An innovative model-based protocol for minimisation of greenhouse gas (GHG) emissions in WRRFs

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Abstract

Water Resource Recovery Facilities (WRRFs) are big contributors to greenhouse gas (GHG) emissions and energy consumption. Aeration is the main source of energy consumption in these facilities and nitrous oxide (N_2O) is the main form of direct emission which is produced during nitrification and denitrification processes through multiple potential pathways. Mathematical modelling is a widely used tool for optimisation of WRRFs and modelling protocols have been developed, which are widely used in the community. However, carbon footprint reduction has not been the main focus of these protocols. In this study, an innovative model-based protocol for minimising GHG emissions of WRRFs was developed using advanced mathematical modelling paradigms. The protocol was constructed based on three different cases for each of which a flow sheet model, a computational fluid dynamics (CFD) model and a knowledge-based risk assessment model were studied together with high frequency data collected by LESSDRONE (an automated wireless tool for measuring direct off-gas emissions). The risk assessment model helps identify high risk conditions while the CFD model provides valuable insights on the impact of hydrodynamics under non-ideal mixing conditions. The flow sheet model is used to test the proposed mitigation strategies and to provide in-silico data for the risk assessment model. The developed model-based protocol provides a robust guideline for water utilities to optimise their operations for minimising carbon

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footprint of WRRFs without compromising their removal efficiencies.

Keywords: carbon footprint, mathematical modelling, N_2O risk assessment, CFD, mitigation strategies

Introduction

Historically, obtaining a high-quality effluent that meets the stringent regulations at the lowest cost has been the focus of process design and optimisation in wastewater treatment plants (WWTPs). More recently, there have been two important evolutions in perspective of a conventional WWTP. One is the focus on recovery rather than removal for water, energy and the nutrients (nitrogen and phosphorus). This has led to the development of new technologies and processes for recovering energy or reusable products. The second evolution is the focus on greenhouse gas (GHGs) emissions and carbon footprint (CF) of water resource recovery facilities (WRRFs) due to concerns with respect to climate change and global warming. About 2-3% of total global GHG emissions are associated to waste and wastewater industry (Maktabifard et al., 2019, Stocker et al., 2013). The total CF of a WRRF is associated with the sum of direct and indirect GHGs emissions from the plant. Direct emissions are related mainly to the biological processes within the WRRF: CO_2 is generated through microbial respiration, N_2O is produced from the nitrification/denitrification stage and CH_4 is formed in the anaerobic zones or by stripping from incoming wastewater. Indirect emissions on the other hand are mainly caused by consumption of electricity and thermal energy, transportation, production of chemicals, or transportation to and from the plant, sludge disposal, etc. CF reduction strategies are focused on the mitigation of direct GHGs emissions (mainly by decreasing N_2O and CH_4 production) and reducing indirect emissions by moving towards an energy neutral WRRF through lower aeration energy requirements and efficient biogas production or utilisation (Ye et al., 2022).

Direct GHGs emissions from activated sludge WRRFs range from 0.9 to 2.2 $kgCO_{2\text{eq}}/m^3$ (Flores-Alsina et al., 2011). The global warming potential (GWP) of CH_4 and N_2O over a 100 years timeline are, respectively, reported to be 27.2 and 273 $CO_{2\text{eq}}$ according to the latest IPCC report (Arias et al., 2021) making N_2O by far the most significant direct form of GHGs emission from WRRFs. It can account up to 78% of total carbon footprint of the plant with nitrification by ammonia oxidizing bacteria (AOB) being the main source of its emissions (Daelman et al., 2013, Kampschreur et al., 2009). N_2O can be produced during the nitrification process through incomplete hydroxylamine oxidation (triggered by high dissolved oxygen concentrations) and/or AOB denitrification (triggered by high nitrite or low dissolved oxygen conditions). However, it is important to mention that N_2O emission can also happen through the incomplete heterotrophic denitrification process by high DO, low pH and/or low

COD/N conditions. Therefore, each direct emission pathway can be dominant depending on the specific operating conditions of a plant. On the other hand, WRRFs are big consumers of energy leading to indirect GHGs emissions. In Europe, annual specific energy consumption in WRRFs is reported in a range of 20-120 kWh per population equivalent (PE) (Mamais et al., 2015). This value in the US is reported to be between 16-71 kWh/PE (Stillwell et al., 2010) while in Australia ranges from 30-120 kWh/PE have been reported (Krampe, 2013). Considering an average total energy consumption of 6454 kWh per capita in Europe, WRRFs are contributing to 1-3 % of total energy consumption. Usually, in WRRFs with activated sludge process (ASP) treatment, aeration is responsible for 50-60% of electricity consumption, 15-25% is associated with sludge treatment and 10-15% to the secondary sedimentation (Mamais et al., 2015). High energy demand of WRRFs will usually lead to more CO_2 production through fossil fuel combustion that is required for providing the energy requirements of the plant.

Mathematical modelling is a widely used approach for optimisation of WRRFs. Many attempts have been made in the past decade to incorporate the biological mechanisms for N_2O emissions within the conventional Activated Sludge Models (ASM) (Vasilaki et al., 2019, Ye et al., 2022). Most of the studies consider only a single pathway for N_2O emissions in the nitrification process by considering either the autotrophic denitrification of nitrite or the incomplete hydroxylamine oxidation (Guo et al., 2012, Mampaey et al., 2013, Ni et al., 2013, Sperandio et al., 2016). Pocquet et al. (2016) introduced a two pathway model which takes both mechanisms into consideration. Only the two pathway model is able to capture both NO and N_2O emissions correctly by formulating the dominant pathway under different operating conditions. In addition, there are only a few studies on the modelling of N_2O production from heterotrophic denitrification pathway and they are all based on lab-scale experimentation (Domingo-Felez and Smets, 2020, Hiatt and Grady, 2008, Pan et al., 2013). Moreover, the abiotic N_2O production can be also included in the mechanistic model (Harper et al., 2015). Massara et al. (2018) incorporated the two pathway model into an ASM2d model for biological phosphorus removal . This model was then used by Solis et al. (2022) to build a benchmark plant-wide mechanistic model of N_2O based BSM2 configuration that can help in identifying the impact of various operatinal and control scenarios on the N_2O emissions. Nonetheless, the lack of a widely-accepted transferable (to different process conditions and reactors) mechanistic model for N_2O and the difficulty to calibrate and validate these models due to lack of extensive experimental data under various dynamic conditions (Vasilaki et al., 2018) have prevented them to be used widely for full-scale mitigation and control strategies (Mampaey et al., 2019).

Moreover, in recent years, some studies have taken the advantage of data-driven techniques to either model N_2O productions in a purely black-box approach or to improve the mechanistic models in a so-called hybrid modelling paradigm (Schneider et al., 2022). Most of these studies have focused on identifying the relashionships between N_2O emissions and other operating parameters of the treatment plants (Bellandi et al., 2020, Song et al., 2020, Vasilaki et al., 2020a). Nevertheless, some quantitative predictive models for N_2O have been developed using machine learning algorithms (e.g. deep neural networks) that show great potential of such methodologies for N_2O applications (Hwangbo et al., 2021, Khalil et al., 2023, Li et al., 2022, Vasilaki et al., 2020b). The main challenge of such an approach however is the availability of long-term operational datasets for training and validation of such models.

With the lack of a comprehensive and validated mechanistic model for N_2O production, Porro et al. (2014) focuses on a knowledge-based approach as a promising methodology for optimisation of GHGs emission in WRRFs. They adapted a knowledge-based risk assessment modelling framework (Comas et al., 2008) originally developed for diagnosing the risk of microbiology related solid separation problems (e.g. filamentous bulking) to predict operating conditions under which the risk of N_2O emission is high in activated sludge systems. While the focus of most mechanistic (and data-driven) models is on N_2O prediction and quantification of its emission, the knowledge-based risk assessment model provides insights on why certain conditions might lead to N_2O emissions. This is helpful for avoiding high-risk conditions and therefore providing a pro-active assessment of N_2O emissions. In addition, some hydrodynamic studies (Qiu et al., 2019, Rehman, 2016, Sperandio et al., 2022) suggest that the N_2O emissions are impacted by local process conditions and the hydraulics and mixing patterns in the bioreactors creating local heterogenities might play an important role in N_2O emissions (depending on the plant's configuration).

Protocols for modelling and optimisation of WRRFs have been developed in the past (Amerlinck et al., 2014, Hulsbeek et al., 2002, Langergraber et al., 2003, Melcer, 2004, Rieger et al., 2012, Vanrolleghem et al., 2003). However, previous protocols were focused on biokinetic parameters and wastewater characterisation, or they were case-specific and could not be generalised. The IWA Good Modelling Practice (GMP) unified protocol (Rieger et al., 2012) proposed a step-wise simulation procedure combining key aspects of the previous efforts. The GMP protocol includes several key elements like strategies for data collection and reconciliation, defining the level of effort (e.g. in calibration or data collection) as a function of objectives, a calibration/validation procedure that includes parameter selection, uncertainty analysis and guidance for interactions between modellers and end-users. Moreover, it includes close interactions between modellers and stakeholders at each step of the protocol. Nevertheless, the ultimate goal of the GMP is still tailored for a better and more systematic model development, calibration/validation, and application. However, a robust model-based protocol focused on troubleshooting and optimisation of WRRFs, in particular with CF minimisation as its main target, is lacking and is therefore the main driver for the present work.

In this study an innovative protocol is introduced focusing on optimisation of WRRFs operating conditions for CF reduction. It is developed within the framework of the EU-Life LESSWATT project and takes advantage of advanced modelling paradigms and extensive data collection for mitigation of energy expenditure and GHG emissions. To develop the protocol different modelling frameworks and innovative measurement campaigns were applied to several case studies in order to analyse the added value and synergy between these different information sources when it comes to mitigation of CF in WRRFs. This paper presents the development of the LESSWATT protocol through results of measurement campaigns and model-based analysis for three selected WRRFs representing different process configurations, different WRRF scales, different levels of data availability and different geographical locations as one of its strong advantages.

Materials and methods

Data collection

The LESSDRONE is an automated wireless self-moving device designed and developed for monitoring direct GHGs emission, DO concentrations and oxygen transfer efficiency in aeration tanks of biological treatment systems (Caretti et al., 2021). It consists of a round steel support frame, six inflatable cylinders (for floating on the surface of the water) and a hood mounted at the center of the frame that captures the off-gas and collects it through a pipe. On top of the frame there are two boxes containing the analysis instruments and the control/positioning devices. The device is equipped with eight motors and can be remotely controlled or pre-programmed to follow a path on the surface of the tank. The gas passes through an anemometer (flow rate measurement) to the sensors for CO_2, CH_4 and N_2O measurements. Gas detection analysis for CH_4 and N_2O is based on non-dispersive infra-red technology which filters a narrow spectral region that overlaps with the absorption band of specific gases (Novagas2 probe, Novasis Innovazione, Italy) while a near infra-red absorption probe is used for CO_2 (GMP251 analyser, Vaisala, Finland). It also contains a probe for DO and temperature measurements (XYO optical oxygen sensor, First Sensor, Germany) in the liquid phase. LESSDRONE evaluates the standard oxygen transfer efficiency of the aeration system in process condition (αSOTE) based on the off-gas method which uses a gas-phase mass balance of oxygen over the liquid volume (ASCE, 1997).

Within this study, the LESSDRONE was positioned at the center of the aeration tanks of different case studies and high frequency data (every 5 seconds) were collected under different operating conditions (e.g. air flow rates and DO setpoints). The N_2O concentration measured in the off-gas and the air flow rate data were used to calculate the N_2O emission rates based on the following equation (Guo, 2014).

$$N_2O_{er} = \frac{[N_2O]}{10^6}\frac{Q_{air}}{A}\frac{28}{0.0224} \tag{1}$$

where N_2O_{er} is the N_2O emission rate ($gN_2O - N/m^2/d$), $[N_2O]$ is the N_2O concentration in the off-gas (ppm), 10^6 is for the ppm unit conversion, Q_{air} is the air flow rate (m^3/d), A is the aerated area (m^2), 28 is the nitrogen mass per mole of N_2O ($gN_2O - N/mol$) and 0.0224 is the molar volume of N_2O gas (m^3/mol).

N_2O risk assessment modelling

The core of the N_2O risk assessment model (Porro et al., 2014) is a knowledge base containing heuristic and empirical knowledge on operating conditions and parameters that are linked to the risk of N_2O production in a WRRF (e.g. via heterotrophic denitrification and AOB nitrification/denitrification). This information is collected from the literature and domain experts. The goal of the risk model is not to make quantitative predictions of N_2O production but to assess whether certain operational and control strategies lead to more or less favourable conditions for N_2O emissions to arise. The risk model is based on principles of fuzzy decision theory. Numerical values of operating conditions and parameters related to N_2O production are translated into low, medium and high risk. The fuzzified input data set is then used to generate a fuzzy output by a set of IF/THEN-based inference rules defined purely based on literature and empirical knowledge. For example, high DO and high nitrite conditions generate a high fuzzy output for risk of N_2O production in denitrification stage. Finally, fuzzy output values are defuzzified into numerical values for further interpretation again based on definition of some membership functions. Consequently, the result of risk assessment modelling is presented as risk score values between 0 and 1, with 1 referring to the highest risk. The two important specific terminologies in this study to represent the risk of N_2O emission are *high DO risk* and *low DO risk*. *High DO risk* refers to the risk of having N_2O emissions caused by conditions where high DO concentrations contribute to one of the pathways of N_2O emissions. This is mainly related to either incomplete hydroxylamine oxidation in the nitrification process or the incomplete heterotrophic denitrification in the anoxic zones. Similarly *low DO risk* is defined for the conditions where low DO concentrations trigger a pathway for N_2O emissions which in this case is through AOB denitrification in the aerobic zones.

The N_2O risk model can be simulated based on data of different type and abundance. It can for example be fed with high frequency measurement data collected by LESSDRONE in order to identify the operating conditions under which the risk of N_2O emission is high. However, simulation data (e.g. output of flow-sheet biokinetic model or CFD model) can be used as input as well. This allows performing operational scenario analysis to define mitigation strategies.

Flow-sheet biokinetic modelling

The ASMs, as the most widely-used mathematical models for describing biological wastewater treatment processes were applied for constructing the flow-sheet biokinetic models in this study (Henze et al., 2000). Flow-sheet models are technical representation of the unit processes and their connectivity for a process train and can be developed in the available commercial WRRF simulators. They include submodels for each unit process (e.g., ASM for activated sludge tanks or a settling model for clarifiers). The choice of ASM version (e.g. ASM1, ASM2d and ASM3) to be used for modelling depends on the features and requirements of the biological process in each case and the objective of the modelling study. In this study, the ASM1 and ASM3 models were used for the Cuoiodepur and San Colombano case studies respectively to account for COD removal, nitrification and denitrification processes. The choice of ASM3 over ASM1 for the case of San Colombano was merely based on the previous available version of the model. For the case of Eindhoven on the other hand, the ASM2d model was used to account for biological phosphorus removal as well. Secondary clarifiers were described with conventional Takacs model (Takacs et al., 1991) in Cuoiodepur and San Colombano case studies, while for the case of Eindhoven a more advanced model of Burger-Diehl (Burger et al., 2011) was used. In the case of Eindhoven, also the primary sedimentation tank was modelled using a modified Tay model (Tay, 1982).

