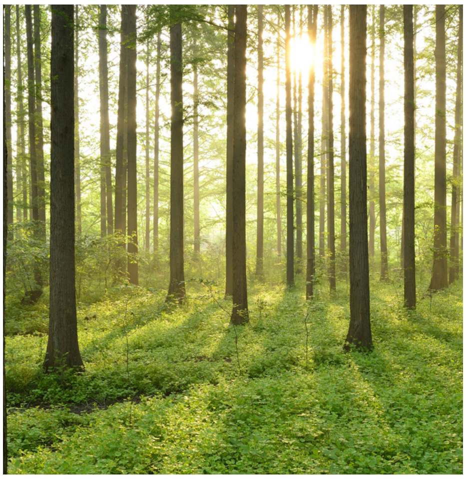
VOC IN BIOGAS PROCESS WATERS

REPORT 2015:221



ENERGY GASES AND LIQUID FUELS

Energiforsk

VOC in Biogas Process Waters

Content of VOC in Process Water from Upgrading Facilities for Compressed Biogas (CBG)

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Authors' foreword

This project was carried out mainly by the authors and staff at the plants where sampling was performed. Valuable contributions were also made by members of the project group, which consisted of:

- Rakel Martinsson, Borås Energi och Miljö AB
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Sammanfattning

Vid anaerob nedbrytning av organiska material bildas biogas som består av metan, koldioxid och mindre mängder av föroreningar såsom svavelväte, vatten, ammoniak och flyktiga organiska föreningar, VOC. Vid uppgradering och komprimering av biogas till fordonsbränsle uppkommer ett processvatten som i olika utsträckning innehåller VOC.

VOC är samlingsnamn för flyktiga organiska föreningar med låg kokpunkt[1]. De kan produceras naturligt av mikroorganismer, växter och frukter eller på syntetisk väg. VOC kan användas som viktiga komponenter i färg, lösningsmedel, parfym, diverse industriella produkter, oljeprodukter mm.

Det finns i dagsläget en osäkerhet kring hur processvattnet bör hanteras på bästa sätt för att minimera påverkan på hälsa och omgivande miljö. En viktig anledning till detta är att det inte är klarlagt vad processvatten från komprimering och uppgradering av biogas innehåller. Koncentrerat processvatten kan ha en stark stickande lukt som kan upplevas besvärande för bland annat driftpersonal vid hantering av vattnet och det finns även oro för negativa hälsoeffekter vid upprepad och långvarig exponering. Vanliga tekniker för hantering av det uppkomna processvattnet vid svenska biogasanläggningar är: behandling på kommunalt reningsverk, utsläpp till recipient eller återföring tillbaka till rötningsprocessen.

En tidigare studie finansierad av SGC/Energiforsk (Arrhenius and Johansson, 2012) visar på att det troligtvis är de ämnen som finns i biogasen innan uppgradering som sedan återfinns i processvattnet. VOC hamnar i biogas genom avgång från det material som rötas. Antingen finns det redan i substratet eller så bildas det av mikroorganismerna under rötningsprocessen.

Mål med detta projekt har varit att:

- Karakterisera processvatten från minst 6 gasuppgraderingsanläggningar (≥ 3 vatten, ≥ 3 amin) och minst ett prov från kondens vid komprimering av biogas med avseende på innehåll av flyktiga organiska föreningar, VOC.
- Sammanställa litteraturstudie:
  - × Tillgängliga tekniker för omhändertagande av uppkommet processvatten. Teknikerna beskrivs avseende möjlighet att rena VOC i vatten, kostnadsnivå och driftsäkerhet
  - × Miljö- och hälsoeffekter av VOC i processvatten
  - × Nedbrytning av ett urval av VOC i anaerob respektive aerob miljö
- Verifiera resultat från litteraturstudie för minst 2 olika tekniker för omhändertagande av uppkommet processvatten
- Skapa ett bra underlag för val av lämpliga analysmetoder samt utgöra ett underlag för bedömning av miljö- och hälsoeffekter av processvatten samt möjliga behandlingsmetoder

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[1] VOC är ett samlingsnamn för flyktiga organiska föreringar, Volatile organic compounds. Det finns olika definitioner, enligt EU direktiv 1999/13/EC är det ämnen som har ett ångtryck på 0,01 kPa eller mer vid 20°C. I detta projekt räknas alla ämnen som har en kokpunkt under 350°C till VOC.

Litteratursammanställning
Under litteraturgenomgången identifierades några viktiga referenser som anses användbara för frågor kring VOC i processvatten:

- Arrhenius and Johansson (2012) “ Karakterisering av föroreningar i biogas före och efter uppgradering till fordonsgas”
- Norberg and Lithner (2013) ” Rening och destruktion av kontaminerat släckvatten”
- Farhadian, Duchez, Vachelard, and Larroche (2008) ” Monoaromatics removal from polluted water through bioreactors—A review”
- Ruiz and Flotats (2014) “Citrus essential oils and their influence on the anaerobic digestion process: An overview”

Flera studier har undersökt innehåll av VOC i biogas, bland annat Arrhenius and Johansson (2012), Moreno et al. (2014), Orzi et al. (2010) Rasi et al. (2011) och Pierucci et al. (2005).

Den stora variation av mängd och specifik VOC som hittats i processvatten gör det svårt att dra generella slutsatser om miljö- och hälsoeffekter. Information om de vanligast förekommande VOC i processvatten som provtagits redovisas i litteratursammanställningen och appendix C. För p-cymen, d-limonen och 2-butanon som är de VOC som hittats i högst koncentration är d-limonen den enda som har allvarligare miljörelaterade riskfraser (R50 och R53).

Utifrån den problematik som finns kring mark och vatten som förorenats med oljeprodukter har det utvecklats ett antal reningstekniker för att rena vatten med organiska föroreningar. Val av reningsmetod bestäms av processvattnets karaktär samt vilken belastning det ger recipient. Möjliga tekniker kan indelas i tre kategorier; fysikaliska, kemiska och biologiska. Fysikaliska tekniker använder de fysikaliska egenskaperna som VOC har för att skilja dem från vatten. Till dessa hör luftnings-, filter- och membran-tekniker. De olika teknikerna har ett stort spann i investerings- och driftkostnad men kan anpassas efter anläggningens behov. Kemiska tekniker som är applicerbara för processvatten är främst av oxidationstyp, vilka tenderar att bli relativt kostsamma för just rening av processvatten.

I biologiska reningstekniker bryts VOC ned i biologiska processer. Dessa tekniker har ett stort spann i investerings- och driftkostnad beroende på hur avancerad anläggningen är. Kostnadseffektiva alternativ kan vara att använda en befintlig biologisk reningsanläggning för samrening. Exempel på samrening är återföring till rötningsprocessen, att sända processvatten till reningsverk eller att bryta ned processvatten i biologiska markbäddar/våtmarker.

Studier på inhibering av anaeroba processer på grund av höga halter av VOC har gjorts vilka visar på stor variation i känsligheten för VOC. Den mikrobiologiska florans sammansättning och yttre faktorer som påverkar denna är viktiga. Exempel på yttre faktorer är reaktorns belastningsgrad av inmatat organiskt material och reaktortemperatur. Det är även känt att mikroorganismer kan anpassar sig och sannolikt är att processvatten med VOC som härrör från substratet är enklare för processen att hantera. Halter på mellan 5 och 500 mg/l VOC har undersökts och visats ha varierande inhiberande effekt på rötningsprocessen.

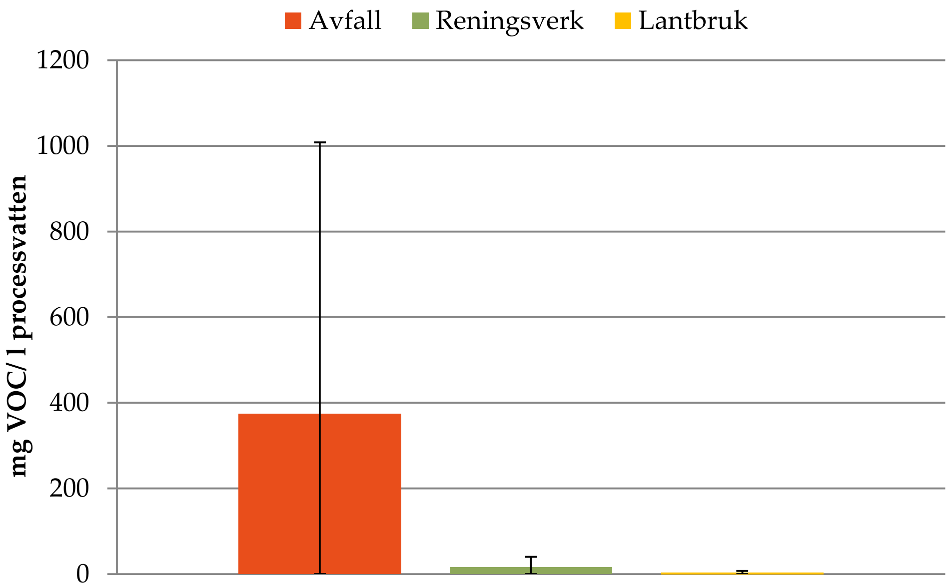
Karakterisering av processvatten
Detta projekt har undersökt både mängd och typ av VOC från nio provtagningsplatser vid åtta biogasanläggningar. Anläggningarna delades in i tre kategorier med avseende

på vilket substrat som huvudsakligen rötas, avfall (mat-, slaktavfall), reningsverk (ARV-slam) och lantbruk (gödsel, grödor, ensilage). Vid sju av åtta biogasanläggningar bestod substratet till minst 10 % av avfall. Hälften av anläggningarna använde aminskrubber och hälften vattenskrubber för att uppgradera gasen till fordonsgas. Ett prov på kondensat togs. En detaljerad beskrivning för hur provtagningen skulle utföras togs fram så att mätfelen skulle bli så små som möjligt, se appendix A och B.

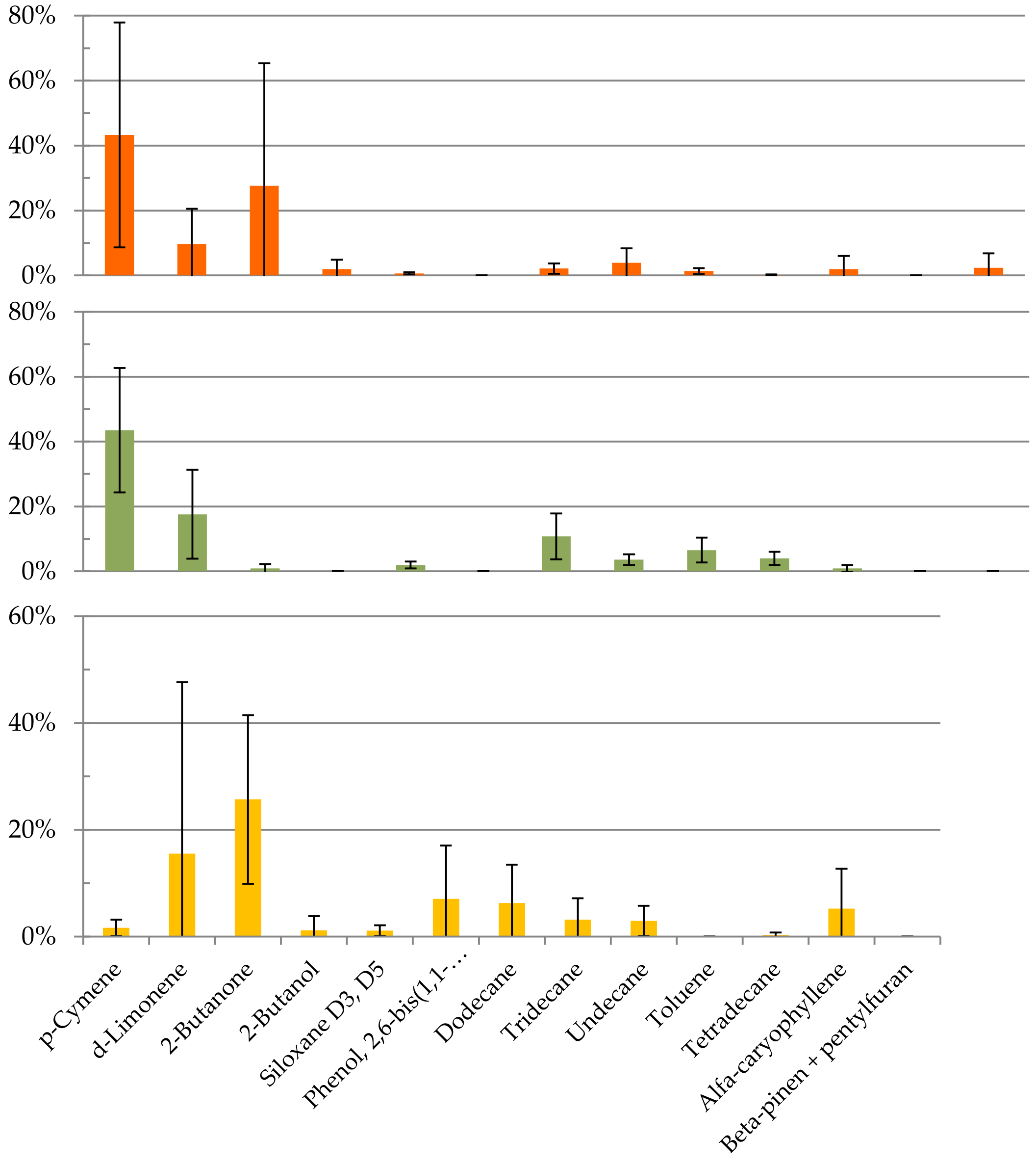
Ingen skillnad kunde ses mellan typ av uppgraderingsteknik (amin- eller vattenskrubber). Användingen av vatten varierade kraftigt mellan varje specifik anläggning. Detta påverkade halten VOC i hög grad. Resultaten från provtagningarna visar att vilket substrat som rötas har stor påverkan på halt av VOC i processvatten, både vad gäller total medelhalt och vilka specifika VOC som återfinns i vattnet, se Figur 1-3. Anläggningar som har avfall (mat- och slakteriavfall) som huvudsubstrat har den högsta halten av VOC och anläggningar som rötar lantbruksavfall den lägsta.

Av de två reningsverk som ingick i studien så hade processvatten från den ena VOC-halter i nivå med anläggningar för avfall och den andra hade halter i nivå med anläggningar för jordbruksavfall. Standardavvikelsen är hög för både totalkoncentrationer och specifika VOC vilket indikerar att anläggningsspecifika data är viktiga för resultatet. Medelhalt av VOC var 27, 17 och 0,7 mg VOC/Nm^3 behandlad biogas för rötning av avfall, reningsverksslam respektive jordbruksprodukter.

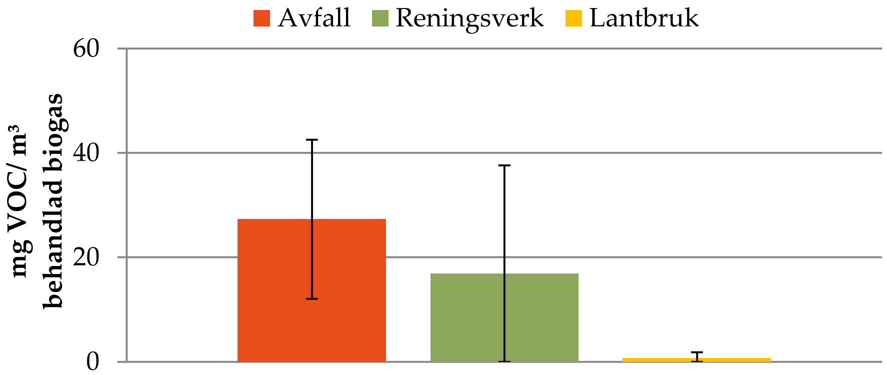
De vanligast förekommande VOC är p-cymen, d-limonen och 2-butanon även om det varierar stort mellan anläggningar, se Figur 2.



Figur 1. Medelhalt av VOC i processvatten från uppgradering av biogas uttryckt som mg/l processvatten. Resultaten uppdelade med avseende på huvudsubstrat och standardavvikelse är markerad med felstaplar.



Figur 2. Genomsnittlig andel av de vanligast förekommande VOC i processvatten från uppgradering av biogas. Resultaten uppdelade med avseende på huvudsubstrat: avfall (🟧), reningsverk (🟩) och lantbruk (🟨).



Figur 3. Medelhalt av VOC i processvatten från uppgradering av biogas uttryckt som mg/m^3 behandlad biogas. Resultaten uppdelade med avseende på huvudsubstrat och standardavvikelse är markerad med felstaplar.

Laboratorieförsök för utvärdering av reningstekniker

Två labförsök genomfördes för att utvärdera reningsteknikerna, adsorption på filter och nedbrytning i anaerob miljö genom satsvisa utrötningsförsök.

I utrötningsförsöken startades tre serier, en kontrollserie utan tillsats av VOC, en serie med en koncentration på 11,6 mg VOC/l och en serie med 238 mg VOC/l. Halterna av VOC som användes i denna studie har i tidigare studier visats kunna vara mer eller mindre hämmande men 238 mg VOC/l har visats tydligt hämmande i tidigare studier. Biogasproduktionen i detta test var dock lika för alla serier med en viss fördröjd produktion i serien med 238 mg VOC/l.

Filterförsöken utfördes med torv och aktivt kol. 3 L tillrett processvatten pumpades två gånger i olika koncentrationer genom 4,5 cm^3 stora filter. Den sista decilitern samlades upp och analyserades på VOC. Värdet jämfördes med ett blankprov som pumpats igenom utan filter. Resultaten visade att både aktivt kol och torv har kapacitet att rena processvatten. Aktivt kol hade högre reningsförmåga för båda koncentrationerna. Båda filtermaterialen hade svårt att effektivt rena 2-butanon som är den mest lösliga av de VOC som testades. Torv hade något lägre reningsförmåga av p-cymen och d-limonen, men högre reningsförmåga av tridekan jämfört med aktivt kol. Den minst lösliga av VOC i det tillredda processvattnet var siloxan som båda filtermaterialen renade till en nivå under analysutrustningens detektionsgräns.

Lämpliga analyser är i första läget breda screeninganalyser för VOC. När väl de vanligaste VOC identifierats kan en mer specifik analys användas så länge inte belastning, substratsammansättning eller andra viktiga förhållanden på anläggningen förändras. Om processvattnet inte förorenats med andra organiska komponenter än VOC kan analyser liknande BOD, COD, eller TOC utföras för att indikera dess innehåll av VOC.

