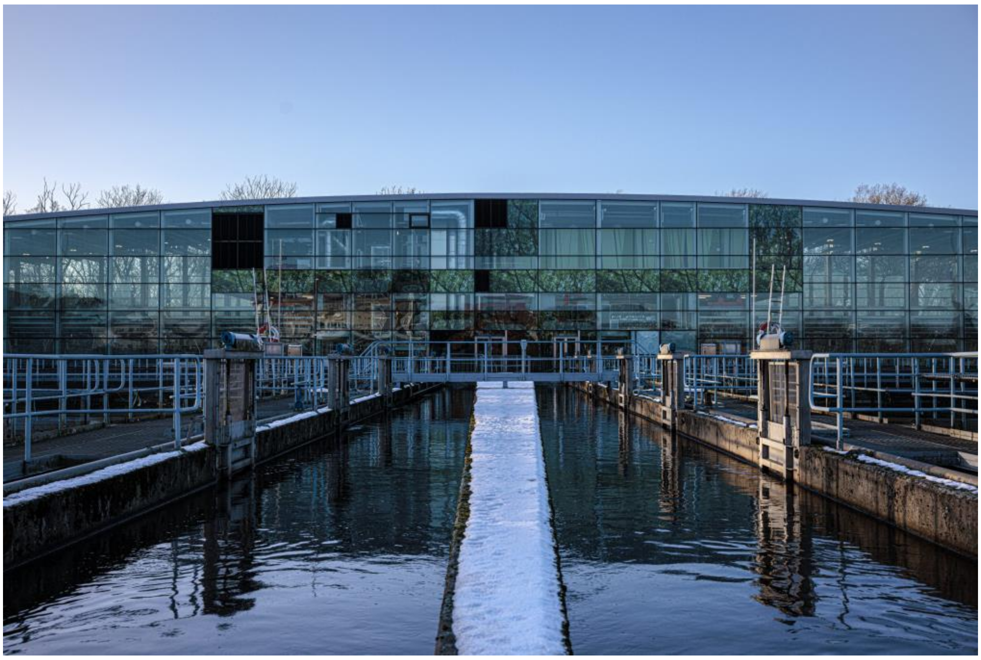

Managing Sustainable Nitrogen Removal from Wastewater

Carbon Sources for Denitrification

Master’s thesis in Infrastructure and Environmental Engineering
& Industrial Ecology

LINNEA KJELLÉN & SOFIA SJÖSTEDT

DEPARTMENT OF ARCHITECTURE AND CIVIL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2025
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MASTER’S THESIS ACEX30

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- Carbon Sources for Denitrification

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and Industrial Ecology

LINNEA KJELLÉN
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ABSTRACT

External carbon sources are essential for effective nitrogen removal in biological post-denitrification at wastewater treatment plants (WWTPs). However, the commonly used fossil-based methanol contributes significantly to the climate impact of WWTPs. This study examined both technical and sustainability aspects of transitioning to more sustainable carbon sources, focusing on methanol and ethanol. Denitrification performance during carbon source transitions was evaluated in laboratory-scale moving bed biofilm reactors (MBBRs), designed to replicate full-scale conditions. Methanol, ethanol, and a methanol/ethanol mixture were tested in a system acclimated to methanol. Results showed comparable performance between the mixture and methanol alone. No major differences were observed when switching from methanol to ethanol. Switching back to methanol resulted in a temporary decrease in performance, suggesting a short acclimation period may be needed. In parallel, a sustainability assessment using a multi-criteria analysis framework was conducted to develop a basis for future evaluation of fossil-free methanol and ethanol alternatives. Relevant options and criteria across ecological, social, and economic dimensions were defined, and both qualitative and quantitative data were collected. Based on the findings, three of the 11 criteria are considered ready for direct application in future assessments. One criterion was excluded due to a confirmed lack of impact, while the remaining seven require additional data or further investigation. All alternatives are recommended for continued evaluation, except recycled ethanol, which requires further testing due to uncertainties related to impurities.

Key words: wastewater treatment, nitrogen removal, denitrification, moving bed biofilm reactor, external carbon source, multi-criteria analysis

Hantering av hållbar kväverening från avloppsvatten

Kolkällor för denitrifikation

Examensarbete inom masterprogrammet Infrastruktur och miljöteknik samt Industriell ekologi

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SAMMANFATTNING

Externa kolkällor används för effektiv kväverening vid biologisk efterdenitrifikation vid avloppsreningsverk. Fossilbaserad metanol som ofta används bidrar dock avsevärt till verkens klimatpåverkan. Denna studie undersökte både tekniska aspekter och hållbarhetsaspekter av övergången till mer hållbara kolkällor, med fokus på metanol och etanol. Denitrifikationsförmågan mellan övergångar av kolkällor utvärderades i laboratorieexperiment som använde sig av Moving bed biofilm reactors (MBBR), utformade för att replikera fullskaliga förhållanden. Metanol, etanol och en blandning av metanol och etanol testades i system som acklimatiserats till metanol. Resultaten visade jämförbar förmåga mellan blandningen och enbart metanol. Inga större skillnader observerades vid övergång från metanol till etanol. Övergången tillbaka till metanol resulterade tillfälligt i lägre denitrifikationsförmåga, vilket tyder på att en kort acklimatiseringsperiod kan behövas. Parallellt genomfördes en hållbarhetsanalys, som delvis följer ramverk för multikriterieanalys, för att utveckla en grund för framtida utvärdering av fossilfria metanol- och etanolalternativ. Relevanta alternativ och kriterier över ekologiska, sociala och ekonomiska dimensioner definierades, och både kvalitativ och kvantitativ data samlades in. Baserat på resultaten anses endast tre av de elva kriterierna vara redo för direkt tillämpning i framtida bedömningar. Ett kriterium bekräftades inte innebära någon påverkan och kan exkluderas framöver, medan de återstående sju kriterierna kräver ytterligare data eller vidare utredning. Alla alternativ rekommenderas för fortsatt utvärdering, förutom återvunnen etanol, som kräver ytterligare testning på grund av osäkerheter relaterade till föroreningar.

Nyckelord: avloppsrening, kväveborttagning, denitrifikation, moving bed biofilm reactor, extern kolkälla, multikriterieanalys

Acknowledgements

We would like to express our sincere gratitude to our supervisor at Chalmers and our mentors at Gryaab for their enthusiasm, valuable insights, and continuous support throughout the project.

Linnea Kjellén & Sofia Sjöstedt, Gothenburg, 2025

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1 Introduction

Today, wastewater treatment plants (WWTPs) face the dual challenge of adapting to more stringent effluent requirements while lowering their carbon footprint.
A significant part of this challenge involves rethinking the use of fossil-based chemicals in treatment processes. This thesis explores how such use can be improved through both practical experiments and a broad sustainability assessment with environmental, social and economic perspectives. The work revolves around a specific WWTP but still provides insights for other treatment plants.

1.1 Background

Nitrogen removal is a critical component of modern wastewater treatment, mainly for preventing eutrophication of oceans and to return nutrients to agricultural processes (Swedish Environmental Protection Agency, 2022). The transformation of nitrogen in wastewater into nitrogen gas can be achieved through nitrification and denitrification processes, such as those implemented in moving bed biofilm reactors (MBBRs) at Rya WWTP (Gryaab, n.d.-a). It is the treatment plant in Gothenburg, operated by Gryaab, that treats wastewater in the larger Gothenburg region.

WWTPs must manage increased loads driven by climate change and population growth while adapting to stricter discharge regulations and striving for greater sustainability (Neth et al., 2022; Sapmaz et al., 2022). Decreasing the use of fossil-based carbon sources is crucial for decreasing the carbon footprint of a WWTP (Gustavsson & Tumlin, 2013). Fossil-based methanol is commonly used as carbon source, for instance in MBBR systems, due to its low cost and high efficiency but poses environmental concerns and potential toxicity risks at high concentrations (Sapmaz et al., 2023; Wang et al., 2021). According to Gryaab (2025), the fossil-based methanol used as external carbon source is the third largest contributor to the climate impact of Rya WWTP, corresponding to 6 000 tons of CO_2-e per year.

Reducing the amount of fossil-based methanol required can be achieved by switching to a non-fossil-based carbon source entirely, or by introducing it in a mix with the methanol. There are many different types of carbon sources you can use, but easily biodegradable chemicals, low-molecular weight are preferable (Fu et al., 2022). In line with this and what is believed to work best at Gryaab, only methanol and ethanol are relevant to this context. In particular, bio-based ethanol emerged as the best potential fossil free carbon source from previous projects including market analysis and simpler sustainability comparisons. Since ethanol is a well-established carbon source (Fu et al., 2022), there is no point in direct comparisons of methanol and ethanol. Further, the technical function with bio-based or fossil based should be the same, hence not requiring testing how bio-based versions compare to fossil versions. How the presented solution with switching to ethanol or to a mix of ethanol and methanol works in practice remains to be determined. To the authors' knowledge this has not been examined in MBBR systems before. Examining the transition from ethanol back to methanol, is also relevant to know more about the implications of switching overall and can potentially help WWTPs make more informed choices of carbon source in case of market availability shifts.

There are many different product alternatives of fossil-free methanol and ethanol available on the market. While the previous comparisons at Gryaab brought forth potential candidates, and to some extent included comparisons between aspects such as cost, technical performance and safety, a more in-depth analysis of the performance and environmental, social and economic sustainability is needed.

Ultimately, the challenge is to determine how switching between methanol and ethanol works in a biological system acclimated to methanol as well as determining which products and sustainability aspects should be considered. This is what this thesis will cover and therefore aid in the research of more sustainable wastewater treatment.

1.2 Aim and objectives

The aim of this thesis is to aid WWTPs in transitioning to sustainable external carbon source usage in post-denitrification processes, by examining process performance when switching carbon sources and assessing relevant carbon source alternatives through sustainability perspectives.

There are two objectives. The first objective is to evaluate, through lab-scale experiments, whether ethanol can be successfully introduced into a post-denitrification process originally designed for methanol, followed by a return to methanol. The comparison includes methanol acting as a reference, alternating between methanol and ethanol, and alternating between a mix of methanol and ethanol. The sub-objectives related to this part are:

- Evaluate key performance indicators for the carbon sources alternatives such as denitrification efficiency, denitrification rate and carbon utilization.
- Assess whether the carbon source transitions have considerable impact on the treatment process.
- Compare and relate performance indicators to existing literature and full-scale WWTP data.
- Provide recommendations for further research on carbon source substitution in denitrification processes.

The second objective is to evaluate and compare several carbon source alternatives through a sustainability analysis, covering environmental, social, and economic dimensions. This is performed using a multicriteria analysis (MCA) approach, with the aim of developing an evaluation basis for future selection. The related sub-objectives are:

- Identify and define relevant external carbon source alternatives.
- Establish a comprehensive list of sustainability criteria for evaluation.
- Gather qualitative and quantitative data to create the evaluation basis.
- Identify key areas for further research and provide guidance on which aspects WWTPs should prioritize for future investigation.

1.3 Limitations

The thesis focuses on carbon source alternatives best suited for Rya WWTP. The process and results are therefore influenced by local considerations relevant for Gryaab. The sustainability analysis includes carbon source alternatives selected from a prior market analysis at Gryaab and does not cover all available products on the market. While the multicriteria analysis (MCA) structure was followed, actual weighting, scoring, and aggregation of results were not performed within the scope of this study. The evaluation basis developed with the MCA methodology in this thesis aim to support future evaluation and decision-making processes.

The laboratory scale experiments focused on the nitrogen removal efficiency. Internal reactor conditions (e.g., pH, temperature variations) and external conditions (e.g., inflow fluctuations) were not fully monitored. Sampling was limited to grab samples.

2 Theory

This section presents the theoretical background relevant for the thesis. It gives an overview of wastewater treatment in general, and with a focus on biological nitrogen removal. It also describes the treatment process design of Rya WWTP including the treatment system moving bed biofilm reactor (MBBR). The post-denitrification MBBR system of Rya WWTP is presented in more detail. The subject regarding different types of fossil-free versions of the carbon sources methanol and ethanol is briefly introduced. Finally, the general methodology of multicriteria analysis is outlined to give context to the sustainability analysis in this thesis.

2.1 Wastewater treatment

Water is an important resource in human societies, and it is thus important to maintain its quality. The water taken from ground- or surface waters will ultimately be returned to the environment after human use (Metcalf & Eddy, 2004; Sonune & Ghate, 2004). This used water is called wastewater. To avoid environmental pollution, wastewater must be treated before being released back into water bodies.

Wastewater can originate from domestic facilities such as households, offices, and schools, but also from industries (Sonune & Ghate, 2004). Other types are stormwater, urban runoff caused by precipitation, and water infiltrating sewage pipes through cracks or other defects. These are part of the municipal sewer system. Wastewater generated from industrial processes may need pre-treatment before reaching the municipal sewer system or require separate handling.

Generally, the main constituents of wastewater are different types of organic material, nutrients, pathogens and metals (la Cour Jansen et al., 2021). To remove these, a combination of physical, chemical and biological processes is used (Sonune & Ghate, 2004). To represent different levels of treatment at WWTPs, the terms preliminary, primary, secondary, and tertiary treatment are commonly used (Meng et al., 2024; Sonune & Ghate, 2004). Which constituents that are removed at which treatment level, and examples of treatment methods for different constituents are summarised in Table 2.1.

Table 2.1. Summary of the conventionally used treatment levels, which wastewater constituents that is removed and which main processes that are commonly used. Compiled with information from Metcalf & Eddy (2004), Meng et al. (2024), Jansen et al. (2019), & Sonune & Ghate (2004).

Level of treatment	Constituent/pollutant removed	Main treatment process
Preliminary	Larger, solid constituents such as grit and sticks, as well as grease	Physical/mechanical
Primary	Suspended solids	Physical
Secondary	Colloidal and dissolved organic material and nutrients	Biological and chemical
Tertiary	Remaining small particles, pathogens	Varies. Combinations of the above or other methods.

Biological wastewater treatment is based on the principle of microorganisms, mostly bacteria, transforming or removing compounds such as organic matter and nutrients present in the wastewater (Metcalf & Eddy, 2004). According to la Cour Jansen et al. (2019), the two main biological treatment methods are activated sludge and biofilters. In activated sludge, reactors contain a sludge consisting of living biomass (bacteria and other microorganisms) as well as inorganic and organic particles. The sludge is kept suspended by stirring or aeration. In biofilter methods, the bacteria are instead densely fixated onto a surface in the form of a so-called biofilm. Sufficient contact between the biofilm and the wastewater is important for pollutant removal and there are different techniques as to how this can be ensured. One is where the medium onto which the biofilm grows is fixed and the water is distributed onto the medium, as in the technology trickling filters; another is where the medium is moving through water, as in the technology moving bed biofilm reactor (MBBR). These biological methods can be used for removal of organic matter and the nutrient nitrogen.

Municipal wastewater is along with agriculture one of the main sources of excessive environmental concentrations of nitrogen (Rahimi et al., 2020). High concentrations of nitrogen being released into freshwater environments can lead to eutrophication. This can in turn lead to algal blooms and oxygen depletion, which ultimately negatively affect aquatic life. Hence, removal of the nitrogen from wastewater is of importance.

2.1.1 Biological nitrogen removal

Nitrogen naturally occurs in several forms and oxidation states, and is a crucial element for microorganisms, plants and animals (Metcalf & Eddy, 2004). Its most commonly occurring forms are ammonia (NH_3), ammonium (NH_4^+), nitrogen gas (N_2) and nitrate (NO_3^-). There are multiple routes in which the nitrogen species are converted from one form to another. The different forms of nitrogen and the pathways between them are typically described with the nitrogen cycle, a simplified version of this is depicted in Figure 2.1. Utilisation of the two processes nitrification and denitrification is commonly used in biological nitrogen removal methods.

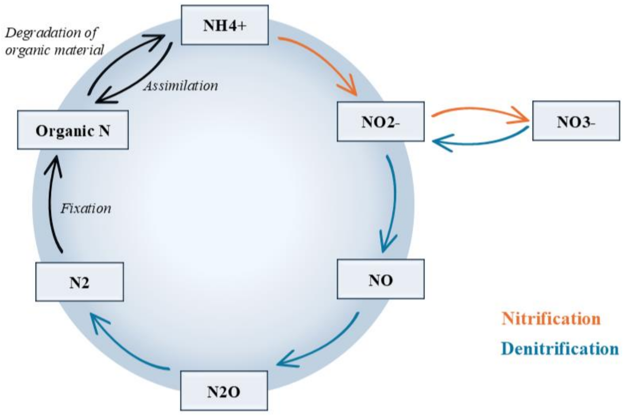

Figure 2.1. Simplified version of the nitrogen cycle, inspired by la Cour Jansen et al. (2021).

Nitrification is a biological process consisting of two steps, where the first step involves ammonium, NH_4^+, being oxidised to nitrite, NO_2^-, by ammonia-oxidising bacteria (AOB) (Rahimi et al., 2020). Secondly, nitrite-oxidising bacteria (NOB) oxidise nitrite to nitrate, NO_3^-, in the presence of oxygen. The second step is faster than the first, making the first reaction the limiting step. The bacteria performing the nitrification steps are groups of autotrophic AOB and NOB, using oxygen as the final electron acceptor (Rahimi et al., 2020). They gain their energy from the ammonia oxidation and acquire carbon from CO_2.

In the denitrification process, bacteria convert nitrate into nitrogen gas, N_2, through the creation of several intermediate products (Meng et al., 2024). The reaction chain can be summarised as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

The denitrification process is anaerobic, since nitrate is used as electron acceptor (Jansen et al., 2019). Many of the denitrifying bacteria can use oxygen as terminal electron acceptor as well, and therefor anoxic conditions are required for the denitrification process to take place (Rahimi et al., 2020; Jansen et al., 2019). Denitrification can be performed by both autotrophic and heterotrophic bacteria, however, heterotrophic denitrifies are more commonly occurring (Rahimi et al., 2020). Heterotrophic bacteria, in contrast to autotrophs, use organic carbon for growth of bacterial cell material (Metcalf & Eddy, 2004). This organic carbon is necessary for denitrification by heterotrophs and cell growth of the bacteria (Rahimi et al., 2020).

The organic carbon used in the denitrification process can either be already present in the incoming wastewater, generated within the wastewater treatment system (at the plant) due to bacterial cell decay, or externally added to the system (Swinarski et al., 2009). External source of organic carbon usage is usually needed when the organic matter content in the influent water is too low, or when the denitrification treatment process is separated from and placed after an aerated treatment process, since the organic material gets consumed in these processes (Fu et al. 2022; la Cour Jansen et al., 2021). Post-denitrification is a used term for when the denitrification treatment process is placed after the aerated nitrification process.

That carbon source substrates have low molecular weight is an important property, since it generally correlates with higher biodegradability by bacteria (Fu et al., 2022). Commonly used carbon sources are for example methanol, ethanol, acetate and glucose (Rahimi et al., 2020). The populations of denitrifying bacteria vary depending on what carbon source is used (Meng et al., 2024). Some populations are more abundant using ethanol, methanol or acetate while others are only more abundant when glycerol is used. The ratio between organic material and nitrogen (C/N ratio) is one of the important parameters affecting the denitrification process (la Cour Jansen et al., 2021). It directly affects the denitrification rate, since it represents the ratio between electron donor and electron acceptor (Güven, 2009). Generally, a C/N-ratio of about 3.5–4.5 is considered sufficient for complete denitrification.

Three commonly used measures of the organic content in water are chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) (Metcalf & Eddy, 2004):

- COD is defined as the oxygen equivalent to the organic material available for chemical oxidation in a water sample (Metcalf & Eddy, 2004). There is no clear definition of soluble and particulate fractions, however, a general partitioning can be made through filtering of the sample. The COD-concentration can potentially include oxidation of inorganic substances as well, due to the measuring method.
- BOD is defined as the amount of dissolved oxygen consumed by microorganisms for biochemical oxidation of organic material (Metcalf & Eddy, 2004). The measurement is dependent on time, with a measurement taken over 5 days being labelled as BOD_5 (Jouanneau et al., 2014). In Sweden, BOD_7 is the standard, whereas in most other parts of Europe, BOD_5 is more common (Swedish Agency for Marine and Water Management, 2016).
- TOC is defined as the total organic carbon present in a water sample (Metcalf & Eddy, 2004). Dissolved organic carbon (DOC) is the measured organic content in which the sample have been filtered through a 0.45 µm pore size filter.

Too low C/N-ratio in the denitrification process medium can lead to reduced denitrification rates or only a partial reaction (la Cour Jansen et al., 2021). This can also result in an increase in intermediate products such as dinitrogen oxide and a decrease in treatment of nitrate. Increased emissions of dinitrogen oxide are something to be avoided, since it is a potent greenhouse gas significantly stronger than carbon dioxide (Zhou et al., 2025). Each intermediate in the denitrification reaction chain can act as electron acceptor, creating competitive conditions for available electron donors (Güven, 2009). The reduction rates of the different reaction steps, such as the rate of nitrate being transformed into nitrite, are affected by the bacterial culture and the wastewater composition. Generally, however, the nitrite reduction rate (NO_2^- to NO) is slower than the nitrate reduction rate (NO_3^- to NO_2^-). This inconsistency can cause accumulation of nitrite in the denitrification medium. Microbial species composition affects nitrite accumulation in the denitrification process (Du et al., 2016; Meng et al., 2024; Rahimi et al., 2020). Some denitrifying bacteria only inhibit the enzymes for reduction of nitrate to nitrite, and not further steps of the reaction chain. If these are abundant, nitrite accumulation is more likely. Other factors affecting nitrite accumulation are limited carbon, pH, nitrate concentration, oxygen concentration and toxic compounds (Rahimi et al., 2020).

