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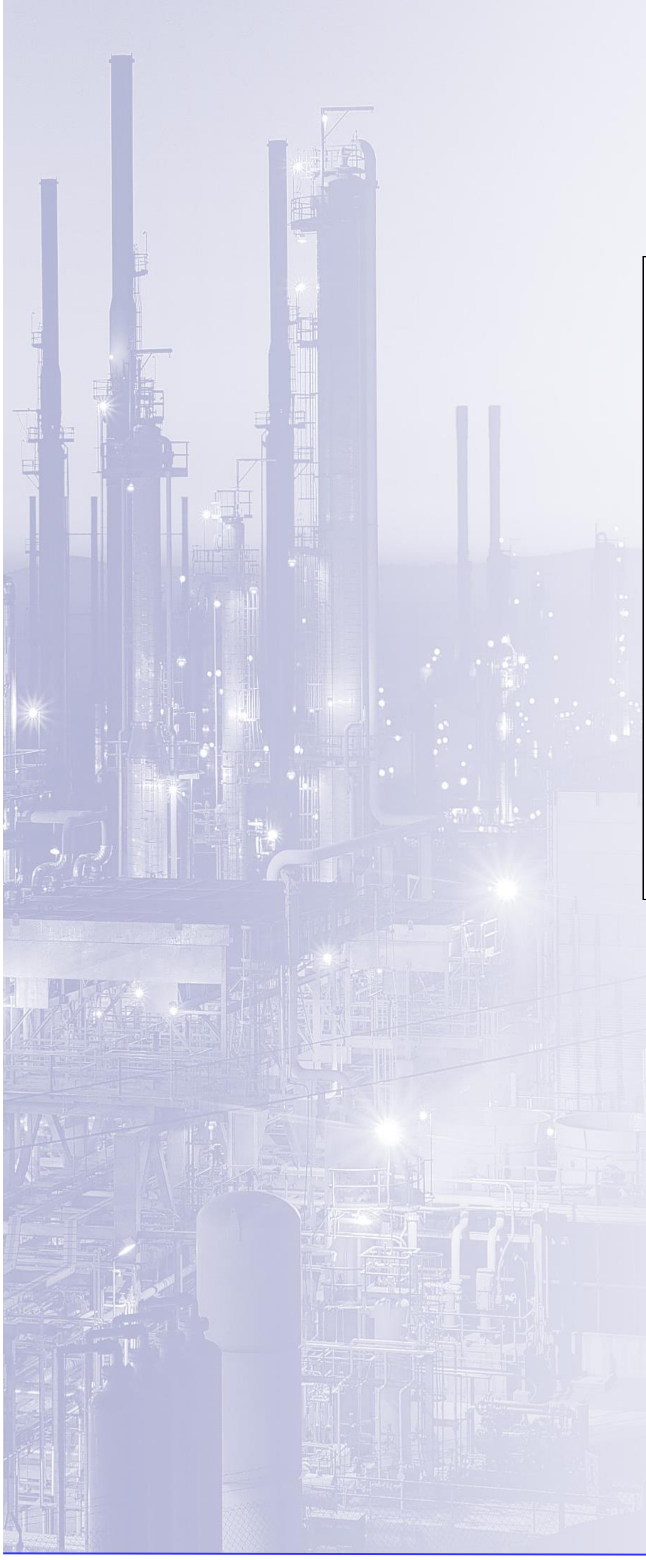

Methods for estimating VOC emissions from primary oil-water separator systems in refineries

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Methods for estimating VOC emissions from primary oil-water separator systems in refineries

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ABSTRACT

This report reviews the different methods available to estimate annual Volatile Organic Compound (VOC) emissions from primary oil-water separator systems in refineries and discusses the results obtained by applying some of these in two field trials carried out in European refineries in 2011.

Average emission estimates over the trial periods were obtained using four published emission factors, three models and an empirical algorithm. DIAL (Differential Absorption LIDAR (Light Detection and Ranging)) was also used to derive estimates of short term emission fluxes from remote measurements of VOC concentration. Each method has been assessed for its adequacy in providing a reasonable estimation of emissions.

KEYWORDS

VOC emissions, wastewater treatment, emission factor, E-PRTR.

INTERNET

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SUMMARY

CONCAWE Report 1/09 *Air pollutant emission estimation methods for E-PRTR reporting by refineries* provides algorithms that can be used by the European oil refining sector to estimate emissions for the purpose of meeting the reporting requirements of the European Pollutant Release and Transfer Register (E-PRTR).

A review of the emission factors for volatile organic compounds (VOCs) provided in Report 1/09 for gravity-type oil-water separator systems identified that these factors may not represent current European refinery practices, having been derived from tests undertaken in the USA over 25 years ago.

This study was initiated to assess how adequately the factors represented the VOC emissions from such systems. A review of the different methods available to estimate VOC emissions was carried out and the following were selected to be applied in two field trials:

- four emission factors (i.e. those published in CONCAWE 1/09 report, US EPA AP-42 chapter 5, VDI 2440 and the UK EI VOC estimation protocol).
- three models (i.e. WATER9, TOXCHEM+, EPA Refinery Wastewater Emission Tool) and
- the Litchfield empirical algorithm.

Additionally, the differential absorption LIDAR (DIAL) facility operated by the UK National Physical Laboratory (NPL) was used to derive estimates of short term fluxes from remote measurement of VOC concentrations.

Measurement campaigns were undertaken over five day periods at the oil-water separator systems in two European refineries. To obtain different climatic conditions, sites were chosen in both northern (Site 1) and southern Europe (Site 2). During the tests the analytical and operational data required as input for the emission factors, models and the algorithm were determined.

A wide range of estimated emission fluxes using the emission factors, models and DIAL methodology was obtained. Reviews of the probable VOC losses from the separator systems at both sites were therefore undertaken. At each site an emission value was determined for the period of the campaigns which was deemed to be the ‘best engineering estimate’. This was used for comparison with the values obtained by each of the other emission estimation methods. As representative inlet samples could not be taken at Site 1 the estimate for that site was derived from the maximum historic rate of free oil recovery and therefore deemed to be the ceiling value for emissions. At Site 2 the quantities of free oil and VOCs entering the system could be quantified. The vapour losses calculated using the Litchfield algorithm and a mass transfer model thus provided the best estimate of average emissions for Site 2.

The NPL DIAL facility was used at both sites, but the situations prevented useful emission estimates, which could be used for comparison with the other techniques, from being derived. At each site, particularly Site 2, the estimates based on DIAL measurements were considered too great a proportion of the VOC loading on the system. A major source of uncertainty with the DIAL methodology is in the calculation to obtain the mass emission flux value. This requires the concentration data across the entire plume cross section to be multiplied by the wind velocity component perpendicular to the DIAL measurement plane. At Site 2 it was very likely that there

were complex air flows in the vicinity of the separator system due to its surrounding topography. These can have resulted in higher uncertainty in the multiplication of the observed plume area and concentration by the reference wind speed than for measurements made in more open areas. In addition, a detailed review of the downwind scans at Site 2 highlighted the probable presence of variable sources upwind of the separator system adding significantly to the measured concentrations.

Both the models and the Litchfield algorithm require concentration data for the hydrocarbons entering the system and thus representative inlet water samples are needed. However, the vast majority of refinery primary waste water treatment facilities do not have an influent sampling point installed. Moreover, these methods only provide spot estimates. During the trial periods it was demonstrated that temporal variations occurred in the oil-in-water concentration values. Thus the results of methods using spot samples should not be extrapolated to provide annual averages of oil in water for these systems unless the required frequency of analysis to obtain a reasonable average has been established.

The Litchfield algorithm provides estimates of VOC loss based on ambient, water and 10% distillation point temperatures. The applicable ranges of the latter two parameters may make the use of the algorithm inappropriate where the temperature of the influent water to the separator system is restricted due to constraints on effluent water discharges or the volatility of the free oil is low due to refinery practices or long residence times in the sewer system.

Compared to WATER9, the EPA Refinery wastewater emissions tool (RWET) was found to be the more user-friendly, having a number of default values already provided as well as the chemical properties for some of the components that were found in the streams at both sites. However, it requires other components to be added by the user, in particular to make up the difference between the total concentration of the specified components and the total measured oil in water concentration. For these campaigns dodecane and icosane (C20) were used as the surrogate compounds to make up this difference. Unlike the other two models, the RWET is very sensitive to the concentrations of these heavier components. The use of the RWET, therefore, requires VOC speciation up to and including C12.

There are concerns that the models have limited capacity to address basins covered by a free oil layer. For these field trials, therefore, estimates of the emissions were made using a combination of both models and Litchfield algorithm. The estimates for the basins covered in free oil were made using the Litchfield algorithm. For the basins covered by an oil sheen (e.g. the API separators at both sites) a mass transfer model was used. At Site 2, where the oil in water concentration could be accurately quantified, this method (using the RWET as the model) was deemed to provide the best engineering estimate of emissions. At Site 1 the combined Litchfield and RWET computations provided one of the closest agreements with the engineering estimate of the maximum emissions.

Four published emission factors were used to estimate the average emissions over the periods of the campaigns.

The factor published by the VDI is based on the exposed water surface area (20 $g/m^2/h$) and provides a fixed emission value for the system. It cannot, therefore, reflect any improvement that the site may make in reducing the amount of oil entering the drains. However, at some refineries, such as Site 2, it is not possible to determine the water flow rate through the system on a routine basis. For those sites where it is also not possible to determine the quantity of oil recovered per annum, the use of the VDI factor is the only practical way to provide an annual VOC emission estimate.

Three published emission factors based on water flow were used to provide estimates for the separator systems at the two sites.

The factor provided in the US EPA AP-42 publication of 0.6 kg/m^3 water treated gives unreasonably high estimates unless the average oil in water concentration is very high (e.g. >3500 mg/l) or very significant perturbations in the oil loading on the system can occur on a frequent basis. In these circumstances the factor can provide an emission estimate ceiling value.

The other factors are provided in CONCAWE report 1/09 and in UK Energy Institute VOC Estimation Protocol. In the latter two factors are provided. For oil in water concentrations ≥880 mg/l, the same factor is given as in CONCAWE report 1/09 of 0.111 kg/m^3 water treated. However, the UK EI publication also provides an emission factor (0.0225 kg/m^3 water treated) which applies where the average oil in water concentration is less than 880 mg/l (~1000 ppmv). This factor is referred to as the 'EI factor' in this report. Although the CONCAWE factor is generally considered applicable to all situations, it too was derived from the Litchfield algorithm. For a water temperature of 35°C and 10% distillation point of 220°C this algorithm shows that the factor is limited to average oil in water concentrations of <3500 mg/l.

Where the complete system has a tightly sealed cover installed, the emissions can be determined by using a vapour retention efficiency of 97%. For other types of cover an efficiency of 90% can be used. Where a system is only partially covered, the emissions estimated for an uncovered system can be pro-rated taking into account both the fraction of area of the system that is covered and the vapour retention efficiency of the type of cover installed.

A decision tree to assist sites in their choice of annual VOC emission estimation for uncovered oil-water separator systems is provided in section 6.5 based on the results of the two field trials.

1. INTRODUCTION

Since 2001, European refineries have been required to report the emissions of a number of pollutants, both to air and water into the European Pollutant Emission Register (EPER [18]). In 2007, the EPER was replaced by the European Pollutant Release and Transfer Register (E-PRTR, [19]) which introduced new substances and increased the amount of information required to be submitted concerning both emissions and the transfer of pollutants and waste.

The information in E-PRTR is publicly accessible and the data can be searched at individual site level and by industry codes that allow aggregated data to be retrieved for industrial sectors. Therefore, it is important that the database contains emission and descriptive data that are as accurate as possible for sector-wide analysis.

Inaccurate emissions data can lead to a false impression of pollution emission levels when the information retrieved is used as a contribution to environmental decision making. Realistic emissions reporting is of key importance in the context of the National Emission Ceiling Directive (NECD, [20]).

CONCAWE identified the need to maintain a compendium of emission factors with associated references for the release of air pollutants emitted by refineries with focus on the refinery relevant substances named in the EPER and E-PRTR. The first report was published in 2005 [1] followed by three updated reports [2], [3], [5], the latest being CONCAWE report 1/09 *Air pollutant emission estimation methods for E-PRTR reporting by refineries* published in 2009.

The review of the emission factors included in the 2009 report identified several areas where some of the emissions factors available were derived from measurements made some years ago and hence potentially not representative of current operating practices.

This report concerns a study to assess the adequacy of the emission factors for annual Volatile Organic Compound (VOC) emission estimates from gravity type oil-water separator systems provided in CONCAWE report 1/09 [5]. The simple emission factor provided in the latter was derived from tests performed over 25 years ago [10].

Other calculation methods range from the simplest empirical algorithm for estimating short term VOC emissions from primary oil-water separator systems (derived by Litchfield in 1971 [22]) to potentially more accurate short term flux estimates which use algorithms or models (e.g. US EPA WATER9). These, however, require an extensive campaign of reliable and representative water sampling and subsequent analysis to be undertaken to provide the data inputs.

Emission fluxes can also be derived from measurements such as remote optical sensing, flux chambers, tracers and mass balancing.

In 2011, field trials were carried out at the primary oil-water separator systems in two European refineries: one in northern Europe (Site 1) and the other in southern Europe (Site 2). The site selection was made in order to study the effects of different operational practices and potential seasonal climatic conditions on the VOC emissions.

At both sites, Differential Absorption LIDAR (DIAL) was used to derive estimates of short term VOC emission fluxes.

Additionally, a portable gas chromatograph (GC) was used to analyse the VOCs emitted from the water/free oil surfaces in the different areas of the separator systems. The analytical parameters and operational data required as inputs for the emission factors, algorithms and models were also determined during the field trials.

This report reviews the different methods available to estimate the VOC emissions from primary oil-water separator systems and discusses the results obtained by applying some of these in the two field trials. Finally, a comparison of the estimates obtained at the two field trials is provided.

2. METHODS FOR ESTIMATING VOC EMISSIONS

Methods for estimating VOC emissions from gravity-type oil-water separators, i.e. API type and tilted plate interceptors (TPIs), include calculating mass emission fluxes from measurements of VOC concentration and air flow rate, undertaking a material balance, using empirical and theoretical algorithms (the most complex of which are available as software packages) or simple emission factors. All of these methods, except for the use of emission factors, provide a short-term estimate of VOC emissions which, due to short-term variations in the incoming separator oil concentration, composition and flow, is very difficult to extrapolate accurately to an annual average. On the other hand, while providing annual emission estimates, emission factors are generic and do not take into account plant specific process and water quality parameters.

2.1. EMISSION MODELS AND ALGORITHMS

2.1.1. Emission models – theoretical algorithms

VOC emissions from gravity type oil-water separators occur due to diffusion and convection. The factors that influence the rate of volatilisation include:

- the properties of the VOC compounds in the water, including their volatility and diffusivity in the water and oil phases;
- the degree of surface coverage and the thickness of any film of oil present on the water surface;
- the concentrations of the compounds in the water and air;
- the temperatures of the water and air;
- the wind speed across the water surface of the separator;
- the degree of turbulence;
- the area and water depth of the separator.

The rate of volatilisation can be determined using mass transfer theory and this is the basis of emission models for water treatment systems. These models use the gas and liquid phase mass transfer coefficients to estimate the overall mass transfer coefficients for each individual VOC. The coefficients are used to calculate the average mass emission rate for each VOC over a period of time. Theoretical algorithms that may be used to estimate VOC emission flux rates are provided in a number of papers (e.g. [11] [12] [13]).

Computer-based emission estimation models have been developed, the two most widely used being WATER9 and TOXCHEM+. The former is a freely available program [14] developed by the US EPA using the algorithms provided in reference 12, whereas TOXCHEM+ is a proprietary software package.

The use of these models requires considerable sampling and analysis to be undertaken in order to obtain sufficiently accurate input data. Obtaining representative samples can present considerable practical difficulties where water flows are not well mixed and/or a free oil layer resides on the water surface.

Concerns have been raised about these models, including their complexity, user friendliness and accuracy, e.g. when an oil phase is present [23]. For standardised reporting purposes in the US, a simplified refinery wastewater emission tool (RWET) has been developed for the EPA [15] which is applicable to uncovered wastewater treatment systems. It is freely available [17] and based upon the algorithms provided in [13]. However, the tool focuses on the individual VOCs listed as hazardous air pollutants (HAPs) in US legislation and surrogates have to be used for non-HAP substances. Moreover, this tool does not take into account the composition of the free oil layer and the suspended oil.

During the two field trials described in this report, sampling and analysis campaigns were undertaken to apply the WATER9 and TOXCHEM+ models. The EPA RWET was also used on a limited basis to allow a comparison with the results from the more complex models.

2.1.2. Emission models – empirical algorithms

A widely used empirical algorithm for gravity type separators is that derived by Litchfield [22]. The tests undertaken by Litchfield used a weighed pan containing influent oil from an actual API separator placed on the water surface of a hot-water bath. The pan was left for a period of 24 hours after which it was re-weighed and the losses calculated.

From these experiments, Litchfield derived the following algorithm:

Loss (% vol) = 0.3356 + 0.05742 TA – 0.05148 TDP10 + 0.3861 TW

where:

TA is the ambient temperature in °C

TW is the influent water temperature in °C and

TDP10 is the 10% distillation point (DP) of the influent oil in °C.

This algorithm permits the volume percentage loss of VOCs from the influent oil to be calculated. Determining the VOC mass emission rate requires data on the influent water flow, concentration of oil in the water and the liquid density of the evaporated hydrocarbons.

The following algorithm to calculate mass emission rate is provided in CONCAWE report 1/09 [5]:

VOC mass emitted (kg/h) = 0.01 x D x V x Loss (% vol)

where:

D is liquid density of evaporated hydrocarbons (kg/m^3) and

V is volume flow rate of hydrocarbons entering the separator (m^3/h).

The Litchfield equation is considerably simpler than the algorithms used, for example, in WATER9. This has raised concerns about its accuracy e.g. it does not take account of the wind speed and the surface area of the separator, both of which have an influence on VOC volatilisation rate. An additional source of error is that the algorithm was derived from tests conducted for periods of 24 hours, this being equivalent to the frequency that oil was skimmed from the API separator being simulated by Litchfield. The oil in the separator, therefore, has a 'residence time' of 24 hours. There are no factors provided for the case where oil is skimmed manually at more frequent intervals or, more likely, where it is skimmed or decanted on a continuous basis.

In addition, the Litchfield method is designed to estimate emissions resulting from evaporation of VOC from an oil layer and may not be suitable for estimating emissions from parts of the separator not covered by free oil. Furthermore, the method does not take into account mass transfer from the water phase into the free oil phase. Obtaining reliable and representative analysis of the oil layer may be difficult as sampling often can only be done in the skimmed oil collection basins which will not contain volatiles which have been already evaporated from the separator system.

The Litchfield algorithm can also be used to estimate emissions from other components of a water treatment system such as equalisation basins and impound basins, etc., which have a free oil film on the water surface.

Data, including those on the separator influents, were obtained during the field trials to permit the use of this algorithm. This algorithm was used to estimate the emission from the primary oil-water separator system components that were covered by an oil layer.

2.2. EMISSION FACTORS

Emissions can be estimated using a simple emission factor relating mass emission to a basic parameter such as water flow. This method is, by far, the simplest way to estimate mass emission fluxes for water treatment systems. However, as the mechanisms for emission generation from these systems are complex, the use of a simple emission factor gives a less accurate estimate than a model, provided that the latter can be populated with accurate input data. Due to the temporal variations in their major input parameters these models cannot be extrapolated to provide accurate annual average emission estimates for this source unless sampling and analysis campaigns are undertaken on a regular basis over the year. Emission factors, therefore, are extensively used by industry in the compilation of emission inventories for water treatment facilities.

2.2.1. Emission factors for primary oil-water separator systems

2.2.1.1. Uncovered gravity type separators

There are two types of emission factor for uncovered gravity type separators: one relates emissions to the flow of water through the separator, while the other relates emissions to the total exposed surface area of the water in the separator system.

a. Emission factors related to water flow

There are a number of published emission factors for uncovered gravity type separators e.g. [16] and [6]. These were reviewed and CONCAWE report 1/09 [5] provides a recommended VOC emission factor of 0.111 kg/m^3 treated water. By comparison, the emission factor published by the US EPA in AP-42 is 0.6 kg/m^3 [16].

A subsequent review by the UK Energy Institute [9] postulated that the factor provided by CONCAWE in report 1/09 is potentially conservatively high and that it appears to be the upper bound for Northern European refineries and not a typical average. The UK Energy Institute has thus recommended that if the average influent oil concentration is known to be less than 880 mg/l (~1000 ppmv) then a factor of 0.0225 kg/m^3 water treated should be used [8]. For influent oil concentration values greater than 880 mg/l, this reference provides the same factor as CONCAWE report 1/09 of 0.111 kg/m^3 water treated.

b. Emission factors related to exposed water area

An emission factor is provided in the German VDI publication reference [24] of 20 g/m^2/h for the exposed area of an uncovered separator system.

Water flows and the exposed areas of the waste water system components were determined during the field trials to permit the use of these simple factors.

2.2.1.2. Covered separators

Emissions from a separator can be reduced by installing a cover, either fixed over the basin or floating on the surface of the water. The fitting of a tightly sealed fixed cover is reported to achieve an emission reduction of 97% [6]. The range of efficiency of a floating cover given in reference [21] is 80% to 90%.

CONCAWE report 1/09 provides emission factors for sealed covers implying an efficiency of 97%. The German VDI factor for all types of covered separators implies an efficiency of 90%.

The separator at Site 1 is uncovered; at Site 2 one of the two separators operating in parallel is tightly covered. Therefore the VOC retention factor provided by CONCAWE was used for Site 2.

2.3. MEASUREMENTS

Uncovered separator basins and other parts of a separator system (e.g. pre-separator, forebay, etc.) are area sources of diffuse emissions and so the total VOC mass emission flux from these cannot be directly measured. Emissions, however, can be indirectly estimated using flux chambers and remote VOC monitoring systems. A tracer method has also been used to determine VOC emissions from an effluent water impoundment basin.

2.3.1. Mass balance

It is theoretically feasible to undertake a material balance on a water treatment facility. However the balance would require measurements of influent and effluent concentrations, compositions and flow rates for each of the constituent parts of the facility and reliable and accurate data on the quantity and composition of the skimmed oil and sludge removed. The large number of required samples, the possible difficulty in the quantification of the amount of skimmed oil, and the potential short term temporal variations make this approach impractical for accurately estimating emissions fluxes. This method, therefore, was not considered during the planning of the field trials.

2.3.2. Flux chamber

A flux chamber comprises a container resting on the surface from which emissions are emanating. Air is drawn into or recirculated through the chamber at a known rate and the emission concentration is measured in the vent flow [7]. Flux chambers are commonly used in dynamic olfactrometry to determine the emissions of several compounds. They have been used to measure VOC emissions from land fill sites where the chamber rests on the soil. Flux chambers have also been designed to float on water and thus could be used for wastewater treatment systems. Potential problems identified with these devices are that both the presence of the chamber and the induced air flow may influence the rate of VOC emission from the water surface. There has been no published data on the comparative performance of different types of flux chamber. At the commencement of the planning of the separator field trials one study of these devices for a soil application was reported to have found considerable variations between both makes and types. It was decided, therefore, not to use a flux chamber during the measurement campaigns.

2.3.3. Remote VOC monitoring systems

Methods for the remote measurement of the concentration of VOC emissions from diffuse sources include fixed open path devices using e.g. differential optical absorption spectroscopy (DOAS) or mobile systems such as Differential Absorption Lidar (DIAL) or solar occultation flux (SOF). These devices enable the line average VOC concentration to be quantified during the period of measurement.

DIAL relies on the scattering of light by the atmospheric aerosol and its absorption by VOCs at a given wavelength. A small part of each laser light pulse sent out is scattered backwards in the direction of the monitoring system. Collection and analysis of the spectral properties of this back-scattered light at two different wavelengths contribute to the measurement. Both wavelengths are equally affected by the scattering effect of the atmospheric aerosols throughout the optical path (also referred to as ‘line of sight’). One wavelength is absorbed by VOCs. As a consequence, the difference in backward scattered light between both wavelengths is proportional to the integrated concentration profile throughout the line of sight. The main advantage over other open-path systems is that DIAL facilities are ’single-ended’; i.e. there is no need for a mirror or retro-reflector to terminate the light path, so these systems can measure upwards permitting measurements across the entire plume. By sampling the returned light pulse rapidly in time it is possible to distinguish how far each part of the light pulse has travelled and hence range resolve the signal.

SOF uses the sun as a light source and determines the total absorption by VOC in the entire column between the sun and the spectrometer. It cannot, therefore, provide the height of a plume, or details of concentration variations along the column length to permit the identification of individual sources contributing to a plume [4]. For these reasons it was decided not to use SOF for the field trials.

To obtain mass emission flux values in a DIAL campaign the concentration data across the entire plume cross section have to be multiplied by the wind velocity component perpendicular to the DIAL measurement plane. This is not easy to determine and remains a key source of uncertainty in overall emission estimation by remote sensing.

CONCAWE and the UK National Physical Laboratory (NPL) are working to develop a protocol to improve the overall methodology.

The DIAL facility operated by NPL was used during the field trials to obtain concentration data. Mass flux estimates were derived from these data using wind field data measured in the vicinity of the primary oil-water separators.

2.3.4. Tracer gas methods

This method involves releasing an inert gas at a fixed flow rate close to the VOC emission source to be estimated. Concentration measurements of the VOC and tracer gas are then made down-wind of the source. The VOC emission rate can be calculated from the ratio of the concentration of the tracer gas to that of the emitted VOCs and the known flow rate of the tracer. This method has been used for an equalisation basin where the tracer gas was released from a large number of points using pipes drilled with very small holes laid alongside and partially across the basin. This method is considered unsuitable for a separator where it is postulated there will be spatial variations in emission flux e.g. along the length of a separator. In addition, emissions of the most suitable tracer gas (SF_6) are no longer permitted. This method, therefore, was not considered during the planning of the field trials.

