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Practical guidance to determine NMVOC emissions from refinery wastewater collection and treatment facilities

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Practical guidance to determine NMVOC emissions from refinery wastewater collection and treatment facilities

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PREFACE

To the reader:

This document has been prepared as a practical guide to help site personnel gain a better understanding of non-methane volatile organic compound (NMVOC) wastewater emissions. The objective is to provide straightforward, executable methods for measuring and assessing emissions at wastewater treatment facilities, based on past practical experience and without requiring specialized equipment and/or extensive scientific expertise.

The methods and procedures detailed within are designed to be implemented on-site using readily available tools and techniques. Rooted in operational best practices, this guidance bridges the gap between technical rigor and practical field application. Rather than serving as an exhaustive, all-encompassing scientific resource, it focuses on accessible and repeatable methods that operational teams can readily apply. The goal is to provide a user-friendly framework for routine emissions evaluation, empowering teams to effectively identify and quantify emissions, consistently monitor and understand process variability, and contribute to ongoing environmental stewardship efforts.

We recognize that wastewater emissions can be complex and variable, and while comprehensive scientific analyses have their place, this guidance document emphasizes simplicity and clarity. It is meant to support initial assessments and provide a foundation upon which more detailed investigations or contractor-led studies may be built if required. Users are encouraged to treat this report as a starting point, complementing existing protocols and further refining methodologies as needed.

It is hoped that this guide will serve as a valuable tool for those responsible for managing wastewater treatment operations, facilitating both the identification of emission sources and the implementation of effective control measures. It is our hope that the insights provided here will lead to improved operational practices and a better understanding of wastewater emissions across various facilities.

Sincerely,

Concawe Special Task Force on Emissions Determination and Reporting (STF-69)

ABSTRACT

Wastewater from refinery operation contains various pollutants that shall be purified prior to wastewater emitted to sea. A major pollutant is hydrocarbon remains. Wastewater collection and treatment facilities in European refineries are generally not fully closed systems and therefore recognized as a non-negligible contributor to the overall site non-methane volatile organic compounds (NMVOC) emissions.

Measurement of emissions from wastewater is often difficult due to their specific location and system configuration. Wastewater collection systems are located across the entire site, and it is not always feasible to measure the emissions. The emissions in wastewater treatment facilities occur at various places, mostly from uncovered areas. They are therefore often diffuse in nature and cannot be measured as point sources, which makes quantification complicated.

The two most common practices used today to estimate emissions from wastewater are emission factors and emission models. Published, general emission factors are not site specific and could result in over- or underestimation of the emissions. They also give no information where emissions occur. Emission models inform where emissions occur but require detailed information on system configuration and operation. Examples of tools to model NMVOC emissions are TOXCHEM and, more specifically for this application, the EPA Refinery Wastewater Emission Tool (RWET). Furthermore, atmospheric dispersion modelling can be used to simulate result of VOC emissions. It is performed with computer programs that include algorithms to solve the mathematical equations that govern the pollutant dispersion. Software using a Gaussian dispersion model (not probabilistic), which most operators are familiar with as it is also used for other purposes can be used for this. Suitable programs are e.g., PHAST, AERMOD, or ADMS. More advanced computational dynamics software can also be used to estimate VOC emissions in complex situations, but this requires more specialistic knowledge and/or contractor to execute. This is outside of the scope of this practical guidance document. To confirm the representativeness of a model a validation with measurements is advised.

This practical guidance document explains how to use ‘simple’ measurements to estimate the NMVOC emissions of wastewater facilities. The measurements should be repeated several times to better understand the NMVOC emission sources and their variability and reduce the uncertainty in estimating annual emissions. Two independent measurement methods are proposed, which should result in comparable emission rates.

In case a higher measurement accuracy is required, the measurements can also be used as a basis to perform specialized measurements by a contractor. The EN 17628 can be used as a framework to execute such measurements for a few complementary methods.

KEYWORDS

Wastewater collection and treatment, Volatile Organic Compounds (VOCs), emissions, emission factors, sampling, modelling, TOXCHEM, RWET, EN 17628

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1. INTRODUCTION

Wastewater from refinery operation contains various pollutants that shall be purified prior to wastewater emitted to sea. A major pollutant is hydrocarbon remains. Wastewater collection and treatment facilities in European refineries are generally not fully closed systems and therefore recognized as a non-negligible contributor to the overall site non-methane volatile organic compounds (NMVOC) emissions.

Measurement of emissions from wastewater is often difficult due to their specific location and system configuration. The emissions occur at various places, mostly from uncovered areas. They are therefore often diffuse in nature and cannot be measured as point sources, which makes quantification complicated.

Measurement technologies are available, such as flux chambers and remote NMVOC monitoring systems, but these technologies are complex to apply and difficult to interpret.

The two most common practices used today to estimate NMVOC emissions from wastewater facilities are published general emission factors and tools to model NMVOC emissions. Examples of tools to model NMVOC emissions are TOXCHEM and, more specifically for this application, the EPA Refinery Wastewater Emission Tool (RWET).

General emission factors are usually expressed as weight of a pollutant emitted per volume throughput or other generally known quantity:

- They are relatively easy to use and do not require detailed information, but they are not site-specific, while configuration of wastewater facilities is often very site-specific.

- There are several recommended emission factors [1], and some could be too conservative, resulting in reported emissions being higher than real emissions. A comparison of emission factors and models/algorithms, based on the results of two field campaigns are reported in Concawe Report 5/14 [2].

- They do not indicate where emissions occur, and hence cannot be used as a starting point for effective mitigation measures for emission reduction.

Emission models:

- They are more representative of actual operations than general emission factors.

- They are however more complex and require very detailed information, both regarding site configuration and wastewater analysis.