2.1.2 Moving bed biofilm reactor systems

Moving bed biofilm reactor (MBBR) is one type of biofilm system that can be used for biological wastewater treatment. The main incentive for its development was the need of a compact technology with limited mechanical issues, which earlier biofilm technologies were prone to having (Dezotti et al., 2017; di Biase et al., 2019; Madan et al., 2022).

In biofilm, microorganisms such as bacteria grow on surfaces in a cluster of bacterial cells and extracellular polymeric substances (Dezotti et al., 2017). This creates a protective environment for the microbial community of the biofilm. Additionally, it contains a high variety of microbial functional groups which generally can imply a greater ability for wastewater pollutant removal.

The MBBR technology consists of biofilm growing on small carriers, usually plastic in a hollow cylinder form, which are kept suspended in the water of the reactor (Madan et al., 2022). Reactors with anoxic conditions need mechanical stirring, while in aerobic reactors biocarrier movement can often be caused by the aeration process. In contrast to treatment processes where the biomass is suspended directly in the water (activated sludge), there is no need for recirculation of biomass due to the biofilm being fixed onto the carrier surface and hence remains in the system (Dezotti et al., 2017). This allows the microbiome to become specialised at the system’s intended purpose, such as nitrogen removal.

The MBBR technology have other advantages against methods where the biomass moves freely in the reactor water. A high biomass concentration leads to a higher treatment capacity per volume, resulting in a compact process where smaller reactor volumes can be used (Madan et al., 2020). Additionally, biofilm systems are more resistant to varying conditions such as fluctuations in temperature, pH, and influent characteristics. However, both operation and investment costs of the MBBR system can be high. Maintenance can be expensive if aeration is used for both providing of oxygen and stirring of biocarriers, as well as the initial costs of biocarriers and reactor construction. Stagnant zones can appear if the hydrodynamics of the reactor is not given enough thought, but to which extent these zones affect the treatment capacity is uncertain (di Biase, 2019).

2.1.3 Rya wastewater treatment plant

Rya wastewater treatment plant (WWTP) receives wastewater from 7 municipalities in the Västra Götaland-province, approximately 800 000 people (Gryaab, n.d.-a). The facility removes BOD, phosphorus and nitrogen from the wastewater. Figure 2.2 show the processes and how they are connected.

The incoming wastewater passes through several treatment processes before being released into the recipient Göta Älv river. Firstly, bar screens remove larger parts such as paper and plastics. The water then goes through primary settling before the biological treatment of BOD and nitrogen and simultaneous precipitation of phosphorus. The biological treatment consists of activated sludge, nitrifying trickling filters, post-nitrifying moving bed biofilm reactor (MBBR) and post-denitrifying MBBR. The final treatment step is disc filters. An overview of the treatment processes is seen in Figure 2.2. Sludge recirculation occurs within the activated sludge process. Some sludge is processed again through the treatment plant. The produced sludge that leaves the process steps is treated and can be used for agricultural purposes.

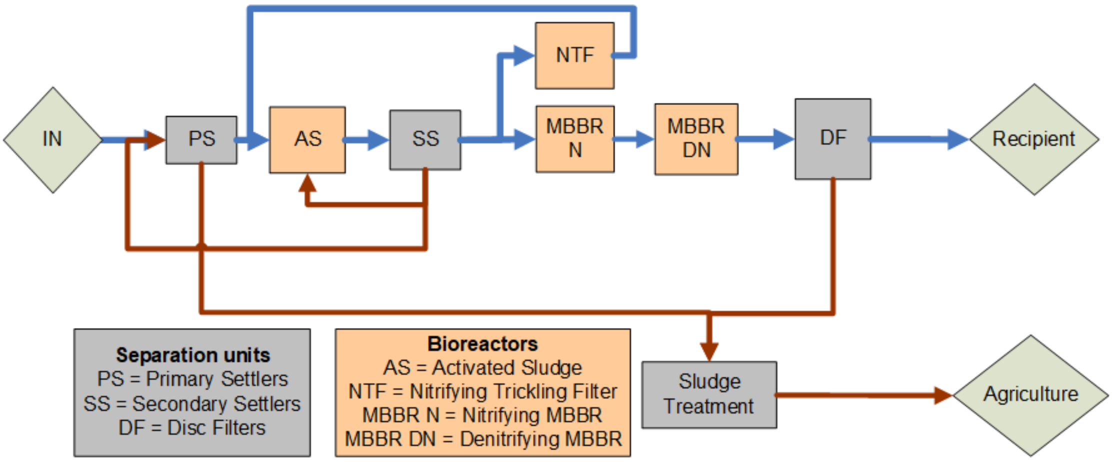

Figure 2.2. Process diagram of the water treatment processes at Rya WWTP.

The post-denitrification is a MBBR system which consists of six basins, so-called lines, each divided into three zones, shown in Figure 2.3. The zones are divided by strainers which allows flow of wastewater but hinders biocarriers. Nitrified water from the trickling filters and nitrifying MBBR is mixed and then distributed into the six lines of the post-denitrification.

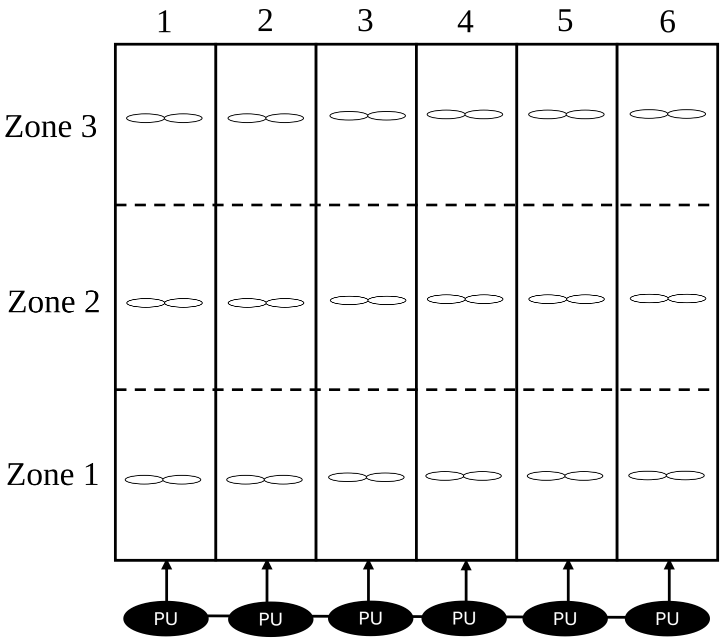

Figure 2.3. Illustration of the lines of the denitrification MBBR process at Rya WWTP, including dosage pumps (PU).

The zones have a filling ratio of 55–58 % carriers, corresponding to about 350–370 m^3. The active area of the biocarriers, that is, the area of the biocarriers onto which the biofilm can grow, is 500 m^2/m^3. Phosphoric acid and external carbon source, currently methanol, is added to the system. These are crucial for the denitrifying bacteria and hence the function of the denitrification process. The external carbon source flow is regulated by the incoming wastewater flow, the incoming nitrate concentration and a set effluent nitrate concentration, as well as the C/N-ratio. Both the carbon source and the phosphoric acid is added into Zone 1. The largest removal of nitrate happens in Zone 1.

2.2 Fossil free versions of methanol and ethanol

Bio-based methanol and ethanol can be produced from biomass that is converted to biofuels through various process. These are categorized as first-generation biofuels which are produced from edible biomass and second-generation biofuels which are produced from non-edible biomass (Bhaskar & Pandey, 2015; Darda et al., 2019; El-Araby, 2024). The first-generation biofuels can be based on for example corn, wheat or sugarcane as feedstock. The second-generation biofuels are made of lignocellulosic biomass from agricultural and forest residues and crops grown for biofuel purposes (Bhaskar & Pandey, 2015; Darda et al., 2019). The forest residues may stem from logging operations or industrial processing of forest biomass (Bhaskar & Pandey, 2015).

Methanol and ethanol can also originate from recycled chemicals, by recovering and processing solvents used in other industries, such as the pharmaceutical sector (Chea et al., 2019). Furthermore, an increasingly common procedure used in the chemical industry is mass-balancing (ISCC, n.d.). It allows the bio-based or recycled feedstocks to be tracked through the whole value chain despite it being mixed with other types of feedstocks.

2.3 Multicriteria analysis

A multicriteria analysis (MCA), or multicriteria decision analysis (MCDA), is a structured decision-making tool used to compare different alternatives based on multiple criteria (Belton & Stewart, 2002; Neth et al., 2023; UK Government, 2009). It is commonly used in sustainability assessments and decision-making processes where options must be evaluated from several perspectives, such as environmental, economic, and social perspectives.

The general MCA process involves defining the problem and objectives, followed by identifying a set of alternatives to achieve those objectives (Belton & Stewart, 2002; Neth et al., 2023; UK Government, 2009). A set of criteria is selected to assess the performance of each alternative. Information of the alternatives is acquired so that each alternative can be scored according to its performance in each criterion, typically using a consistent numerical scale. Weighting is then applied through choosing numerical coefficients to reflect the relative importance of the criteria or differences in performance. An overall score for each alternative is achieved by multiplying its score in each criterion by the corresponding weight, then summing across all criteria. This provides a basis for ranking or selecting alternatives. Finally, the results should be analysed. It is recommended to conduct a sensitivity analysis to tests how changes in scores, weights, or assumptions affect the results which in turn can help assess the robustness of the conclusions. How an MCA process is carried out or by whom can vary. Typically, the process is supported by facilitated workshops involving key stakeholders, especially during scoring and weighting stages.

3 Method

This section presents the methodology used to compare different external carbon sources through laboratory experiments and a sustainability analysis. The experiments are primarily technical while the sustainability analysis covers several perspectives. The alternatives examined in each part differ, but the approaches together offer a comprehensive basis for studying possibilities of switching to lower climate impact carbon source.

3.1 Laboratory experiments

The laboratory experiments investigated the effects of methanol and ethanol as carbon sources in the post-denitrification process. The setup used aimed to reflect the first zone of the post-denitrification process at Rya WWTP as most of the denitrification occurs in zone 1. The methodology for the setup, sampling and analysis and evaluation of the carbon source performance are described below.

3.1.1 Experimental setup

The experiments were conducted using three laboratory-scale continuous stirred tank reactors (CSTR), specifically *Dolly Biogas Reactors* from Belach Bioteknik AB. Each reactor had a total volume of 10 litres. Biocarriers (AnoxKaldnes K1) acclimated to methanol from the first zone of the full-scale MBBR were added. A filling fraction of approximately 50% was used, consistent with full-scale conditions.

The reactors were continuously supplied with influent used in the post-denitrification process. The water passed through an influent buffer tank before being distributed to the reactors via three peristaltic pumps. Each reactor was equipped with an upper and lower stirring blade which was set at constant mixing. All effluent directed to the plant’s wastewater treatment system. See Figure 3.1 for the actual setup and Figure 3.2 for a schematic overview.

Figure 3.1. The experimental setup with reactors and influent arrangement.

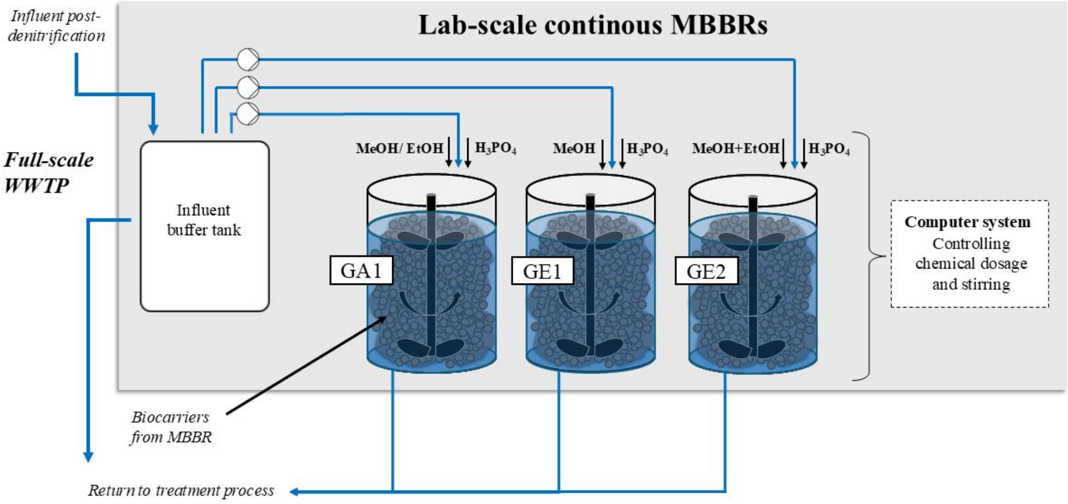

Figure 3.2. Schematic illustration of experimental setup showing what was done in lab-scale and how it relates to the full-scale wastewater treatment plant (WWTP). Including reactor labels (GA1, GE1 and GE2) and flow arrows for water (blue) and chemicals (black).

The experiments were conducted over a period of 82 days between February and May 2025. The average water temperature during the experiment was 16–17°C.

The carbon dosing timeline is summarized in Table 3.1. Initially all reactors were first dosed with methanol to ensure comparability and stable reactor conditions. After this, the first reactor alternated between methanol and ethanol (GA1), the second reactor continued receiving methanol (GE1) and the third reactor alternated between methanol and a mixture of methanol and ethanol (GE2). Transitions from methanol to alternative carbon sources and back were performed once stable reactor performance had been confirmed through analytical results.

Table 3.1. Timeline of experiment showing the duration each reactor was dosed with each carbon source.

Period	Duration	GA1	GE1	GE2
Period 1	Day 1 to 22	Methanol	Methanol	Methanol
Period 2	Day 22 to 50	Ethanol	Methanol	Methanol/ethanol mix
Period 3	Day 50 to 73	Methanol	Methanol	Methanol
Period 4	Day 73 to 82	Increased methanol dosage		

The reactor GE1 which only received methanol, served as the reference in the experiment. This was done to approximate the standard operation at the full-scale treatment plant, where methanol is the carbon source. Since the experimental setup did not include online measurements nor chemical dosing based on incoming nitrate, the reference reactor was critical for interpreting the results. It provided a baseline against which the other configurations used in GA1 and GE2 could be compared to. The reactor GA1 that switched entirely to ethanol is intended to reflect a direct implementation of ethanol in the post-denitrification process. For the mixture in reactor GE2, a methanol/ethanol ratio of 60/40 was chosen to reflect an incremental implementation instead where methanol is still the main carbon source, but the amount is decreased. To understand the impacts of these transitions more and investigate the possibility to go back to methanol, it is switched to methanol once again.

Methanol and ethanol with concentrations >99% were used, sourced from both fossil-based and bio-based origins depending on availability. Due to their high purity, no functional differences in performance were expected between the fossil-derived and bio-based variants of either methanol or ethanol. Additionally, phosphate (85% ortho-phosphoric acid) was added throughout the experiment to ensure biofilm growth.

All chemicals were diluted with deionized water and stored in containers beneath the reactors and prepared throughout the experiment. The carbon sources were diluted to 25% as a standard but were increased to 50% in the last period to investigate the effects of increased carbon dosage. The phosphoric acid was diluted to 5%.

The influent and chemical flow rates were determined based on full-scale design criteria. This meant aiming for a hydraulic retention time around 30 minutes and a C/N-ratio of 4.7. Based on this, the influent flow was set to 250 ml/min.

The chemical dosing was controlled via computer-regulated peristaltic pumps. They operated at a constant speed of 27 rpm and activated intermittently based on pre-set operator parameters. Preliminary test runs using water and various operational settings were conducted to calibrate the dosage pumps. To match the full scale, the diluted phosphoric acid required a flow of 0.001 ml/min, but the minimum flow the pumps provided were 0.006 ml/min. This flow was used, resulting in excess phosphorous in the reactors which was assumed not to affect the process. For carbon dosage, a flow of

0.06 ml/min calculated for methanol diluted to 25% was used for all carbon source configurations. An explanation for this is given at the end of this sub-section.

The corresponding added COD concentrations and C/N ratios that are achieved with the setup are calculated with Equation 3.1 and Equation 3.2 respectively.

$$COD\ added\ [\frac{mg}{l}] = \frac{Q_C\ \cdot \rho_C \cdot dilution \cdot COD\ content}{Q} \tag{3.1}$$

$$\frac{C}{N} = \frac{Q_C \cdot \rho_C \cdot dilution \cdot COD\ content}{\left(c_{NO_3^- - N,in} + c_{NO_2^- - N,in}\right) \cdot Q} \tag{3.2}$$

Q is the target flow to each reactor [l/min], Q_C is the target flow of carbon source to each reactor [l/min], ρ_C is the density of carbon source [mg/l], c is the incoming concentration of NO_3^-–N and NO_3^--N [mg/l]. The dilution is 0.25 (25%) for Period 1-3 and 0.5 (50%) for Period 4. The density and COD-content of ethanol and methanol is seen in Appendix A. The density and COD content of the mix are approximated with the methanol/ethanol proportions (60/40).

Assuming the correct influent and dosage flows are achieved, and that the incoming nitrogen is constant at 13 mg/l, based on WWTP data for the same time period as the experiments, the theoretical COD and C/N values can be seen in Table 3.2. Each parameter is the same for all reactors in Period 1 and 3 when they received methanol (with 25% dilution). The C/N ratio of 4.9, is slightly above the target ratio to have enough carbon. It is the same for GE1 in Period 2 since it continued with methanol. The COD and C/N ratio are doubled when the methanol dilution instead is 50% in Period 4. Because the flows were not altered for the reactors receiving ethanol in Period 2, the added COD and C/N ratio are higher than in the methanol reactor. In this period the C/N ratio theoretically reaches 7.3 for GA1 which received ethanol and 5.8. for GE2 that received the mixture.

Table 3.2. Theoretical COD added mg/l and theoretical C/N-ratio corresponding to the target carbon dosage flow for each reactor in each period. Period 1 = all reactors on methanol, Period 2 = GA1 – ethanol, GE1 – methanol, GE2 – mixture of methanol and ethanol. Period 3 = all reactors on methanol. Period 4, all reactors on methanol with increased concentrations.

	GA1		**GE1**		**GE2**	
Period	**COD**	**C/N**	**COD**	**C/N**	**COD**	**C/N**
Period 1	63.2	4.9	63.2	4.9	63.2	4.9
Period 2	94.4	7.3	63.2	4.9	75.7	5.8
Period 3	63.2	4.9	63.2	4.9	63.2	4.9
Period 4	126.4	9.7	126.4	9.7	126.4	9.7

The dosing with ethanol does in fact require lower flows due to ethanol having higher COD content than methanol. Specifically, the required flow rate for ethanol and the mixture corresponding to the methanol flow rate was 0.041 ml/min and 0.52 ml/min, respectively. Although they differ, the flow rates for each carbon source were not adjusted. The dosing pumps lacked the precision needed to accurately deliver such small flow differences because there were inconsistencies with the provided flows. The intention was to keep the flows constant throughout the experiment, including during the increased dosage phase, where only the dilution of the carbon source was altered. Efforts were made to operate as close to the intended flows as possible. This included tubing maintenance and measuring the carbon flow rates at several points of the experiment. Additionally, to achieve target flows with the determined dilutions, parameters had to be set so that the chemicals were added every 16 minutes, and therefore not continuous dosing.

3.1.2 Sampling, laboratory analysis and data evaluation

Grab samples were collected each morning, five times per week. Samples were collected directly from the reactor outlets and the main influent stream and subsequently filtered through a 0.45 µm filter. The inflow to each reactor was measured during sampling. The analytical parameters and corresponding methods are summarized in Table 3.3.

Table 3.3. Analytical parameters and the analytical methods used in the experiment.

Parameter	Analytical method
Nitrate (NO_3-N)	Using Hach Lange LCK 339/340
Nitrite (NO_2-N)	Using Hach Lange LCK 341
Ammonium (NH_4-N)	Using Hach Lange LCK 304
Phosphate (PO_4-P)	According to SS-EN ISO 6878:2005
Chemical Oxygen Demand (COD)	Using Hach Lange APC114/814.
Dissolved Organic Carbon (DOC)	Using Shimadzu TOC-V analysis.
Total suspended solids (TSS)	According to SS-EN 872:2005 with modification (microwave drying)

All methods required filtration, including COD. Nitrogen compounds were analysed 3–5 times per week. During transitions between carbon sources, additional samples for nitrogen analysis were taken in the afternoon over several days to monitor stabilization. DOC was analysed 2–3 times per week. COD, PO_4-P and suspended solids were analysed once per week. After sampling, COD- and PO_4-P-samples were sent to the Rya WWTP laboratory for analysis. Samples for nitrogen species and DOC were stored in a freezer at -18°C and were slowly thawed and shaken prior to analysis.

The analysis of total suspended solids (TSS) includes using Equation 3.3.
TSS were measured as an indicator of biomass production, to see if there was a difference between methanol and ethanol.

$$TSS\ \left[\frac{mg}{l}\right] = \frac{dry\ weight\ of\ residue\ and\ filter - dry\ weight\ of\ filter}{sample\ volume} \qquad 3.3$$

Phosphorous were only analysed to control if the reactors received enough nutrient. Concentrations measured from the other analyses were used in calculations for further interpretation of the results: denitrification rate, nitrate reduction and parameters related to carbon content.