The commercial wastewater treatment modelling software WEST (MikebyDHI) was used but it should be mentioned that the proposed protocol is not restricted to the use of any specific software for modelling.

The flow-sheet biokinetic models are conventionally constructed using the tank-in-series (TIS) approach in which an activated sludge tank is modelled as a number of completely mixed tanks connected in series. This is a common approach to construct a relatively simple model. However, when variations due to incomplete mixing are high a TIS model is not capable of sufficiently capturing the recirculation and local concentration gradients. This is where hydrodynamic studies are helpful. Computational Fluid Dynamics (CFD) allows for modelling spatial variations inside bioreactors in a very high detail (Jourdan et al., 2019). Consequently, the conventional TIS models can be updated to a compartmental model (CM) based on the results of detailed hydrodynamic modelling in case this is available (Le Moullec et al., 2011). In CM, an activated sludge tank is modelled as a number of conceptual compartments inter-connected with some exchange flow rates that represent the spatial profiles and the effect of mixing patterns in a more realistic way thus improving the prediction power of the model. While for the Cuoiodepur and San Colombano case studies a TIS model was considered sufficient for the purpose of the modelling study, in the case of Eindhoven a compartmental model of the plant was already available through extensive hydrodynamic studies that were done. Therefore, the CM was used in the flow sheet model.

CFD-biokinetic modelling

CFD-biokinetic modelling (Rehman, 2016) was used in this study to assess whether local phenomena due to heterogeneous mixing might play an important role in GHG emissions for the different case studies. On the one hand, this served to evaluate the accuracy of the TIS approach and on the other hand the CFD model data can be used as input to the risk model to calculate local N_2O risks throughout the reactor. A 3D two-phase (gas/liquid) CFD model was used and a standard procedure was followed to develop the geometry and meshing as well as modelling mixing (Eulerian two-fluid model) and turbulence (Realizable k-ϵ model) (Wicklein et al., 2016). CFD simulations were performed in ANSYS, FLUENT software and the post-processing of the data is done in either ANSYS or ParaView.

The CFD models are then extended by an ASM model to account for the biological processes involved. This integration has been done by solving a transport equation for each of the ASM components in which the source term is derived from the mass balance equations. To the standard ASM processes, an extra term is added to account for oxygen mass transfer from gas to liquid phase. Simulations are carried out in a sequential way meaning the the biokinetic part was simulated on top of the frozen converged steady-state hydrodynamic solution. As a result, the output of the CFD-biokinetic model is a snapshot of concentration profiles for ASM components at a specific gas and liquid flow rates (here influent and air flow rates). It is kind of an X-ray scan of the reactor and a very powerful means to analyse what is actually going on in the reactor.

In case of having non-ideal mixing conditions in the reactor, the DO parcels obtained as the output of the CFD-biokinetic model can be fed to the N_2O risk assessment model (Porro et al., 2019). This leads to a risk score at each spatially distributed location across the bioreactor and local operating conditions leading to high emission risk can be investigated.

Case studies

The protocol has been developed through the analysis of N_2O measurements and simulations with different modelling tools for three different WRRFs. Each case study was characterized by different process conditions, process configurations and geographical locations which allowed to develop a protocol for GHG reduction that is generically applicable.

The first case is the Cuoiodepur WRRF located in the community of San Miniato (PI) in Italy. The plant has a capacity of 850,000 PE treating combined industrial and municipal wastewater. The industrial tannery wastewater entering the plant goes through a pre-treatment (fine screening, grit chamber sulfur oxidation and equalization) and primary sedimentation stage after which it is introduced to the denitrification tank. The municipal wastewater is added to the industrial wastewater right after the denitrification and before nitrification/oxidation tank. The configuration of the biological tanks comprises a single denitrification (11000 m^3) and 7 parallel nitrification rectangular tanks (3750 m^3 each). Mixed liqour is recycled from the end of nitrification to the beginning of denitrification. Returned activated sludge goes from underflow of the secondary sedimentation to the denitrifiaction zone. DO is controlled at 2 mg/L inside the aeration zone. A DO probe is located at the end of the nitrification tank. After secondary sedimentation the treated wastewater goes to the tertiary treatment stage for further purification.

The industrial wastewater has almost twice the flow rate of the municipal one with around 700 mg/L of total nitrogen. This high nitrogen load to the plant can induce favorable conditions for N_2O emissions that motivates the study of this case study for developing the protocol.

The second case is the San Colombano WRRF located in Lastra a Signa, Tuscany, Italy. It treats municipal wastewater from the surrounding municipalities with a capacity of 600,000 PE. After a preliminary treatment (coarse and fine screenings and a combined aerated grit, oil and grease removal) followed by primary settling, the wastewater goes through a denitrification-nitrification biological process. There are 3 parallel lines of treatment each consisting of 4 parallel rectangular tanks with the volume of 8500 m^3. Each tank is divided into 6 anoxic zones and one aerobic zone in series (with almost equal anoxic and aerobic volumes). The internal recycle flow goes from the end of aerobic zone to the first 3 anoxic zones and the activated sludge is recycled from secondary clarifiers to the beginning of the denitrification zone. The air flow is regulated by an ammonia-DO cascade controller with ammonia setpoint of 1.5-3 $mgNH_4/L$ which provides a DO concentration range of 0.8-1.2 mg/L. The wastewater goes through a secondary settling tank before being introduced to the chemical disinfection at the end. The DO and NH_4 probes are located at the end of the aerobic section.

The much lower levels of DO compared to the first plant makes this case interesting to study as it is known that too low DO conditions can contribute to the N_2O emissions.

The third case study focuses on the Eindhoven WRRF located in the south of the Netherlands treating municipal wastewater of the surrounding municipalities with the capacity of 750,000 PE. The treatment plant consists of three separate lines each including a primary settling tank, anaerobic/anoxic/aerobic bioreactors and four secondary settling tanks. The acivated sludge tanks are carrousel type reactors with concentric form. The anaerobic, anoxic and aerobic volume of the circular tanks are 3733, 9525 and 16933 m^3 respectively. It also includes chemical dosing in the form of aluminum chloride for improving phosphorus removal. There are two internal recycles; one from anoxic to the anaerobic zone and one from the end of the aerobic back to the anoxic zone. The external activated sludge recycles flows from the underflow of the secondary settling tank to the beginning of the anoxic zone. The aeration system of Eindhoven consists of two sets of diffusers. The summer package continuously aerates the tank while the winter package comes in actions in high load conditions. The aeration is regulated by the presence of an ammonia-DO cascade controller with ammonia setpoint of 1.4 mg/L which controls the setpoint of oxygen between minimum of 0.5 and maximum of 5 mg/L in the aeration zone. The DO and NH_4 probes are located at the end of the aeration summer package.
The particular configuration of the biological tanks including their geometry, circular flow and partial aeration system makes it an intriguing case to study how N_2O emissions can be impacted by those factors. In addition, previous N_2O measurments and N_2O modelling studies on this specific case seemed highly valuable for the development of the protocol.
Table 1 shows the influent charactersitic data for the three case studies that have been used for the development of the protocol.

Table 1: Influent characteristics for the three case studies.

	San Miniato		San Colombano	Eindhoven
Parameter	Industrial	Municipal		
COD $[mg/L]$	13130 ± 4726	266 ± 72	141 ± 54.2	476 ± 139
TSS $[mg/L]$	6279 ± 3847	53 ± 24	65.1 ± 18.4	$211ys \pm 84.8$
NH4 $[mg/L]$	326 ± 137	30 ± 16.8	18.2 ± 5.4	41.3 ± 9.86
TN $[mg/L]$	710 ± 283	41 ± 7.3	21.3 ± 6.8	49.4 ± 14.3
pH	8.2 ± 1.1	7.6 ± 0.4	7.7 ± 0.5	7.75 ± 0.24

Results and discussion

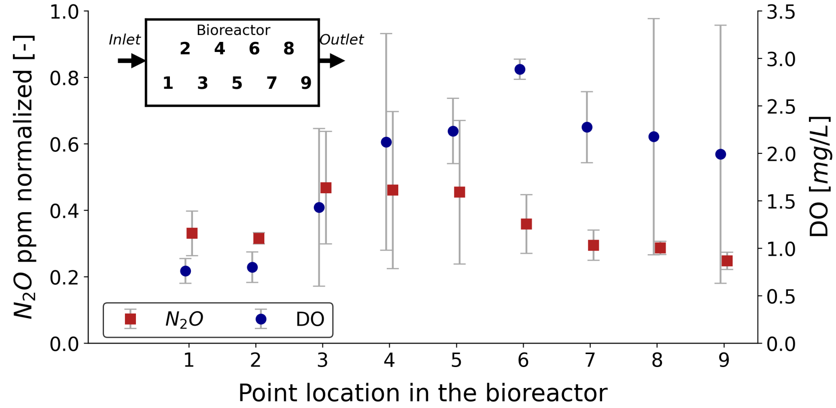
Case study: Cuoiodepur WRRF, Italy

A measurement campaign with LESSDRONE was done in May 2019. The experimental campaign was carried out under normal operating conditions of the plant. During the first half of the measurement campaign N_2O emissions were collected at different locations across the tank in 2-hour intervals (Figure 1a). Overall, emissions are observed across the whole bioreactor in this case although they vary from one point to another and show higher values in the middle of the tank. DO concentrations are generally higher towards the end of the bioreactor where the fixed DO probe is also located (close to the point 9). However, it is not clear at this point whether this observation is due to the incomplete mixing pattern or time-dependent dynamics. Figure 1b shows the temporal variations of the DO for the whole period of the measurement campaign while in Figure 1c a zoomed version can be seen for a period of almost two days during which a stationary test (with fixed location of the LESSDRONE in the middle of the tank between points 4,5, and 6) was performed to have a continuous N_2O measurement for a long period.

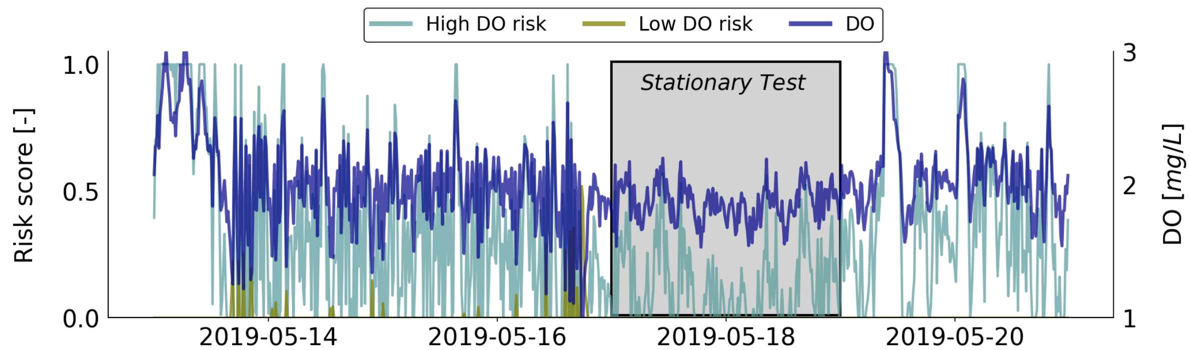
Subsequently, the N_2O risk model framework (Porro et al., 2014) was applied on data collected from the plant's SCADA system. In Figure 1b, high DO and low DO risk scores (i.e. risk due to predominantly high and low DO conditions respectively) predicted by the model as well as measured DO concentrations (by LESSDRONE) are presented. It can be seen that in almost the entire period of the measurement campaign a risk of N_2O emissions due to high DO concentrations ('High DO risk') is predominant. In fact, during the stationary test (Figure 1c) the low DO risk is zero all the time. The measured DO concentration during this period is often higher than 2 mg/L. The N_2O emission rate peaks in many occasions follow the peaks in high DO risk. It is important to note that high risk scores do not always correlate with N_2O emissions. The risk assessment model provides qualitative insights on operating conditions that favors N_2O emissions. Therefore, the magnitude of the peaks observed in the emission rates and risk do not necessarily match. Nevertheless, in most cases when a peak of N_2O emission rate is observed, a peak of high DO risk is visible too. The emission rate data confirm the output of the risk model, i.e. that the plant's current operational strategy is creating favourable conditions for N_2O emission. These findings are aligned with the literature where dominance of hydroxylamine oxidation pathway was reported in high DO (more than 2-2.5 mg/L) concentrations (Ni et al., 2013, Sun et al., 2017, Tumendelger et al., 2014). Hence, if the risk can be reduced, the actual emission can also be mitigated. At this point, reducing aeration as a potential mitigation strategy comes to mind. However, this needs to be done with care as N_2O emissions due to low DO risks also occur in specific periods of the measurement campaign. Before implementing such a significant change in the plant's operation, the mitigation strategy is first tested in a flow sheet model to ensure that reducing the aeration would not have any detrimental effects on the effluent quality. Therefore a flow sheet model was constructed based on ASM1 and calibrated and validated on historical data (see A.1 for more information).

As the LESSDRONE measurement campaign revealed quite some spatial variation in the N_2O emissions, the aeration tank is also modelled using a CFD-biokinetic integrated model to study whether these variations in N_2O emissions are caused by non-ideal mixing conditions (unequal aeration) or simply by the time-varying properties of DO and influent concentrations. This can provide insights into possible effects of local N_2O emission risks or local conditions to be considered when assessing mitigation strategies. Three scenarios are selected to simulate the CFD-biokinetic model reflecting low to high influent flow rate conditions. The results show no indication of mixing issues (such as dead zones or short cuts) with a clear plug flow behaviour in the reactor. The reactor is well mixed over it's depth and width. Moreover, the hydrodynamics do not change significantly with the increase of influent flow rate (Figure A.2.1). Both soluble substrate and ammonia are entirely consumed over the first half of the reactor indicating the presence of more than sufficient DO in the reactor where it is required for COD and nitrogen removal.

The CFD model results confirm that local variations in N_2O emissions are due to temporal dynamics and not spatial heterogeneous zone or similar mixing problems. As aeration is an important source of mixing, it was first tested in the CFD model whether the proposed mitigation strategy (aeration reduction) would not cause any negative effects on the reactor hydraulics. In a 4th scenario, the mitigation strategy with 40% reduction of air flow rate (to test a substantial reduction) was simulated by the CFD model confirming that reducing air flow does not significantly change the reactor's hydraulic behaviour (Figure 2). Figure A.1.3 shows the effluent quality predicted by the flow sheet model comparing the reference scenario (under normal operating conditions) with the mitigation scenario in which the aeration is reduced. The outputs suggest that the 40% aeration reduction has no significant negative impact on the treatment performance (5% reduction in ammonia removal). In addition, the output of the flow sheet model was used as the input of the N_2O risk assessment model (data not shown) to ingestigate the impact of the proposed scenario on the risk of emission. While the low DO risk remained almost unchanged, 20% reduction in the high DO risk was observed (percentage of the time the high DO risk is more than 50%) that suggests the effectiveness of the proposed strategy in reducing high risk operating conditions for N_2O emission.