- They can be used to predict emissions on a daily basis, provided the required inputs are available (e.g. detailed wastewater analyses at system flows).

- They can inform which area(s) of the wastewater collection or treatment is (are) likely to generate significant emissions and hence can be used as a starting point for effective mitigation measured for emission reduction.

Examples of tools to model NMVOC emissions are TOXCHEM and EPA Refinery Wastewater Emission Tool (RWET) [8], the latter being designed specifically for this application. TOXCHEM is based on mass transfer equations and mass balances including the removal mechanism of stripping and volatilization, biodegradation and sorption. RWET is an excel based tool that represents individual components in a typical wastewater treatment system and can estimate emissions for a particular unit. Effluent concentrations from a particular component can then be used as inputs for the next downstream collection or treatment unit.

Furthermore, atmospheric dispersion modelling can be used to simulate VOC emissions. It is performed with computer programs that include algorithms to solve the mathematical equations that govern the pollutant dispersion. Software using a Gaussian dispersion model (not probabilistic), which most operators are familiar with as it is also used for other purposes can be used for this. Suitable programs are e.g., PHAST, AERMOD, or ADMS. Gaussian models cannot back calculate the source from the measured emissions, but with a limited number of sources (1-5), a manual trial-and-error process is possible. More advanced computational dynamics software can also be used to estimate VOC emissions in complex situations, but this requires more specialized knowledge and/or contractor to execute. This is outside of the scope of this practical guidance document.

In order to confirm the representativeness of a model a validation with measurements is advised, but as stated above measurements are not straightforward. This guidance explains how to use ‘simple’ measurements which can be done by site personnel to estimate the NMVOC emissions of wastewater facilities. The measurements should be repeated several times to better understand the NMVOC emission sources and their variability and reduce the uncertainty in estimating annual emissions.

Two independent measurement methods are proposed in this guidance document, which should result in comparable emission rates. The two methods can be used in parallel to compare/confirm emissions or they can be used to validate models like TOXCHEM and RWET [8]. In case a higher measurement accuracy is required, the measurements can also be used as a basis to perform specialized measurements by a contractor. The EN 17628 [3] can be used as a framework to execute diffuse NMVOC measurements using a few complementary methods (i.e., DIAL, SOF, TC and RDM). Guidance on the application of EN 17628 is provided in Concawe report 1/23 [9].

This practical guidance document is structured as follows: background information on the most important parameters influencing NMVOC emissions from wastewater facilities is given in **Section 2**, while details on the two proposed ‘simple’ measurement methods are given in **Section 3** and **Section 4**. The main conclusions are provided in **Section 5**.

2. PARAMETERS INFLUENCING NMVOC EMISSIONS OF REFINERY WASTEWATER FACILITIES

In this Section, important parameters that influence NMVOC emissions from wastewater facilities are described.

The most important parameter is the **quantity of hydrocarbons** in the wastewater. This is reflected in the emission factors for oil-water separators [1]. Today, sites having a well-established “no-oil-to-sewer” program are likely to send, on average, less than 880 mg/l oil to sewer and can use the lowest emission factor of 0.0225 kg/m^3_{ww} [2].

The second parameter influencing NMVOC emissions is the **hydrocarbon volatility,** which is dependent on the composition of the complex organic and inorganic mixture in the wastewater. As wastewater sewers are generally not air-tight and most wastewater treatment facilities have uncovered areas, the most volatile hydrocarbons will readily evaporate. As a rule-of-thumb, one can assume that 100% of C7 and lighter hydrocarbons sent to wastewater will be emitted to air. The ratio is somewhat lower for benzene and any other polar components which can be partially or fully dissolved in the water.

Hydrocarbon volatility is also reflected in the Litchfield equation, which can be used to estimate the emissions from the oil layer in oil-water separators [1][2]. The C8-C20 hydrocarbons will be partially emitted to air and partially removed with the oil. The fraction emitted depends on the system configuration and cannot be estimated precisely without detailed knowledge. As a rule-of-thumb, one can assume that 100% of the heavier than C20 hydrocarbons are not emitted to air but stay in the oil.

The third parameter influencing NMVOC emissions is the **flow turbulence**. Air measurements in the vicinity of water weirs, mixing tanks, etc. indicate that NMVOC emissions are one or more orders of magnitude higher than in the vicinity of quiescent surfaces. Emission factors for uncovered wastewater collection systems and oil-water separators take this indirectly into account, as such factors represent total emissions. Caution should be taken when using the factors for covered systems [1, **table 8**] as these factors assume 97% reduction of emissions compared to uncovered systems, but this reduction is only true if the entire system is covered and generated emissions are collected and abated. Measurements indicate that emissions generated in a covered (but turbulent) area can be emitted downstream in an uncovered (and possibly quiescent) area. Operators using simple methods (i.e., factors) to report NMVOC emissions need to be aware of the effect of turbulence on emissions. Local measurements can confirm the magnitude of emissions and indicate target areas for emission reduction.

Once the above major parameters are well understood for a given system, other factors having an influence on NMVOC emissions (like both water/wastewater and ambient air temperature, surface area of the emitting source, as well as wind speed) should be taken in account. When estimating emissions on daily basis, it is advised to use an emission model.

Emission models take mass transfer into account (i.e., turbulence), which provides site-specific information about emissions in function of the physical processes taking place. The models also incorporate accurate physical-chemical properties (e.g., boiling points, Henry factors) as well as biodegradation and sorption rates. However, the main objective of such models is to provide speciation of NMVOC emissions after the gross amount of oil has been removed, namely after the oil-water separator. The models mainly estimate emissions of the components dissolved in the water and have limited capability to simulate air emissions from the oil layer. If a model (i.e., TOXCHEM or RWET) is used, the recommendation is to also use the Litchfield equation for uncovered oil-water separators to avoid under-estimating the NMVOC emissions [2].