På grund av den stora variationen i typ och halt av VOC så är det svårt att göra allmänna uttalanden om hälso- och miljörisker för VOC-innehållande processvatten. Av de tre vanligaste är det bara d-limonen som utgör en påtaglig risk, i form av dess toxiska påverkan på vattenlevande organismer. Den bryts dock ner relativt fort.

Summary

The aims of this project were to: qualitatively and quantitatively characterise the content of volatile organic compounds (VOC) in the process water produced during upgrading of biogas by amine or water scrubbing techniques and compression of biogas; and describe appropriate methods for management of the process water with respect to process stability and environmental and human impact.

The project consisted of three main parts:

- Characterisation of process water from upgrading facilities using water scrubbing and amine scrubbing with respect to content of VOC
- Literature-based review of available techniques for treatment of VOC in water, environmental and health effects of some relevant VOC in process water and degradation of some VOC in anaerobic and aerobic environments
- Laboratory evaluation of two treatment techniques for process water, in order to verify literature data.

Results from the plants were divided into three categories with respect to the main substrate used at the plant: waste (food and slaughterhouse waste), sewage sludge (sludge) and agriculture (manure, silage, grain). At all plants except one, at least 10% of the substrate mix consisted of waste. The characterisation of process water from upgrading of biogas showed that the content of VOC in process water, both regarding concentration and composition in terms of particular VOC, is dependent on the substrate used at the biogas plant. The characterisation also showed that the VOC content varied greatly between different sampling points for the same main substrate and sampling occasions, indicating that site-specific conditions are important for the results. Biogas plants using waste as the main substrate had the highest concentration of VOC in the process water, while plants using agricultural residues had the lowest levels. The VOC content in process water from the two participating sewage plants differed, with one plant having a VOC content in line with waste biogas plants and the other a VOC content in line with agriculture biogas plants.

The plants in this study used different amounts of water during upgrading, which greatly affected the concentration of VOC. There were no significant differences in content of VOC between upgrading biogas with a water scrubber or amine scrubber.

The quality and quantity of the process water varied widely between plants. Thus decisions on whether and how to treat the process water need to be based on site-specific information. One possible way to treat the process water is to use an existing biological treatment plant, e.g. a digestion process or a sewage plant. Inhibition of VOC in the anaerobic digestion process was studied in biomethane potential tests, but no inhibition was observed for addition of synthetic process water in realistic amounts. Another possible technique for purification is adsorption filters. Filter trials were performed to test the adsorption capacity of activated carbon and peat. Both filter materials adsorbed VOC, but activated carbon had higher removal efficiency.

To perform an appropriate analysis of VOC, it is important to take samples on several occasions and to use appropriate analytical methods. A general recommendation when investigating VOC in process water is to start with a broad screening analysis and then narrow the focus towards a more specific analysis, as long as the substrate mix, organic load and other important process parameters remain constant.

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1 Background

Biogas comprises methane, carbon dioxide and smaller amounts of contaminants such as hydrogen sulphide, water, ammonia and volatile organic compounds (VOC). Compression and upgrading of biogas to vehicle fuel generates process water, which to varying degrees contains the VOC from the gas. In Sweden, the most common techniques for biogas upgrading are water scrubbing and amine scrubbing (Bauer et al., 2013).

Volatile organic compounds are functionally defined according to EC Directive 1999/13/EC (Solvent Emissions Directive) as organic compounds having a vapour pressure of 0.01 kPa or more at 293.15 K (i.e. 20 °C), or having a corresponding volatility under particular conditions of use. In this project, VOC with a boiling point up to 350 °C were analysed.

Volatile organic compounds can be produced naturally by microorganisms during degradation of organic matter or released by plants. They can also be produced by fruits as a defence against microorganisms (Wikandari et al., 2013). There are numerous types of VOC with highly differentiated functionality. Synthetically produced VOC are used in paints, solvents, perfumes, assorted industrial products etc.

The VOC end up in the biogas either by direct evaporation from the substrate or as by-products from the anaerobic degradation (Hecht and Griehl 2009) (Mrowiec et al., 2005).

1.1 CONTENT OF VOC IN PROCESS WATER

Arrhenius and Johansson (2012) investigated the content of VOC in biogas before and after upgrading to vehicle fuel. They found that the VOC found in biogas before, but not after, upgrading most likely ended up in the process water during gas upgrading. The VOC in the biogas were also dependent on the substrate used at the plant.

There are few studies available about the content of VOC in process water from gas upgrading, but the results reported by Arrhenius and Johansson (2012) give a good indication of the substances that can be found. Their results are supported by the fact that process water from biogas upgrading units sometimes has a strong odour, indicating content of specific VOC.

1.2 MANAGEMENT OF PROCESS WATER

Management of process water from the biogas generation and the gas upgrading steps are performed in different ways depending on local conditions and on the quantity and quality of process water produced. Common ways to manage the process water in Sweden are by:

- Sending it to a sewage treatment plant
- Disposing of it in recipient waters
- Returning it to the process
- Using an oil separator in combination with the previous options.

1.3 PROBLEM STATEMENT

It is not completely clear what the process water from compression and upgrading of biogas actually contains. Due to this, there is currently uncertainty about how the process water should be managed to minimise the impact on health, the surrounding environment, and the degradation process in the digester.

2 Aim and goal of the project

The main aim of this project was to characterise the content of VOC’s, both in qualitative and quantitative terms, in the process water generated during upgrading of biogas by amine or water scrubbing techniques and compression of biogas. An additional aim was to identify appropriate methods for management of the process water with respect to process stability, the environmental impact and human health.

In order to achieve this, the following specific objectives were established:

- Characterisation of process water from at least six gas upgrading facilities (≥3 water, ≥3 amine) and at least one sample of condensate with respect to content of VOC
- Literature-based description of:
    - available techniques for treatment of VOC in water, regarding effectivity, cost and reliability
    - environmental and health effects of VOC in process water
    - degradation of some VOC in anaerobic and aerobic environments
- Verification of results from the literature review for at least two different technologies for disposal of process water
- Application of results from the project as a basis for choice of appropriate methods for analysis of process water, for comparing their value in assessing environmental and health effects of process water, and for assessment of possible treatment methods.

3 Review based on literature

A review of available techniques for treatment of process water and of the environmental effects, health effects and degradation of a selection of VOC was performed. More than 100 scientific articles and reports were downloaded, categorised and scrutinised, and selected information was used in this report. The literature chosen for the review was as recent and as broad as possible. Review articles were prioritised. The databases and search engines used were Science Direct, with journal articles from nearly 2,500 journals, and Bing and Google on the internet.

References considered of being of the greatest importance for this report were:

- Arrhenius and Johansson (2012) "Karakterisering av föroreningar i biogas före och efter uppgradering till fordonsgas" (Characterisation of pollutants in biogas before and after upgrading to vehicle fuel)
- Norberg and Lithner (2013) "Rening och destruktion av kontaminerat släckvatten" (Purification and disposal of contaminated process water)
- Farhadian et al. (2008) "Monoaromatics removal from polluted water through bioreactors—A review"
- Ruiz and Flotats (2014) "Citrus essential oils and their influence on the anaerobic digestion process: An overview"

Other studies that have investigated VOC in biogas include Moreno et al. (2014), Rasi et al. (2011), Orzi et al. (2010) and Pierucci et al. (2005).

Information on ecotoxicology and human health effects of the substances most commonly occurring in process water samples was obtained from the following databases:

- European Chemicals Agency ECHA (2015)
- KemI – Swedish Chemicals Agency (KemI, 2015)
- TOXicology Data NETwork (TOXNET, 2015)
- Biopesticides database (BPDB, 2015)
- The Human Metabolome Database (HMDB, 2015)

The HMDB database is described in Wishart et al. (2007).

Examples of relevant key words used during the searches are:

- Removal VOC water (7737 hits on Science Direct)
- Upgrading biogas process water (1901 hits on Science Direct)
- Upgrading biogas water (1961 hits on Science Direct)
- Biogas VOC water (469 hits on Science Direct).

Examples of key words with only a few relevant hits are:

- Biogas process water (18064 hits on Science Direct, but difficult to find interesting articles for this project)
- Upgrading biogas process water VOC screening (46 hits on Science Direct).

3.1 VOC IN PROCESS WATER FROM GAS UPGRADING

No scientific or other reports investigating the content of VOC in process water from upgrading of biogas were found. Some studies investigated the content of VOC in biogas, both before and after upgrading, and also investigated the content of VOC in air close to the substrate before, during and after anaerobic or aerobic digestion. The VOC in process water from upgrading of biogas most likely originates from the biogas that has been upgraded. This chapter presents some studies in which VOC in biogas was examined.

3.2 STUDIES ABOUT VOC IN BIOGAS

As described above, VOC end up in biogas by numerous ways, see section 1. Four studies that investigated the content of VOC in biogas were identified. The studies were:

- Arrhenius and Johansson (2012): They investigated contaminants in biogas before and after upgrading to vehicle fuel. The investigation included samples from a total of nine biogas plants digesting various types of substrates and using amine, water or pressure swing adsorption (PSA) technology for upgrading of the biogas. VOC were detected in biogas before and after upgrading, and the content of VOC was found to be 70-100% lower in the upgraded biogas compared to before upgrading.
- Pierucci et al. (2005): These authors looked at VOC produced during aerobic processing of municipal solid waste (MSW) and concluded that the VOC found in the condensate were similar to those in the gaseous phase, but that more polar compounds such as acids were found in the condensate.
- In Moreno et al. (2014), samples of gas were collected from four different waste products in an MSW treatment plant where both anaerobic and aerobic treatment of MSW were performed. In total, 152 different VOC were identified in the samples.
- Rasi et al. (2011): In a review of trace compounds affecting biogas utilisation, these authors found that VOC such as aromatics and terpenes are common in biogas from landfill. In biogas from sewage plants, common pollutants were H_2S in concentrations up to 1000 ppm and halogenated compounds in low concentrations. They also found that concentrations of silicon compounds (siloxanes) can be quite high in biogas from sewage plants. No mention is made of measurement of VOC in biogas from co-digestion or farm-scale biogas plants.

Some VOC are strongly connected to the substrate being digested. In biogas from digestion of food waste, p-cymene and d-limonene are characteristic VOC (Arrhenius and Johansson, 2012). This was also shown by Moreno et al. (2014), who in addition to p-cymene and d-limonene found pinene to be a distinguishing VOC. Orzi et al. (2010) found p-cymene, d-limonene, 2-butanone and 2-butanol to be the dominant VOC during anaerobic digestion of OFMSW. Pierucci et al. (2005), who investigated VOC produced from aerobic processing of municipal solid waste, found alkanes, terpenes such as α-pinene and d-limonene, benzene and halogen-containing compounds to be the main VOC.

In biogas from sewage plants, alkanes with 9-13 carbons are typical. The content of silicon compounds (siloxanes) can be higher in biogas from sewage plants than from digestion of other substrates, e.g. waste digestion gives a low content of siloxanes. This is due to silicone-containing compounds being used in households and industries (Arrhenius and Johansson, 2012; Rasi et al., 2011). Rasi et al. (2011) also showed that halogenated compounds are low in biogas from sewage plants and co-digestion.

Energy crops and by-products from the food industry result in sulphur compounds and ketones in the biogas (Arrhenius and Johansson, 2012). A ketone is a molecule containing a carbon atom having a double bond to an oxygen atom.

Arrhenius and Johansson (2012) also investigated biogas from anaerobic digestion of manure at two facilities. At the first plant ketones and linear hydrocarbons were detected, while at the second plant terpenes and toluene, which is an aromatic hydrocarbon, were detected.

The typical concentration of VOC in biogas before upgrading was 700 mg/m^3 at waste facilities, 200 mg/m^3 at wastewater treatment plants and 20 mg/m^3 when energy crops and waste from the food processing industry were co-digested (Arrhenius and Johansson, 2012). Orzi et al. (2010) studied VOC emissions from MSW and showed a decrease in VOC emissions from around 3300 ppbv before digestion to around 1500 ppbv after digestion. Looking at specific compounds, p-cymene was found in the highest concentrations post digestion, the concentrations of 2-butanone showed no clear trend during the digestion process and d-limonene and 2-butanol had the highest concentrations before digestion (Orzi et al., 2010).

Arrhenius and Johansson (2012) showed that during upgrading of biogas to vehicle fuel, the VOC in biogas are mainly adsorbed onto activated carbon or zeolites if PSA technology or such filters are used, or alternatively persist in condensation/process water from the upgrading facility.

3.3 ENVIRONMENTAL AND HEALTH EFFECTS OF VOC IN PROCESS WATER

The great variety of VOC found in process water makes it very difficult to state general health and environmental effects by exposure to these VOC without an accurate site-specific investigation covering several sampling periods. Some VOC are highly toxic and some have no known negative health effect. The health and environmental effects of process water depend on the level of exposure, i.e. the exposure time and the type of VOC present, as well as their concentrations (EPA, 2012). At present, there is still a lack of information about the impact of VOC on human health. However, information on individual VOC can be found in the chemical databases mentioned on page 15. To find the specific compound, the CAS number should be used.

The 10 most common VOC found in the characterisation of process water in this project are described in Table 1 and Table 2. More details on these VOC and their environmental and health effects can be found in Appendix C.

A specific value for indoor air quality regarding VOC, namely the Lowest Concentration of Interest (LCI), has been determined for most of the VOC found in process water. These are shown in Table 2. The LCI is a health-based limiting value. It was originally developed as a standard of emissions from building products (Kephalopoulos et al., 2013). The Swedish Work Environment Authority has published regulations and general advice on exposure limits for 400 substances and these also contain advice about sampling of air (Arbetsmiljöverket, 2011).

Table 1. The 10 most common VOC characterised in process water, including some data from safety datasheets (MSDS).

VOC	CAS no.	Appearance	Smell
p-Cymene	99-87-6	Clear, colourless liquid	Sweet, aromatic, with pleasant smell
d-Limonene	5989-27-5	Clear, colourless liquid	Citrus
2-Butanone	78-93-3	Clear, colourless liquid	Strong, acetone-like
2-Butanol	78-92-2	Clear, colourless liquid	Alcohol
Siloxane D3	541-05-9	White crystalline solid	Not specified
Siloxane D5	541-02-6	Colourless liquid	Not specified
Decane	124-18-5	Clear, colourless liquid	Alcohol

VOC	CAS no.	Appearance	Smell
Toluene	108-88-3	Clear, colourless liquid	Sweet, solvents
Acetone	67-64-1	Clear, colourless liquid	Acetone
Pentylfuran	3777-69-3	Clear, colourless liquid	Not specified
Terpinolene/ α-terpinolene	586-62-9	Clear, light-yellow liquid	Pine

Table 2. Properties of the 10 most common VOC characterised in process water, including some data from safety datasheets (MSDS), Lowest Concentration of Interest (LCI), and Predicted No-Effect Concentration (PNEC) values for freshwater

VOC	Boiling point	Solubility	Limit value health, LCI indoor air (µg/m³)	PNEC value for fresh water (µg/L)
p-Cymene	177 °C	23 mg/L	1000[2]	Not found
d-Limonene	175 °C	14 mg/L	5000[2]	5.4
2-Butanone	80 °C	Soluble	5000[2]	55800
2-Butanol	99 °C	Soluble	Not found	47100
Siloxane D3	Not specified	May decompose	Not found	Not found
Siloxane D5	90 °C	<0.01 mg/L at 23 °C	1500[3]	Not found
Decane	174 °C	4 µg/L	Not found	1.2 (soluble part)
Toluene	111 °C	561 mg/L	2900[2]	680
Acetone	56 °C	Soluble	Not found	10600
Pentylfuran	65 °C	Not specified	1200[3]	Not found
Terpinolene/ α-terpinolene	194 °C	7 mg/L	1400[2]	0.634

In the ECHA database, seven of the VOC listed have values for Predicted No-Effect Concentration (PNEC) for water and sediment (ECHA, 2015). The PNEC is the concentration below which exposure to a substance is not expected to cause adverse effects (Finizio and Vighi, 2014). The PNEC value can be used for an assessment if release of e.g. process water to a recipient such as a stream or river may cause negative effects on the environment. If the concentration of a certain compound in the recipient is lower than the PNEC value, then the risk of negative environmental effects in the recipient is low.

The following theoretical example illustrates how release of d-limonene from process water directly into a stream or a river can be calculated. The calculated concentration in the stream can then be compared with the PNEC value for d-limonene in fresh water, which is 5.4 µg/L (ECHA, 2015).

Assumed values

Amount of d-limonene in process water	5 000 µg/L
Flow process water	0.25 L/s
Flow in a little stream	500 L/s
Flow in a river	10 000 L/s

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[2] EU-wide harmonized LCI-values, JRC project, ECA report 29

[3] Belgian limit values for LCI

Calculated values

Flow d-limonene in recipient	1.25 mg/s
Concentration of d-limonene in a little stream	2.5 μg/L
Concentration of d-limonene in a river	0.125 μg/L

The example shows that even if the amount of d-limonene in the process water is high, the flow in a stream/river has to be quite low before there is a potential risk of a negative impact on aquatic life. In the example we assumed that there was no breakdown of d-limonene between the plant and the stream/river, but part of the d-limonene might be decomposed or released to the atmosphere before the river in real life, due to its short half-life in the environment.

3.4 AVAILABLE TECHNIQUES FOR TREATMENT OF PROCESS WATER

There are several different techniques available to treat water contaminated with VOC. This is partly due to a growing problem with contaminated groundwater from, for instance, landfill leachate and oil pollution (Farhadian et al., 2008; Kalmykova et al., 2014). In this report, only applicable techniques for purification of process water from biogas upgrading plants are discussed. The techniques are described below and summarised in Appendix D.

The quality and quantity of the process water produced vary widely from one treatment plant to another and there is no single answer as to which technique is most effective or economical. Decisions on whether and how to treat the process water need to be based on the impact on the recipient in relation to costs (both economic and environmental). Some VOC are easily degradable and common in nature, while others are persistent and toxic. Another aspect is that a high proportion of the VOC may evaporate to the atmosphere if released into recipients. This should be placed in relation to the amounts of specific VOC released to the atmosphere by plants, animals and microbes (Goldstein and Galbally, 2007).

Treatment techniques can be divided into three main categories; physical, chemical and biological. The physical techniques use the physical properties of VOC to transfer them from one phase to another. In chemical and biological methods, the VOC are destroyed either by oxidation or natural degradation.

3.4.1 Physical methods

A very common technique used for removing VOC from water is air stripping. The high vapour pressure of VOC is used to move them from the liquid to the gaseous phase. Higher temperature increases this effect. To ensure that the VOC are not transferred to the atmosphere, this technique needs to be complemented with, for instance, filter cleaning or incineration. Investment in both air stripping and incineration can be costly.