(a)



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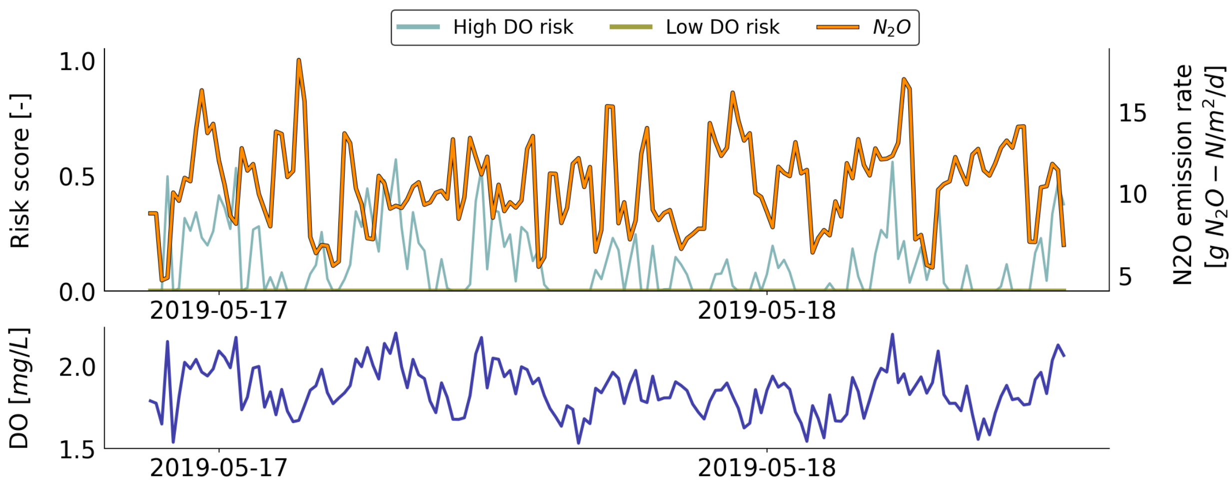


(c)

Figure 1: Cuoiodepur WRRF N_2O risk assessment modelling results under normal operating conditions. (a): Spatial variations of the N_2O and DO in different points of the bioreactor. N_2O concentrations in the off-gas are measured in *ppm* and normalized based on the maximum value observed during the whole period of the measurement campaign (b): N_2O risk score and DO concentration for the whole preiod of the measurement campaign (c): zoomed-in graph for the period of stationary test with continuous N_2O measurements.

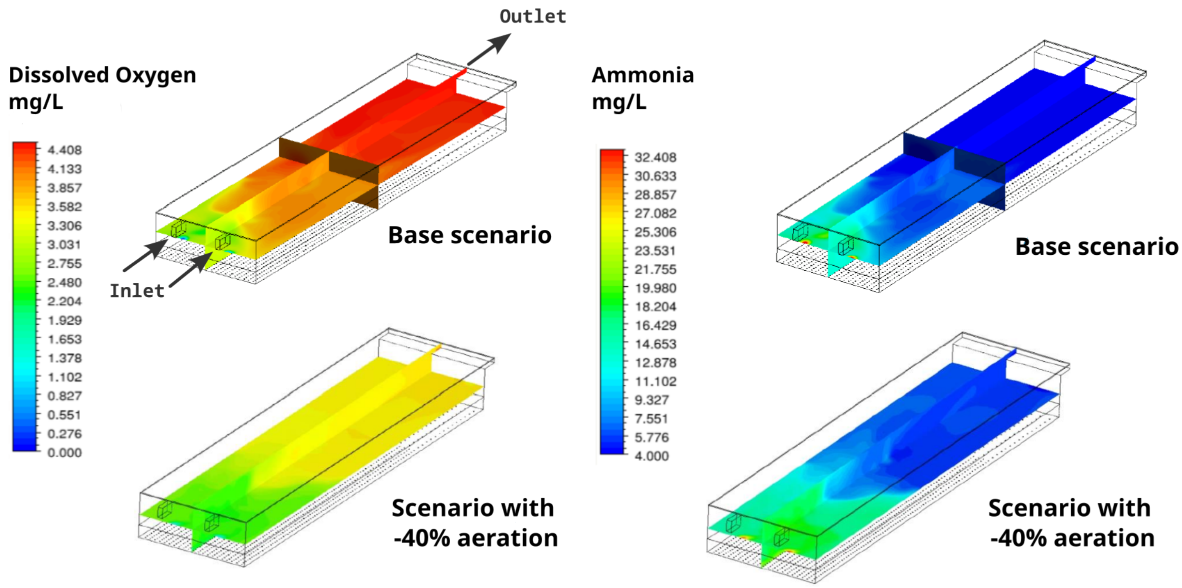
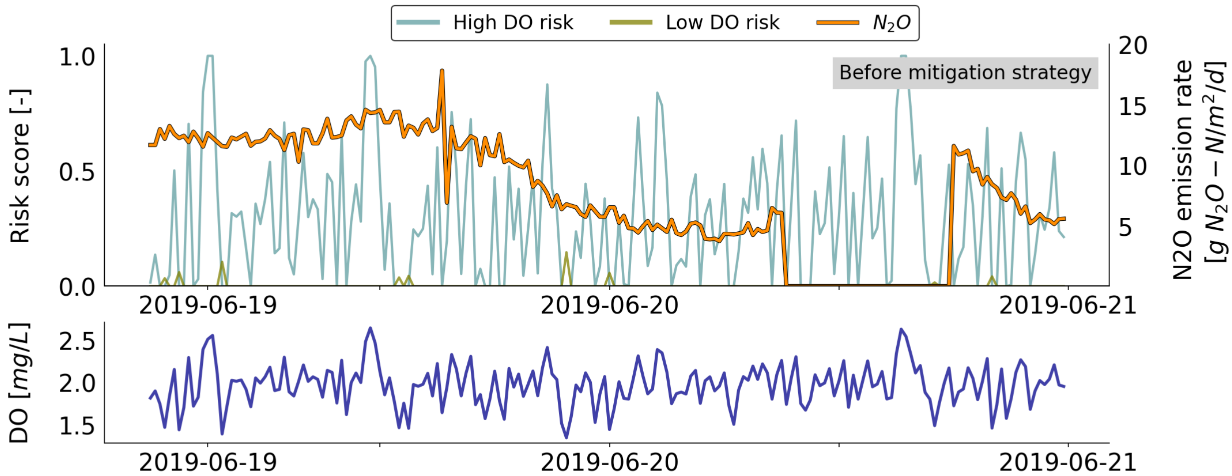
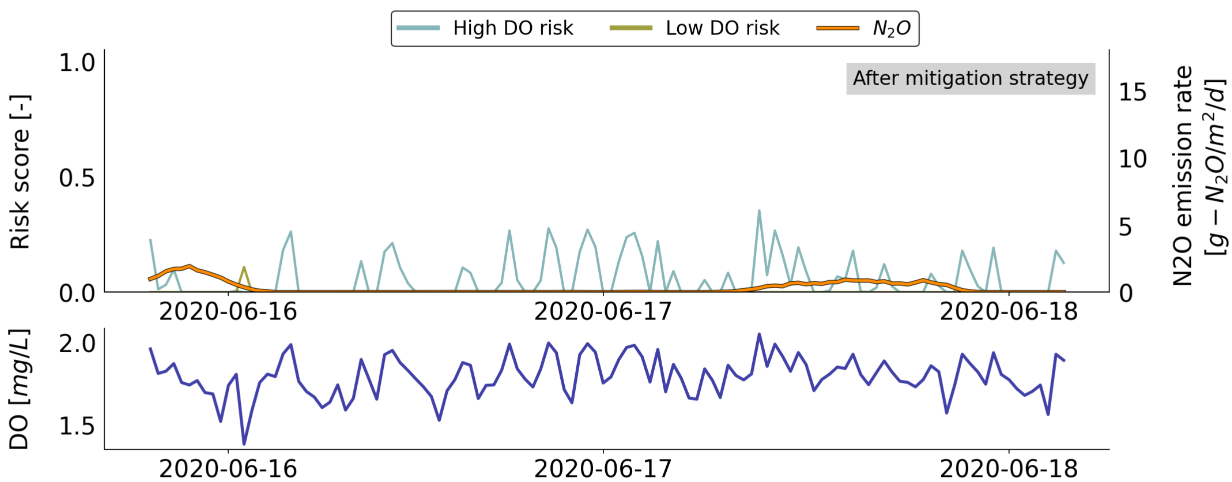


Figure 2: Comparison between two scenarios with high and low aeration in terms of concentration profiles from the CFD-biokinetic model

Finally, a measurement campaign was carried out in June 2019 to assess the impact of the proposed mitigation strategy. In the middle of the test the DO setpoint was reduced from 2 to 1.8 mg/L (in agreement with the operators to test a reduced DO level that seems to be still enough for the treatment performance). The data collected by LESSDRONE was used as the input for the N_2O risk assessment model. Figure 3 shows the results of the N_2O risk model before (Figure 3a) and after (Figure 3b) applying the reduced DO setpoint. The two measurement campaign periods are presenting similar conditions in terms of N loads in the influent (average NH_4 loads to the biological tanks of 190.3 and 193.4 Kg/d before and after the mitigation strategy respectively). However, the COD load in the measurement campaign before applying the mitigation strategy was almost 1.8 times higher than when the mitigation strategy was applied. This leads to having lower COD/N ratio during the application of the mitigation strategy than the time before that. However, this lower ratio did not trigger the incomplete heterotrophic denitrification pathway for N_2O emission since it is still very high because of the high COD contribution from the industrial influent. In the first case, similar to the previous measurement campaign high DO risk is predominant. The actual N_2O emission is also consistently high. Reduction of the DO setpoint as the proposed mitigation strategy decreased the high DO risk significantly. In fact, the percentage of time where the high DO risk is greater than 50% is reduced from 26% in the first scenario to 12% in the scenario with the mitigation strategy applied. The validity of the risk model was confirmed by the measurements that show that the N_2O emission is also reduced considerably. The mitigation strategy in the second scenario was able to keep the emission as low as zero almost all the time. Moreover, the proposed mitigation strategy leads to reduction of 500 $MWh/year$ (394 $tCO_2eq/year$ of indirect emissions, estimated based on the period of the measurement campaign) of energy consumption thanks to the reduced aeration.



(a)



(b)

Figure 3: Results of N_2O risk assessment based on data collected in a new measurement campaign (a): Before application of mitigation strategy (b): After application of mitigation strategy with lower aeration. The period with zero emission during the measurement before application of the mitigation strategy is due to an interruption of LESSDRONE measurements.

Overall, the risk assessment model provided a valuable indication of emission risks and directly allowed to propose a mitigation strategy. The fuzzy rules of the risk model provide a more accurate representation of the risk of emission based on DO and suggest at what DO conditions the risk is higher. CFD model on the other hand allowed to check for local heterogenities and it showed good mixing conditions across the bioreactor. It also helped assess the impact of the aeration reduction (as the proposed mitigation strategy) on the bioreactor's mixing pattern. The combined results of the risk and CFD models provide a powerful tool to see when, where and why the risk of emission is high which cannot be done simply by looking at the DO data itself. Moreover, the flow sheet model provided a great opportunity to test the mitigation strategy prior to the implementation and proved that the performance of the treatment process is not compromised by that. Under the new operating condition both the risk of N_2O emission as well as the actual N_2O emissions measured by LESSDRONE were significantly reduced.

Case study: San Colombano WRRF, Italy

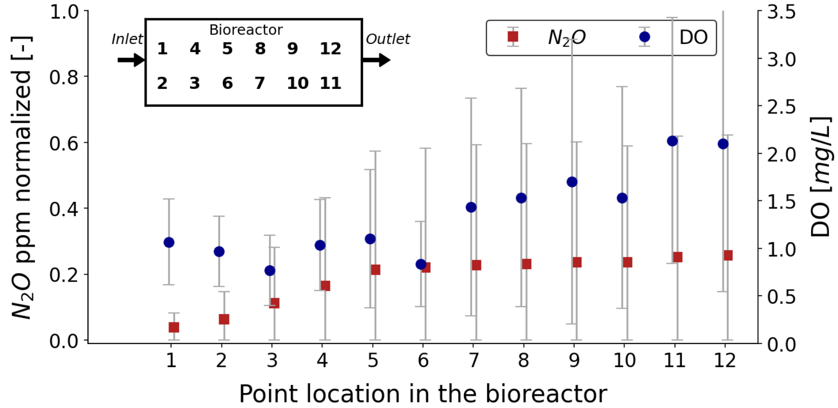
Spatial and temporal data are collected with LESSDRONE in a measurement campaign carried out in April-May 2021. The results of the point tests in various locations across the aeration tank (Figure 4a) shows a non-uniform DO concentration profile. While generally the DO increases across the length of the bioreactor as it is expected (less DO consumption at the end of the tank), some drops are visible (e.g. points 3,6, and 10) which could indicate non-ideal mixing patterns. The N_2O emissions in the off-gas shows a general increasing trend from the beginning to the middle of the tank while in the second half of the tank it remains stable. The temporal dynamics of DO on the other hand (Figure 4b) generally shows a low DO concentration profile over time (less than 1 mg/L) with very high peaks (up to 8 mg/L) happening in multiple occasions. During this period, some high peaks are visible for the N_2O emissions as well. While most of these peaks are related to the periods with very high DO conditions, there are some peaks (e.g. at the beginning of both periods) that occur during low DO conditions.

The N_2O risk assessment model was applied to the DO data collected during this period. Under conditions with high concentrations of DO, high DO risk is observed while for the rest of the measurement period where DO is consistently lower than 1 mg/L the Low DO risk is dominant. This indicates that the nitrifer denitrification due to low DO conditions (DO less than 1-1.5 mg/L) might be the dominant pathway (Aboobakar et al., 2013, Castellano-Hinojosa et al., 2018, Sun et al., 2017, Tumendelger et al., 2014, Wang et al., 2011). The N_2O emission data show sharp peaks in many instances that the risk increases, although not all periods with an elevated risk lead to actual N_2O emissions. Figure 4c shows a zoomed version of the same measurement campaign for 06 May 2021 where a sharp peak of N_2O emission is visible. It seems that when the ammonia peak arrives, DO is consumed rapidly but the controller's response is too late and when there is no ammonia left the DO concentration goes high and the risk transitions into high DO regime. This is due to the fact that in practice there is a minimum air flow rate of around 900-1000 m^3/h which is supplied to the bioreactor even when there is no more ammonia. A sharp peak of N_2O emission is also visible for this period. However, for the rest of the time where low DO risk is dominant not a lot of peaks can be seen for N_2O emission. This can be an indication of having non-ideal mixing conditions in the bioreactor which motivates further application of the CFD model.