3. OVERVIEW OF TEST PROGRAM

The programs for both field trials were developed in order to cover the following main objectives:

- To determine short-term VOC mass emissions from a primary oil-water separator system during both daylight and night-time periods using concentration measurements from DIAL and wind field data;
- To compare results from DIAL methodology with estimates using:
    - Factor of 0.111 kg/m^3 water treated provided in CONCAWE report 1/09 [5].
    - Factor of 20 g/m^2/h provided in VDI publication 2440 [24].
    - Factor of 0.6 kg/m^3 water treated provided in US EPA publication AP-42, Ch. 5 [16].
    - Factor of 0.0225 kg/m3 water treated where the average influent oil in water concentration is <880 mg/l provided in UK Energy Institute publication [8].
    - Litchfield algorithm [22] for the system components covered by an oil layer.
    - TOXCHEM+, WATER9 [14] and US EPA refinery wastewater emissions tool (RWET) [15] [17], for those system components which are covered by an oil sheen or thin free oil layer.
- To determine the speciation of the VOC emissions from the different sections of the separator system using a portable GC/MS.

The collaboration and co-ordination between the CONCAWE special task force members, the NPL DIAL team, the Explorair portable GC/MS team and site personnel were considered of utmost importance. Therefore, several meetings were held between all the participants prior to the field trials in order to cover the operational, safety and practical issues associated with the project.

A rehearsal day was scheduled at least one month prior to the start of each campaign in order to identify any operational or applicability issues that could interfere with the development of the programme.

Besides, during periods of DIAL operation, the project and refinery teams recorded any events around the separator system area potentially impacting VOC emissions. The information was transmitted to NPL in case the planning of the DIAL scans had to be rearranged.

Mass Emission Estimates using DIAL methodology

The DIAL measurement programme was supplied by NPL prior to the campaigns and agreed by the refinery personnel and the CONCAWE special task force members. The basis of the field trials was a five day DIAL programme including concentration measurements from both up and down-wind of the primary oil-water separator system area as well as covering day and night-time periods. Nevertheless, the actual scan opportunities were subject to the atmospheric conditions occurring during the campaign, the constraints imposed by the refinery in terms of safety and the restrictions on where the DIAL van could be placed.

DIAL concentration measurements need to be combined with wind field data in order to calculate the VOC flux. Therefore, accurate and representative wind field monitoring during the scanning period were considered to be of utmost importance. Both portable mini-masts mounted in the vicinity of the separator system and a fixed high mast placed in an area of unperturbed wind field were set up by NPL to monitor wind speed and direction. The locations of these were agreed according to the prevailing wind direction, topography and safety restrictions within the refinery.

These meteorological data were complemented with local measurements of ambient temperature, solar radiation and precipitation recorded at the nearest official or refinery meteorological station.

Air samples were also collected by NPL for subsequent analysis to determine the molecular weight to derive the emission flux in terms of mass and also to correct for the relative aromatic content, as the wavelengths used in their infra-red DIAL are not sensitive to the latter.

NPL provided a detailed report of monitoring and results for each campaign, including concentration measurements and flux calculations.

VOC Emission Speciation

Two options were considered for the determination of the speciation and concentration of the VOC emissions:

- Open-path Fourier transform infrared (OP-FTIR) monitor operated by NPL. This consists of a light source and a receiving telescope that collects and focuses the light beam into the FTIR spectrometer. The light beam is projected across the emission source before being received and analysed by the spectrometer. The disadvantage of this technique is that it only covers one scan line in a fixed position.
- Portable GC-MS system operated by the company Explorair. A total of up to five sampling lines can be installed, either at different locations (to provide an average sample) or all at the same point above the emission source. The vapour is pumped into a GC-MS for analysis.

For the first campaign both techniques were applied in parallel. However, for the second campaign only the GC-MS system was used.

Emission Models - Theoretical and Empirical Algorithms

Three emission models were applied to the system under study (WATER9, TOXCHEM+ and the EPA refinery wastewater emissions tool (RWET)) and the empirical algorithm developed by Litchfield.

During the monitoring periods, sampling and analysis and the recording of the operational conditions required to permit the use of these models and algorithm were undertaken.

4. DESCRIPTION OF THE SITES AND RESULTS OF TESTS

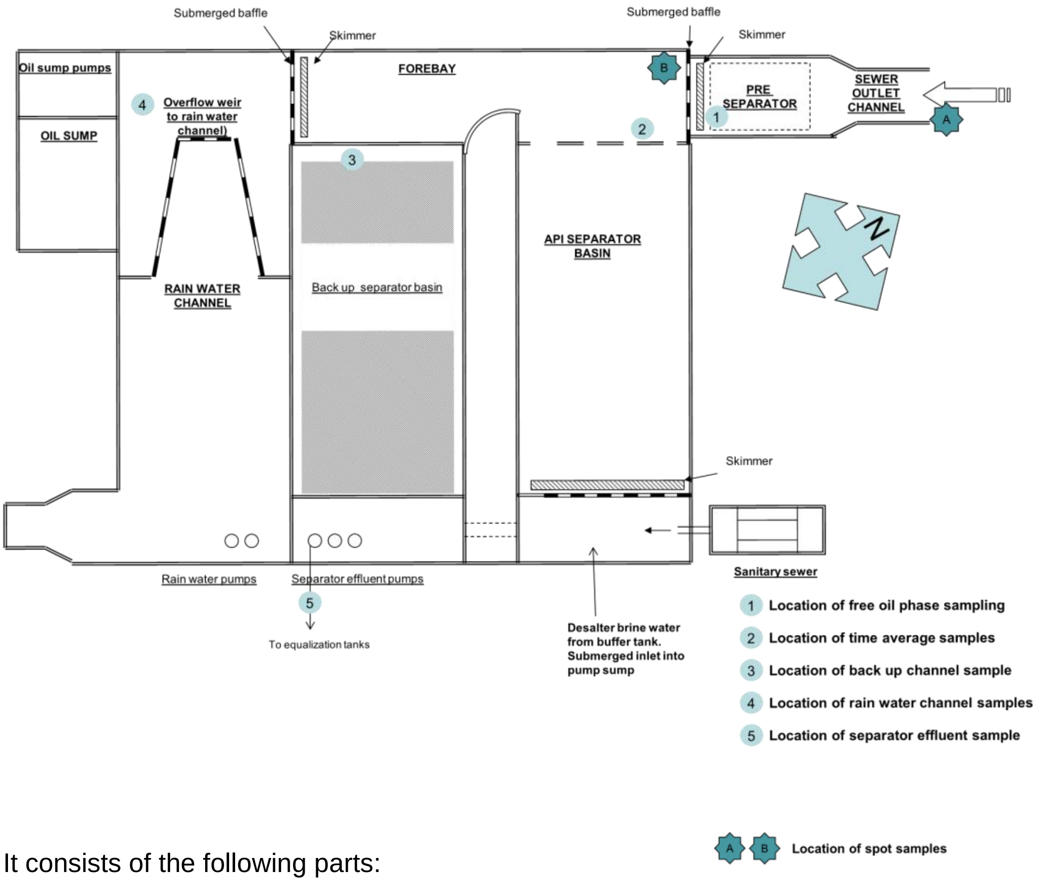
4.1. CAMPAIGN SITE 1

4.1.1. Waste water primary system description

The Site 1 separator consists of basins with a liquid level at ~3.8 meter below grade.

Below is a simplified schematic in top view of the separator area – more details are provided in **Appendix I**.

Figure 1 Scheme of separator area. Site 1



It consists of the following parts:

- An open sewer outlet channel, comprising a length of open drain of 10 m between the mouth of the main refinery sewer and the pre-separator. This has a water depth of about 0.5 m and a water velocity of around 0.13 m/s in dry weather conditions. The residence time is about 3 minutes for normal flow conditions.
- A pre-separator consisting of a basin with a screen to remove floating debris at the inlet and an oil skimmer at the back end. The water depth is around 1.3 m with a water velocity of about 0.03 m/s. In the pre-separator free oil accumulates on the water surface and is removed by a slotted pipe skimmer, which operates in a continuous mode. The pre-separator residence time is around 6 minutes for normal flow conditions.

- A forebay which connects the pre-separator to the API separator basin, a back-up separator basin and a ‘rain water’ channel. The latter has an overflow weir in V-shape. Water depth in the forebay is 1.3 m up to the inlet distributor wall of the API separator. The residence time in the forebay is around 9 minutes during normal flow conditions. At its inlet the back-up separator basin is isolated from the forebay by a gate. The API separator basin is designed to take the normal flow, whereas the rain water channel weir overflows during periods of heavy rain conditions. Before the water flows into the rain water channel it passes an oil skimmer.
- At its inlet the API separator basin is equipped with a flow distributor consisting of a vertical wall with 5 inlet openings of 0.2 m diameter evenly spaced over a width of 6 meter at a water depth of 1.3 m. Water depth in the API separator is 1.9 m (the separator is at lower elevation compared to the forebay floor). The water velocity in the API separator is 0.008 m/s with a residence time of around 1 hour for normal flow conditions. The back end of the separator is equipped with a slotted pipe oil skimmer which continuously removes the free oil layer on top of the water surface.
- At the back end of the API separator basin the water falls over a weir into a pump sump. The height of the weir relative to the water level in the pump sump is about 0.5 m. In the pump sump desalter brine water is also introduced via a submerged pipe. This stream is not routed to the inlet of the separator because it does not contain free oil having been buffered upstream in a very large tank equipped with oil skimming facilities.
- Due to fouling of both the API separator basin and the pump sump the rain water channel V weir was overflowing even in dry weather conditions. In order to avoid this atypical condition a temporary pump was installed in the pump sump during the measurement campaign. This allowed the total influent to flow through the API separator basin. At the end of each day of the measurement campaign, the pump was stopped, resulting in overflow conditions of the V-weir occurring. Consequently fresh oil accumulated on top of the rain water channel between each measurement campaign period.

4.1.2. Overview of campaign

The measurement campaign at the separator area of Site 1 was carried out over 5 days, 3 measurement periods being during the day time and 2 during evening/night time. These daily campaign measurement periods are hereafter referred to as ‘DIAL days’.

- April 13: 11.00 h to 17.00 h
- April 14: 11.00 h to 17.00 h
- April 15: 11.00 h to 17.00 h
- April 18: 18.00 h to 24.00 h
- April 19: 17.00 h to 24.00 h

During the entire campaign the weather was dry. The flow rate through the separator system over the five ‘DIAL days’ ranged from 228 to 256 m^3/h. The flow rate was determined using the flow meter from the equalization tank downstream of the separator to the flotation unit secondary separation stage, subtracting the flow rate of stripped sour water and adjusting for equalization tank level variations.

4.1.3. Sampling undertaken and results

4.1.3.1. Sample points

In order to collect input data for the Litchfield algorithm and the emission estimation models, the following sampling locations were chosen:

- In the open sewer outlet channel (sample point A on **Figure 1**). The intention was to take advantage of the higher turbulence at this point. In this way the sample would be more representative for the two liquid phases which are expected to be present in the pre-separator: a small layer of oil rich emulsion on top and a bulk phase containing emulsified oil droplets suspended in the water phase.
- At the forebay (sample point B on **Figure 1**). This location was selected because it is accessible and is considered to provide a representative sample of the API separator inlet.
- Sampling at points A and B was done by submerging a plastic tube about 0.3 to 0.5 m below the water surface and connecting it to a peristaltic pump discharging the sampled liquid into sampling bottles prepared by the laboratory. During the entire sampling campaign the plastic tubes remained in place at each sampling location.
- Time averaged samples were taken during the entire measurement period on each ‘DIAL day’ at the inlet of the forebay using a peristaltic pump with submerged suction.
- Other sources (stand-by basin, rain-water channel) were also sampled in the same way:
    - Isolated stand-by basin: one sample during the first ‘DIAL day’ at mid-depth.
    - Rain water channel: one sample per ‘DIAL day’ at mid-depth upstream of the V-weir.
- Effluent of the separator was sampled from a sampling point in the discharge pipe of the effluent pumps. This was done once every ‘DIAL day’.
- Free oil sampling was carried out from the surface of the water in the pre-separator near the oil skimmer, in the forebay at sample point B, in the rain water channel and in the API separator basin. This sampling was also undertaken by means of a plastic sampling tube and a peristaltic pump. Again the sampling tubes remained in place during the entire campaign. Free oil was analysed for density and 10% distillation point (DP).
- An oil sample was taken from the oil sump during the first ‘DIAL day’. However, the oil sump accumulates oil over more than one day. Thus, to ensure that representative data were obtained for each ‘DIAL day’ it was decided to use the samples from the oil layer in the pre-separator and the forebay to derive the data for the Litchfield calculations.
- Samples for oil in water (OIW) analysis were collected in glass bottles of 1 litre (pre-filled with some preservative acid). For the speciation analysis small sample bottles were used (also pre-filled with some preservative acid). All sample bottles were provided by the laboratory. During each ‘DIAL day’ samples were stored in a cooled box. At the end of the day the samples were taken to a nearby laboratory and stored in a refrigerator.

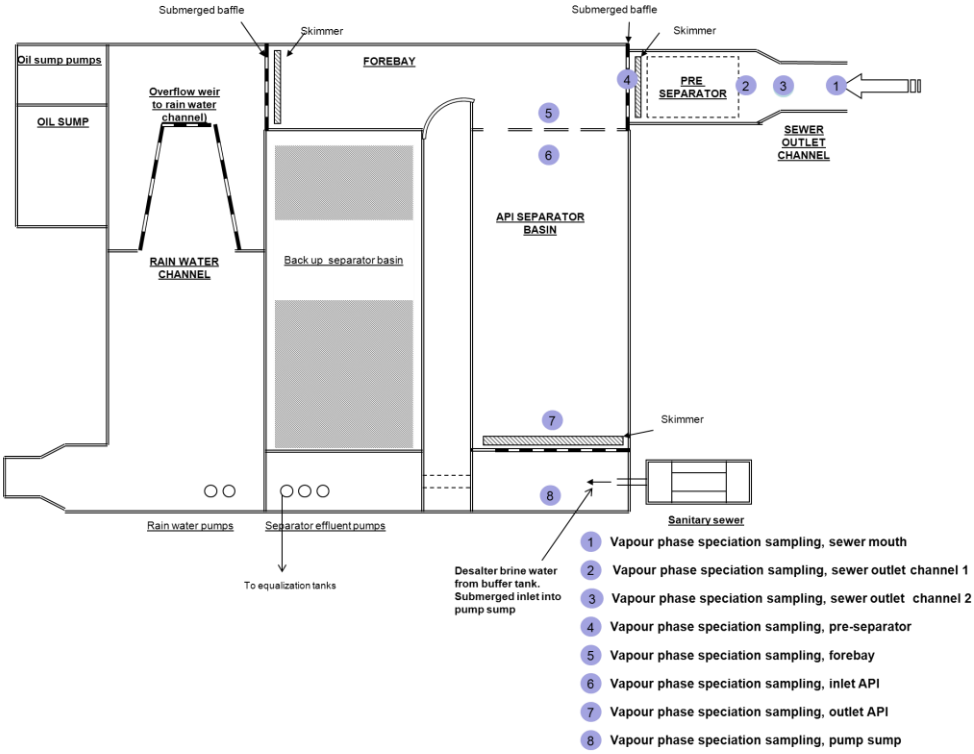
- Sample bottles were labelled with a number, date, time, sample point and an analysis code (i.e. OIW, SPEC, DEN, 10%DP).
- Prior to the campaign a sampling 'rehearsal day' was organised to test the sampling procedures. The opportunity was also taken to establish if very light components (C3 to C5) were present in the emissions. To this end a specific sample container (vial) was used to allow the laboratory to test for the presence of C3-C5 by using head space GC-FID. As no significant quantities of C3 to C5 were detected, as shown in **Table 1**, sampling using the vial was not included in the test program.

Table 1 Average head space GC-FID results. Rehearsal day. Site 1

	C3 hydrocarbons	C4 hydrocarbons	C5 hydrocarbons
µg/L	Not detected	12.0	28.5

- The sampling locations for the vapour phase speciation by GC-MS are shown in **Figure 2**.

Figure 2 Vapour phase speciation sampling points



4.1.3.2. Sampling frequency

The following frequencies were applied. All were spot samples except where otherwise specified:

- Oil in water:
    - Every 2 hours on each ‘DIAL day’ samples were taken at points A and B. Sample point B was sampled approximately 15 minutes after sample point A to take account of the residence time between the two sampling locations. Total number of samples per ‘DIAL day’ for each sampling point was 4 (at start of the DIAL measurements and at two hour intervals thereafter).
    - One time average sample for each ‘DIAL day’ at sampling point B.
    - Rain water channel and separator effluent: 1 sample each ‘DIAL day’.
- Full speciation:
    - Sample Point A: sample taken 2 hours after start of DIAL measurements.
    - Sample Point B: samples taken 2 and 4 hours after start of DIAL measurements.
- Oil phase analysis:
    - Pre-separator: samples taken 3 and 7 hours after start of DIAL measurements each ‘DIAL day’.
    - Rain water channel: sample taken on 3 of the 5 ’DIAL days’.
    - Separator basin: 1 sample taken on one ‘DIAL day’.
    - Separator oil sump: 1 sample taken on one ‘DIAL day’.

4.1.3.3. **Analysis by external laboratory**

The following procedure was applied for the oil in water analysis samples taken at sample points A and B:

- Shake sample.
- Allow settling for 6 minutes (samples labelled ‘A”) and 1 hour (samples labelled ‘B’).
- Determine total oil in water (OIW). This was the sum of the oil content of the oily phase on top and the oil in the aqueous phase. The OIW was analysed by extraction with tetrachloro-ethylene and subsequent infrared spectrometry. This method results in the analysis of only the non-polar hydrocarbons. Polar hydrocarbons are normally also present in refinery waste water but do not contribute significantly to the VOC emissions from the separators because of their high solubility in water and low volatility (the lightest polar molecule possibly present at Site 1 is phenol). This was confirmed by the GC-MS speciation of the vapour space above the separator water level which did not identify any polar hydrocarbons except for MTBE.
- Speciation was done only on the aqueous phase because the amount of free oil was very limited.

4.1.3.4. **Temperature measurement**

Water temperature was measured during the sampling operation by measuring the temperature of the liquid in the sample bottle.

4.1.3.5. Portable GC-MS

Speciation of the vapour phase above the liquid level was carried out on a continuous basis for several hours each 'DIAL day' in various parts of the separator area. Sampling was carried out using plastic tubes located at a distance above the liquid level of ~0.2 to 0.5 m. Two types of GC-MS devices were used:

- μGC-MS for relatively high concentrations (i.e. from 1 ppmv to a few % v/v) but limited to C10 and lighter components with an analysis time of about 3 minutes.
- Fast GC-MS for low concentrations (i.e. down to 1 ppbv) and for heavier compounds (i.e. up to C25) with an analysis each 10 or 15 minutes.

4.1.3.6. Analytical results

Analytical results and temperature data are shown for each 'DIAL day' in **Appendix II**.

The following observations can be highlighted:

a) Oil in water

- Despite the presence of a free oil layer on most of the basin surface the measured oil in water concentrations were relatively low, ranging from :
    - 35 to 470 mg/l for sampling locations A and B.
    - 290 to 740 mg/l for the rain water channel.
    - 86 to 330 mg/l for the separator effluent.
- The above analytical results indicate that the samples from sample point A were probably not providing representative values for the total incoming oil load. This could be explained by the fact that an oil layer was already developed at the sampling location, making it impossible to take a representative sample which included all free oil. Therefore, it was needed to estimate the oil in water in the inlet to the system from the oil being recovered which is registered on a monthly basis. This is estimated to be ~500 mg/l.
- The rain water channel samples typically had higher oil in water numbers. This is believed to have been caused by the presence of a relatively thick oil layer on top of that basin. During the sampling campaign this basin had no flow which may explain the presence of a thicker oil layer as a result of the long oil to water separation time.
- The results from the time-average samples taken at the inlet of the forebay shown in **Table 2** are a good representation of the variability of the oil concentration in the feed to the API separator basin. These samples were taken downstream of the pre-separator skimmer.

Table 2 Results from time average samples

	Time-average sample fore-bay OIW, mg/l	Flow rate through separator m^3/h	T water °C	T ambient air °C
Day 1	160	250	24.0	10.5
Day 2	120	240	24.7	9.5
Day 3	260	256	28.4	12.2
Day 4	110	213	27.2	18.4
Day 5	200	228	28.4	21.8

The above values are all average values over the entire period of the DIAL measurement for each day.

b) Free oil analysis

- The 10% distillation point of the oil layer sampled at the pre-separator and the forebay ranged from 213 to 224°C, with the exception of one sample which had a value of 178°C. These results may indicate that the incoming oil at Site 1 is either weathered in the separator basins and the upstream sewer system or that the oil which enters the sewer is of a high boiling point nature. The average measured oil density was also on the high side (0.86 kg/l) and therefore consistent with the measured boiling point range.

c) Vapour phase speciation by GC-MS

In general the speciation analysis resulted in relative low concentrations of C5 to C6 compared to C7 to C10. By far most of the oil in water consisted of heavier than C10 fractions.

This is consistent with the results from the vapour phase speciation measurements carried out above the liquid surface in the various basins (see detailed results in **Appendix III**.

A summary of the results are provided below:

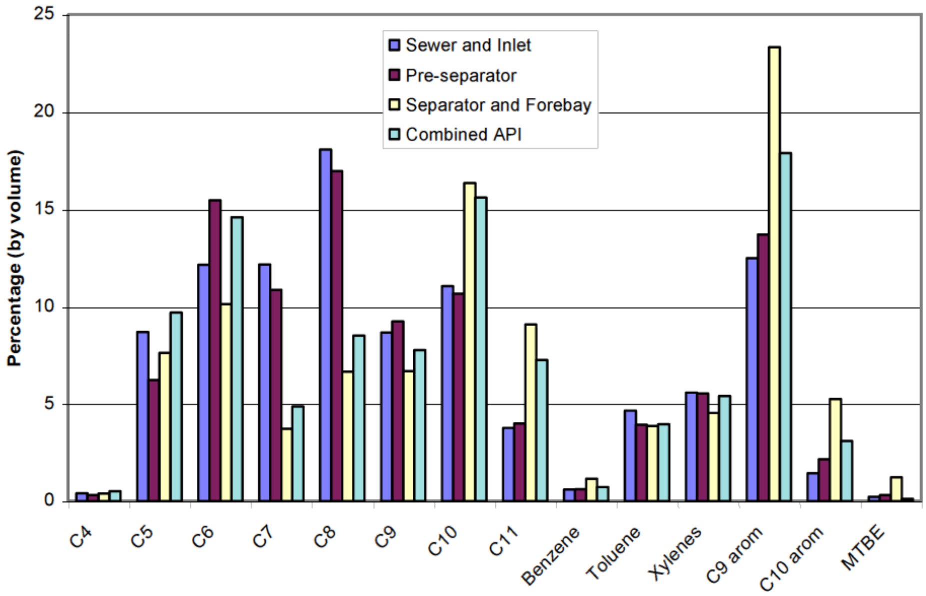
- On ‘Dial day’ 1 a test was carried out to evaluate the effect of the height above liquid level of the sampling point on measured concentrations. A window of 2 m down to 0.1 m above liquid level was tested. This test was done on the pre-separator. Concentrations increased from 2 m to ~0.5 m. No significant change was observed between 0.5 and 0.1 m. It was decided to carry out all sampling at a height of about 0.1 m above the liquid height as this approach resulted in the highest concentrations while still making the sampling practicable.
- The substances which were detected at a relevant concentration can be grouped into the following categories:
    - Alkane and cycloalkane isomers of C4 to C11.
    - Benzene/toluene/ethyl benzene/xylenes (BTEX).
    - C9 aromatics.

  - C10 aromatics.
  - MTBE.

- Overall the measured concentrations varied quite substantially over the 5 'DIAL days'.
- From the speciation within the above mentioned groups it can be concluded that C4 was only marginally present (ranging from 0 to 1% v/v of the total vapour concentration). The same can be said for BTEX. Benzene varied from 0.1 to 2.5% v/v of the total concentration. It has to be noted that during the DIAL campaign no desalter brine was routed to the effluent sump of the separator (its normal destination). This may explain the low concentrations of the light aromatics in the emissions from the pump sump, since desalter brine is a known contributor to the benzene load in waste water upstream of a treatment plant. Furthermore MTBE was not significantly present with the exception of the separator effluent pump sump on 'DIAL day' 2 with a share of 4.6% v/v of the total concentration.
- Furthermore no phenols were detected. At Site 1 the waste water streams containing phenols are not routed to the primary oil-water separator system.
- The highest concentrations were noted for C6 to C10 alkanes and also C9 aromatics. This could be explained either by a low presence of C5 and lighter compounds in the sewer system or by the evaporation in the sewer system of the lighter substances upstream of the separator.
- The concentrations generally decreased over the flow path of the water through the separator system: highest at the sewer mouth, followed by the inlet channel and the pre-separator, with decreases again after the pre-separator skimmer to the forebay and the separator basin. The concentrations measured in the effluent sump of the separator were found to be ~40% higher compared to the separator basin itself, which were likely to be due to the evaporation caused by the turbulence generated by the water falling over the separator effluent weir.
- When comparing the concentrations at the pre-separator obtained during daytime and night time, no clear picture emerged: these were about the same on 'DIAL day' 4, but on 'DIAL day' 5 the night time concentrations dropped to ~50% of the daytime values.
- The last two 'DIAL days' showed substantially higher concentrations (~30000 ppbv at the pre-separator) then during the first 3 days (~6000 to 9000 ppbv at the pre-separator). This could be attributed to the higher water temperature during days 4 and 5 (24.4 to 25.7°C on days 1 to 3 and 27.8 to 29°C on days 4 and 5) and/or to the higher oil in water concentration in the inlet channel (60 to 170 mg/l on days 1 to 3 and 140 to 260 mg/l on days 4 and 5 respectively)
- A vertical scan was carried out at the sewer mouth on day 5. Higher concentrations were measured at the top of the sewer mouth (~130000 ppbv) then at the centre (~54000 ppbv) and the lowest concentrations were measured at 0.1 m above the liquid level (~28000 ppbv) The latter was of the same order as that measured in the open inlet channel and the pre-separator. Furthermore the top of the sewer mouth had relatively more C5 and C6 whereas the point 0.1 m above the water surface had relatively more C9 to C11. This observation is an indication that lighter substances were present in the upper part of the underground sewer pipe.

