EVALUATION OF THE MONITORING SYSTEM FOR VOLATILE ORGANIC COMPOUND (VOC) EMISSIONS AT NATREF, SOUTH AFRICA

M GREEFF

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This study is dedicated to my daughter
Marlie

ABSTRACT

An evaluation of the VOC (Volatile Organic Compound) emissions monitoring system of Natref (National Refiners of South Africa) was conducted to determine the effectiveness of the system. Natref monitors fugitive plant equipment VOC emissions, VOC emissions from the wastewater treatment area and the tank farm as separate entities. The hiatus in the VOC emissions monitoring system is the absence of an overall VOC emission scenario at Natref. Data of VOC emissions from Natref's field data were used to determine the overall VOC emission scenario at the refinery. Since no control guidelines are available for VOC emissions in South Africa, it was necessary to benchmark with refineries in the USA and Western Europe to determine how effective Natref's VOC emissions monitoring system is. The percentage VOC emissions at Natref from the three areas fell outside the benchmark ranges and different scenarios were simulated to determine the possible causes. The results of this evaluation brought to light inadequacies in the VOC emissions monitoring system at Natref and an estimated loss of approximately three million rand per annum due to VOC emissions. The absence of a coherent picture of VOC emissions at the refinery can lead to sub-optimal expenditure of resources to reduce VOC emissions. The value of a monitoring system lies therein that information obtained from it can be used to implement effective control measures in order to make a contribution to the protection of the environment and therefore towards sustainable development.

OPSOMMING

Die monitering stelsel vir VOV (Vlugtige organiese verbindings) emissies by Natref (Nationale Petroleum Raffineerders van Suid Afrika) is geevalueer om te bepaal hoe effektief die stelsel is. Natref moniteer VOV emissies vanaf die aanleg toerusting, die water behandelingsarea en die tenkplaas afsonderlik. Die leemte in Natref se monitering stelsel is die afwesigheid van 'n globale oorsig ten opsigte van VOV emissies. Data van VOV emissies, verkry vanuit Natref se beskikbare metings en bepalings is gebruik om 'n globale oorsig vir VOV emissies te bepaal. Aangesien geen beheer riglyne ten opsigte van VOV emissies vir Suid-Afrika beskikbaar is nie, was dit nodig om Natref se VOV emissies met raffinaderye in die VSA en Wes Europa te vergelyk. Die persentasie bydrae van elk van die areas tot die globale emissie-situasie val buite die reikweidte gevind vir oorsese raffinaderye. Verskillende modelle is geevalueer om die moontlike oorsake vir die verskille tussen VOV emissies by Natref en oorsese raffinaderye te bepaal. Die evaluering toon dat die omvang van die monitering stelsel vir VOV emissies by Natref nie uitgebreid genoeg is nie en 'n beraamde verlies van ongeveer drie miljoen rand per jaar as gevolg van VOV emissies. Die bestaande monitering stesel kan daartoe lei dat hulpbronne verkeerdelik aangewend word in pogings om VOV emissies te beheer. Die waarde van moniteringstelsels lê daarin dat inligting daaruit verkry aangewend kan word tot omgewingsbewaring en volhoubare ontwikkeling.

PREFACE

Goals

Industries and governments endeavour to achieve economic growth and the protection of the environment by focusing on sustainable development. Industries, including refineries, are developing environmental management programmes to monitor their impacts on the environment, and to implement control measures to minimise their effects on the environment. Impacts on the environment caused by refineries are water pollution, air pollution and solid wastes. Volatile organic compounds (VOC), which are hydrocarbon compounds that vaporise into the atmosphere, are one form of air pollution found in a refinery.

The aim of this dissertation is to evaluate the effectiveness of the VOC emissions monitoring system implemented at Natref, a refinery in South Africa. The aim will be met by achieving the following objectives:

- Estimating fugitive, wastewater treatment area and tank farm VOC emissions, and determining each area's contribution to the total VOC emissions at Natref.
- Comparing the overall VOC emission scenario found at Natref with findings of VOC emissions at refineries abroad.

Structure of dissertation

This dissertation is in article format. In the article manuscript the causes of VOC emissions and methods to estimate VOC emissions, for the three areas mentioned above, are discussed. VOC emissions at Natref are estimated for the three areas and then combined to determine the overall extent of VOC emissions at Natref, and to benchmark with refineries abroad. Conclusions and recommendations based on the results are made. Figures, tables and graphs are inserted into the text for user friendliness. Attached to the article manuscript are appendixes containing Natref's field data that are summarised in the tables and graphs in the text.

This article is aimed at the peer review magazine, Hydrocarbon Processing. Since this journal requires a somewhat unusual style, this article manuscript is written in the generic style and references are according to the guidelines of the North West University.

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ABBREVIATIONS

API - American Petroleum Institute
CDU - Crude Distillation Unit
EPA - Environmental Protection Agency of America
ISO - International Standards Organisation
LDAR - Leak Detection and Repair
LR - Leak Rate
Natref - National Petroleum Refiners of South Africa
NO_x - Nitrogen oxide compounds
O_3 - Ozone
PLV - Preloading Vapour
ppmv - Parts per million by volume
RVP - Reid Vapour Pressure
SCI - Sasol Chemical Industries
SV - Screening Value
TVP - True Vapour Pressure
USA - United States of America
VOC - Volatile Organic Compounds

LIST of VARIABLES

			Units for equations	SI units
LR	-	Leak Rate	kg/hr	kg/s
SV	-	Screening value	ppm	ppm
x	-	Ambient temperature	°F	K
y	-	10 % distillation point	°F	K
z	-	Waste water temperature	°F	K
ρ	-	Density	kg/m^3	kg/m^3
Ef	-	Filling emissions as a percentage of the volume loaded	%	%
C_s	-	Vapour concentration at saturation	bar	Pa
C_p	-	Average preloading vapour (fraction)	-	-
V_b	-	Fraction of tank volume containing saturated vapour	-	-

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1. Introduction

Volatile organic compounds (VOC's) are hydrocarbon compounds that combine with nitrogen oxides and other airborne chemicals in the presence of sunlight (photochemical reactions) to form ozone in the troposphere. Another definition for volatile organic compounds (VOC's) is: any compound of carbon, whose vapour pressure at 20 °C exceeds 0.13 kPa (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate) that participates in atmospheric photochemical reactions (Harmse, Rowe & Cox, 2002). Examples of common VOC's include benzene, toluene, xylene, naphtha, ethylene oxide, methyl ethyl ketone, acetone, 1,3 butadiene and other light hydrocarbon compounds (Chang, Lo, Jo & Wang, 2003; Concawe, 1999).

VOC's are sensory irritants, causing dry eyes, irritation to the upper respiratory tract, headaches and a rough tongue (Meininghaus, Koumiali, Mandin & Cicolella, 2003; Yang, Wang, Chun, Chen, Huang & Cheng, 1997). Some VOC's cause liver, kidney and brain damage and are carcinogenic (Heja, Hussain & Khan, 2003; Muller, Diab, Renedell & Hounsome, 2003; Rigger, 1992). VOC emissions have also been implicated as a major precursor in the production of photochemical smog in the presence of oxides of nitrogen (NO_x), which causes atmospheric haze, eye irritation and respiratory problems (Chang *et al.*, 2003; Sillman, 1999; Jenkin & Clemitshaw, 2000; Wadden, Scheff & Uno, 1994; Siegell, 1998, Grover & Gomaa, 1994/95). Ozone (O_3) is a primary component of photochemical smog and is also a health threat if present in high concentrations. High concentrations of ground level ozone can result in nausea, lung damage, cancer, injury to plants, crops and vegetation and certain man-made materials (Benoit, 1995; Fourie, 2000).

VOC emissions also impact on the earnings of a company since VOC's are products lost to atmosphere therefore a company cannot realise the profit on these products (Parker, 1997). The reduction of VOC emissions by industry is therefore gaining importance, and control standards or limitations on VOC emissions are becoming more stringent worldwide (Hill, 2002; Grover *et al.,* Winter 1994/95; Jagiella & Kliclman, 1994; Ammann, Koch, Maniatis & Wise, 1995). Any industry processing hydrocarbon compounds is expected to cause VOC emissions. Refineries process crude oil, which consists of hydrocarbon compounds.

Studies done on refineries and surrounding residential areas have shown that refineries are a major source of VOC emissions (Cetin, Odabasi & Seyfioglu, 2003; Kebede, Schreiner & Huluka, 2002; Escalas, Guadayol, Cortina, Rivera & Caixach, 2003; Kenski, Wadden & Scheff, 1995; Wadden *et al.*, 1994; Hill, 2002). It is therefore important for refineries to monitor, control and reduce their VOC emissions as part of their environmental management programme.

Most industries and governments are focusing on sustainable development to ensure economic growth as well as protection of the environment. Industries, including refineries, are developing environmental management programmes to monitor their impacts on the environment, and to implement control measures to minimise their effects on the environment (Gomaa & Allawi, 1994). Impacts on the environment caused by refineries include water pollution, air pollution (including VOC emissions) and solid wastes.

Refineries and other industries in South Africa have been following the same trend. Natref (National Petroleum Refiners of South Africa)[1] implemented an environmental management programme, ISO 14001 in 1998. VOC emissions are measured and reported by the refinery as part of their environmental management programme.

Currently no official regulations for VOC emissions have been published for South Africa. The National Environmental Management Air Quality Bill (National Environmental Management: Air Quality Bill, 2003) of the Republic of South Africa provides ambient air quality guidelines for ozone (O_3), oxides of nitrogen (NO_x) and other air pollutants, but none for VOC's. Since VOC emissions have been implicated as a major precursor in the production of ozone in the presence of oxides of nitrogen (NO_x) (Chang *et al.*, 2003; Sillman, 1999; Jenkin *et al.*, 2000; Wadden *et al.*, 1994; Siegell, 1998), it makes sense to limit VOC emissions as well.

The drive for sustainable development, the absence of guidelines for VOC emissions and the fact that VOC emissions are controlled by refineries abroad, led to limited monitoring of VOC emissions by refineries in South Africa.

VOC emissions from the wastewater treatment area, storage tanks and product loading area were estimated in studies done by Natref during 1999, 2000 and 2001

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[1] Description of Natref, see page 6

(Grant, 1999; Mncube, 2001; Oosthuizen, 2000; Oosthuizen & Mncube, 2001). From July 2000, Natref started to monitor and report fugitive VOC emissions, VOC emissions from the wastewater treatment area and VOC emissions from the tank farm on a continuous basis, using point measurements.

With the publishing of the Air Quality Bill, Natref raised the questions:

- How effectively are VOC emissions monitored at Natref?
- What conclusions can be drawn from the results for VOC emissions reported by Natref?
- What is the overall situation concerning VOC emissions at Natref?
- How do VOC emissions at Natref (and therefore refineries in South Africa) compare to VOC emissions at refineries abroad?

To evaluate the effectiveness of the VOC emissions monitoring system at Natref it is necessary to benchmark with refineries abroad since no environmental guidelines concerning VOC emissions are available for South Africa. This can only be done optimally if the overall situation concerning VOC emissions at Natref is known. Refineries are similar in construction and close contact exists between the environmental departments of refineries in South Africa, therefore the situation concerning VOC emissions at one refinery in South Africa, will also be an indication of the situation at other refineries in South Africa.

Currently the overall situation concerning VOC emissions at Natref (the total VOC emissions at Natref site, in Sasolburg during stable operations excluding VOC emissions due to product spills) is not determined in the VOC emissions monitoring system implemented at the refinery and therefore the questions raised cannot be answered adequately. In order to answer these questions it is the aim of this evaluation to address this hiatus in Natref's VOC emissions monitoring system.

The information resulting from this evaluation can then be used as a starting point to improve VOC emissions monitoring systems, determine the capital loss represented by VOC emissions, assist refineries to implement control measures, influence future ambient air guidelines for VOC emissions in South Africa and to benchmark with refineries abroad.

2. Goals and objectives

The goal of this study is to determine the overall situation concerning VOC emissions at Natref, which in turn will enable the evaluation of the VOC emissions monitoring and control system at Natref.

To achieve this goal the following objectives are set for this study:

- Explain how VOC emissions are estimated at Natref.
- Combine all the available VOC emissions data of the refinery to determine the overall extent of VOC emissions at Natref.
- Determine the cost (loss) VOC emissions presents to Natref.
- Benchmark (compare) Natref's VOC emissions with those available for refineries abroad.
- Simulate different VOC emissions scenarios to evaluate the overview of VOC emissions at Natref.

3. Materials and methods.

The evaluation of the VOC emissions monitoring and control system at Natref was done using point measurements of VOC emissions taken by Natref for studies done in 1999, 2000, 2001 and values reported for VOC emissions by the refinery as part of their environmental management programme (Grant, 1999; Mncube, 2001; Oosthuizen, 2000; Oosthuizen *et al.*, 2001). These data will be referred to as: 'Natref's field data' in the rest of this evaluation.

To transform Natref's field data into meaningful information, the data were reworked using methods, recommended by the EPA (Environmental Protection Agency of America, protocol 453) and in the Concawe manuals (best practices used in Western Europe) (Concawe, 1986; Concawe, 1987; Concawe, 1999). Natref's field data were ordered into the same sections as done by refineries abroad in order to benchmark with these refineries.

VOC emissions are mainly the lighter hydrocarbons (components with low boiling points) that vaporise at ambient temperatures, i.e. petrol components (starting at butanes, pentanes to hydrocarbon chains containing 13 carbon molecules). Therefore to determine the cost (loss to the refinery) represented by VOC emissions, the price of petrol is used for the purpose of this study. The price received by the refinery for petrol does not fluctuate as much as the retail price since it is influenced by the import price of the final products from the Middle East. Currently the price for petrol is R 1700 per ton of petrol as supplied by Natref's Planning and Scheduling department. This price will have to be updated when required for further studies.

