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Risk assessment for emissions from hot heavy fuel oil during barge loading

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ABSTRACT

A series of emissions, occupational exposures, and mutagenic hazard studies were conducted to assess the risk associated with the loading of commercial Heavy Fuel Oils onto barges on the inland waterways. This report summarises the results from the laboratory investigations, exposure monitoring studies, and mathematical modelling exercise aimed at documenting the potential inhalation exposure, fractional release and intrinsic hazards of HFO vapours and aerosols under barge loading conditions. Analytical methodologies were developed to quantify HFO vapour and aerosol air concentrations, and an industrial hygiene assessment and worker exposure monitoring were conducted during actual loading operations. The results indicated that during the loading of hot commercial HFO on inland waterway barges:

- The emissions resulted in low workplace exposures, well below limit values set by the American Conference of Governmental Industrial Hygienists
- There was no release of detectable amounts of benzo(a)pyrene
- There was no mutagenic risk to workers based on the mutagenicity assays conducted on fume condensates generated under similar operating conditions which was corroborated with low total concentrations of aromatic compounds and low overall fluorescence in the fumes
- There was no substantial contribution to air emissions relative to other types of petroleum hydrocarbon cargos.

Therefore, based on these findings, the risk for workers handling commercial grade HFOs, as well as the environmental risks, during a barge loading operation on inland waterways do not pose a health concern. These studies did not indicate a need for additional control measures on the emissions of hot HFOs during barge loading beyond normal good operational industrial hygiene practices.

KEYWORDS

Occupational inhalation exposure, emission factor, PAH, total hydrocarbon, mutagenicity, naphthalene, heavy fuel oil, barge loading

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CONTENTS

			Page
SUMMARY			**V**
1.	**INTRODUCTION AND OBJECTIVES**		**1**
2.	**PROJECT OUTLINE**		**4**
	2.1.	EXPOSURE SAMPLING AND ANALYTICAL METHODS DEVELOPMENT	4
	2.2.	VAPOUR CONDENSATE GENERATION AND CHARACTERIZATION	4
	2.3.	WORKPLACE SAMPLING AND ANALYSIS	4
	2.4.	HAZARD INFORMATION REFINEMENT BY MUTAGENICITY TESTING	5
	2.5.	EMISSIONS ESTIMATION	5
	2.6.	INTEGRATION OF INFORMATION TO INFORM RISK ASSESSMENT	5
3.	**MATERIALS AND METHODS**		**6**
	3.1.	SAMPLING METHOD	6
	3.2.	CONDENSATES	8
	3.3.	SAMPLE ANALYSIS	9
	3.3.1.	Boiling point distribution	9
	3.3.2.	Fluorescence	10
	3.3.3.	Total hydrocarbons	10
	3.3.4.	(Polycyclic) Aromatic Hydrocarbons	11
	3.3.4.1.	Bulk products and condensates	11
	3.3.4.2.	Workplace samples	11
	3.4.	MUTAGENICITY TESTING	12
	3.5.	EMISSIONS ESTIMATION	12
4.	**RESULTS**		**14**
	4.1.	BULK SAMPLES AND CONDENSATES	14
	4.1.1.	Boiling point distribution	14
	4.1.2.	Fluorescence	16
	4.2.	PERSONAL AND AREA SAMPLES	17
	4.2.1.	Total Hydrocarbons (THC)	17
	4.2.2.	Aromatic hydrocarbon exposures	19
	4.3.	MUTAGENICITY TESTING	23
	4.4.	EMISSION ESTIMATION	26
5.	**DISCUSSION**		**27**
	5.1.	EXPOSURE ANALYSIS	27
	5.2.	MUTAGENICITY TESTING	28
	5.3.	EMISSIONS ESTIMATION	29
	5.4.	STUDY STRENGTHS AND LIMITATIONS	32