- The results of the GC-MS speciation are represented in graphical form in **Figure 3** below which shows the relative proportions of the substances identified in the vapour space above the system liquid levels.

Figure 3 GC-MS speciation results (%v). Site 1



- The average liquid density of the evaporated VOCs was determined at 758 kg/m^3 based on averaging the results obtained from the GC-MS measurements in the vapour phase above the basin liquid surface (see **Table 32** in **Appendix III**).

4.1.4. Results from estimates using emission factors and algorithms

Table 3 shows the VOC emission estimates for the various 'DIAL days' based on the analytical results and different simple estimation factors or calculation methods. The results are expressed in kilograms per hour.

Table 3 Emission estimates. Daily averages. Site 1

kg/h	Sewer outlet +Pre-separator	Entire System			
	Litchfield	CONCAWE report factor	UK EI factor	EPA AP-42 factor	VDI factor
13/04/2011	- [1]	27.7	5.6	149.3	12.4
14/04/2011	- [1]	26.6	5.4	144.0	12.4
15/04/2011	2.2	28.4	5.7	152.0	12.4
18/04/2011	1.8	23.6	4.8	128.0	12.4
19/04/2011	0.9	25.3	5.1	136.0	12.4
Average	1.6	26.3	5.3	141.9	12.4

Table Note1. Not determined since analytical results were out of applicability limits.

It should be noted that the Litchfield equation results in negative numbers for some of the 'DIAL days' mainly because the water temperature was less than the lower boundary condition for which the equation was derived.

The estimate using the VDI method is based on a total basin surface area of 621 m^2.

The US EPA AP-42, UK EI and CONCAWE methods are based on the average water flow rate during each 'DIAL day' period of the measurement campaign.

4.1.5. Results from estimates using models

The emission estimation models only provide the estimated air emissions of individual substances and not of the total VOCs. Thus, the individual substance concentration data in the waste water at the inlet of the oil-water separator system are required.

Individual substances of specific interest mainly belong to the categories below. In addition some specific lighter substances potentially present in refinery waste water have been considered:

- C6 to C10 aromatic hydrocarbons.
- C5 to C10 non aromatic hydrocarbons.
- Naphthalene.
- CS_2.
- Acetone.
- MTBE.

It should be noted that the above hydrocarbons are mostly of the non-polar type. Polar substances such as phenols were not included since the streams containing these are not treated in the gravity type oil-water separator system at Site 1.

The models do not use vapour-liquid equilibrium data for the substances contained in the free oil layer. Therefore, they are expected to be more limited in their capability for dealing with basins covered by a free oil layer.

Therefore, the models were used to estimate the emissions from the primary oil-water separator system components which are covered only by a thin oil layer: the forebay and API basins.

Throughout the DIAL campaign the sum of the concentrations of the above mentioned substances in the inlet to the forebay and API basin ranged from 1 to 37 mg/l, with 5 out of 10 analyses below 3 mg/l. On the other hand the total hydrocarbon concentration in the waste water samples ranged from 37 to 350 mg/l. Consequently the majority of the hydrocarbons analysed in the waste water samples were heavier than C10. For the purpose of running the models it was assumed that the hydrocarbons which were heavier than C10 consisted equally of C12 and C20.

The analytical results of the waste water speciation used in the models are included in **Appendix IV**.

4.1.5.1. WATER9

Apart from the concentration of hydrocarbons in the waste water the following process operating conditions, equipment characteristics and meteorological data are required as input to the WATER9 model.

- Water flow rate;
- Inlet composition;
- Surface area of basins;
- Percentage oil coverage in the separator basin;
- Wind velocity;
- Height of overflow weir;
- Waste water temperature;
- Air temperature.

From this list surface oil coverage, wind velocity and water temperature are the most sensitive parameters with respect to the estimated VOC emissions.

Appendix IV and **Appendix V** document the input parameters and the modelled cases. Several cases were run based on waste water analytical data for the forebay for each of the 5 ‘DIAL days’.

Overall the estimated VOC emissions range from 0.03 to 0.28 kg/hour with an average of 0.1 kg/h over the entire campaign, representing 0.8% VOC loss.

4.1.5.2. TOXCHEM+

The TOXCHEM+ program uses mass transfer calculations to estimate VOC emissions to air based on influent composition data for individual substances, similar to WATER9.

The program partitions the substances over 3 phases: water, free hydrocarbon and solid phase (typically sludge).

Partitioning to the free hydrocarbon phase is based on the octanol-water partitioning coefficients for the various substances submitted as input to the program.

The mass transfer from the water phase to air is based on the Henry’s coefficient for the various substances.

Mass transfer from the free oil phase to air is not based on oil phase vapour-liquid equilibrium data for the various substances. Instead a default approach is used: based on the % oil coverage provided as input by the user, the mass transfer to air (as calculated based on the Henry coefficients) is corrected with an ‘oil coverage correction factor’. For a 100% oil covered basin this correction factor is 2, regardless of the vapour-liquid equilibrium characteristics of the individual substances.

The above means that the program is primarily designed to calculate the emission for cases without free oil coverage and for substances below their solubility limit in water. This characteristic makes the program less suitable for oil covered separator basins since:

- The mass transfer from the water phase to the free oil phase is not treated according to the solubility limits of the substances involved. So if a concentration above the solubility limit is provided in the input, the program will treat this as a dissolved substance.
- The mass transfer from the free oil phase to the air is not based on vapour/liquid equilibrium data but a default correction factor is applied to the amount vapourised from the water phase.

The required input to TOXCHEM+ is:

- Water flow rate;
- Substance speciation;
- Wind velocity;
- Water temperature;
- Basin surface area;
- Percentage of free oil coverage of the basin;
- Overflow weir height and width;
- Influent water suspended solids content.

Based on the octanol-water partitioning data, the calculated fraction of each substance partitioned to free oil is very small (< 0.004), whereas the fraction partitioned to solids depends on the type of substance based on an assumed suspended solids content. These varied from 0.026 for benzene to 0.36 for C12.

Appendix VI documents the input parameters and the modelled cases. Several cases were run based on waste water analytical data for the forebay for each of the 5 'DIAL days'.

The calculated emissions for the various 'DIAL day' cases obtained by TOXCHEM+ varied from 0.07 to 0.7 kg/hour with an average of 0.2 kg/hour that represents 0.9% loss. This can be compared to 0.03 to 0.3 kg/hour using WATER9 for the same conditions and water quality data.

4.1.5.3. Refinery wastewater emissions tool (RWET)

The refinery wastewater emission tool (RWET), developed for the US EPA, is an Excel based model with separate sheets representing individual components in a typical wastewater treatment system. The modules allow the estimation of air emissions for each particular component of the system as well as the effluent concentrations which can then be used as inputs for the next downstream collection or treatment unit. The calculations are primarily based on those presented in US EPA AP-42 [13] but also include updates deemed more accurate in the literature. The equations are provided in US EPA (2011) [15].

In this study, the module in the RWET for the estimation of emissions from oil-water separators was used.

The tool focuses on individual VOCs listed as hazardous air pollutants (HAPs) in US legislation. As published, it requires the input of concentration data for 22 individual HAPs plus n-butane. However, the model is very much more user friendly than WATER9 as the chemical properties of these 23 components are provided. Other hydrocarbons can be added as influent components but the properties of these must be inserted by the user.

For this project, four additional compounds were added to the specified influent constituent list: heptane, octane, dodecane and icosane (C20), the properties of these compounds can be found in **Appendix VII**. As in WATER9 and TOXCHEM+, it was assumed that the hydrocarbons which were heavier than C10 represented the difference between the sum of the concentrations of the listed compounds and the total oil in water concentration. This delta was assigned to C12 and C20. Unlike the other models where the ratio of this assignment had little effect on the results, for the RWET the C12:C20 ratio has a significant impact on the emission estimates. The ratio was varied, therefore, until the sum of the emission estimates for the C10 and heavier hydrocarbons was the same fraction of the total emissions as that determined from the GC-MS speciation. For Site 1 the C12:C20 ratio used for the RWET was 4:96.

The tool provides a list of critical inputs that the user must populate with site specific data. For the separator module these are:

- Surface area;
- Waste water flow;
- Wind speed;
- Fraction of oil in water (v/v) (i.e. OIW concentration in volume terms as fraction – a default of 0.001 is given in the RWET equivalent to 1000 ppmv);
- Oil layer thickness: for the basins considered to be covered only by an oil sheen a value of 0.1 cm was used.

A list of default variables and constants is also provided for the user to check and amend if required.

Using the average constituent concentrations over the campaign period the RWET provided an estimate of VOC emission flux of 1.8 kg/h. The result obtained is shown in **Table 4**.

Table 4 RWET result. Site 1

	Emissions [kg/h]
Forebay + API basin	1.8

4.1.6. Results from estimates using DIAL methodology

The campaign consisted of upwind and downwind measurements during five days. In total 142 scans were produced from seven positions of the DIAL truck depending on the wind direction: see wind roses in **Appendix VIII**.

The measured DIAL concentrations were combined with wind vector data from a fixed wind mast located near the separator area.

Wind data at the fixed mast were available at 3m and 11m elevation. For the emission calculations a correlation was used to determine the wind speed at the various heights of the plume. The resolution of the DIAL scan is approximately 3.75m x 3.75m. A grid of these dimensions is built and a concentration value, based on an interpolation (developed by NPL) of the path integrated concentration for each scan line, is assigned to each grid cell.

To obtain emission rates (flux), the NPL DIAL method multiplies the concentration of each cell of the grid by the perpendicular component of the wind speed assigned to the same cell.

A correction factor of 1.19 has been applied by NPL to the results to correct for the fact that the DIAL concentration measurements are based on the absorption coefficient for standard composition similar to gasoline vapour (unleaded petrol), whereas the real composition differs from that standard composition.

The correction factor above is derived from downwind sorption tube sampling of the ambient air at two meters elevation around the primary oil-water separator system subsequently analysed by gas chromatography. In **Figure 4** below the results of the sorption tube sampling are represented as a percentage distribution of the group of substances which were identified. It should be noted that C4 appears in this graph; this results from the presence of C4 upwind.

Figure 4 Summary of the sorption samples speciation analysis. Site 1

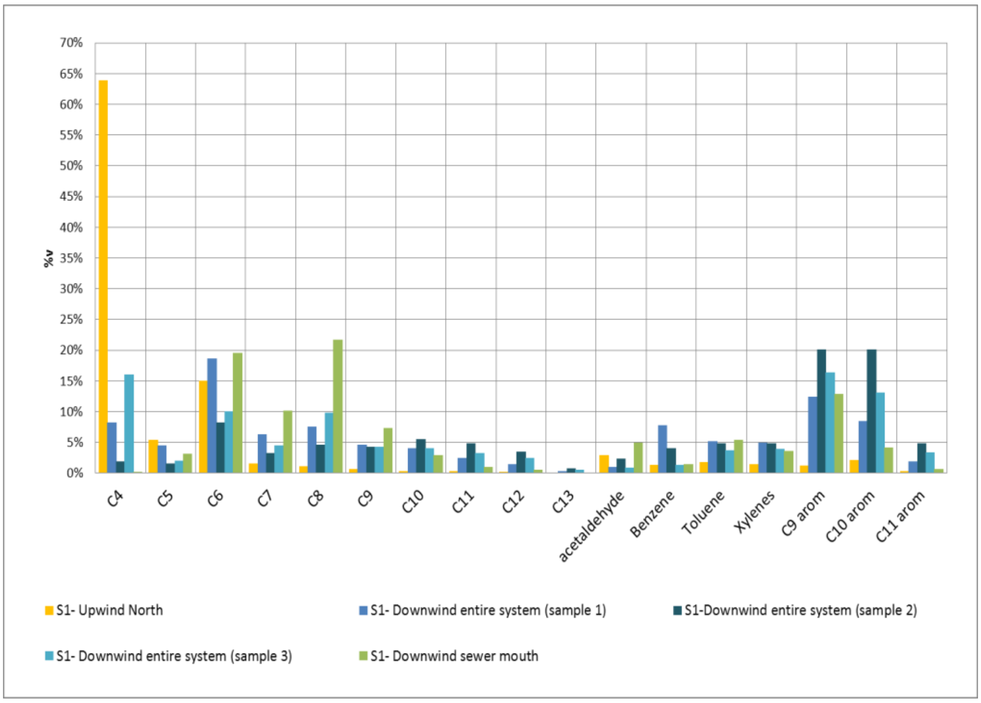
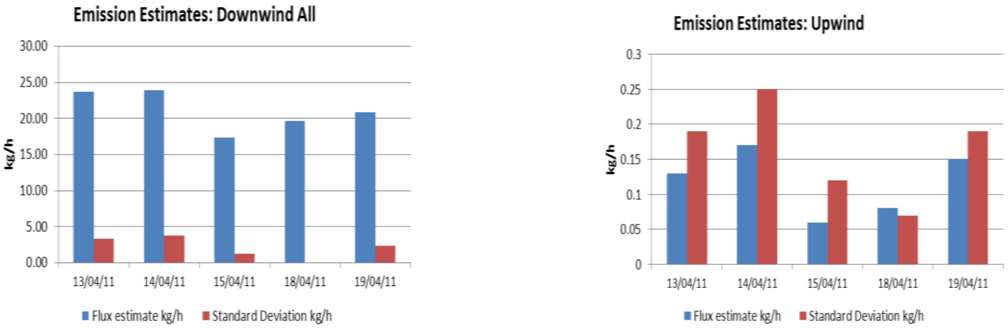


Figure 5 shows that upwind scans did not result in significant calculated VOC fluxes. The downwind calculated average fluxes for the entire separator system range from 17.3 kg/h to 23.9 kg/h. This range does not take into account the results obtained scanning only parts of the system, e.g. the inlet channel. **Figure 5** also shows the standard deviation for the set of emission fluxes derived from all scans. The standard deviation should not be mistaken to represent the uncertainty for the application of DIAL methodology to derive emission estimates. The detailed results are included in **Appendix IX**.

The range may represent the variability of emissions caused not only by the changes in operating conditions, waste water composition and atmospheric conditions but also by the intrinsic uncertainty of the methodology. Therefore, it is not possible to distinguish the intrinsic method uncertainty from the observed range of the calculated emission.

Figure 5 Summary NPL estimates Site 1. Upwind and Downwind estimates



4.1.7. Overview of estimates

Table 5 Overview of estimates for Site 1 - Algorithm and models

kg/h	Litchfield	WATER9	TOXCHEM +	RWET
Sewer outlet + Pre-separator	1.6	-		
Forebay + API basin	-	0.1	0.2	1.8
Entire System	-	1.7	1.8	3.4

The estimates from the entire system were calculated combining the results from Litchfield which had been applied to the sewer and pre-separator basin and the models WATER9, TOXCHEM+ and RWET which were applied to the forebay and API basin.

The approximate maximum mass loss by balance was calculated from the maximum historic average oil recovered registered by the refinery and the maximum percentage oil loss calculated by Litchfield (sewer and pre-separator) and TOXCHEM+ (forebay and API basin).

Table 6 Overview of estimates for Site 1 - Emission factors and DIAL methodology results

kg/h	CONCAWE report factor	UK EI factor	EPA AP-42 factor	VDI	NPL
Entire system	26.3	5.3	141.9	12.4	21.1

	Oil in water (kg/h) [1]	Max. % loss [2]	Maximum VOC loss (kg/h)
Approximate maximum mass loss by balance	≤140	4.9	6.1

Table Notes:1. Sum of VOCs in body of water from OIW concentration measurements and maximum free oil recovery rate from historic data.
2. Sum of maximum volume loss values from Litchfield algorithm and TOXCHEM+.

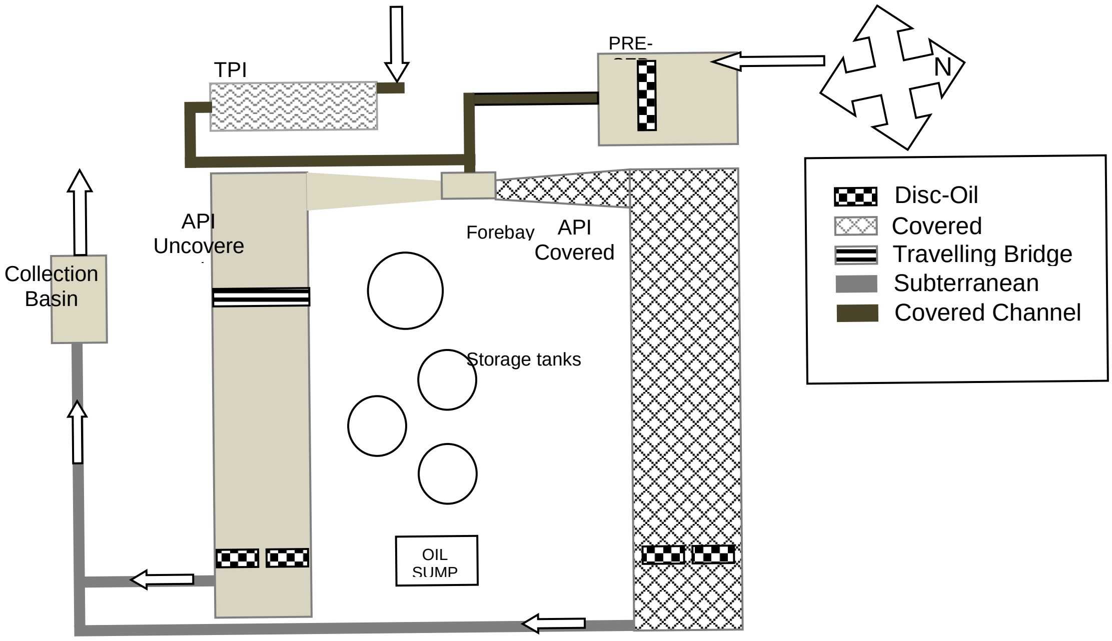
4.2. CAMPAIGN SITE 2

The second field trial was carried out in a southern European refinery during mid-September 2011. Site selection and trial timeframe were made in order to cover operational practices and meteorological conditions which were different from Site 1.

4.2.1. Waste water primary system description

In this site the gravity type oil-water separation system comprises: a tilted plate interceptor (TPI), a pre-separator equipped with discoil skimmers, and two API gravity separators: one is covered (API#1) and the other is uncovered (API#2). Both gravity separators are equipped with discoil skimmers and the API#2 also has a travelling bridge. A schematic description of the system is shown in **Figure 6**.

Figure 6 Schematic of separator area. Site 2



- The TPI and the pre-separator work in parallel and treat different streams:
  - The TPI treats waste water coming from three different origins: tank drains, selective hydrogenation units and lube oil area. The tank and desalter drains streams are fed to the main TPI inlet channel through a closed pipe system that discharges into the open channel creating a high turbulence area where the streams merge.

    Water depth in the tilted plate interceptor is around 2 m.

    The oil recovered is sent to an uncovered oil sump situated by the TPI. From there it is pumped to the main oil sump of the separator unit which is also uncovered.

    The transfer of oil from the TPI sump into the main sump and from the main sump to the slop tanks is done in a batch mode without flow measurement.

- The pre-separator receives the waste water from several units in the refinery. The main inlet to the pre-separator is an open channel leading to a weir over which the water falls into the pre-separator creating an area of high turbulence. The oil is skimmed by a set of discoils located at the back end of the pre-separator. The water depth is about 2 m. The outlet streams from the TPI and the pre-separator converge in a small basin (referred to in this description as the “forebay”) situated just upstream from both API inlet channels. From the forebay the water flows into the API separators approximately at the same rate. The API#1 channel is tightly covered and it is equipped at the back end with a set of discoils.
- The API#2 channel is uncovered and equipped with a travelling bridge for oil skimming and sludge scraping. In addition, there is a discoil skimmer set at the back end of the channel.

The dimensions of both separators are similar, being approximately 11 by 35 m. Unlike Site 1 the water level in the API separators is close to grade.

The outlet stream from both API separators is collected in a pump sump (collection basin) before being sent to the pH adjustment basin and the DAF secondary system. The sump also collects a waste water stream coming from the sour water stripping (SWS) unit.

- The oil recovered from APIs, the TPI and the pre-separator is collected in an uncovered sump. The sump also receives on a regular basis oil discharges from tankers coming from other parts of the refinery.
- The oil from the oil sump is pumped into a series of small storage tanks for further re-processing. They act as decanters, the oil goes from one tank to the other by gravity and the water is removed from the bottom of each one.

The water flow into the TPI and the pre-separator is unknown, and is not registered by the refinery in normal operation. However, the combined flow into the primary oil-water separator system can be derived from the inlet flow to the DAF system which is equipped with flow meters at the inlet of each cell.

The DAF secondary treatment system is located in another area of the refinery. It is fed from the primary oil-water separator system outlet through three intermediate basins. The DAF system also treats an extra stream coming from the sour water stripper unit whose flow can be calculated from a mass balance upstream. Therefore, to calculate the inlet flow to the primary oil-water separator system it is sufficient to subtract the sour water stripper flow stream from the total inlet to the DAF system.

The individual flow rates to the TPI and the pre-separator had to be calculated using measurements of the conductivity and chlorine content made in both streams and in the forebay where the streams are mixed.

The system is in a depression about two meters below the surrounding refinery ground level. It can be operated with one of the APIs out of operation, but this can only be undertaken during periods of no rainfall to ensure that the system does not flood.

The prevailing wind direction is in a line over the TPI and the uncovered API (API#2). There are non-volatile product storage tanks and a large pipe rack in the prevailing upwind area of the system and refinery plant downwind, so there are relatively impervious wind barriers both up and down wind in the prevailing direction.

There is a meteorological station at the refinery which registers temperature, precipitation and relative humidity every 15 minutes. In addition, there is an official meteorological station near the site where solar radiation data, temperature, wind direction, wind speed, atmospheric pressure, precipitation and relative humidity are registered every 15 minutes.

4.2.2. Overview of campaign

The second field trial took place from the 13th September 2011 to the 17th September 2011. The primary objectives were to estimate emissions from:

- The entire system in normal operation;
- The system with only the uncovered API (API#2) in operation;

- The system with only the covered API (API#1) in operation;
- The entire system in normal operation during night time;
- If feasible, to differentiate the emissions between system components.

Therefore the following schedule was planned;

13-09-2011	8:00 to~18:00h	only covered separator (API#1) in operation.
14-09-2011	8:00 to~18:00h	both separators (API#1 and API#2) in operation.
15-09-2011	8:00 to~18:00h	only uncovered separator (API#2) in operation.
16-09-2011	8:00 to~18:00h	only uncovered separator (API#2) in operation.
17-09-2011	17:00 to~02:00h	both separators (API#1 and API#2) in operation.

The total periods indicated above include the time required to set up the DIAL and the portable gas chromatograph which was between two and three hours each ‘DIAL day’. The NPL DIAL operated for approximately 7 hours per day.

A meeting between all the participants in the project was held one month prior to the start of the campaign in order to review all the associated safety issues. At the same time the possible locations for the DIAL truck, portable gas chromatographs and wind masts were agreed.

4.2.3. Sampling undertaken and results

4.2.3.1. Sample points

All the sampling was undertaken manually by contractors (SGS) at the points requested by CONCAWE and agreed with the refinery personnel. The sample bottles and preservative procedures for every analysis were provided by SGS.

The locations and sampling procedure were chosen to ensure that the samples were as representative as possible.

- Pre-separator inlet (sample point A): the samples were taken at one of the points where the turbulence was higher due to a change of direction of the inlet channel.
- TPI inlet (sample point B): the sampling point was located just downstream of the point where the different inlet streams to the TPI merge. High turbulence and mixing rate were ensured due to the fact that two of the inlet streams fall into the inlet channel from a piping system.
- TPI outlet (sample point C): the sampling point was situated just at the TPI outlet before it merged with the pre-separator outlet.
- Pre-separator outlet (sample point D): the sampling point location was selected to be immediately downstream of the pre-separators discoil and before the outlet stream merged with the TPI outlet.

- Forebay (sample point E): the sampling was carried out at the point where the highest turbulence was found after the pre-separator and TPI outlet meet and before the inlet to the API.
- API separator outlets (sample points F and G): The water samples were taken just after the discoil discharge where a high turbulence was found.
- Free oil sampling (sample points I, J and K): the oil was taken directly from oil recovered by the discoil skimmers, so the sample was as “fresh” as possible.
- Free oil sampling from TPI (sampling point L): the free oil was sampled from the oil intermediate sump where the oil recovered in the TPI was discharged.

As for Site 1, prior to the campaign a sampling ‘rehearsal day’ was organised to test the sampling and to undertake a full speciation analysis of the water stream going into the separators. The results of the analysis were used to limit the species to be analysed during the campaign to those found during the rehearsal period.