4. VOC emissions at Natref, South Africa

4.1 Description of Natref:

Natref is a typical refinery, but in contrast to many others, it is not situated on the coast but approximately 500 km inland at Sasolburg in the Free State. Crude oil is distilled to produce petrol, diesel, jet fuel and other products. Crude oil that arrives by ship at Durban is pumped to storage tanks in Durban. When the crude oil is required at the refinery, it is pumped through an underground pipeline to Natref, where it is stored in tanks before being distilled in the crude distillation unit (CDU) (See Figure 1). The intermediate products (that require further processing in downstream conversion units), by-products (i.e. liquefied petroleum gas, fuel oil, paraffin etc.) and final products (petrol, jet fuel and diesel) are stored in tanks before they are further treated or supplied to the market. Products leave the refinery via pipeline, rail or road tankers. The wastewater generated in the refinery is partly treated to remove hydrocarbon compounds before it is sent to Sasol Chemical Industries (SCI) for further treatment. Other waste products such as flue gas (from burning fuel gas and fuel oil and incinerating off-gases) are released into the air and sludge from cleaning tanks etc. is land farmed. For the purpose of this study, only the VOC emissions at Natref are evaluated.

The generation of VOC emissions at refineries is divided into three areas in order to supply practical guidelines for monitoring these emissions (Siegell, 1998; Siegell, 1996; Siegell, 1995). VOC emissions that occur due to product spills and start-up and shutdown operations are not included in the day-to-day monitoring of VOC emissions from normal operation. The areas, that covers the entire refinery are:

- Fugitive VOC emissions,
- VOC emissions from the wastewater treatment area, and,
- VOC emissions from storage tanks and product loading area (tank farm).

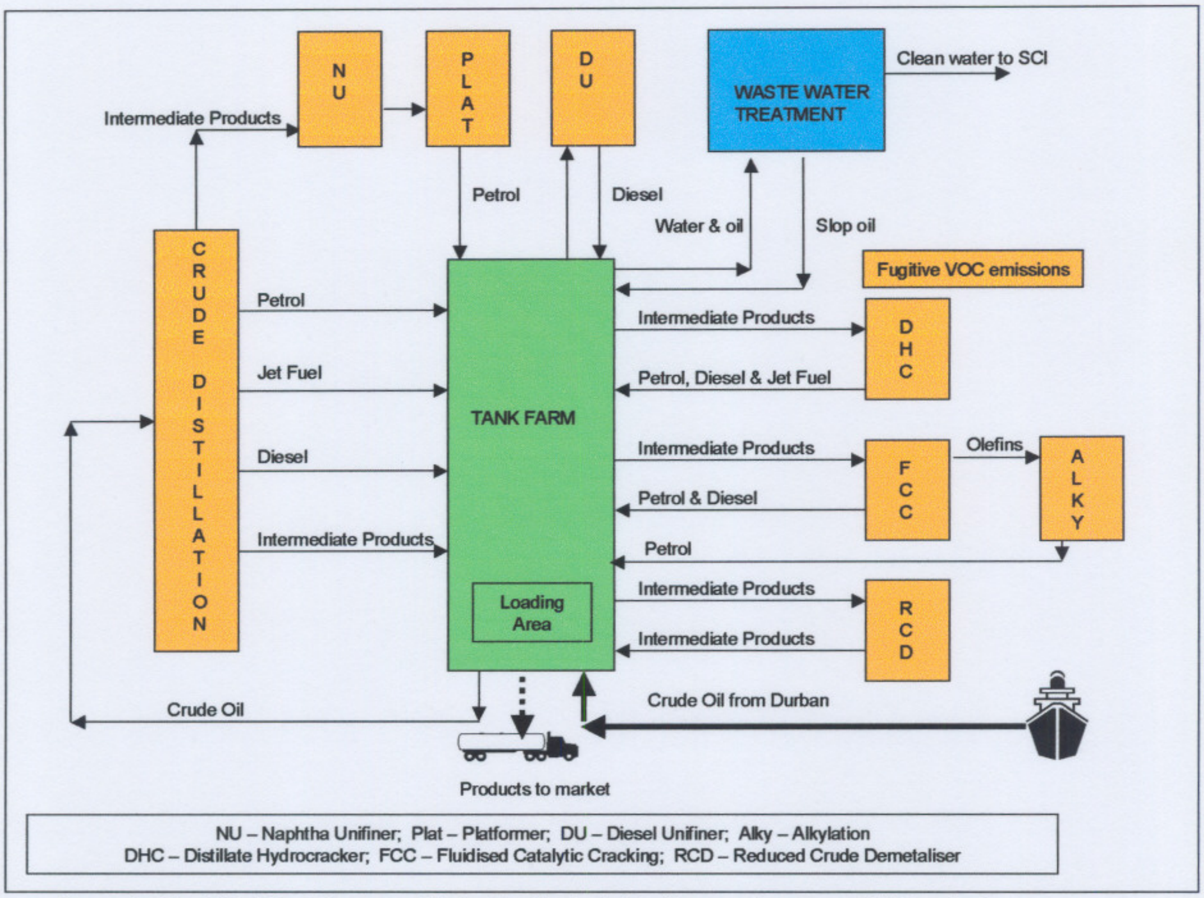


Figure 1: Simplified flow diagram of Natref to illustrate the three main areas of VOC emissions

According to a study done on six refineries abroad (Exxon, USA) (Siegell (1), 1997), 40 – 60 % of the total VOC emissions were generated from fugitive emissions, 10 – 15 % from the wastewater treatment area and 30 – 45 % from the tank farm (including product loading) (Siegell (1), 1997; Siegell, 1995). The percentage of VOC emissions from each area is influenced by the pollution control regulations that are applicable in the areas where the refinery is situated.

4.2 <u>Fugitive VOC emissions</u>

Fugitive VOC emissions refer to hydrocarbon products that leak from process equipment and piping auxiliaries such as relief valves, compressors, valves, drains, pumps and flanges (referred to as 'ancillary equipment' for this discussion) (Siegell (2), 1997; Siegell, 1995). Although the individual leaks are usually quite small, the total VOC emissions from the ancillary equipment are high because so many are found in a refinery (Siegell, 1995; Park, Chah, Choi, Kim & Yi, 2002; Concawe, 1999).

Valves are only one source of fugitive emissions, but it is estimated that valves account for 50 – 60 % of the fugitive emissions and that the major portion of fugitive emissions originates at only a small fraction of the valves. Less than 1 % of valves in gas/vapour service can account for over 70 % of fugitive emissions at a refinery (Siegell, 1996; Harrison, 2004; Siegell (2), 1997; Concawe, 1999).

To reduce fugitive VOC emissions at refineries, the first step is to implement a LDAR (Leak Detection And Repair) programme. A LDAR programme entails the measuring of VOC emissions from ancillary equipment and repairing all process equipment that have VOC emissions greater than 10 000 ppmv (parts per million by volume). 10 000 ppmv is also called the leak definition concentration (Siegell (2), 1997; Siegell, 1995, Concawe, 1999). A simple LDAR programme has an annual cost of approximately R 300 000 (Siegell, 1995). When an LDAR was implemented at a refinery a reduction of 50 – 75 % in the fugitive VOC emissions were found, compared to fugitive VOC emissions calculated using average emission factors for different ancillary equipment (Siegell, 1995).

Fugitive VOC emissions can be determined using two methods. Guidelines on how to apply these methods are set out in the EPA manuals (EPA, 1995, Protocol 453). Method 1 (used in this study): Product leaks are measured at the ancillary equipment and the results are accumulated to get the total VOC emissions for the refinery. This method could give an under-prediction of the fugitive VOC emissions since it is impractical to do measurements on all the ancillary equipment due to the large numbers of such ancillary equipment in a refinery.

Method 2: Use emission factors developed for individual ancillary equipment. The emission factor for each type of ancillary equipment is multiplied with the number present in the refinery and the results are then added to get the total fugitive VOC emissions for the refinery. This method may result in over-predicting fugitive VOC emissions since ancillary equipment may not leak as much as the factors suggest.

Natref implemented a LDAR (Leak detection and repair) programme in the year 2000 using method 1. Personnel from Natref's environmental department measure the VOC emissions every six months at 2000 to 2500 valves in the refinery, which are approximately 1.5 m above the ground. Every time leak measurements are taken, different valves, except for those identified as high-risk valves (valves in gas / vapour service) are evaluated.

A measuring instrument (Industrial Scientific ATX pump), approved by the EPA is used to measure the VOC emissions at the valves. Guidelines provided by the EPA indicate where measurements are to be taken at the valves and how to convert the measured values (also referred to as screening values) from ppmv to a leak rate in kg/hr (See correlations in Table 1).

The sum of the leak rates for all the valves is reported as the fugitive VOC emissions at Natref. Values are reported in tons/day and the average value for the year is determined by multiplying the average of the monthly values by 12. (See results in Table 2).

Table 1: Petroleum Industry leak rate versus screening value correlations.

Equipment type/service	Leak rate correlation* Kg/hr
Valves (all)	$LR = 2.29E\text{-}06 \times (SV)^{0.746}$
Pump seals (all)	$LR = 5.03E\text{-}05 \times (SV)^{0.610}$
Others	$LR = 1.36E\text{-}05 \times (SV)^{0.589}$
Connectors (all)	$LR = 1.53E\text{-}06 \times (SV)^{0.735}$
Flanges (all)	$LR = 4.61E\text{-}06 \times (SV)^{0.703}$
Open-ended lines (all)	$LR = 2.20E\text{-}06 \times (SV)^{0.704}$

* Not a correlation in the statistical sense

Where LR = Leak rate (kg/hr)
SV = Screening value (ppmv)

The LDAR programme does not replace standard operation procedures employed by the operations department to ensure equipment integrity and safety of personnel. (Operators report leaks found on equipment in order for the maintenance department to repair the leaks. The rate at which these leaks are repaired depends on the priority given to the leak by the operator. The size, type of product and equipment leaking determines the priority of the leaks.)

Table 2: Fugitive VOC emissions at Natref. (Summarised from Appendix 1)

Year	Emissions Ton/yr	Cost R/yr
Jul '00 – Jun '01	110	187 000
Jul '01 – Jun '02	146	248 200
Average	128	217 600

The following can be concluded from the values reported for fugitive VOC emissions at Natref:

- Guidelines indicating whether the specific values for fugitive VOC emissions at Natref are high or low are not readily available. Fugitive VOC emissions are discussed in relation to the rest of the VOC emissions at a refinery and this comparison indicates that the fugitive VOC emissions at Natref are much lower than the benchmark range (See discussion on page 23 to 26).
- Natref reports the fugitive VOC emissions for the refinery based on results from 2000 to 2500 valves, while the EPA methods include pump seals, flanges etc. (EPA, Protocol 453, 1995). This will lead to an underestimation of the fugitive VOC emissions at the refinery.
- The loss due to fugitive VOC emissions at Natref seems too low compared to studies done in refineries abroad (Siegell, 1995; Siegell, 1996; Harrison, 2004; Siegell (1), 1997; Concawe, 1999). If the results for fugitive VOC emissions are correct, it is not economically feasible to implement an LDAR programme at Natref to reduce fugitive VOC emissions since the cost to reduce it is more than the apparent loss (R 250 000 versus R 300 000).
- According to Natref's environmental department, the LDAR program implemented has already resulted in an improvement in the level of VOC emissions measured at high-risk valves. This statement has to be verified since the results indicate an increase in fugitive VOC emissions for the past two years.
- The ancillary equipment (valves, flanges etc.) used at Natref are standard design (installed when the refinery was built in 1970, and not replaced with the latest environmentally friendly designs), therefore the low fugitive VOC emissions seem questionable (See discussion on page 23 – 26).

- Is the LDAR programme implemented by Natref comprehensive enough? Determining the fugitive VOC emissions using emission factors (second method) could give Natref an indication of the expected fugitive VOC emissions (worst-case scenario). The LDAR programme can then be improved to represent the fugitive VOC emission more accurately.

In the following section the VOC emissions from the wastewater treatment area are discussed:

4.3 Waste water treatment

Water generated and used in refineries is contaminated with hydrocarbons (Escalas *et al.*, 2003). The processed water is collected and treated to remove oil (hydrocarbons) and other contaminants before it is released back into the environment (or in Natref's case, further treatment at another company).

The most common wastewater treatment system used by refineries worldwide is an API (American Petroleum Institute) separator (See Figure 2). The API separator works on the principle of gravity separation. The system provides an environment where solids can be settled coincidentally with the separation of oil (oil floats on water) in the influent water. An API separator consists of:

- An open rectangular basin
- Inlet water and oil-water separation chambers
- Flight scrapers for removing sludge (oil) from the surface of the water
- Sludge collection pit
- Oil skimming device
- Ponds for storage of water after passing through open separator
- Slop tanks to store the recovered oil

The main advantage of the API separator is that it can intercept large volumes of water, oil and solids. The main disadvantage is that it requires a large area of land and it can only remove comparatively large oil droplets. It is mainly from these large open areas (ponds and separators) that hydrocarbon components (VOC's) evaporate into the atmosphere and pollute the air.

VOC emissions from the API separator are measured separately, since its contribution to the total VOC emissions can be quite high (10 – 15 %) (Jagiella *et al.*, 1994; Siegell, 1995; Concawe, 1999). The VOC emissions from the wastewater treatment unit can be significant if proper housekeeping and control measures are not implemented at a refinery (Bianchi *et al.*, 1997; Siegell, 1995; Siegell, 1996; Siegell (1), 1997; Escalas *et al.*, 2003, Jagiella *et al.*, 1994).

The wastewater produced at Natref is treated in an API separator and is then sent to Sasol Chemical Industries (SCI) for further treatment.