Other techniques use the low water solubility of VOC for adsorption to different filter media. Adsorption methods do not convert the VOC and the filter needs to be treated when consumed in order to divest its load of VOC. Different activated carbon media have been proven to be efficient for this kind of process water, because of their high porosity and large activated surface (Farhadian et al., 2008; Le Cloirec, 2012). Other materials used for adsorption are bark and peat. For better performance, the organic matter is sometimes treated and the surface is ‘activated’, e.g. activated carbon (Dias et al., 2007). Bark and peat are cheaper than activated carbon, but most often not as effective.

Other media used for adsorption of VOC are different kind of treated zeolites. The use of zeolites for adsorption of VOC from air is well-established. The VOC accumulate onto the zeolite and are then incinerated (Nikolajsen et al., 2006). It is less common to use zeolites as adsorbents for VOC in water purification. According to Levchuk et al. (2014), use of zeolites is twice as expensive as use of activated carbon, but the life time is much longer for zeolites. Pore size and hydrophobicity are important factors for good functionality.

To improve the filtering capacity, a pretreatment step may be necessary, e.g. a sand filter for removal of precipitated particles. Sand filtration alone is not a well-proven method for VOC removal (Kalmykova et al., 2014), but slow sand filtration with an active biofilm is a proven method (Arvin et al., 2004).

Different membrane filtration techniques and reverse osmosis are efficient for removal of VOC (Farhadian et al., 2008). In membrane filtration, the water is pressed through membranes with different characteristics and pores of different sizes to match the target pollutant being removed from the water. The techniques have high investment and operating costs (Norberg and Lithner, 2013).

Pervaporation is an advanced membrane technique where high pressure is used to give partial vaporisation of the VOC over a membrane. The membrane can be chosen to match the target pollutant being removed from the water. Pervaporation techniques are used in the field for purification of water contaminated with VOC (Hitchens et al., 2001), but no full-scale units currently exist in Sweden (in 2015).

3.4.2 Chemical methods

Chemical methods for removal of pollutants include coagulation, flocculation, precipitation, addition of ion exchanger and chemical oxidation. Some oxidation techniques are efficient for removal of VOC in water (Tiburtius et al., 2005), while others are less successful (Farhadian et al., 2008; Kalmykova et al., 2014; Le Cloirec, 2012; Norberg and Lithner, 2013) and are not further discussed here.

Oxidation methods use the highly reactive radical ·OH for oxidation of VOC to CO_2 and water. The ·OH radical can be generated in several different ways, for instance:

- By addition of reagents, e.g. Fenton's reagent, O_3, O_2 or H_2O_2
- Using an energy source such as UV light
- Using a catalyst (e.g. TiO_2)
- A combination of all these methods in advanced oxidation processes (AOPs).

However, AOPs have the disadvantages that it is difficult to degrade all compounds completely and the resulting secondary degradation compounds might be difficult to control. AOPs are also somewhat energy consuming. Tiburtius et al. (2005) compared different AOPs and showed that a combination of Fenton's reagent and UV light gave almost complete degradation of water contaminated with BTX (benzene toluene and xylene). They also showed that sunlight improved the oxidation, which could reduce the amount of energy that needs to be added to the process.

3.4.3 Biological methods

Biological methods use biological processes to degrade and remove pollutants from water. They can be carried out in more or less controlled forms. In Sweden, common biological techniques are biofilters, activated sludge treatment, anaerobic digestion process for biogas production, infiltration into soil and soil absorption systems.

It is well documented that bacteria, fungi, archaea and other microorganisms can degrade VOC (Battersby and Wilson, 1989; Farhadian et al., 2008; Wilson et al., 2012), with bacteria playing the largest role. The stability and diversity of species in a bacterial community and the amount and structure of the VOC present affect how effective and stable the degradation process is (Monlau et al., 2014). Biological degradation of VOC by microorganisms depends on a number of factors such as available compounds for electron acceptors, macro- and micronutrients, carbon source (VOC often act as a carbon source) and environmental factors such as pH, temperature, salinity, alkalinity, pressure etc. (Farhadian et al., 2008). These factors affect the activity and growth of the microorganisms as well as the *state* of the compound. During aerobic degradation, O_2 is the primary electron acceptor, while usual alternative electron acceptors during anaerobic degradation are nitrate, Fe (III), sulphate and CO_2 (Farhadian et al., 2008).

3.4.3.1 Degradation with activated sludge techniques/aerobic bioreactors

Aerobic biological techniques with activated sludge processes, such as the moving bed biological reactor (MBBR), fluidised bed reactor (FBR), submerged fixed film reactor (SFFR) and fixed film activated sludge (FAS) show good removal of hydrocarbons with efficiencies of up to 99% (Farhadian et al., 2008). Microorganisms that grow on a carrier material have been proven to be more resistant to toxins than microorganisms in free solution. Examples of carrier materials are GAC, polyurethane (PU), polystyrene (PS), wood, sand, kaolin, ceramic, polyvinylchloride (PVC) and polyethylene (PE) (Farhadian et al., 2008).

Many studies do not mention or do not include vaporisation or sorption to organic matter of VOC. It is thus difficult to determine how much VOC has actually been degraded by microorganisms.

Simonich et al. (2002) showed almost complete degradation of fragrance material in water in activated sludge plants, carousel plants, oxidation ditch plants, trickling filter plants, rotating biological contactor plants and lagoons. In most sewage plants in Sweden, the activated sludge process is commonly used for treatment of wastewater and could thus be used for purification. However, as described above, there is a major risk that the VOC will evaporate during the different aeration steps.

Treatment with aerobic bioreactors can be efficient and show high capacity. However, this is an expensive solution if the treatment plant is built solely for process water. If connected to an existing plant, it is a cost-effective solution.

3.4.3.2 Constructed soil adsorption systems, wetlands and reed beds

A common way to treat different types of wastewater is to use nature's common way of degrading organic matter in different soil-based and/or aquatic systems. This is widely used partly due to low energy requirements and low investment costs (Vymazal, 2009). In Sweden, where the climate limits degradation during winter, parameters such as retention time have to be taken into account. The most widely implemented techniques for different wastewater types in Sweden are soil absorption techniques, constructed wetlands and reed beds (Norberg and Lithner, 2013; Ridderstolpe, 2009a). Other techniques include lagoons, ponds, phytoremediation etc.

There are different data on how efficient soil-based systems are at degrading organic pollutants such as VOC (Norberg and Lithner, 2013; Vymazal, 2009). The microorganisms often degrade organic matter better in small soil-based water treatment systems than in sewage plants, due to better functioning and more complex composition of the microbial population (Palm et al., 2012). Evaporation of VOC to air is not always investigated, however.

During infiltration of wastewater into soil for adsorption, the degradation of organic matter persists in the unsaturated soil layer. Reports show high evaporation of VOC from such treatments (Tyler et al., 1991).

In constructed wetlands, the wastewater comes into contact with a network of aerobic, anoxic and anaerobic zones, which facilitates degradation. There are some great wetlands for treatment of wastewater from petrochemical industries, one of the largest of which, in the United Kingdom, has an area of 49 000 m^2 (Vymazal, 2009).

3.4.3.3 Anaerobic treatment

Degradation of volatile organic compounds is well established in research (Ahn et al., 2009; Battersby and Wilson, 1989; Healy and Young, 1979; Lawrence, 2006; Lovley, 2000) and anaerobic bioreactors are a proven technology for water containing a high level of impurities. The process converts the hydrocarbons to volatile fatty acids (VFA), which are then converted to CH_4 and CO_2.

It is more complex to degrade VOC than for instance VFA and this can be used as an indicator of process imbalance (Hecht and Griehl 2009). External factors such as temperature that affect how sensitive the microbial community is to VOC are also important (Levén and Schnürer, 2005).

Process water is often produced at biogas plants using CSTR (continuous stirred tank reactor) and if the process water is produced in reasonable amounts it can be degraded as a small part of the substrate (see sections 3.4 and 5.2).

The benefits compared with aerobic bioreactors are low energy requirements, the production of energy-rich biogas and low production of sludge. Concerns are the need for a longer start-up time to build biomass and that anaerobic bioreactors are more sensitive to changes in e.g. temperature and may need to be heated compared with aerobic bioreactors. Examples of reactors for this kind of water include HAIB (horizontal immobilised anaerobic bioreactors) and UASB (upflow anaerobic sludge blankets) (Farhadian et al., 2008).

3.5 INHIBITION OF ANAEROBIC DIGESTION PROCESS BY VOC

As described, VOC are a natural degradation product and intermediary in the anaerobic degradation process. Other VOC are directly produced from the waste, e.g. fruit, as protection against microbial degradation and are hence directly harmful for the process in high concentrations (Wikandari et al., 2013).

The structure and properties of VOC vary greatly. Their inhibitory effect in the anaerobic process is dependent on functional groups, chain structure and whether they contain other elements such as nitrogen, sulphur, halogens etc. Halogenated VOC are reported to be more inhibitory to the anaerobic process than if no element is added (Battersby and Wilson, 1989; Chen et al., 2008; ECHA, 2015).

The VOC can also be more or less hydrophobic. If they are hydrophobic, they easily adsorb to organic matter and can accumulate to inhibitory concentrations (Chen et al., 2008; Monlau et al., 2014). The hydrophobic nature is itself a factor affecting the toxicity for microorganisms (Ruiz and Flotats, 2014).

Temperature is an important factor for how the microbial community can handle VOC. Levén and Schnürer (2005) showed mineralisation of benzoic acid, phthalic acid, methyl phthalate, phenol, m- and p-cresol in mesophilic culture, but only mineralisation of benzoic acid in thermophilic culture.

Table 3 lists some selected VOC likely to be found in process water from biogas upgrading, together with the findings on their inhibitory effect. Such tables can be misleading, however, since the bacteria and archaea adapt to their environment. Inoculum and organic loading rate are thus important factors, together with experimental set-up, for the sensitivity of bacterial cultures to VOC.

Table 3. Inhibition of anaerobic processes by different VOC.

Substance	Concentration/ content	Comment	Reference
Terpene – limonene	10 mg/L	Anaerobic ethanol production Reduced microbial activity observed at10 mg/L.	(Grohmann et al., 1994)
Terpene – limonene	50 mg/L	Mesophilic AD, sewage sludge. Significant reduction in gas production (58%) at a load generating a concentration of 50 mg/L.	(Mizuki et al., 1990)
Terpene – limonene	450-900 µg/L	Thermophilic AD. Suggested threshold level of d-limonene for inhibiting AD lies between 450 and 900 µL/L.	(Forgács, 2012)
Terpene – car-3-ene, myrcene, α-pinene	5, 50 & 500 mg/L	Thermophilic AD. Inhibition of 77-95% at concentrations of 500 mg/L. Inhibition of 9-63% at 5 mg/L.	(Wikandari et al., 2013)
Citrus essential oils (VOC originating from fruits)	24–192 mg/L	Review of effect of citrus essential oils on the anaerobic process. Results show some controversy regarding the limiting dosage of limonene for a stable process.	(Ruiz and Flotats, 2014)
Aldehyde – E-2-hexenal, hexanal, nonanal	5, 50 & 500 mg/L	Thermophilic AD. Inhibition of 84-100% at concentrations of 500 mg/L. Inhibition of 5-22% at 5 mg/L.	(Wikandari et al., 2013)
Alcohol – octanol	5, 50 & 500 mg/L	Thermophilic AD. Inhibition of 99% at concentrations of 500 mg/L. Inhibition of 69% at 5 mg/L.	(Wikandari et al., 2013)
Aldehyde – furfural, 5-HMF[4], syringe-aldehyde, vanillin	3 and 10 g/L	Inhibition either shown as lower gas yield or longer lag phase.	(Monlau et al., 2014)

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[4] 5-HMF: 5-hydroxymethyl-2-furfural

4 Material and methods

4.1 CHARACTERISATION OF PROCESS WATER WITH RESPECT TO CONTENT OF VOC FROM GAS UPGRADING FACILITIES

In total, nine different sampling points for process water was identified at eight Swedish biogas plants, as shown in Table 4. The sampling points were chosen to achieve a variety of conditions regarding type of substrate digested and technique used for upgrading the biogas.

Table 4. Sampling points at full-scale biogas plants in the project.

Main substrate	Technique for upgrading
Agriculture main substrate	Amine
Agriculture main substrate	Water
Agriculture main substrate	Water
Waste main substrate	Amine and water
Waste main substrate	Amine
Waste main substrate	Water
Waste main substrate	Water
Sewage sludge main substrate	Amine
Sewage sludge main substrate	Amine

The samples were taken from used process water from the upgrading facility and sampling was performed by staff at each plant. If the flow was more than ≈ 0.5 L/ minute, the sample was retrieved from a partial flow. At sampling, the use of plastics was minimised to avoid loss of VOC from the water sample. The samples were collected and filled to the top of two 100-mL glass bottles and then immediately sent to SP's laboratory in Borås.

The sampling was performed by following a detailed instruction and sampling protocol, in order to ensure low uncertainty during sampling and also to ensure that the samples were taken in a uniform manner, see Appendix A and Appendix B (both in Swedish).

Samples of process water were taken in August and November 2014. The process water was analysed for content of VOC at SP's laboratory in Borås, see section 4.2. The results from the samplings were compiled and processed at Tekniska verken in Linköping AB.

To identify the VOC that were dominant in the process water, the proportions of the most common VOC in the process water were calculated for each sample. The average individual percentage distribution for the dominant VOC was then calculated for all samples in each substrate category.

4.2 ANALYSIS OF VOC IN PROCESS WATER

Analysis of volatile organic compounds (VOC) was performed by gas chromatography/mass spectrometry (GC-MS) via a purge and trap method (TD-GC-FID/MS) and following guidelines in ISO 16000-6:2011 (ISO, 2011).

The VOC present in the 100-mL water samples were extracted by bubbling air through a known volume of water (a fraction of the water collected at the plant) introduced into a 100-mL glass bottle with a gas phase on the top of the water. The VOC were then captured on an adsorbent tube filled with Tenax, which is capable of quantitatively adsorbing non-polar or slightly polar substances with boiling point in the range 70-320 °C (typically containing 6 to 20 carbon atoms). Two extractions were performed in succession; the purpose of the second extraction was to check whether VOC were quantitatively removed from the water.

Analysis of the Tenax tubes was then carried out by so-called thermal desorption (Markes TD100 desorber), where the adsorbed substances were released by heating the sorbent tubes and then transferred to a cold trap for focusing. The trap was then rapidly heated up again and VOC were released and reached a gas chromatography (GC) column for separation. The column effluent was split into two streams for the detection of individual components, one stream passing through a flame ionisation detector and the other stream through a mass spectrometer.

The fragmentation pattern in the mass spectrum provided information about the structure of the eluted substances, so that they could be identified using a database of compound mass spectra.

The analyses were performed on an Agilent Technologies gas chromatograph 6890N equipped with a flame ionisation detector and a mass spectrometer 5975C inert MSD in the so-called "Electron impact mode". The GC column is a non-polar capillary column (5% phenyl polysilphenylene-siloxane, BPX5, 50 m long, 0.32 mm internal diameter, 1 μm film thickness).

4.3 LABORATORY TRIALS SIMULATING WATER TREATMENT TECHNIQUES

Two different trials were performed to simulate treatment of process water. The techniques chosen were adsorption to organic filters and anaerobic digestion, to simulate the recirculation of process water back to the digestion process. In the anaerobic digestion trial the main objective was to determine whether the biological process was inhibited by VOC.

A synthetic model solution with five selected VOC was prepared at two different concentrations to mimic process water. The VOC were chosen and added in realistic amounts corresponding to those found in most of the process water from the plants investigated in this study in one solution, and at unnaturally high concentrations in another solution (Table 5). The process water with realistic levels of VOC was used in the filter trials and the process water with high levels of VOC was used for both the filter trials and anaerobic digestion trials.

The added VOC were pipetted to tap water 1 cm below the surface in 1-L bottles. When all VOC had been added, the bottle was properly closed and firmly shaken.

In both solutions of the prepared process water, a film on the water was detected, indicating that the VOC were not all completely dissolved. This was expected, since the addition rate was higher, and sometimes much higher, than the solubility of the VOC.

All the water samples used in the trials were extracted from 1 cm below the surface of the water in the 1-L bottles. Analyses of this water showed lower levels of VOC compared with the total amount added, due to the film on the surface (Table 5). The calculations in coming sections are based on values from the laboratory analyses.

Table 5. Properties of prepared synthetic solution for simulation of process water.

VOC	**Concentrations analysed in laboratory (mg/L)**		**Total concentration added (mg/L)**	
	Realistic level (for filter trials)	High level (for filter and inhibition trials)	Realistic level (for filter trials)	High level (for filter and inhibition trials)
d-Limonene	**2.4**	**44**	20.2	202
p-Cymene	**4.6**	**166**	19.8	206
Tridecane	**0.47**	**82**	5.3	53
2-butanone	**16.6**	**183**	29.8	302
Siloxane D4	**0.27**	**8**	2.9	9.5
Sum of VOC	**24.3 mg/L**	**483 mg/L**	78 mg/L	772 mg/L

4.3.1 Filter trials with activated carbon and peat

Tests investigating adsorption of VOC by activated carbon and peat were performed on laboratory scale at Tekniska verken biogas laboratory in Linköping. The activated carbon and peat used were selected in cooperation with the suppliers, Chemviron Carbon (activated carbon) and Axon miljöteknik (peat).

The filters were prepared by using a petrol filter for general purposes, see Figure 1.

Figure 1. Petrol filter used as container for filter material in the experiments testing adsorption of VOC by activated carbon and peat.

The filter materials were stuffed between the particulate filter and the glass tube, resulting in a volume of 4.5 cm^3. The prepared VOC water (see section 4.3) was pumped through the filter using a peristaltic pump (Pharmacia Biotech pump P-1) at a rate of 0.6-0.7 L/hour. The water was pumped from the bottom to the top of the filter in saturated conditions, in order to avoid loss by evaporation to the atmosphere. The tubes used were confirmed as having low permeability to VOC. At the pump Tygon R-3603 (inside ø 3.2 mm) tubing was used and between bottles, pump and filter hard PTFE tubing was used (inside ø 3.0 mm). The total length of tubing from bottle of prepared VOC water to bottle of filtered water was approximately 1 m.