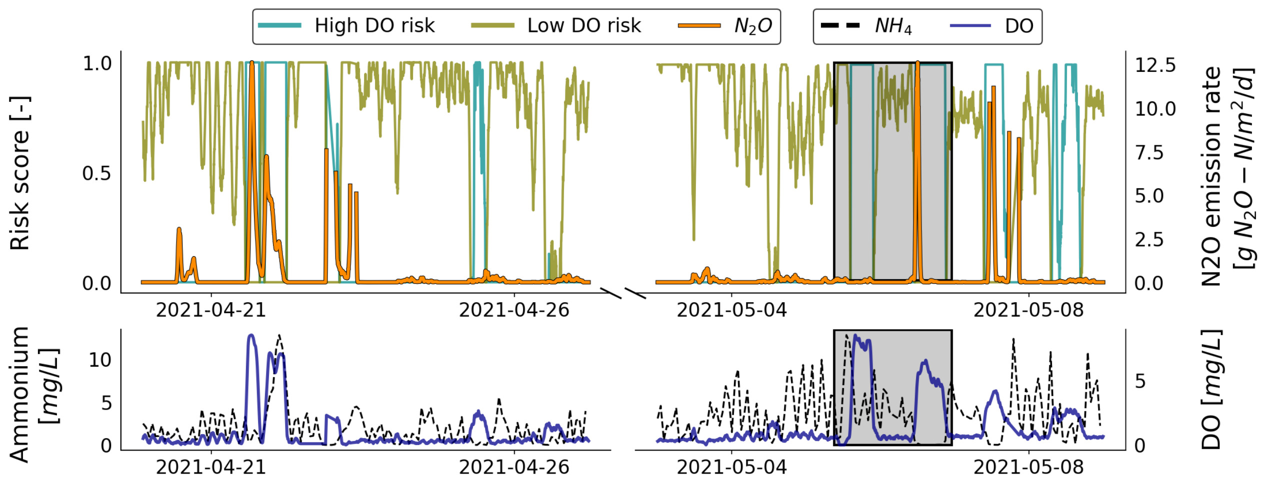
The low DO values can be also related to the location of the DO probe which is at the top end of the bioreactor. This could not be optimal due to potentially non-ideal mixing patterns thus being not the best representative of the DO in the tank. Moreover, a slight increase in nitrate can be seen before the N_2O emission peak. The nitrate sensor is located in the last compartment of the anoxic zone. This increase could indicate incomplete denitrification happening at the end of the anoxic zone (where back flow from aeration zone occurs) that could contribute to N_2O production which will be eventually emitted in the aeration section (Aboobakar et al., 2013, Kampschreur et al., 2009).

It seems that reducing the DO set point range in the ammonia-DO cascade controller should allow to eliminate peaks of emission risk due to Low DO risk conditions as well as high DO risks related to overaeration after the ammonia peak is gone. On the other hand, overaeration after the ammonia peak leads to moving into high DO risk regime. However, it is still difficult to propose a clear mitigation strategy as local variations could be in place that impacts the observations.

In order to investigate the local variations in detail, the entire bioreactor including both anoxic and aerobic zones was modelled using a CFD-biokinetic model. The results (Figure B.2.1) show that the DO concentrations of greater than 2 mg/L are visible in almost all the aerobic section. A reversed flow pattern is seen from the beginning of the aerobic zone back to the last two compartments of the anoxic zone. This back flow hampers the denitrification and increases the volume of nitrification. As a result, high DO concentration (Figure B.2.1a) is visible in the last two compartments of the anoxic zone, specially near the top of the bioreactor. COD is almost completely consumed in the anoxic zone having low concentration at the inlet. Similarly, ammonium nitrification starts in the last two compartments of the anoxic zone and is almost completely consumed in the aerobic section (Figure B.2.1b). Although nitrate is consumed in the anoxic zone, there is a higher concentration near the end of this section due to the back flow from the aerobic zone (Figure B.2.1c). Interestingly, at the top end of the bioreactor, a small area with very low concentration of DO is visible (Figure B.2.1a). This is precisely where the DO probe is located and could thus explain why the controller does not function optimally. The hydrodynamic study shows that the current operational and control strategy may lead to high DO concentrations that are not measured by the DO probe. This could indicate risk for N_2O emission due to high DO concentrations and explain the discrepancy between the risk model results (indicating very frequent low DO risk) and the actual N_2O emission data (indicating that most emissions are associated to periods of higher DO values). Another explanation for this could be that ammonia is not being converted when DO is low and therefore no N_2O is being



(a)



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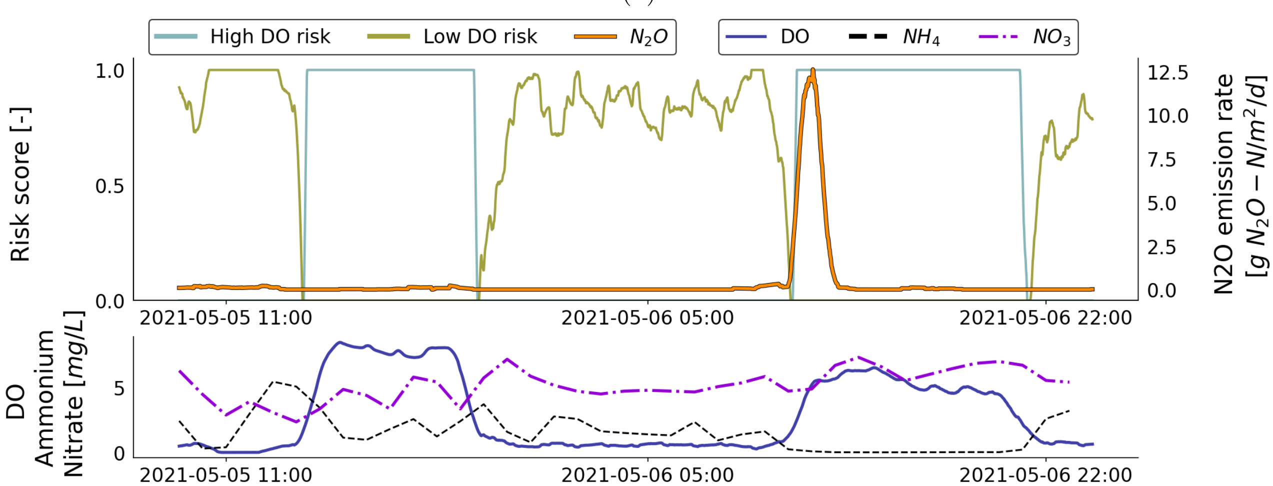


(c)

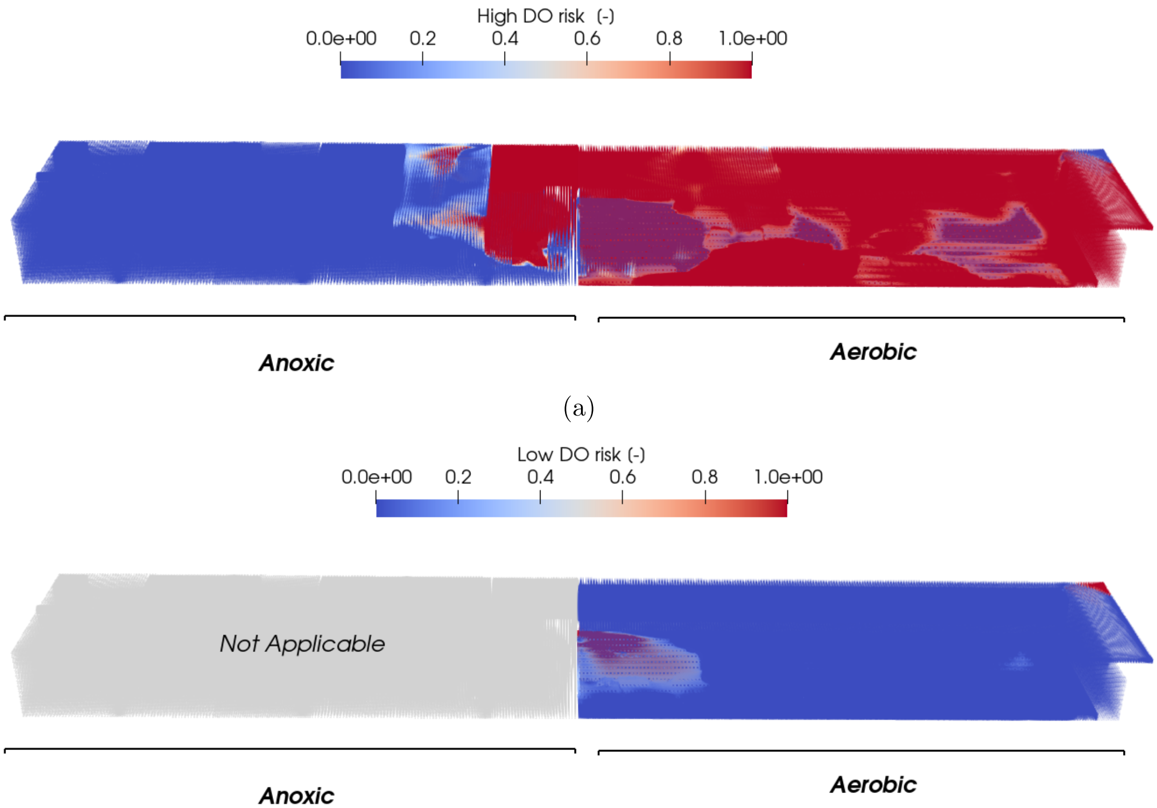
Figure 4: Results of the measurement campaign with LESSDRONE in April-May 2021. a) The results of the point tests at various locations across the bioreactor. N_2O concentrations in the off-gas are measured in *ppm* and normalized based on the maximum value observed during the whole period of the measurement campaign b) N_2O risk assessment modelling results for the whole period of the measurement campaign. c) Zoomed version for 06 May 2021.

produced. On the other hand, when DO increases ammonia comes down and consequently N_2O goes up for a brief period of time until ammonia is being consumed and drops to zero. Occasional emissions during low DO conditions could be also related to N_2O production triggered by the denitrification pathway.

In order to investigate the impact of local variations on the N_2O risk, a novel approach was used by integrating the CFD-biokinetic and N_2O risk assessment models. The DO parcels obtained as the output of the CFD-biokinetic model are fed to the N_2O risk assessment model (Porro et al., 2019). This leads to a risk score at each spatially distributed location across the bioreactor. This way, the zones with high N_2O risk can be identified and further investigated for high risk operating conditions.

Figure 5 shows the results of the CFD-biokinetic coupled with the N_2O risk assessment model in terms of high DO and low DO risk conditions. High DO risks are visible across the aeration zone of the bioreactor. However, there are some areas with very low high DO risk near the bottom of the tank and where the DO probe is located at the top end of the bioreactor. High DO risk is observed also in the last two compartments of the anoxic zone where the back flow from the aeration zone is happening. This can explain the observed high nitrate concentrations at the end of the anoxic zone which indicated the potential N_2O emission related to this region. On the other hand, the low DO risk (Figure 5b) is not present in the aerobic zone except for a small area near the bottom at the beginning of the aeration zone and where the DO probe is located (low DO risk is not a factor in anoxic zone and therefore is not applicable to that part). It is important to note that the CFD-biokinetic simulation is a snapshot in time which means that at the specific time where DO is quite high across the aerobic tank (after the ammonia is consumed), the low DO risk is not present significantly. However, the small areas with low DO risk indicate that under low DO concentrations (e.g., a lot of instances observed in Figure 4b) the low DO risk will be dominant in the bioreactor and potantially increase the N_2O emissions.

The ammonia-DO cascasde controller operates with the ammonia set point of 1.5-3 mg/L. This leads to having low DO concentrations (as low as 0.3 mg/L) most of the time. Consequently, low DO risk regimes are dominant. However, in many instances, high DO peaks (as high as up to 8 mg/L) are observed, most probably due to having a minimum air flow supply all the time. This means that when ammonia is consumed at the end of the anoxic zone, the DO increases and high DO risk regimes are unavoidable. Moreover, having high DO and nitrate at the end of the anoxic zone due the back flow from aerobic part, might provoke N_2O emissions due to



(b)

Figure 5: CFD-risk assessment modelling results for a) high DO risk and b) low DO risk conditions.

incomplete heterotrophic denitrification (Kampschreur et al., 2009). The non ideal mixing conditions at the end of the anoxic and beginning of the aerobic zones lead to having both high DO and low DO risk regimes in that area.

It seems that high DO risk regimes can be prevented by increasing the DO before ammonia peaks rather than after the ammonia is consumed. Moreover, the minimum air flow rate to the bioreactor can be reduced to avoid overaeration of the system when ammonia is consumed. On the other hand, low DO conditions can be avoided by increeasing the minimum DO concentration in the controller (e.g. from 0.3 to 1 mg/L). This strategy was tested with the flow sheet model (data not shown) in which the DO was controlled to be no less than 1 mg/L. The simulated output was then used as the input of the N_2O risk model. This showed a 50% reduction in low DO risk condition (percentage of time where low DO risk is greater than 50%) for a year of dynamic simulation. In addition, reducing the ammonia set point range in the controller can prevent low DO conditions too. This scenario was also tested with the flow sheet model (data not shown) by reducing the range of ammonia set point from 1.5-3 mg/L to 1-2.5 mg/L. The results of the simulation show no significant change to COD removal and an improvment for ammonia removal by 13%. The output of the flow sheet model was tested with the risk assessment model too. Although the results show insignificant differences, a slight decrease (by 5%) is observed in Low DO risk conditions.

Although there were no new measurement campagin carried out in this plant, the mitigation strategy by decreasing the set point range of ammonia from 1.5-3 mg/L to 1-2.5 mg/L was tested in a previous campagin (in July 2020) in order to potentially limit low DO conditions. The data from this period (which had similar conditions in terms of COD and N load) is used for further analysis and comparison with the simulation studies. The results (Figure 6) show that during the measurement campaign with the mitigtaion strategy, periods with DO concentrations lower than 1.0 mg/L decreased from 93.8% to 78.8% of the time. Consequently, the low DO risk of N_2O emission was reduced by 25% during the mitigation strategy. Although, small peaks of N_2O emission were still observed during the mitigation strategy (low DO risk was still high in some instances), no period with high peak of N_2O emission (more than 0.5 in the normalized data) was observed during the application of the mitigation strategy. However, the slight increase in the aeration leads to an increase of energy consumption by 105 $MWh/year$ (33 $tCO_2eq/year$ of indirect emission).

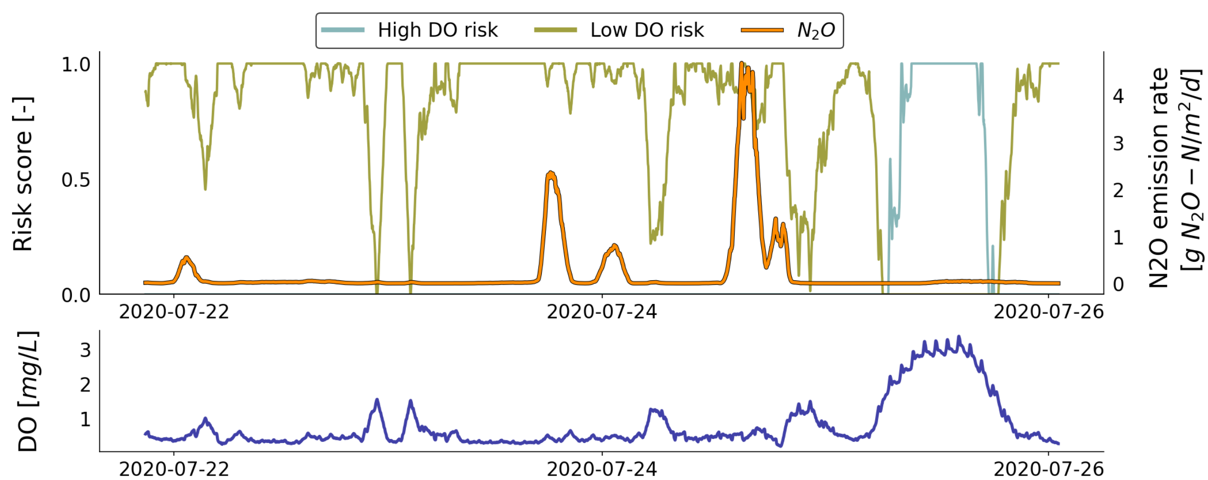


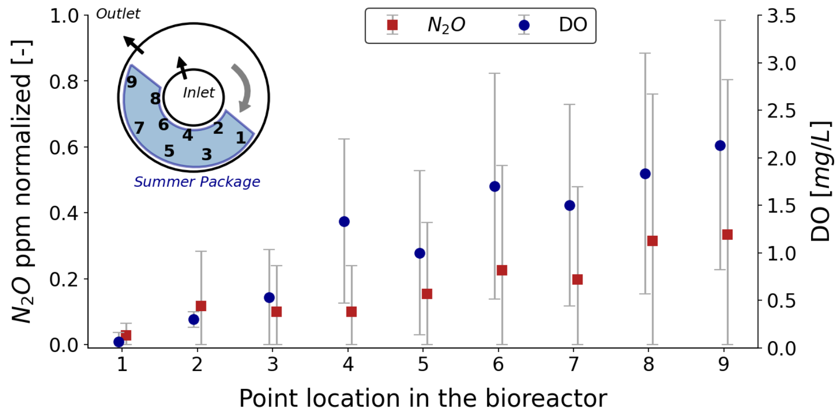
Figure 6: Data from a measurement campagin carried out in July 2020 with the application of the mitigation strategy and the results of the N_2O risk assessment modelling for the same period for San Colombano WRRF.