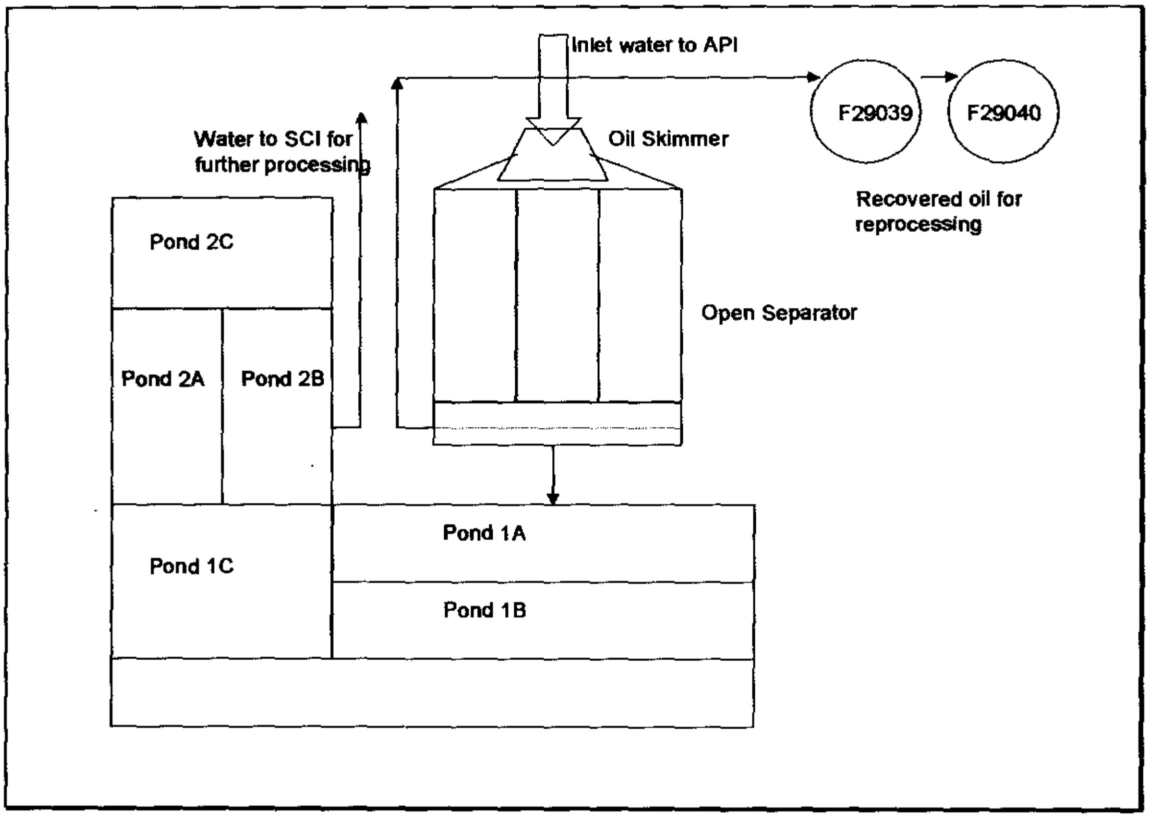


Figure 2: API Separator at Natref.

4.3.1 Estimating the VOC emissions from the wastewater treatment area.

It is very difficult to estimate the VOC emissions from an API area because of the large surface area that is exposed to the atmosphere. Methods that are used by refineries worldwide to estimate VOC emissions from the API separator are the Litchfield equation (Method 1) (Concawe, 1987), emission factors (Method 2) (Grover *et al.*, Winter 1994/95) and the fence-line method (method 3, currently used by Natref).

Method 1 - Litchfield equation:

The Litchfield equation is an equation that takes into account the 10% distillation point of the oil in the water (the temperature at which 10 % of the oil has evaporated), the ambient air temperature and wastewater temperature and the oil content of the wastewater. The Litchfield equation estimates the percentage of oil in the wastewater that evaporates into the atmosphere (See Table 4 for values of constants).

Litchfield equation: $\text{Loss } (\%) = -6.6339 + 0.0319x - 0.0286y + 0.2145z$

Where:
Loss = volume % of oil lost to atmosphere from oil in influent
x = ambient air temperature, °F
y = 10 % distillation point, °F
z = waste water temperature, °F

It should be noted that neither the wind velocity nor separator surface area are included in this correlation although both are expected to have an influence on the volume of oil evaporating (Concawe, 1987).

Method 2 - Emission factors:

Another way to estimate the VOC emissions from the API area is to use emission factors. The values for emission factors are found in Table 3. If no control measures (i.e. installing covers over the API separator (Siegell, 1995)) are implemented to reduce the VOC emissions from the API separator, the uncontrolled emission factor is used otherwise the controlled emission factor is used. (Grover *et al.*, Winter 1994/95)

For Natref, the uncontrolled emission factor was used to estimate the VOC emissions from the API separator because no control measures, such as sewer system suppression and covers have been implemented yet (See Table 5 for results).

Table 3: Emission factors

Type of VOC emissions	Emission Factor (lb VOC emissions/1000 gallons of waste water)	Emission Factor (kg VOC emissions/m^3 waste water)
Uncontrolled	5	0.5992
Controlled	0.2	0.024

Method 3: Fence-line method:

The fence-line method is used by industry to measure (online measuring equipment is available) air pollutants (including VOC emissions) that leaves the site to have an indication of pollution levels the surrounding area will experience. This methods takes into account the dilution effect of air pollutants by air. No reference in the literature could be found where the fence-line method is used by a refinery to estimate the VOC emissions from the wastewater treatment area. Members of the refinery staff at Natref indicated that it is the method used in their monitoring system.

Natref personnel measure VOC emissions (with the Industrial Scientific ATX pump) on a monthly basis, upwind and downwind from the API ponds at a height of approximately 1.5 m above the ground. The difference in the values is then reported as the VOC emissions from the wastewater treatment area.

4.3.2 VOC emissions from the API separator at Natref.

The Litchfield equation and the emission factors were used to calculate the VOC emissions from the API separator in a survey done by Natref during December 2000/ January 2001. Since July 2000 Natref has been measuring the VOC emissions from the API area, every month using the fence-line method. These values are reported in the VOC emissions monitoring system as the VOC emissions from the wastewater treatment area. In the following paragraphs the methods are compared:

Litchfield equation:

For the purpose of this study, the VOC emissions for the API area were estimated using the Litchfield equation for the period 1998 to 2002 using Natref's field data (Mncube, 2001). The VOC emissions were estimated using the monthly average volume flow of wastewater to the API separator, the measures oil concentration in the wastewater and the percentage of oil lost to atmosphere as calculated with the Litchfield equation (concentration measured and % loss calculated in the December 2000/January 2001 survey) (See Table 5 for results).

The values for the constants in the Litchfield equation were measured in Natref's laboratory (analysing samples of the water and oil going to the API separator), during the survey done by Natref in December 2000/January 2001 to determine the VOC emissions from the wastewater treatment area.

Table 4: Values used for Litchfield equations' constants (Natref's VOC emissions report, 2001, See Appendix 2)

	To calculate Natref's API emissions	**General values for European refineries (Concawe Reports)**
x , °F (°C)	77 (25)	55 (13)
y , °F (°C)	194 (90)	250 - 325 (121 – 163)
z, °F (°C)	89.6 (32)	75 (24)
% Loss as calculated with the Litchfield equation	9.5	3.9*
Density (kg/m^3)	746	600
Oil in effluent/m^3 water (mg/l)	5600	2000 *

* Concawe Report No 87/52, 1987: 21

Table 5: VOC emissions from the API separator at Natref (Summarised from Appendix 2)

Year	Litchfield Equation Ton/yr	Emission Factors Ton/yr	Fence line Ton/yr	Average* Ton/yr	Cost R/yr (R1700/t)
Jul '98 – Jun '99	571	862		717	1 218 900
Jul '99 – Jun '00	544	821		682	1 159 400
Jul '00 – Jun '01	576	870	117	723	1 229 100
Jul '01 – Jun '02	544	821	109	683	1 161 100
Average	559	844	113	701	1 192 125

* Average of Litchfield and emission factor results

Discussion of results:

- The VOC emissions estimated with the different methods vary significantly, causing concerns regarding the accuracy of the methods used. The VOC emissions estimated with method 2 (uncontrolled emission factors) are 51% higher than when estimated using method 1 (Litchfield equation). But the fence-line method's results are 80 % less than the VOC emissions estimated using the Litchfield equation. This raises the question: which of these methods should be used to estimate the VOC emissions at Natref's API separator?
- The values in Table 4 indicate that the wastewater at Natref contains far more (180 % more) oil than what is recommended for European refineries. The oil in the wastewater has a higher concentration of light hydrocarbon components (y), and the ambient temperature (x) and wastewater temperature (z) are higher than those experienced by Western European refineries (Concawe, 1986; Concawe, 1999). These differences indicate that the expected VOC emissions from the API separator at Natref will be higher than those of Western European refineries (Cetin *et al.*, 2003).
- Since the size of the API separator and the wind speed is ignored with the Litchfield equation, the VOC emissions as compared to the emission factor method may be under-predicted.
- The VOC emissions calculated with the emission factor are in the correct order of magnitude for the volume of wastewater treated in the API separator (Grover *et al.*, Winter 1994/95). The emission factors seem to take into account the size of the API separator.

- Although the fence-line method takes the wind speed into account to a certain extent, the VOC emissions measured with the fence-line method are much lower compared to the other methods. This conflicts with expectations that the VOC emissions from the API separator will be high. The dilution effect that is present with this method probably causes the VOC emissions to be underestimated. To use the method in this manner seems questionable.
- The reasons for Natref's decision to use the fence-line method in the VOC emissions monitoring system to measure the VOC emissions from the wastewater treatment area are not clear. A justification for the use of this method could not be found in the literature and indications are rather that refineries abroad use the other two methods.
- The loss could be estimated at 1 million rand, which can be used to justify projects to reduce the VOC emissions from this area.
- For the rest of this study, the average of the VOC emissions estimated with the Litchfield equation and emission factors will be used.

The third area that contributes to VOC emissions at a refinery is the tank farm and loading area. The investigation into this area is presented in the following paragraphs:

4.4 *Tank farm*

The tank farm refers to all the tanks in which crude, intermediate and final products are stored and it includes the product loading area, where products are loaded into rail cars and road tankers. Measurements abroad show that the tank farm can make a significant contribution (30 – 45 %) to the VOC emissions of a refinery, especially if no control measures are implemented. Before VOC emissions became known as an important pollutant, refineries began implementing control measures in this area, in order to reduce product losses (Siegell, 1998; Siegell, 1995; API Publication, 1993; Concawe, 1986). The drive to reduce VOC emissions was an economic rather than an environmental one.

4.4.1 Storage tanks

The main factors affecting evaporation of products and therefore VOC emissions from tanks are product properties (i.e. liquid composition, vapour pressure and product temperatures), the vapour-liquid interface (i.e. area and time of exposure between vapour and liquid phases), environmental aspects (i.e. volume of vapour phase, temperature changes in vapour space and ambient air, operating pressure of tank and wind speed) and the condition of the tanks (i.e. corroded) (Concawe, 1986). Typically, VOC emissions from storage tanks range between 10 to 15 % of total plant VOC emissions (Siegell, 1995).

Three types of tanks are generally found in refineries to store products i.e. floating roof tanks, fixed roof tanks with internal floating covers and fixed roof tanks (Figure 3). VOC emissions from floating roof tanks and fixed roof tanks with internal floating covers are less than those from fixed roof tanks (smaller contact area between product and air). VOC emissions occur from the tanks due to the following mechanisms:

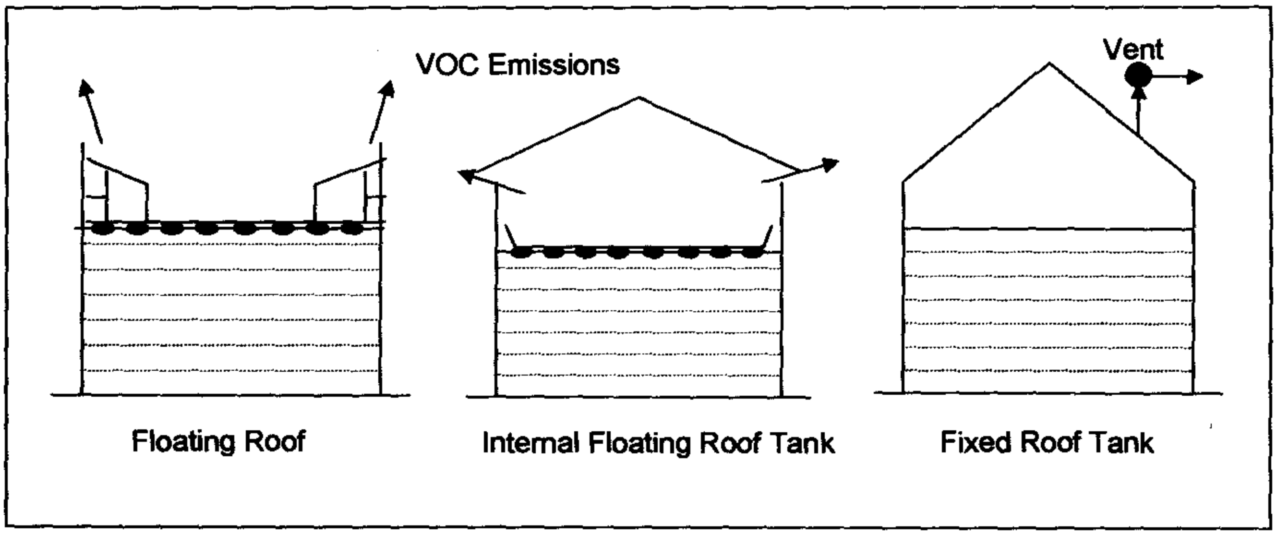


Figure 3: Types of storage tanks.

- Standing storage emissions

  VOC emissions from floating (internal and external) roof tanks are caused by the evaporation of liquid product through the flexible peripheral seals, deck structure and fittings such as manholes, gauge pipes, hatches and roof support columns or legs. The wind has a significant influence on the magnitude of these emissions.

- Breathing emissions

  In fixed roof tanks vaporised products escape through vents, fitted with pressure/vacuum relief valves. VOC emissions are caused by temperature variations of the content of the tanks due to the diurnal cycle and changes in the barometric pressure, which in turn cause expansion and contraction of both liquid and vapour in the tanks. Meteorological factors such as wind, sunshine and rain on the outside surfaces of the tank will influence the magnitude of the breathing emissions.