A 3-L portion of the process water was pumped through each filter material, which according to information provided by the manufacturers led to a total load of 1/3 of the filter's total capacity for absorption of the VOC in the run with general concentrations of VOC. The last 100 mL were pumped to a special bottle and sent for analysis of VOC to SP's laboratory in Borås. A control run was made where 1 L was pumped through the filter without material and the last 100 mL was saved in a bottle and sent for VOC analysis to SP's laboratory in Borås, see section 4.2.

Table 6. Details of the filter experiment testing adsorption of VOC by activated carbon and peat.

Filter material	Flow	Amount of filter material cm^3, g	Process water passing through the filter	Concentration of process water
Reference	≈ 1 L/h	None	1 L	24 and 483 mg/L
Activated carbon	≈ 0.7 L/h	4.5 cm^3/ 2.45 g	2.8 L	24 and 483 mg/L
Peat	≈ 0.6 L/h	4.5 cm^3/ 2.15 g	2.8 L	24 and 483 mg/L

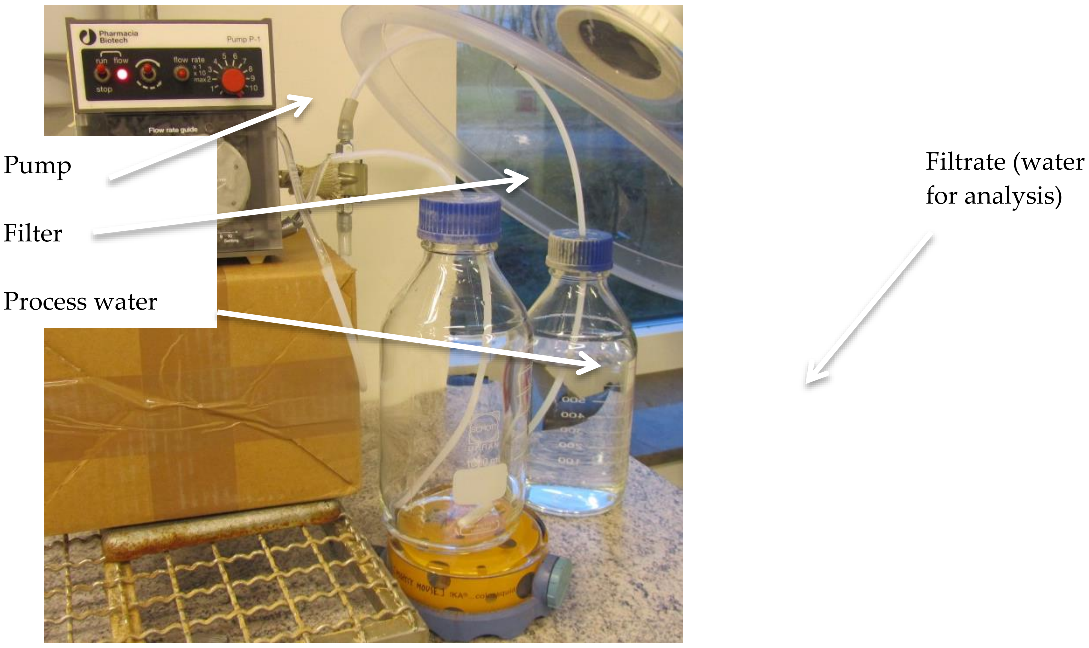

Figure 2. Experimental set-up used for investigation of adsorption of VOC onto activated carbon and peat.

4.3.2 Anaerobic digestion trials simulating recirculation of process water to the digestion process

Inhibition of VOC in the anaerobic digestion process was studied in modified biomethane potential (BMP) tests. In BMP tests, biogas is produced from substrate and inoculum in batch systems. To ensure a good environment for the microorganisms, inoculum from a mesophilic process with waste as main substrate, micro and macro nutrients are added to the process (Nilsson Påledal et al., 2013).

Four series were started:

- One control series without addition of VOC
- Two series where the intention was to have high but realistic amounts of VOC in the digestion process; see assumptions below for generation of realistic concentrations of VOC. In one series, gas measurements were performed. In the other series, the content of VOC in the biogas produced was analysed. Analysis of VOC in sludge and gas was performed to detect degradation of VOC.
- One series with very high amounts of VOC, to observe whether VOC inhibit the biogas process.

In order to simulate a realistic load of VOC to the process, the following assumptions were made. To ensure that the results on whether the process was inhibited or not were clear, the calculated concentration was increased three-fold.

- Organic loading rate: 3.5 kg volatile solids (VS)/ m^3 day
- Specific biogas production: 800 m^3 biogas/kg VS
- VOC in raw gas: 100 mg/m^3 biogas (and all VOC end up in process water)
- The dose of process water used in BMP tests corresponded to 3 weeks of production of process water in one series and maximum possible amount of process water in one series.

The test set-up is described in Table 7.

Table 7. Experimental set-up for biomethane potential (BMP) tests.

	Description	Substrate	Added amount of prepared process water	Gas measurement
Series 1	Control	Cellulose, starch, fat, gelatine	-	Yes
Series 2	+ addition of VOC-solution in a high amount	Cellulose, starch, fat, gelatine	12 mL	Yes
Series 3	+ addition of VOC-solution in a very high amount	Cellulose, starch, fat, gelatine	247 mL	Yes
Series 4	+ addition of VOC-solution in a high amount	Cellulose, starch, fat, gelatine	12 mL	No (VOC capture in TENAX tubes and biogas in Al-balloons)

Analyses of VOC were made on prepared VOC solution, inoculum before start-up, biogas after digestion and sludge after digestion. The analyses were performed at SP's laboratory in Borås, see section 4.2.

The BMP tests were performed in the system AMTPSII ©, BioProcess Control Sweden AB, Lund, see Figure 3. The biogas produced flowed through a bottle filled with NaOH solution to capture carbon dioxide (CO_2). The methane gas continued to a flow cell for continuous measurement of the volume of gas produced and was recalculated according to standard temperature and pressure (1013.25 hPa and 0 °C). The experiment lasted until the net biogas production from the substrate ceased, 22 days after start-up.

Figure 3. The AMTPSII system used for performance of the biomethane potential (BMP) tests.

5 Results and discussion

The impact of VOC on the surrounding environment varies greatly, depending on their structure, size, charge and concentration. The focus of this report is on the VOC found in high amounts in process water.

Results from the plants were divided into three categories with respect to main substrate used at the plant, waste (food and slaughterhouse waste), sewage sludge (sludge) and agriculture (manure, silage, grain). At all plants except one, at least 10% of the substrate mix consisted of waste.

5.1 CHARACTERISATION OF PROCESS WATER FROM GAS UPGRADING FACILITIES WITH RESPECT TO CONTENT OF VOC

There were large differences in the quantity of water required during upgrading of biogas at the different plants using water and amine scrubbing (see Figure 4 and Figure 5, respectively). For both the water and amine scrubber techniques there was an upgrading facility which used much more water than the others and can be regarded as an outlier. Apart from these two facilities, the average water use for plants in this study was 0.4 L/m^3 treated biogas for water scrubbers and 0.03 L/m^3 treated biogas for amine scrubbers.

Due to the difference in water use at different upgrading facilities, the VOC concentrations are expressed both in mg VOC/L process water and mg VOC/m^3 treated raw biogas in this report, to avoid false effects from different dilutions.

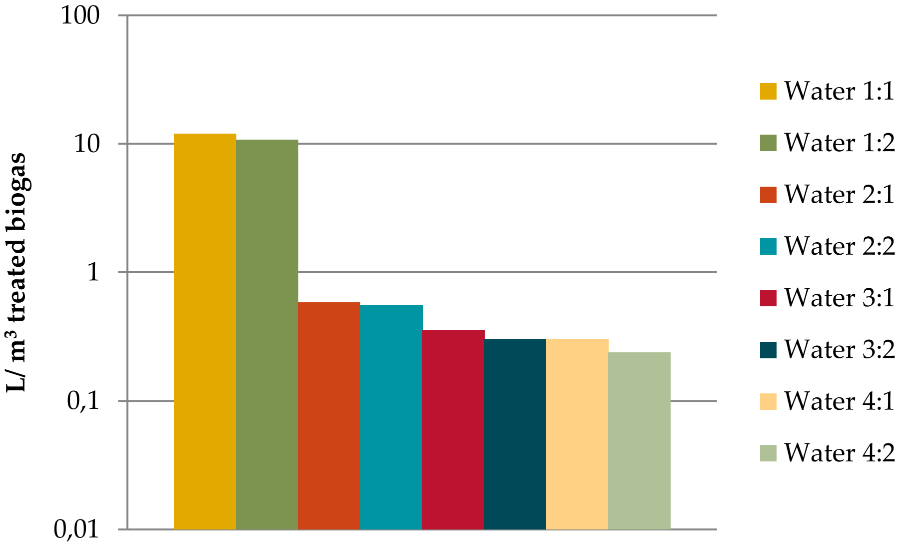

Figure 4. Water use per m^3 treated biogas for the water scrubber techniques investigated in the study. Two measurements were made at each upgrading facility.

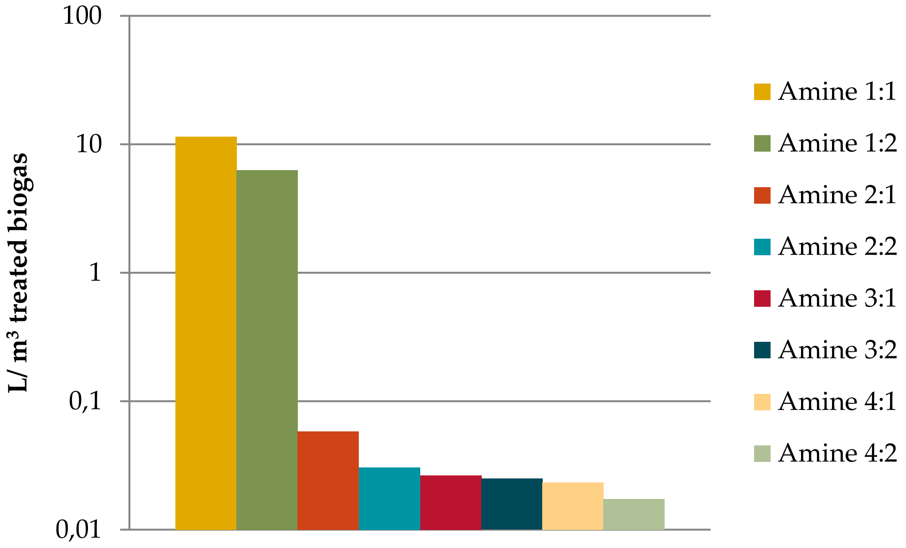

Figure 5. Water use per m³ treated biogas for the amine scrubber techniques investigated in this study. Two measurements were made at each upgrading facility.

5.1.1 Content of VOC in process water from upgrading facilities

The average content of VOC in process water from upgrading of biogas, expressed in mg VOC/L process water and mg VOC/m³ treated raw biogas, is shown in Figure 6 and Figure 7, respectively. The average proportions of the most common VOC, separated according to main substrate, are shown in Figure 8.

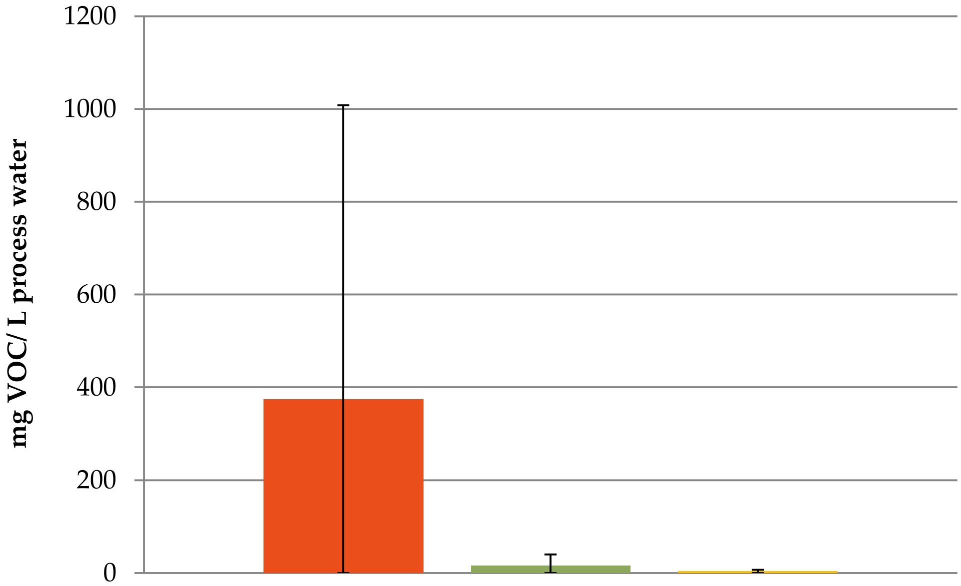

Figure 6. Average content of VOC in process water from upgrading of biogas, expressed as mg/L process water. Results separated with respect to main substrate: waste (🟧), sewage sludge (🟩) and agriculture (🟨). Upper and lower standard deviations are marked with deviation bars.

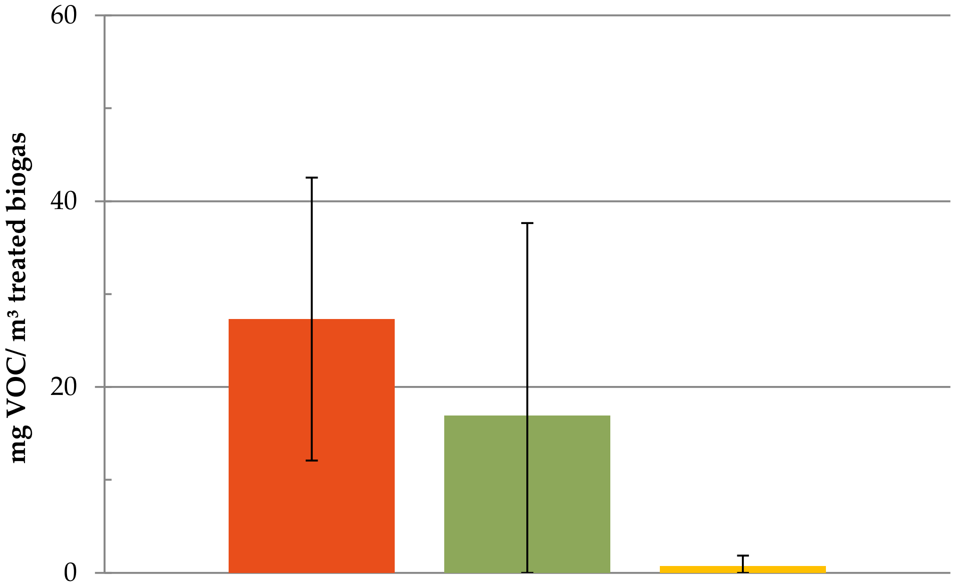

Figure 7. Average content of VOC in process water from upgrading of biogas, expressed as mg/m³ treated biogas. Results separated with respect to main substrate: waste (🟧), sewage sludge (🟩) and agriculture (🟨). Upper and lower standard deviations are marked with deviation bars.

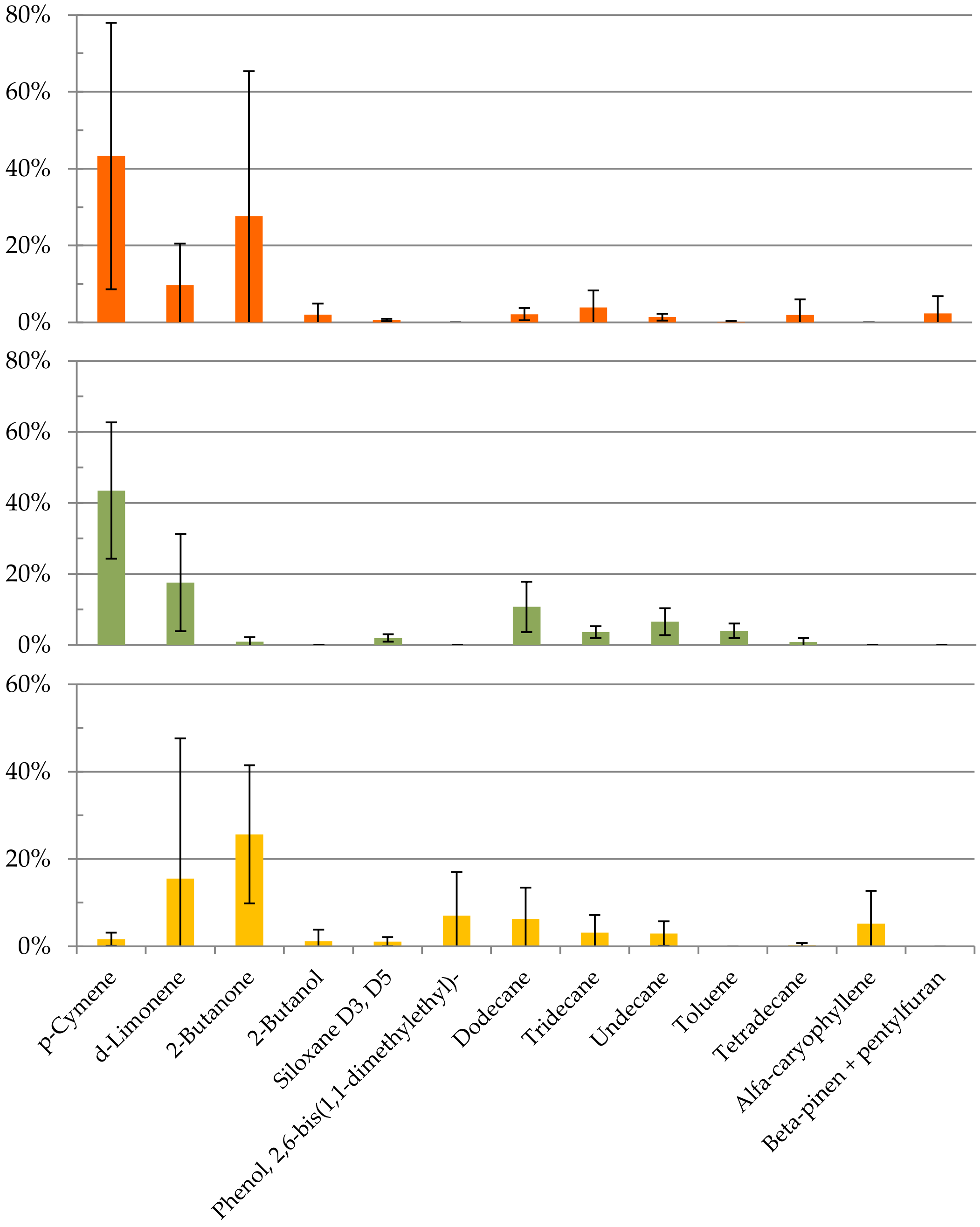

Figure 8. Average share of most common VOC in process water from upgrading of biogas. Results separated with respect to main substrate: waste (🟧), sewage sludge (🟩) and agriculture (🟨). The values are calculated as the average of the percentage distribution for each sample.