In summary, the measured data and the N_2O risk assessment results show significant variations in the DO concentrations that lead to having both low DO and high DO risk regimes frequently. Nevertheless, the low DO risk is dominant throughout the plant operation. However, not a lot of instances with high emission are observed during low DO periods. Even though the risk and the emission are not expected to correlate all the time, this can suggest that the emission is prevented in most cases which might be due to local variations in DO profile that is not reflected in the DO probe data. The CFD-biokinetic coupled with the risk assessment model provided valuable insights on the mixing conditions. In particular, it showed that although the high DO risk is dominant when the ammonia is consumed, some regions can still provoke low DO risk conditions specially near the beginning of the aeration zone. In addition, the N_2O emissions might be happening already in the last two compartments of the anoxic zone due to high DO conditions because of the back flow from aerobic zone. Although strategies for reducing high DO risk was not tested in practice, a mitigation strategy for avoiding low DO conditions was tested both with flow sheet model and in a measurement campaign. The results showed noticeable improvement in both risk and emission reduction.

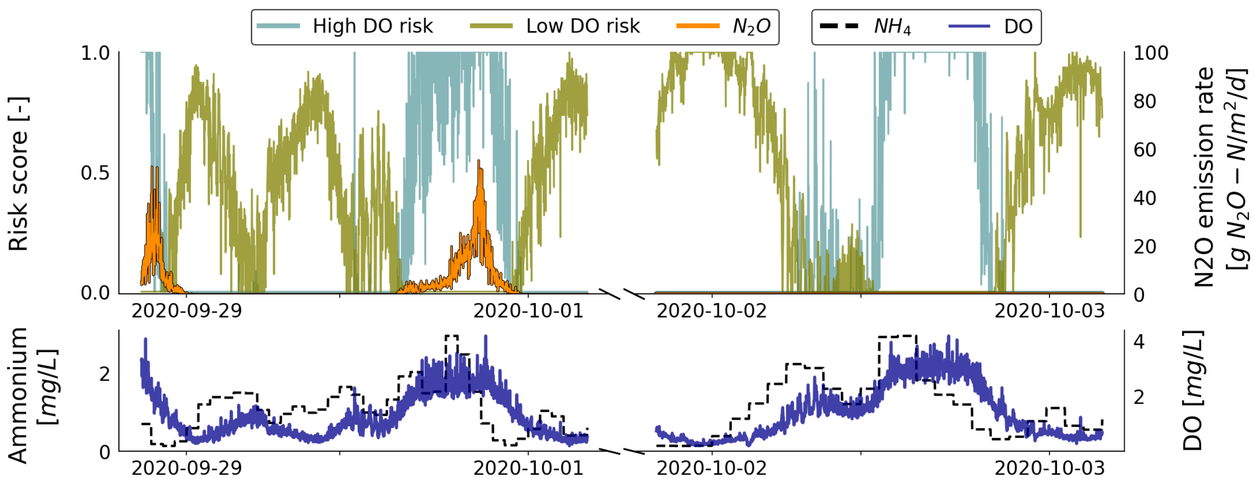
Case study: Eindhoven WRRF, The Netherlands

A measurement campaign was carried out at the Eindhoven WRRF in September-October 2020. The results of the spatial mesurement through the point tests at various locations in the aeration zone (Figure 7a) of the bioreactor show considerable varioations in both average DO concentrations and N_2O concentrations in the off-gas. Generally, DO and N_2O concentrations increase moving from the beginning towards the end of the aeration zone. It seems that high DO concentrations are providing more favorable conditions for N_2O emissions here. This can be related to the increase in ammonium oxidation towards the end of the tank with higher DO concentrations (due to higher nitrification rate). The dynamic data collected through the stationary tests (with fixed location of the LESSDRONE in the center of the aeration zone between points 4,5, and 6) appear to have high fluctuations of DO concentration over time (Figure 7b). However, N_2O emission is generally low and only occasional peaks are visible in the data. The N_2O risk assessment modelling framework was applied to the collected data from Eindhoven. It can be seen (Figure 7b) that under normal operating conditions of the plant both high DO risk and low DO risk are present without one being the predominant one for the entire period of testing. Most of the time the DO concentration is either too high or too low so that the risk of N_2O emission remains high in a lot of instances. These results indicate a need to assess the N_2O production in more detail by considering the local variations, the specific nitrification rates which can be linked to ammonia concentrations, and the location of the DO probe that might impact the measurements.

The CFD-biokinetic model of Eindhoven bioreactor showed high variations in the DO concentration profile across the bioreactor (Figure C.2.1). Therfore, the integrated CFD-risk assessment model was also applied to this case.



(a)

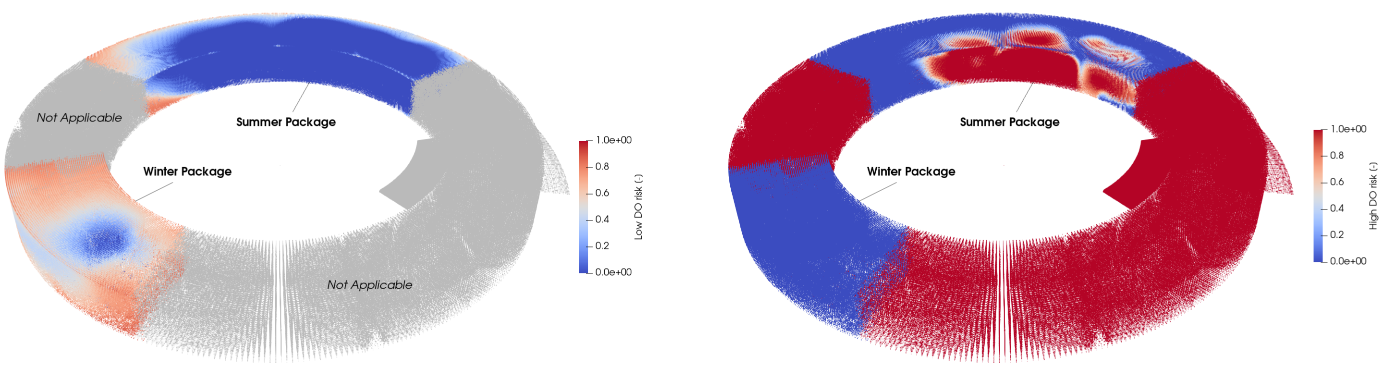


(b)

Figure 7: N_2O risk assessment modelling results for the Eindhoven WRRF under normal operating conditions. (a) The results of the point tests at various locations across the bioreactor. N_2O concentrations in the off-gas are measured in *ppm* and normalized based on the maximum value observed during the whole period of the measurement campaign (b) N_2O risk assessment modelling results.

The winter package and the beginning of the summer package mostly show high risk due to low DO concentrations (Figure 8a), and the risk decreases in the direction of flow with the lowest risk near the end of the bioreactor (end of summer package). This supports data from previous N_2O measurement campaigns where higher emissions at the beginning of the aeration zone were seen. The low DO risk factor does not exist in the parts of the bioreactor where there are no diffusers (and they act almost like an anoxic zone) because the lower the DO concentration is for the denitrification, the better it is for avoiding N_2O productions. The high DO risk in the aerobic zone (Figure 8b), is mostly restricted to one larger area at the end of the reactor (middle to end of the summer package). This can be compared to the period in Figure 7b where the DO concentration is high (more than 2 mg/L) and a peak of N_2O was observed after the ammonia peak in high DO risk regime (based on LESSDRONE measurements collected in the middle of the aeration summer package). The integrated CFD-risk model confirms the possibility of N_2O being produced simultaneously from low DO, and from high DO concentrations (so from both AOB pathways) in different parts of the bioreactor. Ribeiro et al. (2017) observed the same pattern where highly dynamic DO conditions triggers both incomplete hydoxylamine oxidation and AOB denitrification during the nitrification process. This means that lowering DO to mitigate High DO risk can exacerbate the Low DO risk in the other part of the bioreactor. The high DO risk shows high values in the anoxic zones of the bioreactor. This can be explained by the average DO concentrations in those regions which is not significantly low (0.67 mg/L). However, it is important to keep in mind that high risk does not equate to high N_2O emissions 100 percent of the time and that the CFD simulations shown below are an instantaneous snapshot in time. At this specific time step/snapshot, it was observed that the nitrate concentrations in the anoxic zones were low, which means that there is not a lot of N_2O to be produced due to incomplete heterotrophic denitrification from high DO conditions (Ahn et al., 2010, Kampschreur et al., 2009).

As a result, when mitigating N_2O by reducing low DO risk for Eindhoven WRRF, the DO setpoints need to be picked carefully so high DO concentrations do not dominate and then risk starts to increase from high DO. This advanced modelling approach led to a better understanding of how hydrodynamics can potentially impact N_2O production/mitigation and predictions of N_2O risk.



(a) (b)

Figure 8: CFD-biokinetic integrated with risk assessment model for Eindhoven WRRF. a): Low DO risk b): High DO risk. Low DO risk factor does not exist in the anoxic zones (gray area in figure a)

As a potential mitigation strategy, reduction of the DO control range was proposed. This means the maximum DO setpoint needs to be decreased and the minimum DO setpoint needs to be increased. Therefore, the maximum and minimum DO setpoints were changed to 3 mg/L (from 5 mg/L) and 1 mg/L (from 0.5 mg/L) respectively. This new scenario is first tested with the calibrated and validated flow sheet model of the plant to see the impact of DO setpoint change on the performance of the treatment process. The simulated DO concentrations by the flow sheet model for the proposed mitigation strategy was then used as the input of the N_2O risk assessment model to investigate high DO and low DO risk conditions under new DO profile. The results (Figure C.1.4) show the output of the models for DO concentrations, effluent ammonia and N_2O risk scores comparing the base case scenario with normal operating condition and a new scenario with the application of the mitigation strategy. Although on some occasions the ammonia concentration in the effluent is higher than the base case scenario, overall the performance of the treatment is not significantly compromised (average ammonia removal dropped from 94.2% to 93.5%) which suggests that the potential mitigation strategy could be implemented while maintaining acceptable removal efficiency. Moreover, the new controller settings was able to reduce the risk of N_2O emission. The percentage of time for high DO and low DO risks of greater than 50% were reduced by 5% (from 16% to 11%) and 12% (from 43% to 31%) respectively. In addition, the new control settings led to about 5% reduction in aeration energy consumption.

Figure 9 shows the result of the risk model based on the data collected with LESSDRONE during a measurement campaign in which the proposed mitigation strategy has been applied. The test started under normal operating condition of the plant and after one day the mitigation strategy was applied. Then the setpoints were set back to the previous values under normal operation for another day and after that the mitigation strategy was once again tested. It can be seen that in both cases where the mitigation strategy is applied the risk of N_2O emission due to both high DO and low DO conditions are significantly reduced. The percentage of time for high DO and low DO risks of greater than 50% during the implementation of the new control strategy were in fact reduced by 12% (from 22% to 10%) and 14% (from 40% to 26%) respectively. In addition, the actual energy consumption for the aeration is reduced by 3600 $MWh/year$ (2991 $tCO_2eq/year$ of indirect emissions). However, during the first period of applying the mitigation strategy, there is still a peak of N_2O emission visible. Looking at the data of the ammonia and nitrate and comparing them to the second period in which the mitigation strategy was applied, it is difficult to formulate a hypothesis on what exactly is the cause of this N_2O peak. It is important to mention that this period of testing was heavily influenced by rain events. The presence of rain event may have made the controller work sub-optimally. Nonetheless, looking at the actual N_2O emission data, the percentage of time during which N_2O emission is observed was reduced from 22.8% for normal operating condition period to 4.5% during the period of mitigation strategy. This shows that a reduction in the risk scores for both low DO and high DO conditions contributes to having lower N_2O emissions in general with the application of the proposed mitigation strategy.

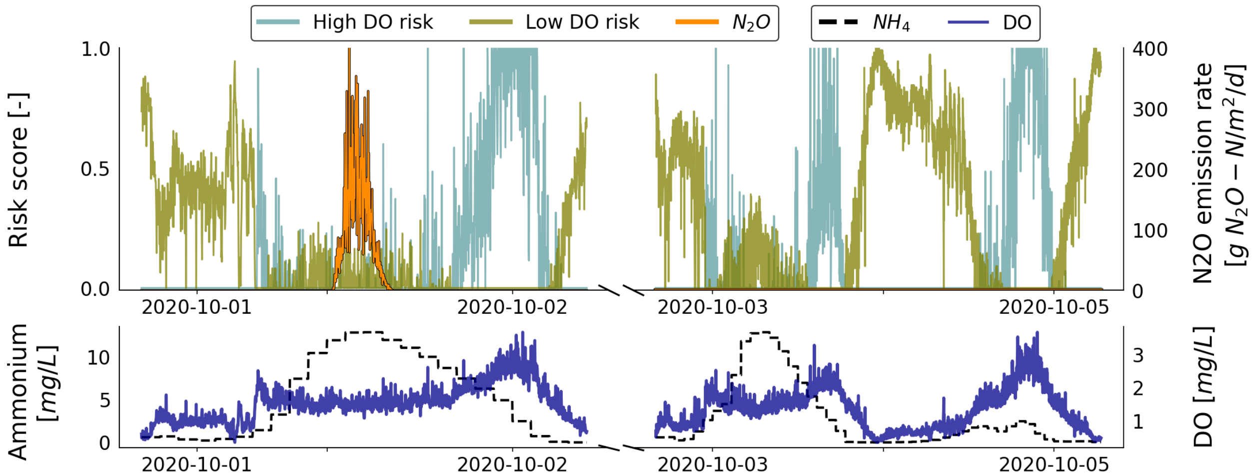


Figure 9: N_2O risk assessment modelling results for the Eindhoven WRRF with the application of the proposed mitigation strategy. The mitigation strategy was applied once beween 2020-10-01 and 2020-10-02 and then again between 2020-10-03 and 2020-10-05. The period between them (not shown in the graph) was operated with the original DO set point range.