The vapour phase speciation programme was agreed once the possible locations for the equipment were established in the safety meeting. The main areas monitored were:

- The pre-separator: samples from the inlet, middle and outlet were analysed separately. A period of average sampling was also undertaken.
- TPI: four point average sampling of the TPI basin (five lines used but two combined at one location).
- Forebay: one point sampling.
- Uncovered API: five point average sampling.

Additionally, some sampling was undertaken to try to evaluate the influence of the height of sampling above the water level on the concentration.

A summary of the VOC emission speciation programme is shown in **Table 7.**

Table 7 Vapour speciation programme. Site 2

Day	Sampling Points	Observations
13-09-2011	Collection Basin	Measurements to evaluate the influence of the height on concentration
14-09-2011	Average API#2	
	Forebay	
	Average TPI	
15-09-2011	Pre separator	Sampling points were installed in the inlet, middle and exit of the pre-separator. Measurements of the average of all sampling point were also performed.
	Oil sump	

Schematics showing the positions of the sampling points are given in **Figure 7** to **Figure 9**.

Figure 7 Sampling points for GC-MS speciation uncovered API. Site 2. Four sampling lines.

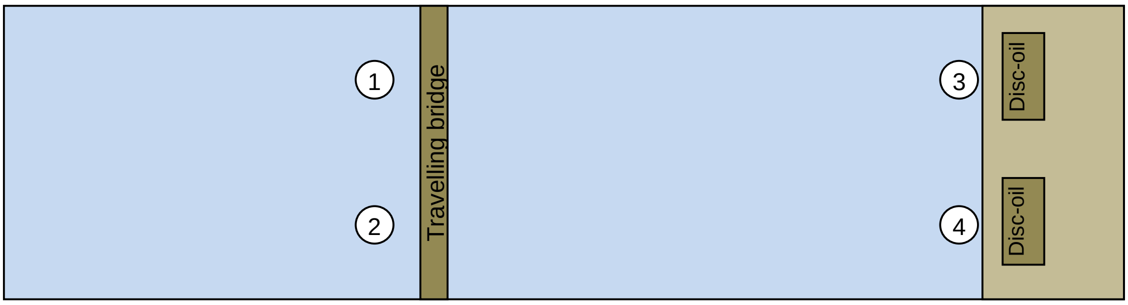


Figure 8 Sampling points for GC-MS speciation TPI. Site 2. Four sampling lines.

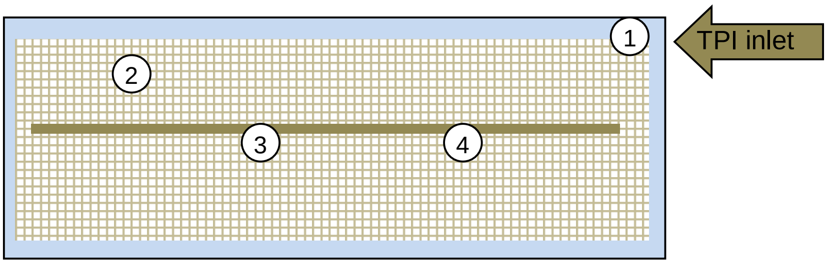
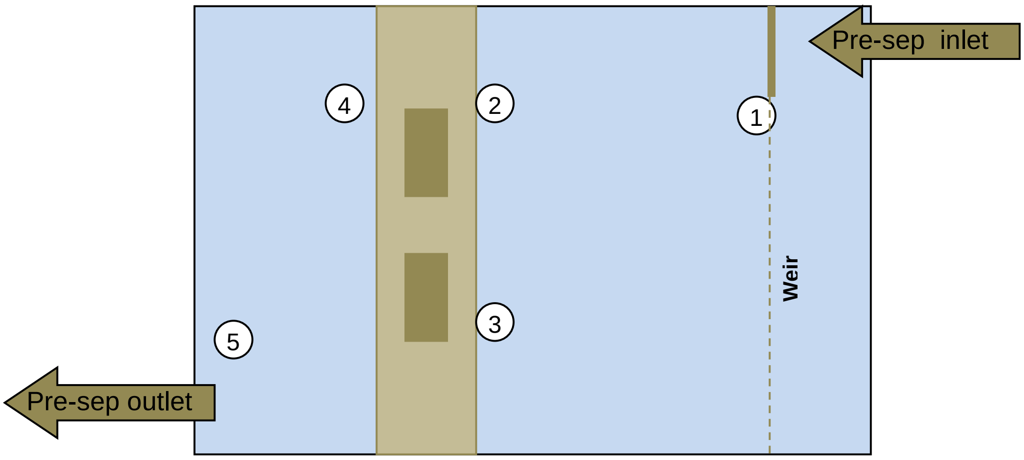


Figure 9 Sampling points for GC-MS speciation pre-separator. Site 2. Five sampling lines. Inlet sampling (1), middle sampling (2, 3) and outlet sampling (4, 5)



4.2.3.2. Sampling frequency

The sampling frequency established for every point and analysis is detailed below. The sampling frequency is referred to the starting time of DIAL measurements. All samples were spot samples. No average sampling was performed at Site 2:

- Oil in water:
    - Samples taken every 2 hours at points A, B and E each ‘DIAL day’. Total number of samples per ‘DIAL day’ for each sampling point was 4 (at start of DIAL measurements and at 2 hour intervals thereafter).
    - One sample taken each ‘DIAL day’ at sampling points F and G.
- Full speciation:
    - Samples taken at points A, B and E 3 hours after start of DIAL measurements.
    - One sample of the oil phase taken at sampling points A and B on day 2.
- Oil recovered analysis (10% distillation point and density):
    - Samples taken three and seven hours after the start of DIAL measurements each ‘DIAL day’ at sample points I, J, K and L.
- Conductivity and chlorine analysis:
    - Samples taken every 2 hours at sample points C, D and E each ‘DIAL day’. Total number of samples per ‘DIAL day’ for each sampling point was 4 (at start of DIAL measurements and at 2 h intervals thereafter).

The sampling was undertaken as planned except for the first day, 13th September, when a power supply problem delayed the programme for four hours resulting in one of the sample sets being skipped.

4.2.3.3. Analysis by external laboratory

The procedure applied for the oil in water analyses on samples taken at sampling points A and B was the same as described in section 4.1.3.3.

All the sampling was performed manually using new 5 litre plastic bottles with samples being transferred to smaller glass bottles for further analysis. These bottles were pre-labelled by the laboratory with a number, date, hour, sample point and a code (OIW, SPEC, DEN, 10%DP).

4.2.3.4. Temperature measurement

The water and free oil temperature were measured by SGS for each sample immediately after the sampling.

The ambient air temperature data were obtained from the refinery meteorological station.

4.2.3.5. Portable GC-MS

Speciation of the vapour phase above the liquid level was undertaken as at Site 1 (see section 4.1.3.5) during ‘DIAL days’ 1 to 3. Sampling was carried out using a total of five lines which could be located at a distance above the liquid level of ~0.05 to 0.2 m.

The average liquid density of the evaporated VOCs for each basin was calculated by averaging the results obtained from the GC-MS measurements in the vapour phase above the liquid surface (see **Table 8**).

Table 8 Average liquid density of evaporated VOC. Site 2

kg/m³	Pre-separator	TPI	API
Evaporated VOC liquid density	744	735	757

This table shows that the evaporated VOC liquid density increased from the inlet of the system through to the APIs.

4.2.3.6. Analytical results

The detailed analytical results, temperature and speciation data are shown in **Appendix II**.

The following conclusions can be drawn:

a. Oil in water

- The oil in water results of the TPI and pre-separator inlet were very variable. The quality of the incoming water was dependent on the upstream operation. In the case of the TPI the fluctuations were greater due to the tank drain discharges that are not performed continuously but in a batch mode. The maximum and minimum values registered during the campaign are shown below together with the average value:

  – TPI inlet: 22,000 mg/l to 14 mg/l with an average for all 5 ‘DIAL days’ of 2,488 mg/l.

The highest results were found the first day when the average concentration was around 14,000 mg/l. Thereafter the average oil in water content decreased to 500 mg/l.

  – Pre-separator inlet: 6,200 mg/l to 36 mg/l, with an average of 943 mg/l.

The highest concentrations were also found the first day. The fluctuations registered were not as important as for the TPI.

- As shown below the TPI and pre-separator are efficient at removing the oil from heavy loaded streams, the concentrations observed in the forebay generally being much lower than those registered in the pre-separator and TPI inlet:

  – Forebay: 400 mg/l to 7 mg/l, with an average of 105 mg/l.

  The free oil removal performance appears to be lower for low inlet concentrations.

- In general, there was no consistent percentage reduction in the oil concentration in the outlet of the API separators compared to the influent samples (forebay). This was probably due to a different period between the inlet and effluent samples being taken to the residence time of the water in the API. Thus fairly rapid changes in the influent stream were not reflected in the effluent sample.

The effluent samples were taken 3 hours after the first forebay sample was taken. The residence time of the separators depends on the inlet flow to the system and whether just one or both separators are in operation. It can vary from 1.5 hours to 7 hours, the average being 2 hours when one separator is working and 4 hours when both on them are in operation.

- Covered API outlet: 7 mg/l to 410 mg/L with an average of 161 mg/l.
- Uncovered API outlet: 37 mg/l to 160 mg/L with an average of 101 mg/l.

b. Water phase speciation

- The water speciation results show a very variable composition of the hydrocarbons in the water entering the system, but in general, the main compounds found were aromatics, phenols and methyl ethyl ketone (MEK).
    - The MEK is used in the dewaxing process in the lube oils unit and it is expected to be found in the inlets of the API, the TPI and the pre-separator. The concentration of MEK at the TPI inlet was higher than at the inlet of the pre-separator.
    - The phenols are produced in several units of the refinery and are also expected in streams entering both the TPI and API separators.
    - There was a higher concentration of light hydrocarbons (C5s) in the TPI inlet than at the pre-separator inlet.

c. Free oil analysis

- The oil recovered from the covered and uncovered APIs present very different densities and 10% distillation points.
    - Covered API: range of density from 0.8806 kg/l to 0.9230 kg/l.
    - Uncovered API: range of density from 0.8922 kg/l to 0.9786 kg/l.
    - Covered API: range of 10% distillation point from 106°C to 306°C.
    - Uncovered API: range of 10% distillation point from 98°C to 182°C.

  Some samples had values of density close to 1.0 and distillation points close to 100°C, indicating that these samples had significant water content and therefore they were not representative of the oil recovered.
- The oil recovered at the TPI had lower density and 10% distillation point values than the oil recovered at the pre-separator:
    - Pre-separator: range of density from 0.8634 kg/l to 0.9508 kg/l with an average of 0.9106 kg/l.
    - TPI: range of density from 0.8087 kg/l to 0.8467 kg/l with an average of 0.8285 kg/l.
    - Pre-separator: range of 10% distillation point from 99°C to 264°C. The average value, discarding those values close to 100°C which are considered not to be representative of the oil recovered, was 220°C.

  - TPI: range of 10% distillation point from 86°C to 143°C. The average value, discarding those ~100°C, was 138°C.

The oil and water speciation analyses identified that this was probably due to the light hydrocarbons and solvents in the TPI inlet which are assumed to come from the lube oil de-waxing process. Besides, two of the three waste water streams going to the TPI are transported through a closed pipe system; therefore the light ends content at the TPI are expected to be higher.

Furthermore, the oil speciation analysis were coherent with the 10% distillation points and density results, confirming a higher content of lighter components (light hydrocarbons and solvents) in the oil recovered at the TPI.

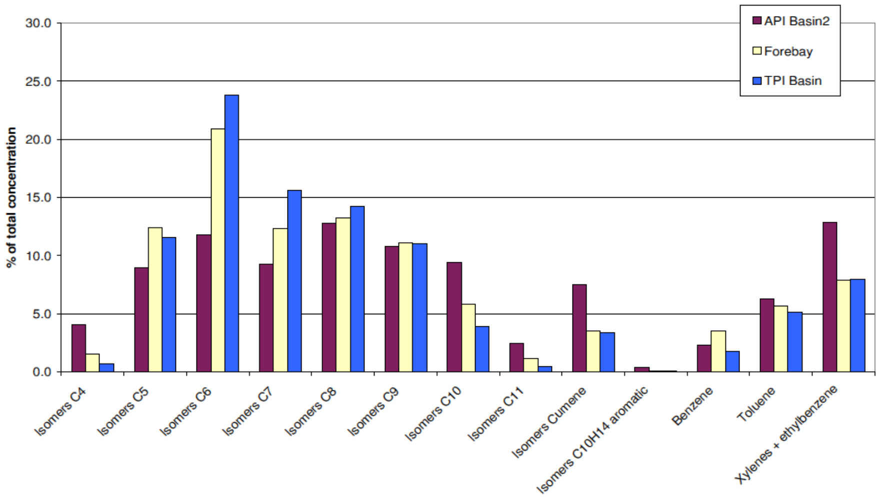
d. Vapour phase speciation by GC-MS

- The results of the GC-MS vapour phase speciation measurements were consistent with the results observed in the water and oil phase.
  - The concentration of VOCs was highest at the pre-separator and the TPI and lowest at the uncovered API. The pre-separator registered the highest concentration being approximately 100 times higher than the concentration at the API separator.
  - No phenols or ketones were detected, but this is expected due to their high solubility in water.
  - The results registered during the pre-separator sampling showed a high variability of the concentration during the analysis period (1.5h). This was also in agreement with the high variability of the water analysis results.

The sampling undertaken at different distances from the water surface in the collection basin showed the expected decrease in concentration when increasing the sampling height.

The results of the GC-MS speciation are represented in graphical form in **Figure 10** which shows the relative proportions of the substances identified in the vapour space above the system liquid levels. The detailed results can be found in **Appendix III.**

Figure 10 GC-MS speciation results (%v). Site 2



4.2.4. Results from estimates using emission factors and algorithms

Table 9 shows the VOC emission estimates for the various ‘DIAL days’ based on the analytical results and different simple estimation factors or calculation methods. The results are expressed in kilograms per hour.

Table 9 Emission estimates. Daily averages. Site 2

kg/h	Pre-separator		TPI		Entire system			
	Litchfield	VDI	Litchfield	VDI	CONCAWE report factor	UK EI factor	EPA AP-42 factor	VDI
13/9/2011	2.0	2.0	385.9	1.1	1.0	7.1	5.7	11.1
14/9/2011	1.5	2.0	1.0	1.1	40.0	8.1	216.3	11.1
15/9/2011	18.0	2.0	2.9	1.1	44.7	9.1	241.4	11.1
16/9/2011	2.4	2.0	45.5	1.1	44.0	8.9	237.9	11.1
17/9/2011	0.3	2.0	3.2	1.1	43.6	8.8	235.4	11.1
Average 5 days	4.9	2.0	87.7	1.1	34.7	8.4	187.3	11.1
Average excluding day 1	5.6	2.0	13.2	1.1	43.1	8.7	232.8	11.1

Table Note: 1. VDI factor provides total estimate including the oil sump area.

The source of the highest emission on a daily basis according to Litchfield estimate was the TPI; this was due mainly to the high oil in water concentration registered in the samples taken on the first day. The average for the campaign period decreased from 88 kg/h to 13 kg/h when the first day samples are not taken into account in the calculation.

The VDI method is based on a total basin surface area of 895 m^2. The surface area of each basin is provided in **Appendix X**.

The EPA, UK EI and CONCAWE methods are based on the average water flow rate during each day of the measurement campaign. For this site, because there is both a covered and uncovered API, these methods result in an over-estimate of the emission rate. This is because they can only be applied to systems which are either totally uncovered or covered. In the latter case an emission reduction factor of 97% is applied to the entire system.

In this case, the accuracy of the estimates could be improved by pro-rating the factors by the surface areas. At Site 2, 42% of the surface area of the system is tightly covered. Assuming that the efficiency of the cover is 97%, the factors would need to be adjusted to (100 – 42) + (42 *0.03) = 59% of their values for the totally uncovered situation. This would reduce, for example, the estimate using the CONCAWE factor to an average VOC flux of 20.4 kg/h over the 5 day campaign.

The UK EI emission factor of 0.0225 kg/m^3 water treated is applicable only where the average oil in water influent concentration is < 880 mg/l. As the average concentration at Site 2 was in excess of this value the EI factor has been included in **Table 9** for completeness only.

4.2.5. Results from estimates using models

Following a review of the complexity and the results obtained from implementing the models at Site 1, only the US EPA Refinery Wastewater Emissions Tool (RWET) was used at Site 2.

4.2.5.1. Refinery wastewater emission tool (RWET)

As mentioned in section 4.1.5.3, this model requires as input the concentration values for several substances.

As for Site 1, four additional compounds were added to the specified influent constituent list: heptane, octane, dodecane (C12) and icosane (C20). The concentrations of dodecane and icosane where calculated to represent the difference between the sum of the concentrations of the listed compounds and the total oil in water concentration. As with Site 1 the ratio of C12 to C20 was set so that the ratio of the estimated emissions of the C10 and heavier hydrocarbons to the total equalled that determined from the VOC speciation undertaken by GC-MS (section 4.2.3.6.d). At this site the C12:C20 ratio was 7:93.

Using the average compositional data for the entire 5 day campaign, the RWET estimated emission from the uncovered API basin was 4.5 kg/h. For the covered basin an emission reduction of 97% was assumed. Overall, this resulted in a total emission estimate for the two API basins of 4.6 kg/h.

Table 10 RWET results. Site 2

	Emissions [kg/h]
API basins (covered and uncovered)	4.6

4.2.6. Results from estimates using DIAL methodology

The DIAL campaign took place in parallel with the analytical sampling and vapour speciation analysis.

The main objective of the campaign was to assess emissions rates from the primary waste water treatment area and to try to identify and differentiate the estimates from each potential emission source.

The measurements of VOC concentrations were made from different locations using DIAL scans downwind and upwind in a vertical plane. In total 160 scans were produced from three positions of the DIAL truck depending on the wind direction, which was highly variable. The wind roses produced by NPL for the campaign days are shown in **Appendix VIII**.

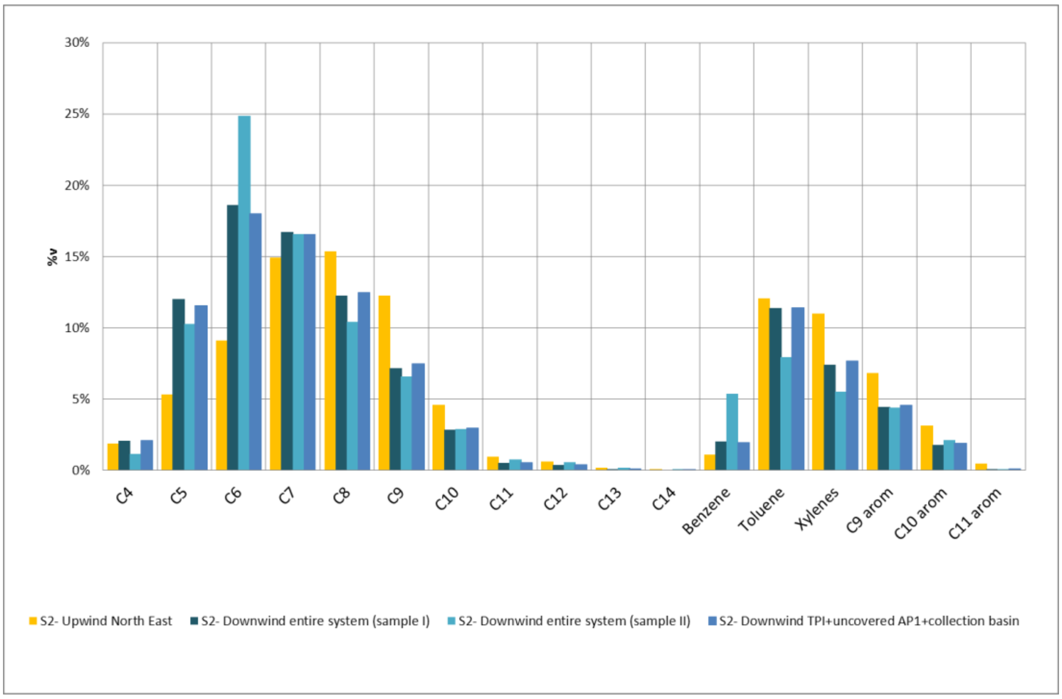
The emission rates reported were estimated by combining the concentrations measured with the wind velocity and direction registered by a wind mast located in an unperturbed wind field some distance from the primary oil-water separator system.

A summary of the results is included in **Appendix IX**.

A correction factor of 0.95 has been applied by NPL to the results shown in the appendix to correct for the fact that the DIAL concentration measurements are based on the absorption coefficient for a standard composition similar to gasoline vapour, whereas the real composition differed from that standard composition.

The correction factor above was derived from sorption tube sampling of the ambient air at two meters elevation around the primary oil-water separator system subsequently analysed by gas chromatography. More than 100 substances were identified; for simplicity they have been grouped by families in **Figure 11** below. These results are consistent with the GC-MS speciation of the vapours emitted. The yellow bars represent the composition of the upwind emissions being sampled.

Figure 11 Sorption tubes GC analysis results. Site 2



The following conclusions can be drawn from the results in **Appendix IX**:

The DIAL methodology provided very high emission estimates: as shown above, some of the results from the NPL DIAL are as high as 660 kg/h. A comparison between the hydrocarbons entering the system and the emissions estimated was conducted. This showed that the emission estimates reported are, in some of the cases, greater than the average mass rate of oil entering the system over the test period.

- A number of upwind sources were identified which were very significant in comparison to the estimated emission rates for the separator system.
  - Some upwind sources identified were:
    - An emission from a western source as high as 100 kg/h.
    - A source to the east of the separator system was estimated to emit almost 40 kg/h.
    - The emergency basin situated to the south of the separator system area appeared to be a smaller source with emissions estimated to be up to 15 kg/h.
  - Additionally, a northern source was identified from the DIAL concentration profiles and was estimated to be about 170 kg/h.
  - Given the limited number of upwind scans no insight could be gained into the variability of these upwind sources with time.

  - Only a limited number of upwind scans were performed for the corresponding set of downwind scans. Furthermore, during one DIAL day there were no upwind scans undertaken.
  - This shows that at Site 2 there were a number of significant sources in the vicinity of the separator system. For the effective application of DIAL methodology at Site 2 more information would be needed on these sources which would require exhaustive surveys of their size and variability. Since this was not achieved during the actual campaign, the lack of data concerning the upwind sources could be a major contributor to the overall uncertainty of the emission estimates.

- To calculate the emission flux the actual plume is represented as a grid with cells of 3.75m x 3.75m. A concentration value based on an interpolation of the path integrated concentration for each scan line is assigned to each grid cell.

  To obtain emission rates the concentration of each cell of the grid is combined with the component of the wind speed which is perpendicular to the plane of the scan lines. This introduces another element of uncertainty because:

    - The wind speed is assumed to change in the vertical direction, not taking into account variations in the other dimensions.
    - The wind speed variation with height is calculated using a logarithmic equation based on only two measurement points (3m and 11m) from the fixed mast in the undisturbed wind field.
    - The wind direction is considered to vary only with time and not spatially.

  The above mentioned elements of uncertainty may be reinforced by the specific topography of the separator system which is in a depression with surrounding obstacles that create a complex, highly turbulent wind field. In addition, the meteorological conditions occurring during the campaign were likely to induce convective conditions which also resulted in turbulent conditions and highly variable concentrations.

- It was not possible to clearly differentiate the individual emission sources due to limited locations for the DIAL van and the wind direction.

- The estimates from the measurements made during the day and up to 01:00 at night when both separators were in operation were similar even though the ambient temperatures registered were slightly different (average day 31°C, average night 26°C). Moreover, the oil in water analyses reveals that the oil loading on the system during the night time measurements was lower than during the day.

4.2.7. Overview of estimates

In **Table 11** an overview of the estimates obtained considering the five campaign days is shown. In order to be able to compare the results estimated by the different methods, the results from all of the downwind results provided by NPL have been averaged.

Table 11 Overview of estimates for Site 2 - Litchfield and RWET

kg/h	Litchfield	RWET
Pre-separator	4.9	
TPI	87.7	
API basins	-	4.6
Entire System	97.2	

Table 12 Overview of estimates for Site 2 - Emission factors and DIAL methodology results

kg/h	CONCAWE report factor	CONCAWE report factor pro-rated	UK EI factor	EPA AP-42 factor	VDI	NPL
Entire system	34.7	20.4	8.4	187.3	11.1	193.4

5. DISCUSSION

5.1. SITE 1

The primary waste water treatment facilities at Site 1 comprise a relatively small pre-separator followed by a forebay acting as a feed to either the main API separator basin, a stand-by basin or a storm-water bypass channel. The pre-separator, forebay and API all have oil skimmers. As the refinery is located on flat terrain and the waste water system relies on gravity flow through the drains and sewers, the water level in the water treatment facility is almost four metres below grade.

In the vast majority of refinery primary waste water treatment facilities there is no sampling point installed to obtain an inlet water sample. However, Site 1 is unusual in having an open stretch of sewer immediately prior to the pre-separator which provides access to obtain an inlet sample. Although this stream appeared turbulent, free oil could be discerned on the water surface. Water samples taken in this sewer were from the bulk of the water stream and thus did not include the free oil. Consequently it is believed that the values of oil in water (OIW) concentration at the inlet to the system result in an under-estimate of the VOC load on the pre-separator. This has an impact on using the algorithms and models such as Litchfield and WATER9 which require a value of OIW concentration to permit the estimation of VOC mass fluxes.

The sampling of the water flow into the main API basin was undertaken near to the exit of the pre-separator and close to the submerged API inlet diffuser pipes and so can be considered to have provided representative OIW concentrations for both the API and forebay.