- Withdrawal and Displacement emissions

  In floating (internal and external) roof tanks the film of liquid product that adheres to the surface of the tank walls and any tank roof support columns, evaporates after the withdrawal of liquid product. The magnitude of these emissions is influenced by the surface condition of the tank, for instance the presence of rust or a tank lining.

  In fixed roof tanks air is taken in through the vents as the tank is emptied. The dilution of the hydrocarbon vapour-air mixture will lead to further evaporation from the surface of the liquid to restore vapour-liquid equilibrium. This will lead to an increase in pressure, which in turn leads to VOC emissions when the pressure valve setting of the tanks are exceeded (air/vapour mixture is expelled to reduce the pressure).

  Displacement emissions occur when the air-vapour mixture is expelled through the vent when the fixed roof tanks are filled with liquid product again.

VOC emissions from storage tanks can either be measured or estimated using the methodology as set out by the American Petroleum Institute's "Manual for Evaporation loss from External Floating roof tanks" and "Evaporation loss from fixed roof tanks". The equations in these manuals take into account physical properties of the products, nature of the given storage tank and external meteorological factors (API Publication, 1991; API Publication, 1997). VOC emissions are estimated using zero-wind-speed and wind-speed-dependent factors for the tank rim and type and number of deck fittings (i.e. manholes, guide poles support columns, vacuum breakers etc.) present. The withdrawal, breathing and standing storage VOC emissions are estimated and the values added for every tank.

There are 92 tanks at Natref's site including fixed roof tanks, fixed roof tanks with internal floating roofs and floating roof tanks. All the floating roof tanks have been fitted with secondary seals (extra seal around periphery of tank to reduce product losses) to reduce the VOC emissions and therefore product losses. Final product tanks are emptied two to three times a week when product is sent to the market and are expected to have higher VOC emissions than intermediate product tanks.

During the first quarter of 1999 Natref conducted a survey to estimate VOC emissions from the storage tanks, using the methodology in the API manuals. Problems encountered during the survey included the collection of physical properties of the products in the tanks such as RVP (Reid Vapour Pressures), vapour molecular weights and distillation information. Extremely limited vapour molecular weight data were available because it was not required for other purposes and it is very difficult to obtain representative samples for analysis.

From the survey it was found that the highest VOC emissions came from tanks containing crude oil and petrol components. The findings from this survey are summarised in Table 6 (Natref VOC emissions report, 1999).

Table 6: VOC emissions from storage tanks at Natref (Natref VOC emissions report, 1999, Summarised from Appendix 3)

Product	Final Product Ton/yr	Product Components Ton/yr	Total Ton/yr	Cost R/yr
Petrol	155	120	275	467 500
Jet fuel	0.6	0.02	0.62	1 054
Diesel	3	5	8	13 600
Crude oil			47	79 900
Intermediates			28	47 600
Total			358.62	609 654

The results confirm that lighter hydrocarbon compounds (with lower boiling points, petrol components) evaporate first (Benoit, 1995). Since crude oil contains the whole spectrum of hydrocarbons it is expected to have high VOC emissions. Since the greater majority of VOC emissions are petrol components, the use of the petrol price to determine the loss to the refinery due to VOC emissions is acceptable.

Since July 2000 Natref has been measuring (with the Industrial Scientific ATX pump) the VOC emissions twice a year at the vents, sample points and standing pipes of the final product storage tanks (these tanks are emptied and filled more often than other intermediate product tanks). These results are then reported as the storage VOC emissions and have been constant at 1 ton/day from 2000 to 2002. The average loss on a yearly basis is 365 ton/yr and compare well with the loss (359 ton/yr) found in the 1999 storage tank survey (Natref VOC emissions report, 1999). This represents a monetary loss of R 620 500 per year.

The emissions from the loading area, when loading products into rail cars and road tankers, are combined with the tank farm emissions for monitoring purposes. The estimation of VOC emissions from product loading is covered in the following paragraphs.

4.4.2 Product loading.

When product is loaded into rail cars and road tankers, hydrocarbon vapours are expelled into the atmosphere (Benoit, 1995). Loading operations are a large potential source of VOC emissions. Typically VOC emissions from loading operations range between 20 to 30 % of plant VOC emissions (Siegell, 1995).

VOC emissions are caused by the expulsion of a volume of vapour due to the addition of a similar volume of liquid. This mechanism is similar to emissions from the filling of fixed roof tanks. The quantity and composition of the vapour emissions expelled will depend on the previous product contained, any cleaning prior to loading, new material being loaded, method of loading and any vapour collection or control devices used (Siegell, 1995; Concawe, 1986).

The vapour expelled during loading consists of two components. Initially, they are predominantly due to the vapour formed by the evaporation of the previous product (unless the holding vessel was cleaned). Later in the loading process the emissions are predominantly the vapour generated during the loading of the new liquid (Siegell, 1995; Concawe, 1986).

The volume of VOC emissions is mostly influenced by the turbulence created when products are loaded. Emissions will be higher when more turbulence is present during loading due to the increase in evaporation and entrainment of liquid droplets in the vapour/air mixture.

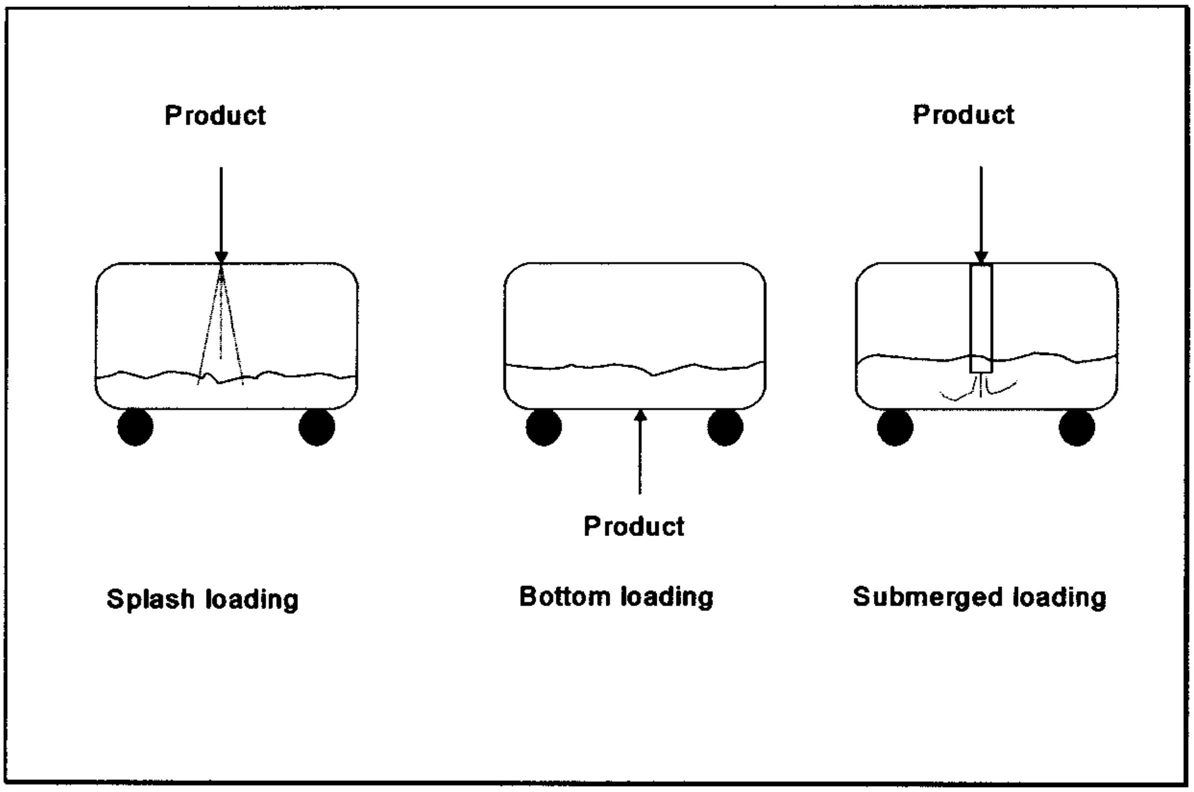


Figure 4: Loading methods for rail cars and road tankers

Product can be loaded in three different ways (See Figure 4). Splash loading is when liquid is poured from the top into the rail car or road tanker. Bottom loading is when liquid enters the tanker at the bottom while submerged loading is when the fill pipe extends to 0.3 – 0.6 m above the bottom of the road tanker or rail car (API Publication, 1993; Concawe, 1986). VOC emissions from splash loading are the highest while it is the lowest with bottom loading. Submerged loading reduces the VOC emissions by 60 – 65 % compared to splash loading.

VOC emissions from the loading area can either be measured (with the Industrial Scientific ATX pump), or estimated using the methodology as set out in the Concawe manual (Concawe, 1986). The equation in the manual takes into account vapour-liquid equilibrium conditions, the physical properties of the products that are loaded, the previous tank content and the degree of splashing that is present when loading.

The following equation was used to estimate the filling VOC emissions that occur when loading road tankers and rail car compartments (Concawe 1986):

$$E_f = 0.45 * C_s \left[C_p + V_b \left(\frac{1 - C_p}{1 - Cs} \right) \right]$$

where: E_f = Filling emissions expressed as a volume percentage of liquid loaded.

C_s = Vapour concentration at full saturation as a volume fraction, which can be taken as equal to the gasoline TVP (true vapour pressure) in bar.

C_p = Average PLV (preloading vapour) concentration expressed as a fraction of full saturation.

V_b = the parameter representing the fraction of the tank volume containing saturated vapour as a result of splashing during filling. (0.13 for road tankers with bottom loading and 0.18 for rail cars with submerged loading)

Assumptions on which the equation is based:

- The previous consignment of product (petrol, jet fuel or diesel) was unloaded completely from the compartments at discharge locations.
- There is only one point of discharge for road tankers and rail cars.
- The factor 0.45 is related to the vapour/liquid volume equivalents is still valid for Natref conditions.

At Natref, road tankers are bottom loaded and rail cars are submerged loaded, with a fill pipe that extends to 0.3 – 0.6 m above the bottom of the tank. The fill pipe is below the liquid level for the majority of the loading time. The filling methods used at Natref are dictated by the mechanical construction of the rail cars and road tankers.

During December 2000 Natref conducted a survey to estimate VOC emissions from the loading area for June 1998 to July 2000, using the methodology as set out in the Concawe manual. (See Table 8 for results) Problems encountered included obtaining physical properties of products and measuring of V_b and C_p (faulty apparatus). Therefore average values, as determined for Western European refineries were used for C_p and V_b (Concawe, 1986). See Table 7 for constants of the equation.

Table 7: Constants used to estimate % E_f for rail car and road tanker loading (Natref VOC emissions report, 2000)

	C_p	V_b		C_s	% E_f	
		Rail Cars	Road Tankers	TVP Bar	Rail Cars	Road Tankers
Petrol	0.15	0.18	0.13	0.41	0.0755	0.0622
Jet Fuel	0.01	0.18	0.13	0.41	0.0576	0.0421
Diesel	0.005	0.18	0.13	0.41	0.0569	0.0414
General values suggested for Western Europe *					0.061	0.05

* (Concawe, 1986)

Since July 2000 Natref has been measuring (with the Industrial Scientific ATX pump) the VOC emissions at the loading area, every month. These results are reported as the loading VOC emissions at Natref. The total VOC emissions for the year were determined by multiplying the average of the monthly values by 365. (See Table 8, July 2000 to June 2002). A vapour recovery unit at the rail loading area was installed at Natref in 2002 and Natref reported a reduction in VOC measured around the rail cars.

Table 8: VOC emissions from loading operations at Natref. (Natref VOC emissions report, 2000, Summarised from Appendix 1 & 4)

	Petrol Ton/yr	Jet Fuel Ton/yr	Diesel Ton/yr	Total Ton/yr	Cost R / yr
Jul '98 – Jun '99	318	58	209	586	996 200
Jul '99 – Jun '00	279	58	216	553	940 100
Jul '00 – Jun '01	Measurements not taken for individual products.			691	1 174 700
Jul '01 – Jun '02				459	780 300
Average	299	58	213	572	972 825

- The survey indicated that petrol is the highest source of VOC emissions.
- The higher value for E_f, compared to European refineries can be attributed to the value used for the TVP of petrol (Oosthuizen *et al.*, 2001). This is possible when Natref is able to blend a greater volume of butane into petrol as compared to European refineries.

- The estimated VOC emissions compare well with the VOC emissions measured during July 2000 to June 2002.
- The loss experienced by the refinery due to these product losses is nearly 1 million rand per annum. This monetary loss can probably justify the expansion of the vapour recovery unit to the road loading (Benoit, 1995).

4.4.3 Combined VOC emissions for the tank farm.

The combined VOC emissions from the storage tanks and loading area are presented in Table 9:

Table 9: VOC emissions for the tank farm at Natref (Summarised from Appendix 1, 3 & 4)

Year	Storage Ton/yr	Loading Ton/yr	Total Ton/yr	Cost R / yr
Jul '98 – Jun '99	338	586	924	1 570 800
Jul '99 – Jun '00	365	553	918	1 560 600
Jul '00 – Jun '01*	365	691	1056	1 795 200
Jul '01 – Jun '02*	365	459	824	1 400 800
Average	358	572	931	1 581 850

* Measured results

- No guidelines are available to indicate whether the specific values for VOC emissions from the tank farm at Natref are high or low.
- As expected, the VOC emissions from the storage tanks are less than from the loading area (Siegell, 1995). The VOC emissions from the storage tanks are approximately 40 % of the total VOC emissions from the tank farm. This coincides with the fact that more control measures have been implemented on the storage tanks of the refinery.
- The greatest reduction in VOC emissions from the tank farm can be achieved by introducing control measures in the loading area. The vapour recovery unit installed in 2002 is expected to reduce the VOC emissions from the loading area.
- Natref loses approximately 1.6 million rand due to VOC emissions from the tank farm. The losses incurred from the tank farm are higher than the fugitive VOC

emissions and VOC emissions from the wastewater treatment area, justifying the additional expenditure by refineries to reduce VOC emissions from the tank farm.