In this case, the risk assessment model showed that both high DO and low DO risk conditions are happening frequently and in combination with the measurement data on DO and N_2O emissions helped direct the study towards checking local variations. Only two emission peaks were observed during the high DO risk conditions but the risk model suggests that both incomplete hydroxylamine oxidation and AOB denitrification pathways can be triggered by high fluctuations in the DO concentrations. The integrated CFD-risk assessment model provided insights on the impact of DO gradients on the local N_2O emission risk and how application of a certain mitigation strategy (e.g. reducing the DO set point in the aeration control) could potentially have negative impact on other regions inside the bioreactor. The validated flow sheet model allowed testing the proposed mitigation before the implementation and showed that the performance of the treatment process is not compromised by that. In addition, it provided valuable input on how the mitigation strategy potentially reduce the risk of N_2O emissions due to either high DO or low DO regimes.

LESSWATT protocol

Based on the step-wise analysis of the different case studies and the subsequent insights that were obtained, a protocol is proposed for a structured exploration and diagnosis of operational and control strategies leading to unwanted N_2O emissions. The main objective of the LESSWATT protocol is to target CF reduction of WRRFs by minimising N_2O emissions and energy expenditure.

Figure 10 shows the scheme of the LESSWATT protocol with the corresponding data requirements for each step.

After defining the specific objective of the project, boundaries of the modelling study need to be selected (step 0). In some cases, only a part of the treatment line might have to be considered. For instance, assessing only the aeration zone might be sufficient when the N_2O emission is dominant in this section.

In the first step (1a), an N_2O risk assessment modelling framework (Porro et al., 2014) is used to assess whether certain operating conditions create an elevated risk of N_2O. Initially, the risk model is applied to historical data (using available sensor data at the plant or by conducting a measurement campaign to collect high frequency data) to evaluate current operational strategies. Alternatively, a more detailed analysis of the system's emission risks is achieved by coupling the N_2O risk model to a flow sheet model (step 1b). A calibrated and validated flow sheet biokinetic model of the biological treatment line is developed based on the historical data following the general GMP protocol (Rieger et al., 2012). Note that a flow sheet model is not strictly necessary to apply the N_2O risk assessment and define potential mitigation strategies. However, the use of a flow sheet model has the distinct advantage that more data on additional operational scenarios can be provided to the N_2O risk model and more importantnly it allows virtual testing of possible mitigation strategies.

It might be already possible at this stage to propose a mitigation strategy if the N_2O emission patterns can be explained by high-risk operating conditions detected by the model (going directly to step 4). This can happen for example where the bioreactor is completely and well mixed. So, both the DO and N_2O measurements reliably represent the local concentration profiles inside the bioreactor. However, as was shown by the case studies of San Colombano and Eindhoven plants, this is not always the case. It can happen that the model detects a low-risk condition based on DO measurements but the N_2O data shows high emissions in the same operating condition. In these situations where some difficult-to-explain discrepancies are present, it is important to look at the hydrodynamics and mixing patterns inside the bioreactor using a CFD-biokinetic model (Rehman, 2016). The results of this step show whether the bioreactor is not completely mixed and if there are some dead zones affecting the presence of air in those regions. In case of having very high local variations inside the bioreactor, two important additional steps can be followed. The flow sheet biokinetic model of the plant which is conventionally developed with a tank-in-series (TIS) approach can be updated to a compartmental model (CM) based on the results of CFD-biokinetic model leading to a more accurate description of hydrodynamics in the flow sheet model (step 3a). The second additional step is to use the concentration profiles calculated by the CFD-biokinetic model (instead of the measured data) as the input for the N_2O risk model (step 3b). This integrated CFD-biokinetic-N_2O risk model (Porro et al., 2019) calculates the risk scores for N_2O emission spatially across the bioreactor. As a result, the effect of mixing patterns and local conditions on the risk of emission are identified which will be highly valuable for proposing more complex mitigation strategies. Moreover, these hydrodynamic studies lead to understanding the impact of sensor location in not-completely mixed tanks and how this can be optimised to have a better representation of the dominant reactor conditions.

Combining the results of the risk assessment model (fed by different experimental and simulated data sources) with expert knowledge, one or more potential mitigation strategies are defined for reducing the N_2O emissions and energy expenditure of the plant (step 4). Before applying the proposed mitigation strategies on the full-scale plant (which might entail some risks of sub-optimal performance), they are evaluated by the use of calibrated/validated flow sheet model and/or the CFD-biokinetic model to see the impact of the proposed actions on the performance of the treatment process (step 5). This ensures the ability to implement some mitigation strategies without compromising the treatment efficiency and still being able to meet the effluent quality regulations. Finally, the chosen strategy is applied in practice and if desired, a new measurement campaign can be performed to confirm N_2O emission reduction with the new operational setting (step 6).

There have been many studies on the monitoring of N_2O emissions from WRRFs and potential mitigation strategies that can be applied to tackle that (Vasilaki et al., 2019). These studies focus on testing differnte operational conditions either by implementing them in practice (Mampaey et al., 2016) or by simulating them with the mechanistic models of N_2O emissions (Kampschreur et al., 2009, Ni et al., 2015, Rodriguez-Caballero et al., 2015). Nevertheless, there is no widely-accepted guideline on definition of mitigation strategies that can be applied in full-scale systems and how they impact on the performance of the treatment process (Vasilaki et al., 2019). In addition, the mechanistic models only focus on prediction of N_2O and do not provide much insights on why the emission happens under certain operating conditions. The use of the risk assessment model in the LESSWATT protocol provides a powerful tool on investigating why certain operating conditions of the plants leads to high risk of N_2O emissions. The knowledge base of the risk include all potential factors that impact various pathways of the N_2O emissions. Even though in this study only DO data were used for the risk predictions, it is still an appropriate factor to look at since DO is one of the most important factors on the emissions through both denitrification and nitrification processes and most of the studies in the literature have focused on aeration control strategies and DO concentrations as a mitigation strategy (Vasilaki et al., 2019). Of course, in the presence of data for other risk factors (e.g. nitrite) the risk model can be adapted according to accomodate for that. Moreover, despite the presence of some studies on the spatial variations of the N_2O emission in the bioreactors (Ahn et al., 2010, Ni et al., 2015, Pan et al., 2016), they only focus on point measuremnts at the surface of the bioreactors at different locations. The hydrodynamic studies proposed by the LESSWATT protocol takes advantage of the power of CFD simulations in order to investigate the spatial variations of the risk of N_2O emissions across all directions within the bioreactors. The combination of the risk assessment model with the hydrodynamic studies of the bioreactors provides a valuable way of understanding why and when operating conditions at WRRFs will allow high risk of N_2O emissions.

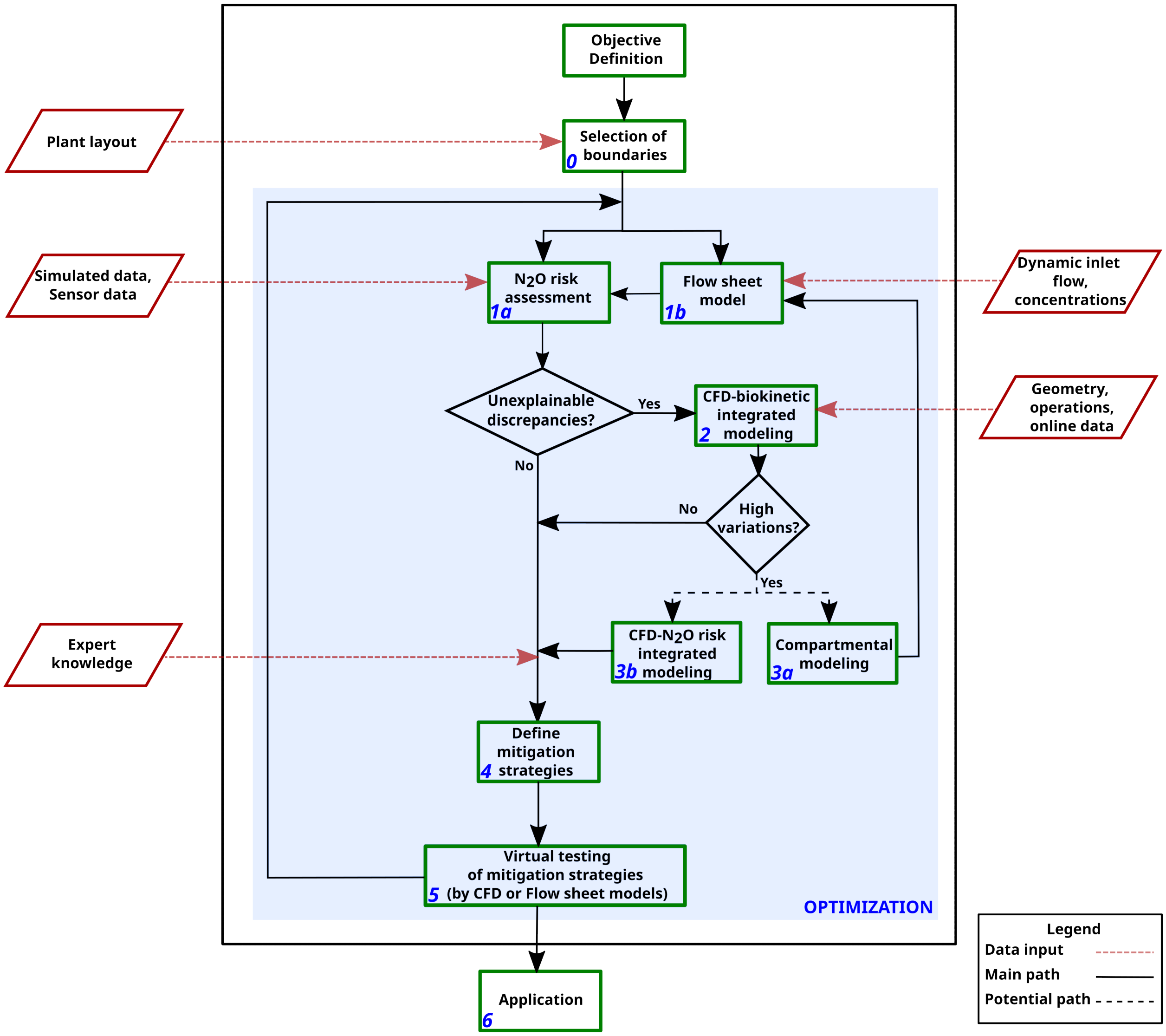


Figure 10: LESSWATT model-based protocol scheme for optimisation of WRRFs targeting CF reduction.

Conclusions

The current study presents a comprehensive approach for optimisation of water resource recovery facilities (WRRFs) focusing on carbon footprint (CF) reduction. Extensive experimental and modelling studies on N_2O emission were performed for three WRRFs with different operating conditions, configurations and geographical locations. These analysis led to the development of an innovative model-based protocol to assist WRRFs in the assessment and mitigation of N_2O emissions. The protocol takes advantage of advanced mathematical modelling tools to analyse the risk of N_2O emissions in WRRFs and to propose mitigation strategies for tackling CF minimisation of WRRFs.

After objective definition and performing a mass balance over the biological treatment line, the LESSWATT protocol proceeds with the application of a knowledge-based fuzzy N_2O risk assessment framework to identify operating conditions under which the risk of direct N_2O emission is high. The risk model can be performed on historical data as well as on simulated flow sheet data. The latter allows for more extensive scenario testing. A mitigation strategy could be potentially proposed at this point. However, in many situations incomplete mixing patterns inside the bioreactors leads to difficult-to-explain discrepancies. CFD-biokinetic integrated modelling (potentially coupled with the N_2O risk assessment model) can provide invaluable insights on the local variations and the effect of sensor location on the collected data. The proposed mitigation strategy/ies can be virtually tested with a developed flow sheet kinetic model and if applicable also with a CFD-biokinetic model to investigate the expected impact of the mitigation strategy on the performance of the treatment process.
The results showed that the use of advanced modelling paradigms proposed by the LESSWATT protocol can help operators and utilities to not only mitigate the direct and indirect GHGs emissions of their plant but also reduce their energy expenditure (and consequently cost) by optimising the performance of their process.

The application of the proposed protocol for three case studies showed that a better understanding of high-risk operating conditions allows to define improved aeration controls leading to around 10% reduction in indirect emission (mainly due to reduction in the aeration energy consumption in WRRFs with over-aeration) and up to 50% reduction in direct emissions (mainly due to reduction in the N_2O emission) of a WRRF on a yearly basis.

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Appendix A Case study: San Miniato WRRF, Italy

A.1 Flow sheet model

A mass balance over the biological section of the treatment plant was built and the flow rates and wastewater compositions of the influent to the bioreactor as well as those of the internal and external recycles were obtained. The historical data of the plant were used to calibrate and validate a modified-ASM1 flow sheet model of the biological treatment line. The plant was modelled using the conventional TIS approach. Overall, the flowsheet model shows a good agreement to the experimental data (Figure A.1.1). The model was calibrated based on the historical data of the plant. Respirometric experiments were carried out in the lab to properly calibrate the kinetic and stoichiometric parameters for heterotrophic and autotrophic biomass.

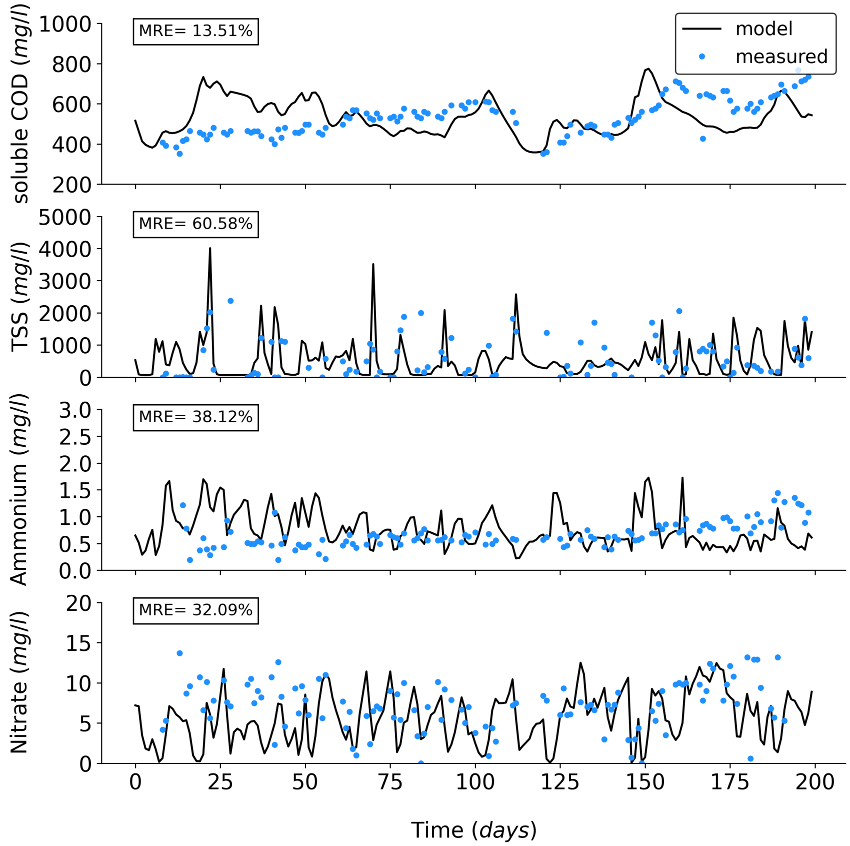


Figure A.1.1: Effluent prediction of the calibrated and validated flow sheet model for Cuoiodepur WRRF compared to the daily grab sample data (2-4 measurements per week). MRE: Median Relative Error. Note: high concentrations of COD and TSS in the effluent are originated from the industrial flow coming to the plant. The effluent goes through the tertiary treatment processes before discharging.