3. NMVOC EMISSION ESTIMATION USING WASTEWATER SAMPLING

Analysing wastewater samples from the various areas of the collection and treatment system is an important step in understanding and estimating NMVOC emissions. Several sampling campaigns should be performed over the period of emission estimation (typically a year) to compensate for sampling challenges and/or to account for process variability. During such sampling, the wastewater treatment operation should be kept as representative as possible (i.e., normal incoming hydrocarbon pollution load) to ensure average conditions.

The main considerations are listed below:

- Sampling the main sewers allows identifying the main pollution sources and making an approximate mass balance. Guidance on what to analyse and how to take representative samples is provided in **Appendix A**. Note that a large fraction of the C7 and lighter components and a smaller fraction of C8-C12 components can evaporate in underground wastewater collection systems (network of drains, sewers, lift stations, manholes, sumps and junction boxes) before reaching the wastewater treatment area. In a measurement campaign on a refinery up to 50% of C7 and lighter and 10-20% of C8-C12 was found to be evaporated. The magnitude of emissions from the collection system is dependent upon the built-in controls to minimize contact with the air, such as water seals.

- Sampling in-between the various steps of the wastewater treatment will enable understanding of the hydrocarbon quantity removed from the wastewater in each step. Depending on their volatility and on system design (e.g., turbulence and uncovered or covered units), the removed hydrocarbons can be emitted to air or be recovered in the oil phase. Using a few aromatic components as “model components” for other components with similar volatility and combining this information with the total hydrocarbons allows a rough estimation of the fraction emitted to air versus the fraction going to oil.

- The sampling results, in combination with the wastewater flow, allows to estimate the emission mass rate i.e., g/h) of light speciated components like benzene, toluene, ethylbenzene, xylenes (as BTEX). Based on the ratio between total hydrocarbons and speciated components, the total NMVOC emission rate can be estimated. Guidance for data analysis and interpretation is provided in **Appendix C.**

- Following the guidance for wastewater sampling and analyses in **Appendix A** will inform on emissions of C5 and heavier components. For many refineries the C2-C4 hydrocarbons are under normal operating conditions not present in significant quantities and can therefore be neglected. In case of specific operations on your site e.g. handling of non-refinery wastewaters this may not be the case and may need to be quantified separately. Emissions from the light aromatic components can be estimated more precisely with gas chromatography - mass spectrometry (GC-MS) as there are fewer isomers.

- Developing a wastewater mass balance requires knowledge about the flows, but these may not be measured at all locations. What works well is to start with the known or measured flowrates, and then use any surrogate information to estimate the missing data.

It shall be noted that an estimated emission is representative for the measurement period. To extrapolate to annual emissions, it will be required to repeat the measurements to reduce the uncertainty. The number of measurements will depend on the extent of the hydrocarbon concentration variations in the wastewater. They should be made at regular intervals to also capture the effect on emissions of seasonal meteorological variations (e.g., insolation, rainfall, etc.)

Appendix B provides a non-exhaustive list of the main sources of hydrocarbons to sewers in typical refineries. **Appendix C** provides a methodology for the entire wastewater sampling effort.

4. NMVOC AIR EMISSION MEASUREMENTS IN WASTEWATER SYSTEMS

Air concentration measurements indicate the location and importance of NMVOC emissions, total NMVOC or specific components like benzene. The main challenge in wastewater systems is to calculate an accurate emission rate (kg/s) from the air concentration measurements. This calculation will require additional information e.g., wind speed and direction, information on NMVOC emissions from nearby sources, knowledge of concentration in the emission plume and a form of dispersion modelling.

Measurement of NMVOC concentration at an individual point in air can be done with various methods. Optical Gas Imaging (OGI) can be used to screen for emission plumes, EPA Method 21 (‘sniffing’) can be used to locate and classify equipment leaks and passive sorption tubes or sensors/analysers can be used for diffuse area emissions. Measurements enabling average concentrations over a scan area (e.g., through a plume) can be made using optical techniques like Solar Occultation Flux (SOF) and Differential Absorption Lidar (DIAL). The latter two are described in EN 17628:2022 [3]. The most suitable method to use will depend on the measurement objective as well as the system configuration.

Below a suggested approach for NMVOC emission measurement in the wastewater collection and treatment systems is provided.

Wastewater collection systems are located across the entire site. It is preferred to measure the emissions of the collection system components using Method 21 and/or OGI. A pragmatic approach could be taken by measuring the components with the highest potential emissions like larger oily water collection sumps. Measuring the emissions separately from other sources located nearby is however not always feasible and some sources will require more frequent measurement to better understand the emission source and their variability (e.g., intermittent sources).

To minimize emissions from wastewater collection systems containing elevated hydrocarbon concentrations, the components (e.g., network of drains, sewers, lift stations, manholes, sumps and junction boxes) should be fitted with emission control devices such as submerged weirs or water seals on manholes or sealed covers with vent line to atmosphere or control device. If all components are routinely checked and defects repaired across the entire collection system, the emissions can be considered negligible. For all other cases, an emission rate can be calculated either from Method 21 measurements using correlations between the measured concentration and the emission rate to atmosphere or by using leak/no leak factors for OGI measurements. In locations where measurements are not feasible it is advised to use default emission factors to estimate the emissions from the wastewater collection system. It is recommended to use EPA-450/3-85-001A factors [4] instead of those in the EPA AP-42 [5] as the factors in the former more closely resemble Method 21 results.

Drain systems on clean water/storm water (which have no or limited presence of hydrocarbons during normal operating conditions) are not expected to be significant emission sources and can be considered negligible.