Denitrification rates of the biofilm in the reactors were calculated according to Equation 3.4 and Equation 3.5.

$$r_{NO_3^-} = \frac{(c_{NO_3^- - N,in} - c_{NO_3^- - N,out}) \cdot Q}{V \cdot a_s} \qquad 3.4$$

$$V = \varphi \cdot V_r \qquad 3.5$$

Where r_{NO3^-} is the denitrification rate [g/m^2·d], Q is the flow rate [l/d], c is the in-and outflow NO_3^--N concentrations [g/l], V the wet volume of the bioreactor [m^3], a_s the specific surface area of the biocarriers [m^2/m^3], φ the filling degree of the biocarriers and V_r the total volume of the reactors [m^3].

Nitrate reduction was calculated in percentage, as demonstrated in Equation 3.6.

$$NO_{3,Reduction}^- = \frac{(c_{NO_3^- - N,in} - c_{NO_3^- - N,out})}{c_{NO_3^- - N,in}} * 100 \qquad 3.6$$

Where c is the in-and outflow NO_3^--N concentrations [g/l].

The COD input concentrations and C/N-ratio that are theoretically achieved in the setup (presented above in Table 3.2), was calculated with Equation 3.1 and 3.2. To better analyse the carbon content achieved in the experiment, the same equations are used to determine the added COD and C/N ratio depending on measured values. This means the same equations are used but with a change of input parameters where Q instead is the measured flow to each reactor [l/min], Q_C is the measured flow of carbon source to each reactor [l/min] and c is the measured incoming concentration of NO_3^--N and NO_3^--N [mg/l].

To get the corresponding DOC input concentrations a COD/DOC ratio calculated with the measured concentrations of COD and DOC. It is only the average ratios in each reactor within Period 2 that are used to get the COD/DOC ratios for methanol, ethanol and the mixture. Thereafter the estimated DOC is calculated with Equation 3.7

$$DOC\ added\ [\frac{mg}{l}] = \frac{COD\ added}{\frac{COD}{DOC}\ ratio} \qquad 3.7$$

Concerning COD or DOC input, the added concentration in each reactor is added to the respective incoming concentration to achieve a total carbon input of either COD or DOC in each reactor. This is compared to the effluent COD or DOC concentrations to study how much carbon is used related the total carbon content.

The results of the experiment were supplemented with current and historical data from the full-scale WWTP, obtained through internal databases and targeted measurement campaigns. These data were used to complement the experimental results regarding influent conditions. Access to the WWTP's routine influent monitoring allowed for a greater number of data points than those captured through the experiment's grab samples alone, as it included measurements from days without experimental sampling. Additionally, it was used for evaluating the findings by assessing expected variability in incoming wastewater, as well as what can be considered typical effluent values, particularly in the first post-denitrification zone this setup aimed to replicate.

In addition, a literature review was conducted to further interpret and contextualize the experimental results by comparing them to other studies involving methanol and ethanol in MBBR systems or other biological nitrogen removal processes.

3.2 Sustainability analysis

The methodology to assess carbon source alternatives through sustainability perspectives partially follows a multicriteria analysis (MCA) approach, and it will be referred to as such throughout the thesis. The key steps include formulation of the aim, specification of alternatives, definition of the criteria set, and data acquisition. Finally, the findings are summarized and reflected upon. The outcome is intended to serve as a structured evaluation basis for comparing the proposed alternatives. While a complete MCA typically includes scoring the alternatives, and weighting criteria to produce a composite sustainability score, this thesis focuses on establishing the foundation for such an evaluation rather than performing the full MCA.

The alternatives, prerequisites, and criteria were gradually developed in parallel with data collection. This iterative structure meant that the different components of the assessment evolved together. Data gathering informed the selection of criteria, while the selected criteria and alternatives also guided which types of information were sought. Therefore, more details on methodology are presented in the Results and discussion section, but the main methodology and overall approach are outlined here.

Note that the alternatives in the MCA are separate from the configurations tested in the laboratory experiment. The experimental results were not part of the main basis for the MCA, although they provided some points of discussion for certain alternatives.

3.2.1 Aim formulation

The aim formulated specifically for the sustainability analysis was to develop an evaluation basis for comparing bio-based or recycled alternatives to the fossil-based methanol currently used in post-denitrification at the Rya WWTP, considering ecological, social, and economic aspects. The analysis concerns consumption over a one-year period, with 2024 used as the reference year.

3.2.2 Specification of alternatives and prerequisites

Initial concepts for potential alternatives (various forms of ethanol and methanol) were identified based on previous studies and a market analysis performed at Gryaab 2024, and consultations with Gryaab personnel. This analysis mainly covers specific product alternatives but alternatives reflecting design options were considered as well, where representative products were chosen.

The alternatives were determined and further specified during the project through continued consultations and reviewing previous internal reports regarding the carbon source alternatives. This included determining the specific products to be included in each alternative and how they are meant to be implemented at the plant and other prerequisites. Similar products for a certain supplier or from different suppliers were combined into one alternative and representative information were chosen for each alternative with more than one product. The alternatives are described in the thesis, but the suppliers are not mentioned here for confidentiality reasons.

3.2.3 Selecting and defining criteria

The development of the criteria list involved reviewing Gryaab's prior studies and market analysis, as well as academic literature regarding MCA applications in water treatment contexts. This literature review served to understand commonly used criteria in comparable assessments and provided a conceptual basis for structuring and justifying the selection of criteria in this study.

Initially, a broader list of criteria was compiled (Appendix B), capturing general sustainability aspects that could be of interest when choosing carbon source at a WWTP. This list draws significant inspiration from Backeström and Ceder (2022) who established a comprehensive set of criteria for sustainability assessments in the water and environmental sectors. Their list together with criteria used previously at Rya WWTP (when comparing technologies for pharmaceutical removal and future effluent compliance) served as key references for identifying relevant criteria in this study.

The criteria proposed by Backeström and Ceder (2022) were intended for water-related MCAs, and some were applied specifically in their evaluation of infiltration and water reuse. Besides expanding that list with criteria and applying own interpretations, the context of the included studies is also emphasised here. Authors such as Malmquist (2006), Marques et al. (2015), and Zheng et al. (2016) provided comprehensive criteria lists suggested for water services and sustainable urban water management. Criteria were also identified in more specific MCA contexts, including soil remediation alternatives (Rosén et al., 2015), retrofitting of WWTPs (Machado et al., 2020) and resource recovery from water bodies (Johannesdottir et al., 2021). Additional contributions in the current work were found related to sustainability assessment of sludge management (Sabet et al., 2025), MCAs comparing WWTP technologies (Castillo et al., 2016; Omran et al., 2021), and an MCA on industrial water reuse (Isaac et al., 2022). Although some studies focus on contexts other than WWTPs the criteria are considered relevant to the topic and may offer valuable insights for sustainability assessments when evaluating carbon sources.

For selecting the criteria to be included in this thesis, the relevance of each criterion in the general criteria list was evaluated based on comparability and significance, meaning that alternatives could be meaningfully assessed using the same criteria and focusing on aspects expected to vary across the alternatives. The selection was also based on available data for the products provided by the suppliers (see Appendix C). The criteria selection process is detailed further in the Results and discussion, where the included and excluded criteria are discussed under each sustainability dimension. Each selected criterion was then clearly defined and categorized under one of the three sustainability dimensions environmental, social, or economic.

3.2.4 Data acquisition

Data to support the developed evaluation basis were collected through a combination of methods.

Consultations were held with Gryaab personnel to gain operational insights into how carbon sources are handled at the facility, including aspects of implementation, daily operations, and supply logistics. Discussions also addressed how new products and sustainability efforts are communicated internally and externally, particularly in relation to media, public interest, and stakeholder engagement.

Relevant internal studies conducted by Gryaab were reviewed, including a market analysis. These documents provided foundational information for evaluating existing options and supplier characteristics. To complement existing knowledge and gather updated or missing information, targeted questionnaires were distributed during this thesis work. These were adapted to gather both new information and follow-up data where prior responses were incomplete. Appendix C summarizes the content of the market analysis and the questionnaires.

A targeted literature review was conducted to supplement practical insights and provide a broader context. This review covered topics including:

- Denitrification processes and external carbon source application (particularly within MBBR systems),
- Environmental and safety impacts of various carbon source types
- Usage trends and reported preferences from other WWTPs,
- Environmental implications such as recipient water impacts, sludge characteristics, and resource use
- Health and safety considerations relevant to WWTP operations.

The first topic was reviewed in parallel with the literature work supporting the experimental component of the thesis. While some sources contributed to both aspects, they are applied differently depending on context.

Calculations were carried out based on supplier data, literature, and other collected inputs. These calculations were used to support selected criteria with assumptions stated where necessary. Due to the evolving nature of the analysis, calculations cannot be described upfront, as they are closely tied to the iterative definition of criteria. They are brought up in the Results and discussion and in presented in detail in Appendix D.

3.2.5 Results and reflections of the evaluation basis

The data were gathered using structured templates to ensure systematic compilation. However, some qualitative and discussion-based data could not be easily quantified. In such cases, these findings were included to reflect uncertainties, highlight aspects that are difficult to assess at present, or identify areas where further clarification is expected in future evaluations.

Although formal MCA scoring and weighting were not performed, practical considerations for applying the evaluation basis in Gryaab’s continued work or other WWTPs considering alternative external carbon sources are discussed.

4 Results and discussion

This chapter presents the results and discussions for the laboratory experiments and the steps of the MCA. Discussions are integrated throughout the results where relevant but are further developed in dedicated sections at the end of each part. In the MCA section it is highlighted how the findings related to the laboratory experiments informed the sustainability assessment.

4.1 Laboratory experiments

The results from the laboratory experiments are presented and discussed. It includes measured parameters and calculated performance indicators. Data points where the inflow occasionally was completely stopped were removed.

The results are compared to findings in the literature and to data from the full-scale WWTP. The influence of the experimental setup on the results is discussed, along with sources of uncertainty. Based on the findings, recommendations are provided for future research on the transition of carbon source in denitrification processes.

4.1.1 Influent and carbon dosage flows

Influent flows to the reactors are shown in Figure 4.1. The target flow was 0.25 l/min, and most inflows were within a range of 0.24–0.27 l/min, apart from some outliers. Reactor GE1 had the most operational problems with regards to inflow, as can be seen in the diagram below.

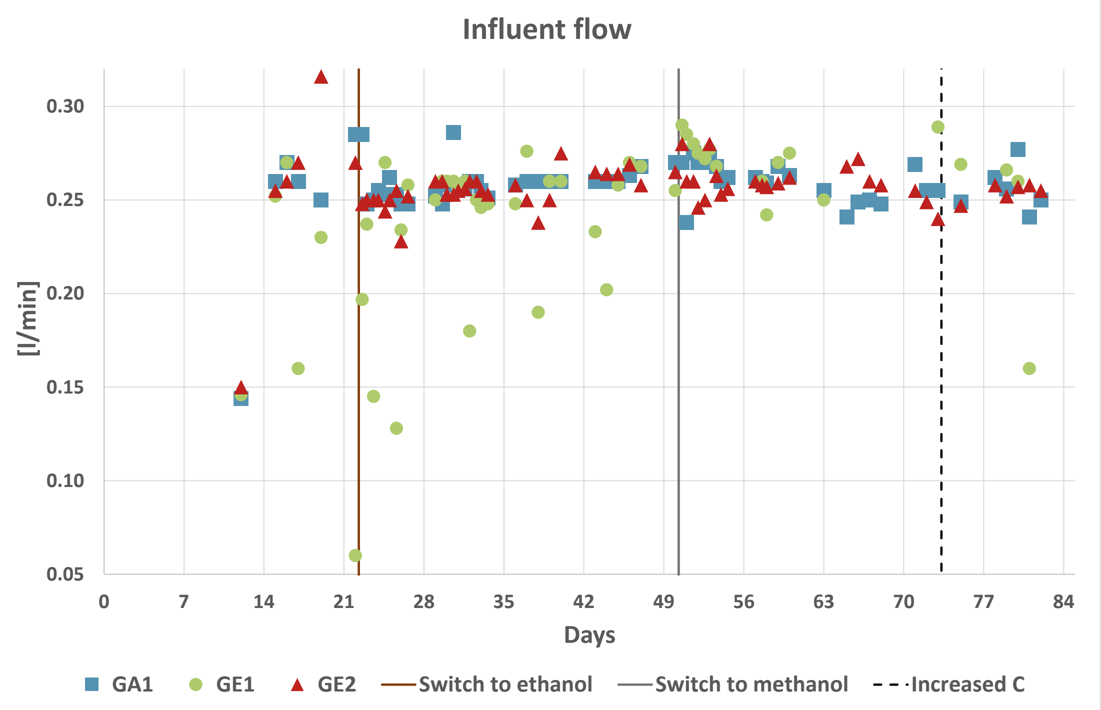

Figure 4.1. Influent flow to the reactors. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol

reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

Table 4.1 show that the measured carbon dosage flows. The measurements are quite uncertain due to difficulties in accurately setting and measuring the small flows, so these should be seen as estimated averages. However, it can be stated that the flows generally are slightly lower than the target flow of 0.06 ml/min for all reactors. It was seemingly always lower in reactor GA1. Only measurements after the prior testing were included in these calculations. The average flows in Period 1 might be a bit higher than the averages presented here, depending on how long the initial pump calibration stayed consistent. For Period 4, adjustments of the tubing finally gave flows closer to the target flow.

Table 4.1. Average carbon dosage flows for each reactor and period in ml/min.

	GA1	**GE1**	**GE2**
Period 1	0.038	0.048	0.050
Period 2	0.039	0.045	0.047
Period 3	0.047	0.055	0.051
Period 4	0.054	0.065	0.055

4.1.2 Organic carbon

Figure 4.2 and Figure 4.3 show the measured COD and DOC concentrations in the influent, the effluent of the reactors and the calculated total carbon input. The average COD/DOC ratios calculated for Period 2 that was used for calculating the added DOC were 2.75 mg/l for methanol, 2.56 mg/l for ethanol and 2.71 for the mix.

No substantial changes in effluent COD or DOC concentrations were observed after switching carbon sources. If carbon was being used inefficiently after a switch, one would expect clear patterns of increased organic content in the effluent compared to before the switch, but this was not seen in the transition points.

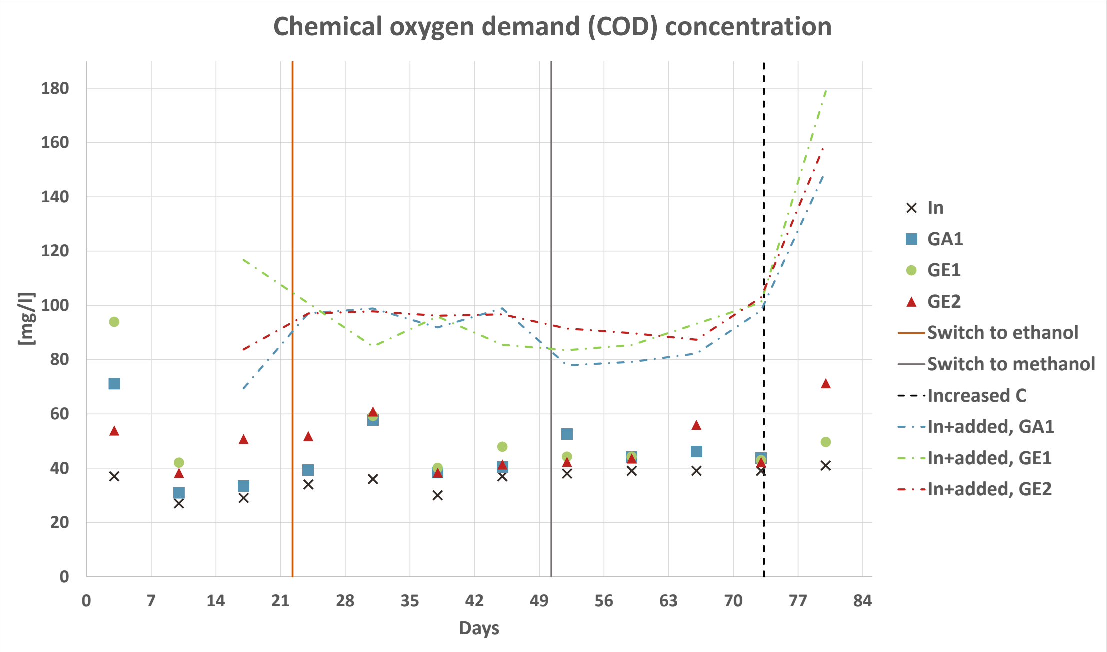

Figure 4.2. Concentrations of chemical oxygen demand in influent and reactor effluent. Including total input of carbon (incoming concentration + added carbon). Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

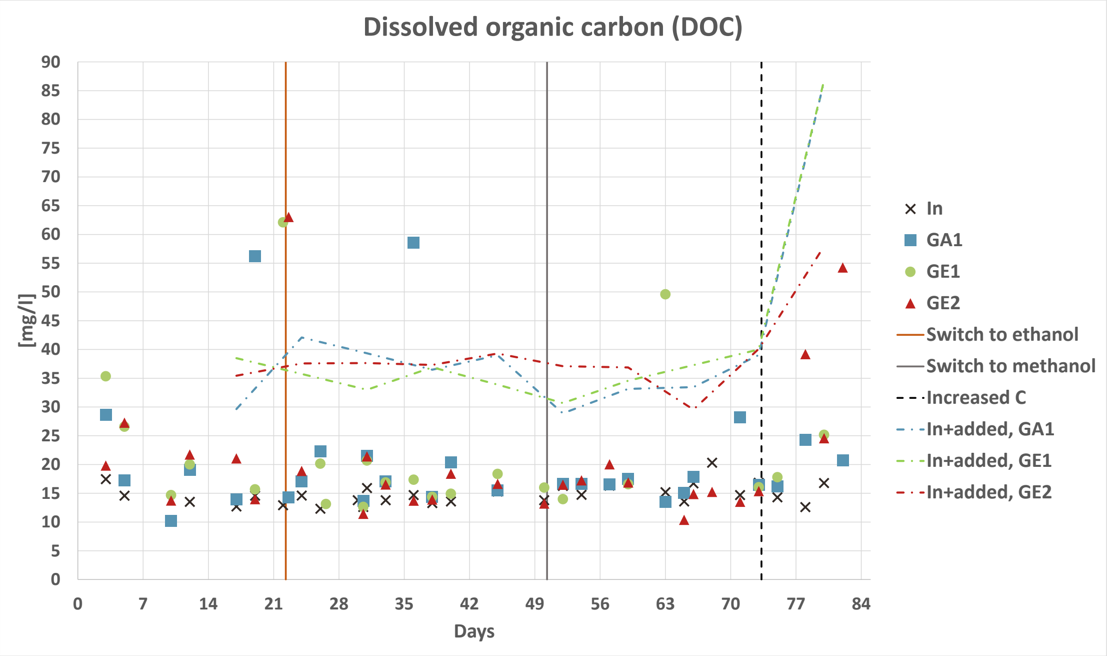

Figure 4.3. Concentrations of dissolved organic carbon in influent and reactor effluent. Including total input of carbon (incoming concentration + added carbon). Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

Occasional peaks in reactor effluent concentrations of COD and DOC are observed at specific times. These correspond to periods of reduced flow due to operational issues with the influent pumps. While these outliers exist, the general trends are more relevant. DOC concentrations are typically between 10–20 mg/L and COD concentrations are generally around 37 mg/L.

For each reactor and period, DOC and COD show parallel fluctuations patterns in the influent and effluent on the dates where both are sampled, see Figure 4.4.

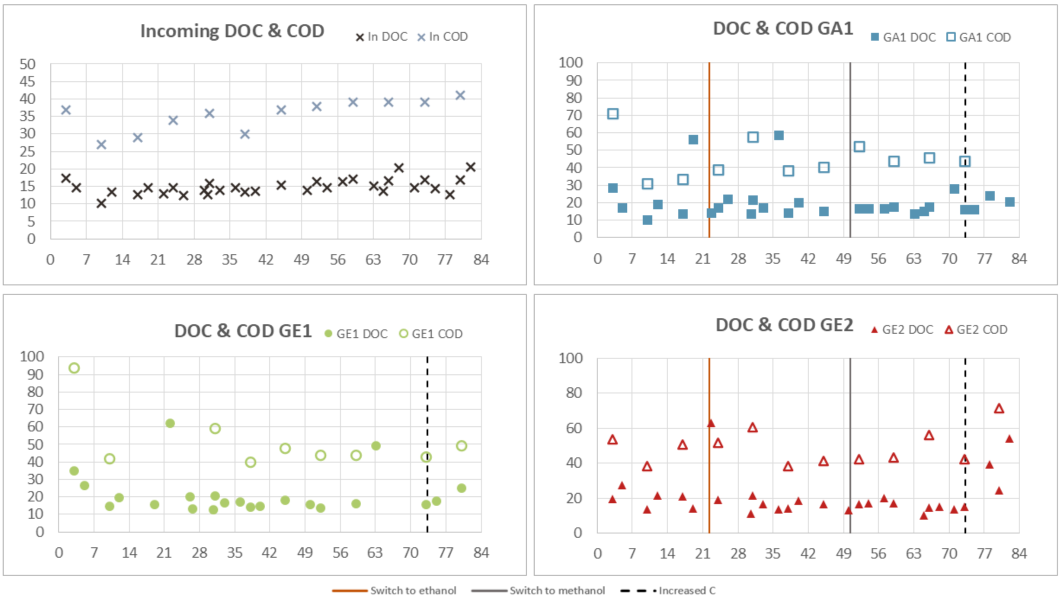

Figure 4.4. Concentrations of dissolved organic carbon (DOC) and chemical oxygen demand (COD) in the influent and each reactor. The y-axis is the concentrations in mg/l and x-axis the days. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

The COD measurements are consistently higher than DOC because COD captures all oxidizable substances, including inorganic and non-dissolved organics, whereas DOC only includes dissolved organic carbon. Note that both DOC and COD analyses were performed on filtered samples. As a result, COD does not provide information about particulate matter.