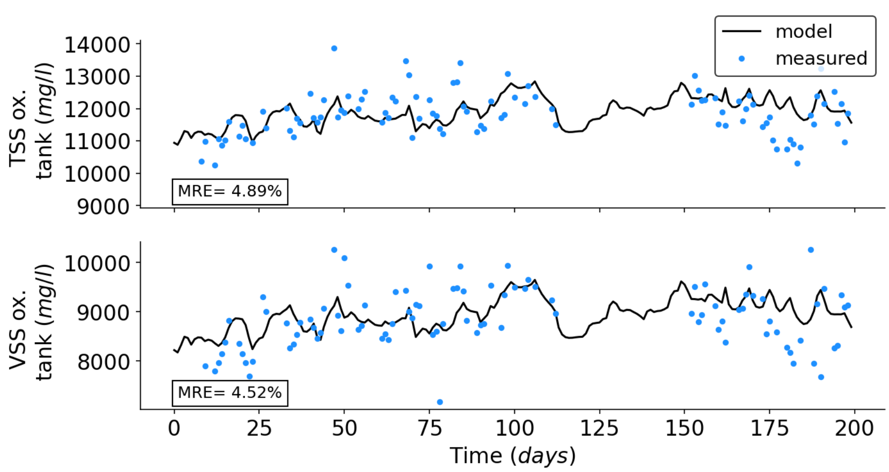


Figure A.1.2: TSS and VSS predictions of the calibrated and validated flow sheet model for Cuoiodepur WRRF. MRE: Median Relative Error.

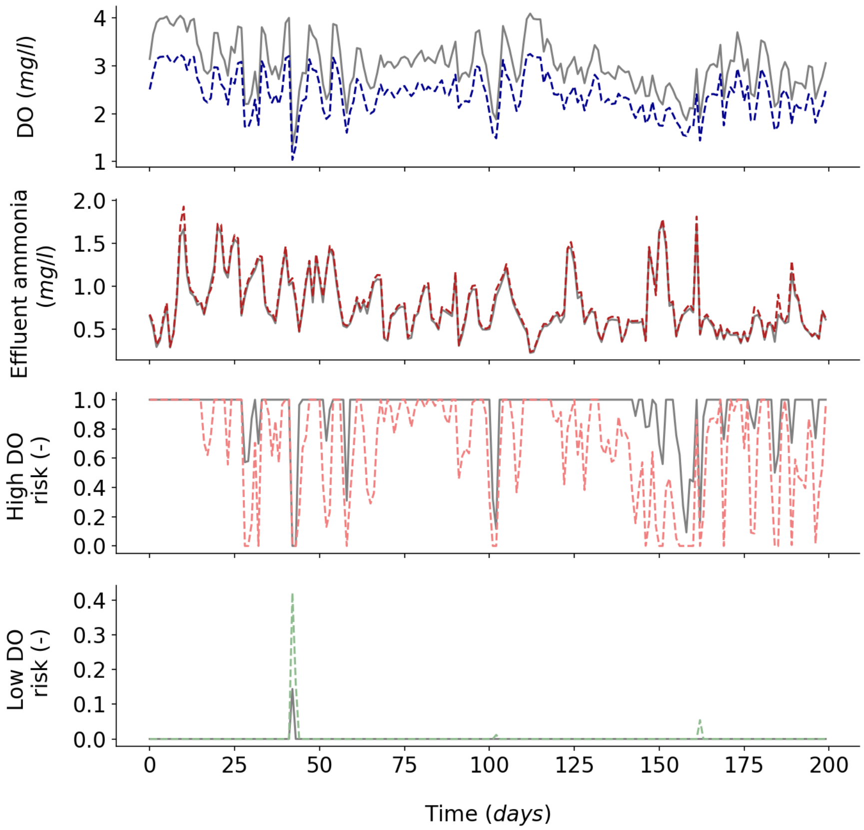


Figure A.1.3: Testing the proposed mitigation strategy using the flow sheet model of Cuoiodepur WRRF and risk assessment model with simulated data, Solid lines: Reference scenario, Dashed lines: mitigation strategy. The DO concentration is the average DO values in three compartments of the aerobic reactor. The higher DO values in the output of the model compared to the DO probe measurement (generally around 2 mg/L based on the controller setpoint) is related to the impact of higher concentrations in the other parts of the tank.

A.2 CFD-biokinetic model

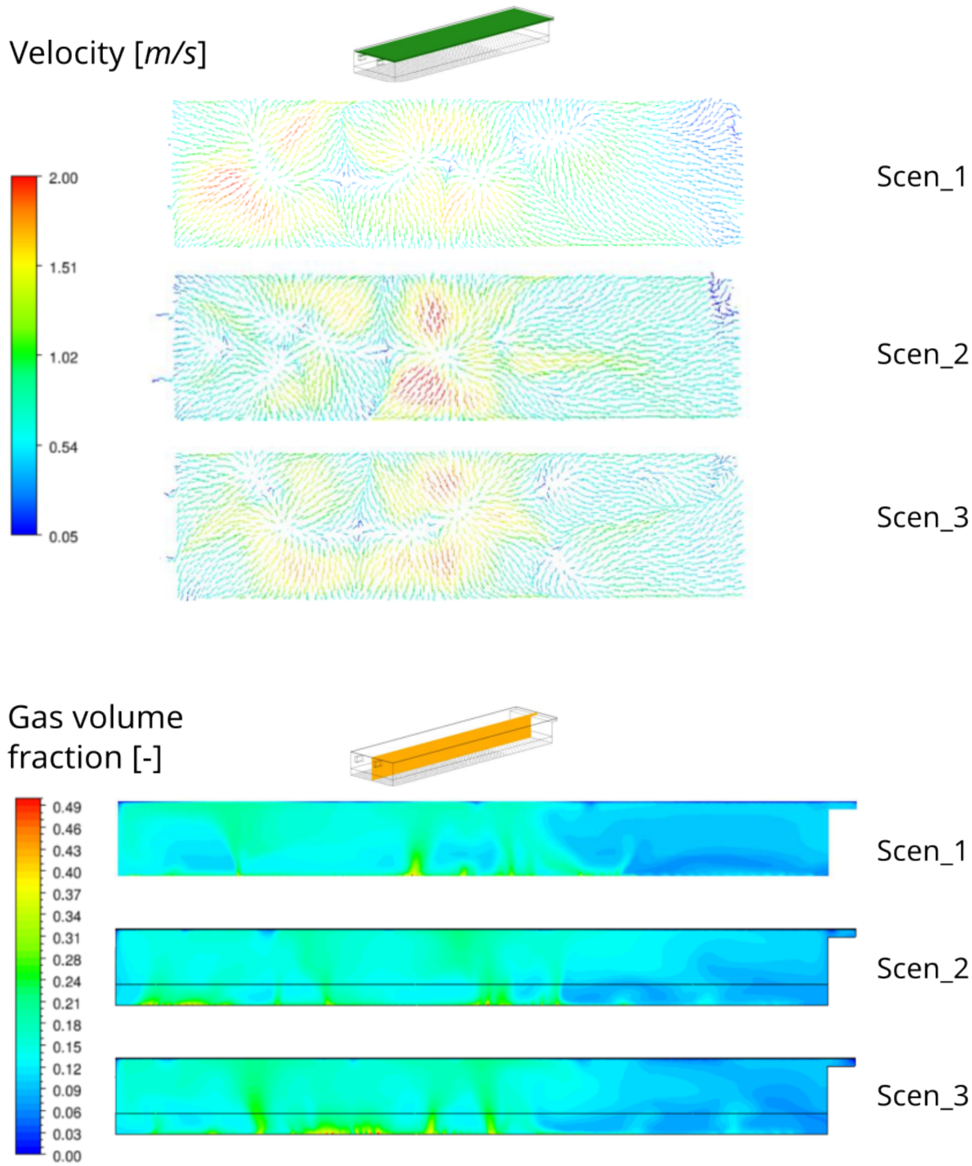


Figure A.2.1: CFD results of Cuoiodepur WRRF aeration tank for Scenario 1 (Scen_1): Low influent, Scenario 2 (Scen_2): Medium influent, Scenario 3 (Scen_3): High influent flow rates.

Appendix B Case study: San Colombano WRRF, Italy

B.1 Flow sheet model

After performing the mass balance of the biological line, all flows and compositions are obtained for the influent to the bioreactor and for all recycle flows. Also in this case, a TIS approach has been considered for constructing the flow sheet model. A modified-ASM3 model has been calibrated and validated based on the historical data of the plant resulting in a good fit between the model output and the measured data (Figure B.1.1) The choice of the ASM version here was based on previous modelling studies that had been done on the plant prior to the start of this study.

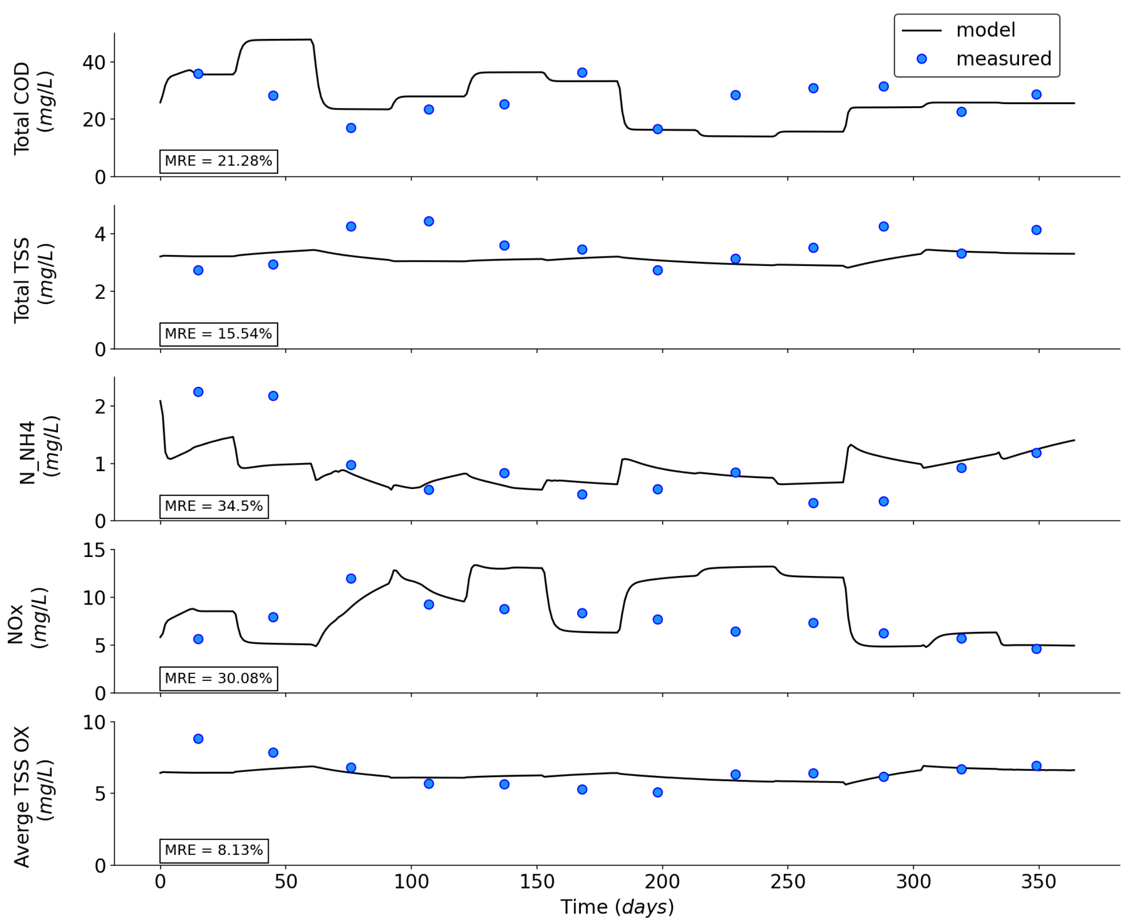
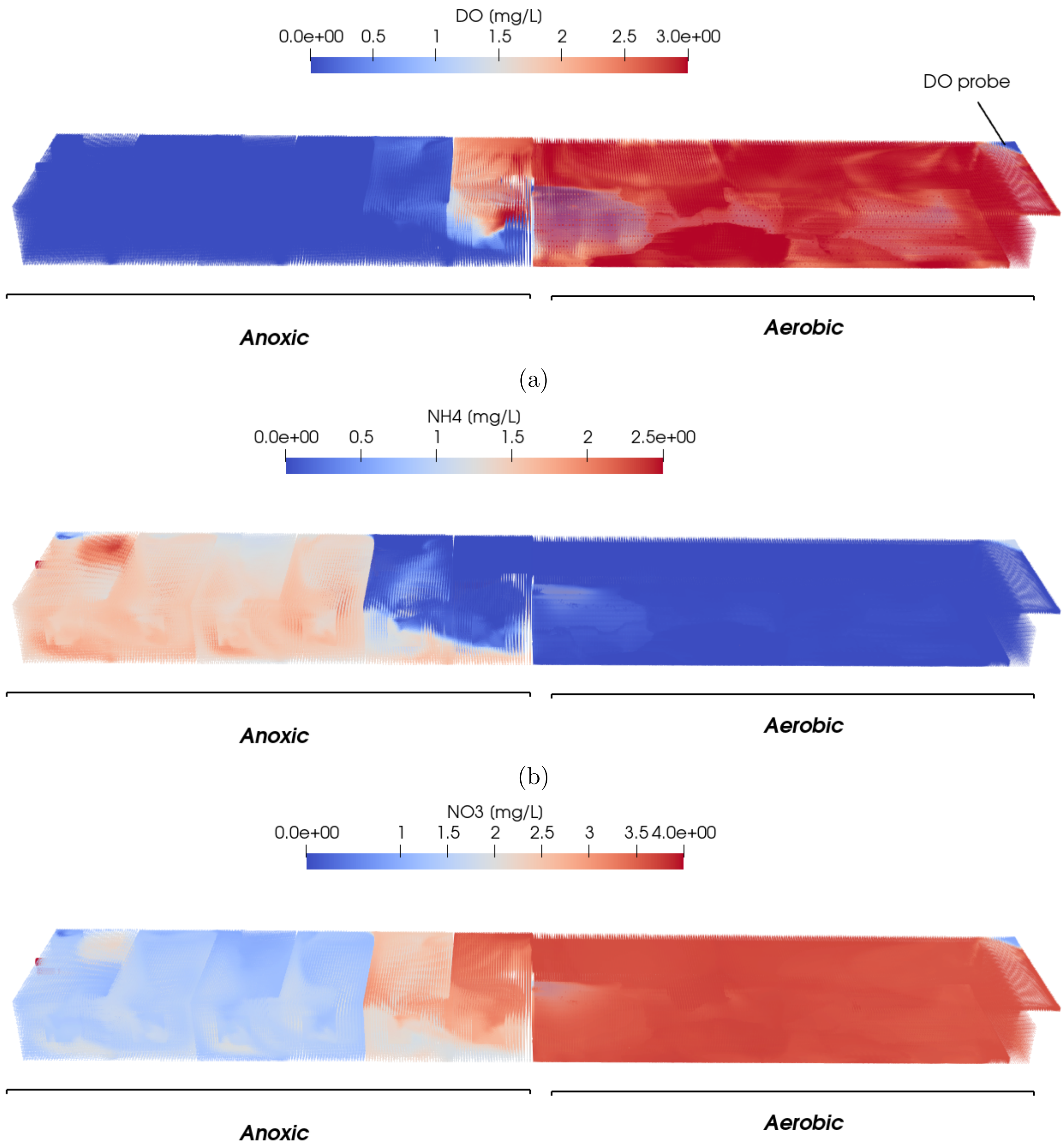


Figure B.1.1: Effluent parameters and Oxidation tank TSS predicted by the calibrated and validated flow sheet model of San Colombano WRRF compared to monthly grab samples. MRE: Median Relative Error.