The average value of the OIW concentration at the pre-separator inlet over the five ‘DIAL days’ was 159 mg/l, the value in the forebay from the time-average sampler was 127 mg/l and the average water flow rate was 250 m^3/h. The average computed oil mass flow rates into the pre-separator and API were therefore 40 kg/h and 32 kg/h respectively. These rates, however, only account for the dissolved VOCs and emulsified oil. As mentioned above, the actual mass flow rate of oil entering the pre-separator would have been greater due to the free oil on the inlet stream which could not be directly measured. The historic average oil recovery rate from the system at Site 1 is ≤100 kg/h, so during the campaign at Site 1 it was judged that the average oil mass flow rate into the pre-separator would have been ≤140 kg/h, equivalent to an average oil in water concentration of ≤560 mg/l.

Some variations in the OIW concentrations were noted. For the forebay, where a time-average sampler was used, the range of spot readings varied up to 6.4 times the average daily value.

The other parameters measured were the water and ambient temperatures and the 10% distillation point (DP) of the oil sampled from the free oil layer in the pre-separator, this being deemed to represent the inlet oil to the system. Values of these parameters are required for the Litchfield equation which gives a value of the oil loss to atmosphere in percent volume terms. Applying this factor to the amount of oil entering the system provides the VOC emission flux estimate. The water flow was determined from the level in a holding tank downstream of the API and flow meters at the second stage DAFs.

Litchfield derived his algorithm using test conditions reflecting those in an API separator at a US refinery in the 1970s. This algorithm was used in the development of a number of emission factors for uncovered API separator systems [10]. The factor in the CONCAWE report 1/09 [5] is 0.111 kg/m^3 water treated. This is also provided in the UK EI publication reference [8] for systems with average OIW concentrations ≥880 mg/l. For systems with lower OIW concentrations the factor provided in reference [8] is 0.0225 kg/m^3 water treated. The US EPA AP-42 [16] provides a factor of 0.6 kg/m^3 water treated.

In the original derivation of the factor of 0.111 kg/m^3 water treated, the values in the Litchfield algorithm for water, ambient and 10% distillation point temperatures were 48.9°C, 18.3°C and 148.9°C respectively, giving a volume loss of 12.6%. At Site 1, the conditions were very different to these: the average water temperature over the five day period was 26.5°C, with a range of 24°C to 29°C and the average ambient temperature was 16.5°C. The average value of the 10% distillation point of the free oil from the pre-separator was 210°C (range: 178°C to 224°C). This is almost 40% greater than the one used in deriving the factor in CONCAWE report 1/09. Either the residence time of the oil in the sewer was sufficiently long for it to have lost its light ends before entering the separator system or the refinery operating practices limit the amounts of light product entering the drains. An alternative explanation is that the 10% DP temperature used in deriving the factor was not representative of current conditions, having been obtained from test data at US refineries in the 1980s.

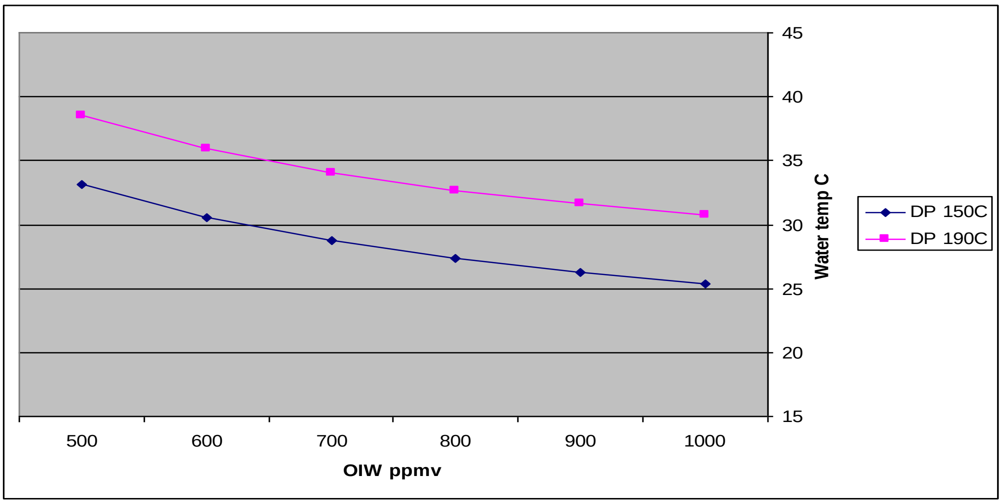
The combination of lower water temperature and higher 10% distillation temperature at Site 1, compared to Litchfield’s original test conditions, resulted in his algorithm providing negative loss values for the first two days of the campaign. Results for the other three days ranged from zero to 3.1% volume loss, the latter being on the day that the value of the 10% distillation point was at its lowest at 178°C. These values indicate that for some days of the campaign at Site 1 the Litchfield algorithm was outside of the limits of its applicability.

The calculation of the mass emissions from the volume % loss values provided by Litchfield requires a value for the liquid density of the evaporated hydrocarbons. This was determined from the vapour speciation provided by the GC-MS analyses. The values varied from 748 kg/m^3 at the sewer mouth/inlet channel to 770 kg/m^3 at the API separator, demonstrating that the emitted vapours became heavier as the water travelled from the inlet to the outlet of the system. The average from all of the samples taken was 758 kg/m^3. By comparison the default value provided in CONCAWE report 1/09 is 660 kg/m^3. This confirms that the volatility of the oil present in the system was lower than had previously been considered “typical” for European refinery waste water systems.

Applying the Litchfield % loss values resulted in estimated daily average VOC emissions ranging from zero (where negative values were set to zero) to 2.2 kg/h, with an average of 1.6 kg/h.

The UK Energy Institute factor of 0.0225 kg/m^3 water treated, for systems with average OIW concentrations less than 880 mg/l, was also derived using the Litchfield algorithm. However, providing this factor as a ceiling for VOC loss if the OIW concentration is less than 880 mg/l is too simplistic because the emissions are also dependent on the water temperature and the 10% distillation point temperature. **Figure 12** shows the values of OIW concentration and water temperature, for two different 10% distillation point temperatures, which provide VOC emissions of 0.0225 kg/m^3 water treated using the Litchfield algorithm (at an air temperature of 10°C).

Figure 12 Relationship between OIW concentration and water temperature to provide a VOC loss of 0.0225 kg/m^3 of water treated



The average OIW concentration at the inlet of the system was ≤560 mg/l. As the average water and the 10% distillation point temperatures were 26.5°C and 210°C respectively, **Figure 12** indicates that the EI factor could be used at Site 1.

The average water flow through the system during the test period was 250 m^3/h. The three factors considered, therefore, gave the following VOC emission estimates: US EPA AP-42 [16] 141.9 kg/h, CONCAWE [5] 26.3 kg/h and EI [8] 5.3 kg/h.

The method for estimation set out in VDI publication 2440 [24], uses the exposed water area of the system. This method provides a fixed value for the system, independent of any improvement that the site may make in reducing the amount of oil entering the drains. The estimate obtained by this method was 12.4 kg/h.

Modelling of emissions was undertaken using WATER9 and TOXCHEM+. These models require individual component concentrations and thus additional samples were taken from the inlet to the pre-separator and the forebay for detailed compositional analyses. There was, for each sample, a difference between the total concentration of the components nominated in the models and the corresponding OIW concentration. To compensate, the delta was assigned to dodecane (C12) and icosane (C20) in equal proportions. Sensitivity studies were undertaken and this assignment had little impact on the model results.

The EPA refinery wastewater emission tool (RWET) [15] was also used. This tool requires the input of concentration data for 22 individual components classified in the USA as hazardous air pollutants (HAPs) plus n-butane. It permits other compounds to be nominated to represent the difference between the sum of the concentrations of these compounds and the total OIW concentration. For this exercise, heptane, octane, dodecane and icosane were assigned as these compounds. Unlike the other two models the RWET was very sensitive to the ratio assigned to the C12 and C20 components input to make up the difference between the total concentration of the hydrocarbons nominated in the models and the measured total OIW concentration. This ratio was set to ensure that the estimated emission of C10 and heavier hydrocarbons as a fraction of the total was equal to that determined by the GC-MS speciation survey.

The models are primarily designed to calculate the emissions using the Henry coefficients of the speciated substances with a default approach to correct for free oil coverage. Correspondingly, the models do not use vapour-liquid equilibrium data for the substances contained in the free oil layer. They are expected, therefore, to be limited in their capability for dealing with basins covered by more than a thin free oil layer.

The models were, therefore, used to estimate the emissions from the components of the separator system which were covered only by a very thin oil layer or oil sheen i.e. the forebay and API basin, using the analytical data from the forebay samples. For these components, the following average emission rates were estimated: WATER9 0.1 kg/h, TOXCHEM+ 0.2 kg/h and EPA RWET 1.8 kg/h. Using the value from the application of the Litchfield method for the sewer outlet/pre-separator of 1.6 kg/h provides a range of total emission rates using the models from 1.7 kg/h to 3.4 kg/h.

The DIAL was used over the five day campaign to provide estimates of emission fluxes derived from measured hydrocarbon concentrations and wind field data. The wind speed and direction data were derived from a fixed mast in the undisturbed wind field.

The DIAL methodology provided calculated estimates of fluxes from both upwind sources and downwind of the system. For the latter, scans were made downwind of the entire system as well as of sub-components of the system. Consistent very low fluxes (0 to 0.1 kg/h) were estimated for upwind sources from a number of different wind directions. There were differences in the estimates for the individual sub-components of the system made during the campaign, possibly because of the temporal variations in OIW concentrations. An alternative reason may be that the DIAL scan lines were made directly across the facility in order to try to differentiate between the emission sources and thus were too close to the sources to provide clear demarcation of the plumes.

The DIAL provided six periods during the five day campaign when scans were downwind of the entire system. The wind directions for these periods were varied. The VOC emission rates determined for these periods ranged from 17.3 kg/h to 23.9 kg/h, with an average of 21.1 kg/h.

Due to the wide range of estimated emission fluxes obtained using the emission factors, models and DIAL, a review of the maximum probable VOC losses from the separator system was undertaken. Long term refinery data indicate that the average amount of oil recovered in the system has been between 70 kg/h to 100 kg/h. Records of refinery operations over the campaign period did not identify any reasons why the separator system should have been operating at abnormally high inlet oil loading. The upper value of 100 kg/h was therefore assumed as the average rate of recovered oil for the period of the campaign. VOC emissions occur due to evaporation from the oil layer and from volatilisation of the VOCs in the water phase. The maximum values of these during the campaign, calculated using the Litchfield algorithm and the TOXCHEM+ model, were 3.6% and 1.3% respectively. The maximum assumed total % volume loss of the inlet VOCs, therefore, was 4.9% volume being the sum of these two values. The average oil mass flow rate into the pre-separator was ≤140 kg/h, comprising free oil <100 kg/h from historic data and dissolved/emulsified oil from measured OIW concentration data of 40 kg/h. During the campaign, the average oil density was 0.86 kg/l and the average liquid density of the evaporated VOCs was 0.76 kg/l. Based on mass balance, measurements and the use of an empirical algorithm, the best engineering estimate of the maximum VOC emission rate during the campaign period is thus = 0.049*140*0.76/0.86, being equal to 6.1 kg/h.

Comparison of this maximum VOC flux rate with that computed using the AP-42 factor (141.9 kg/h) indicates that the latter is unrealistically high at this site, being of the same order of magnitude as the amount of VOCs entering the system. The CONCAWE factor estimated VOC emissions of 26.3 kg/h, being 4.3 times the maximum value derived above, whereas the estimate using the EI factor (5.3 kg/h) was reasonable at about 0.87 times. The value derived from the VDI factor (12.4 kg/h) is about twice the maximum emission estimate.

WATER9, TOXCHEM+ and the RWET were only used to estimate the emissions from the forebay and API basins. A total emission estimate was derived by combining the model estimates with that obtained using the Litchfield algorithm for the sewer outlet/pre-separator. The total emission value obtained by summing the RWET plus Litchfield estimates indicates an average emission rate of 3.4 kg/h, being 0.56 times the maximum flux rate derived above.

The average DIAL estimate of VOC emissions indicated a flux about 3.5 times the maximum rate derived from engineering judgement. There are a number of sources of uncertainty with the DIAL methodology, as outlined in CONCAWE report 6/08 [4]. A key one is in the calculation to obtain the mass emission flux value. To achieve this, the concentration data across the entire plume cross section have to be multiplied by the wind velocity component perpendicular to the DIAL measurement plane. Constraints for the location of the DIAL facility at Site 1 due to the plant and storage surrounding the separator system meant that scan lines had to be made relatively close to the basins and so the plumes were possibly closer to ground level than was optimal for this estimation method. Further work should be undertaken to model the plumes for this location to ascertain what impact the below-grade source location had on plume shape and dispersion.

5.2. SITE 2

The core components of the system at Site 2 are the same as at Site 1. In addition there is a tilted plate interceptor (TPI) the effluent of which combines with the flow from the main pre-separator in a very small basin, equivalent to the forebay at Site 1. There are also two API separators operating in parallel, one of which is fitted with a tight cover.

The system is gravity fed and in a depression some metres below the surrounding grade level. This permits the water level to be close to the top of the basins. The APIs are situated at a lower level than the pre-separator and forebay and the water streams are fed into these basins above their water levels via weirs or open pipes. There was no problem, therefore, in obtaining representative water samples at Site 2.

At Site 2 there are a number of streams entering the system and the flows of water through these into the pre-separator and the TPI are impossible to determine on a routine basis. Although the flow into the downstream secondary DAFs is measured, it includes an additional stream with low OIW concentration levels coming from the sour water stripper (SWS) which is added to the effluent from the API separators. During the campaign the flow of the water from the SWS was estimated by mass balance. Furthermore, the split between the TPI and pre-separator flows had to be derived from a conductivity balance between the two streams and the combined flow to the API separators.

The OIW concentrations were measured at two hourly intervals (as for Site 1). Very significant variations were observed, particularly at the inlet to the TPI. The stream to this separator includes tank drains which are intermittent sources of oil with potentially large variations in the quantity of oil entering the sewer system. The range of the TPI inlet OIW concentration was from 14 mg/l to 22,000 mg/l, with averages of 14,000 mg/l on the first day and 2500 mg/l over the five day period of the field trial. If the first day when the maximum OIW concentrations occurred was excluded, the average for the last four days was 500 mg/l. By comparison the range for the pre-separator inlet over the five day campaign period was lower at 36 mg/l to 6200 mg/l, with an average of 940 mg/l. The average OIW concentration over this same period at the convergence of the streams from the TPI and pre-separator inlet into the API separators was ~100 mg/l.

The temporal variations in the OIW concentrations demonstrate the difficulties with using spot samples to generate long term average emissions from waste water systems.

The average ambient temperature over the five day campaign was 30°C, with the average water temperatures at the inlets to the pre-separator and TPI being 31°C and 44°C respectively. The average 10% distillation point temperatures of the free oil sampled from these system components were 220°C and 138°C. These show the significant difference in the constituents of the oil in the two main streams entering the system.

The values of these parameters are well within the range of the Litchfield algorithm. The algorithm was used to estimate the emissions from the system components with a free oil layer, i.e. the pre-separator and the TPI. The average results for the five day campaign are; pre-separator 4.9 kg/h and TPI 87.7 kg/h. On this basis, the TPI was the major overall emitter. On a daily basis the estimates for the emissions from the TPI were 386 kg/h, 1 kg/h, 3 kg/h, 46 kg/h and 3 kg/h. This shows the impact of the abnormally high peak loading of oil on the TPI on the first day of the campaign. The reason for this is unknown and hence it is not possible to forecast the frequency at which such peaks may occur.

Emission estimates were also made using three factors; those from the US EPA AP-42, CONCAWE and VDI publications [16], [5] and [24]. The estimates were made for the entire 5 day period of the test campaign and for the last four days. During the first day there was a very significant perturbation in the load conditions on the TPI. These load conditions were very much higher than during the last four days when, although there were temporal variations in OIW concentrations, the range in variation as a percentage of the average concentration value was approximately similar to that at Site 1.

The EI factor for separators with inlet OIW concentrations less than 880 mg/l [8] was not considered since the average concentration at Site 2 exceeded that value.

The estimates using the EPA factor in AP-42 [16] gave an average emission of 187 kg/h for the five day period and 233 kg/h for the four day period. The estimate increased, although the oil loading was lower, because of increased volumes of water treated.

The estimates for the two test periods derived using the factor in CONCAWE report 1/09 [5] were 35 kg/h and 43 kg/h respectively. However, this factor applies to system with no covered areas. It results, therefore, in an over-estimate of the emission rate at Site 2 since one separator basin is covered, the other separator basin and the rest of the system components being open. To improve the accuracy of estimation using the CONCAWE method for this situation the factor was pro-rated using the ratio of the area of the covered API to the total surface area. This resulted in revised emission estimates of 20.4 kg/h and 25.3 kg/h taking account of the assumed efficiency of the tightly sealed API cover of 97% [5].

The VDI publication [24] provides factors related solely to the total water surface area covered by free oil. The emission estimate using the VDI emission factor was, therefore, a constant value of 11 kg/h for the period of the two API separators being in operation. Unlike the factors related to waste water treated, the VDI method permits both covered and uncovered API separators to be accounted for separately.

In practice the only factor that can be used at the refinery to determine the annual VOC emissions from the primary waste water treatment system is that published by the VDI, as it is not possible to determine the quantity of water treated.

Following a review of the data requirements of the models used at Site 1 and their applicability, only the US EPA Refinery Wastewater Emissions Tool (RWET) was used for the uncovered separator basin at Site 2 and the result used to calculate the emissions from the covered basin. The average emission rate for the two API separators was estimated to be 4.6 kg/h. Summing this estimate with those for the pre-separator and TPI derived using the Litchfield correlation provides an average total flux estimate for the system over the five day campaign of 97.2 kg/h. The average for the last four days of the campaign was 23.3 kg/h. These two values are deemed to be the best estimates of the emissions from the system, being based on measurements, e.g. of OIW concentrations in fully representative water samples, and the use of an empirical algorithm.

At Site 1 there were few structures surrounding the waste water treatment system permitting the NPL DIAL to undertake upwind scans for a wide range of wind directions. The situation at Site 2 was very different, with the system enclosed in a depression surrounded on two sides by high, relatively solid structures (e.g. process plant, storage tanks, pipe racks) which presented significant obstructions to the wind flow, especially in the prevailing direction. On the third side there was a steep embankment. This resulted in very restricted locations for the DIAL van to operate, with an inability to undertake upwind scans for some quadrants.

The initial analyses of the scan results produced some very high emission estimates. In order to assess these, in the first case the flows of oil through the system were estimated for some of those scans providing the maximum emission estimates. A number of the influent oil mass flow rates were found to be less than the estimated VOC emission rates. Further analyses were made for four periods during the five day campaign when scans were downwind of the entire system. The wind directions for these periods were either east or west/north west. The VOC emission rate estimates for these periods were 660.3 kg/h, 190.2 kg/h, 154.1 kg/h and 72.7 kg/h. The approximate quantities of oil entering the system during these periods were 349 kg/h, 321 kg/h, 27 kg/h and 49 kg/h respectively. It can be seen that there is no correlation between the rate of oil entering the system and the estimated emissions.

The measurements were for wind directions in which the system is sheltered by the structures on either side of the depression in which it is located. It is very possible that the complex flow in the basin could result in low local wind speeds and vertically advected plumes that would lead to over-estimation of emissions when multiplying the observed plume area and concentration by the reference wind speed. In addition, a detailed review of the downwind scans highlighted the probable presence of upwind sources adding significantly to the measured concentrations. These contributions were not constant in time and spatially not clearly distinct from the plumes associated with the separator system components. Nevertheless it was possible to assume a partition and explore some revisions to the estimated emissions. However, there were insufficient data from the upwind scans to permit the variations in emissions from these sources to be completely accounted for.

The circumstances at Site 2, therefore, prevented the DIAL providing useful emission estimates which could be used in comparison with the other techniques. It is recommended that further work be undertaken to model the wind field within the separator area at Site 2 to gain a better understanding of the limitations of the use of the DIAL technique within such possibly complex plume structures.

6. CONCLUSIONS

This project has enabled a number of different techniques to be used to estimate VOC emissions from the primary oil-water separator systems at two European refineries. The techniques used were remote monitoring (DIAL), models (WATER9, TOXCHEM+ and the EPA Refinery Wastewater Emissions Tool), a simple empirical algorithm to determine VOC loss (Litchfield) and four published emission factors.

6.1. COMPARISON OF EMISSION ESTIMATES

6.1.1. Site 1

A summary of the average results obtained for the five day test period using the different estimation methodologies, plus a best engineering estimate of the maximum emission rate, are shown for Site 1 in **Table 13**.

Table 13 Comparison of average emission estimates at Site 1

Method	Average emission estimate [kg/h]
Remote monitoring with DIAL	21.1 [1]
Models plus empirical algorithm [2]	
WATER9 + Litchfield	1.7
TOXCHEM + Litchfield	1.8
RWET + Litchfield	3.4
Emission factors [3]	
US EPA AP-42 [16] (0.6 kg/m^3 water treated)	141.9
CONCAWE [5] (0.111 kg/m^3 water treated)	26.3
UK EI [8] (0.0225 kg/m^3 water treated)	5.3
VDI [24] (20 g/m^2/h)	12.4
Best engineering estimate of maximum emission rate based on mass balance, measurement and empirical algorithm.[4]	6.1

Table notes:

1. Downwind scans of entire system only made on days 2, 3, 4 and 5
2. Estimation of emissions using the models was made solely for the basins covered in an oil sheen. The emission estimate for the pre-separator was derived from the Litchfield algorithm. The sum of these provides the estimate for the total system.
3. Average oil in water concentration during campaign was ≤ 560 mg/l
4. Based on the maximum historic rate of free oil recovery and the measured concentrations of dissolved and emulsified oil in the body of the water. Maximum vapour losses calculated using the Litchfield algorithm and the TOXCHEM+ model. These are supported by measurements of the volatility and density of the free oil and liquid density of evaporated VOCs.

Comparison of the results from the application of the different methodologies with the best engineering estimate of emissions indicates the closest agreements for Site 1 are the estimate using the UK EI factor and the combined RWET/Litchfield computations.

6.1.2. Site 2

A summary of the results obtained using the different estimation methodologies are shown for Site 2 in **Table 14**.

Table 14 Comparison of average emission estimates at Site 2

Method	Average emission estimate kg/h	
	5 days	Excluding day 1[1]
Remote monitoring with DIAL	- [2]	193.4
Model plus empirical algorithm [3] RWET + Litchfield	97.2	23.4
Emission factors		
US EPA AP-42 [16] (0.6 kg/m^3 water treated)	187.3	232.8
CONCAWE [5] (0.111 kg/m^3 water treated)	34.7	43.1
CONCAWE adjusted for partial coverage system	20.4	25.3
VDI [24] (20 g/m^2/h)	11.1	11.1

Table notes:

1. VOC input loadings to the TPI and pre-separator on day 1 averaged 2500 kg/h and 120 kg/h respectively compared to averages of 136 kg/h and 93 kg/h during days 2 to 5. The average TPI influent oil in water concentration on day 1 was 14,000 mg/l and for the entire campaign was 2500 mg/l. For days 2 to 5 it averaged 500 mg/l. The average pre-separator influent oil in water concentration over the entire five days was 940 mg/l.
2. Downwind scans of entire system only made on days 3, 4 and 5.
3. Estimation of emissions using the RWET was made solely for the uncovered API separator basin which had an oil sheen. The emissions from the covered separator were estimated using a value for emission reduction of 97%. The emission estimates for the pre-separator and TPI were derived from the Litchfield algorithm. The sum provides the estimate for the total system. For the two periods of the campaign considered, these values are deemed to be the best estimates of the emissions from the system, being based on measurements, e.g. of OIW concentrations in fully representative water samples, and the use of an empirical algorithm.

Comparison of the results from the application of the different methodologies with the best engineering estimate of emissions over the five day campaign indicate that it falls between the EPA AP-42 factor and the CONCAWE factor. For the period in which a significant perturbation in oil loading occurred the AP-42 factor provides a conservative emission estimate ceiling value. For the period in which the oil loading was more stable the CONCAWE factor adjusted to account for the partially covered area of the system at Site 2 is close to the expected emissions. Of the factors, the adjusted CONCAWE factor, therefore, is considered to provide the most representative estimate of the system emissions during the more stable period of oil loading.

6.2. REMOTE MONITORING

The NPL DIAL facility was used at both sites. At each, particularly Site 2, the DIAL methodology provided estimates that engineering judgement considered too great a proportion of the measured, or derived, VOC loading on the system. A major source of uncertainty with the DIAL methodology is in the calculation to obtain the mass emission flux value. This requires the concentration data across the entire plume cross section to be multiplied by the wind velocity component perpendicular to the DIAL measurement plane. At Site 2 it is very likely that there were complex air flows in the vicinity of the separator system due to its surrounding topography. These can have resulted in higher uncertainty in the multiplication of the observed plume area and concentration by the reference wind speed than for measurements made in more open areas.

Another source of uncertainty arises from the presence of upwind sources particularly if these are time varying or physically close to the source being monitored. At Site 1, there was no evidence that upwind sources affected the results. At Site 2, however it is certain that the concentrations measured were affected by local time-varying sources giving rise to plumes not clearly distinct from the plumes associated with the separator system components. Emissions from these sources, therefore, are likely to have added significantly to the measured concentrations.

The need to scan within the separator depression at Site 2 was the result of constraints on the location of the DIAL facility and also on the range of potential scan directions due to the surrounding plant and storage. The latter meant that it was not possible to undertake upwind scans covering all wind directions at Site 2. Similar constraints at Site 1 meant that scan lines had to be made relatively close to the basins and so the plumes were possibly closer to ground level than was optimal for this technique.