Effluent COD concentrations are typically just above the background level, indicating that most of the added carbon was used effectively and that there is enough carbon. Effluent DOC, on the other hand, is sometimes lower than in the influent. A lower effluent DOC than influent suggest excessive consumption of dissolved available carbon, potentially indicating carbon limitation. There are also instances where effluent DOC exceeds the estimated total influent DOC. There are not measurements for both DOC and COD on these days to compare them. They are likely related to lower flows or possibly measurement variability.

To see if the carbon concentrations in the reactors varied due to the intermittent dosing regimen, additional sampling of DOC at several times during the 16-minute dosing cycle was performed. It was observed that the added carbon reaches a peak in the first few minutes and is then consumed during the cycle, ending up just above or just below the incoming concentration (see Appendix E). Unlike the reactor-samples, the influent was just analysed once for this date. However, the incoming concentration is not expected to vary in such a short time frame. Following this test, samples were consistently taken just before new carbon dosing, to capture conditions near the end of the cycle. This change in sampling strategy was intended to reduce variability and possibly clarify both carbon and nitrogen trends, though this was not clearly reflected in the data. While short-term variability is visible, these differences likely do not impact the overall conclusions.

The calculated C/N-ratios are seen in Figure 4.5. Considering the WWTP guideline of 4.7, values well below this likely indicate underdosing. In Period 4, the ratio increased significantly when switching to higher carbon dosing. The decreasing trend that follows is due to slightly higher incoming flow and nitrogen.

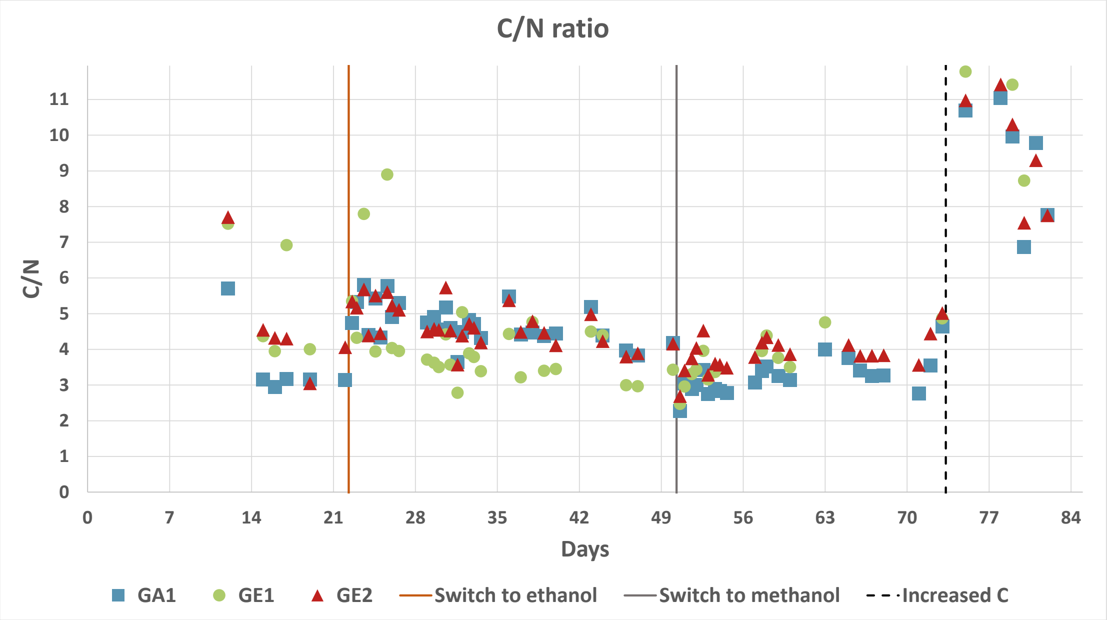

Figure 4.5. Estimated added carbon to incoming nitrogen ratio. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

It was established in Section 4.1.1, that each period is affected by variations in influent and carbon dosage flows and that they differ from the target flows. This causes some uncertainties with all calculations dependent on these flows (added COD, added DOC and C/N ratio).

4.1.3 Ammonium

Influent and effluent concentration of NH_4^+-N for the reactors can be seen in Figure 4.6. These concentrations stayed relatively low for large parts of the experiment. Higher effluent concentrations seem to be connected to higher influent concentrations.

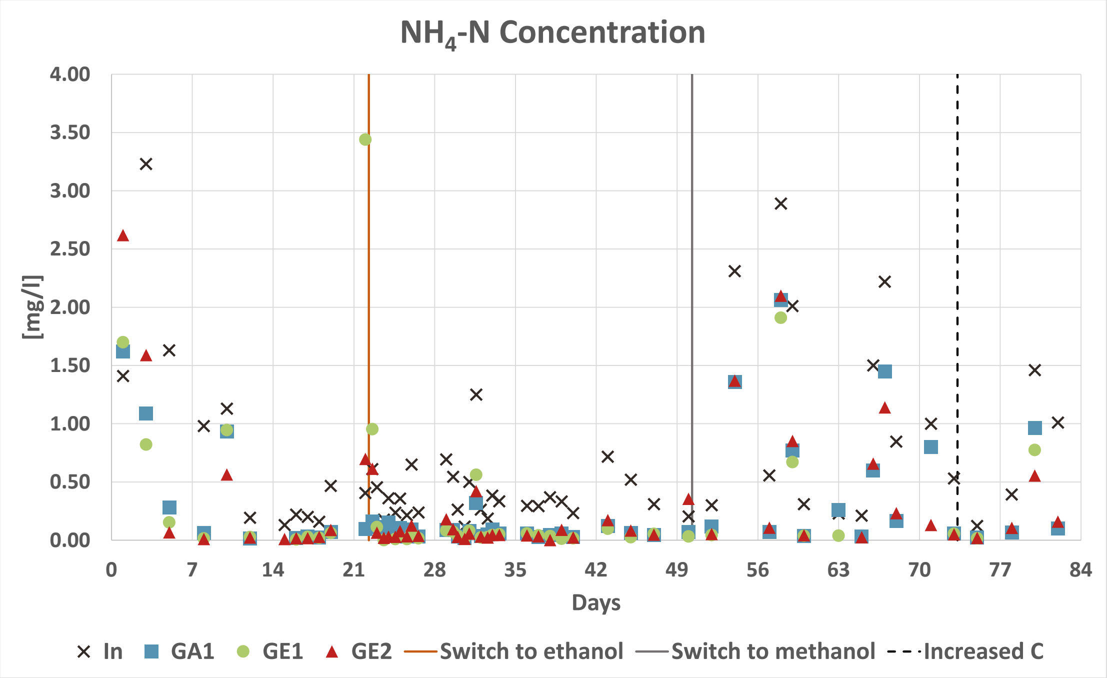

Figure 4.6. Influent and effluent NH4+-N-concentrations for the reactors. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

4.1.4 Nitrite

Influent and effluent concentration of NO_2^--N for the reactors can be seen in Figure 4.7. Most of the measured concentrations are between 0.035 and 1.7 mg/l. This variation is similar to an earlier measurement campaign in the full scale MBBR denitrification from 2018–2019, where nitrite concentrations in Zone 1 varied between 0.023 and 1.8 mg/l. The range is therefore considered reasonable, but the results also show that effluent nitrite concentrations increased throughout the test period for all three reactors. After increasing the external carbon source dosage, the concentrations started declining. This indicates that the nitrite accumulation was caused by a too low carbon source dosage.

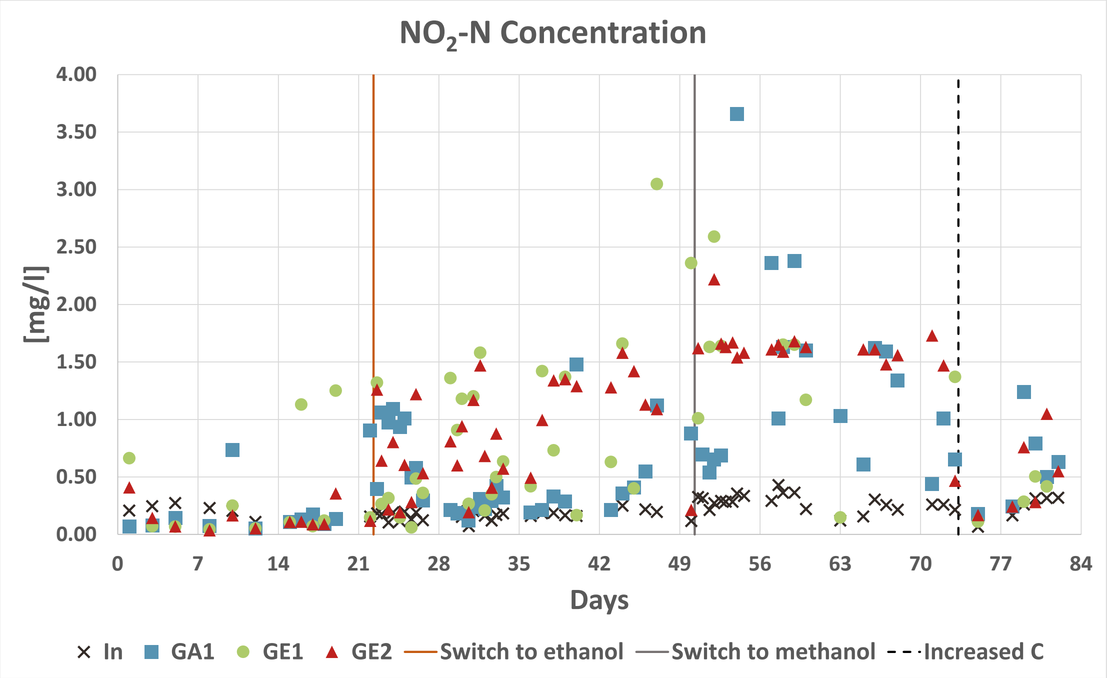

Figure 4.7. Influent and effluent NO2--N-concentrations for the reactors. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

Rocher et al. (2015) explains differences in nitrite accumulation at different C/N ratios. While nitrite accumulation occurs whenever there is a lack of carbon, it may be high residual NO_3^- and little NO_2^- in cases with strong carbon deficiencies. This is because both the denitrification rate and the production of intermediate species is slow. With moderate underdosing, the concentration of NO_2^- is higher. This ratio is supposedly sufficient for removing nitrate but not for eliminating intermediate NO_2^- in the process. However, Du et al. (2016) found that the C/N-ratio did not influence the nitrite accumulation. The authors note that this differs from earlier experiments that have shown increased nitrite accumulation for high and low C/N-ratios.

Since this study switched between methanol and ethanol, it is difficult to know if the increasing nitrite concentrations were only caused by a low C/N-ratio. Nitrite accumulation could be caused by a combination of factors. For instance, it can involve aspects such as pH, nitrate concentration and presence of oxygen or toxic compounds (Rahimi et al., 2020). However, the results strongly indicate that the increase in nitrite concentration over time mainly was caused by a low dosage of carbon source.

4.1.5 Nitrate

Figure 4.8 show the influent and effluent concentrations of NO_3^--N. The nitrate concentration is consistently reduced from the influent to effluent. Although the reduction varies, this indicates the biofilm have denitrification capacity throughout the entire experiment.

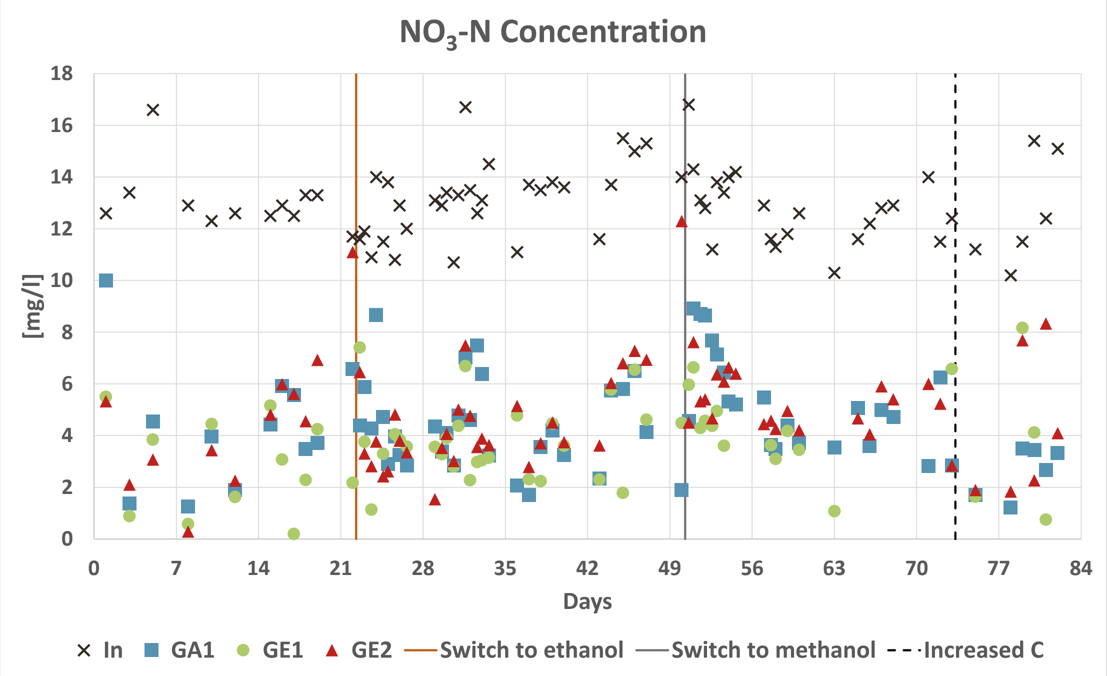

Figure 4.8. Influent and effluent NO3--concentrations for the reactors. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

Looking at the reduction of NO_3^--N-concentration shown in Figure 4.9, a decline in reduction can be observed in the reactor operating on only ethanol, GA1, after the switch back to methanol. There is also a reduction after the switch to ethanol, however, there is large variation in values throughout that period. For the reactor receiving a mix of ethanol and methanol, the nitrate reduction seems to be unaffected by the switches. Another observation is dips in reduction occurring prior to any changes in dosing, which are believed to be caused by flow, stirring or dosing inconsistencies. One aspect to consider is that all switches occurred on Mondays, where these issues were usually worse since there were no maintenance of the reactors during the weekends. This potentially makes these concentrations less representative of the impacts of switching carbon source.

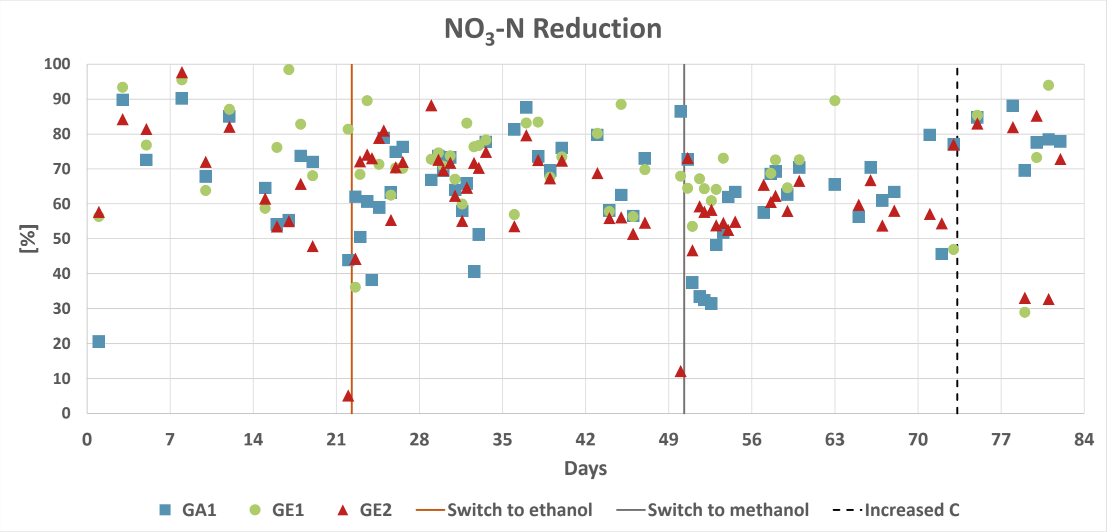

Figure 4.9. Removal efficiency (%) of NO3--N-concentration for the reactors. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

The lower reduction in GA1, the reactor that switched between methanol and ethanol dosing, seems to persist for two to three days until it increases again, as seen in Figure 4.10. This finding is put in relation to other studies, described further down in Section 4.1.9.

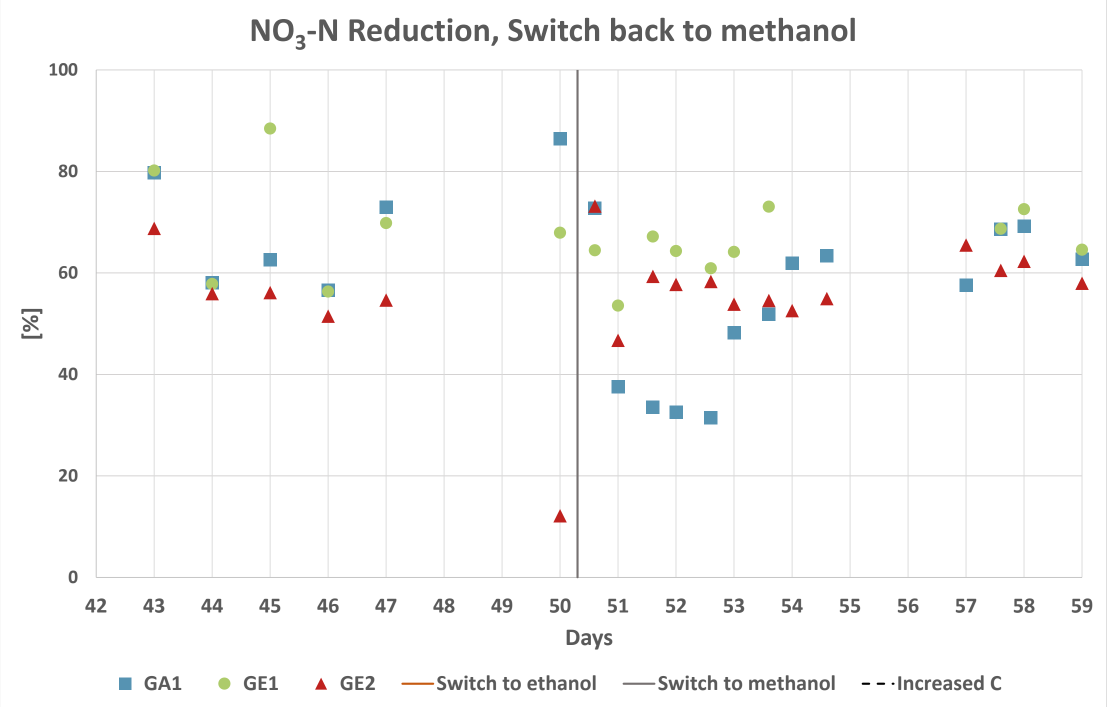

Figure 4.10. Removal efficiency (%) of NO3-N concentration for the reactors. Focus on the days around the switch back to methanol. GA1 - Ethanol, GE1 - Methanol reference, GE2 - Mix of ethanol and methanol.

Figure 4.11 show how the denitrification rates changed over time for the different reactors. A decrease in the denitrification rate was observed in GA1 when switching from ethanol back to methanol, following a pattern comparable to the one seen in nitrate reduction.

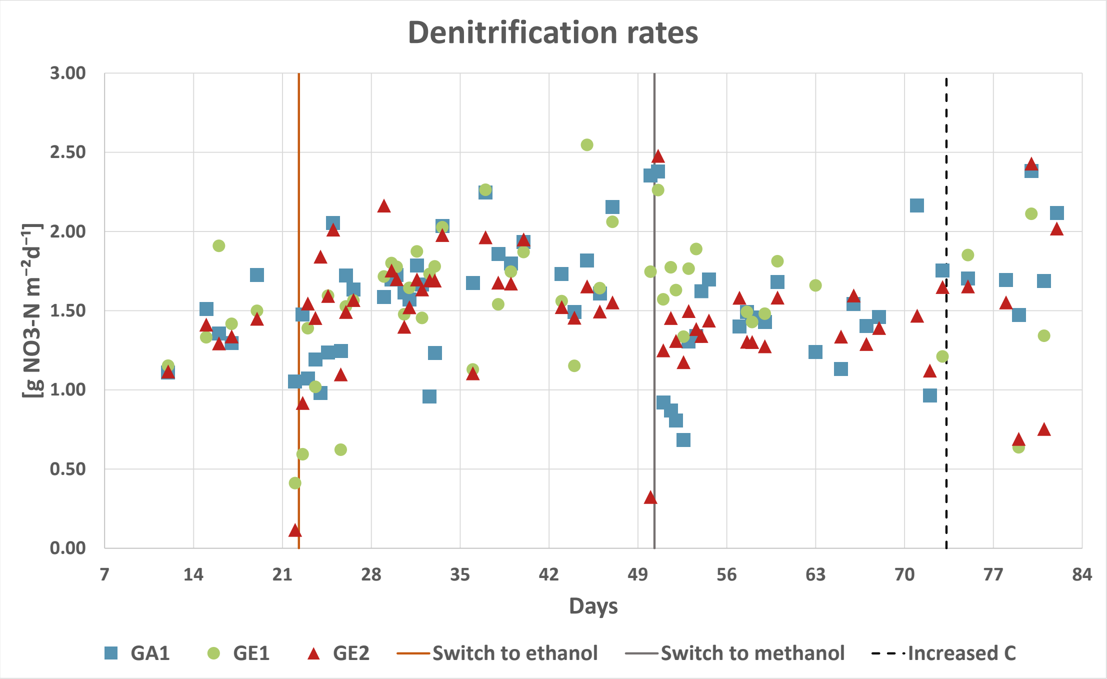

Figure 4.11. Denitrification rates for the reactors. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

The mean values of the denitrification rate along with standard deviation are summarized in Table 4.2.