Wastewater treatment facilities are often located in an area with limited obstacles and away from process units. In the latter circumstances the “area measurement” techniques SOF, DIAL and Reverse Dispersion Modelling (RDM) [3] can be used to determine a quantitative estimate of the total emissions from the area (total NMVOC or total “single speciated NMVOC” e.g., benzene). Area measurements techniques are however costly and only offered by a limited number of specialized contractors. The measurement period is usually short (1 hour to a day), and a single measurement campaign will be of limited use for annual emission reporting, especially if the process conditions in the wastewater facilities are variable and the measurement uncertainty is not well understood. Furthermore, area measurement techniques do not allow to locate high emission spots within the wastewater treatment facilities unless you can use a drone with sensors. So, this may require the use of a portable NMVOC monitor (FID/PID or OGI) to individually screen each source. Before considering the use of area measurement techniques it is therefore proposed to better quantify wastewater treatment emissions with simpler techniques first.

The suggested approach is a simplified version of RDM. It uses a number of passive tubes or sensors (with data logging) spread around the emission sources. These may comprise, for example, just the oil-water separator or include a limited number of other emission sources within the wastewater treatment facility or the immediate vicinity. It assumes that the wind field in the area is the same as measured elsewhere in the “undisturbed field”. This is generally acceptable when the number of high structures (which can modify the wind pattern) is limited in the vicinity of wastewater treatment facilities. It uses a Gaussian dispersion model (not probabilistic), which most operators are familiar with as it is also used for other purposes. Such a model cannot back calculate the source from the measured emissions, but with a limited number of sources (1-5), a manual trial-and-error process is possible. Suitable programs are e.g., PHAST, AERMOD, or ADMS.

The potential emission areas should initially be screened at least two times (**Table 1, Appendix D**) using a portable detector e.g., a PID (Photo Ionization Detector) prior to the placement of the tubes or sensors. This will assist in determining their best locations. Historic weather data as well as the weather predictions will also help in defining the most promising timeframe and location for the passive tubes/sensor measurements. Highest measurement accuracy will be obtained when the wind is predominantly from the same direction with a wind speed >2 m/s and <10 m/s. These measurements should be repeated several times over the period of a year to better understand the NMVOC emission sources and their variability and reduce the uncertainty in estimating annual emissions. This simple measurement approach can be seen as the first step to help building a better model or design specialized measurement campaigns to be performed by a contractor if a higher accuracy is required.

Secondary treatments deserve a particular consideration, because the emission contains necessarily CO_2 and water vapor, which interfere in the Infrared-based methodologies. Also, Method 21 is thought for small leaks, rather than for vast surfaces.

In **Appendix D** more details are provided for application of the methodology.

5. CONCLUSIONS

Measurement of emissions from refinery wastewater is often difficult due to their specific location and system configuration. The emissions in wastewater treatment facilities occur at various places, mostly from uncovered areas. They are therefore often diffuse in nature and cannot be measured as point sources, which makes quantification complicated.

Wastewater collection systems are located across the entire refinery site. To minimize emissions from wastewater collection systems containing elevated hydrocarbon concentrations, the components (network of drains, sewers, lift stations, manholes, sumps and junction boxes) should be fitted with emission control devices such as submerged weirs or water seals on manholes or sealed covers with vent line to atmosphere or control device. It is preferred to measure emissions of the collection system using EPA Method 21 or OGI. When this is not practically feasible default emission factors (from EPA-450/3-85-001A) can be used to estimate the emissions.

The two most common practices used today to estimate emissions from wastewater treatment facilities are emission factors and emission models. Examples of tools to model NMVOC emissions are TOXCHEM and EPA Refinery Wastewater Emission Tool (RWET) [8], the latter being designed specifically for this application. TOXCHEM is based on mass transfer equations and mass balances including the removal mechanism of stripping and volatilization, biodegradation and sorption. RWET is an excel based tool that represents individual components in a typical wastewater treatment system and can estimate emissions for a particular unit. Effluent concentrations from a particular component can then be used as inputs for the next downstream collection or treatment unit.

Furthermore, atmospheric dispersion modelling can be used to simulate VOC emissions. It is performed with computer programs that include algorithms to solve the mathematical equations that govern the pollutant dispersion. Software using a Gaussian dispersion model (not probabilistic), which most operators are familiar with as it is also used for other purposes can be used for this. Suitable programs are e.g., PHAST, AERMOD, or ADMS. Gaussian models cannot back calculate the source from the measured emissions, but with a limited number of sources (1-5), a manual trial-and-error process is possible. More advanced computational dynamics software can also be used but this is outside of the scope of this practical guidance document. In order to confirm the representativeness of a model, a validation with measurements is advised, but as stated above measurements are not straightforward.

This guidance explains how to use ‘simple’ measurements which can be done by site personnel to estimate the NMVOC emissions of wastewater facilities. The measurements should be repeated several times to better understand the NMVOC emission sources and their variability and reduce the uncertainty in estimating annual emissions.

Two independent measurement methods are proposed in this guidance document, which should result in comparable emission rates. The two methods can be used in parallel to compare/confirm emissions or they can be used to validate models like TOXCHEM and RWET [8]. In case a higher measurement accuracy is required, the measurements can also be used as a basis to perform specialized measurements by a contractor. The EN 17628 [3] can be used as a framework to execute diffuse NMVOC measurements using a few complementary methods (i.e., DIAL, SOF, TC and RDM). Guidance on the application of EN 17628 is provided in Concawe report 1/23 [9].