It is recommended that further work be undertaken to model the wind field within the separator area at Site 2 to gain a better understanding of the limitations of the use of the DIAL technique within complex plume structures. Work could also be undertaken to model the shape and dispersion of plumes from below-grade source locations such as the basins at Site 1.

6.3. MODELS AND ALGORITHMS

At Site 1 it was very difficult to obtain a representative sample of the water at the inlet to the system to determine accurately the total oil entering the system. This information was required to permit emission estimation using either the Litchfield algorithm or the models. Moreover, the complex models, such as WATER9, also required extensive sampling and analysis campaigns to provide VOC speciation data.

Both Litchfield and the models provided spot estimates. Both sites, particularly Site 2, demonstrated that wide temporal variations occurred in the oil-in-water concentration values. Thus the results of methods using spot samples cannot accurately be extrapolated to provide accurate annual averages, unless sampling and analysis efforts are repeated at regular intervals over the year.

The Litchfield algorithm provides estimates of VOC loss based on ambient, water and 10% distillation point temperatures. The applicable ranges for these may make the use of the algorithm inappropriate where the temperature of effluent water discharges are restricted and/or the volatility of the free oil is low due to refinery practices or long residence times in the sewer system.

In addition, there are concerns that models, such as WATER9, have limited capacity to address basins covered by a free oil layer.

Compared to WATER9 the EPA Refinery Wastewater Emission Tool (RWET) was considered more user-friendly, having chemical properties already provided for a number of the components that were found in the streams at both sites. However, it requires other components to be added where these are not already specified in the model and also to make up the difference between the total concentration of the specified components and the total measured OIW concentration. For these campaigns dodecane and icosane were added to compensate for this delta. The RWET is very sensitive to the concentrations of these heavier components. For the use of the RWET it is recommended to carry out the speciation of the hydrocarbons in the water at least up to C12.

Where separator system basins are covered by free oil and refineries have data on the quantity of oil recovered from the separator system, the Litchfield algorithm can be used to estimate annual VOC emissions. Regular measurements of ambient, water and 10% distillation point temperatures and oil density would be required to permit the computation of the annual average VOC loss from the oil recovered.

In the case of a separator system consisting of basins covered by a free oil layer and basins only covered by an oil sheen this method can be enhanced by using a combination of Litchfield for the former and a mass transfer model for the latter. The models, however, require representative samples to be taken for compositional analysis.

These approaches can be used either as a basis for an annual emission estimate if regular sampling and compositional analysis is undertaken over the year or to verify the validity of estimates obtained by using emission factors.

To compute mass emissions rates from the volume loss determined by the Litchfield algorithm requires a value for the liquid density of the evaporated VOCs. A default value is provided in CONCAWE report 1/09 [5] of 660 kg/m^3. At Site 1 the average value determined from the GC-MS speciation survey was 758 kg/m^3. At Site 2 the average value for the VOCs emitted from the TPI was 735 kg/m^3 and from the pre-separator was 744 kg/m^3. It is recommended that the default value is revised to 745 kg/m^3, being the average of these three values, when the CONCAWE report is next updated.

6.4. EMISSION FACTORS

The factor published by the VDI in reference [24] is based on water surface area and provides a fixed emission value for the system. Like the emission factors based on waste water flow rate it cannot reflect any improvement that the site may make in reducing the amount of oil entering the drains. Where it is also not possible to determine the quantity of oil recovered per annum, the use of the VDI factor is the only practical way to provide an annual emission estimate.

Three published emission factors based on water flow were used to provide estimates for the total separator systems at the two sites.

The factor provided in the US EPA AP-42 publication [16] of 0.6 kg/m^3 water treated gives unreasonably high estimates unless the average OIW concentration is very high (e.g. >3500 mg/l) or very significant perturbations in the oil loading on the system can occur on a frequent basis. In these circumstances the factor can provide a conservative emission estimate ceiling value.

The other two factors are provided in CONCAWE report 1/09 [5] and in UK Energy Institute publication [8]. In the latter two factors are provided. For OIW concentrations ≥880 mg/l, the same factor is given as in CONCAWE report 1/09 (0.111 kg/m^3 water treated). However, the UK EI publication also provides an emission factor (0.0225 kg/m^3 water treated) which applies where the average OIW concentration is less than 880 mg/l (~1000 ppmv). Care has to be taken with this factor as it is too simplistic to relate emissions solely to OIW concentration because the emissions are also dependent on the water temperature and the 10% distillation point temperature. Moreover, although the CONCAWE factor is generally considered applicable to all situations, it too was derived from the Litchfield algorithm. This indicates that for a water temperature of 35°C and 10% distillation point of 210°C it is limited to average OIW concentrations of <3500 mg/l.

During the two field trials there were periods of time when the average influent oil in water concentrations were within the ranges of application of the three factors. At Site 1 during the whole campaign the average OIW concentration was less than 880 mg/l and so within the range of the EI factor. At Site 2, during test days 2 to 5 the average concentration was between 880 and 3500 mg/l and thus the CONCAWE factor was applicable. At Site 2 the very heavy oil loading on day 1 resulted in the average OIW concentration over the entire 5 day period being at the bottom end of the range for the AP-42 factor. For each of these periods the appropriate factor is deemed, by comparison with the best engineering estimates, to have provided an adequate estimate of the VOC emissions.

Where it is not feasible to measure influent OIW concentrations it is necessary to establish which of the factors is applicable. Where the volume of oil recovered is known, the average OIW concentration in the inlet stream can be determined. Otherwise, a qualitative assessment of the average input conditions to the waste water treatment system and review of the operating practices at the refinery need to be undertaken to determine the potential range of the influent OIW concentration and thus identify which factor to use.

The accuracy of the estimation can be improved by undertaking regular measurements of the temperatures of the water and the 10% distillation point and density of the free oil in the system. These would permit a site to use the Litchfield algorithm to calculate the average mass loss from the influent oil. An estimate of annual emissions can then be determined using an average value for the influent OIW concentration determined from a qualitative assessment.

Where the quantity of water treated can be determined, consideration can be given to improving further the emission estimate by undertaking periodic emission calculations with a model using compositional data obtained through sampling of the inlet water to those basins which are covered only by a sheen of oil. The resultant average emission estimate is then summed with the average result obtained from using the Litchfield correlation. Significant analytical effort is required as speciation data for the VOC components in the water phase are needed up to and including C12. A review of the results of a number of emission calculations can be used to establish the frequency of sampling depending on the variations in the estimates derived from the model. Moreover, the additional effort to improve the VOC inventory may not be considered beneficial where the emission estimate for the VOCs in the water phase is relatively small and possibly within the error band for the Litchfield calculations

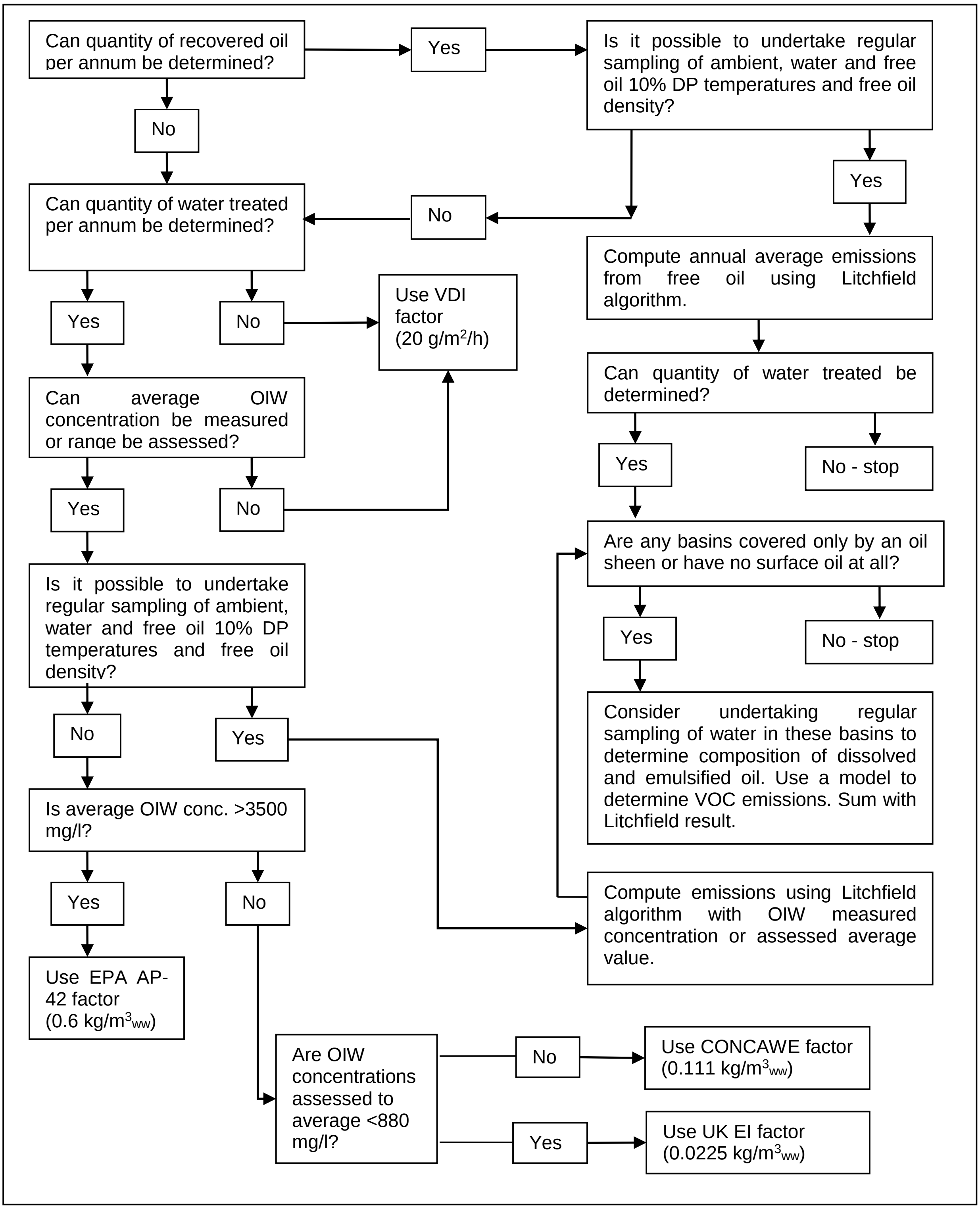
6.5. DECISION TREE

A decision tree for supporting the selection of the methodology used by refineries in their estimation of annual VOC emissions from uncovered primary oil-water separator systems based on the results from the two campaigns is provided in **Figure 13**.

Where the complete system has a tightly sealed cover installed, the emissions can be determined by assuming a vapour retention efficiency of 97% [5]. For other types of cover an efficiency of 90% can be assumed [24].

Where a system is only partially covered, the emissions estimated for an uncovered system can be pro-rated taking into account the fraction of area of the system that is covered and the vapour retention efficiency of the type of cover installed.

Figure 13 Decision tree for guidance in determining emissions from uncovered systems



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8. GLOSSARY

BTEX	Benzene, toluene, ethylbenzene, and xylenes
DAF	Dissolved air flotation
DIAL	Differential absorption LIDAR
DP	Distillation point
EI	Energy Institute
E-PRTR	European Pollutant Release and Transfer Register
FTIR	Fourier transform infrared
GC-FID	Gas chromatography–Flame Ionisation Detector
GC-MS	Gas chromatography–mass spectrometry
HAP	Hazardous Air Pollutants
LIDAR	Light Detection and Ranging
MEK	Methyl ethyl ketone
MTBE	Methyl tert-butyl ether
NECD	National Emission Ceiling Directive
NPL	UK National Physical Laboratory
OIW	Oil in Water (comprising free and suspended oil and dissolved hydrocarbons)
OP-FTIR	Open-path Fourier transform infrared
RWET	Refinery wastewater emissions tool
SWS	Sour water stripper
TPI	Tilted plate interceptor
UK	United Kingdom
US	United States
US EPA	United States Environmental Protection Agency
VDI	Verein Deutscher Ingenieure - Association of German Engineers
VOC	Volatile Organic Compound

9. REFERENCES

1. CONCAWE (2005) Air pollutant emission estimation methods for EPER and PRTR reporting by refineries. Report No. 9/05. Brussels: CONCAWE

2. CONCAWE (2005) Air pollutant emission estimation methods for EPER and PRTR reporting by refineries (revised). Report No. 9/05R. Brussels: CONCAWE

3. CONCAWE (2007) Air pollutant emission estimation methods for E-PRTR reporting by refineries. Report No. 3/07. Brussels: CONCAWE

4. CONCAWE (2008) Optical methods for remote measurement of diffuse VOCs: their role in the quantification of annual refinery emissions. Report No. 6/08. Brussels: CONCAWE

5. CONCAWE (2009) Air pollutant emission estimation methods for E-PRTR reporting by refineries. Report No. 1/09. Brussels: CONCAWE

6. CPPI (2005) Code of practice for developing an emission inventory for refineries and terminals, Rev. 9. Ottawa: Canadian Petroleum Products Institute

7. Eklund, B. (1992) Practical guidance for flux chamber measurements of fugitive volatile organic emission rates. *Journal Air & Waste Management* *42*,*12*

8. EI (2010) Protocol for the estimation of VOC Emissions from petroleum refineries and gasoline marketing operations. London: Energy Institute

9. EI (2011) VOC emissions from refinery effluent water systems. London: Energy Institute

10. EPA (1985) VOC emissions from petroleum refinery wastewater systems – background information for proposed standards. EPA-450/3-85-001a. North Carolina: US Environmental Protection Agency

11. EPA (1990) Industrial wastewater volatile organic compound emissions – background information for BACT / LAER determinations. EPA-450/3-90-004. Cincinnati: US Environmental Protection Agency

12. EPA (1994) Air emissions models for waste and wastewater. EPA-453/R-94-080A. North Carolina: US Environmental Protection Agency

13. EPA (1995/8) Compilation of air pollutant emission factors. Vol 1: Stationary point and area sources. Chapter 4.3: Waste water collection, treatment and storage. Publication AP-42. North Carolina: US Environmental Protection Agency

14. EPA (2006) Emissions factors software and tools. WATER9 version 3.0. North Carolina: US Environmental Protection Agency http://www.epa.gov/ttn/chief/software/water/water9_3/index.html

15. EPA (2011) Emission estimation protocol for petroleum refineries – version 2.1.1. North Carolina: US Environmental Protection Agency

16. EPA (1995/2008) Compilation of air pollutant emission factors. Vol 1: Stationary point and area sources. Chapter 5.1: petroleum refining. Publication AP-42. North Carolina: US Environmental Protection Agency

17. EPA (2011) Refinery wastewater emission tool. North Carolina: US Environmental Protection Agency http://www.epa.gov/ttn/chief/efpac/esttools.html

18. EU (2000) Commission Decision 2000/479/EC of 17 July 2000 on the implementation of a European pollutant emission register (EPER) according to Article 15 of Council Directive 96/61/EC concerning integrated pollution prevention and control (IPPC). Official Journal of the European Communities No. Ll92, 28.07.2000

19. EU (2006) Regulation (EC) No. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC. Official Journal of the European Union No. L33, 04.02.2006

20. EU (2001) Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001 on national emission ceilings for certain atmospheric pollutants. Official Journal of the European Communities No. L309, 27.11.2001

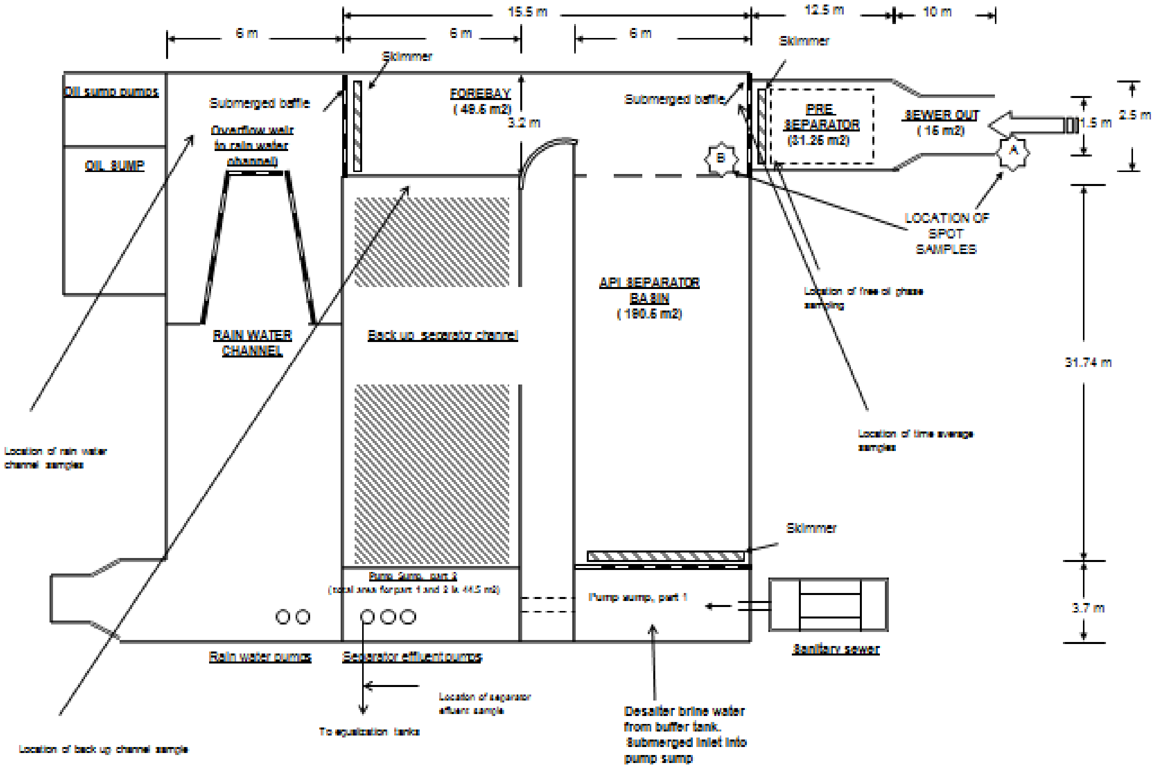
21. EU (2003) Reference document on best available techniques for mineral oil and gas refineries. European IPPC Bureau

22. Litchfield, D. K. (1971) Controlling odors and vapors from API separators. *Oil & Gas Journal Nov 1, 60-62*

23. Soyars, B. and Hopperton, M. (2010) Defensible emission calculations for petroleum refinery wastewater systems. National Petrochemical & Refiners Association Environmental Conference, San Antonio, September 20 - 21, 2010

24. VDI (2000) Emission control mineral oil refineries. Report No. 2440. Düsseldorf: VDI

APPENDIX I SITE 1 PRIMARY OIL-WATER SEPARATOR SYSTEM AREA DETAILS



PRESEPARATOR + SEWER OTLET AREA = 51.25 m2
API BASIN+ FOREBAY + PUMP SUMP AREA = 285 m2

APPENDIX II ANALYTICAL DATA: SITES 1 AND 2

Table 15 Site 1 – Oil in water concentration, mg/l. Samples taken from water below free oil layer

Location	Type of sampling	Time of sampling	"DIAL day"				
			Day 1	Day 2	Day 3	Day 4	Day 5
Sewer outlet	Spot	Start of day	210	120	41	420	380
	Spot	+ 2 hours	110	170	60	260	140
	Spot	+ 4 hours	74	120	35	54	140
	Spot	+ 6 hours	55	70	100	150	470
Forebay	Average	-	160	120	260	110	200
	Spot	Start of day	190	810	43	190	340
	Spot	+ 2 hours	140	54	51	350	110
	Spot	+ 4 hours	40	130	37	47	180
	Spot	+ 6 hours	43	39	56	110	200
Rainwater basin	Spot	-	740	410	510	330	290
API outlet	Spot	-	330	220	110	230	86

Note: Speciation and water flow rate for Site 1 provided in Appendix IV.

Table 16 Site 1 – Density (ρ), kg/l and 10% distillation point (DP) °C of oil sampled from free oil layer

Location	Time of sampling	Parameter	"DIAL day"				
			Day 1	Day 2	Day 3	Day 4	Day 5
Pre-separator	+ 3 hours	ρ	0.86	0.866	0.819	0.862	0.876
		10% DP	214.0	213.3	215.6	-	223.7
	+ 7 hours	ρ	-	0.868	0.915	0.862	0.929
		10% DP	-	217.0	-	178.4	-
Rainwater basin	-	10% DP	-	-	227.8	228.9	-
API basin	-	ρ	0.887	-	-	-	-
	-	10% DP	241.3	-	-	-	-
Oil sump	-	ρ	0.864	-	-	-	-
	-	10% DP	229.6	-	-	-	-

Table 17 Site 1 – Water and ambient air temperature data, °C

Location	Time of sampling	"DIAL day"				
		Day 1	Day 2	Day 3	Day 4	Day 5
Sewer outlet	Start of day	22.4	23.9	24.4	29.1	29.7
	+ 2 hours	24.8	24.4	25.7	27.8	29.0
	+ 4 hours	23.7	25.5	31.9	27.2	27.9
	+ 6 hours	24.8	25.1	31.5	24.9	27.0
Forebay	Start of day	21.8	24.5	24.2	28.2	29.0
	+ 2 hours	24.1	24.3	26.2	28.9	29.4
	+ 4 hours	25.1	25.3	33.5	27.5	28.3
	+ 6 hours	24.8	26.1	30.8	27.5	24.9
Rainwater basin	-	-	20.0	20.4	20.5	-
API outlet	-	-	-	-	-	26.4
Ambient	Start of day	9.0	7.7	9.6	20.8	25.0
	+ 2 hours	10.0	8.3	11.5	20.3	23.6
	+ 4 hours	12.0	9.7	14.0	18.0	20.2
	+ 6 hours	13.0	12.0	14.8	16.0	18.6

Table 18 Site 2 – Total oil in water concentration, mg/l

Location	Time of sampling	"DIAL day"				
		Day 1	Day 2	Day 3	Day 4	Day 5
Pre-sep inlet	Start of day	1700	200	55	43	310
	+ 2 hours	2200	68	320	520	120
	+ 4 hours	6200	2300	2600	85	36
	+ 6 hours	-	810	110	190	47
TPI inlet	Start of day	1000	94	840	640	14
	+ 2 hours	16000	650	25	820	52
	+ 4 hours	22000	240	220	48	110
	+ 6 hours	-	110	530	3700	180
Forebay	Start of day	24	180	22	42	400
	+ 2 hours	-	170	69	58	38
	+ 4 hours	37	210	65	51	83
	+ 6 hours	-	150	260	38	85
Outlet covered API	+ 3 hours	7	410	-	-	65
Outlet uncovered API	+ 3 hours	-	37	130	76	160

Table 19 Site 2 – Water and ambient temperature data, °C

Location	Time of sampling	"DIAL day"				
		Day 1	Day 2	Day 3	Day 4	Day 5
Pre-sep inlet	Start of day	30.2	30.0	29.0	29.0	31.0
	+ 2 hours	30.2	31.6	31.3	30.8	28.3
	+ 3 hours	31.9	33.2	31.4	31.6	30.5
	+ 4 hours	32.2	32.2	31.4	30.2	29.6
	+ 6 hours	-	31.6	32.1	31.0	29.4
TPI inlet	Start of day	47.0	44.8	38.1	42.6	44.4
	+ 2 hours	46.4	45.3	43.5	44.8	41.2
	+ 3 hours	46.4	47.0	43.7	41.0	36.1
	+ 4 hours	45.5	47.8	44.9	45.3	40.5
	+ 6 hours	-	44.8	45.6	55.4	41.1
Forebay	Start of day	43.4	40.3	34.2	35.8	42.5
	+ 2 hours	45.0	41.5	36.5	37.5	39.9
	+ 3 hours	43.7	43.4	36.6	37.1	38.6
	+ 4 hours	46.6	43.1	37.4	37.9	40.2
	+ 6 hours	-	43.6	37.5	45.7	41.2
Outlet covered API	+ 3 hours	38.2	36.8	-	-	33.6
Outlet uncovered API	+ 3 hours	-	41.7	37.5	36.9	37.8
Ambient	Start of day	30.2	27.0	24.7	22.9	29.9
	+ 2 hours	32.9	30.4	28.5	26.6	27.4
	+ 3 hours	32.9	31.3	29.5	28.0	26.1
	+ 4 hours	33.9	32.1	30.4	29.4	25.4
	+ 6 hours	-	33.4	31.6	31.3	23.0

Table 20 Site 2 – Water flow data, m^3/h

Location	Time	"DIAL day"				
		Day 1	Day 2	Day 3	Day 4	Day 5
Pre-sep inlet	Start of day	28	-	-	94	58
	+ 2 hours	30	-	71	100	75
	+ 4 hours	40	-	-	13	42
	+ 6 hours	-	246	260	146	59
TPI inlet	Start of day	146	-	-	64	232
	+ 2 hours	130	-	99	85	295
	+ 4 hours	240	-	192	175	362
	+ 6 hours	-	78	-	207	185
Forebay	Start of day	173	319	236	157	290
	+ 2 hours	160	237	171	185	370
	+ 4 hours	280	257	452	188	404
	+ 6 hours	-	323	386	353	245

Table 21 Site 2 – Density (ρ), kg/l, 10% distillation point (DP), °C and temperature of recovered oil (T_{OIL}), °C

Location	Time of sampling[1]	Parameter	“DIAL day”				
			Day 1	Day 2	Day 3	Day 4	Day 5
Pre-separator	+ 3 hours	ρ	0.937	0.936	0.934	0.863	0.879
		10% DP	247.5	264.0	141.5	99.2	200.5
		T_{OIL}	33.9	32.4	34.1	31.8	29.1
	+ 7 hours[2]	ρ	0.951	0.94	0.884	0.87	0.883
		10% DP	-	-	141.7	228.0	218.0
		T_{OIL}	31.7	33.7	38.4	32.3	28.1
TPI	+ 3 hours	ρ	0.842	0.846	0.811	0.828	0.822
		10% DP	142.9	137.0	88.7	98.4	98.5
		T_{OIL}	41.0	41.4	37.7	38.9	31.8
	+ 7 hours[2]	ρ	0.842	0.847	0.811	0.809	0.822
		10% DP	133.3	138.4	89.9	86.4	96.6
		T_{OIL}	37.6	41.2	39.1	35.8	32.6
Covered API	+ 3 hours	ρ	0.923	0.91	-	-	0.889
		10% DP	306.3	223.2	-	-	157.9
		T_{OIL}	36.8	36.3	-	-	31.6
	+ 7 hours[2]	ρ	0.908	0.921	-	-	0.9
		10% DP	181.0	235.9	-	-	106.0
		T_{OIL}	37.1	35.9	-	-	38.0
Uncovered API	+ 3 hours	ρ	-	0.976	0.892	0.896	0.918
		10% DP	-	97.7	126.9	182.1	127.3
		T_{OIL}	-	41.9	32.6	35.2	36.6
	+ 7 hours	ρ	-	0.979	0.928	0.897	0.9
		10% DP	-	104.2	101.0	175.6	142.9
		T_{OIL}	-	41.4	38.4	36.6	37.6

Table Notes:
1 – Time of sampling after start of “DIAL day”.
2 – Sampling undertaken five hours after start of “DIAL day” on day 1.