B.2 CFD-biokinetic model



(c)

Figure B.2.1: CFD-biokinetic results of San Colombano WRRF bioreactor for a) DO, b) Ammonia and c) Nitrate concentration profiles.

Appendix C Case study: Eindhoven WRRF, The Netherlands

C.1 Flow sheet compartmental model

A mass balance on the whole biological treatment line leads to obtaining all required flow rates and wastewater compositions in important parts of the treatment plant like recycle ratios and influent going into the bioreactor. A flow sheet model of the Eindhoven plant has already been developed during past modelling studies. This model is based on ASM2d to describe biological phosphorus removal and was first designed with the TIS approach, calibrated and validated based on the historical data of the plant providing relatively good fit to the experimental data (De-Mulder, 2019). Extensive CFD-biokinetic modelling studies have also been carried out for this plant with the aim of understanding mixing patterns inside the aerobic bioreactor (Rehman, 2016). The outcome of the CFD-biokinetic studies (Figure C.2.1) showed that the circular bioreactor is not completely mixed and there are quite a lot of variations in local DO concentrations. This led to an important update of the flow sheet model by upgrading it to a compartmental model (CM) (De-Mulder, 2019). The whole aerobic bioreactor that was previously modelled as 4 tanks in series is now modelled having various compartments connected to each other through exchange flow rates. Overall, introducing the CM improved the prediction power of the model especially for nitrate prediction which was a weak point of the TIS model (Figure C.1.1-C.1.3). Predictions of DO concentration and air flow rates in the aerobic tank are also significantly improved.

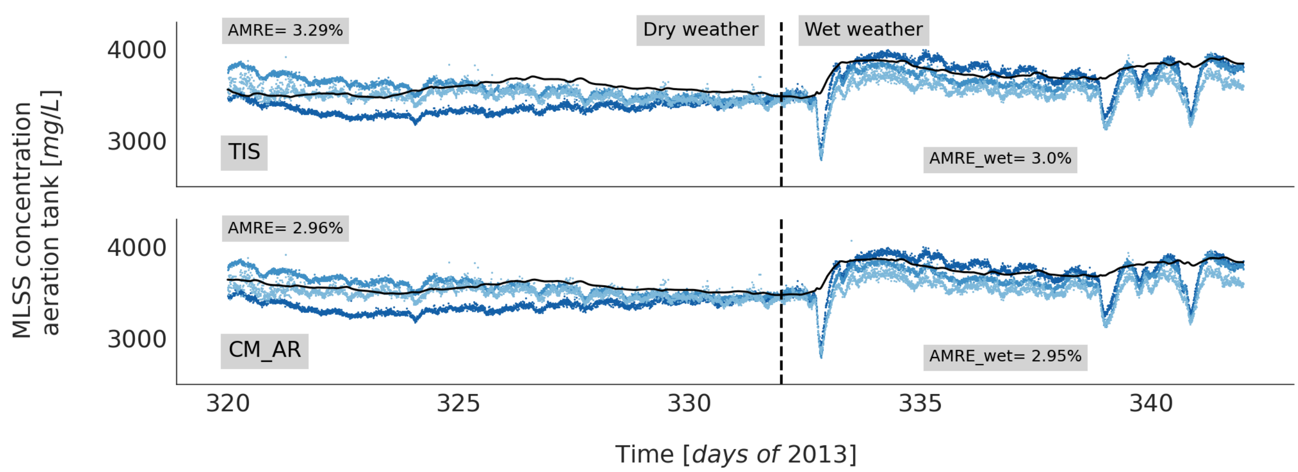


Figure C.1.1: TSS concentration in the aeration tank of Eindhoven WRRF predicted by the calibrated and validated flow sheet compartmental model. AMRE: Average Median Relative Error (over 3 treatment lanes). TIS: tanks-in-series model, CM_AR: compartmental model of the aeration tank.

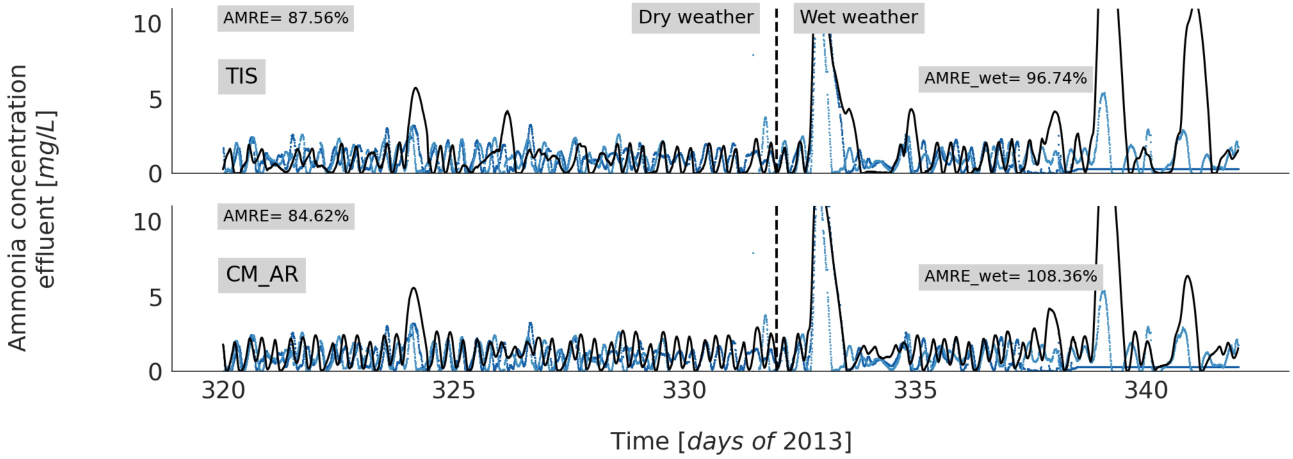


Figure C.1.2: Ammonia concentration in the effluent of Eindhoven WRRF predicted by the calibrated and validated flow sheet compartmental model. AMRE: Average Median Relative Error (over 3 treatment lanes). TIS: tanks-in-series model, CM_AR: compartmental model of the aeration tank.

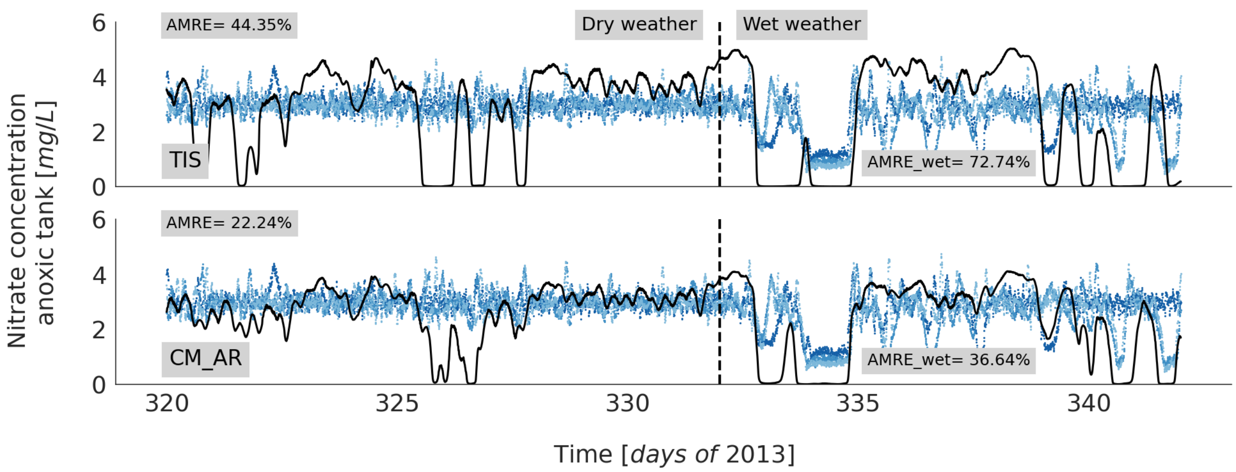


Figure C.1.3: Nitrate concentration in the anoxic tank of Eindhoven WRRF predicted by the calibrated and validated flow sheet compartmental model. AMRE: Average Median Relative Error (over 3 treatment lanes). TIS: tanks-in-series model, CM_AR: compartmental model of the aeration tank.

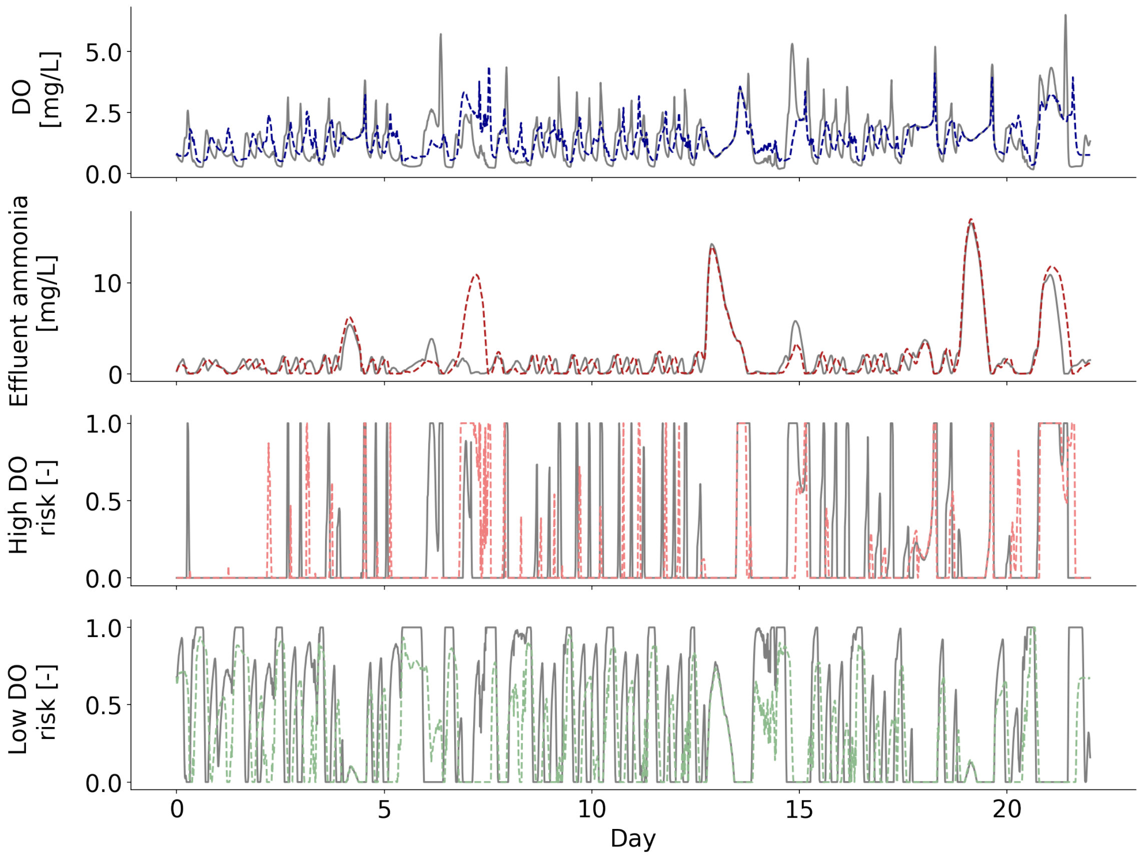
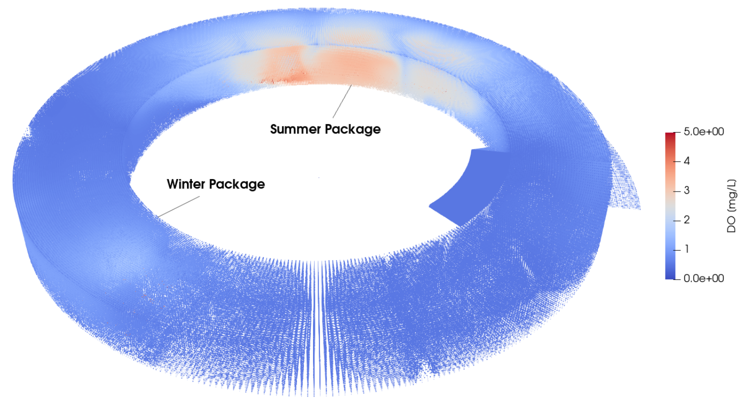
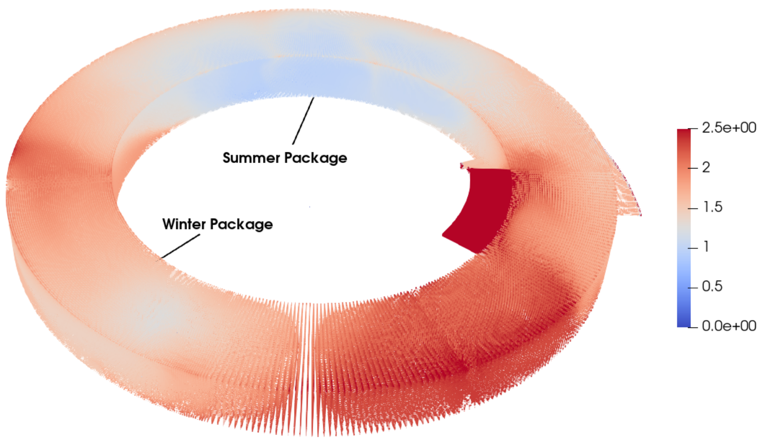


Figure C.1.4: Testing the proposed mitigation strategy using the flow sheet model of Eindhoven WRRF and risk assessment model with simulated data, Solid lines: Reference scenario, Dashed lines: mitigation strategy.

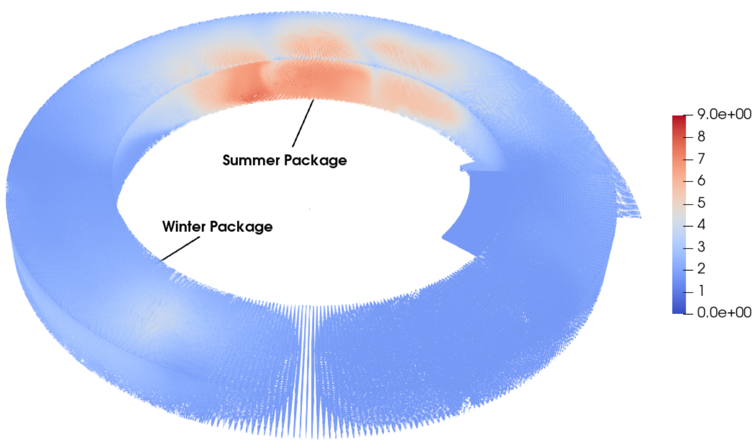
C.2 CFD-biokinetic model



(a)



(b)



(c)

Figure C.2.1: CFD-biokinetic results of Eindhoven WRRF bioreactor for a)DO, b)Ammonia and c) Nitrate concentration profiles.