The overall VOC emissions situation at Natref is discussed in the following section:

5. The overall VOC emission scenario at Natref

At Natref the VOC emissions from each sector are monitored as separate entities. The contribution of each to the total VOC emissions at the refinery is not presented in the current Natref VOC emissions monitoring system. In this section the percentage contribution of VOC emissions from each area to the total VOC emissions is determined and compared to findings of studies done for refineries in the United States (Siegell, 1997). The USA refineries are subject to different pollution control regulations causing differences in VOC emissions from the three areas for these refineries (Siegell, 1995). Note that the benchmark ranges are also influenced by control regulations applicable worldwide. This study presents the first coherent overall view of the VOC emission scenario at Natref. Results are presented in Table 10, Table 11, Graph 1 and Graph 2.

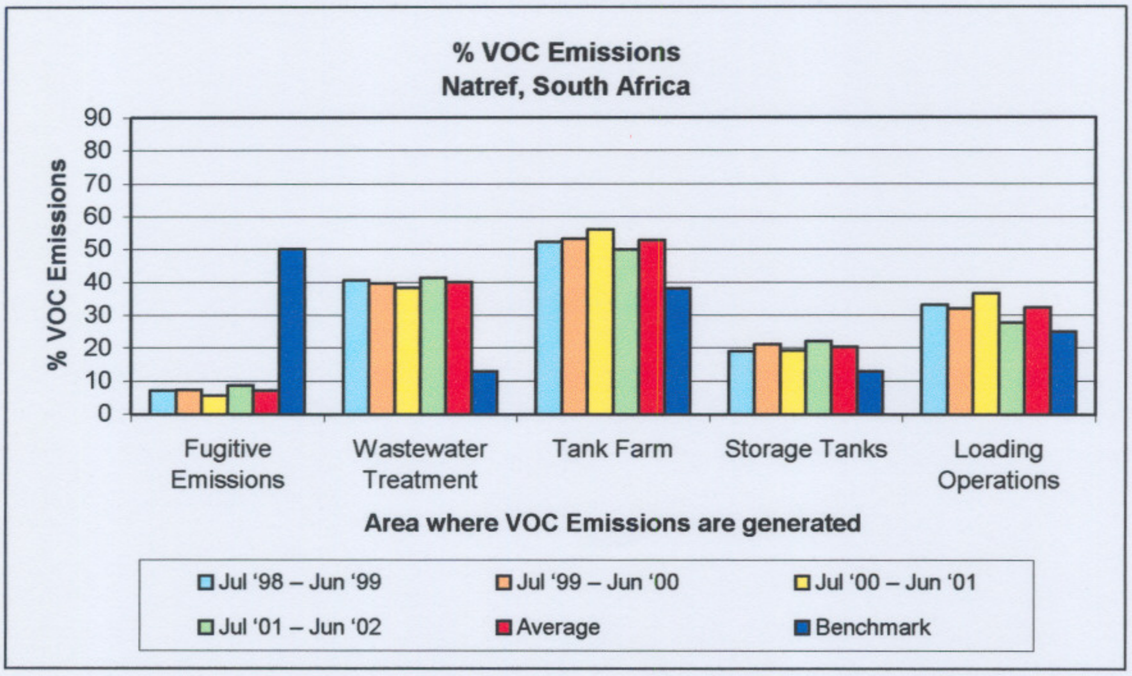
Table 10: Combined VOC emissions at Natref. (Based on results of Tables 2,5 & 9)

Year	Fugitive Ton/yr (%)	Wastewater Ton/yr (%)	Tank Farm Ton/yr (%)	Total Ton/yr (%)	Cost R / yr
Jul '98 – Jun '99	128* (7)	717 (41)	924 (52)	1769	3 007 300
Jul '99 – Jun '00	128* (7)	682 (39)	918 (53)	1729	2 939 300
Jul '00 – Jun '01	110 (6)	723 (38)	1056 (56)	1889	3 211 300
Jul '01 – Jun '02	146 (9)	683 (41)	824 (50)	1653	2 810 100
Average values	128 (7)	701 (40)	931 (53)	1760	2 992 000
Benchmark Range**	(40 – 60)	(10 – 15)	(30 – 45)		

* Average of July 2000/June 2001 and July 2001/June 2002

** Range seen at refineries abroad (Siegell, 1995; Siegell, 1996; Siegell (1), 1997)

Graph 1: % VOC Emissions at Natref, South Africa



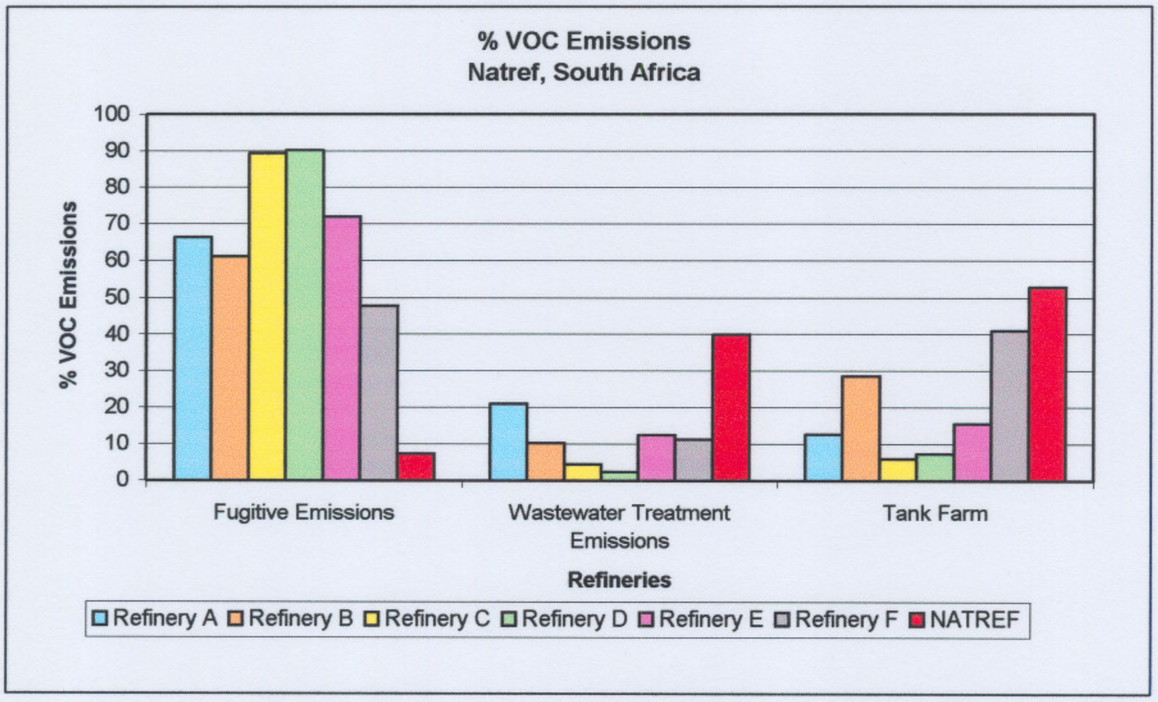
- At Natref the % VOC emissions from the tank farm were the highest and fugitive emissions the lowest. This contradicts findings of studies done at refineries in Europe and the United States (Siegell, 1995; Siegell, 1996; Concawe, 1999). The greatest discrepancies lie between fugitive VOC emissions and VOC emissions from the wastewater treatment area.
- In terms of operations Natref does not differ significantly from refineries abroad nor does it have any control measures implemented concerning fugitive VOC emissions (state of the art emission prevention ancillary equipment is not used in the refinery). Therefore the low contribution of fugitive VOC emissions to the total VOC emissions does not make sense, raising questions regarding the adequacy of the measuring process. The findings confirm that there are shortcomings (do measurements only at some valves) in the LDAR program used to estimate the fugitive VOC emissions at Natref.
- The low level of fugitive VOC emissions compared to that experienced by refineries abroad causes the percentages of VOC emissions from the other areas to be drawn askew.

- VOC emissions from the wastewater treatment area are higher than the benchmark range. Based on the findings concerning the factors influencing VOC emissions from this area it seems possible and is even expected. (High temperatures, lighter oil components and higher oil concentration in the wastewater) (Cetin *et al.*, 2003) (See Table 4).
- The differences in the factors influencing the VOC emissions from the wastewater treatment area easily account for the higher percentage VOC emissions from the wastewater treatment area at Natref. (40% instead of 10 – 15 %).
- The 8% deviation between the VOC emissions from the tank farm and the highest point of the expected range does not seem excessive. It can probably be accounted for by differences in control measures implemented at Natref and those implemented by refineries abroad.
- The results indicate that Natref loses approximately 3 million rand per annum due to VOC emissions. This monetary loss is probably conservative (due to low VOC emissions' results) and can be used to justify the implementation of control measures to reduce VOC emissions at the refinery.

Table 11: Comparison of % VOC emissions at Natref with refineries in the USA (Siegell, 1995)

Refinery	**Fugitive %**	**Wastewater %**	**Tank Farm %**
Refinery A	66	21	13
Refinery B	61	10	29
Refinery C	89	5	6
Refinery D	90	2	7
Refinery E	72	13	16
Refinery F	48	11	41
NATREF	**7**	**40**	**53**

Graph 2: Comparison of % VOC emissions at Natref with USA refineries.



The low level of fugitive VOC emissions is questionable. The surmise that the methodology to determine fugitive VOC emissions is not extensive enough, raises the question as to what the overall VOC emission scenario at Natref would be if the percentage fugitive VOC emissions is adjusted to fall within the benchmark range. In the following section a simulation of results is presented in order to address this question.

6. Simulation of the results

The absence of a coherent overall view of VOC emissions at Natref can lead to resources allocated erroneously. This must be avoided and a simulation can assist in obtaining a more representative picture. This will in turn lead to optimal expenditure on control measures.

In this section a few different scenarios will be explored. For the fugitive VOC emissions at Natref to fall within the range of 40 – 60 % of the total VOC emissions, the measured fugitive VOC emissions (in ton/hr) should be increased by 90 %. Methods available to estimate VOC emissions are not exact. This is due to difficulties experienced to obtain representative samples, physical properties of products and evaporated hydrocarbons etc. (Concawe, 1986; Concawe, 1987, Concawe, 1994; Siegell (1), 1997; Siegell 1995). Other uncertainties in methods used to estimate VOC emissions for the three areas are therefore included in this simulation. This is done to determine the contribution of these uncertainties to the overall VOC emission results.

Uncertainties are presented for different scenarios and each scenario is simulated with and without a 90% increase in the fugitive VOC emissions. The results of the different scenarios are presented in Table 12 and Table 13. The results of scenario 1 are also presented in Graph 3 and Graph 4.

Table 12: Modelled scenarios for the total VOC emissions at Natref.

Scenario	Change from original overall VOC emission results at Natref.*	Area where change is applied.
Scenario 1	Fugitive VOC emissions (tons/hr) are increased by 90%. Compare with results found in the study.	Fugitive VOC emissions
Scenario 2	Using the VOC emissions as measured with the fence-line method to determine overall situation.	Wastewater treatment area.
Scenario 3	Using the VOC emissions as estimated with the Litchfield equation (ignoring the results of emissions factor method) to determine the overall situation.	Wastewater treatment area.
Scenario	**Change from original overall VOC emission results at Natref.***	**Area where change is applied.**
Scenario 4	Using a density of 600 kg/m^3 for the evaporated hydrocarbons, as suggested in the Concawe manual instead of 746 kg/m^3 (density of petrol) to estimate the VOC emissions with the Litchfield equation (Concawe, 1986; Concawe, 1987; Natref's VOC emissions report, 2001). Taking the average of the results based on the Litchfield equation and the emission factor method to determine the overall situation.	Wastewater treatment area.
Scenario 5	The same as Case 4, but ignoring the results from the emission factor method.	Wastewater treatment area.

* Each case is done with and without increasing fugitive VOC emissions by 90%.

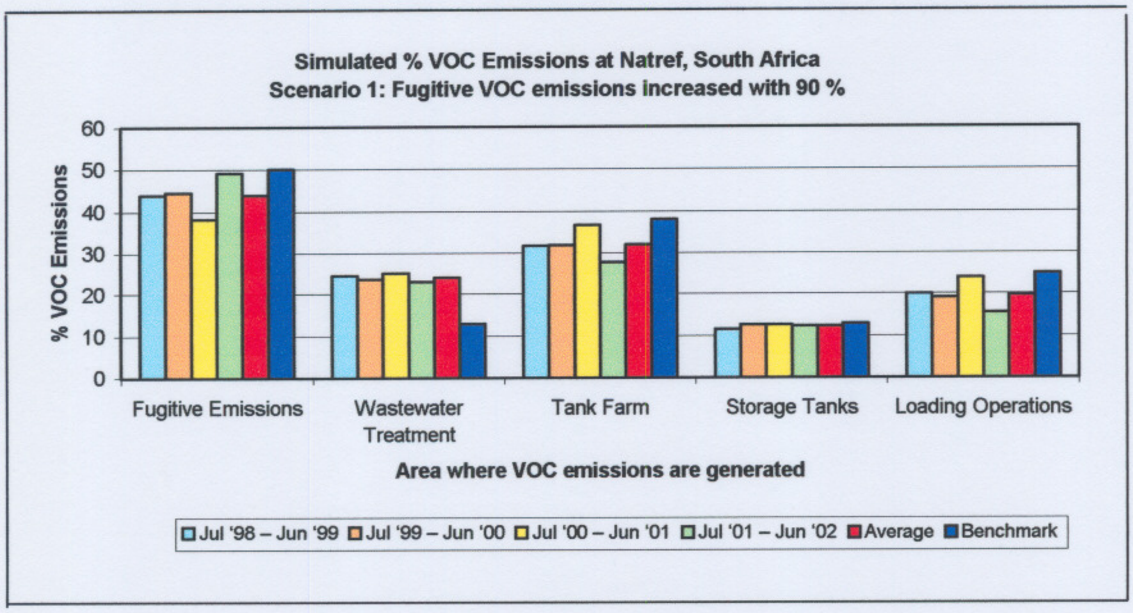
Table 13: Results of modelled scenarios for total VOC emissions at Natref.