The results show clear differences in average levels of VOC content between different substrate groups, both in total concentrations and specific VOC. However, it is important to point out that standard deviations were high. Plants which use waste as the main substrate, such as food and slaughterhouse waste, also had the highest average content of VOC in process water. When substrate from agriculture, like manure, silage or grains, was used the content of VOC was low. The standard deviation was high for both total content and specific substances, indicating that site-specific conditions have an important impact on the results.

In this study the most common VOC were in general p-cymene, d-limonene and 2-butanone, but this varied even between duplicates (see sections below for each substrate type). p-cymene and d-limonene are known to be common VOC during digestion of food waste (Arrhenius and Johansson, 2012) and food waste was used to varying degrees (at least 10%) at eight of the nine sampling points used for process water.

2-butanone is known to be a common VOC during digestion of manure (Arrhenius and Johansson, 2012; Murphy et al., 2014). The presence of 2-butanone can thus be explained by digestion of manure or slaughterhouse waste, which may contain traces of manure or intestines and is used as substrate at seven of the nine sampling points in this study. It can also be explained by digestion of food waste, since 2-butanone has been identified as a common VOC during digestion of the organic fraction of MSW (Orzi et al., 2010).

The results varied considerably both between plants utilizing the same main substrate but also between the two sampling dates for the same sampling point. This indicates that a number of analyses at different times are required in order to make an accurate characterisation with low uncertainty of the average VOC content in process water.

5.1.2 Waste biogas plants

Average content of VOC in process water from upgrading of biogas at waste biogas plants, expressed in mg VOC/L process water and mg VOC/m^3 treated raw biogas, is shown in Figure 9 and Figure 10, respectively. Sample 2:2 was identified as an outlier, based on both its content and its incidence of VOCs. Therefore, the average value was also calculated without the outlier and this average value was used for the comparison in Figure 6 and Figure 7. Incidence of the most common VOC in process water is shown in Figure 11.

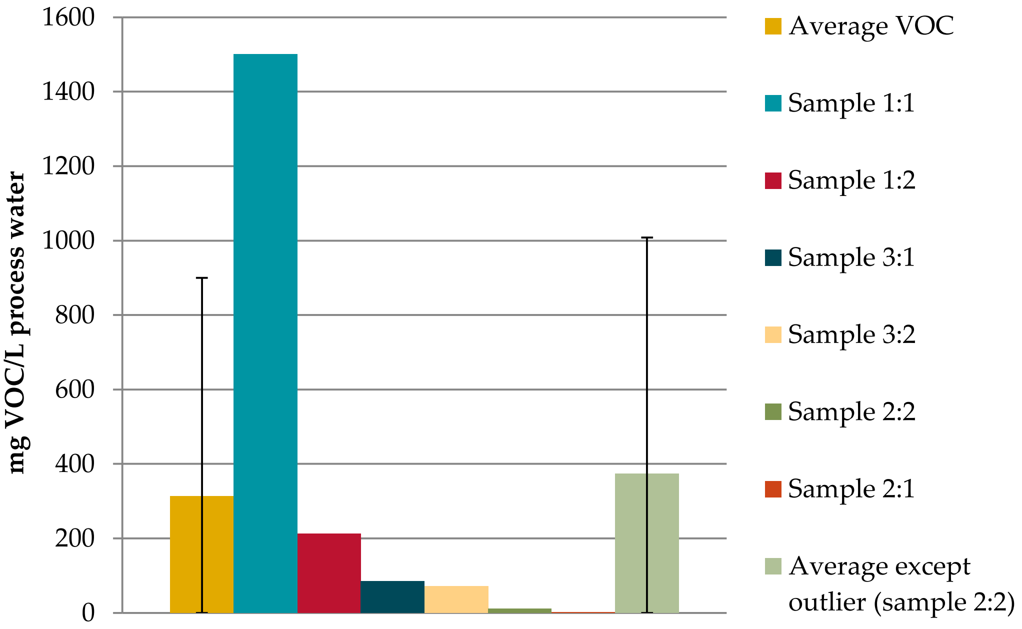

Figure 9. Content of VOC in process water from upgrading of biogas, expressed as mg/L process water, in plants where waste is the main substrate. The bars are shown from highest to lowest value.

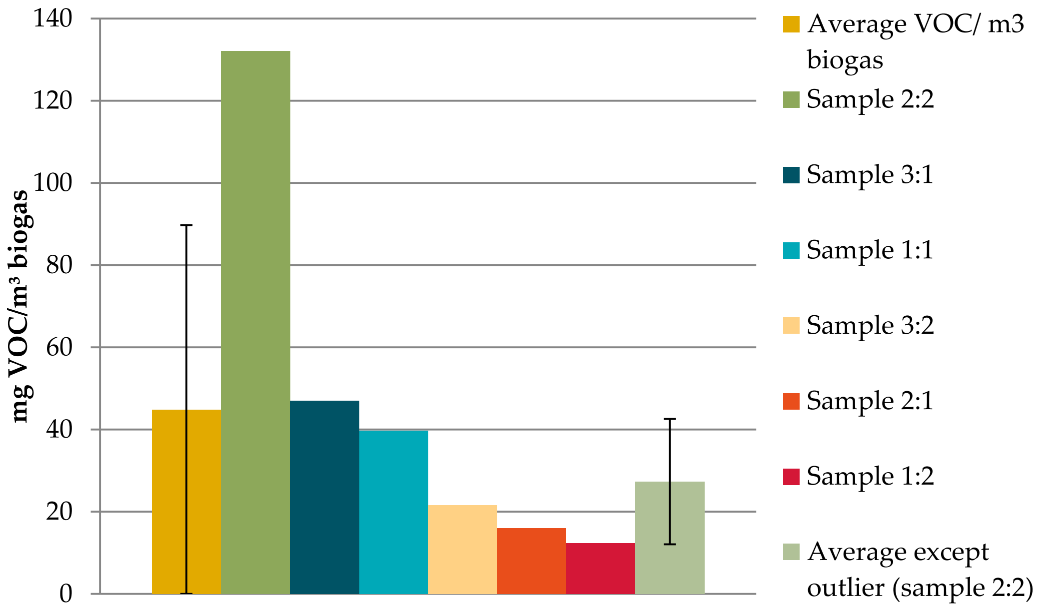

Figure 10. Content of VOC in process water from upgrading of biogas, expressed as mg/m³ treated biogas, in plants where waste is the main substrate. The bars are shown from highest to lowest value.

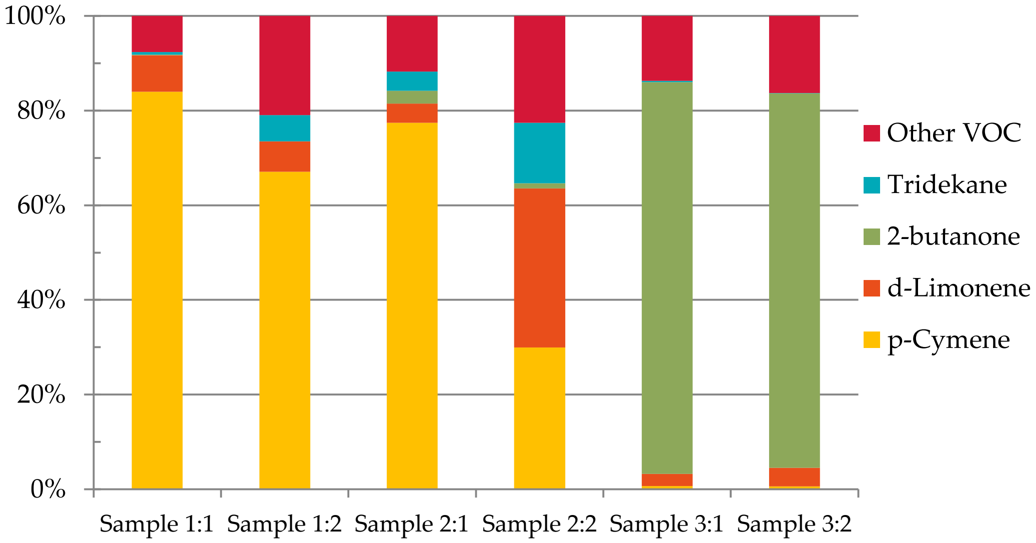

Figure 11. Incidence of the most common VOC in process water from upgrading of biogas in plants where waste is the main substrate.

When calculated per litre process water, the difference between the lowest and highest content of VOC in process water was about 100-fold, 1.5 mg/L compared with 1500 mg/L. The reason for this difference was mainly that different amounts of water were used in the upgrading facility, since these two sampling points came from the same biogas plant and at the same time. When calculated with respect to m³ treated biogas, the difference for these two sampling points was much smaller, 16 compared with 40 mg/m^3 treated biogas. The highest and lowest values were 47 and 12 mg VOC/m^3 treated biogas, respectively, i.e. about 250-fold smaller than when the content of VOC was expressed as mg VOC/L process water. The variation between the sampling occasions was larger than the difference between sampling points. This indicates that a number of analyses are required on different occasions in order to make an accurate characterisation of the average VOC content in process water from one upgrading facility.

The incidence of different VOC showed similar results for the same sampling point at different times, but it was possible to distinguish different sampling points, indicating that each upgrading facility/biogas plant has a specific pattern of appearance of different VOC in water, at least as long as the substrate mix is mainly the same. In four of the samples p-cymene and d-limonene were the most common VOC, comprising 60-90% of the total amount of VOC. This is in line with results for VOC in biogas reported by Arrhenius and Johansson (2012). In two of the samples the content of 2-butanone corresponded to 80% of the total amount of VOC, indicating that the substrate composition was different at this sampling point. Arrhenius and Johansson (2012) did not find 2-butanone in the biogas from waste plants in their study, but it has been identified as a common VOC by Orzi et al. (2010). This difference in VOC content between the present study and that by Arrhenius and Johansson (2012) is probably due to the fact that less than half the participating plants in the previously performed study participated in both studies and that the total number of plants and sampling points in both studies was too few. It is also noteworthy that the two studies analysed VOC in different media; water (this study) and gas (Arrhenius and Johansson, 2012).

5.1.3 Sewage biogas plants

The average content of VOC in process water from upgrading of biogas at sewage biogas plants, expressed in mg VOC/L process water and mg VOC/m^3 treated raw biogas, is shown in Figure 12 and Figure 13, respectively. The incidence of the most common VOC in process water is shown in Figure 14.

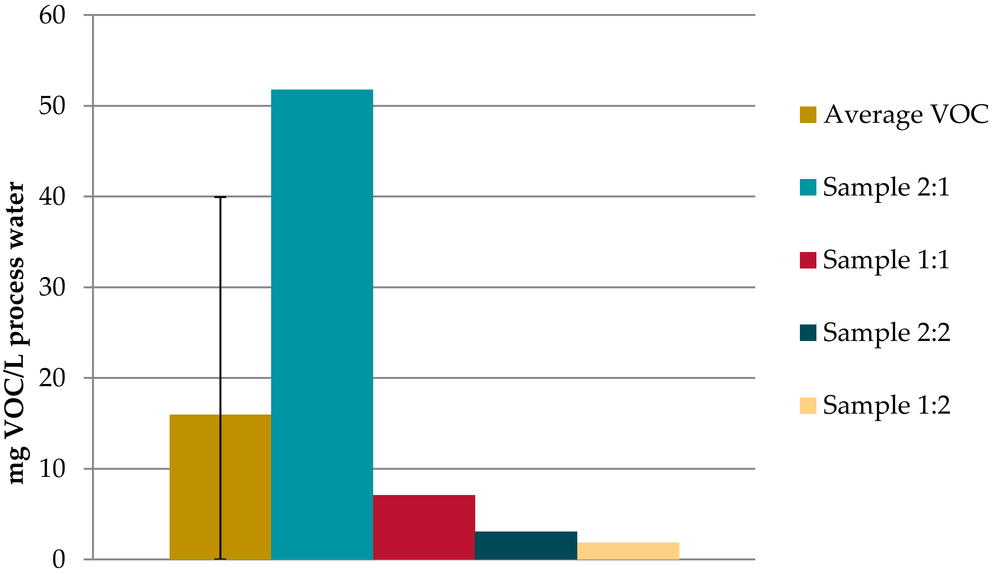

Figure 12. Content of VOC in process water from upgrading of biogas, expressed as mg/L process water, in plants where sewage sludge is the main substrate. The bars are shown from highest to lowest value.

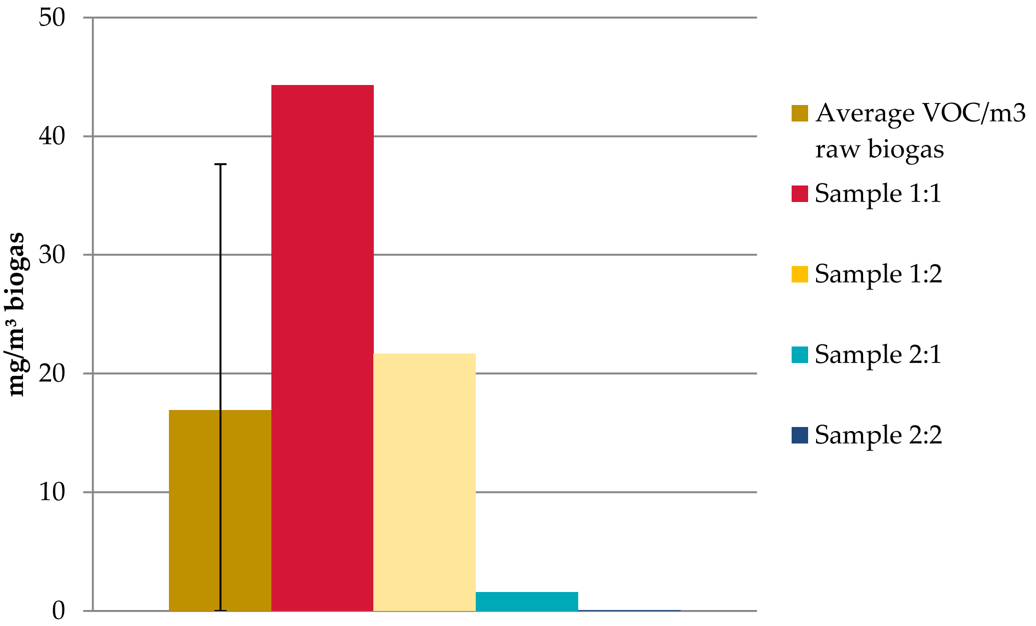

Figure 13. Content of VOC in process water from upgrading of biogas, expressed as mg/m³ treated biogas, in plants where sewage sludge is the main substrate. The bars are shown from highest to lowest value.

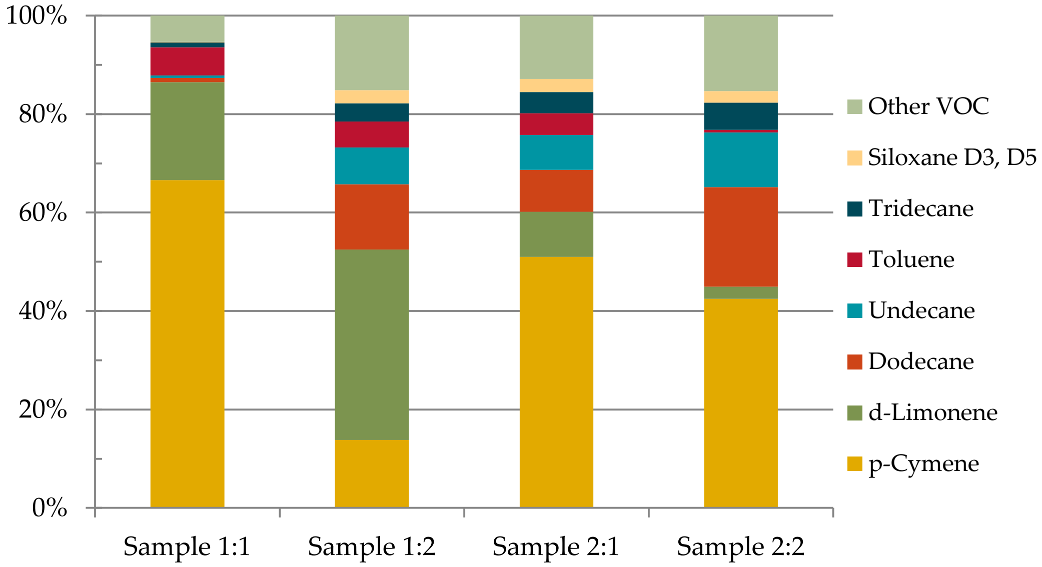

Figure 14. Incidence of the most common VOC in plants where sewage sludge is the main substrate.

The average level of VOC at sewage plants was lower than the VOC content at waste biogas plants, but higher than that at agriculture biogas plants. However, by comparing separate values for mg VOC/m³ treated biogas, it is clear that the VOC content at the two participating sewage plants differed. One plant had a VOC content that was in line with waste biogas plants, while the content at the other plant was in line with agriculture biogas plants.

The difference between the two sewage biogas plants could be due to the fact that upgrading facilities at both plants upgrade biogas partly originating from the digestion of waste. Both plants use amine scrubbers for upgrading, but the amount of water used for upgrading is different.

Since only two sewage plants were included in the study, which both additionally received gas from waste digestion plants at their upgrading facility, it is not possible to make an accurate characterisation of the average VOC content in process water from sewage plants. In order to do so, more participating sewage plants would be required, where some of these plants only digest sewage sludge, and also more samples at different times from each sampling point.

P-cymene, d-limonene, dodecane and undecane were the most common VOC in all samples. A large proportion of the p-cymene and d-limonene probably originates from biogas produced from food waste. Siloxanes were found in all samples from sewage biogas plants, but did not represent more than 2.7% of the total amount of VOC. Siloxanes are commonly found in biogas from sewage plants (Arrhenius and Johansson, 2012; Rasi et al., 2011).

If the sewage plants in this study had only used sewage sludge as substrate, the fraction of siloxanes would probably have been higher.

5.1.4 Agriculture biogas plants

Average content of VOC in process water from upgrading of biogas in agriculture biogas plants, expressed as mg/L process water and mg/m^3 treated biogas, is shown in Figure 15 and Figure 16, respectively. The incidence of the most common VOC in the process water is shown in Figure 17.