Table 4.2. Mean denitrification rate in NO_3-N/m^2d and standard deviation (std). Period 1 - All reactors on methanol, Period 2 - GA1 on ethanol, GE1 on methanol, GE2 on ethanol- and methanol mix. Period 3 - All reactors on methanol. Period 4 - All reactors on methanol, increased dosage.

	GA1		**GE1**		**GE2**	
Period	**Mean**	**Std**	**Mean**	**Std**	**Mean**	**Std**
Period 1	1.3	0.2	1.3	0.5	1.1	0.5
Period 2	1.6	0.4	1.6	0.4	1.6	0.4
Period 3	1.4	0.4	1.6	0.3	1.4	0.3
Period 4	1.8	0.3	1.5	0.6	1.5	0.7

The denitrification rates seem to increase from Period 1 to Period 2, however, they increase for all reactors and not only the ones receiving ethanol. Thus, it is unlikely that the change in carbon source is the main cause for the increase in denitrification rates. For GA1 and GE2, the reactors receiving ethanol and mix of ethanol and methanol, the denitrification rates decrease when switching back to methanol. In an earlier pilot MBBR study, denitrification rates were reported to be higher for ethanol than methanol

(Bill et al., 2009). However, as seen in Figure 4.11 and the standard deviation values (Table 4.2), there is quite a large variation in values during the experiment.

The mean values of denitrification rate for the whole experiment were 1.55 g NO_3-N/m^2d for GA1, 1.57 for GE1 and 1.50 for GE2. The mean value of denitrification rate in Zone 1 of the full-scale denitrification MBBR for 2024 was 1.9 g NO_3-N/m^2d. Based on this, it seems like the denitrification rate of neither of the reactors are reaching the levels of the full-scale denitrification process. However, given the small scale of the laboratory reactors and other differences between the lab- and full-scale, the results indicate a relatively high level of treatment performance.

4.1.6 Phosphorus

Phosphorus, PO_4-P, was measured once a week to make sure there was enough for bacterial growth. The results can be seen in Figure 4.12.

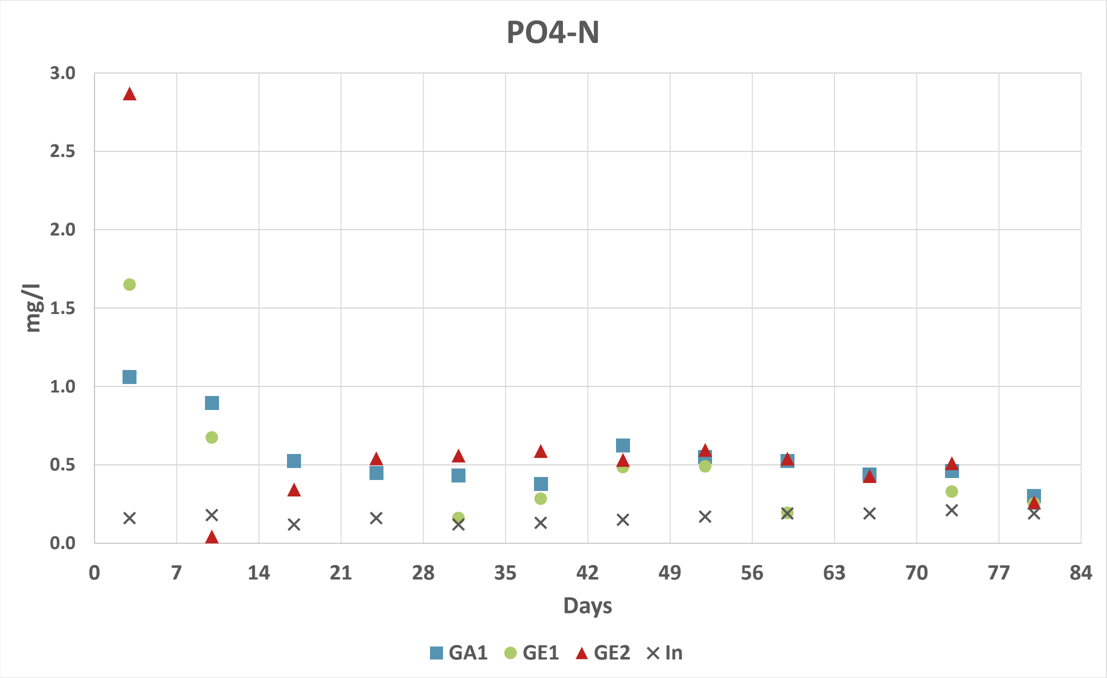

Figure 4.12. Measured PO4-P for the three reactors.

As mentioned in the methodology, phosphoric acid was overdosed in the reactors. This was assumed to not impact the results. For the first week, the difference between the influent and effluent concentrations are quite large. After the second week and the rest of the experiment, the difference is smaller. This could indicate that the biomass adapted to the higher dosage of phosphorus and started using higher amounts. However, the lack of consistent samples makes the indications uncertain.

4.1.7 Suspended solids

Suspended solids were measured during the experiment and some variations were observed, see Figure 4.13. However, due to the limited number of data points and the lack of clear trends or correlations, no meaningful conclusions could be drawn.
Other studies using lab-scale MBBRs found that more biomass was produced when using ethanol as carbon source (Cheng et al., 2023; Torresi et al., 2017). This could not be seen from the TSS parameter in this study. It was visually observed though, and through the increase in reactor maintenance required, that biomass increased over time in all reactors.

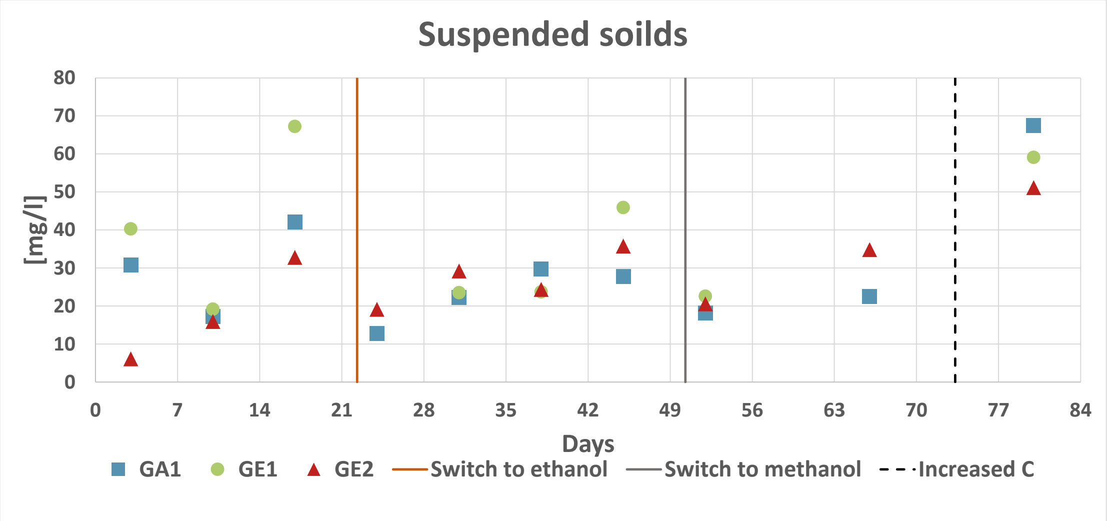

Figure 4.13. Concentration of suspended solids in the effluent. Vertical lines indicate changed carbon dosage (Switch to ethanol means for GA1 - methanol to ethanol, GE1 - Methanol reference, GE2 - Methanol to mix of ethanol and methanol. All reactors are dosed with methanol after the second line).

4.1.8 Uncertainties

Uncertainties in this study arise from the absence of statistical analysis and certain limitations in the experimental setup. Statistical analysis was not performed due to a limited number or samples for certain periods and analytical parameters, the overall exploratory nature of the study, and time constraints. This limits the certainty of the results, particularly with respect to variations within and between reactors and during transition periods. The experimental design aimed to reflect realistic operational conditions at a real WWTP and to test whether added carbon could be fully utilized, particularly during carbon source transitions. However, in practice, it became evident that a more robust and precise setup would have been beneficial.

A main challenge was to achieve accurate and continuous carbon dosage due to technical limitations of the equipment. The flow suitable for methanol was therefore used for all carbon sources. However, ensuring the exact same COD content between carbon sources were not considered a priority, given that the focus was on studying the transitions of carbon sources. Dosing flows were measured during the experiment at different occasions and showed varying flows and were generally lower than intended. Fine-tuning was difficult due to both equipment limitations and the inherently small volumes involved. Calculations involving carbon input (e.g., C/N ratios, COD added) which are dependent on the carbon dosage flows were uncertain as a result.

To avoid altering too many parameters mid-experiment, increasing the methanol concentration was chosen as a practical approach to investigate its effect, particularly on nitrite accumulation, which appeared to decrease with higher carbon availability. While further dilution of methanol to allow higher flows might have been ideal, to also have more continuous dosing, limitations in the pump and tubing setup made this infeasible. Higher flows caused displacement of the dosing tubes during testing prior to the experiments.

There were issues with the influent as well, as the pumps stopped providing flow, particularly the one connected to reactor (GE1). Flow inconsistencies were particularly evident in the morning. Several attempts were made to fix the pump or tubing, but issues remained throughout the experiment.

Other operational issues include stirring inefficiencies and technical constraints of the reactors. The reactors are quite small, and not originally designed to house biocarriers. The internal pipes and such hindered free movement of the carriers. Stuck biocarriers caused stops in stirring, but there were also some technical issues with the stirrers. It possibly contributed to stagnant zones and low flows. As mentioned in the theoretical background, stagnant zones can appear in MBBR systems but the knowledge on whether this affect the overall nitrogen removal performance is uncertain (di Biase, 2019). However, it is possible that stagnant zones in this study could have affected the process due to the small size of the reactors. Additionally, biomass seemed to build up over time in all the reactors, which eventually caused issues with blockages in the outlets, requiring increased maintenance.

The results showed variability during and between days across the reactors. It may be partly due to natural variations but is also likely tied to operational fluctuations and measurement uncertainties. Sudden low or high concentrations of nitrogen species right before or after a switch are considered less representative of the impacts of carbon transitions. This is because the changes were made after the weekends (without reactor maintenance).

Concerning measurement frequencies, nitrogen was the most frequently analysed parameter and was the only one measured twice daily during transition phases. In contrast, DOC was still only measured once per day during these periods, and overall, it was analysed less frequently than nitrogen. This limited the ability to capture fluctuations in DOC concentrations. This along with the limited number of samples for COD, only once weekly, may not provide sufficient data to accurately assess carbon dynamics. The resolution for suspended solids was also low, with measurements conducted only on a weekly basis, making it difficult to draw reliable conclusions from the data. Furthermore, the study relied solely on grab sampling, which even for parameters measured twice daily may not fully reflect the system's variability. The frequency of the analyses was constrained by the scope of this thesis.

Certain NO_2^- measurement values were outside of the measuring range of the measuring kit used for the spectrophotometry instrument. For some samples, the spectrophotometer showed an approximate concentration outside of the measuring range, while for other samples the absorbance was too high for it to provide any value at all. The samples with too high absorbance were diluted and run in the instrument again. The samples outside of the measuring range, but still given an approximate value of the concentration, were too many to be able to dilute and measure again within the time scope of the study. Therefore, a set of representative samples were diluted and measured again and compared with the approximative values. In this aspect, the approximate values were deemed to be sufficiently accurate and were consequently used as data points in the laboratory results. Nonetheless, these nitrate concentration values have only been used for general discussions on concentration fluctuations over time. For more detailed analysis and use of specific values, all samples could be diluted and re-measured.

4.1.9 Relevance to full-scale systems and previous research

The results indicated an effect when switching carbon source from ethanol to methanol when going back to methanol. Several studies have observed that methanol generally requires a longer acclimatization period compared to ethanol (Bill et al., 2009; Christensson et al., 1994; Gavazza Dos Santos et al., 2004; Zhang et al., 2024). This means how long it takes for the bacteria to get used to the new substance. The laboratory experiments showed a noticeable drop in denitrification capacity during the first few days of transitioning from ethanol back to methanol.

Only two studies were found that explored the ability of switching between methanol and ethanol. Cherchi et al. (2009) tested various acclimated and non-acclimated biomass with several carbon sources in laboratory scale Sequencing Batch Reactors (SBR). Among them are methanol, ethanol, and a commercial alcohol mix that contains methanol. It was suggested that both methanol and ethanol could be used right away in the biomass acclimated to the alcohol mixture. Ethanol could be used directly in the methanol acclimated sludge. Methanol was however not tested on ethanol acclimated sludge. Mokhayeri et al (2008) found that ethanol could be utilized on methanol-acclimated biomass with a similar denitrification rate to that of methanol on methanol-acclimated biomass. Using methanol on ethanol-acclimated biomass resulted in lower denitrification rates but still worked and showed quite fast acclimatisation. They suggest that the two substrates could be interchanged to grow respective populations with a short acclimatisation period.

While these experiments used another technique, their results also point to possibilities with carbon source interchangeability, at least in the short-term response. This, together with the results in the current thesis, may mean that the acclimatisation period to methanol is not as long as expected. Assuming that the acclimatization time is a few days, implementing a switch of carbon source in the large-scale process might be deemed acceptable to do once. If the plan instead is to be able to switch back and forth between different carbon sources, it could potentially affect the yearly mean value too much.

The results are considered highly relevant to the full scale. Although denitrification performance is somewhat lower in the lab, the results come quite close when considering differences in size and setup between the lab-scale and full-scale systems.

4.1.10 Contributions to Research and Future Directions

Previous experiments at Gryaab or the reviewed literature have primarily employed batch testing using denitrification capacity tests, with few efforts directed at continuous-flow MBBR systems operating with real wastewater. While both methanol and ethanol are well-established carbon sources for denitrification, comparative studies rarely focus solely on transitions between the two. Instead, the research tends to evaluate alternative or bio-based carbon sources or combining conventional sources with emerging ones. The dynamics of switching between methanol and ethanol, especially in continuous systems, remain underexplored. This study therefore contributes to the growing body of knowledge on post-denitrification in continuous biofilm systems by addressing an area that has seen limited experimental focus.

Despite the practical limitations of the current experimental setup, this study provides valuable insights. Several key areas are proposed for further study. Future experiments should prioritize securing a stable and representative setup, with continuous and accurately controlled inflow and carbon dosing. This includes using appropriate tubing and pumps capable of handling the correct flow rates, and ensuring consistent carbon availability (i.e., excess COD) to evaluate performance under ideal conditions. More frequent or even continuous (online) monitoring is recommended to better capture short-term variations, transition dynamics, and potential lag effects. Grab sampling in its current form may miss critical fluctuations, particularly around carbon source switches. Additionally, incorporating gas monitoring (e.g., N_2, N_2O) would allow for a more detailed understanding of denitrification performance and pathways, particularly with regard to environmental impacts.

Future studies should incorporate statistical analysis to increase confidence in the results. Analysing the microbial communities could provide deeper insights into their response to changes in carbon source. This could help determine whether bacteria adapt over time, how communities shift during repeated or short-interval transitions, and how such shifts correlate with performance. Lastly, future work should use different methanol-to-ethanol ratios in the mixture and observe whether performance stabilizes after repeated switches with all options.

4.2 Multicriteria analysis

The following sections present the results and discussion regarding the MCA. First an overview of what information was available regarding product alternatives is presented. Afterwards the sub-chapters cover the main steps of selecting and defining alternatives and criteria and developing the evaluation basis. Given the iterative nature of the MCA, these sections contain methodology details as well. The final section summarizes key findings of the evaluation basis and discusses the relevance of each criterion and alternative. It includes guidance for WWTPs on interpreting the results and determining the next steps for further evaluation.

4.2.1 Available data from suppliers

Appendix C summarizes what information has been requested and provided in the previous market analysis or in this work. Overall, in the previous assessment, sufficient product data were available to categorize the carbon sources into different alternatives and to support calculations and evaluations in several criteria. For the current assessment, updated or additional information was requested from suppliers. This included details on transport (location and means), types and quantities of raw materials, associated production processes (e.g., feedstocks, methods, and energy consumption), full product specifications, safety data sheets, pricing, and deliverable volumes. Comments are also included in the appendix, regarding the data availability and usage of the information in the MCA. Further discussion about data availability is held in Section 4.2.5.

4.2.2 Alternatives and prerequisites

The alternatives that have been chosen for evaluation in this thesis are seen in Table 4.3.

Table 4.3. The chosen alternatives, including description of type of product and how many products and suppliers are involved.

Alternative	Description
1. Fossil-based methanol	Fossil methanol, supplied by the current provider and represents continued operation as at the present Rya WWTP.
2. First-generation bio-ethanol	Bio-ethanol derived from cereal-based feedstocks, primarily wheat. It includes two products from two different suppliers.
3. Second-generation bio-ethanol	Bio-ethanol derived from forestry industry residue. Includes two products from two different suppliers.
4. Recycled ethanol	Ethanol used in other industries, such as pharmaceutical industry, prior to recycling. It includes two products from the same supplier.
5. Mass-balanced bio-methanol	Includes two mass-balance certified products from two different suppliers.
6. Second-generation bio-methanol	Bio-methanol derived from forestry industry residue. It concerns only one product from a single supplier.
7. Methanol and ethanol in separate lines	It involves using three dosing lines with first-generation bio-ethanol (as in Alternative 2) and three lines with fossil methanol (as in Alternative 1).

Some product characteristics are presented in Appendix F. All alternatives, except the recycled ethanol has purities above 99%. Besides varying concentration, this alternative contains impurities. One of the included products contains 1–30% isopropanol (propan-2-ol), depending on batch, while the other contains 3.1% acetone. One of the included products in Alternative 3 potentially contains a small amount of metal concentrations.

The products originate from seven different companies, including both Swedish and international actors. These represent a range of sectors such as chemical industries, agricultural and forestry cooperatives, biorefineries, and companies specializing in solvent recycling and processing.

All alternatives are initially regarded as technically and economically feasible for application at Rya WWTP because the assessment focuses solely on variants of methanol and ethanol, which in general are well-established carbon sources.

Alternative 7 does not include any additional products to those evaluated in the other alternatives. While various product combinations could be theoretically assessed in this alternative, only fossil-based methanol and biobased ethanol was chosen. This option is included rather to represent design options for using ethanol and methanol simultaneously. This alternative could also be applied for representing a transition period from fossil-based methanol to biobased ethanol. The COD demand is assumed to be split equally between the two carbon sources, unlike the other alternatives in which the sole carbon source should make up the whole COD demand.

The assumptions underlying the evaluation are the following:

- All alternatives are assumed capable of achieving the same annual average treatment efficiency after a sufficient acclimatization period, although the required quantity of carbon source may vary.
- Fossil-free methanol and fossil-free ethanol with high purity (>99%) are assumed functionally equivalent to their fossil-based counterparts.
- The alternatives are evaluated as if they were already implemented at the treatment plant.

The first assumption is necessary to enable a fair, structured comparison between the options within an MCA framework. This approach is consistent with similar MCA studies in the wastewater sector, where certain performance variables are held constant to avoid introducing case-specific complexity or undermining comparability. In practice there are expected differences in denitrification effectiveness among the alternatives, but here the focus is instead of the amounts required to achieve the same level of nitrogen removal.

With the second assumption, the recycled ethanol (Alternative 4) with lower purity, requires assumptions about the technical function. The COD-content is comparable to methanol (see Appendix F). Assuming the COD is easily available, this provides some indication of functionality of this alternative. This underlines the choice of including it in the analysis. However, it is further assessed in the evaluation basis, including other relevant assumptions.

The third assumption is needed to make simplifications. This thesis does not address detailed infrastructure-specific adjustments which are dependent on further investigation and expert review and thus fall outside the current scope. However, the implementation for each alternative were conceptualized, see Figure 4.14. Their application is assumed to take place in the existing post-denitrification facility using current carriers. In Alternative 1–6 a single carbon source is added to all treatment lines using existing dosing pumps. Both storage tanks are used for the same carbon source.

Alternative 7 likely requires facility adaptation to handle both carbon sources independently, such as:

- Separate delivery logistics and transport handling.
- Separate storage tanks for each carbon source.
- Potentially additional pumps and structural support for unloading.
- New or modified physical infrastructure (valves, pipes etc.) or operational schemes to manage separate dosing system from the tanks to the dosing pumps.

Furthermore, if two tanks are no longer jointly used (as in dual carbon source scenarios), the existing booster pump may no longer be necessary. Unused pipes or other equipment under such configurations may also require decommissioning.