	VOC emissions results Fugitive VOC's as estimated			**VOC emissions results Fugitive VOC's increased by 90%**		
	Fugitive	**Waste water**	**Tank Farm**	**Fugitive**	**Waste water**	**Tank Farm**
Scenario 1	**7***	**40***	**53***	44	24	32
Scenario 2	11	10	79	55	5	40
Scenario 3	8	35	57	46	20	34
Scenario 4	8	38	54	45	23	33
Scenario 5	9	30	62	48	17	35

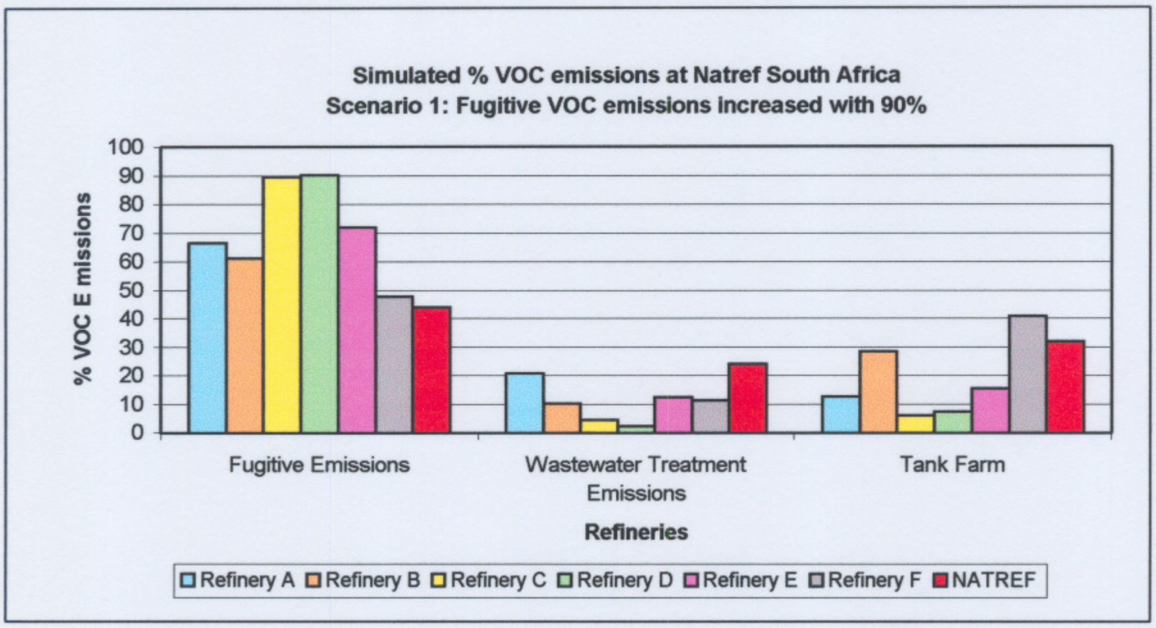
* Overall VOC emission scenario based on results of current VOC emissions monitoring system at Natref.

- If the fugitive VOC emissions (ton/hr) are increased by 90 %, the percentages of the other two areas are adjusted downward (See Graph 3 and Graph 4). The contributions from all three areas to the overall VOC emission scenario are more in line with the benchmark ranges and the results compare more favourably with those of refineries abroad.
- The results of the simulation (with the exception of Scenario 2) are very similar, indicating that the other uncertainties present have a relatively small impact on the results.
- In Scenario 2 the percentage of the wastewater treatment area reduces to the lower limit of the benchmark range. This is in conflict with expectations of high VOC emissions due to higher temperatures experienced and higher oil in water concentration at Natref.

Graph 3: Simulated % VOC Emissions at Natref, South Africa



Graph 4: Comparison of Natref's simulated VOC emissions with USA refineries



The results of the simulation move the percentages in the overall VOC emission scenario at Natref closer to the benchmark ranges confirming that the surmise concerning the extent of the methodology to measure fugitive VOC emissions is legitimate. The results seem to be more realistic if the construction of and conditions at Natref are considered.

7. Conclusion and recommendations.

ISO 14001 environmental management system has been implemented at Natref, indicating a commitment from Natref to protect the environment. Only if the steps forming the basis of any environmental management system are followed pertinently in the VOC emissions scenario, can effective monitoring and control measures be implemented. The steps are:

- Assess the environmental risks of the installation (including VOC emissions, see introduction).
- Plan all preventative measures against pollution (VOC emissions) for continuous improvement.
- Apply minimising strategies and implement control operations.
- Verify the performance of the process by direct and indirect monitoring.
- Review results.
- Improve the VOC emissions monitoring system.

The effectiveness of any industry's and therefore Natref's environmental management programme depends greatly on the monitoring systems, the accuracy of measurements and methods used. Benchmarking with similar industries assists in obtaining reliable results, identifying additional control measures required and improving current monitoring systems.

Before this study was done, very few conclusions could be made on the effectiveness of the control and estimation of VOC emissions at Natref, because by considering the VOC emissions from the three areas separately, Natref overlooked inaccuracies in the monitoring process, resulting in the VOC emissions monitoring system being ineffective.

The results of the study bring to light the following problems regarding the effectiveness and accuracy of VOC emissions monitoring at Natref.

- The biggest problem seems to be with the determination of fugitive VOC emissions. The percentages of fugitive VOC emissions at Natref are much lower compared to refineries in the USA and Western Europe. The low percentages of fugitive VOC emissions causes the VOC emissions from the wastewater treatment area and tank farm to be apparently higher than what is expected, when compared to refineries abroad.

- Natref uses the fence-line method to determine the VOC emissions from the wastewater treatment area. This method gives lower results than the Litchfield equation and emission factor method probably due to the dilution of hydrocarbon vapours.
- Factors (oil content of water, temperatures etc.) influencing evaporation of oil at the wastewater treatment area suggest that the VOC emissions may be higher than the benchmark range, strengthening the surmise that the results obtained with the fence-line method are questionable.
- The results from the tank farm seem to be in order with no significant problems identified in this area. This can probably be attributed to more control measure implemented due to the economic drive that existed prior to the environmental drive.
- Natref may implement control measures to reduce VOC emissions in areas that have a lesser impact on the environment, based on the results from the existing VOC emissions monitoring system.

The following recommendations are made to enable Natref to determine VOC emissions more accurately and to improve the current VOC emissions monitoring system. The results can be used to identify areas that have the biggest impact on air pollution and to implement control measures optimally.

Fugitive emissions:

- Conduct a comprehensive study estimating the fugitive VOC emissions using emission factors for all the ancillary equipment (valves, relief valves, vents, flanges, pumps etc.) in order to have a baseline (initial results before control actions) with which the measured results from the LDAR can be compared.
- Develop and implement a more comprehensive LDAR programme. Monitor the effectiveness of and improvements achieved with the LDAR programme to enable Natref to continuously improve it (identify high risk equipment and evaluate them every six months, as well as adding new ones).
- When the LDAR programme is working satisfactorily, other control measures can be implemented such as: upgrading valve packing and pump seals of those equipment that have the highest fugitive VOC emissions.

Wastewater treatment:

- Natref has to monitor the properties for the Litchfield equation (volume of wastewater generated, the oil concentration in the wastewater, density of oil, 10 % distillation point of oil, the ambient air and water temperatures) continuously, because this is the first step in controlling VOC emissions from the wastewater area. If these properties are not known, no control measures can be justified, implemented or improved.
- The most effective way to reduce the VOC emissions from the wastewater treatment area is to reduce the oil concentration in the wastewater and the volume of wastewater generated in the refinery. Western European refineries have reduced the oil content in wastewater (after treatment in an API unit) from 30 mg/l in 1981 to 3.7 mg/l in 1997 by proper housekeeping. The oil content in the wastewater can be decreased by reducing oil contamination of storm and cooling water and to implement proper operating procedures for equipment in the refinery. If this is achieved the reduction of VOC emissions from the wastewater treatment area will be significant.
- Confirm whether the fence-line method is accepted as best practice by refineries abroad and if so, evaluate the way Natref applies this method to determine the VOC emissions from the wastewater treatment area.
- After the recommendations mentioned above are implemented Nafref can implement more costly control methods, such as adding covers to the API separators. Covers on API separators could reduce the VOC emissions from the API with approximately 90 %.

Tank farm:

- The improvement resulting from the vapour recovery unit that was installed in 2002 on the rail loading area needs to be confirmed in order to extend it to road tanker loading.
- It will be worthwhile to connect tanks with high VOC emissions (tanks containing crude oil, petrol and petrol components) to the vapour recovery unit in order to reduce VOC emissions from the storage tanks.
- Include VOC emissions from crude tanks in the monitoring system since the crude tanks are also a big source of VOC emissions.

The current VOC emissions monitoring system at Natref is inadequate, which leads to ineffective control measures and a misrepresentation of the VOC emissions to themselves, the public and government. Sustainable development can only be achieved if industries reflect the correct and complete effect of their impacts to themselves, the public and government.

The combined results can assist Natref in developing and improving the monitoring programme for VOC emissions and therefore their environmental management system. The improved results can be used to identify the real problem areas and to implement control measures where the biggest reduction in the VOC emissions will be achieved.

In this study the methods used by the refinery to estimate the VOC emissions from each area were discussed and the results obtained with the methods were combined and benchmarked with refineries abroad. The information obtained by achieving the first three objectives highlighted inefficiencies around Natref's VOC emissions monitoring system. It can be assumed that similar situations concerning VOC emissions exist at other refineries in South Africa since environmental departments from different industries, environmental protection groups and their consultants and government agencies are working closely together.

Large chemical industries in South Africa have committed themselves to sustainable development and by implementing an improved VOC emissions monitoring system Natref can make important contributions to sustainable development.

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APPENDIX 1

Fugitive Emissions

2000/2001 RESULTS			Jul-00	Aug-00	Sep-00	Oct-00	Nov-00	Dec-00	Jan-01	Feb-01	Mar-01	Apr-01	May-01	Jun-01
Parameters			1	2	3	4	5	6	7	8	9	10	11	12
Effluent to Sasol (m^3/month)			127161	127161	117488	127380	130110	129587	129587	140731	119692	87914	87914	113861
Slop Transferred ex API (m^3/month)			1225.8	668.21	1135.5	1131.2	626.6	1051	495	827	1067	1504	1651.2	1474.8
Total effluent (m^3/month)			128386.8	127829.21	118623.5	128511.2	130736.6	130638	130082	141558	120759	89418	89565.2	115335.8
Total effluent (kg/month)														
Litchfield:	x °F		y °F	z °F										
	77		194	89.6										
% Oil in effluent	5600	mg/l												
% Loss volume of inlet oil	9.4932													
Volume of oil in water (m^3/month)			718.96608	715.843576	664.2916	719.66272	732.12496	731.5728	728.4592	792.7248	676.2504	500.7408	501.56512	645.88048
% Loss by Litchfield (m^3/month)			68.252888	67.9564624	63.0625302	68.319021	69.5020867	69.449669	69.154089	75.254951	64.197803	47.536326	47.61458	61.314726
Take density as	746	kg/m^3												
Emission factors: Controlled (m^3/month)	0.024	kg/m^3	4.1304064	4.11246788	3.81630563	4.1344086	4.20600322	4.2028311	4.1849437	4.5541448	3.885008	2.8767185	2.88145416	3.7105351
Emission factors: Uncontrolled (m^3/month)	0.5992	kg/m^3	103.12248	102.674615	95.2804306	103.2224	105.00988	104.930683	104.48409	113.70181	96.995701	71.822072	71.9403054	92.639694

Fugitive emissions	**t/day**		**0.3**	**0.3**	**0.3**	**0.3**	**0.3**	**0.3**	**0.3**	**0.3**	**0.3**	**0.30**	**0.3**	**0.3**
VOC emissions ex road and rail loading	t/day		2.20	1.73	1.83	1.38	1.91	1.87	1.71	2.13	2.06	2.53	1.91	1.46
VOC emissions ex API area	t/day		0.30	0.30	0.30	0.30	0.30	0.30	0.15	0.25	0.30	0.45	0.45	0.45
VOC emissions ex storage	t/day		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Total VOC emissions	t/day		3.80	3.33	3.43	2.98	3.51	3.47	3.16	3.68	3.66	4.28	3.66	3.21