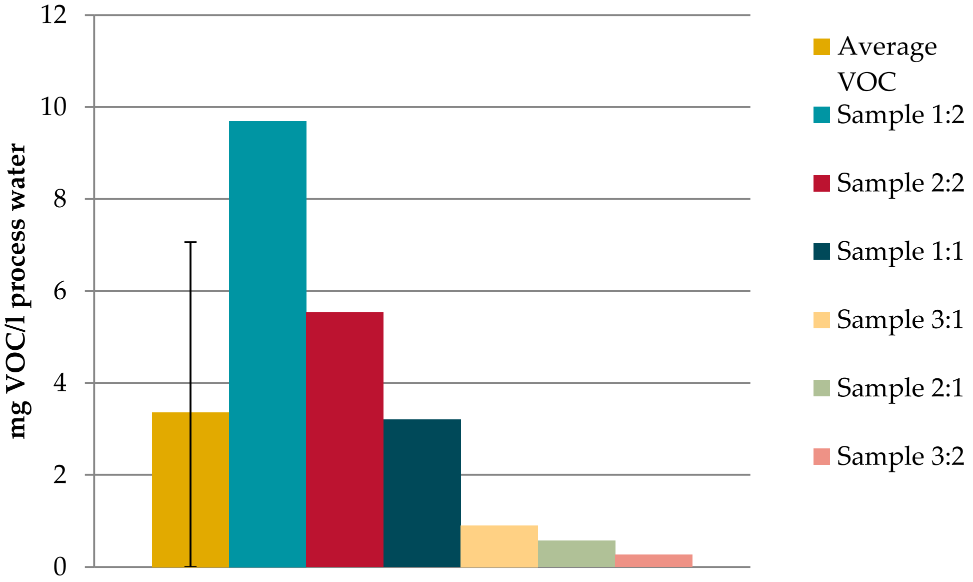

Figure 15. Content of VOC in process water from upgrading of biogas, expressed as mg/L process water, in plants where agricultural residues are the main substrate. The bars are shown from highest to lowest value.

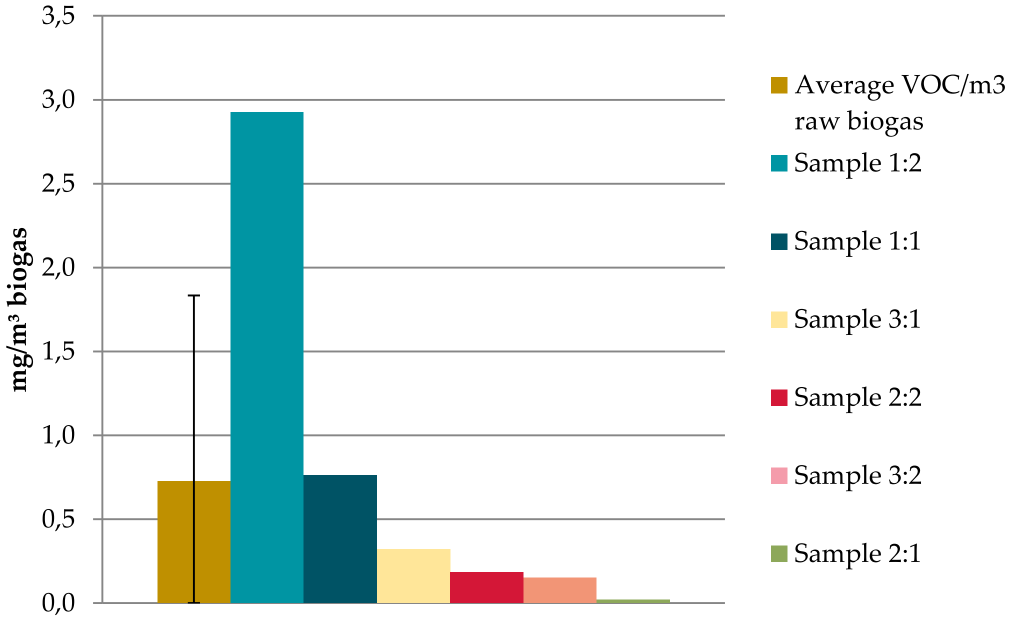

Figure 16. Content of VOC in process water from upgrading of biogas, expressed as mg/m³ treated biogas, in plants where agricultural residues are the main substrate. The bars are shown from highest to lowest value.

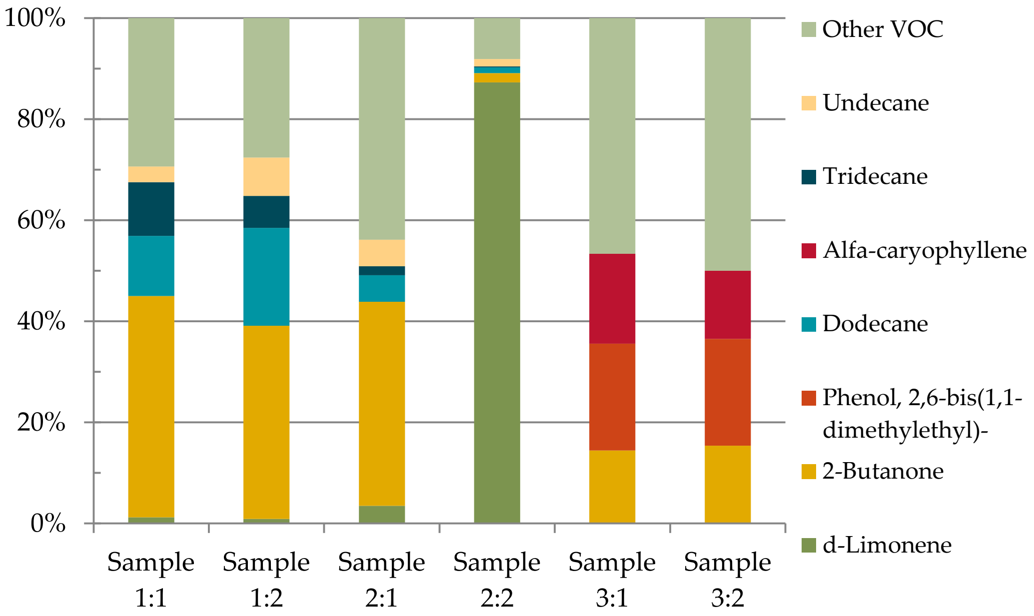

Figure 17. Incidence of the most common VOC in plants where agricultural residues are the main substrate.

The number of samples was too small to make an accurate characterisation of the average VOC content in process water from one upgrading facility, but the amount of VOC was generally very low compared with waste and sewage biogas plants, whether expressed as mg VOC/L water or mg VOC/m³ treated biogas. The content in water was on average 99% lower than at waste plants and 80% lower than at sewage plants. Expressed as mg VOC/m³ treated biogas, the average is 98% lower than at waste plants and 95% lower than at sewage plants.

The incidence of the most common VOC showed similar results for two out of three sampling points at different times. At the third point, the fractions of different VOC varied between the two sampling times, with d-limonene detected in a much higher amount at the second sampling time. Other VOC were detected in the same order as at the first sampling time.

It was also possible to distinguish the sampling points from each other, indicating that each upgrading facility/biogas plant has a specific pattern for the presence of VOC in water as long as the main substrate is the same.

2-butanone was the most common VOC in three out of six samples and was also detected in the other three samples. This is in line with results for VOC in biogas in Arrhenius and Johansson (2012) and Murphy et al. (2014).

5.1.5 Condensed water from biogas

During the cooling of the biogas condensed water is formed. One sampling point for this water was analysed in the project for plants with waste as the main substrate. The incidence of the most common VOC in condensed water is shown in Figure 18.

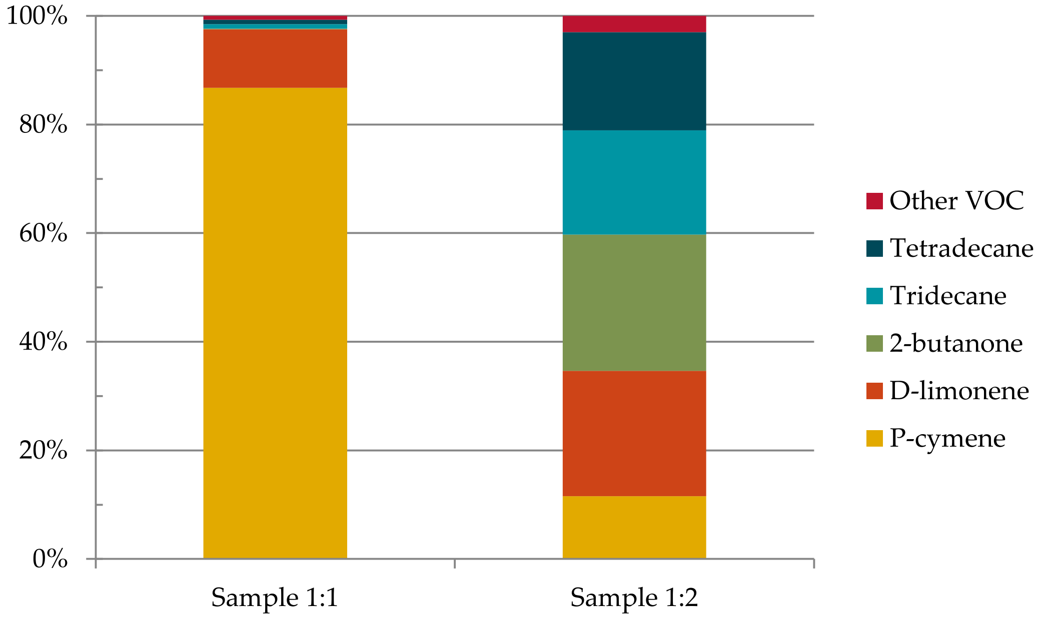

Figure 18. Incidence of the most common VOC in condensed water.

The amount of VOC in the samples differed greatly between the sampling times, but both samples had a high amount of VOC, 479 and 36 500 mg VOC/ L or 21 and 1 740 mg VOC/m^3 treated biogas. The difference was mainly due to a large difference in the amount of p-cymene, while other VOC were present in the same order of magnitude at the two sampling times. The number of samples was too small to make an accurate characterisation of the average VOC content in condensed water from one facility due to both varying results and few samples.

5.1.6 Comparison of water scrubber and chemical scrubber

Due to different use of amounts of water at different plants and upgrading facilities, only results expressed as mg VOC/m^3 treated biogas are discussed in this section. In total, eight samples from the water scrubber technique were analysed (four with waste and four with agricultural residues as main substrate). In total, eight samples from the amine scrubber technique were analysed (four with sewage sludge, two with agricultural residues and two with waste as the main substrate). Average values in mg VOC/m^3 treated biogas for the two upgrading techniques are shown in Figure 19.

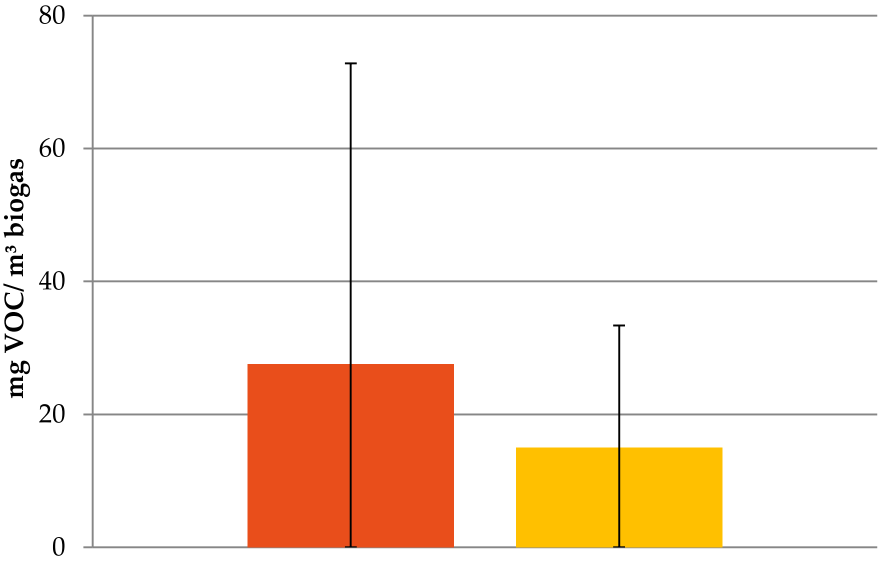

Figure 19. Average content of VOC in process water from upgrading of biogas, expressed as mg/m^3 treated biogas. Results separated with respect to upgrading technique: water scrubber (🟧) and amine scrubber (🟨). Upper and lower standard deviations are marked with deviation bars.

The content of VOC was on average similar when comparing process water from the water and amine scrubber techniques. A likely explanation for the few differences between the techniques is that different substrate types were used at the plants, rather that the upgrading technique itself, see previous paragraph.

5.2 FILTER TRIALS WITH ACTIVATED CARBON AND PEAT

The synthetic process water flowed through the filters at both normal and high concentrations and the amount of VOC left in the filtrate was compared against a blank sample. Results are presented in Figure 20. The flow rate and amount of filter material was not optimised for the specific material. Furthermore, it should be stressed that the volume and not the weight was the same for the two materials. The amount used was 2.45 and 2.15 g, for activated carbon and peat respectively. The presented results are intended to show tendencies and not to be used to calculate specific adsorption values.

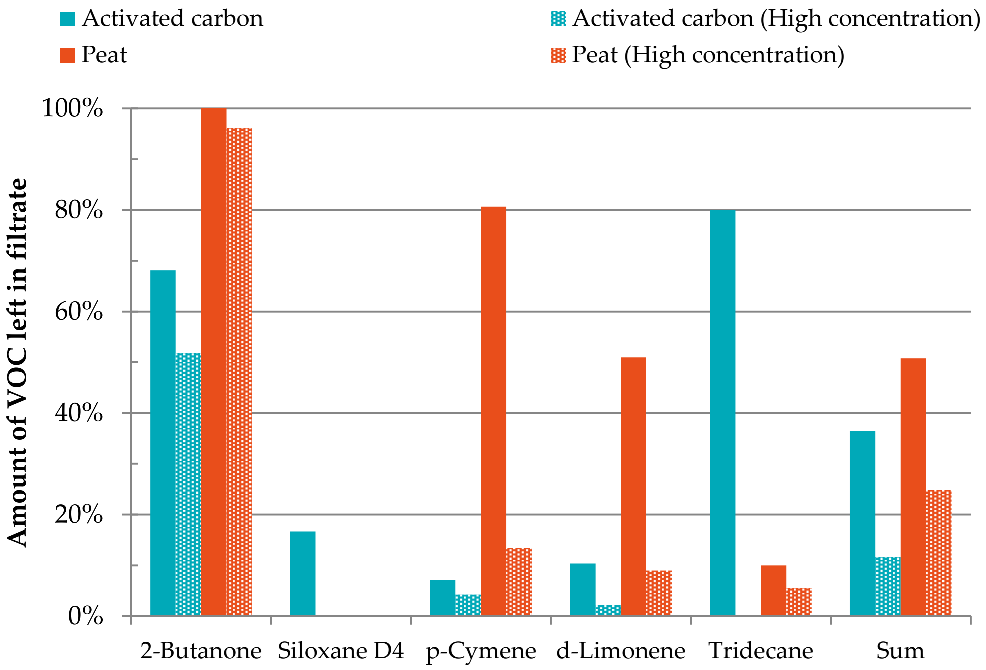

Figure 20. Amount of VOC in the filtrate, compared with a blank run, with simulated process water in realistic (24 mg VOC/L) and high (483 mg/L) concentrations.

The results showed that activated carbon had the potential to reduce all five VOC tested by at least 50% in one of the two trials (realistic and high concentration). Peat showed potential to reduce all five VOC except for 2-butanone. Activated carbon had better adsorption than peat for all VOC, irrespective of concentration, except for tridecane.

Both filters readily adsorbed siloxane D4, which was the least water-soluble of the VOC applied (see Table 2 and Table 5). Similarly, both filters had difficulties in reducing the concentration of 2-butanone, which is the most polar and the most water-soluble of the VOC tested. The reduction of p-cymene and d-limonene was high in all trials except one with a peat filter and realistic VOC concentrations. This might also be explained by the solubility of the VOC, since in realistic concentrations p-cymene and d-limonene are dissolved in the water phase.

On average, activated carbon reduced VOC by 64% for process water with a realistic level of VOC and 88% for process water with a high level of VOC. Peat reduced the VOC by 49% for process water with a realistic level of VOC and 75% for process water with a high level of VOC.

The amount of peat used in the trials was 12% less than activated carbon regarding weight. Since peat is a cheaper filter material than activated carbon, even if the reduction of VOC was lower than for activated carbon, it would still be interesting to perform more detailed investigations to find out whether peat can be a cost-effective solution for treatment of process water from upgrading facilities.

5.3 ANALYSIS OF INHIBITION OF THE BIOGAS PROCESS BY ADDITION OF VOC

Biomethane potential tests were performed to simulate the recirculation of process water back to the anaerobic process in the digesters and investigate the risk of inhibition of the microorganisms in the digester. Final concentrations of VOC in the anaerobic tests are shown in Table 8.

Table 8. Final concentrations of VOC in biomethane potential (BMP) tests.

	Concentration (mM)*	Concentration (mg/L)	Amount of VOC in relation to inoculum and substrate (mg/g VS)
Series 2 – VOC in high amount	0.12	11.6	0.6
Series 3 – VOC in very high amount	2,4	238	13.2

*A model molar mass of 100 g/mol was used, which is a weighted average of the molar masses of the individual substances in the VOC solution

Results from the BMP test with addition of VOC solution are shown in Table 9 and Figure 21.

Table 9. Accumulated methane gas production in biomethane potential (BMP) tests.