While the implementation is not part of the analysis, it needs to be mentioned that for any alternative, the facility must be compatible with the selected carbon source. As Rya WWTP is already configured for methanol, modifications (e.g., physical adjustments, inspections and permits) would be necessary to accommodate ethanol. During consultations on how to apply the alternatives it was stressed that construction works require shutting down the facility. The more complicated reconstruction, the longer the shutdown, which could significantly affect treatment results.

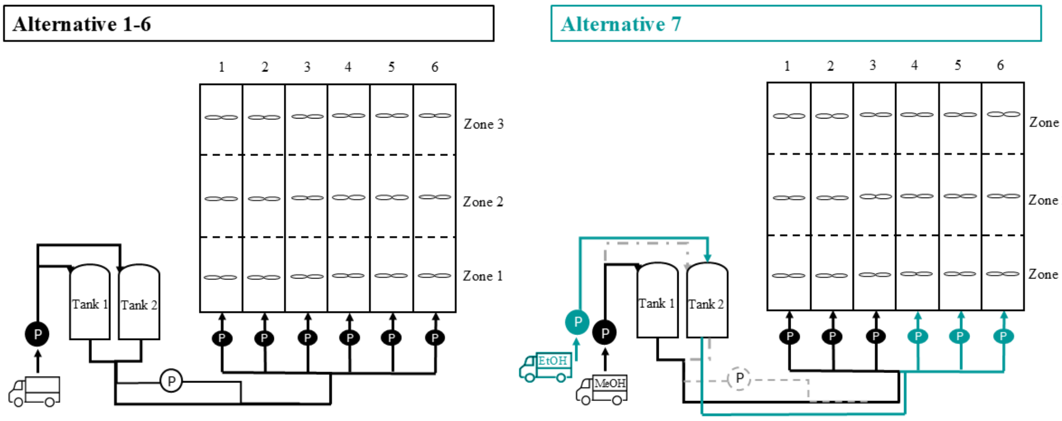

Figure 4.14. Conceptual overview of how the alternatives can be implemented at the WWTP, containing the six post-denitrification lines, along with pumps (P) for dosing, pumping from the truck and a booster pump in the middle. The pipe systems led between the lines and the two storage tanks are shown. On the left, each carbon source is used in the entire system. On the right, methanol and ethanol are used separately. Green indicates new changes and dashed lines the structures that potentially becomes unused in this alternative.

Other alternatives that represent the design or transition aspects, like Alternative 7, were initially considered. Further discussions on this along with other choices for alternatives is held in Section 4.2.5.

4.2.3 Chosen criteria

The general criteria that can be relevant when studying carbon sources was studied and summarized, see Appendix B. From this, the chosen criteria and the definitions included in this assessment are presented in Table 4.4. The explanations of included or excluded criteria follows bellow the table.

Table 4.4. Chosen criteria for the multi-criteria analysis.

Criteria	Definition
Ecological dimension	
Impact on recipient	Impact on recipient through changes of BOD- and copper concentrations in effluent.
Climate impact	Total greenhouse gas emissions from production, transportation and respiration of carbon source.
Circularity regarding nutrients and other resources	Impact on sludge quality in relation to amount of nutrients that can be recirculated to agriculture.
Other environmental impacts	Environmental aspects not considered in the other criteria.
Social dimension	
Perception in society	Society’s opinion and possible concerns regarding the choice of carbon source.
Working environment	Influence on the working environment at Gryaab during daily operations regarding handling and transportation of carbon source as well as lab analyses.
Safety	Safety aspects and risks to the facility or personnel at Gryaab.
Economic dimension	
Annual cost	Annual cost based on operation.
Operational reliability	Operational reliability of the system.
Flexibility	Flexibility of the system to switch from one type of carbon source to another.
Vulnerability	Vulnerability regarding future market availability.

In this study, all alternatives involve liquid carbon sources used for biological treatment within a WWTP. This homogeneity limited the range of relevant criteria, as many differences commonly found in broader MCA applications, for instance fundamentally different technologies or chemicals, were not applicable here. Because of this, many process-related criteria were excluded, only leaving the ones which are relevant when comparing usage of a sole carbon source (Alternative 1–6) to the simultaneous use of ethanol and methanol (Alternative 7). The following sections discusses specific criteria in detail related to the sustainability dimensions.

Ecological dimension

Within the ecological dimension, the criteria deemed most relevant were related to impact on receiving water and sludge circulation as well as climate impact. The other ecological criteria were excluded or restructured.

Waste generation was excluded because the carbon sources are not expected to generate substantial waste, nor is there believed to be a difference between using one or two carbon sources. Waste-related impacts are considered only related to impurities in the products which are instead evaluated under the sludge-related criterion or Recipient impact.

No significant differences in energy consumption are expected across the alternatives in the use phase. There is not enough information about the products to evaluate the ecological impacts of the production besides through the criterion Climate impact, given by the companies.

The assessment did not continue with any standalone criteria related to the usage of materials, resources or chemicals. The focus lies on the impacts or risks associated with their use in the denitrification process which are more meaningfully categorized under other criteria.

Land use and water use were not assessed as separate criteria due to lack of detailed data. However, potential impacts are considered under a consolidated criterion referred to as Other environmental impacts.

Social dimension

Definitions and indicators for social sustainability criteria are highly context dependent. Many aspects that were presented in the general criteria list were excluded because they are too abstract or difficult to assess meaningfully within the scope of this analysis. The criteria relating to work environment, health and safety were considered to have more clear definitions and are directly relevant to WWTP operations and therefore included. Health and safety were combined into just the Safety criterion.

When it comes to end users, the service access and quality are assumed to remain unchanged, aside from any potential impacts on receiving waters, which are already accounted for under ecological criteria. However, social perceptions and public opinion regarding the origin and production of carbon sources may be relevant. General attitudes toward fossil-based or bio-based products, especially those derived from food crops are frequently discussed in the literature and media. These issues could influence stakeholder or public sentiment and are therefore acknowledged in the assessment through the criterion Perception in society.

While the appropriate measures regarding regulation and classifications need to be in line when introducing a new carbon source or process design, any legislation or policy aspects are not covered because the assessments assume they are already implemented.

Economic dimension

The economic dimension can encompass a wide range of factors, including strictly monetary aspects and technical-operational considerations. In this assessment, the focus was narrowed to costs of the product use. The primary economic criterion is the annual cost associated with each carbon source alternative.

Flexibility in terms of reliability of the process during varying operation conditions is deemed less relevant when comparing the current alternatives. Since all alternatives involve the same treatment technique and similar chemicals, no significant differences are expected in how they respond to variations in flow, temperature, or other operational factors.

Flexibility with a focus on adaptability is however more interesting. In this context the ability of adjusting the system means the ability of a WWTP to switch between carbon sources. The desire to avoid reliance on a single carbon source was expressed by WWTP staff during this thesis. This is relevant in scenarios regarding market-driven shifts in product availability or pricing. It also allows a WWTP to reconsider a carbon source that initially appeared to be the most sustainable or cost-effective, should future conditions or improved evaluations suggest otherwise. Therefore, the ease of switching between methanol- and ethanol-based carbon sources was evaluated. This evaluation did not focus on detailed physical or technical requirements, which are already addressed in the prerequisites. This assessment focused on general discussions of the implications of switching between methanol to ethanol and vice versa, rather than evaluating each specific product combination in detail. This approach avoids creating a complex matrix of product-specific switch scenarios and instead captures overall process adaptability. The drivers behind a switch are assessed in relation to the Vulnerability criterion.

Finally, a separate criterion, Operational Reliability, was developed to reflect several technical aspects regarding the carbon sources. Ease of implementation was only partially considered in relation to switching between alternatives. Broader aspects tied to ease of implementation, like initial startup complexity or long-term integration into the facility were not evaluated, as the analysis assumes the alternatives are already introduced. Ease of operation is not included further but is reflected to some extent in both Operational reliability and the Work environment criterion within the social dimension, regarding practical handling and process safety. Other aspects, such as physical system robustness, were excluded from this analysis as the alternatives involve similar types of carbon sources with no expected significant impact on the durability of the WWTP.

4.2.4 Evaluation basis

In this section, the acquired information for the different criteria is compiled along with discussion on the results. First a main calculation relevant for several criteria is presented.

Many criteria are based on the amounts required of each alternative to satisfy the COD demand to reach sufficient treatment. The amounts required are based on the annual COD demand 2024 for the WWTP which was 3 599 tonnes, and the COD content of the products (see Appendix F), the resulting annual demands based on this are seen in the Table 4.5.

The methanol-alternatives require the largest amount of product at 2 399 tonnes/year, followed by recycled ethanol at 2 384 tonnes/year. Why it is so similar despite being an ethanol alternative is due to this alternative having a similar COD-content to methanol. “Pure” ethanol contains more COD per g product and therefore requires less product to reach the same COD demand, being around 1 700 tonnes/year. Less amount of either substance is required in Alternative 7 when the COD demand is split between both carbon sources.

Table 4.5. The calculated annual demand of each alternative, related to the COD demand of the WWTP.

Alternative	Product demand 2024 [tonnes/year]
1. Fossil-based methanol	2 399
2. First-generation bio-ethanol	1 731
3. Second-generation bio-ethanol	1 756
4. Recycled ethanol	2 384
5. Mass-balanced bio-methanol	2 399
6. Second-generation bio-methanol	2 399
7. Methanol and ethanol in separate lines	
Methanol	1 200
Ethanol	878

To get the same demand of the carbon sources when using two carbon sources, a higher proportion of the COD demand would be fulfilled by ethanol and less of methanol. They get roughly the same demand of approximately 1 000 tonnes/year when the COD demand is met by 42% methanol and 58% ethanol (in proportions). Here the same amount would be held in each storage tank which might be logistically beneficial. However, in terms of the dosing, this division would be hard to achieve when half of the lines are dosed by methanol and half by ethanol. If instead, two lines are used for methanol and four lines are used for ethanol then the demands would be approximately 800 tonnes/year and 1 170 tonnes/year respectively. These aspects are only brought up to put in perspective the differences with methanol and ethanol and to highlight other options that might streamline the operational procedure and logistical aspects.

4.2.4.1 Impact on recipient

Regarding impact on recipient from increased concentrations of impurities in effluent, two alternatives were considered relevant for further assessment: one which contained other types of organic substances, and one that contained copper trace concentrations.

The alternative with recycled ethanol consists of two different products, one of which contain the impurity isopropanol, and the other the impurity acetone. These are organic substances which could contribute to increased BOD-concentrations in effluent if they are not consumed. The calculations represent a worst-case scenario based on the following assumptions: The product with isopropanol contains the highest fraction of impurity, 30%; no impurity is consumed in the MBBR denitrification process; everything reaches recipient. BOD-concentrations were calculated for each day of 2024 using data for flows and methanol dosage. Calculation steps are described in detail in Appendix D. Mean values, along with standard deviation and 90th percentile, of the increased BOD-concentrations are shown in Table 4.6.

Table 4.6. Calculated BOD-concentrations from the products of the recycled ethanol alternative, in mg BOD_7/l.

	Product with isopropanol [mg BOD_7/l]	Product with acetone [mg BOD_7/l]
Mean value	8.4	1.3
Standard deviation	3.6	0.57
90th percentile	13	2.1

Comparing these values with the emissions regulation of BOD_7 for Rya WWTP, 10 mg BOD_7/l, both impurities will immensely increase the effluent BOD_7-concentrations from the WWTP. Hence, for the recycled ethanol alternative to be considered as an option, its impurities must firstly be established as a functioning external carbon source. If they are not consumed at a high rate and instead reaches recipient, it will result in Rya WWTP not reaching their emissions regulation.

One study using isopropanol in batch tests and pilot scale found that isopropanol as carbon source led to increased effluent BOD concentrations (Hwang et al., 1994). Other examples of isopropanol or acetone were not identified in the literature and further testing should be conducted to confirm the effect on BOD with isopropanol and acetone.

One of the products of the second-generation bio-ethanol alternative contained small amounts of copper. Two scenarios were used for this: one where all the additional copper from the carbon source ends up in the effluent water, and one where all the copper ends up in the sludge. Calculated values for the copper concentration in effluent water is shown in Table 4.7. Given the low values, it is likely that this will not affect the recipient.

Table 4.7. Calculated additional copper concentration in effluent water.

	Copper concentration in water [µg/l]
Mean value	0.0015
Standard deviation	0.00064
90th percentile	0.0023

4.2.4.2 Climate impact

Climate impact for the alternatives is given in tonnes of CO_2-equivalents per year, shown in Figure 4.15. Greenhouse gas emissions from production, transport and respiration of carbon source are included. For more detailed calculations and assumptions, see Appendix D. The alternatives with fossil methanol have a significantly higher climate impact than the rest of the alternatives, especially the one with only fossil methanol. Recycled ethanol along with second-generation bio-ethanol and bio-methanol have the lowest climate impact.

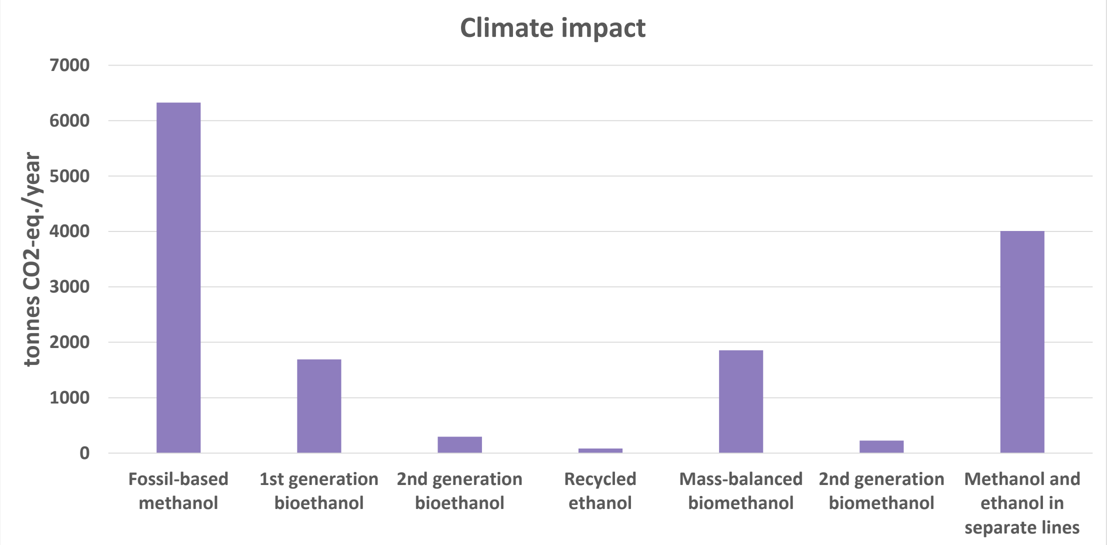

Figure 4.15. Climate impact in tonnes CO2-eq./year for the alternatives.

Among the non-fossil alternatives, the mass-balanced bio-methanol and the first-generation bio-ethanol have the highest impact. The climate impact of the production process is very similar between the two alternatives, however, the mass-balanced stands out in terms of the impact from transportation. The transportation phase account for almost 15 percent of its total climate impact. The products representing the mass-balanced alternative are shipped from much further away in comparison to the products in the first-generation bio-ethanol alternative.

For the recycled ethanol alternative, transportation also constitutes a large share of the total climate impact, about 20 percent. These products are not shipped a long way, but the specified climate impact from the production process is very low compared to all other alternatives.

The climate impact of each product’s production processes was provided by its manufacturer. No additional insight into these figures was requested, and it was assumed that the manufacturers had included both direct and indirect greenhouse gas emissions. Respiration of carbon source was only relevant for the fossil methanol and was included in the total climate impact of the production process.

4.2.4.3 Circularity regarding nutrients and other resources

For this criterion, focus was on examining whether possible metal content in the alternatives could affect the amount of sludge from the WWTP that could be used on agricultural land. One of the products from the second-generation bio-ethanol alternative had metal concentrations in the specified content and was therefore evaluated further. The criterion for impact on recipient included a scenario where all the copper ended up in the effluent water. In this criterion, the possible scenario of all the copper ending up in the sludge is considered.

Copper concentrations in sludge intended to be spread on agricultural land is regulated by Swedish law (SFS 1998:944). Additionally, the sludge from Gryaab is certified by REVAQ, which regulates sludge from WWTPs to be used on farmland (Gryaab, n.d.-

c). Taking the Swedish law and REVAQ regulations into account, the concentration of copper in the sludge cannot exceed 409 mg/kg total solids (TS). If the concentration is larger than this value, the amount of sludge recirculated to agriculture must be reduced. The mean value of copper concentration in the sludge from Rya WWTP year 2024 was 381 mg/kg TS (Gryaab, n.d.-b). Table 4.8 summarizes the calculated additional concentration of copper along with the threshold values and mean value of sludge from Rya WWTP 2024.

Table 4.8. Copper concentrations in the sludge.

	Copper concentration in sludge [mg/kg TS]
Calculated value	0.00628
Mean value Rya WWTP 2024	381
Threshold value for equal amount of recirculated sludge	409
Threshold value by Swedish law (SFS 1998:944)	600

According to these calculations, the additional copper from the alternative carbon source is unlikely to have any impact on the copper concentration in the sludge. Hence, the amount of sludge that can be recirculated can remain unchanged. Given that all alternatives can provide the same amount of sludge to be recirculated, this criterion does not necessarily have to be included in the further steps of the multi-criteria analysis.

4.2.4.4 Other environmental impacts

In this criterion, literature was used to identify other potential environmental concerns for the alternatives. However, it was not possible to provide a comprehensive or fully comparable assessment due to limited data availability. Most suppliers only provided general product information, with little or no detail on specific raw materials or production processes. Nonetheless, a few potential concerns are briefly discussed.

Both fossil and biobased fuels have other environmental impacts than effects on the climate. Fossil fuels and their production have effects such as air pollution, contaminated water and land, and destruction of habitats (Hao & Van Brown, 2019). Biofuel production can have environmental impacts such as effects on land use, water use and water quality (Delucchi, 2010). Additionally, the use of fertiliser for cultivation of crops for biofuel can lead to eutrophication. According to Delucchi (2010), higher land- and water use is required for biofuel production in comparison to petroleum equivalents.

While land use requirements are not directly a problem in themselves, they are an indicator of impacts related to land use such as biodiversity, loss of habitat, ecosystem services, and soil erosion (Delucchi, 2010). Using yield factors of wheat-based bio-ethanol in the EU predicted for 2030 by Leal et al. (2013), a general calculation of land use requirements for the alternatives was conducted. This is presented in Table 4.9.

Table 4.9. Land use for the different alternatives, in m^2 land/m^3 external carbon source.

Alternative	Land use requirement [m^2/m^3]
1. Fossil-based methanol	-
2. First-generation bio-ethanol	7 360 000
3. Second-generation bio-ethanol	-
4. Recycled ethanol	-
5. Mass-balanced bio-methanol	-
6. Second-generation bio-methanol	-
7. Methanol and ethanol in separate lines	3 680 000

Due to a lack of information regarding the economic values or mass values of main and residual products it was difficult to make allocation based on these factors. Therefore, for the alternatives based on residual products, the entire land use was chosen to be allocated to the main product. It should be noted that, while these product alternatives were not assigned any land use requirements in this assessment, they may have been had a different allocation been used. The recycled ethanol and fossil-based methanol were assumed not to contribute to any land use requirements.

When it comes to the use of water, its impact is highly dependent on conditions such as climate, crop type, soil characteristics, and agricultural practices (Chiu et al., 2016; Chiu et al., 2012). Consequently, the region in which the cultivation takes place along with the water availability in that region is important knowledge. A large majority of the alternatives included in the multi-criteria analysis are produced in the Northern European region. According to Mekonnen (2011), Nordic Europe have lower artificial irrigation usage compared to many other parts of the world. However, there could still be risk of water stress in western Europe, including for example Denmark, for cultivation of some crops (Gerbens-Leenes & Hoekstra, 2012). This is mostly due to large industrial and environmental water requirements. The issue is further complicated by climate change, which effects could result in changes in precipitation patterns (Delucchi, 2010).

Once again, due to the lack of information regarding the different product alternatives, such as exactly what type of raw material that is used, waste streams, as well as yield factors, discussions on this subject become general. Therefore, calculations were mainly excluded from this criterion.

4.2.4.5 Perception in society

Public awareness and engagement regarding the choice of carbon sources for denitrification is assumed to be limited. While the environmental and social drawbacks of fossil-based options are well documented, concerns have also been raised in the literature about biomass-based alternatives.

With first-generation biofuels, the food versus fuel conflict may arise (Bhaskar & Pandey, 2015; Darda et al., 2019; El-Araby, 2024; Kampman et al., 2010). This issue means that crops suitable for food production is used for producing biomass for biofuels or bioenergy, potentially affecting food availability, security and prices. It also relates to indirect land use changes and greenhouse gas emissions. This can occur if the production of crop-based biofuels takes place on agricultural land previously used for food, which is pushed elsewhere, far away or even into non-agricultural land (Directorate-General for Energy, 2017).

The food versus feed/fuel issue is one reason for preferring second-generation. However, second-generation requires more advanced processing and is more costly than first-generation biofuels (Darda et al., 2019; El-Araby, 2024). Second-generation biofuels may instead be associated with concerns of deforestation (Darda et al., 2019; El-Araby, 2024). However, this is less relevant considering the included products are based on forest residues Additionally, there may be opinions about suitability of end use for the biofuels within transportation or industrial activities and competition between sectors (Directorate-General for Energy, 2017; Kampman et al., 2010) to consider.