Total	Average	2001/2002 RESULTS	Jul-01	Aug-01	Sep-01	Oct-01	Nov-01	Dec-01	Jan-02	Feb-02	Mar-02	Apr-02	May-02	Jun-02	Total	Average
2000/01	**2000/01**	**Parameters**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**2001/02**	**2001/02**
1438586	119882.17	Effluent to Sasol	142756	72212	75477	79541	119310	121215	129960	121448	117863	121971	130247	127934	1359934	113327.83
12857	1071	Slop Transferred ex API	1000	853	0	841	987	852.7	1000	608	1961	1460	449	860	10872	906
1451443.3	120954		143756	73065	75477	80382	120297	122067.7	130960	122056	119824	123431	130696	128794	1370805.7	114234
	120953.61															114233.81
8128.0825	677.34021	Volume of oil in water (m^3/month)	805.034	409.164	422.6712	450.139	673.663	683.5791	733.376	683.514	671.0144	691.214	731.8976	721.246	7676.5119	639.70933
771.61513	64.301261	% Loss by Litchfield	76.4234	38.84276	40.12502	42.7326	63.9522	64.89353	69.6209	64.8873	63.70074	65.6183	69.4805	68.4694	728.74663	60.728886
46.695227	3.8912689	Emission factors: Controlled (m^3/month)	4.62486	2.350617	2.428214	2.58602	3.87014	3.927111	4.21319	3.92673	3.854928	3.97097	4.204697	4.14351	44.100988	3.6750823
1165.8242	97.152014	Emission factors: Uncontrolled (m^3/month)	115.467	58.68706	60.62442	64.5642	96.6246	98.04687	105.189	98.0375	96.24469	99.1419	104.9773	103.45	1101.0547	91.754555
110	**0.30**	**Fugitive emissions**	**0.40**	**0.40**	**0.40**	**0.40**	**0.40**	**0.4**	**0.4**	**0.4**	**0.40**	**0.40**	**0.40**	**0.4**	**146**	**0.40**
691	1.89	VOC emissions ex road and rail loading	0.89	0.99	1.12	1.22	2.09	1.27	1.48	1.12	1.55	1.52	1.26	0.59	459	1.26
117	0.32	VOC emissions ex API area	0.30	0.26	0.30	0.25	0.30	0.26	0.30	0.18	0.59	0.44	0.14	0.26	109	0.30
365	1.00	VOC emissions ex storage	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	365	1.00
1283	3.51	Total VOC emissions	2.59	2.65	2.82	2.87	3.79	2.93	3.18	2.70	3.54	3.36	2.80	2.25	1079	2.96

APPENDIX 2

Wastewater Treatment

VOC EMISSIONS FROM WASTEWATER TREATMENT AREA

DESCRIPTION	VALUES	UNITS
% Oil in effluent	5600	mg/l
% Loss volume of inlet oil	9.4932	
Take density as	746	kg/m3
Emission factors: Controlled (m3/month)	0.024	kg/m3
Emission factors: Uncontrolled (m3/month)	0.5992	kg/m3

Date	Effluent	Slop Oil	Total	Litchfield	Emission	Litchfield	Emission
	m^3/month	m^3/month	m^3/month	m^3/month	m^3/month	t/month	t/month
Aug-94	103119.00	1513.00	104632.00	55.62	84.04	41.50	62.70
Sep-94	111511.00	581.00	112092.00	59.59	90.03	44.45	67.17
Oct-94	116737.00	669.10	117406.10	62.42	94.30	46.56	70.35
Nov-94	110960.00	1183.00	112143.00	59.62	90.08	44.47	67.20
Dec-94	111609.00	1378.00	112987.00	60.07	90.75	44.81	67.70
Jan-95	122076.00	1055.00	123131.00	65.46	98.90	48.83	73.78
Feb-95	107104.00	501.00	107605.00	57.20	86.43	42.67	64.48
Mar-95	93905.00	613.00	94518.00	50.25	75.92	37.48	56.64
Apr-95	106809.00	849.00	107658.00	57.23	86.47	42.70	64.51
May-95	91013.00	662.00	91675.00	48.74	73.63	36.36	54.93
Jun-95	95119.00	813.00	95932.00	51.00	77.05	38.05	57.48
Total	**1169962.00**	**9817.10**	**1179779.10**	**627.19**	**947.62**	**467.89**	**706.92**
Average	**106360.18**	**892.46**	**107252.65**	**57.02**	**86.15**	**42.54**	**64.27**
Jul-95	73322.00	848.00	74170.00	39.43	59.57	29.41	44.44
Aug-95	66585.00	598.30	67183.30	35.72	53.96	26.64	40.26
Sep-95	65427.00	970.40	66397.40	35.30	53.33	26.33	39.79
Oct-95	68341.00	813.30	69154.30	36.76	55.55	27.43	41.44
Nov-95	102375.00	884.70	103259.70	54.89	82.94	40.95	61.87
Dec-95	102375.00	669.50	103044.50	54.78	82.77	40.87	61.74
Jan-96	99838.00	596.50	100434.50	53.39	80.67	39.83	60.18
Feb-96	124913.00	901.00	125814.00	66.89	101.06	49.90	75.39
Mar-96	111810.00	399.50	112209.50	59.65	90.13	44.50	67.24
Apr-96	117001.00	755.00	117756.00	62.60	94.58	46.70	70.56
May-96	91233.70	651.50	91885.20	48.85	73.80	36.44	55.06
Jun-96	64895.00	987.20	65882.20	35.02	52.92	26.13	39.48
Total	**1088115.70**	**9074.90**	**1097190.60**	**583.29**	**881.28**	**435.13**	**657.44**
Average	**90676.31**	**756.24**	**91432.55**	**48.61**	**73.44**	**36.26**	**54.79**
Jul-96	46290.00	1104.00	47394.00	25.20	38.07	18.80	28.40
Aug-96	80380.00	705.80	81085.80	43.11	65.13	32.16	48.59
Sep-96	72229.00	477.40	72706.40	38.65	58.40	28.83	43.57
Oct-96	67172.00	427.40	67599.40	35.94	54.30	26.81	40.51
Nov-96	87431.00	1122.00	88553.00	47.08	71.13	35.12	53.06
Dec-96	87431.00	948.40	88379.40	46.98	70.99	35.05	52.96
Jan-97	77516.00	475.80	77991.80	41.46	62.64	30.93	46.73
Feb-97	77034.00	411.60	77445.60	41.17	62.21	30.71	46.41
Mar-97	73200.00	525.00	73725.00	39.19	59.22	29.24	44.18
Apr-97	74037.00	350.00	74387.00	39.55	59.75	29.50	44.57
May-97	59954.00	661.80	60615.80	32.22	48.69	24.04	36.32
Jun-97	59954.00	677.00	60631.00	32.23	48.70	24.05	36.33
Total	**862628.00**	**7886.20**	**870514.20**	**462.78**	**699.21**	**345.24**	**521.61**
Average	**71885.67**	**657.18**	**72542.85**	**38.57**	**58.27**	**28.77**	**43.47**

Date	Effluent	Slop Oil	Total	Litchfield	Emission	Litchfield	Emission
	m^3/month	m^3/month	m^3/month	m^3/month	m^3/month	t/month	t/month
Jul-97	59954.00	777.00	60731.00	32.29	48.78	24.09	36.39
Aug-97	70973.00	565.60	71538.60	38.03	57.46	28.37	42.87
Sep-97	0.00	648.00	648.00	0.34	0.52	0.26	0.39
Oct-97	111722.00	535.20	112257.20	59.68	90.17	44.52	67.26
Nov-97	117455.00	620.00	118075.00	62.77	94.84	46.83	70.75
Dec-97	116344.00	534.00	116878.00	62.13	93.88	46.35	70.03
Jan-98	77034.00	850.00	77884.00	41.40	62.56	30.89	46.67
Feb-98	119691.00	870.00	120561.00	64.09	96.84	47.81	72.24
Mar-98	117207.00	906.00	118113.00	62.79	94.87	46.84	70.77
Apr-98	82604.00	900.00	83504.00	44.39	67.07	33.12	50.04
May-98	108059.00	810.00	108869.00	57.88	87.45	43.18	65.23
Jun-98	122201.00	1096.10	123297.10	65.55	99.03	48.90	73.88
Total	**1103244.00**	**9111.90**	**1112355.90**	**591.35**	**893.46**	**441.15**	**666.52**
Average	**91937.00**	**759.33**	**92696.33**	**49.28**	**74.46**	**36.76**	**55.54**
Jul-98	118123.00	786.30	118909.30	63.21	95.51	47.16	71.25
Aug-98	115478.00	742.60	116220.60	61.79	93.35	46.09	69.64
Sep-98	116906.00	696.00	117602.00	62.52	94.46	46.64	70.47
Oct-98	121696.00	829.06	122525.06	65.14	98.41	48.59	73.42
Nov-98	125687.00	734.01	126421.01	67.21	101.54	50.14	75.75
Dec-98	125687.00	1083.11	126770.11	67.39	101.82	50.28	75.96
Jan-99	129348.00	1198.04	130546.04	69.40	104.86	51.77	78.22
Feb-99	121829.00	1532.78	123361.78	65.58	99.09	48.92	73.92
Mar-99	121829.00	977.94	122806.94	65.29	98.64	48.70	73.59
Apr-99	113875.00	756.28	114631.28	60.94	92.07	45.46	68.69
May-99	118303.00	800.00	119103.00	63.32	95.67	47.23	71.37
Jun-99	99834.00	515.40	100349.40	53.35	80.60	39.80	60.13
Total	**1428595.00**	**10651.52**	**1439246.52**	**765.13**	**1156.03**	**570.79**	**862.40**
Average	**119049.58**	**887.63**	**119937.21**	**63.76**	**96.34**	**47.57**	**71.87**
Jul-99	107463.00	1286.34	108749.34	57.81	87.35	43.13	65.16
Aug-99	107463.00	977.00	108440.00	57.65	87.10	43.01	64.98
Sep-99	121334.00	1262.00	122596.00	65.17	98.47	48.62	73.46
Oct-99	117784.00	739.50	118523.50	63.01	95.20	47.00	71.02
Nov-99	115929.00	460.80	116389.80	61.88	93.49	46.16	69.74
Dec-99	111635.00	578.50	112213.50	59.65	90.13	44.50	67.24
Jan-00	111635.00	951.00	112586.00	59.85	90.43	44.65	67.46
Total	**793243.00**	**6255.14**	**799498.14**	**425.03**	**642.17**	**317.07**	**479.06**
Average	**113320.43**	**893.59**	**114214.02**	**60.72**	**91.74**	**45.30**	**68.44**
Jul-00	127161.00	1225.80	128386.80	68.25	103.12	50.92	76.93
Aug-00	127161.00	668.21	127829.21	67.96	102.67	50.70	76.60
Sep-00	117488.00	1135.50	118623.50	63.06	95.28	47.04	71.08
Oct-00	127380.00	1131.20	128511.20	68.32	103.22	50.97	77.00
Nov-00	130110.00	626.60	130736.60	69.50	105.01	51.85	78.34
Dec-00	129587.00	1051.00	130638.00	69.45	104.93	51.81	78.28
Jan-01	129587.00	495.00	130082.00	69.15	104.48	51.59	77.95
Feb-01	140731.00	827.00	141558.00	75.25	113.70	56.14	84.82
Mar-01	119692.00	1067.00	120759.00	64.20	97.00	47.89	72.36
Apr-01	87914.00	1504.00	89418.00	47.54	71.82	35.46	53.58
May-01	87914.00	1651.20	89565.20	47.61	71.94	35.52	53.67
Jun-01	113861.00	1474.80	115335.80	61.31	92.64	45.74	69.11
Total	**1438586.00**	**12857.31**	**1451443.31**	**771.62**	**1165.82**	**575.62**	**869.70**
Average	**119882.17**	**1071.44**	**120953.61**	**64.30**	**97.15**	**47.97**	**72.48**

Date	Effluent	Slop Oil	Total	Litchfield	Emission	Litchfield	Emission
	m^3/month	m^3/month	m^3/month	m^3/month	m^3/month	t/month	t/month
Jul-01	142756.00	1000.00	143756.00	76.42	115.47	57.01	86.14
Aug-01	72212.00	853.00	73065.00	38.84	58.69	28.98	43.78
Sep-01	75477.00	0.00	75477.00	40.13	60.62	29.93	45.23
Oct-01	79541.00	841.00	80382.00	42.73	64.56	31.88	48.16
Nov-01	119310.00	987.00	120297.00	63.95	96.62	47.71	72.08
Dec-01	121215.00	852.70	122067.70	64.89	98.05	48.41	73.14
Jan-02	129960.00	1000.00	130960.00	69.62	105.19	51.94	78.47
Feb-02	121448.00	608.00	122056.00	64.89	98.04	48.41	73.14
Mar-02	117863.00	1961.00	119824.00	63.70	96.24	47.52	71.80
Apr-02	121971.00	1460.00	123431.00	65.62	99.14	48.95	73.96
May-02	130247.00	449.00	130696.00	69.48	104.98	51.83	78.31
Jun-02	127934.00	860.00	128794.00	68.47	103.45	51.08	77.17
Total	**1359934.00**	**10871.70**	**1370805.70**	**728.75**	**1101.06**	**543.64**	**821.39**
Average	**113327.83**	**905.98**	**114233.81**	**60.73**	**91.75**	**45.30**	**68.45**