Substrate	Accumulated production of methane gas (NmL CH_4/g VS)
Series 1 - Control	546 ± 7
Series 2 – VOC in high amount	549 ± 12
Series 3 – VOC in very high amount	547 ± 15

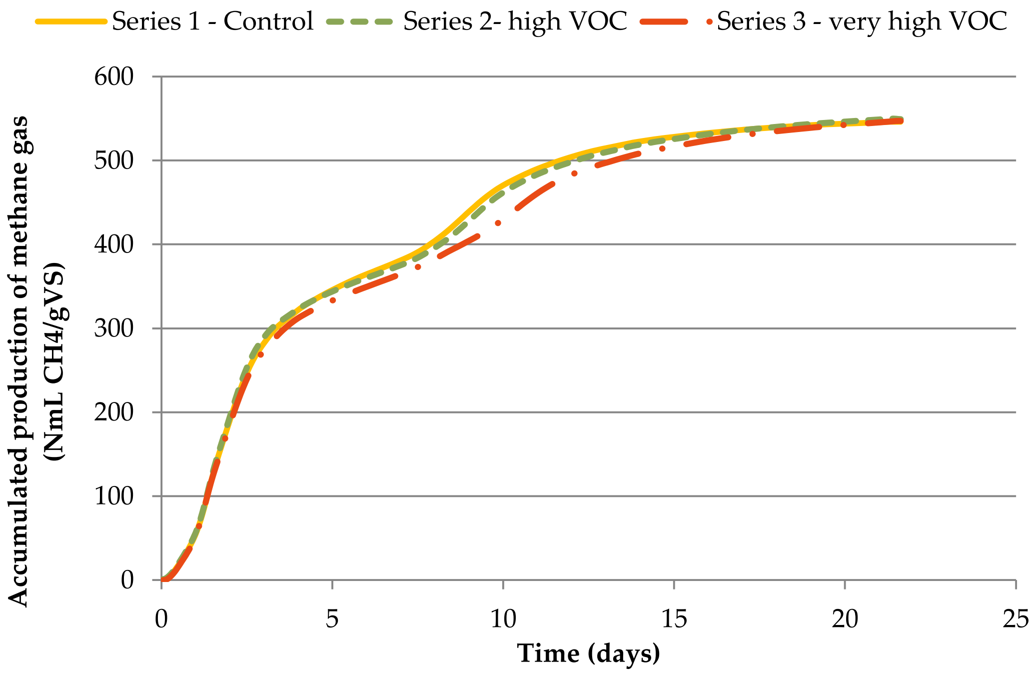

Figure 21. Accumulated production of biomethane from: the control series; series 2, with VOC in solution in high amounts; and series 3, with VOC in solution in very high amounts. Values are given in NmL CH_4/g VS.

The concentrations of VOC used in both series 2 and 3 have in earlier studies been shown to be inhibitory to varying degrees (see Table 3). However, no inhibition was observed here for series 2. Many studies show a clear, in some cases total, inhibition of anaerobic digestion at concentrations in the same magnitude as in series 3. The biogas production for the three replicates in series 3 showed tendencies for inhibition, manifested by lower production between days 5-10. The production recovered over time and total gas production was finally equal for all series. One explanation for the lack of response to VOC could be that the inoculum might have acclimatised to VOC and that the favourable conditions used in BMP trials made it possible to produce biogas.

The measurements of VOC in series 4 before and after the BMP test are shown in Table 10.

Table 10. Measured VOC before and after the biomethane potential (BMP) test.

	VOC in bottles before BMP test (inoculum + VOC addition) (µg)	VOC in bottles after BMP test (µg)	VOC sampled on Tenax tubes (µg)
Series 4	6200	3150	5

The measurements of VOC showed that about half of the added VOC were still left in the bottle after the BMP test had ended. Only about 0.1% of the original content of VOC in the bottles was measured in the Tenax tubes, so the other half had either been degraded by microorganisms or left the bottles without being captured by the Tenax tubes. Alternatively, the inoculum, a complicated sample matrix, could have affected the VOC analysis in some way. Of the five VOC added, only p-cymene and d-limonene could be detected in the samples analysed after the BMP test.

5.4 APPROPRIATE METHODS FOR ANALYSIS OF VOC IN PROCESS WATER

This project clearly showed that the content of VOC in process water is dependent on substrate used at the biogas plant. However, it also showed that the VOC content varies widely between different sampling points for the same main substrate, and also between different samples in time at the same sampling point.

To perform an appropriate characterisation, it is important to carry out sampling on several occasions and also to use analytical methods that can measure the compounds targeted in the investigation. A general recommendation for such an investigation is to start with a broad screening analysis and, after some sampling rounds, move to a narrower and more specific analytical method, since wide screening analyses are often more expensive than narrow, specific analyses. It may also be possible to use simpler methods of analysis that measure the total content of carbon, e.g. total organic carbon (TOC) or chemical oxygen demand (COD), or easily degradable organic material, e.g. biological oxygen demand (BOD). If simpler methods are used, it is important to be aware that in general they are not developed for volatile compounds, which can evaporate during preparation and analysis. Moreover, simpler methods cannot separate VOC from other sources of carbon, e.g. foam or microorganisms in the water. If simpler methods for analysis are used it is suggested that a wide screening analysis of VOC be performed initially together with the simpler method to investigate the correlation.

The highest amounts of VOC in process water occur at waste biogas plants, where p-cymene, d-limonene and 2-butanone are most common. They accounted for at least 60% of the total amount of VOC in the samples in this study. These results indicate that if waste is a large part of the substrate, the most important substances to analyse in the process water are p-cymene, d-limonene and 2-butanone. These VOC are not included in standard analyses at the major Swedish laboratories, however. At sewage plants, the most common VOC were p-cymene, d-limonene, dodecane and undecane and therefore it is important to include these in analysis of process water. At agriculture biogas plants, the amount of VOC was very low compared with waste and sewage plants, meaning that the need for further investigations of process water was low.

5.4.1 Alternative methods for analysis

Biological oxygen demand is a measurement of the amount of oxygen required by microorganisms to degrade the organic carbon in solution. It is a common way of measuring organic carbon, and the standard measure is the amount of oxygen required by microorganisms over 5 or 7 days. When trying to measure VOC with this method it is important to know that VOC present in high concentrations might inhibit the microorganisms that degrade the organic carbon, giving a false low value. Dilution can be used in the analysis so that the concentrations of the microorganisms are lower.

Chemical oxygen demand is used as an indirect measurement of the amount of organic compounds in water. It is expressed in mg/L, also referred to as parts per million (ppm), which indicates the mass of oxygen consumed per litre of solution. The basis for the COD analysis is that nearly all organic compounds can be fully oxidised to carbon dioxide with a strong oxidising agent under acidic conditions.

Total organic carbon analysis requires the organic carbon to be completely oxidised to carbon dioxide, which is then measured. An alternative method is to analyse TOC as the difference between amount of total carbon and amount of inorganic carbon (carbon dioxide, carbon monoxide, inert carbon, cyanide and cyanate).

6 Conclusions

This characterisation of process water from upgrading of biogas showed that the content of VOC, both regarding total concentration and specific VOC, in process water is dependent on the substrate used at the biogas plant. Biogas plants using waste as the main substrate had the highest concentration of VOC in the process water and plants that use agricultural residues had the lowest levels. The characterisation also showed that the content varied greatly between different sampling points with same main substrate and sampling occasions at the same sampling point. This indicates that site-specific conditions are important for the results.

The upgrading plants in this study used different amounts of water during upgrading, which greatly affected the concentration of VOC. There were no significant differences in content of VOC in process water from a water scrubber or amine scrubber.

To perform an appropriate characterisation, it is thus important to take samples on several occasions and also to use analytical methods which can measure the compounds interesting for the investigation. A general recommendation for such an investigation is to start with a broad screening analysis and then narrow the focus to a specific analytical method.

There are several different techniques available to treat water contaminated with VOC and the quality and quantity of the process water produced affects the choice of treatment technique. Decisions on whether and how to treat the process water need to be based on the impact on the recipient in relation to costs (both economic and environmental). Possible ways for treatment of the process water can be to use an existing biological purification plant, e.g. recycling of process water to the digestion process, or sending it to a sewage plant. Inhibition by VOC of the anaerobic digestion process was investigated in BMP tests, but no inhibition could be observed for addition of synthetic process water in a realistic amount.

Filter trials testing the adsorption capacity of activated carbon and peat showed that both filter materials adsorbed VOC, but activated carbon had higher removal efficiency.

The great variety of VOC found in process water makes it very difficult to state general health and environmental effects from exposure, without an accurate site-specific investigation including several sampling periods. Some VOC are highly toxic and some have no known negative health effect. Of the three most common VOC found in process water (p-cymene, d-limonene and 2-butanone), d-limonene is the only one with more serious risk phrases (R50 and R53).

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Appendix A. Sampling protocol for process water (in Swedish)

Information om biogasanläggningen

Företag	**Provtagningsplats (skrubber/ amin/ annat)**
Provtagare (namn)	**Kontaktuppgifter**
Väder (temp etc.)	**Datum och tid**
Provtagningspunkt (flöde/ brunn, beskrivning, bifoga gärna en skiss)	
Totalt flöde av processvatten (l/s, l/min)	**Flöde vid provpunkt om T-rör på ledning/ slang/ rör (ej brunn)**
Fri fas i brunn (Ja/ Nej)?	**Om Ja, bedömning av andel fri fas av totalt processvatten**
Flöde biogas gasuppgradering (in och/eller ut)	**Metanhalt rågas**
Iakttagelser vid provtagning	
Speciella noteringar vad gäller driftdata (var det något speciellt just denna dag/ vecka)	

Företag	**Uppgiftslämnare**
Substrat 1	**Andel av substratmix (%)**
Substrat 2	**Andel av substratmix (%)**
Substrat 3	**Andel av substratmix (%)**
Rötningstemperatur	**Hygienisering (Ja/ Nej, metod?)**
Beskrivning uppgraderingsprocess	
Nuvarande hantering av processvatten	
Finns restriktioner från miljömyndigheten gällande hantering av processvatten? Om ja, vilka?	

Appendix B. Instructions for sampling of process water (in Swedish)

I projektet kommer flyktiga organiska föroreningar (VOC) i processvatten att undersökas. VOC är flyktiga organiska föreningar som vid normala förhållanden har ett så högt ångtryck att de kan sprida sig i luften och har en kokpunkt lägre än cirka 250°C enligt EU direktiv om färg (Directive 2004/42/CE). I detta projekt kommer VOC med kokpunkter upp till 350 °C att analyseras. Lösligheten i vatten är i allmänhet låg. VOC kan förekomma i fri fas på vattenytan, t.ex. bensin eller olja på vatten.

Provtagning kommer utföras som stickprov vid två tillfällen (augusti och oktober/ november) på samma provtagningsplats. I paketet finns provkärl som rymmer 100 ml var, provtagningshandskar och provtagningsprotokoll.

Provtagningsplats

Kontinuerligt flöde – rör/ ledning

Försök i första hand att finna en plats där det går att ta prov från ett kontinuerligt vattenflöde från processen utan stillastående vatten (rör, slang, ledning). På så sätt är det möjligt att ta ett prov som är representativt för hela flödet.

Stillastående vatten - brunn

Om det inte finns någon plats där provtagning på flödande vatten går att utföra så får provtagning ske på mer eller mindre stillastående vatten i brunn eller motsvarande. Provet kan ge en god bild över mängden föroreningar i vattnet, men det finns risk för att VOC kan avdunsta eller lägger sig som fri fas i brunnen vilket gör det svårare att få ett representativt prov för hela flödet.

Provtagningsinstruktion

Allmänt

Även små mängder VOC från t.ex. olja, verktyg, maskiner kan förorena provet och leda till falskt höga värden. Därför är det viktigt med rena händer och kropp, rena kläder och att använda skyddshandskar vid provtagning, t.ex. engångshandskar av Nitril som skickas med tillsammans med provkärlen.

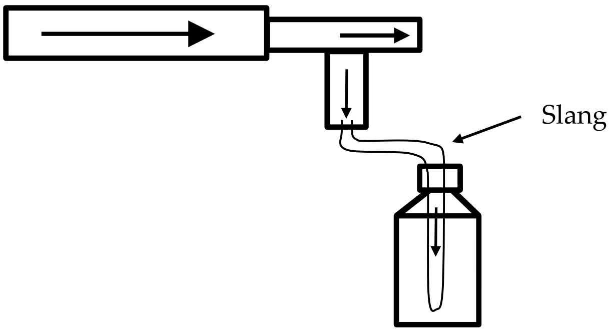
Provet är en ögonblicksbild, därför är det viktigt att förhållandena är så lika genomsnittliga driftsförhållanden som möjligt vid provtagningstillfället. Det är också viktigt att ni noterar det som eventuellt skiljer sig från en ”normal” produktionsdag på anläggningen.

Protokoll som ska fyllas i samband med provtagning skickas med i paketet och skickas även ut via e-post. Skicka gärna en kopia på provtagningsprotokollet med provflaskorna till SPs laboratorium.

Flaskorna ska toppfyllas helt för att undvika avgång av VOC till luft ovanför provet och skickas omgående till SPs laboratorium för analys. Skicka paket så tidigt som möjligt i veckan, ej senare än onsdag!

Provtagning av kontinuerligt flöde – rör/ ledning

Om flödet är högt kan ett delflöde skapas med hjälp av ett T-rör, kulventil och ett kortare rör/slang se Figur A 1.



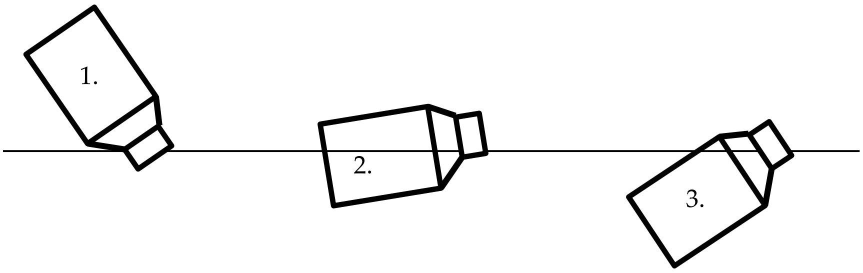
Figur A 1. Provtagning av kontinuerligt flöde från rör/ slang/ ledning. Undvik att vattnet utsätts för luft så att VOC kan avgå till luften innan provet når provkärlet.

Flödet för provtagning bör vara lågt, gärna lägre än 0,5 l per minut. Använd om möjligt delar av metall istället för plast då VOC kan binda till plastytor. Uppskatta totala flödet och eventuellt delflöde för provtagning genom att t.ex. använda en hink, mäta volymen och sedan tiden det tar för att fylla den. Märk flaskan på bifogad etikett med företag/ anläggning, provplats, tidpunkt och provtagare. **Toppfyll 2 flaskor och skicka omgående in dem till SPs laboratorium (flaska 2 är backup om det skulle strula vid analys av flaska 1).**

Provtagning av stillastående vatten - brunn

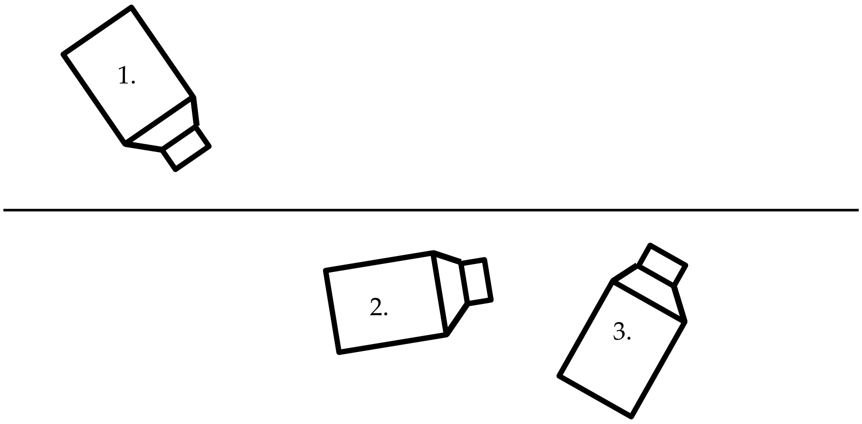
Om det inte finns någon bra plats där provtagning på flödande vatten går att utföra så får provtagning ske på mer eller mindre stillastående vatten i brunn eller motsvarande. Först ska en bedömning göras om det finns någon form av fri fas (skiktning, oljehinna) på ytan (förhoppningsvis finns inte någon fri fas), om ja så behöver omfattningen uppskattas (djup och utbredning jämfört med övrigt vatten i brunnen). Om ni bedömer att det går att ta ut prov som till största delen innehåller endast den fria fasen så ska prov på både den fria fasen och vatten under den fria fasen, om nej så tas prov endast ut på vatten 2-5 cm under vattenytan.

Ett prov på eventuell fri fas tas ut genom att hålla flaskans öppning precis invid vattenytan, se figur A 2. Det räcker med en toppfylld flaska för eventuellt prov från fri fas.



Figur A 2. Provtagning av fri fas i brunn. För ned flaskan med mynningen nedåt i vattnet. Vänd sedan flaskan långsamt åt sidan. Underkant av mynningen i nivå med underkant av fri fas.

Efter att prov tagits ut på eventuell fri fas ska vattnet i brunnen provtas. Om det finns fri fas på ytan är det extra viktigt att ingen ytfilm kommer in i flaskan när den sänks ned i vattnet. Det kan åstadkommas genom att korken får sitta kvar på flaskan när den sänks ned i vattnet. Överkant av flaskans mynning ska vara 2-5 cm under vattenytan när locket tas av och vatten flödar in i flaskan. Sätt på locket när flaskan fortfarande är under vattenytan, se figur A 3.



Figur A 3. Provtagning av processvatten i brunn. Det är viktigt att inte ytfilm/ fri fas kommer in i flaskan.

Märk flaskan på bifogad etikett med provplats tidpunkt och provtagare. **Toppfyll 2 flaskor och skicka omgående in dem till SPs laboratorium (flaska 2 är backup om det skulle strula vid analys av flaska 1).**

Appendix C. Environmental and health effects of selected VOC

p-Cymene

p-Cymene is used as a solvent, chemical intermediate for p-cresol, carvacrol and other organic compounds and also as a fragrance agent in commercial and consumer products. p-Cymene is found to occur naturally in many woody plants and trees and is released through volatile emissions and occurs naturally as part of essential oils. (TOXNET, 2015). p-Cymene can also be used as a fungicide in agriculture (BPDB, 2015). p-Cymene does not have any ecotoxicological risk phrases.

<u>Data from safety datasheet (MSDS):</u>

CAS. no.	99-87-6
Appearance	Clear, colourless liquid
Smell	Sweet, aromatic, with pleasant smell
Boiling point	177 °C
Solubility	23 mg/L
Risk phrase	R10[5]

<u>Data from BPDB:</u>

Degradation: No data

Acute toxicity mammal: 4750 mg/kg (BPDB, 2015) and (ECHA, 2015)

Acute toxicity fish: 48 mg/kg

Acute toxicity *Daphnia*: 6.5 mg/kg

<u>Data from Toxnet:</u>

Human health effects: p-Cymene is reported to be a primary skin irritant

Stability: 83-95% degraded in 14 days

Toxicity green algae: 49000 µg/L, EC50

Toxicity opossum shrimp s: 4400 µg/L, LC50

Toxicity *Daphnia magna*: 6500 µg/L, LC50

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[5] R10 – Flammable

d-Limonene

d-Limonene is used in flavourings, fragrances, cosmetics, as a solvent, wetting agent and as both an active and inert ingredient in pesticides. It is used as an insecticide, insect repellent, and animal (dog and cat) repellent. d-Limonene is found naturally in citrus fruits and is emitted to the environment from plants and the combustion of wood (TOXNET, 2015).

d-Limonene has the ecotoxicological risk phrases R50 and R53, which makes it a problematic substance for the environment. d-Limonene is very toxic to aquatic animals and can cause mortality in fish (fathead minnow) already at levels of 0.25 mg/L. LC50 is 0.72 mg/L (ECHA, 2015). ECHA has set the assessment factor to 50 for freshwater and the PNEC[6] value for freshwater (aqua) is 5.4 µg/l. The decomposition is, according to ECHA, 0.05-0.4 mg/L/h, which indicates that limonene has a short half-life in the environment.