This analysis does not assess current public opinion but speculates on potential concerns that could emerge if these issues gain visibility in media or public discourse. At present, there is no evidence that the public holds specific views on the biomass-based carbon sources. Furthermore, there is a lack of sufficient information to make any assumptions about how society might perceive the other alternatives.

4.2.4.6 Working environment

General considerations regarding the working environment can be made for methanol and ethanol. In this criterion, all methanol-based alternatives are evaluated similarly, regardless of their origin or specific product. The same approach is applied to ethanol-based alternatives, with an exception to the recycled ethanol.

The typical COD-content for ethanol is 2.1 kg COD/kg product, higher than that of methanol of 1.5 kg COD/kg product. The specific products in the alternatives were reported to have similar values with the exception that recycled ethanol (Alternative 4) has a COD-content like methanol, see Appendix F. As mentioned, higher COD-content requires less product and therefore fewer deliveries. In turn, this would reduce the frequency with which employees manage the chemical (carbon source), thereby presumably decreasing the safety risk.

As stated in relation to the laboratory experiments, ethanol is associated with a higher biomass production compared to methanol (Cheng et al., 2023; Torresi et al., 2017). While the current experiment did not confirm this, there might be noticeable differences if the experiment was conducted for longer or used more data points. Additionally, there might be differences in the full-scale. More biomass production could potentially result in more regular maintenance of equipment, which would affect the work environment. However, the potential difference between methanol and ethanol in this aspect is considered small.

The recycled ethanol alternative may require more laboratory analyses during operation due to its impurities. This would apply particularly to the product with varying content (1-30% isopropanol), to monitor denitrification performance. Additional laboratory analyses could potentially be needed at delivery as well, if the manufacturer does not specify the specific content at each batch delivered.

For the alternative with methanol and ethanol in separate lines, the considerations of ethanol and methanol apply. An additional aspect with this alternative is the assumption that it requires more complex operation, running two separate systems at once whereas handling of sole carbon sources of either methanol or ethanol is assumed to be easier.

4.2.4.7 Safety

Only a limited safety comparison could be made between the alternatives due to missing product-specific data, such as complete safety data sheets. Instead, general safety aspects relevant for methanol and ethanol in WWTPs were considered. However, fully assessing the risks, including physical system requirements, necessary permits, and classification standards, were not part of this assessment and would require expert evaluation.

Risks associated with handling, such as spillages, exposure or explosions while unloading and transport, are important to consider. Ethanol was already described to require less handling in the working environment, but it may for that reason also offer a safety advantage. Nevertheless, any new plant components required for any of the alternatives are expected to be designed in a way that minimizes serious risks regardless of the selected carbon source. Residual risks remain if operational routines are not followed or in the event of accidents. Exposure risks can be assessed through safety data sheets of methanol and ethanol, see Appendix A. Both are highly flammable and explosive liquids, but they differ in that methanol poses greater health hazards, while ethanol is more flammable.

Because the alternatives include methanol and ethanol, the facility must be appropriately designed to avoid explosion risks. Environments where flammable gases and vapours may be present must be analysed and classified into hazardous zones (ATEX-IECEx, n.d.; MSB, 2024). See Table 4.10 for the definition of the zones and how it can be applied in a WWTP.

Table 4.10. Definitions of explosion classification zones with examples at a wastewater treatment plant (WWTP).

	Definition	**Examples at a WWTP**
Zone 0	"An area in which an explosive gas atmosphere is present continuously or for long periods" (ATEX-IECEx, n.d.)	The inside of a tank/pump storing the carbon source
Zone 1	"An area in which an explosive gas atmosphere is likely to occur in normal operation" (ATEX-IECEx, n.d.)	The immediate vicinity of the tank, including connected openings/vents
Zone 2	"An area in which an explosive gas atmosphere is not likely to occur in normal operation and, if it occurs, will only exist for a short time" (ATEX-IECEx, n.d.)	The surrounding area adjacent to Zone 1.

This classification, known as EX-classification, depends on several factors including the materials present, the likelihood and type of potential release, and environmental conditions such as temperature, pressure, and ventilation. It guides the selection of appropriate safety equipment and operational procedures.

Besides the EX-classification of the area, the specific chemical used is categorized into temperature class and explosion groups. Ethanol and methanol have been categorized in the same temperature class, T2, but ethanol has a higher explosion group (IIB) than methanol (IIA) (CML EX, n.d.). The temperature class corresponds to an ignition temperature between 300 and 450 °C (CML EX, n.d.; Räddningverket, 2004). Explosion Group II applies to flammable liquids, and the subgroups (IIA, IIB, IIC) further differentiate the risks (CML EX, n.d.; Räddningverket, 2004). If both substances are used in the same installation, equipment must be selected according to the substance with the highest risk, in this case IIB (ethanol). Equipment certified for IIB can also be used for IIA substances, but not the other way around.

In summary, ethanol likely entails more stringent facility requirements related to explosion safety, while methanol poses more serious health hazards. Both risks must be carefully evaluated during the detailed design phase of the facility.

4.2.4.8 Annual cost

The calculated annual costs for the different alternatives are shown in Figure 4.16. See calculations in Appendix D. The currently used fossil methanol has the lowest cost. The second-generation bio-ethanol alternative has by far the highest cost.

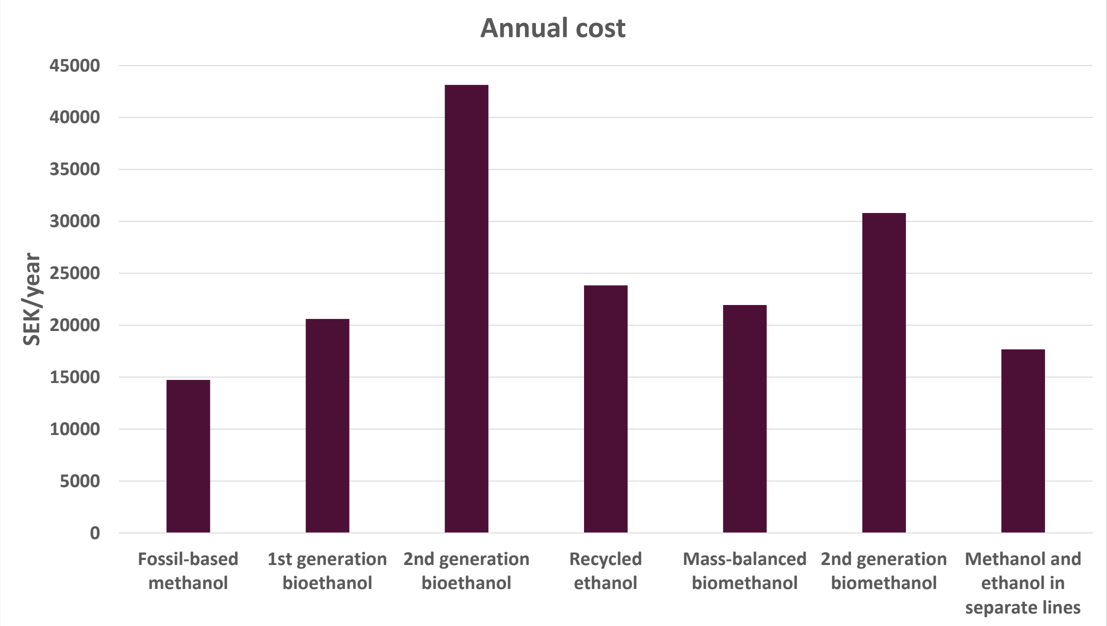

Figure 4.16. Annual cost in SEK/year for the alternatives.

The cost for the second-generation bio-ethanol is more than twice the cost for the first-generation bio-ethanol, and the second-generation bio-methanol has the second highest cost of the alternatives. Chiu et al. (2016) labels first-generation biofuels as more cost competitive. One reason for the price difference could be because of the advanced processing required for turning the biomass to biofuel (Darda et al., 2019; El-Araby, 2024).

4.2.4.9 Operational reliability

Fossil-based methanol (Alternative 1) is used at Rya WWTP today and is otherwise a well-established and reliable option for denitrification (Bill et al., 2009; Brozinčevi et al., 2024; Fu et al., 2022). Alternative 5 and 6, while not yet tested are assumed to perform similarly based on the analysis prerequisites. The same assumption is made for Alternative 2 and 3 (first- and second-generation bio-ethanol), where ethanol also is well-established with high operational reliability (Bill et al., 2009; Brozinčevi et al., 2024; Fu et al., 2022).

Alternative 4, on the other hand, involves untested recycled ethanol products that contain higher levels of impurities and water than the other options. The composition of these products varies, which could affect treatment performance, for example, through fluctuating COD levels or the presence of compounds like isopropanol and acetone. The study by (Hwang et al., 1994) found, besides the increased BOD (see Section 4.2.4.1), that isopropanol was ineffective as a carbon source for denitrification. The isopropanol was in the process converted into acetone, which performed better. Regardless of whether further testing of isopropanol or acetone show that either can function as an external carbon source, the variability in composition raises concerns about process stability. There is uncertainty around whether bacteria can consistently utilize these compounds, or whether they might disrupt microbial communities in the biofilm.

One relevant full-scale case exists. Klagshamn WWTP, a smaller Swedish plant using the MBBR process, has employed ethanol derived from pharmaceutical and agro-industrial by-products (VA SYD, 2024). Although their suppliers differ from those considered in this study, some of the ethanol they use shares similarities with the products in Alternative 4. In 2023, Klaghamn's COD demand was approximately 756 tonnes 2023 (VA SYD, 2024), significantly lower than Rya WWTP (at 3 599 tonnes 2024). Experience at Klagshamn WWTP indicated that variability in ethanol quality contributed to fluctuations in treatment performance (Mases et al., 2012). The quality of the ethanol product can vary between 25% and 85%, and the COD content between 500 and 2200 mg/L (Mases et al., 2012). Starch or alcohol-based by-products are often present, which are believed to be less biodegradable. The recycled ethanol considered in this study also contains varying levels of impurities. The impurities are expected to complicate the measurement of COD and potentially impact the quality of the treated effluent. As a conservative assumption the variation in recycled ethanol composition is treated as a potential risk to process reliability.

Alternative 7, which involves operating two different carbon sources at once require testing. The laboratory experiments can only inform the sustainability assessment in terms of switching between carbon source, not simultaneous use in separate systems. If the operation setups of alternating between, or mixing methanol and ethanol were kept as alternatives in the assessments, the results and experiences could be used more directly. While general experiences with methanol and ethanol have been considered, denitrification rates were assumed to be sufficient across all alternatives for comparison purposes. Thus, differences in denitrification efficiency were not quantitatively compared. It should be noted, however, that ethanol generally demonstrates higher denitrification effectiveness (Bill et al., 2009). In this assessment this is reflected in its higher COD content and lower dosing requirements, as discussed earlier.

4.2.4.10 Flexibility

While system modifications are important in any type of switch of carbon source, a prerequisite of this analysis was that all alternatives are already implemented. Therefore, these requirements only become relevant when evaluating flexibility in case a future switch is needed. As mentioned, the discussions of the actual requirements are limited. Much more details on the treatment plant and expert opinions are needed to formulate a more comprehensive evaluation of the physical alterations needed. Only general comments are made about the ease of adapting the system. In this criterion, just one future switch is considered because several switches back and forth would essentially lead to no differences between the alternatives within the MCA.

Switching from methanol to ethanol may require new safety assessments and permits and ethanol often needs to be denatured. Ethanol also poses a higher fire risk and may trigger stricter classification requirements like EX-zone, as noted under the safety criterion (see Section 4.2.4.7). Systems used with both methanol and ethanol should be designed to meet the most stringent safety standard, typically ethanol’s. Therefore, transitioning from ethanol to methanol is assumed to be easier from a system perspective. In contrast, a switch from methanol to ethanol may involve significant retrofitting, increased safety measures, and component replacements. This adds cost, complexity, and time. Major retrofits could require the plant to shut down for extended periods, potentially several months, affecting treatment performance, emissions compliance, and overall operations. This makes any retrofit a significant decision, not a simple swap.

If a facility is already designed to accommodate both ethanol and methanol, switching between them would be more straightforward. Alternative 7 is assumed to be the most flexible, as the facility is expected to already be equipped to handle both carbon sources. If minor system modifications are still needed, the plant could likely remain operational during adjustments.

In addition to physical infrastructure, it is crucial that the biofilm can effectively utilize the new carbon source. The alternatives analysed are assumed, per the study's prerequisites, to be able to replace the current fossil-based methanol after an initial acclimatization period. Even if this is an extensive acclimatization period, it is considered acceptable when committing to a new source once. However, in the context of flexibility the focus shifts. A quick transition becomes more critical, and prolonged acclimatization periods can pose operational risks.

As established previously, the fossil-based or fossil-free alternatives are assumed to behave the same, except for Alternative 4 which is more unclear due to the impurities. It was described in the laboratory results that literature states methanol typically has longer acclimatisation period. However, this thesis found it might not be very long in the current system, in fact only a few days. Though the adaption to ethanol seemed to be a faster in the experiment.

Information about another WWTP does however indicate much less complicated circumstances regarding using methanol and ethanol in the same facility.
Klagshamn WWTP, mentioned with Operational reliability (see Section 4.2.4.9), was originally designed to utilize methanol but later switched to ethanol (Täljemark et al., 2004; VA SYD, 2024). The facility is still technically capable of handling methanol (VA SYD, 2024). No specific technical specifications or modifications were identified in connection with previous or future transitions between carbon sources at this WWTP, suggesting that the plant can switch between them without major adjustments. The ethanol currently used is considered technical-grade ethanol and classified as waste (VA SYD, 2024). It is noted that handling procedures comply with applicable regulations, although no further details are provided.

Despite the uncertainties with physical requirements, Alternative 7 stands out as the most flexible alternative, where operational continuity and adaptability to supply changes are critical. It is both in terms of infrastructure assuming it has minimal system rebuilds, and with maintaining functionality with the bacteria because of the system already partly running on a specific carbon source can potentially continue while the other part of the system acclimates.

4.2.4.11 Vulnerability

This criterion is both quantitative and qualitative. Quantitative estimations were made on how long the storage lasts at the WWTP in case deliveries are stopped because of market availability issues for instance. The calculations, assumptions and results are presented in Appendix D.

These calculations, only led to small differences in this vulnerability aspects between the alternatives. All methanol options were estimated around 24 days, and all ethanol options besides recycled ethanol would last a few more days, around 33 days. The recycled were estimated at 26 days. Why it appears in the middle of methanol and ethanol is due to having similar COD content/yearly demand to methanol, but a high density, which lowers the estimated flow. While requiring less carbon source, having half the storing capacity compared to the sole carbon sources, the methanol in Alternative 7 depletes just as fast as the one in Alternative 1. Likewise, the ethanol in this alternative lasts 33 days. The difference is quite small between the alternatives.

For the qualitative assessment, assumptions were made on market availability. Here the current availability refers to the reference year 2024. It was evaluated based on supplier inputs or assumptions in case this was lacking. Future availabilities were assumed, based on Gryaab’s previous assessments combined with literature or supplier information. The assumptions are summarized in Table 4.11, afterwards follows the explanations.

Table 4.11. Assumed current and future product availability in each alternative. Current refers to the reference year 2024.

Alternative	Current availability	Future availability
1. Fossil-based methanol	Meets current demand.	Expected to be phased out.
2. First-generation bio-ethanol	Assumed to meet 2024 demand. One product confirmed availability, the other is inferred from product marketing as a carbon source.	Assumed to have many other suppliers with sufficient quantities. May potentially be phased out by second-generation ethanol.
3. Second-generation bio-ethanol	One product meets 2024 demand, the other lacks clear data but it is assumed to reach current demand.	Multiple suppliers likely exist, but high cost may limit use.
4. Recycled ethanol	One product exceeds 2024 demand while the other would require multiple input streams.	Current or similar alternatives seem to have varying content and varying availability.
5. Mass-balanced bio-methanol	Lack of clear data for both included products raise uncertainty with current availability.	Lack of clear data regarding mass balanced products as a whole raise uncertainty with future availability.
6. Second-generation bio-methanol	Availability is assumed to be low.	The availability of other types of bio-methanol may however increase.
7. Methanol and ethanol in separate lines	The lower demand for each carbon source might make it easier to find new products or suppliers. For the actual products see the related alternatives.	The same assumption as for the current availability.

The premise of the thesis is reducing the use of fossil-based methanol, therefore the assumption that it will be phased out as a carbon source is applied to Alternative 1. Further, the current demand and previous year’s demand is met.

It has been generally noted, particularly within the context of Gryaab’s projects, that the availability of bio-methanol based on biomass (Alternative 6) is currently limited. Other types of bio-methanol might be of interest instead. In their previous assessments, a few actors stand out for future considerations for bio-methanol production within Scandinavia. They are shifting toward producing methanol based on carbon dioxide and hydrogen in energy processes. This is commonly known as e-methanol and is showing promising development (Nemmour et al., 2023).

In previous assessments at Gryaab it was mentioned that bio-ethanol and bio-methanol can be produced from residual streams generated by Swedish pulp mills through various industrial processes. It was also stated that the process related to methanol production was stated to be more prevalent in Sweden today. Therefore, it is assumed that this could enhance the availability of bio-methanol from domestic sources.

Various fossil-free ethanol blends based on pharmaceutical residues (as in Alternative 4), or other waste-derived streams are seemingly available on the market. However, they often vary in content and contain impurities. Furthermore, products like these seem to have varying or limited availability, potentially necessitating multiple input streams.

There may be many other suppliers of first-generation ethanol to deliver sufficient amounts. However, the food vs fuel concerns related to first-generation ethanol is generally what led to the development of second-generation bio-ethanol (El-Araby, 2024). If second-generation is continuously seen as the more sustainable option in this regard it may impact availability of first-generation. On the other hand, second-generation ethanol also significantly more expensive, which was highlighted in Section 4.2.4.8, potentially limiting its practical application.

There was a lack of clear information from suppliers as well as in the literature about the availability of the mass-balanced alternatives, hence the current availability is unclear and no assumptions about future availability could be made.

For Alternative 7, the availability is dependent on included products, but considering the operation design it is required less of each carbon source, potentially making it easier to find new products or suppliers to supply the lower demand.

4.2.5 Uncertainties and limitations

This evaluation involved several limitations and uncertainties that should be acknowledged. A full MCA, including scoring, weighting, and aggregation of results, was not conducted within the scope of this thesis. As such, the outcomes should be considered as a foundation for further analysis rather than a complete sustainability assessment.

One of the major limitations was the lack of detailed and consistent data for the alternatives, particularly regarding the environmental impact of production processes. In the questionnaires sent out during this study, not all suppliers responded, and some responses were incomplete. This may partly be due to the limited timeframe of the thesis, and confidentiality reasons. The lack of some specific data limited the ability to assess certain environmental criteria, such as resource and energy use. Additionally, parts of the assessments relied on assumptions, often based on worst-case scenarios. These assumptions were necessary to proceed with the analysis, but they introduce a degree of uncertainty in the results. Sensitivity analyses were not conducted to explore the impact of these assumptions. For some of the qualitative criteria, such as in Perception in society or Vulnerability, the lack of available data resulted in assessment focused on speculations regarding possible aspects of relevance.

As seen in appendix C, data on ISSC certification status of the products was included in the earlier assessment but not in the current one. This is a certification system for sustainable feedstocks (El-Araby, 2024). Among the fossil-free alternatives, recycled ethanol is not eligible for ISCC certification due to its classification as a waste product. For first- and second-generation ethanol, supplier responses were inconsistent without more details. Some indicated full certification, while others stated that only parts of the product were certified. Due to these uncertainties, and because the thesis does not explore procurement frameworks or legal requirements in depth, comparing ISCC status of the alternatives was not included in any criteria. Although it was not part of this MCA, it is important to determine whether non-certified, yet potentially sustainable, products can be accepted under current or future procurement policies of WWTPs.

When it comes to the alternatives, the fossil methanol was only included to represent the continued use of the today's methanol and to act as a reference point. The evaluation of the fossil methanol mainly captured its climate impact, while other potentially negative sustainability aspects might be less represented in the selected criteria. Since it is already decided to phase out this carbon source, it was not a priority in the assessment to capture all aspects of this. Instead, criteria and data collection focused on the other alternatives.

The structure of the alternatives contained some discrepancies. Firstly, a majority of the alternatives consists of two products. These products were deemed similar and were hence combined to limit the number of alternatives. Consequently, in quantitative assessments such as Climate impact and Annual cost, mean values of the two products were used. For the most part, there were not large differences in values between the products within an alternative. In the few cases where there was a difference, it was considered to not affect the end-result to any larger extent.

Secondly, the analysis included different types of alternatives, the product-focused ones in Alternative 1-6 and the design-focus in Alternative 7. For the latter to be included in criteria based on product specific data, representative products for ethanol and methanol had to be chosen. Theoretically, various product combinations could be assessed in this alternative. To more easily display the differences with using two carbon sources, the thesis uses one example only. Fossil methanol was chosen as this could represent a transition period, and the first generation bio-ethanol was chosen for the ethanol part, because it was during the consultations considered one of the most likely options considering only price and market availability.