6. GLOSSARY/ABBREVIATIONS

AERMOD	A steady-state plume model that incorporates air dispersion based on planetary boundary layer turbulence structure and scaling concepts, including treatment of both surface and elevated sources, and both simple and complex terrain
ADMS	Advanced Dispersion Model Software (used to model the air quality impact of existing and proposed industrial installations)
DAF	Dissolved Air Flotation
DIAL	Differential Absorption Lidar
DP	Distillation Point
Emission factor	Weight of pollutant emitted per volume throughput or other generally known quantity
FID	Flame Ionization Detector
GC	Gas Chromatography
GC-MS	Gas Chromatography - Mass Spectrometry
NMVOC	Non-Methane Volatile Organic Compound
OGI	Optical Gas Imaging
OIW	Oil In Water
PAH	Polycyclic Aromatic Hydrocarbon
PHAST	Is a discharge, dispersion, fire, explosion and toxic modelling software using free-field empirical and Computational Fluid Dynamics (CFD) methods.
PID	Photo Ionization Detector
RDM	Reverse Disperse Modelling
RWET	Refinery Wastewater Emission Tool
SOF	Solar Occultation Flux
TC	Tracer Correlation
TOXCHEM	Software for estimating VOC air emissions from wastewater collection, preliminary / primary / secondary treatment and disposal facilities
UK IE	United Kingdom Energy Institute
VDI	Verein Deutscher Ingenieure - Association of German Engineers

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8. APPENDIX A: WASTEWATER SAMPLES AND ANALYSES FOR NMVOC EMISSIONS ESTIMATION

To better understand the hydrocarbon composition of the major incoming wastewater streams, it is useful to initially sample those streams separately either upstream or upon entering the wastewater facilities. Wastewater samples should be taken at the entrance of the wastewater facilities and between each treatment step. It is recommended to maximize the use of regular sample points and, where other locations are needed, carefully select them where mixing occurs.

After selecting the areas from where to take water samples, focus should be on how to best take the samples and what to analyse for.

Potential issues and possible mitigations when taking wastewater samples are shown below:

Table A1 Issues and mitigations during wastewater sampling

Potential issue	**Mitigation**
Wastewater not well mixed (e.g., oil layer at the top) resulting in a not representative sample	Take sample where the water is most turbulent (e.g., pump discharge, weir chute) Consider changing to another well-mixed location
Sample location incorrectly recorded. Highest risk for locations where sampling is not routinely undertaken	Field visit with operator or virtual with pictures to agree on exact location to take sample. Have bottles pre-labelled for custody
Sample degradation before analysis	Especially sensitive for some parameters (like BTEX). Adhere to the analytical methods requirement (correct bottle, preservation chemicals, conservation time) General guidelines in EN ISO 5667-2; specific guidelines for each analytical method

Besides the analyses particularly relevant for estimating the NMVOC emissions (e.g., volatiles, BTEX, hydrocarbons) it is recommended to also analyse for the “typical” wastewater parameters. This provides a means to assess the representativeness of the sample against what is expected (based on routine analyses or on expected contamination).

Table A2 Recommended wastewater relevant parameters for analyses

Parameter	**Method**	**Total + Filtered**	**Remarks**
Total suspended solids (TSS)	EN872	N/A	To check sample representativeness

Total Petroleum Hydrocarbons (mineral oil)	EN93772	Yes	Extraction followed by GC (C10-40 fraction). Possibility to ask for a split in C10-C12; C12-C20; C20-C30; C30-C40
Benzene, toluene, ethylbenzene, xylenes (as BTEX)	EN15680	Yes	Important to acidify sample to pH=2
Volatile hydrocarbons (C5-C9)	Headspace GC	Yes	No EN method, but local methods available.
Individual components	Headspace GC-MS	No	For components to be reported individually by the permit (NMVOC speciation)
Polycyclic aromatic hydrocarbons (PAH)	EN17993	Yes	Important to acidify sample to pH=2

Note: For samples containing significant amounts of oil, it is advised to analyse the sample before and after filtration. This gives a proxy of the split between dissolved and not dissolved hydrocarbons. Filtration is typically done with a 0.45 µm filter. Note that some of the lightest hydrocarbons (like benzene) can be partially lost during filtration.

‘Oily’ water is collected at several places in the wastewater collection and treatment system. When large open oil sumps are present at the facility, it may be relevant to analyse the oil fraction of such sample to estimate the volatile hydrocarbon content as well as the average boiling range (e.g., for applying the Litchfield equation). In case oil sumps are covered and small, these sources can be omitted in a first pass assessment (as limited emissions are expected).

Samples of oil sumps need to be centrifuged to separate oil, water and solids [6]. Then the oil phase can be analysed using typical hydrocarbon liquid methods (see below). Centrifuging DAF (Dissolved Air Flotation) sludge samples is usually not feasible: they tend to form emulsions preventing 3-phase separation. If DAF float is stored in an open tank, NMVOC emissions will occur. A conservative estimate is to assume the same oil composition as for the API samples and to model it as API separator.

For samples after treatment in a flotation unit, it is not needed to filter them before analyses, as little oil/solids are expected.

Table A3 Recommended parameters for analyses of the oil phase

Parameter	**Method**	**Remarks**
BTEX, individual components	GC-MS	For components to be reported individually by the permit (NMVOC speciation)
Distillation curve	ASTM D2887	Gives true boiling point curve. Important to record per 1% the first 10% of the distillation curve

Note: The above methods for the oil phase can also be used for characterizing liquid hydrocarbon products in tanks for NMVOC estimation using, for example, the US EPA TANK programs/equations [7].

9. APPENDIX B: MAIN SOURCES OF HYDROCARBONS TO SEWER

This Section lists the continuous (or regular) sources of hydrocarbons sent to sewer. Infrequent activities (like equipment opening and cleaning) can also send hydrocarbons to sewer and thereby generate NMVOC emissions. They are not covered here as these are specific for each activity and require detailed knowledge of the activity to quantify.