Table 22 Site 2 – Oil in water speciation data (concentration in µg/l), "DIAL day" 1

Compound	Pre-sep inlet[1]	Forebay[2]	Compound	Pre-sep inlet	Forebay
Benzene	1100	460	All C9s normal and cyclo.	12	21
Toluene	660	1500	All C10s normal and cyclo.	12	21
Styrene	76	40	Undecane	6	8
Isopropyl benzene	6	32	2,2,4-Trimethyl pentane	6	6
Diethyl benzene	20	14	Methyl-t-butyl ether	3	6
m+p-Xylene	8800	1400	Carbonyl sulfide	70	66
o-Xylene	4400	800	1,3-Butadiene	15	15
Ethyl benzene	270	510	Naphthalene	2000	170
n-Propyl benzene	1	49	Phenol	21	720
p-Isopropyl toluene	39	4	o-Cresol	37	560
sec-Butyl benzene	1	4	m+p-Cresol	41	680
1-Ethyl-2-methyl benzene	120	79	2,6-Dimethyl phenol	10	10
1-Ethyl-3-methyl benzene	370	220	o-Ethyl phenol	10	22
1-Methyl-2-propyl benzene	15	6	2,4+2,5-Dimethyl phenol	20	85
1-Methyl-3-propyl benzene	7	3	m+p-Ethyl phenol	20	70
1,2,4-Trimethyl benzene	2600	280	2,3+3,5-Dimethyl phenol	20	64
1,3,5-Trimethyl benzene	610	66	3,4-Dymethyl phenol	10	41
Methyl ethyl ketone	20	4100	1-Naphthol	50	20
2-Methyl-4-pentanone	35	35	Biphenyl	88	25
3-Methyl-2-butanone	35	35	Tetralin	290	29
Acetone	1700	1100	Monoethanolamine	150	150
C5 (n-pentane)	9	46	Diethanolamine	20	160
All C6s normal and cyclo.	40	40	Acetic acid	43	40
All C7s normal and cyclo.	9	23	Butyric acid	0	0
All C8s normal and cyclo.	12	15	Propionic acid	1	2

Table Notes:
1. Sample taken 3 hours after start of "DIAL day".
2. Sample taken 2 hours after start of "DIAL day"

Table 23 Site 2 – Oil in water speciation data (concentration in µg/l), “DIAL day” 2

Compound	Pre-sep inlet	TPI inlet	Forebay	Compound	Pre-sep inlet	TPI inlet	Forebay
Benzene	1600	7600	4800	All C9s normal and cyclo.	170	12	15
Toluene	2800	3300	3000	All C10s normal and cyclo.	130	45	34
Styrene	4	86	60	Undecane	110	6	6
Isopropyl benzene	42	25	25	2,2,4-Trimethyl pentane	6	6	6
Diethyl benzene	46	45	26	Methyl-t-butyl ether	3	5	5
m+p-Xylene	2500	1000	1100	Carbonyl sulfide	97	125	220
o-Xylene	1200	580	600	1,3-Butadiene	15	15	15
Ethyl benzene	780	420	400	Naphthalene	70	830	450
n-Propyl benzene	81	53	51	Phenol	32	5600	2300
p-Isopropyl toluene	10	4	5	o-Cresol	48	2500	1600
sec-Butyl benzene	14	3	6	m+p-Cresol	53	2400	1400
1-Ethyl-2-methyl benzene	140	110	97	2,6-Dimethyl phenol	10	42	37
1-Ethyl-3-methyl benzene	720	300	270	o-Ethyl phenol	20	59	120
1-Methyl-2-propyl benzene	47	10	9	2,4+2,5-Dimethyl phenol	23	230	180
1-Methyl-3-propyl benzene	16	8	5	m+p-Ethyl phenol	20	110	50
1,2,4-Trimethyl benzene	480	210	260	2,3+3,5-Dimethyl phenol	20	160	170
1,3,5-Trimethyl benzene	130	52	61	3,4-Dymethyl phenol	10	33	35
Methyl ethyl ketone	30	1600	30	1-Naphthol	20	20	20
2-Methyl-4-pentanone	35	35	35	Biphenyl	48	35	17
3-Methyl-2-butanone	35	35	35	Tetralin	130	32	25
Acetone	200	2600	220	Monoethanolamine	150	150	150
C5 (n-pentane)	10	170	76	Diethanolamine	20	20	20
All C6s normal and cyclo.	68	72	53	Acetic acid	50	29	35
All C7s normal and cyclo.	190	9	9	Butyric acid	0.2	0.2	0.2
All C8s normal and cyclo.	130	12	12	Propionic acid	1	2	2

Note: Samples taken 3 hours after start of “DIAL day”.

Table 24 Site 2 – Oil in water speciation data (concentration in µg/l), "DIAL day" 3

Compound	Pre-sep inlet	TPI inlet	Forebay	Compound	Pre-sep inlet	TPI inlet	Forebay
Benzene	450	7300	3800	All C9s normal and cyclo.	39	270	17
Toluene	340	4600	1900	All C10s normal and cyclo.	100	190	55
Styrene	2	350	67	Undecane	100	84	6
Isopropyl benzene	9	41	15	2,2,4-Trimethyl pentane	63	6	9
Diethyl benzene	35	220	17	Methyl-t-butyl ether	3	6	4
m+p-Xylene	560	2600	890	Carbonyl sulfide	96	210	126
o-Xylene	290	1200	450	1,3-Butadiene	15	15	15
Ethyl benzene	19	940	280	Naphthalene	70	1700	390
n-Propyl benzene	10	61	94	Phenol	10	6000	1600
p-Isopropyl toluene	5	8	3	o-Cresol	27	3100	850
sec-Butyl benzene	7	10	3	m+p-Cresol	46	2500	870
1-Ethyl-2-methyl benzene	46	310	60	2,6-Dimethyl phenol	10	47	16
1-Ethyl-3-methyl benzene	330	1200	200	o-Ethyl phenol	10	57	22
1-Methyl-2-propyl benzene	34	24	5	2,4+2,5-Dimethyl phenol	22	190	78
1-Methyl-3-propyl benzene	10	23	3	m+p-Ethyl phenol	20	100	57
1,2,4-Trimethyl benzene	200	490	160	2,3+3,5-Dimethyl phenol	20	110	62
1,3,5-Trimethyl benzene	48	130	40	3,4-Dymethyl phenol	10	37	28
Methyl ethyl ketone	33000	3000	640	1-Naphthol	20	20	20
2-Methyl-4-pentanone	35	35	35	Biphenyl	7	28	5
3-Methyl-2-butanone	35	35	35	Tetralin	12	46	10
Acetone	250	2200	360	Monoethanolamine	150	150	150
C5 (n-pentane)	9	110	110	Diethanolamine	20	20	22
All C6s normal and cyclo.	50	130	64	Acetic acid	12	13	10
All C7s normal and cyclo.	9	240	26	Butyric acid	0.2	0.2	0.2
All C8s normal and cyclo.	28	480	12	Propionic acid	1	1	1

Note: Samples taken 3 hours after start of "DIAL day".

Table 25 Site 2 – Oil in water speciation data (concentration in µg/l), "DIAL day" 4

Compound	Pre-sep inlet	TPI inlet	Forebay	Compound	Pre-sep inlet	TPI inlet	Forebay
Benzene	420	4800	3500	All C9s normal and cyclo.	50	22	36
Toluene	140	900	620	All C10s normal and cyclo.	34	32	36
Styrene	3	31	29	Undecane	120	6	6
Isopropyl benzene	14	13	13	2,2,4-Trimethyl pentane	6	6	6
Diethyl benzene	36	18	15	Methyl-t-butyl ether	2	3	3
m+p-Xylene	650	860	830	Carbonyl sulfide	68	101	80
o-Xylene	350	500	430	1,3-Butadiene	15	15	15
Ethyl benzene	68	230	250	Naphthalene	85	300	210
n-Propyl benzene	22	20	23	Phenol	16	2100	1800
p-Isopropyl toluene	7	2	2	o-Cresol	27	1100	810
sec-Butyl benzene	18	2	3	m+p-Cresol	44	1200	740
1-Ethyl-2-methyl benzene	45	57	48	2,6-Dimethyl phenol	10	22	20
1-Ethyl-3-methyl benzene	280	160	150	o-Ethyl phenol	10	29	21
1-Methyl-2-propyl benzene	32	4	4	2,4+2,5-Dimethyl phenol	35	110	71
1-Methyl-3-propyl benzene	13	2	2	m+p-Ethyl phenol	20	60	47
1,2,4-Trimethyl benzene	240	160	150	2,3+3,5-Dimethyl phenol	20	89	85
1,3,5-Trimethyl benzene	59	36	36	3,4-Dymethyl phenol	10	38	15
Methyl ethyl ketone	690	32000	26000	1-Naphthol	50	20	20
2-Methyl-4-pentanone	35	35	35	Biphenyl	68	9	8
3-Methyl-2-butanone	35	35	35	Tetralin	120	15	18
Acetone	200	1200	940	Monoethanolamine	150	150	150
C5 (n-pentane)	6	62	66	Diethanolamine	20	93	20
All C6s normal and cyclo.	40	40	40	Acetic acid	10	6	15
All C7s normal and cyclo.	25	9	13	Butyric acid	0.2	0.2	0.2
All C8s normal and cyclo.	32	12	12	Propionic acid	1	1	1

Note: Samples taken 3 hours after start of "DIAL day

Table 26 Site 2 – Oil in water speciation data (concentration in µg/l), “DIAL day” 5

Compound	Pre-sep inlet	TPI inlet	Forebay	Compound	Pre-sep inlet	TPI inlet	Forebay
Benzene	500	5000	5000	All C9s normal and cyclo.	36	36	23
Toluene	200	1900	1400	All C10s normal and cyclo.	20	29	28
Styrene	2	860	360	Undecane	6	8	6
Isopropyl benzene	15	32	22	2,2,4-Trimethyl pentane	6	6	6
Diethyl benzene	18	40	25	Methyl-t-butyl ether	2	2	2
m+p-Xylene	880	1600	1300	Carbonyl sulfide	69	112	84
o-Xylene	480	870	690	1,3-Butadiene	15	15	15
Ethyl benzene	190	630	470	Naphthalene	63	1300	750
n-Propyl benzene	30	160	74	Phenol	10	1500	5400
p-Isopropyl toluene	4	4	3	o-Cresol	33	890	2100
sec-Butyl benzene	8	5	1	m+p-Cresol	48	920	1600
1-Ethyl-2-methyl benzene	74	150	90	2,6-Dimethyl phenol	10	19	24
1-Ethyl-3-methyl benzene	220	430	250	o-Ethyl phenol	10	31	40
1-Methyl-2-propyl benzene	10	8	6	2,4+2,5-Dimethyl phenol	20	110	120
1-Methyl-3-propyl benzene	4	7	3	m+p-Ethyl phenol	20	63	97
1,2,4-Trimethyl benzene	270	300	210	2,3+3,5-Dimethyl phenol	20	110	230
1,3,5-Trimethyl benzene	65	83	55	3,4-Dymethyl phenol	10	31	29
Methyl ethyl ketone	3400	130000	13000	1-Naphthol	20	20	20
2-Methyl-4-pentanone	35	35	35	Biphenyl	6	11	6
3-Methyl-2-butanone	35	35	35	Tetralin	15	10	10
Acetone	200	1400	1100	Monoethanolamine	150	150	150
C5 (n-pentane)	6	91	83	Diethanolamine	20	28	20
All C6s normal and cyclo.	40	40	40	Acetic acid	10	9	20
All C7s normal and cyclo.	9	19	13	Butyric acid	0.2	0.2	0.2
All C8s normal and cyclo.	12	28	12	Propionic acid	1	1	1

Note: Samples taken 3 hours after start of “DIAL day

APPENDIX III VAPOUR PHASE SPECIATION RESULTS

Table 27 Site 1 - Results of GC-MS speciation (mean concentration, ppbv), “DIAL day” 1

Compounds	Pre-Separator			
	2m	0.5m	0.1m	Average all sampling points
Isomers C4	15	27	28	12
Isomers C5	188	381	381	182
Isomers C6	535	974	993	215
Isomers C7	236	400	398	79
Isomers C8	412	627	621	151
Isomers C9	362	557	535	145
Isomers C10	615	912	819	280
Isomers C11	242	345	312	121
Isomers Cumene	683	974	892	280
Isomers C10H14 aromatic	100	153	140	46
Benzene	32	43	48	13
Toluene	149	240	226	52
Xylenes + Ethyl benzene	325	497	443	99
MTBE	5	20	20	3
TOTAL	*3897*	*6151*	*5855*	*1677*

Table 28 Site 1 - Results of GC-MS speciation (mean concentration, ppbv), “DIAL day” 2

Compounds	Pre-Separator	Forebay	API Inlet	API Outlet	Pump Sump
Isomers C4	16	5	4	3	29
Isomers C5	242	98	59	66	598
Isomers C6	1056	106	75	85	1155
Isomers C7	249	36	28	34	421
Isomers C8	572	65	59	64	590
Isomers C9	664	74	53	58	650
Isomers C10	871	155	141	141	1748
Isomers C11	318	74	92	95	735
Isomers Cumene	948	215	233	225	1882
Isomers C10H14 aromatic	302	48	58	52	337
Benzene	32	7	6	7	260
Toluene	244	27	16	19	916
Xylenes + Ethyl benzene	387	35	29	31	803
MTBE	6	1	0	2	487
TOTAL	*5906*	*947*	*852*	*882*	*10611*

Table 29 Site 1 - Results of GC-MS speciation (mean concentration, ppbv), “DIAL day” 3

Compounds	Average (4 API basin sampling points without pump sump)	Average (all API basin sampling points)	Sewer mouth
Isomers C4	33	44	119
Isomers C5	823	1188	2853
Isomers C6	1690	2278	8345
Isomers C7	513	698	2358
Isomers C8	968	1116	3688
Isomers C9	733	958	2757
Isomers C10	1490	2017	3967
Isomers C11	640	1016	1166
Isomers Cumene	1726	2657	4257
Isomers C10H14 aromatic	332	481	475
Benzene	53	100	284
Toluene	379	670	1484
Xylenes + Ethyl benzene	485	687	1801
MTBE	6	13	43
TOTAL	*9870*	*13923*	*33597*

Table 30 Site 1 - Results of GC-MS speciation (mean concentration, ppbv), “DIAL day” 4

Compound	Pre-separator (day time)	Sewer outlet + sewer mouth	Sewer mouth	Pre-separator (night time)
Isomers C4	17	16	10	11
Isomers C5	545	212	136	570
Isomers C6	4147	1680	1430	3663
Isomers C7	4874	3473	3464	4658
Isomers C8	8082	5996	5833	7860
Isomers C9	3022	2575	2654	2759
Isomers C10	1869	2884	3235	1628
Isomers C11	531	1044	1184	435
Isomers Cumene	3348	2845	3498	2579
Isomers C10H14 aromatic	251	298	484	189
Benzene	39	67	63	30
Toluene	808	775	748	693
Xylenes + Ethyl benzene	855	863	1269	645
MTBE	9	6	4	7
TOTAL	*28397*	*23043*	*24010*	*25793*

Table 31 Site 1 - Results of GC-MS speciation (mean concentration, ppbv), "DIAL day" 5

Compounds	Pre-separator (day time)	Sewer outlet (2 sample points)	Top of the sewer mouth	Middle of the sewer mouth	Sewer mouth	Pre-separator (night time)
Isomers C4	150	133	1232	291	79	48
Isomers C5	4472	2811	25173	6038	1673	1195
Isomers C6	5065	3231	15353	5279	2447	1776
Isomers C7	4501	2798	15195	6101	3088	1704
Isomers C8	5274	3231	19961	8664	4716	2355
Isomers C9	1821	1213	8795	4307	2543	1015
Isomers C10	1705	1240	11886	6343	3373	965
Isomers C11	706	551	3773	1910	1143	457
Isomers Cumene	2730	1944	13158	7214	3960	1838
Isomers C10H14 aromatic	376	247	1173	795	480	236
Benzene	325	215	713	297	160	96
Toluene	1511	1036	6713	2858	1639	668
Xylenes + Ethyl benzene	956	755	6833	3864	2322	667
MTBE	344	164	283	96	49	59
TOTAL	*29879*	*20429*	*129230*	*53843*	*27624*	*13032*

Table 32 Site 1 - Liquid density of evaporated VOCs

Sampling Location	"DIAL day"	VOC Liquid Density (kg/m^3)	Additional Information
Sewer mouth	3	749	
	4	765	
	5	742	top
	5	758	centre
	5	767	average
Sewer outlet channel + sewer mouth	4	748	
Sewer outlet channel	5	709	Average of 2 points
Pre-separator	1	769	2m above surface
	1	764	0.5m above surface
	1	761	0.1m above surface
	1	757	Average of 5 points
	2	769	
	4	750	
	4	744	
	5	738	
	5	757	
Forebay	2	768	
API	2	780	inlet
	2	776	outlet
	3	760	Average of 4 points
	3	764	Average including pump sump
Pump sump	2	779	
AVERAGE		*758*	

Table 33 Site 2 - Results of GC-MS speciation (mean concentration, ppbv), “DIAL day” 1

Compounds	Collection basin (at 0.7 meters above surface)	Collection basin (at 0.05 meters above surface)	Collection basin (at 2 meters above surface) Open space
Isomers C4	200	496	316
Isomers C5	483	1355	653
Isomers C6	673	1966	1048
Isomers C7	637	1364	910
Isomers C8	1028	1772	1304
Isomers C9	1066	1704	1395
Isomers C10	871	1130	1012
Isomers C11	377	470	422
Isomers Cumene	1045	1200	1063
Isomers C10H14 aromatic	73	92	79
Benzene	376	383	287
Toluene	884	1165	992
Xylenes + Ethyl benzene	1330	1631	1334
ETBE	56	49	35
Methyl mercaptan	5	0	6
Isomers C10H14 non-aromatic	113	130	119
TOTAL	*9218*	*14907*	*10974*

Table 34 Site 2 - Results of GC-MS speciation (mean concentration, ppbv), "DIAL day" 2

Compounds	Average API	Average Forebay	Average TPI
Isomers C4	239	1240	3442
Isomers C5	532	10283	57438
Isomers C6	698	17273	118321
Isomers C7	547	10189	77434
Isomers C8	755	10964	70591
Isomers C9	641	9175	54730
Isomers C10	559	4807	19192
Isomers C11	146	930	2241
Isomers Cumene	443	2902	16841
Isomers C10H14 aromatic	22	67	406
Benzene	134	2936	8900
Toluene	371	4699	25365
Xylenes + Ethyl benzene	762	6499	39391
ETBE	8	223	291
Methyl mercaptan	0	24	0
Isomers C10H14 non-aromatic	64	501	1906
TOTAL	*5920*	*82711*	*496488*

Table 35 Site 2 - Results of GC-MS speciation (mean concentration, ppbv), “DIAL day” 3

Compounds	Pre-separator inlet	Pre-separator middle	Pre-separator outlet	Pre-separator Average of 5 sampling points
Isomers C4	3930	6657	6953	10519
Isomers C5	28559	47646	60697	80919
Isomers C6	37361	76089	66836	121787
Isomers C7	19081	40284	34991	64890
Isomers C8	26343	61648	38720	80561
Isomers C9	19080	52384	27268	56533
Isomers C10	13521	20491	16198	26116
Isomers C11	3399	3509	3034	4977
Isomers Cumene	15923	17936	12612	27563
Isomers C10H14 aromatic	672	534	495	893
Benzene	5421	12896	6764	13807
Toluene	18716	30662	18074	43536
Xylenes + Ethyl benzene	30533	44161	26611	69256
ETBE	853	2432	1733	2252
Isomers C10H14 non-aromatic	1042	1176	978	1467
TOTAL	*224435*	*418505*	*321963*	*605076*

APPENDIX IV WATER9 INPUT DATA, SITE 1

Table 36 Site 1 – Input data for WATER9 and TOXCHEM+
(Speciation data in **Tables 37 to 39**)

"DIAL day"	Sampling Location	Time after start of test (h)	Model "stream name"	Water Temp. (°C)	Air Temp. (°C)	Water Flow Rate (l/s)	Wind Speed at 10m (m/s)	Oil in Water Conc. (mg/l)
1	Sewer outlet	2	A1	24.8	10	68.6	3.6	110
	Forebay	2	B1_2	24.1	10	68.6	3.6	140
		4	B1_4	25.1	12	68.6	3.6	40
2	Sewer outlet	2	A2	24.4	8	68.3	2.2	170
	Forebay	2	B2-2	25.3	8	68.3	2.2	54
		4	B2_4	26.1	9	68.3	2.2	130
3	Sewer outlet	2	A3	25.7	10	70.3	1.4	60
	Forebay	2	B3_2	26.1	10	70.3	1.4	51
		4	B3_4	33.5	12	70.3	1.4	37
4	Sewer outlet	2	A4	27.8	20	59.2	3.2	260
	Forebay	2	B4_2	28.9	20	59.2	3.2	350
		4	B4_4	27.5	28	59.2	3.2	47
5	Sewer outlet	2	A5	29.0	23	63.1	2.8	140
	Forebay	2	B5_2	29.4	23	63.1	2.8	110
		4	B5_4	28.3	20	63.1	2.8	180

Table 37 Site 1 – Oil in water speciation data (concentration in mg/l), “DIAL days” 1 and 2

Compound	“DIAL day” 1			“DIAL day” 2		
	Location / Time after start of “DIAL day” (h) / Model “stream name”			Location / Time after start of “DIAL day” (h) / Model “stream name”		
	Sewer outlet, +2, A1	Forebay, +2, B1_2	Forebay, +4, B1_4	Sewer outlet, +2, A2	Forebay, +2, B2_2	Forebay, +4, B2_4
Benzene	0.079	0.2	0.16	0.19	0.19	0.31
Toluene	0.0095	0.029	0.086	0.17	0.15	0.45
Ethyl benzene	0.0011	0.0048	0.0005	0.022	0.0005	0.052
m+p-Xylene	0.14	0.76	0.29	0.36	0.27	0.33
o-Xylene	0.11	0.48	0.21	0.3	0.22	0.33
Styrene	0.0005	0.0005	0.0005	0.0013	0.0005	0.004
n-Propyl benzene	0.00093	0.019	0.0034	0.084	0.0096	0.016
Isopropyl benzene (cumene)	0.0011	0.0005	0.0034	0.028	0.0081	0.0088
p-Isopropyl toluene (cymene)	0.007	0.18	0.046	0.092	0.018	0.0098
n-Butyl benzene	0.202	4.39	0.87	0.522	0.352	0.226
sec-Butyl benzene	0.004	0.19	0.018	0.025	0.14	0.008
tert-Butyl benzene	0.0005	0.0073	0.00076	0.00077	0.00093	0.00054
1,2,4-Trimethyl benzene	0.17	3.0	0.44	0.61	0.37	0.38
1,3,5-Trimethyl benzene	0.085	0.77	0.18	0.38	0.195	0.13
1-Ethyl-3-methyl benzene	0.2	1.8	0.37	1.0	0.43	0.33
1-Ethyl-2-methyl benzene	0.081	0.63	0.14	0.35	0.16	0.11
1,2,3-Trimethyl benzene	0.092	0.9	0.23	0.46	0.16	0.11
Diethyl benzene (isomers)	0.084	1.6	0.29	0.95	0.14	0.084
Carbonyl sulphide	0.00084	0.0023	0.00098	0.0005	0.0005	0.0005
Acetone	0.05	0.05	0.05	0.05	0.05	0.05
Methyl-t-butyl ether (MTBE)	0.11	0.05	0.094	0.045	0.29	0.76
2-Butanone (MEK)	0.05	0.05	0.05	0.05	0.05	0.05
4-Methyl-2-pentanone (MIBK)	0.05	0.05	0.05	0.05	0.05	0.05
Naphthalene	0.025	0.24	0.33	0.53	0.001	0.001
Pentane	0.0015	0.0046	0.0021	0.003	0.023	0.0029
Hexane	0.0033	0.0096	0.0047	0.015	0.0096	0.011
Heptane	0.028	0.47	0.11	0.33	0.13	0.05
Octane	0.025	1.1	0.14	0.49	0.09	0.03
Nonane	0.11	6.9	0.64	3.0	0.27	0.075
Decane	0.42	13.0	1.5	6.5	0.71	0.19
SUM	*2.14*	*36.89*	*6.31*	*19.41*	*4.36*	*4.05*
Dodecane (estimate)	53.9	51.6	16.8	75.3	24.8	63.0
Icosane (estimate)	53.9	51.6	16.8	75.3	24.8	63.0