Data from safety datasheet (MSDS):

CAS no.	5989-27-5
Appearance	Clear, colourless liquid
Smell	Citrus
Boiling point	175 °C
Solubility	14 mg/L
Risk phrase	R10 R38 R43 R50/53[7]

Data from ECHA

Very toxic to aquatic organisms (R50) and may cause long-term adverse effects in the aquatic environment (R53)

Stability
Exp 1: The observed volumetric biodegradation rate and soil-normalised biodegradation rate were determined to be 0.38 mg/L/h and 1.9 µg/g/h. Exp 2: Maximum degradation rate in experiments 1, 2A and 2B were 0.044, 0.40 and 0.137 mg/L/h, respectively. Exp 3: 41-98% degradation by biochemical oxygen demand was reached in 14 days

Under the test conditions, d-limonene was readily degraded by indigenous soil microorganisms.

Toxicity

NOEC: 0.250 mg/L mortality fathead minnow

NOEC: 0.074 mg/L mortality *Daphnia* 48h

Data from Toxnet

Stability*:* 83-95% degraded in 14 days

Toxicity: *Daphnia magna*: 577 µg/L, LC50

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[6] Predicted No Effect Concentration

[7] R10 – Flammable, R38 – Irritating to skin, R43 - May cause sensitization by skin contact, R50/R53 Very toxic to aquatic organisms May cause long-term adverse effects in the aquatic environment

2-Butanone

2-Butanone is used as a solvent for extractions in e.g. the pharmaceutical industry. In Sweden it is used in products such as paints and adhesives, but the major use is as a solvent in the plastics industry. 2-Butanone is a common denaturant and occurs often in products containing ethanol (KemI, 2015). 2-butanone occurs naturally as a metabolic by-product of plants and animals and is released into the atmosphere by volcanoes and forest fires (TOXNET, 2015).

ECHA has set the assessment factor to 1 for freshwater and the PNEC value for freshwater (aqua) is 55.8 mg/L.

Data from safety datasheet (MSDS):

CAS no.	78-93-3
Appearance	Clear, colourless liquid
Smell	Strong, acetone-like
Boiling point	80 °C
Solubility	Soluble in water
Risk phrase	R11, R36, R66, R67[8]

Data from ECHA

Stability: >98 % degraded in 28 days, readily degradable

Toxicity

Fathead minnow: LC50 2993 mg/L 96h

Daphnia: EC50 308 mg/L, 48 h

Data from KemI

Not classified as dangerous to the aquatic environment

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[8] R11 – Highly flammable, R36 – Irritating to eyes, R66 – Repeated exposure may cause skin dryness or cracking, R67 – Vapors may cause drowsiness and dizziness

2-Butanol

2-Butanol occurs naturally in apple and pear aromas, as well as chicken manure. Butanols are mainly used as synthesis products and solvents. Among synthetic products are plasticisers (dibutyl phthalate), flavours and perfumes (esters) and glycol ethers. As a solvent, butanols can occur in paint and varnish, glue, paint remover, pesticides and pharmaceuticals. Among other uses, it is a component of hydraulic fluid and emulsifiers, an octane-enhancing agent in gasoline and as a denaturant for ethanol for the heat pump system (KemI, 2015).

ECHA has set the assessment factor to 1 for freshwater and the PNEC value for freshwater (aqua) is 47.1 mg/L.

<u>Data from safety datasheet (MSDS):</u>

CAS no.	78-92-2
Appearance	Clear, colourless liquid
Smell	Alcohol
Boiling point	99 °C
Solubility	Soluble in water
Risk phrase	R10, R36/37, R67[9]

<u>Data from ECHA</u>

Stability*:* 82% degraded in 5 days, readily degradable

Toxicity

Fathead minnow: LC50 2993 mg/L 96 h

Daphnia: EC50 2300 mg/L 24 h

<u>Data from KemI</u>

Not classified as dangerous to the aquatic environment

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[9] R10 – Flammable, R36 – Irritating to eyes, R37 – Irritating to respiratory system, R67 – Vapors may cause drowsiness and dizziness

Siloxanes

A siloxane is a chemical compound containing silicon, oxygen and methyl groups (CH_3). They are used in many different applications such as cosmetics and hygiene products, products for removal of paint from brushes, food additives, implants in cosmetic surgery, coating of needles, pacemakers, manufacture of pacifiers, as additives in paints, oils and for dry cleaning (Arrhenius and Johansson, 2012).

Table A 1. Cyclic and linear types of siloxanes.

Cyclic siloxanes	CAS	Linear siloxanes	CAS
D3: hexamethylcyclotrisiloxane	541-05-9	L3: octamethyltrisiloxane	107-51-7
D4: octamethylcyclotetrasiloxane	556-67-2	L4: decamethyltetrasiloxane	141-62-8
D5: decamethylcyclopentasiloxane	541-02-6	L5: dodecamethylpentasiloxane	141-63-9
D6: dodecamethylcyclohexasiloxane	540-97-6	L6: tetradecamethylhexasiloxane	107-52-8

The siloxanes found in samples taken within this project were siloxane D3 and D5.

No risk phrases for Siloxane D3-D5

<u>Siloxane D3</u>

CAS no.	541-05-9
Appearance	White crystalline solid
Smell	Not specified
Boiling point	Not specified
Solubility	May decompose

No data in ECHA, TOXNET or KemI

<u>Siloxane D5</u>

CAS no.	541-02-6
Appearance	Colourless liquid
Smell	Not specified
Boiling point	90 °C
Solubility	< 0.01 mg/L at 23 °C

Data from TOXNET

Stability

Dimethyl siloxanes in general are highly resistant to biodegradation.

Decane

Decane is an alkane hydrocarbon with the chemical formula $C_{10}H_{22}$ and has 75 structural isomers. These isomers are flammable liquids. Decane is a component of gasoline (petrol). Like other alkanes, it is nonpolar and does not dissolve in polar liquids, such as water.

ECHA has set the assessment factor to 1 for freshwater and the PNEC value for freshwater (aqua) is 1.2 µg/L (counted as the soluble part).

<u>Data from safety datasheet (MSDS):</u>

CAS no.	124-18-5
Appearance	Clear, colourless liquid
Smell	Alcohol
Boiling point	174 °C
Solubility	4 µg/L
Risk phrase	R10, R65[10]

<u>ECHA</u>

Stability*:* 77-83% degraded in 28 days

Readily degradable

Toxicity

The insolubility of decane means that LL50 (Lethal Loading) is counted, and not what is actually dissolved in the water.

Oncorhynchus mykiss: LL50 >1000 mg/L 24, 48, 72, 96 h

Daphnia magna: The saturated exposure solution at a loading of 1000 mg/L did not produce immobility in the test organisms after a 48-hour exposure (EL50 >1000 mg/L 48 h)

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[10] R10 – Flammable, R65 – Harmful: May cause lung damage if swallowed

Toluene

Toluene is released into the atmosphere principally from the volatilisation of petroleum fuels, toluene-based solvents and thinners and from motor vehicle exhausts. Toluene production and use as an intermediate in the production of benzoic acid, benzaldehyde, benzene, explosives, dyes and many other organic compounds may also result in its release to the environment through various waste streams. Toluene has been detected in emissions from volcanos, forest fires and crude oil (TOXNET, 2015).

ECHA has set the assessment factor to 1 for freshwater and the PNEC value for freshwater (aqua) is 0.68 mg/L.

<u>Data from safety datasheet (MSDS):</u>

CAS no.	108-88-3
Appearance	Clear, colourless liquid
Smell	Sweet, solvent
Boiling point	111 °C
Solubility	561 mg/L
Risk phrase	R11, R38, R48/20, R63, R65, R67[11]

<u>ECHA</u>

Toxicity

Oncorhynchus kisutch: LC50 5.5 mg/L 96 h

Daphnia: EC50 270 mg/L 24 h

<u>Data from Toxnet</u>

Ecotoxicity in water (LC50):

313 mg/L 48 hours *Daphnia*

17 mg/L 24 hours fish (Blue gill)

13 mg/L 96 hours fish (Blue gill)

56 mg/L 24 hours fish (Fathead minnow)

34 mg/L 96 hours fish (Fathead minnow)

56.8 mg/L any hours fish (Goldfish)

Stability

Half-life in water 12 and 90 days in two different studies

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[11] R11 – Highly flammable, R38 – Irritating to skin, R48/20 – Danger of serious damage to health by prolonged exposure by inhalation, R63 – Possible risk of harm to the unborn child, R65 – Harmful: may cause lung damage if swallowed, R67 – Vapors may cause drowsiness and dizziness

Acetone

Acetone is used as an extracting reagent and starting material or intermediate in the manufacture of chemical products. Acetone occurs naturally as a metabolic by-product of plants and animals and is emitted into the atmosphere by volcanoes and forest fires (TOXNET, 2015).

ECHA has set the assessment factor to 50 for freshwater and the PNEC value for freshwater (aqua) is 10.6 mg/L.

<u>Data from safety datasheet (MSDS):</u>

CAS no.	67-64-1
Appearance	Clear, colourless liquid
Smell	Acetone
Boiling point	56 °C
Solubility	soluble in water
Risk phrase	R11, R36, R66, R67[12]

<u>ECHA</u>

Toxicity

Pimephales promelas: LC50 6210 mg/L 96 h

Oncorhynchus mykiss: LC50 5540 mg/L 96 h

<u>Data from Toxnet</u>

Ecotoxicity in water (LC50): 5540 mg/L 96 hours (Trout).

8300 mg/L 96 hours (Blue gill).

7500 mg/L 96 hours (Fathead Minnow).

79 mg/L any hours (Water flea).

Stability: 84% degraded in 20 days

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[12] R11 – Highly flammable, R36 – Irritating to eyes, R66 – Repeated exposure may cause skin dryness or cracking, R67 – Vapors may cause drowsiness and dizziness

Pentylfuran

Pentylfuran is a colourless to light yellow liquid. It is not known to be produced by mammalian metabolism. 2-Pentylfuran is found in alcoholic beverages. 2-Pentylfuran occurs in many foods including coffee, potatoes, tomatoes, roasted filberts and soybean oil and is a component of aroma of these foods. 2-Pentylfuran is a flavouring ingredient and belongs to the family of furans. These are compounds containing a furan ring, which is a five-member aromatic ring with one oxygen atom, four carbon atoms (HMDB, 2015).

<u>Data from safety datasheet (MSDS):</u>

CAS no.	3777-69-3
Appearance	Clear, colourless liquid
Smell	Not specified
Boiling point	65 °C
Solubility	Not specified
Risk phrase	R22[13]

No data in ECHA, TOXNET or KemI.

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[13] R22 – Harmful if swallowed

Terpinolene/ α-Terpinolene

Terpinolene is used in the production of resin polymers, essential oils and flavours. Terpinolene is a member of the monoterpine family and is found in many trees and plants including spruce, redwood, pine, aspen and cedar (TOXNET, 2015). Terpinolene is used as a fungicide in wood-oil and in agriculture (BPDB, 2015).

ECHA has set the assessment factor to 1000 for freshwater and the PNEC value for freshwater (aqua) is 0.634 µg/L.

Data from safety datasheet (MSDS):

CAS no.	586-62-9
Appearance	Clear, light yellow liquid
Smell	Pine
Boiling point	194 °C
Solubility	7 mg/L
Risk phrase	R10[14]

Data from ECHA

Stability

Exp 1: At 2 mg/L test concentration, greater than 10% degradation was reached by Day 2 and greater than 60% biodegradation was reached by Day 9. Therefore, terpinolene monoconstituent was readily biodegradable.

Toxicity

Very toxic to aquatic organisms (R50) and may cause long-term adverse effects in the aquatic environment (R53).

Danio rerio (Zebrafish): LC50 0.805 mg/L 96 h

Daphnia: EC50 0,. 34 mg/L 48 h

Data from Toxnet

Toxicity*: Daphnia*: 612 µg/L, 48 h,

Toxicity: Fathead minnow: 720 µg/L, 48 h

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[14] R10 – Flammable

Appendix D. Summary of techniques for treatment of process water

Table A 2 Summary of techniques for treating process water

Technique	Description	Capacity (flow, amount of VOC, concentration of VOC)	Advantages/Drawbacks
Physical			
Air stripping	Transfers VOC in water from liquid phase into an air stream.	Capacity of great variance.	The air from the air stripping needs to be treated, e.g. by incineration.
Filter technique - Active carbon	VOC adsorb onto the activated carbon.	Filter can be adjusted to match flow and concentration.	The method is proven to be efficient (Kalmykova et al., 2014; Le Cloirec, 2012; Ridderstolpe, 2009b). Filter need to be disposed in a proper way when saturated. Expensive in relation to other filter materials.
Filter technique - Bark, peat, cork	VOC adsorb onto the material.	Filter can be adjusted to match flow and concentration.	The material is available in large bulk and thus less expensive than for instance activated carbon. The capacity of the filter material can be low or is not always investigated/ uncertain (Kalmykova et al., 2014; Pintor et al., 2012). If the organic material is treated capacity increases (Dias et al., 2007).
Membrane technique - Reverse osmosis	With applied pressure over a semipermeable membrane particles are removed.	Can be adjusted to match flow and concentration.	An efficient technique for treatment of VOC (Farhadian et al., 2008; Norberg and Lithner, 2013). Requires high pressure and because of that has high operating costs.

Technique	Description	Capacity (flow, amount of VOC, concentration of VOC)	Advantages/Drawbacks
Membrane technique - Nanofiltration	With applied pressure over a semipermeable membrane particles are removed.	Can be adjusted to match flow and concentration.	An efficient technique for treatment of VOC (Farhadian et al., 2008; Norberg and Lithner, 2013). Requires high pressure and because of that has high operating costs. Because of larger pores than reverse osmosis the energy demand is lower for nanofiltration but also lower ability to separate VOC
Membrane technique - Ultrafilter	With applied pressure over a semipermeable membrane particles are removed.	Can be adjusted to match flow and concentration.	An efficient technique for treatment of VOC (Farhadian et al., 2008; Norberg and Lithner, 2013). Requires high pressure and hence has high operating costs. Because of larger pores than nanofilters and reverse osmosis, the energy demand is lower for ultrafilter but also lower ability to separate VOC.
Membrane technique - Pervaporation	High pressure is used to have partial vaporisation of the VOC over a membrane.	Little or no experience on treating process water in full scale.	High potential and research shows good results (Hitchens et al., 2001). New technique, no full-scale units in Sweden yet. High cost for investment and maintenance.
Oil separator	The surface water where oil-like substances accumulate is separated off.	Requires an arrangement so that a still water surface is achieved.	Dissolved compounds are not removed from water (Kalmykova et al., 2014). Large risk that the VOC accumulated on the surface evaporate.

Technique	Description	Capacity (flow, amount of VOC, concentration of VOC)	Advantages/Drawbacks
Chemical			
Chemical oxidation	- Fenton's reagent (hydrogen peroxide and iron solution) - O_2, O_3, H_2O_2, Cl_2 -AOP		Addition of chemicals needed. Might give undesired residuals. High cost because of addition of chemicals and/or energy. UV treatment decreases energy costs.
Biological			
Soil adsorption systems, wetlands and reed beds	VOC is degraded by microorganisms, plants or plankton in different constructed environments.	Retention time needs to be high due to low activity during winter season in Sweden.	High risk of evaporation to atmosphere. Method used all over the world, often in warmer climates. Low energy requirements. Retention time needs to be taken into account (Vymazal, 2009)
Activated sludge processes / Aerobic bioreactors	Microbial degradation by microorganisms in aerobic environment. Carrier material can be used to make the process more robust. Used in sewage plants.	If sent to sewage plant, their requirements need to be met.	Shows high potential for treatment (Simonich et al., 2002). Risk that VOC evaporates during aeration. Expensive solution if treatment is built for solely process water. If connected to WWTP no investment costs needed.

Technique	Description	Capacity (flow, amount of VOC, concentration of VOC)	Advantages/Drawbacks
Anaerobic digestion	Microbial degradation by microorganisms in anaerobic environment	If the process water is recirculated to the anaerobic digestion plant the flow of process water cannot be too high due to dilution.	There is little or no risk of inhibition by VOC in the amounts measured in this project. Cost effective if a process already exists.

VOC IN BIOGAS PROCESS WATERS

Innehållet av flyktiga organiska ämnen (VOC) i processvatten från biogasuppgradering har genom denna studie blivit utforskat. Undersökningen visar att vad man matar biogasanläggningen med har stark påverkan på både koncentration och innehåll av VOC i processvattnet. En viktig faktor är också anläggningens vattenförbrukning. Biogasanläggningar som använder avfall som huvudsakligt substrat visades sig ha högst halt VOC i processvatten medan anläggningar med jordbruksavfall som huvudsubstrat hade lägst. Resultaten varierade dock starkt mellan olika provtillfällen och mellan olika anläggningar. För att få mer enhetliga resultat behövs troligen längre provserier, som tar hänsyn till hur anläggningen är byggd och körs.

Den stora variationen gör det svårt att ge generella råd om miljö- och hälsorisker förknippade med dessa processvatten. Av de tre vanligast förekommande är det dock bara limonen som kan orsaka miljöskada, genom sin toxiska påverkan på vattenlevande organismer. Limonen förekommer naturligt i citrusfrukter.

Ett möjligt sätt att behandla processvatten är att använda en biologisk reningsanläggning, exempelvis en rötningsprocess eller ett avloppsreningsverk. Studien visade genom att köra satsvisa rötningsförsök att det är fullt möjligt att mata tillbaka vattnet i biogasanläggningen utan att rötningsprocessen påverkas negativt. En annan möjlig reningsmetod är användningen av filter. Test gjordes med filter gjorda av aktivt kol och torv. Båda materialen tog bort VOC ur processvattnet, men aktivt kol var effektivare än torv.

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