Process water

In refineries there are two main types of process water: desalter water (also called desalter brine) and stripped sour water. Together they often constitute 50-80% of the organic pollution which the wastewater treatment facilities need to handle.

Desalter water

This is the most contaminated stream of significant flow in a refinery. Typically, 2-4 wt.% water is used to remove the metals and salts from crude. Typical contaminants in the desalter brine are oil (including BTEX and polycyclic aromatic hydrocarbons (PAH)), chlorides, metals, sulphides and mercaptans, ammonia and amines, solids and ions from salts.

Sour water

Sour water is generated at the overhead drums of distillation columns and is produced when sour gases are water washed. Sour gases are generated in hydrotreating units, cracking- and coking units. Sour waters are generally collected and sent to one or more stripping units to remove hydrogen sulphide (H_2S) and ammonia (NH_3). Hydrocarbons are not (well) removed in typical stripping towers, designed with limited trays and reflux. Typical contaminants in the stripped sour water are: H_2S, NH_3, amines, metals. The stripped sour water originating from heavy conversion processes (cracking and coking) also contains HCN and cyanides, BTEX and PAH, as well as phenols and other polar species like organic acids.

Scrubber water

For refineries using scrubbers to clean waste gases, the wastewater generated is a low flow but highly contaminated stream, with a composition like sour water.

Water from flare seal drums

This stream is often highly contaminated but of limited volume.

Spent caustic

Caustic is used to wash products or acid gases, and becomes contaminated with metals, sulphides and organics. When large volumes of spent caustic are generated, they need to be treated (typically by oxidation) before being sent to the site wastewater treatment. Some sites have opted to send their spent caustic to external treatment (e.g., from alkylation units). Limited amounts of spent caustic can be used at the wastewater treatment as source of alkalinity (to increase the pH upstream the biological treatment unit). Depending on the site practice, spent caustic can be a significant source of (light) organics.

Product and crude external floating roof tanks

Such tanks need to be drained on a regular basis, as some rainwater gets into the tank and settles at the bottom. Water is not desired in a pipe-still and neither in the finished products (a maximum amount of water is part of the product specifications). If tank drainage is not done carefully (e.g., fully attended by the operator who stops the flow as soon as he sees oil) it can result in significant hydrocarbons sent to sewer. For finished products (clean service), “smart” valves can automatically close when they detect the oil/water interface. These valves are not suitable for crude service. A good procedure is to drain crude tanks into a slop tank first, which can accommodate some oil, and only drain the slop tank itself to sewer, with full attendance. In sum, depending on the site practices, drain material from product and crude external floating roof tanks may be a significant source of hydrocarbons in the feed to the wastewater treatment.

Wastewater tanks, process water tanks and slop tanks

For the tanks having an oil layer at the top (most of the time), it is recommended that emissions are estimated as if they were hydrocarbon tanks. A sample of the oil layer can be analysed to determine the volatility of the hydrocarbons (see **Appendix A**). For slop tanks with varying composition, it is recommended to model them as crude tanks or based on information from sample analyses (requires multiple samples).

Some wastewater / process water tanks are open (no roof). If they have an oil layer, the same recommendations as for API separators apply. Storm water tanks or equalization tanks in the wastewater treatment facilities have typically no oil layer. NMVOC emissions could still come from dissolved hydrocarbons, especially if the tank is mixed. Taking wastewater samples from the inlet and the outlet of the tank is the easiest way to estimate NMVOC emissions.

Process water tanks can be: (stripped) sour water tanks, desalter brine tanks, coker cutting water tanks.

Wastewater tanks, process water tanks and slop tanks are typically drained to sewer (or to the next wastewater treatment step) via a nozzle located close to the bottom, and the drained water normally contains low amounts of oil and solids. However, the presence of emulsions or the accumulation of solids at the bottom of the tank can deteriorate the water quality. This should be considered when designing the sampling campaign.

10. APPENDIX C: ESTABLISHING AND EXECUTING A WASTEWATER SAMPLING PLAN

Step 1: Use a site plot plan to identify potential critical areas

All sources of hydrocarbons to sewer should be identified in the plot plan (refer to **Appendix B** for main sources). A good understanding of the sewer network and its components is also required (field survey or via pictures). Uncovered or unsealed components such as sumps, weirs, lift stations, and junction boxes in the collection system need to be identified. Sumps are typically below-ground collection basins for a plot area, offering residence time and allowing oil/solids separation. Sumps can be open, covered or covered with emission control. For a site having no sumps, locate the manholes of main sewer sections. Identify whether some streams are piped to the wastewater treatment inlet rather than coming via the sewer system. This distinction is important to understand where emissions of the most volatile hydrocarbons take place.

Step 2: Analyse available data from wastewater treatment process

Most sites have analytical data from the process units (e.g. stripped sour water, desalter brine) and from the wastewater treatment, used for follow-up and optimization of the process. Historical data should be mined to understand the pollution load and variability, the type of pollution, etc. A preliminary mass balance can be established on this basis. Rainwater patterns should be understood when creating the flow balance (e.g., does it rain all the year or only during some months? Should sampling be done during dry weather or during rain or both?).

Step 3: Define wastewater sampling plan

If historical data are very limited, or if the number of places to be sampled is very high (>20 points), consider splitting the campaign into two or more sub-campaigns for better work management, especially if the samples are sent to an external lab for analysis.

There are several objectives for the sampling plan:

- establish or improve the mass flow contaminant balance,
- understand the location of the NMVOC emissions,
- identify and quantify the hydrocarbons sent to sewer,
- identify and quantify the hydrocarbons remaining in the water after emissions to atmosphere have occurred at points throughout the journey from source to the wastewater treatment outlet.