Average effluent, m3/hr 144.6637184

APPENDIX 3

Storage Tanks

VOC Emissions from storage tanks at Natref:
In-house study done in June 1995

Service	Tank no	Loss Ton/yr	Service	Tank no	Loss Ton/yr
Crude oil	F29101	9.340	**Other products:**		
Crude oil	F29107	9.340	Butane	F29050	#
Crude oil	F29108	9.340	Butane	F29051	#
Crude oil	F29109	9.340	Butane	F29054	#
Crude oil	F29113	4.832	Propane	F29052	#
Crude oil	F29114	4.832	Propane	F29053	#
Petrol component:			Straight run Bit 80/100	F29301	#
Alkylate rundown	F29004	12.470	Straight run Bit 80/100	F29302	#
Alkylate rundown	F29005	12.470	Straight run Bit 80/100	F29315	#
Hi octane platformate	F29006	3.650	Straight run Bit 80/110	F29045	#
Lo octane platformate	F29007	2.950	Blown Bitumen 40/50	F29303	#
Lo octane platformate	F29008	2.950	Blown Bitumen 40/50	F29304	#
CDU LSR rundown	F29009	0.059	Blown Bitumen 40/50	F29316	#
CDU LSR rundown	F29010	0.059	Bitumen 60/70	F29305	#
CDU LSR rundown	F29011	0.059	Bitumen 60/70	F29306	#
LFCC rundown	F29012	16.110	Straight run Bit 150/200	F29317	#
LFCC rundown	F29013	16.110	Bitumen Kero	F29307	#
LFCC rundown	F29014	16.110	Refinery fuel oil	F29037	0.001
Sasol petrol comp	F29029	18.660	Refinery fuel oil	F29056	0.001
Sasol petrol comp	F29030	18.660	Heavy fuel oil	F29103	0.640
Ron 95 Unleaded pet	F29059	18.280	Heavy fuel oil	F29310	0.00076
Ron 91 Unleaded pet	F29106	27.320	Heavy fuel oil	F29313	0.00438
Ron 92 Unleaded pet	F29112	27.320	Heavy fuel oil	F29314	0.00438
Premium 93	F29117	27.320	**Intermediate products:**		
Premium 93	F29118	27.320	Slop	F29003	24.400
Premium 93	F29119	27.320	Slop	F29039	0.003
Kerosene products:			Slop	F29040	0.003
Power kerosene	F29031	0.004	Slop	F29209	0.0003
Illuminating paraffin	F29033	0.190	Slop oil	F29060	0.001
Illuminating paraffin	F29033	0.190	Slop oil	F29061	0.001
Jet fuel	F29597	0.060	Platformer feed	F29015	0.010
Jet fuel	F29598	0.060	Naphtha Unifiner feed	F29016	0.123
Jet fuel	F29602	0.060	DU Kero feed	F29017	0.022
Diesel products:			RCD feed - Vac bott	F29018	0.016
DSL rundown	F29022	0.017	RCD feed - Vac bott	F29019	0.075
DSL rundown	F29023	0.017	RCD feed - Red crude	F29046	0.050
HFCC rundown	F29026	0.940	RCD start up	F29057	0.002
HFCC rundown	F29027	0.940	FCC feed	F29102	0.630
HFCC rundown	F29028	0.940	FCC feed	F29104	0.630
HFCC rundown	F29308	0.0005	FCC feed	F29110	0.630
Eco diesel	F29032	1.970	Wax Oil	F29605	0.005
Straight run LCO	F29035	0.007	Mixed Olefins	F29058	#
Straight run LCO	F29036	0.007	DHC Feed	F29105	0.630
Finished diesel	F29048	0.680	Transit tank	F29047	#
Finished diesel	F29116	0.680	Sulphur	F29081	#
Finished diesel	F29120	1.970	Sulphur	F29082	#
Cat poly diesel	F29115	0.151	**Total VOC emissions**		358.62

APPENDIX 4

Product Loading

Assumptions:					
	Cp	Vb-rail	Vb-road	Cs	Density (kg/m3)
Petrol	0.15	0.18	0.13	0.41	748.4
Jet Fuel	0.01	0.18	0.13	0.41	790.9
Diesel	0.005	0.18	0.13	0.41	848.4

Petrol transported by rail cars: July 1998 - June 1999

Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.18	0.15	0.41	0.076	19665.276	14.851
August	0.18	0.15	0.41	0.076	19665.276	14.851
September	0.18	0.15	0.41	0.076	19665.276	14.851
October	0.18	0.15	0.41	0.076	19665.276	14.851
November	0.18	0.15	0.41	0.076	19665.276	14.851
December	0.18	0.15	0.41	0.076	19665.276	14.851
January	0.18	0.15	0.41	0.076	19665.276	14.851
February	0.18	0.15	0.41	0.076	19665.276	14.851
March	0.18	0.15	0.41	0.076	19665.276	14.851
April	0.18	0.15	0.41	0.076	19665.276	14.851
May	0.18	0.15	0.41	0.076	19665.276	14.851
June	0.18	0.15	0.41	0.076	19665.276	14.851
			Total VOC emissions in m3		235983	178
			Total VOC emissions in ton			133

Petrol transported by rail cars: July 1999 - June 2000

Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.18	0.15	0.41	0.076	16811.808	12.696
August	0.18	0.15	0.41	0.076	18485.145	13.960
September	0.18	0.15	0.41	0.076	17867.631	13.494
October	0.18	0.15	0.41	0.076	17049.200	12.876
November	0.18	0.15	0.41	0.076	17655.979	13.334
December	0.18	0.15	0.41	0.076	17001.746	12.840
January	0.18	0.15	0.41	0.076	17348.076	13.101
February	0.18	0.15	0.41	0.076	18885.882	14.263
March	0.18	0.15	0.41	0.076	18278.494	13.804
April	0.18	0.15	0.41	0.076	19151.454	14.463
May	0.18	0.15	0.41	0.076	11078.644	8.367
June	0.18	0.15	0.41	0.076	17127.640	12.935
			Total VOC emissions in m3		206742	156
			Total VOC emissions in ton			117

Petrol transported by road tankers: July 1998 - June 1999

Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.13	0.15	0.41	0.062	33249.937	20.691
August	0.13	0.15	0.41	0.062	33249.937	20.691
September	0.13	0.15	0.41	0.062	33249.937	20.691
October	0.13	0.15	0.41	0.062	33249.937	20.691
November	0.13	0.15	0.41	0.062	33249.937	20.691
December	0.13	0.15	0.41	0.062	33249.937	20.691
January	0.13	0.15	0.41	0.062	33249.937	20.691
February	0.13	0.15	0.41	0.062	33249.937	20.691
March	0.13	0.15	0.41	0.062	33249.937	20.691
April	0.13	0.15	0.41	0.062	33249.937	20.691
May	0.13	0.15	0.41	0.062	33249.937	20.691
June	0.13	0.15	0.41	0.062	33249.937	20.691
			Total VOC emissions in m3		398999	248
			Total VOC emissions in ton			185

Petrol transported by road tankers: July 1999 - June 2000

Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.13	0.15	0.41	0.062	28425.309	17.689
August	0.13	0.15	0.41	0.062	31254.578	19.450
September	0.13	0.15	0.41	0.062	30210.490	18.800
October	0.13	0.15	0.41	0.062	28826.691	17.939
November	0.13	0.15	0.41	0.062	29852.629	18.577
December	0.13	0.15	0.41	0.062	28746.456	17.889
January	0.13	0.15	0.41	0.062	29332.028	18.253
February	0.13	0.15	0.41	0.062	31922.853	19.865
March	0.13	0.15	0.41	0.062	30905.173	19.232
April	0.13	0.15	0.41	0.062	32381.170	20.151
May	0.13	0.15	0.41	0.062	18731.708	11.657
June	0.13	0.15	0.41	0.062	28959.317	18.021
			Total VOC emissions in m3		349548	218
			Total VOC emissions in ton			162

Jet fuel transported by rail cars: July 1998 - June 1999						
Month	**Vb**	**Cp**	**Cs**	**Ef %**	**Volume in m3**	**Ef in m3**
July	0.18	0.01	0.41	0.058	10750.379	6.189
August	0.18	0.01	0.41	0.058	10750.379	6.189
September	0.18	0.01	0.41	0.058	10750.379	6.189
October	0.18	0.01	0.41	0.058	10750.379	6.189
November	0.18	0.01	0.41	0.058	10750.379	6.189
December	0.18	0.01	0.41	0.058	10750.379	6.189
January	0.18	0.01	0.41	0.058	10750.379	6.189
February	0.18	0.01	0.41	0.058	10750.379	6.189
March	0.18	0.01	0.41	0.058	10750.379	6.189
April	0.18	0.01	0.41	0.058	10750.379	6.189
May	0.18	0.01	0.41	0.058	10750.379	6.189
June	0.18	0.01	0.41	0.058	10750.379	6.189
			Total VOC emissions in m3		129005	74
			Total VOC emissions in ton			55

Jet fuel transported by rail cars: July 1999 - June 2000						
Month	**Vb**	**Cp**	**Cs**	**Ef %**	**Volume in m3**	**Ef in m3**
July	0.18	0.01	0.41	0.058	10919.340	6.286
August	0.18	0.01	0.41	0.058	11502.846	6.622
September	0.18	0.01	0.41	0.058	10705.963	6.163
October	0.18	0.01	0.41	0.058	11310.119	6.511
November	0.18	0.01	0.41	0.058	11164.534	6.427
December	0.18	0.01	0.41	0.058	11298.690	6.505
January	0.18	0.01	0.41	0.058	11848.300	6.821
February	0.18	0.01	0.41	0.058	11717.521	6.746
March	0.18	0.01	0.41	0.058	10661.546	6.138
April	0.18	0.01	0.41	0.058	10540.899	6.068
May	0.18	0.01	0.41	0.058	4293.113	2.472
June	0.18	0.01	0.41	0.058	11581.287	6.667
			Total VOC emissions in m3		127544	73
			Total VOC emissions in ton			55

Jet fuel transported by road tankers: July 1998 - June 1999						
Month	**Vb**	**Cp**	**Cs**	**Ef %**	**Volume in m3**	**Ef in m3**
July	0.13	0.01	0.41	0.042	749.141	0.315
August	0.13	0.01	0.41	0.042	813.360	0.342
September	0.13	0.01	0.41	0.042	829.804	0.349
October	0.13	0.01	0.41	0.042	800.092	0.337
November	0.13	0.01	0.41	0.042	815.921	0.343
December	0.13	0.01	0.41	0.042	855.705	0.360
January	0.13	0.01	0.41	0.042	831.315	0.350
February	0.13	0.01	0.41	0.042	737.548	0.310
March	0.13	0.01	0.41	0.042	728.978	0.307
April	0.13	0.01	0.41	0.042	805.912	0.339
May	0.13	0.01	0.41	0.042	750.725	0.316
June	0.13	0.01	0.41	0.042	818.002	0.344
			Total VOC emissions in m3		9537	4
			Total VOC emissions in ton			3

Jet fuel transported by road tankers: July 1999 - June 2000						
Month	**Vb**	**Cp**	**Cs**	**Ef %**	**Volume in m3**	**Ef in m3**
July	0.13	0.01	0.41	0.042	760.915	0.320
August	0.13	0.01	0.41	0.042	801.577	0.337
September	0.13	0.01	0.41	0.042	746.046	0.314
October	0.13	0.01	0.41	0.042	788.146	0.332
November	0.13	0.01	0.41	0.042	778.001	0.327
December	0.13	0.01	0.41	0.042	787.350	0.331
January	0.13	0.01	0.41	0.042	825.650	0.348
February	0.13	0.01	0.41	0.042	816.536	0.344
March	0.13	0.01	0.41	0.042	742.951	0.313
April	0.13	0.01	0.41	0.042	734.543	0.309
May	0.13	0.01	0.41	0.042	299.166	0.126
June	0.13	0.01	0.41	0.042	807.043	0.340
			Total VOC emissions in m3		8888	4
			Total VOC emissions in ton			3

Diesel transported by rail cars: July 1998 - June 1999						
Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.18	0.005	0.41	0.057	19091.715	10.869
August	0.18	0.005	0.41	0.057	19091.715	10.869
September	0.18	0.005	0.41	0.057	19091.715	10.869
October	0.18	0.005	0.41	0.057	19091.715	10.869
November	0.18	0.005	0.41	0.057	19091.715	10.869
December	0.18	0.005	0.41	0.057	19091.715	10.869
January	0.18	0.005	0.41	0.057	19091.715	10.869
February	0.18	0.005	0.41	0.057	19091.715	10.869
March	0.18	0.005	0.41	0.057	19091.715	10.869
April	0.18	0.005	0.41	0.057	19091.715	10.869
May	0.18	0.005	0.41	0.057	19091.715	10.869
June	0.18	0.005	0.41	0.057	19091.715	10.869
			Total VOC emissions in m3		229101	130
			Total VOC emissions in ton			97

Diesel transported by rail cars: July 1999 - June 2000						
Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.18	0.005	0.41	0.057	18359.552	10.452
August	0.18	0.005	0.41	0.057	21891.034	12.462
September	0.18	0.005	0.41	0.057	20191.256	11.495
October	0.18	0.005	0.41	0.057	20835.955	11.862
November	0.18	0.005	0.41	0.057	21345.483	12.152
December	0.18	0.005	0.41	0.057	20375.108	11.599
January	0.18	0.005	0.41	0.057	22752.850	12.953
February	0.18	0.005	0.41	0.057	20225.982	11.514
March	0.18	0.005	0.41	0.057	20023.307	11.399
April	0.18	0.005	0.41	0.057	19437.025	11.065
May	0.18	0.005	0.41	0.057	8741.323	4.976
June	0.18	0.005	0.41	0.057	22017.767	12.535
			Total VOC emissions in m3		236197	134
			Total VOC emissions in ton			100

Diesel transported by road tankers: July 1998 - June 1999						
Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.13	0.005	0.41	0.041	30217.077	12.501
August	0.13	0.005	0.41	0.041	30217.077	12.501
September	0.13	0.005	0.41	0.041	30217.077	12.501
October	0.13	0.005	0.41	0.041	30217.077	12.501
November	0.13	0.005	0.41	0.041	30217.077	12.501
December	0.13	0.005	0.41	0.041	30217.077	12.501
January	0.13	0.005	0.41	0.041	30217.077	12.501
February	0.13	0.005	0.41	0.041	30217.077	12.501
March	0.13	0.005	0.41	0.041	30217.077	12.501
April	0.13	0.005	0.41	0.041	30217.077	12.501
May	0.13	0.005	0.41	0.041	30217.077	12.501
June	0.13	0.005	0.41	0.041	30217.077	12.501
			Total VOC emissions in m3		362605	150
			Total VOC emissions in ton			112

Diesel transported by road tankers: July 1999 - June 2000						
Month	Vb	Cp	Cs	Ef %	Volume in m3	Ef in m3
July	0.13	0.005	0.41	0.041	29058.260	12.022
August	0.13	0.005	0.41	0.041	34647.651	14.334
September	0.13	0.005	0.41	0.041	31957.357	13.221
October	0.13	0.005	0.41	0.041	32977.742	13.643
November	0.13	0.005	0.41	0.041	33784.189	13.977
December	0.13	0.005	0.41	0.041	32248.345	13.342
January	0.13	0.005	0.41	0.041	36011.675	14.899
February	0.13	0.005	0.41	0.041	32012.319	13.244
March	0.13	0.005	0.41	0.041	31691.538	13.111
April	0.13	0.005	0.41	0.041	30763.611	12.727
May	0.13	0.005	0.41	0.041	13835.175	5.724
June	0.13	0.005	0.41	0.041	34848.235	14.417
			Total VOC emissions in m3		373836	155
			Total VOC emissions in ton			115