Table 38 Site 1 – Oil in water speciation data (concentration in mg/l), "DIAL days" 3 and 4

Compound	"DIAL day" 3			"DIAL day" 4		
	Location / Time after start of "DIAL day" (h) / Model "stream name"			Location / Time after start of "DIAL day" (h) / Model "stream name"		
	Sewer outlet, +2, A3	Forebay, +2, B3_2	Forebay, +4, B3_4	Sewer outlet, +2, A4	Forebay, +2, B4_2	Forebay, +4, B4_4
Benzene	0.25	0.24	0.16	0.0008	0.0036	0.0005
Toluene	0.34	0.27	0.18	0.0005	0.0005	0.0005
Ethyl benzene	0.072	0.04	0.031	0.0005	0.0005	0.0005
m+p-Xylene	0.39	0.32	0.22	0.0039	0.0097	0.0022
o-Xylene	0.24	0.21	0.16	0.013	0.029	0.0066
Styrene	0.0063	0.0027	0.003	0.0005	0.0005	0.0005
n-Propyl benzene	0.055	0.027	0.02	0.0005	0.0005	0.0005
Isopropyl benzene (cumene)	0.019	0.013	0.0095	0.0005	0.0005	0.0005
p-Isopropyl toluene (cymene)	0.019	0.011	0.0079	0.007	0.0086	0.0042
n-Butyl benzene	0.522	0.268	0.211	0.142	0.213	0.069
sec-Butyl benzene	0.025	0.013	0.0094	0.0016	0.0028	0.0005
tert-Butyl benzene	0.00077	0.00062	0.00052	0.0005	0.0005	0.0005
1,2,4-Trimethyl benzene	0.61	0.42	0.32	0.0038	0.0084	0.0013
1,3,5-Trimethyl benzene	0.2	0.16	0.12	0.079	0.12	0.047
1-Ethyl-3-methyl benzene	0.48	0.39	0.26	0.037	0.075	0.02
1-Ethyl-2-methyl benzene	0.16	0.13	0.099	0.066	0.095	0.042
1,2,3-Trimethyl benzene	0.16	0.13	0.11	0.063	0.088	0.038
Diethyl benzene (isomers)	0.19	0.1	0.086	0.069	0.089	0.046
Carbonyl sulphide	0.0038	0.0042	0.0031	0.0005	0.0007	0.0005
Acetone	0.05	0.05	0.05	0.05	0.05	0.05
Methyl-t-butyl ether (MTBE)	0.038	0.044	0.033	0.037	0.043	0.033
2-Butanone (MEK)	0.05	0.05	0.05	0.05	0.05	0.05
4-Methyl-2-pentanone (MIBK)	0.05	0.05	0.05	0.05	0.05	0.05
Naphthalene	0.9	0.24	0.21	0.0063	0.0073	0.003
Pentane	0.0029	0.0078	0.0038	0.0029	0.0043	0.0022
Hexane	0.0074	0.0061	0.0043	0.0016	0.0003	0.0013
Heptane	0.11	0.064	0.043	0.055	0.096	0.056
Octane	0.14	0.044	0.028	0.087	0.11	0.045
Nonane	0.29	0.1	0.061	0.16	0.23	0.069
Decane	1.8	0.2	0.13	0.25	0.44	0.092
SUM	*7.18*	*3.61*	*2.67*	*1.24*	*1.83*	*0.73*
Dodecane (estimate)	26.4	23.7	17.2	129.4	174.1	23.1
Icosane (estimate)	26.4	23.7	17.2	129.4	174.1	23.1

Table 39 Site 1 – Oil in water speciation data (concentration in mg/l), "DIAL day" 5

Compound	"DIAL day" 5		
	Location / Time after start of "DIAL day" (h) / Model "stream name"		
	Sewer outlet, +2, A5	Forebay, +2, B5_2	Forebay, +4, B5_4
Benzene	0.015	0.011	0.00062
Toluene	0.0033	0.0025	0.00039
Ethyl benzene	0.0005	0.0005	0.0005
m+p-Xylene	0.026	0.017	0.0024
o-Xylene	0.073	0.075	0.024
Styrene	0.0005	0.0005	0.0005
n-Propyl benzene	0.0007	0.00062	0.0005
Isopropyl benzene (cumene)	0.00098	0.0008	0.0005
p-Isopropyl toluene (cymene)	0.014	0.012	0.012
n-Butyl benzene	0.358	0.271	0.274
sec-Butyl benzene	0.0061	0.0041	0.0021
tert-Butyl benzene	0.0008	0.00072	0.00064
1,2,4-Trimethyl benzene	0.022	0.015	0.0049
1,3,5-Trimethyl benzene	0.14	0.15	0.13
1-Ethyl-3-methyl benzene	0.12	0.11	0.05
1-Ethyl-2-methyl benzene	0.12	0.12	0.12
1,2,3-Trimethyl benzene	0.12	0.11	0.098
Diethyl benzene (isomers)	0.17	0.13	0.14
Carbonyl sulphide	0.00068	0.00072	0.0005
Acetone	0.05	0.05	0.05
Methyl-t-butyl ether (MTBE)	0.067	0.067	0.075
2-Butanone (MEK)	0.05	0.05	0.05
4-Methyl-2-pentanone (MIBK)	0.05	0.05	0.05
Naphthalene	0.001	0.016	0.011
Pentane	0.0031	0.007	0.0075
Hexane	0.0014	0.0031	0.003
Heptane	0.072	0.13	0.13
Octane	0.15	0.17	0.17
Nonane	0.42	0.32	0.35
Decane	0.72	0.43	0.41
SUM	*2.78*	*2.33*	*2.17*
Dodecane (estimate)	68.6	53.8	88.9
Icosane (estimate)	68.6	53.8	88.9

APPENDIX V WATER9 MODELLING RESULTS. SITE 1

The model consists of 3 distinct zones:

1. Flow distribution zone
2. Oil separation zone
3. Overflow weir zone

Simulation of one specific zone of the separator can be done by setting the surface area of one of the two zones equal to zero. A simulation without the outlet zone can be done by setting the effluent overflow height to zero.

Simulations have been carried out using the process conditions and analytical test data as shown in **Appendix IV.**

Test data are characterised by the date of sampling and by the sampling location denoted as ''forebay' being representative for the outlet of the pre-separator and for the inlet to the API separator.

At the forebay samples have been taken 2 and 4 hours after start of the DIAL measurements.

In addition, for the following 3 parameters fixed values have been used.

Air Temperature - fixed at 15°C.

Air Humidity - fixed at 60%.

Water pH - fixed at 7.5.

Several approaches can be used to simulate the emissions from the Site-1 separator.

- CASE 1A – This case is based on assuming the sewer outlet and pre-separator area as the flow distribution zone of the model (surface area 51.25 m^2), with the forebay and the API basin as the oil separation zone of the model (surface area 285 m^2) with 50% oil sheen coverage for the latter zone and an outlet weir height equal to 20 cm. Simulations have been carried out for each of the analytical test datasets, thereby assuming that sampling location B (see **Appendix I**) also represents the inlet of the model.
- CASE 1B – The same as case 1A but with oil sheen coverage of 100% and an outlet weir height equal to 50 cm.
- CASE 2 – This case uses the sewer outlet (surface area 15 m^2) as the flow distribution zone in the model and the pre-separator, forebay and API basin (surface area 271.25 m^2) comprising the oil separation zone of the model. Oil sheen coverage is assumed to be 100 % for the latter zone. The outlet weir is set at 50 cm. In this case the analyses have only been undertaken using the data from sampling location “sewer outlet”.
- CASE 3A – This case models the sewer outlet (surface area 15 m^2) as the flow distribution zone and pre-separator (surface area 31.25 m^2) as the oil separation zone with 100% coverage by oil sheen and the outlet weir set to 0 cm. Data from the “sewer outlet” sampling point have been used.
- CASE 3B – The model uses a reduced size sewer outlet (surface area 1 m^2) as the flow distribution zone and the forebay plus the API basin (surface area 240 m^2) as the oil separation zone with 100% oil sheen coverage and an outlet weir equal set at 50 cm. Data from sampling point “forebay” have been used.

Results from cases 3A and 3B have to be summed to obtain the model results for the entire separator area.

Modelling results for the various cases are shown in the following tables:

Table 40 Site 1 – Results of WATER9 computations for Cases 1A and 1B

“DIAL day”	Stream Name	Hydrocarbon Load kg/h	Calculated Emissions Case 1A kg/h	Calculated Emissions Case 1B kg/h
1	A1	27	0.07	0.11
	B1_2	35	0.28	0.48
	B1_4	10	0.08	0.13
2	A2	42	0.15	0.24
	B2_2	13	0.08	0.13
	B2_4	32	0.14	0.23
3	A3	15	0.07	0.11
	B3_2	13	0.05	0.09
	B3_4	9	0.05	0.08
4	A4	55	0.09	0.13
	B4_2	75	0.13	0.19
	B4_4	10	0.03	0.05
5	A5	32	0.07	0.11
	B5_2	25	0.07	0.10
	B5_4	41	0.08	0.12

Table 41 Site 1 – Results of WATER9 computations for Case 2

“DIAL day”	Stream Name	Hydrocarbon Load kg/h	Calculated Emissions kg/h
1	A1	27	0.09
2	A2	42	0.22
3	A3	15	0.10
4	A4	55	0.10
5	A5	32	0.09

Table 42 Site 1 – Results of WATER9 computations for Cases 3A and 3B

"DIAL day"	Stream Name	Hydrocarbon Load kg/h	Calculated Emissions Case 3A kg/h	Calculated Emissions Case 3B kg/h
1	A1	27	0.02	-
	B1_2	35	-	0.45
	B1_4	10	-	0.13
2	A2	42	0.04	-
	B2_2	13	-	0.12
	B2_4	32	-	0.21
3	A3	15	0.02	-
	B3_2	13	-	0.08
	B3_4	9	-	0.08
4	A4	55	0.03	-
	B4_2	75	-	0.12
	B4_4	10	-	0.04
5	A5	32	0.02	-
	B5_2	25	-	0.08
	B5_4	41	-	0.09

APPENDIX VI TOXCHEM+, SITE 1

The TOXCHEM+ programme is similar to WATER9 in that it is based on mass transfer calculations to estimate VOC emissions to air using influent composition data for individual substances.

The programme partitions the substances over 3 phases: water, free hydrocarbon and solid phase (typically sludge).

Partitioning to the free hydrocarbon phase is based on the octanol-water partitioning coefficients for the various substances submitted as the inputs to the programme.

The mass transfer from the water phase to air is based on the Henry's coefficient for the various substances.

Mass transfer from the free oil phase to air is not based on vapour-liquid equilibrium data for the various substances. Instead a default approach is used: the mass transfer to air, as calculated based on the Henry coefficients, is corrected with an 'oil coverage correction factor' based on the oil coverage input value provided by the user. For a 100% oil covered basin this correction factor is 2, regardless of the vapour-liquid equilibrium characteristics of the individual substances.

The above means that the programme is primarily designed to calculate the emissions for cases without free oil coverage and for substances below their solubility limit in water. This characteristic makes the programme less suitable for oil covered separator basins since:

- The mass transfer from the water phase to the free oil phase is not treated according to the solubility limits of the substances involved. So if a concentration above the solubility limit is provided in the input, the programme will treat this as a dissolved substance.

- The mass transfer from the free oil phase to the air is not based on vapour/liquid equilibrium data. Instead a default correction factor is applied to the amount vaporised from the water phase.

The required input to TOXCHEM+ is:

- Water flow rate
- Substance speciation
- Wind velocity
- Water temperature
- Basin surface area
- Percentage of free oil coverage on the basin
- Overflow weir height and width
- Influent water suspended solids content

As is shown in **Table 43**, the calculated fraction of each substance partitioned to free oil is very small and the fraction partitioned to solids depends strongly on the type of substance. Heavier substances partition to a larger extent to the solids phase.

Table 43 Site 1 – Results of TOXCHEM+ computations: partitioning of compounds to the different phases

Compounds	Fraction evaporated to the air	Fraction left in water effluent	Fraction collected as oil	Fraction collected in the sludge
Benzene	0.068	0.903	0.004	0.026
Toluene	0.061	0.891	0.004	0.044
Ethyl benzene	0.056	0.874	0.003	0.067
m-Xylene	0.055	0.871	0.003	0.071
o-Xylene	0.057	0.884	0.003	0.055
Styrene	0.057	0.884	0.003	0.055
n-Propyl benzene	0.048	0.843	0.003	0.105
Cymene	0.038	0.783	0.003	0.176
Butyl benzene	0.043	0.796	0.003	0.158
1,2,3-Trimethyl benzene	0.043	0.801	0.003	0.154
1,3,5-Trimethyl benzene	0.046	0.798	0.003	0.153
4-Ethyl toluene	0.046	0.826	0.003	0.125
1,2,4-Trimethyl benzene	0.047	0.841	0.003	0.109
Carbonyl Sulphide	0.050	0.936	0.004	0.010
Acetone	0.034	0.952	0.004	0.010
MTBE	0.059	0.915	0.004	0.022
MEK	0.045	0.941	0.004	0.011
MIBK	0.053	0.928	0.004	0.016
Naphthalene	0.048	0.870	0.003	0.078
n-Hexane	0.058	0.894	0.004	0.044
Heptane	0.038	0.774	0.002	0.185
Octane	0.046	0.845	0.003	0.105
Nonane	0.026	0.700	0.002	0.272
Dodecane	0.015	0.625	0.001	0.359

The model has been applied to a surface area of 336 m^2. A weir height of 50 cm has been used. The first surface region (the “oil distribution zone”) comprises the sewer outlet and pre-separator with combined surface area of 51.25 m^2. The second surface region (the “oil film separation zone”) comprises the forebay, the API basin and the API pump sump with a combined surface area of 285 m^2. The emissions have been calculated for both 100% free oil coverage and with no free oil and are provided in **Table 44**. For the sake of comparison the results obtained by WATER9 (case 1B) are also shown.

Table 44 Site 1 – Results of TOXCHEM+ computations

"DIAL day"	Stream Name	VOC Load kg/h	TOXCHEM+				WATER9	
			100% oil coverage		No free oil coverage		Case 1B	
			Estimated Emissions kg/h	Fraction of load emitted	Estimated Emissions kg/h	Fraction of load emitted	Estimated Emissions kg/h	Fraction of load emitted
1	A1	27	0.58	0.021	0.29	0.011	0.11	0.004
	B1_2	35	0.89	0.026	0.45	0.013	0.48	0.014
	B1_4	10	0.23	0.024	0.12	0.012	0.13	0.013
2	A2	42	0.67	0.016	0.34	0.008	0.24	0.006
	B2_2	13	0.20	0.015	0.10	0.008	0.13	0.010
	B2_4	32	0.46	0.014	0.23	0.007	0.23	0.007
3	A3	15	0.22	0.015	0.11	0.007	0.11	0.007
	B3_2	13	0.16	0.013	0.08	0.006	0.09	0.007
	B3_4	9	0.13	0.014	0.07	0.007	0.08	0.009
4	A4	55	1.20	0.022	0.60	0.011	0.13	0.002
	B4_2	75	1.42	0.019	0.71	0.010	0.19	0.003
	B4_4	10	0.18	0.018	0.09	0.009	0.05	0.005
5	A5	32	0.62	0.019	0.31	0.010	0.11	0.003
	B5_2	25	0.40	0.016	0.20	0.008	0.10	0.004
	B5_4	41	0.62	0.015	0.31	0.008	0.12	0.003

APPENDIX VII CHEMICAL PROPERTIES FOR USE IN RWET

Table 45 Default values for properties of additional compounds used in the Refinery Wastewater Emission Tool

	Heptane	Octane	Dodecane	Isocane
CAS No.	142825	111659	112403	112958
Molecular weight	100.0	114.3	170.0	282.6
Vapour pressure (mmHg)	4.60E+01	1.70E+01	2.75E-01	1.4E-04
Henry's law constant (atm-m^3/mol)	2.02E+00	3.87E+00	6.64E-02	3.10E+00
Di,w (cm^2/sec)	7.60E-06	7.10E-06	5.90E-06	-
Di,a (cm^2/sec)	9.30E-02	7.60E-02	4.36E-02	3.50E-02
log(Kow)	3.2	3.6	5.3	11.3
Kb,max (gVO/g-s)	1.18E-05	1.18E-05	1.18E-05	-
Ks, (g/m^3)	15.3	15.3	15.3	-

APPENDIX VIII WIND ROSES SITE 1 AND SITE 2

Figure 14 Wind roses. Site 1

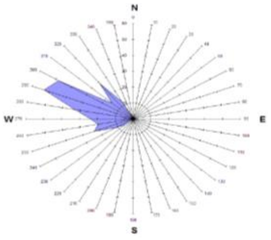
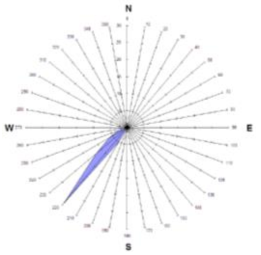
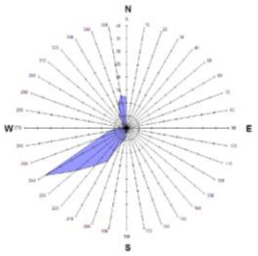
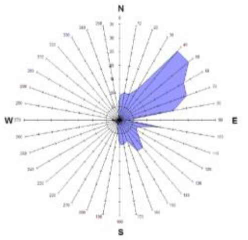
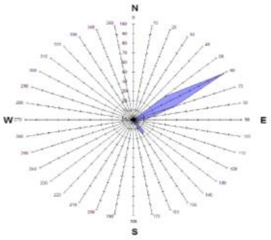
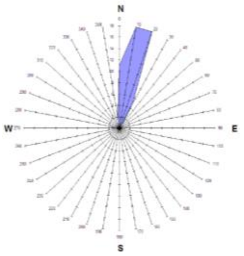
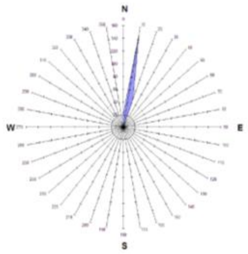
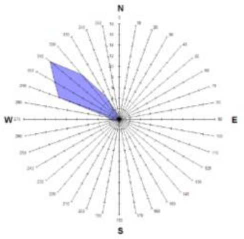
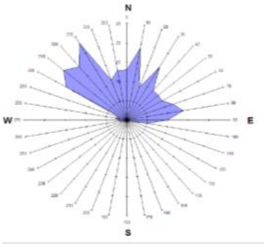
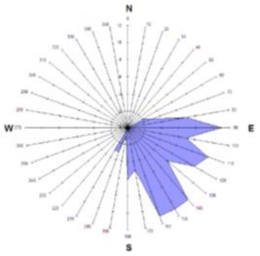
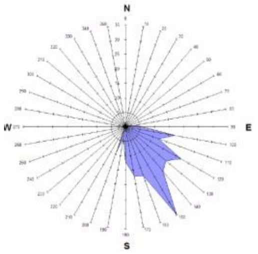
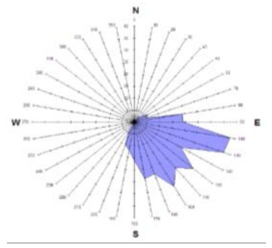
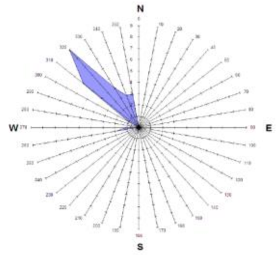
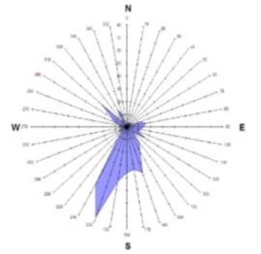
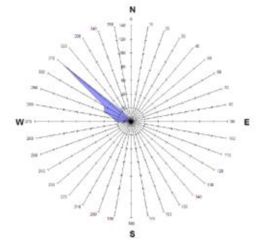
13th April. 11:05-17:02h Height 11m Average wind for period 3.6 m/s at 292.4 degrees	14th April. 11:03-12:12h Height 11m Average wind for period 2.2 m/s at 229.6 degrees	14th April. 13:24-17:14h Height 11m Average wind for period 1.7 m/s at 257.4 degrees	15th April. 10:23-17:01h Height 11m Average wind for period 1.4 m/s at 77degrees
			
18th April. 18:13-00:01h Height 11m Average wind for period 3.2 m/s at 75.7degrees	19th April. 16:52-18:09h Height 11m Average wind for period 2.8 m/s at 18 degrees	19th April. 18:44-23:36h Height 11m Average wind for period 3.5 m/s at 16.1 degrees	
			

Figure 15 Wind roses. Site 2

13th September 12:38-13:56h Height 11m Average for period 2.5 m/s at 310.9 degrees	13th September 14:19-18:54h Height 11m Average for period 1.7 m/s at 7.2 degrees	14th September 12:04-14:05h Height 11m Average for period 2.0 m/s at 136 degrees	14th September 14:48-18:38h Height 11m Average for period 2.4m/s at 145.8 degrees
			

15th September 10:48-16:56h Height 11m Average for period 2.0 m/s at 134.3 degrees	16th September 10:09-10:42h Height 11m Average for period 1.7 m/s at 324.7 degrees	16th September 10:40-16:45h Height 11m Average for period 1.2 m/s at 195.2 degrees	17th September 19:05-00:55h Height 11m Average for period 2.4 m/s at 305.3 degrees
			

APPENDIX IX SUMMARY OF DIAL RESULTS

Table 46 Site 1 - Summary of NPL estimates of emission rates

Date	Description	Flux estimate kg/h	Standard deviation	No. of scans
13/04/2011	Upwind west	0.00	-	1
	Upwind north west	0.38	-	1
	Upwind west north west	0.00	-	1
	Upwind west south west	0.20	0.20	2
	Downwind all except west of the system	16.00	2.70	6
	Downwind all	23.70	3.30	10
14/04/2011	Upwind south south west	0.00	-	1
	Upwind south west	0.23	0.26	2
	Downwind all except pre-sep and sewer outlet	16.00	3.30	3
	Downwind all	23.90	3.78	10
	Downwind rain water basin	1.49	0.59	3
	Downwind sewer outlet	1.20	0.23	3
	Downwind all except rain water basin	10.00	1.52	2
15/04/2011	Upwind east	0.39	-	1
	Upwind east north east	0.00	-	1
	Upwind north east	0.13	-	1
	Upwind north north west	0.10	0.10	2
	Upwind south	0.00	-	1
	Downwind all	17.30	1.27	2
	Downwind all except (sewer + pre-sep + forebay)	11.50	4.88	5
18/04/2011	Upwind east	0.05	0.05	2
	Upwind east north east	0.00	-	1
	Upwind north east	0.15	0.01	2
	Downwind all	19.60	-	1
	Downwind all except rain water basin	12.20	3.36	3
	Downwind rain water basin	4.20	0.97	3
	Downwind sewer and pre-sep	4.00	1.10	6
19/04/2011	Upwind north	0.15	0.19	3
	Downwind all	20.90	2.34	10
	Downwind sewer outlet + pre-sep	3.50	0.53	3
	Downwind all except rain water basin	15.10	1.79	6

Table 47 Site 2 - Summary of NPL estimates of emission rates

Date	Observations	Flux estimate kg/h	No. of Scans	Standard Deviation	Sources to be subtracted
13/09/2011	Upwind west	99.3	3	13	-
	Upwind north west	8.7	1	-	-
	Downwind all except half (E) of uncovered API. Uncovered API was not in operation	151.4	4	61	Upwind west & upwind north
	Downwind east of covered API	76.5	5	11	Upwind east & upwind north
	Downwind east of. uncovered API that was not in operation	46.6	1	-	Upwind east
	Downwind of pre-sep	190.6	3	61	Upwind west
	Downwind of pre-sep + half of covered API	32.8	1	-	Upwind north
14/09/2011	Downwind of all except pre-sep	91.5	3	25	Upwind south & upwind east south east
	Downwind east of uncovered API and oil sump	86.2	3	18	Upwind south & upwind east south east
	Downwind TPI and uncovered API	129.6	8	32	Upwind east south east
	Upwind south	14.4	5	10	-
15/09/2011	Downwind all. only uncovered separator in operation	660.3	4	104	Upwind east
	Downwind uncovered API + oil sump	100.7	13	13	Upwind east south east & upwind east
	Downwind uncovered API + TPI	357.7	5	95	Upwind south & upwind south east
	Upwind south	11.1	3	5	-
16/09/2011	Downwind All, Only uncovered API in operation	190.2	4	36	Upwind west & upwind north west
	Downwind east of uncovered separator + oil sump	59.0	8	25	Upwind west , upwind north west, upwind north & upwind south west
	Upwind east	38.0	1	-	-
	Upwind south east, wind changing	37.8	3	21	-
17/09/2011	Downwind all, both APIs in operation, night, high emissions	154.1	14.0	49.8	Upwind west
	Downwind all, both APIs in operation, night, low emissions	72.7	10.0	41.3	Upwind west

APPENDIX X SURFACE PRIMARY OIL-WATER SEPARATOR, SITE 2

Table 48 Surface primary oil-water separator, Site 2

Basin	Surface m^2
Pre-separator	100
TPI	53
API covered	376
API uncovered	321
Oil Sump	45
TOTAL	*895*

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