Step 4: Take the samples and send them for analysis

We recommend at least 3 sampling campaigns on different days. Ideally, the sampling dates should be selected when site operations are representative for normal operation, i.e., all units running, no upset in the critical process units (desalter, sour water strippers) or in the wastewater treatment facilities.

Follow the recommendations of **Appendix A**.

Step 5: Analyse the data

Analytical data will be combined with process data like flow rates to establish the mass contaminant balance. As flows are not measured at all locations, start with the known or measured flowrates, and then use any surrogate information to estimate the missing data.

It is likely that some reasonable assumptions will need to be made before a final (average) mass contaminant balance is established. Data variability, sampling errors, etc. can occur. As a mitigation step, a minimum of 3 sampling campaigns over the period of a year is recommended. Some redundancy between the suggested analyses could also be useful in case of atypical results (e.g., BTEX is part of the C6-C9 volatiles; analyses on total and filtered samples). If air measurements and modelling campaigns (**Section 4** and **Appendix D**) are also undertaken, it is advisable to execute these in parallel with the wastewater sampling campaigns.

Step 6: Interpret the results

The delta of hydrocarbon load between the inlet and outlet of a given process step represents the sum of hydrocarbons going to air, to oil or to sludge. Tools to model NMVOC emissions (e.g., TOXCHEM) can be used to provide the split. In the absence of such tools, some judgement is required to estimate the amount going to air.

It can be assumed that 100% of “lighter than C7” hydrocarbons sent to wastewater will be emitted to air. The ratio is somewhat lower for benzene and any other polar components which partially or fully dissolve in the water and are emitted with “stripping”. In the absence of tools to model NMVOC emissions, a conservative assumption is to consider that all BTEX lost from the total dissolved amount (filtered sample analysis) are emitted to air, while the rest stays in the oil phase.

The less polar C7-C20 hydrocarbons will be partially emitted to air but are mainly staying in the oil. One way to estimate the fraction emitted to air is to look at the oil composition change between the treatment steps: the total amount of oil in the samples decreases along the treatment steps (as oil is being removed in the API separator and in the DAF, but the oil also becomes heavier because of emissions to air. A close look to the fate of the various hydrocarbon fractions C8-C9, C10-12, C12-20, C20+ between each treatment step allows to assign a fraction emitted to air.

A reasonable estimate is also to assume that 100% of the “heavier than C20” hydrocarbons are not emitted to air but stay in the oil.

In the US, operators are requested to report NMVOC emissions for many individual substances, including PAHs. This task can only be performed with tools to model NMVOC emissions.

To use these results for reporting the annual emissions will require measurements to be repeated, especially if the process conditions are variable.

11. APPENDIX D: NMVOC MEASUREMENTS IN AMBIENT AIR AND SIMPLIFIED REVERSE DISPERSION MODELLING

The method proposed for measuring emissions from wastewater treatment facilities is a combination of NMVOC measurements in ambient air and a simplified version of Reverse Dispersion Modelling (RDM).

The simplified modelling will have a gap with application of RDM methodology as described in EN 17628:2022 [3]. Following that standard, the dispersion model to be used shall be fit for purpose and validated. To validate a model for NMVOC that works in a complex industrial environment (near units, with obstacles in the area etc.) is however a complicated task. This is beyond the scope of this guidance document, which presents a methodology which can be performed by site personnel.

Wastewater treatment facilities are often located in an area with limited obstacles and away from process units. If measurements in such areas are taken during dominant wind conditions (>2 m/s and <10 m/s), a simplified RDM method using a steady-state, Gaussian plume dispersion model should be able to estimate the NMVOC emissions with a higher accuracy and a much lower uncertainty than would be obtained by using emission factors. Depending on site specific conditions (like obstacles in the area, possible interacting/upwind sources), it should be decided if it is worthwhile to pursue a simplified modelling approach. In **Table D1**, conditions for applying the simplified modelling approach are described. Alternatively, a more complex RDM model can be used to obtain more specific emission data. This may require use of a specialist contractor for the data analyses and modelling.

In any case it is advised to execute the wastewater sampling method in **Section 3** and **Appendix C** in parallel with air measurements and modelling, to compare/validate the order of magnitude of the calculated and modelled emissions.

It should be noted that a derived emission rate only represents the emissions in the measurement period. To use these for reporting the annual emissions will require measurements to be repeated especially if the process conditions are variable and the measurement uncertainty is to be understood better.

Table D1 **Conditions for applying the simplified modelling approach**

Parameter	Applicable condition	Explanation & Tips	Limitations/ Mitigations
Planning phase (± 1-2 months before start of measurement campaign)	Screen potential emission areas with a portable detector e.g. PID/FID. Measure at least two times (with week in between) close by the open areas. Screen for presence of any upwind / interacting sources in the area around the wastewater treatment facilities.	Highest emissions often found in areas of air/water contact (e.g., turbulent flow, at weirs or screw pumps) The screening will give an indication of the highest NMVOC emission locations /mass rates. Any potential interacting NMVOC emissions from the nearby surroundings	Confirm that emission 'hot spots' are consistent. A max factor 10 concentration variation is acceptable. More measurements required if variations are larger to confirm concentration difference persistent over time. If interacting NMVOC sources are present, determine if these can be eliminated during measurements.