Other alternatives that represent the design or transition aspects, like Alternative 7, were initially considered. One concept involved dosing methanol and ethanol across all post-denitrification lines, either by mixing them directly in a shared storage tank or by storing and dosing them separately, allowing the mixing to occur within the process lines. These configurations would closely resemble the laboratory-tested mixture, particularly if using the same 60/40 methanol-to-ethanol ratio. The laboratory results demonstrated that such a mix could be technically effective for nitrogen removal. However, unlike the laboratory experiments, the MCA does not evaluate denitrification performance directly, as it assumes equal treatment efficiency across all alternatives. Nonetheless, insights from the experimental work were initially believed to be relevant if this mixed approach remained part of the assessment.
However, during consultations regarding practical implementation, it became evident that mixing methanol and ethanol is currently considered unfeasible at the treatment plant. Such a setup with mixing methanol and ethanol, specifically in the same tanks were believed to remove control over what is dosed and was considered logistically difficult. Dosing them separately were believed to have substantial physical and economic requirements, such as doubling the number of dosage pumps. While this alternative was excluded from the current MCA due to perceived complexity at this

stage, it is still relevant to the broader study and the laboratory experiments. However, all physical changes required in the system need further consideration.

Alternating between methanol and ethanol was another idea discussed in the early stages. However, it was not pursued as a separate alternative in the MCA, as it is not currently considered a stable long-term strategy. Instead, the potential for switching carbon sources is treated as a flexibility aspect and incorporated as part of the evaluation criteria. While Alternative 7 that is included may also contain implementation challenges, it is seen as the most viable option for having two carbon sources.

4.2.6 Further directions relating to the evaluation basis

To support future decisions at Gryaab or other WWTPs, the sustainability implications and technical performance of carbon sources must be better understood. Switching to an alternative must align with long-term operational goals and environmental commitments.

General recommendations for future work are the following:

- Complete the MCA process, including structured scoring and weighting of criteria, involving stakeholders in a transparent process.
- Collect more detailed data. Especially on production processes, supply chains, energy and resource use, and emissions.
- Include sensitivity analyses to evaluate the robustness of results under different assumptions.

With the current alternatives and the development of evaluation basis, some more specific recommendations can be made. To start, the criteria recommended to be included for further assessments are:

- Impact on recipient
- Climate impact
- Annual cost

All these criteria could be compared in clear terms and are of great importance when choosing carbon source.

One criterion can be left out: Circularity regarding nutrients and other resources. Only one alternative had potential metal contents but proved to give almost no impact on metal content in the sludge. The other alternatives are assumed to have no impact on the sludge.

The rest of the criteria need further consideration to confirm their relevance to the evaluation of carbon source, which are:

- Other environmental impacts
- Perception in society
- Working environment
- Safety
- Reliability in operation

- Flexibility
- Vulnerability

The criterion Other environmental impacts, mainly concern land use and water footprint, related to first generation bio-ethanol. Some considerations for other alternatives were identified in the literature, though more product information (origin and conversion processes) is required to relate it further to the alternatives.

A few different aspects could be highlighted in Perception in society, but at this stage it was also mostly relevant for the first generation bio-ethanol. Further assessments can confirm if there are other aspects and determine the role of societal perception in this issue.

For working environment and safety, the general discussions of methanol and ethanol are considered relevant in future evaluation, but more details should be gathered of product information to really define the similarities and differences between the carbon sources. An important aspect going forward is having expert evaluation of the safety requirements.

To evaluate Operational reliability, future assessments should consider whether to continue using simplified approaches like this MCA, without evaluating actual denitrification rates, or to conduct laboratory experiments to gain direct knowledge of each alternative's denitrification performance and impacts on the process. Regardless, the assumption that the varying content and impurities with recycled ethanol compromises the reliability, need to be confirmed.

In the Flexibility criterion, care must be taken in how it is defined and evaluated. In this assessment, it was kept general for both methanol and ethanol to avoid creating a complex matrix for each individual product. However, if WWTPs want to have flexibility when switching between carbon sources, more detailed information is needed, particularly regarding physical infrastructure requirements and permitting processes or legislation aspects.

While Vulnerability is considered an important criterion, it requires a more robust and consistent method of assessment, especially concerning current and future market availability.

All alternatives are recommended to be kept in further assessments except for recycled ethanol, which needs further testing to determine how the impurities impact the treatment processes. The fossil methanol should only be included to serve as a reference to the other alternatives. When it comes to the more design-oriented alternative, with using methanol and ethanol in separate lines, this assessment highlights the broad implications of using two carbon sources at once. Going forward, one could input the information from the different products as a sensitivity analysis to study variations in this alternative. One could also look at different proportions required for each of the carbon sources. Other design alternatives could be further assessed, such as mixing methanol and ethanol, if evaluations of what is required of the facility to handle different carbon source reveals that large infrastructural changes are not required, therefore making such an option more economically feasible.

5 Conclusion

This thesis explored the use of different carbon sources in biological nitrogen removal at wastewater treatment plants (WWTPs), with a particular focus on methanol and ethanol. Laboratory-scale experiments using continuous MBBR systems provided insights into the effects of switching between carbon sources (between methanol and ethanol and a mixture of methanol and ethanol). In parallel, a sustainability analysis was conducted to develop a basis for evaluating carbon sources. This was done using a multicriteria analysis framework, including several ecological, social and economic criteria. It focused on developing an evaluation basis in which alternatives of various fossil free versions carbon sources can be compared. The alternatives compared in the sustainability analysis are separated from the laboratory work but both parts are equally important to achieve the aim of aiding WWTPs in transitioning to sustainable external carbon source usage in post-denitrification processes.

The laboratory results showed that there was nitrogen removal in all reactors throughout the experiment, regardless of carbon source transitions. Despite not quite reaching the full denitrification performance as the full scale process the setup aimed to replicate, the experimental system worked well considering the small scale. However, the trends observed for nitrite accumulation and measurements of organic carbon, point to slight underdosing of carbon during the experiment. This seemingly only affected nitrite and not the nitrate removal. Overall, the results suggests that a MMBR system accustomed to methanol is not affected in denitrification performance when using a mixture with main parts methanol and a smaller part ethanol, or by switching from methanol to ethanol. However, a small decrease in denitrification performance was observed during a few days, when switching back to methanol after a period of ethanol dosage. This indicates the need of a short acclimation period for the MBBR biofilm when switching from ethanol to methanol as carbon source.

In total, 11 criteria were selected for the MCA, covering ecological, social, and economic dimensions. Among these, the most clearly quantifiable criteria which is recommended to be used directly for further assessments concern climate impact, annual costs and impact on recipient (related to effluent BOD concentrations). Only one criterion was concluded to be less relevant. This was a criterion evaluating effects on the sludge and subsequent impact on nutrient recycling, though only a potential issue for one alternative, the outcome was that it had no impact and can be excluded for further analysis.

The relevance of the other criteria and the evaluation of the alternative performances in these criteria need to be further assessed. These generally had a lack of data, which made the assessment difficult, and many assumptions were required. These include assessments of land use and material use, perception in society, market availability. Furthermore, the technical aspects or related to the operation (work environment, safety, flexibility of adapting the current system) were hard to set specific things for each alternative due to a lack of data but also due to the similarities between the alternatives.

All alternatives are recommended for further assessment, except recycled ethanol, which requires additional testing due to potential effects from impurities. Fossil methanol should be retained as a reference. Additionally, the design-focused alternative using methanol and ethanol in separate denitrification lines highlights the broader implications of dual carbon source use.

Several areas for further research and development were identified. Future laboratory work should prioritize an improved experimental setup, with more analyses. For continuation of the sustainability assessment, additional collection of data and a full multi-criteria analysis should be completed to allow for a thorough evaluation of the alternatives.

Ultimately, this study demonstrates the value of combining practical testing with holistic sustainability assessments. The findings indicate what seems to work technically, and highlights what is important in the MCA going forward and therefore provides relevant insights to aid WWTPs in the transition to sustainable carbon source usage.

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7 Appendices

Appendix A

Properties of methanol and ethanol

Property	Methanol	Ethanol
Density	792 kg/m^3	789 kg/m^3
COD content	*1.5 g COD/g methanol*	*2.1 g COD/g ethanol*
Flash point	9.7 °C	12 °C
Upper/lower flammability limit	6 %V/36%V	3.5%V/19%V
Autoignition temperature	455 °C	425 °C
Hazard statements	H225 Highly flammable liquid and vapour. H301+H311+H331 Toxic if swallowed, in contact with skin or if inhaled. H370 Causes damage to organs.	H225 Highly flammable liquid and vapour. H319 Causes serious eye damage/eye irritation.

Appendix B

General Criteria list

Considered criteria that could be relevant when studying carbon sources are summarized, with significant inspiration from Backeström and Ceder (2022). Where appropriate, certain criteria have been grouped under broader categories or presented as sub-criteria. Additional descriptions are provided for some criteria. References indicate where each criterion has been proposed or used in earlier MCAs. Afterwards follows the reference list (confined in this appendix).

Criteria	Description	Reference
ECOLOGICAL DIMENSION		
Environmental Impact on Receiving Waters*		[1], [2], [3], [4], [5], [6], [7], [8], [9], [10]
Impact on sludge and Nutrient Recovery		[1], [3], [6], [7], [9]
Resource use and efficiency:		
Energy use*		[1], [2], [5]
Natural resource use/ non-renewable resource use		[1], [3], [4]
Material use		[1], [2]
Water use or efficient use of water		[1], [2], [3]
Chemical use*		[1], [9], [11]
Land use		[1], [9]
Impact on sludge properties or circularity*		
Climate impact*	*Emissions of greenhouse gases*	[1], [3], [4], [7], [10]
Waste generation*	*Total or non-recyclable waste generation*	[4]
SOCIAL DIMENSION		
Work environment*		[1], [2]
Health and safety*		[1], [2], [3], [4], [7], [8], [9]
Policies, legislation and Institutional Support*		[1], [2], [3]
Stakeholder Confidence and Collaboration		[1], [3]
Local acceptance/perception in society*		[1], [4], [6], [7], [8], [9]
User Impact and Service Quality and accessibility		[1], [2], [3], [4], [6]
Local environment quality and amenity	*Effects on e.g. recreational values, noise or/and the accessibility of the area*	[1], [4]
Equity	*Effects on vulnerable groups in the society*	[1], [4], [5]
ECONOMIC DIMENSION		
Costs:		

Cost of environmental impact		[1], [3], [8]
Annual cost*		[1], [2], [3], [5], [6], [7], [9]
Transportation costs		[1], [3]
Social profitability		[1], [4]
Land cost		[9]
Economic performance of production and waste management		[9]
Expenditure related to workforce skills and safety considerations		[2], [5], [8], [9], [10], [11]
Investment		[2], [5], [9], [10], [11]
Maintenance/operation/monitoring costs*		[5], [8], [9]
Financial risk	*In general, or tied to risk for operational stops etc.*	[1], [2], [3], [6], [7]
Technical function:		
References for technical function*		
Flexibility -adaptability*	*The ability to adjust the established system.*	[2], [6], [7]
Flexibility – reliability*	*Process performance during varying operation conditions*	[1], [2], [3], [5], [8], [9], [10]
Physical durability of the system	*Physical durability and robustness of the system*	[2], [3], [5], [9]
Ease of implementation or operation (convenience)	*It can also cover the compatibility to current system and action plan, the construction.*	[1], [2], [3], [9], [10]
Vulnerability*	*Related to the market availability of the required materials/chemicals*	[1]

* Included in MCAs at Gryaab regarding new treatment techniques.

References in the table:

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Appendix C

Summary of requested information of suppliers - with x marking if it concerns the market analysis performed at Gryaab 2024 (A-24), or the current thesis' multicriteria analysis (MCA-25), including general comments on supplier responses and usefulness in the current analysis.

Type of information	**A-24**	**MCA-25**	**Comments**
Product name, chemical name and manufacturer	x		Sufficient information was provided to form the alternatives in the MCA.
Location of manufacturing and transport	(x)	x	Partly included in the market analysis, though not as a separate question. Sufficient information for all products was not provided, requiring assumptions in calculations.
Mode of transportation		x	Sufficient information was not provided, requiring assumptions in calculations.
Chemical properties (Quality, impurities, water content, COD content)	x		There was sufficient information useful in various steps of the MCA.
Raw material used	x	x	There was varying amounts of detail but was partly useful in the MCA.
Amount of raw material required for production		x	Sufficient information was not provided
Energy consumption during manufacturing and type of electricity used.		x	Sufficient information was not provided.
By-product origin and process	x	x	Not relevant for all; among those for whom it was, sufficient information was not provided.
Full product specification and safety data sheet (SDS)	x	x	Not all suppliers provided full documentation.
Occupational safety considerations (beyond SDS content)	x	x	Not all suppliers commented on safety classification or additional workplace considerations.
Approximate price (EUR/kg)	x	x	Sufficient information was provided to be evaluated.
International Sustainability and Carbon Certification (ISCC) - certification status	x		Not all suppliers provided information on certification. Though, it was not used further in this assessment.
Emission factor, CO_2 equivalent for production or respiration	x	x	There was sufficient information for evaluation, though with uncertainties. Suppliers seem to account for climate impact in different ways. Updated information asked specifically for cradle-to-gate emissions of the product (from raw material extraction to finished product leaving for delivery to customer) indicated in g CO2 eq/kg product.
Estimated annual delivery volume	x	x	Some suppliers did not provide this information. It was used to evaluate market availability with assumptions.

Appendix D

Calculations in the sustainability analysis

Product demand

A product demand for 2024 was calculated using the yearly COD demand 2024 and the COD-content of each product (found in Appendix F) with

$$product\ demand\ \left[\frac{tonnes}{year}\right] = \frac{COD\ demand\ [tonnes/year]}{COD\!-\!content\ of\ product\ [\frac{kg\ COD}{kg\ product}]}$$

Impact on recipient

Data on flows and dosed mass of COD at Rya WWTP for each day of 2024 were acquired from internal documents. Amount of impurity in product content was given by the manufacturers. Concentration of impurity for each day was calculated in the following steps:

$$Amount\ of\ carbon\ source\ dosed\ \left[\frac{kg}{d}\right] = \frac{Dosed\ COD\ [kg\ COD/d]}{COD\!-\!content\ of\ product\ [\frac{kg\ COD}{kg\ product}]}$$

$$Amount\ of\ BOD\ \left[\frac{mg}{d}\right] = Amount\ of\ carbon\ source\ dosed\ \left[\frac{kg}{d}\right] \cdot Share\ of\ impurity\ in\ product\ [-] \cdot BOD - content\ of\ impurity\ \left[\frac{g\ BOD}{g\ impurity}\right] \cdot 1\ 000\ 000$$

$$BOD - concentration\ \left[\frac{mg}{l}\right] = \frac{Amount\ of\ BOD\ \left[\frac{mg}{d}\right]}{Flow\ [l/d]}$$

Mean, standard deviation and 90th percentile values were calculated using Excel.

BOD-values for each impurity were derived from product safety datasheets.
In these safety datasheets, it was not specified if the values represented BOD_5 or BOD_7. Since it was non-Swedish safety datasheets, it was assumed that it represented BOD_5. The calculated BOD-values were converted into BOD_7 using a BOD_7/BOD_5-ratio provided by Svenskt Vatten (Report 2023-1, “Resilient dimensionering av avloppsreningsverk”).

Climate impact

The climate impact consists of the emissions from production and the transports. Emissions for the production [gCO2-e/kg product] was given from the manufacturers. The emissions from transports were calculated.

Assumptions:

- The manufacturers included both direct and indirect greenhouse gas emissions.
- Respiration of carbon source was only relevant for the fossil methanol and was included in the total climate impact of the production process.
- The number of transports for current methanol usage is 4 times every 3 weeks, making it 1.33 times per week. This is 69.3 transports in a year.

- One truck carries 34 tons of liquid carbon source.
- The starting point from which the product is sent was assumed if not clear by production information of the manufacturer. The thesis will not share such company information.

The number of transports for the other products was estimated with

$$current\ no.of\ transports\ per\ year = \frac{annual\ demand\ of\ fossil\ methanol}{annual\ demand\ of\ the\ product}$$

The number of transports for each alternative is shown in the table.

Alternative	Transports per year
1. Fossil-based methanol	69.3
2. First-generation bio-ethanol	50.0
3. Second-generation bio-ethanol	50.7
4. Recycled ethanol	68.9
5. Mass-balanced bio-methanol	69.3
6. Second-generation bio-methanol	69.3
7. Methanol and ethanol in separate lines	
Methanol	34.7
Ethanol	25.4

An online calculation tool (NTMCalc Basic 4.0 Environmental Performance Calculator) was used to determine emissions in kg CO2-e per trip. Emissions from production and transport was converted to kg CO2-e per year.

The total emissions in tonnes CO2-e/year are calculated with

$$total\ emissions\ = production\ emissions + transport\ emissions$$

Circularity of nutrients

It was assumed that all copper ends up in the sludge, and no copper goes with the effluent water from the post-denitrification process.

$$Copper\ concentration\ in\ sludge\ \left[\frac{mg\ Cu}{kg\ TS}\right] = \frac{Total\ amount\ of\ copper\ from\ carbon\ source\ [mg\ Cu]}{Total\ amount\ of\ sludge\ to\ digestion\ Ryaverket\ 2024\ [kg\ TS]}$$

Annual cost

The annual cost for each alternative is calculated with

$$Annual\ cost\ \left[\frac{SEK}{year}\right] = price\ of\ product\ [\frac{SEK}{kg}] \cdot\ product\ demand\ \left[\frac{tonnes}{year}\right]$$

The product prices for each alternative were based on supplier-provided information. While exact prices are not disclosed due to confidentiality, approximate price ranges are presented in Appendix F.

Vulnerability - Calculations of how long storage lasts

Assumptions:

- There are two storage tanks of 100 m^2 each, resulting in each alternative with one carbon source (Alternative 1-6) having a total storage volume of 200 m^2, whereas Alternative 7 stores methanol and ethanol in one tank each.
- The tanks can be filled and emptied entirely.

Calculations:

$$No. of\ days\ until\ tanks\ are\ empty = \frac{Total\ storage\ volume\ [m3]}{Flow\ [\frac{m3}{day}]}$$

Where the flow is calculated with

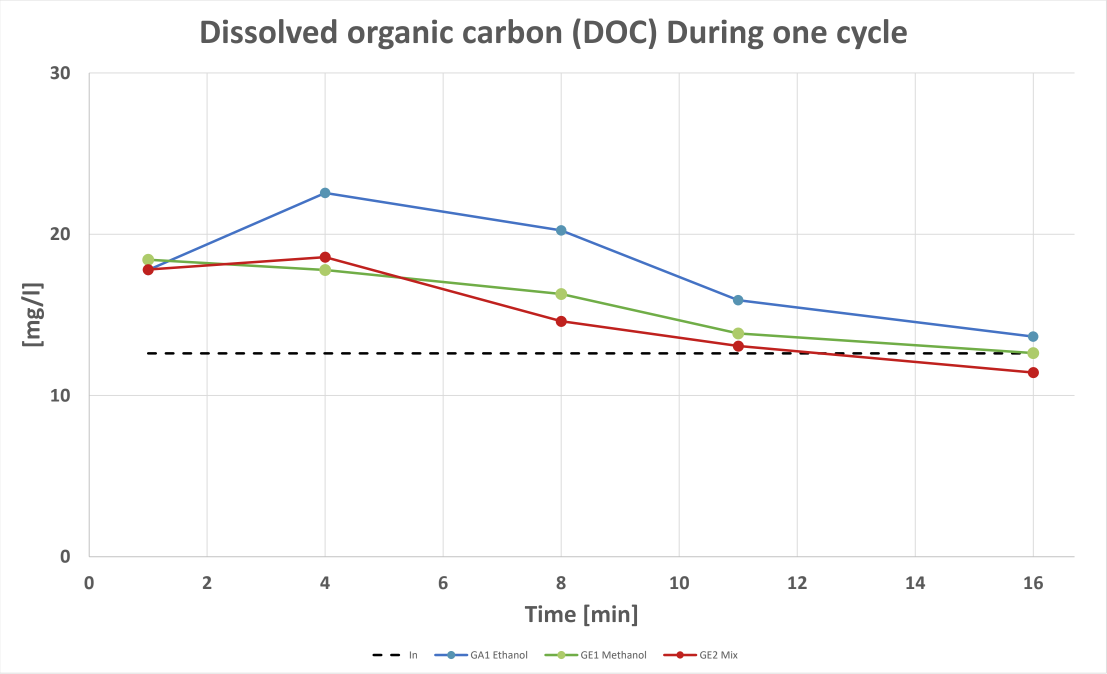
$$Flow\ [\frac{m3}{day}] = \frac{demand\ of\ carbon\ source\ \left[\frac{kg}{year}\right]/365}{density\ [\frac{kg}{m3}]}$$

The resulting number of days until storage runs out according to these calculations are seen in the table below:

Alternative	Storage lasts [days]
1. Fossil-based methanol	24.1
2. First-generation bio-ethanol	33.3
3. Second-generation bio-ethanol	32.8
4. Recycled ethanol	25.7
5. Mass-balanced bio-methanol	24.1
6. Second-generation bio-methanol	24.1
7. Methanol and ethanol in separate lines	
Methanol	24.1
Ethanol	32.8

Appendix E

Diagrams of experimental results – Additional test of dissolved organic carbon



Appendix F

Properties of product alternatives (Alternative 1-6) in the sustainability analysis

Alternative	Purity [%]	COD-content [kg COD/kg product]	Density [kg/m3]	Approximate price ranges [SEK/kg]
1. Fossil-based methanol	>99	1.5	792	5–10
2. First-generation bio-ethanol	>99	2.08	789	10–15
3. Second-generation bio-ethanol	>99	2.05	789	22–27
4. Recycled ethanol	50–81	1.51	840	7–12
5. Mass-balanced bio-methanol	>99	1.5	792	5–15
6. Second-generation bio-methanol	>99	1.5	792	10–15

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