	Investigate, if any potential interacting (intermittent/continuous) emission sources are present in the area. Assessment of likely wind conditions, such as prevailing seasonal wind, and suitable positions for the siting of a meteorological station.	should be taken in account. Potential sources e.g., vacuum truck unloading station, tank cleaning operation, known leaks/emissions (determined in LDAR program), etc. Use should be made of historical meteorological data where available.	If not, determine if measurement can be done during specific wind direction/conditions. If possible, place the monitors such that downwind monitors are not significantly affected by the emissions from interacting NMVOC sources.
Parameter	**Applicable Condition**	**Explanation & Tips**	**Limitations/Mitigations**
Oil in water content (OIW)	Stable and representative OIW content is present in the wastewater.	If not available, consider collecting OIW data of the wastewater over a longer period to determine the representative conditions. Ensure effective wastewater management procedures are in place to minimize contamination (oil, solids) of wastewater over the long-term.	Avoid measurements during known activities with releases to sewer (e.g., equipment cleaning). With high variations in (certain) wastewater streams, emissions also vary a lot, which may result in higher uncertainty of modelled results especially if passive monitors are used. For highly variable streams use of sensors with data logging is therefore advised.
Passive tubes/ monitors	Suitable for short measurement periods (one or more days) and when the wind is predominantly from the same direction. The passive monitors should not be saturated at the end of the measurement period. Various capacities are available, select the type based on measurement duration and expected concentration.	Captures the cumulative NMVOC in the area and provides the average concentration for the measurement period. Use 5-10 monitors (up- and downwind) of a specific emission source in the wastewater facilities (e.g., oil separator), or sources which have been identified in the vicinity. Consider executing one or a few measurements away from the source (10-50 m) as input for the simple dispersion model. Passive tubes can be sent to various labs for NMVOC	With highly variable wind and highly fluctuating emissions (variable wastewater oil loads) the uncertainty can be very high. In that case the use of sensors with data logging should be considered.

		desorption and GC-MS analysis. Passive tubes are cheap and easy to install. Data analyses are easy.	
Parameter	**Applicable Condition**	**Explanation & Tips**	**Limitations/Mitigations**
Sensors with data-logging	Suitable for both short and longer measurement periods. Able to capture variations better during the measurement period. Requires electricity (or battery), shelter box to protect against rain, sensor calibration, statistical validation of data.	Record the concentration in function of time and provide results coupled with time-series, allowing to see concentration variability. Sensors are more costly than passive monitors especially if placed in ATEX zones. A combination of passive tubes and sensors can be used for cost effectiveness.	Data handling is more complex. It is more work to gather the data (the sensors need daily follow-up), analyse and interpret the data (involves statistical validation). If sensors are sensitive enough it may be possible to install them outside ATEX area. Alternatively, sample lines can be run from the sensor to the desired sampling location, taking care to avoid adsorption or contamination.
Wind	Measurements taken when the wind is predominantly from the same direction with wind speed >2 m/s and <10 m/s (at 10 m height) are of good quality to use in the modelling.	Prerequisite when using simple steady-state Gaussian models which are most suitable for point source dispersion calculations along a straight- line plume. This requires flexibility in execution timing of measurements campaign.	Before the start of the campaign check the meteorological data. A 2 to 3 days forecast is a good indication and avoids anticyclonic (low wind) periods. Several measurement windows are required to ensure sufficient data is captured during dominant wind for calculating / modelling the emissions.
NMVOC back-ground	NMVOC background emissions should be < the emissions of the source to be measured.	During planning phase, determine if potential interacting sources can be eliminated or worked around.	Place monitors such that these are not affected by the interacting source at the dominant wind direction during the campaign. Consider placement of additional monitors around the area of measurement with at least one monitor between the interacting source and the wastewater facilities. If useful place additional monitors upwind of the source of interacting.
		During the measurement campaign, use portable NMVOC monitors daily to measure background emissions in the area.	If a persistent unexpected emission peak is detected and cannot be mitigated, abort the campaign. Replan the measurements during different

			wind conditions or when source is not emitting.
Parameter	**Applicable Condition**	**Explanation & Tips**	**Limitations/Mitigations**
Obstacles	No high structures (>4 m) in the direct vicinity of the wastewater treatment unit (<30 m).	High structures / obstacles can modify the local wind pattern. This is especially important if they are in the line of the dominant wind. In that case steady-state Gaussian models may not be accurate enough as they assume that the wind in the area is the same as measured further away in the "undisturbed field".	If there is an obstacle, install the meteorological station and sensors / passive monitors at least 4 meters away from the obstacle. If the above conditions cannot be met, a more complex model should be considered e.g., a Lagrangian model.
Meteo-rological station	Deploy a meteorological station (preferable at 10 m height but at least >3 m) with wind direction and speed as a minimum.	This should be in a clear/free space area near the facility to be studied. Alternatively, make use of site meteorological station. If applicable, correct wind speed for height.	May be required to deploy a metrological station with direct turbulence measurement or solar radiation for higher accuracy of modelled results.
Data gathering & analyses	Screen emission areas with a detector e.g., a PID at the beginning and end of the campaign and compare with data gathered during planning phase.	Air concentration measurements are a direct indication of the location (source) and importance of emissions.	Large open area emissions may be highly variable (e.g., fully uncovered oil separator).
	Execute minimum of 3 measurement campaigns over a year and target for periods of 3-5 days for each campaign.	To gather sufficient measurement data to calculate / model the data.	Steady-state simple model cannot back-calculate the source from the measured emissions, but with a limited number of sources (1-5), a manual trial-and-error process is possible. Having one or a few measurements further in the dispersion plume can improve model results (more constraints in the trial-and-error method).
	Use a simple, steady-state dispersion model.	Different programs can be used, e.g., AERMOD, PHAST or ADMS.	
	In same timeframe, analyse water samples of measured locations.	To compare / validate the order of magnitude of the calculated, modelled emissions (see also **Appendix A**).	Steady-state Gaussian model may not be accurate enough. In that case a more complex model to be considered e.g., a Lagrangian model.

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