6. CONCLUSIONS 33

7. REFERENCES 34

APPENDIX 1 Final report HFO fume collection and analysis Appendix 1-1

APPENDIX 2 Final report Phase 2: HFO fume collection and analysis at 70, 80 and 90°c Appendix 2-1

APPENDIX 3 Evaluation of the Mutagenic Activity of Fume Condensates of Heavy Fuel Oil in the Bacterial Reverse Mutation Test (modified according to ASTM E1687-10) Appendix 3-1

APPENDIX 4 HFO Emissions during Barge Loading Operations on Inland Waterways – Final Report Appendix 4-1

APPENDIX 5 Human Carcinogenicity Of Naphthalene Appendix 5-1

SUMMARY

The emissions, exposures, and mutagenic hazards associated with the loading of heavy fuel oil (HFO) onto inland waterway barges were investigated in a series of studies initiated out of risk-related questions. The report summarizes the results from laboratory investigations, monitoring studies, and mathematical modelling exercises aimed at documenting the inhalation exposure, fractional release and intrinsic hazard of vapours and aerosols released when commercial grade UN 3082 HFOs are loaded onto an inland barge docked at a bulk storage terminal. The primary goal of these studies was to assess whether the inhalation of these hydrocarbons poses a health risk to operators who are responsible for the bulk loading onto barges. Since commercial grade HFOs are a combination of unblended C_{20}–C_{98} refinery residues and a more volatile C_9–C_{28} cutter stock used to improve handling, HFOs were assumed to have the potential for atmospheric release of some hydrocarbons. This concern for measurable release was based, in part, on the increased volatility that would be expected when HFOs are heated to their typical loading temperature of 70–90 °C. Until now, however, the nature and magnitude of these releases and any resulting worker exposures had not been widely reported.

Using a specially designed sampler capable of collecting hydrocarbon vapour and aerosols, personal exposure measurements were assessed for on-board (crew) and onshore refinery/terminal personnel responsible for operations during five barge loading events. The samples were analysed for both total hydrocarbons and a select number of indicator aromatic hydrocarbons (AHs) such as naphthalene and polycyclic aromatic hydrocarbons (PAHs) that included pyrene and benzo[a]pyrene. The level of hydrocarbon exposures from vapours and aerosols for on-board employees ranged from about 0.46–16 mg/m^3, which was well below the occupational exposure limit of 100 mg/m^3 set by the ACGIH (American Conference of Governmental Industrial Hygienists) for diesel fuel as an 8-hour TWA and considered applicable to the emissions of hot heavy fuel oil in this project. Personnel exposures to pyrene and benzo[a]pyrene vapour were below the limit of quantitation (mostly in the range of 0.01-0.07 µg/m^3), whereas naphthalene vapour exposures up to 0.2 mg/m^3 were observed with no exceedances of the German 8-hr time-weighted average exposure limit of 0.5 mg/m^3 or 50 mg/m^3 recognized in other European countries including France and The Netherlands. Most worker exposure samples for aerosol were at concentrations near or below the limit of quantitation of approximately 0.01 mg/m^3. Measured exposure levels of onshore workers were lower than for those working on-board the barges.

Because the personal air samples did not provide sufficient material for further detailed analyses such as the boiling point distribution, fluorescence, and mutagenicity, fume condensates were generated in the laboratory from samples of three separate commercial grade HFOs collected at barge loading terminals. These condensates were used as surrogates to represent the emissions during barge loading. These condensates were generated at temperatures of 70, 80, and 90 °C to cover the range of temperatures that can typically exist during HFO loading**.** Measured loading temperatures on-board the barges ranged from 72 to 81 °C. Fluorescence measurements indicated that the condensates contained far less potentially carcinogenic 4–6 ring PAHs than the bulk material. Similarly, a comparison of the chemical analysis results of condensates and bulk HFO samples indicated that levels of PAHs of concern were much lower in the condensates. Mutagenicity was determined with a bacterial reversed mutation assay optimised to detect mutagens that may be present in petroleum substances. None of the condensates were

mutagenic in this assay and the condensate generation temperature had no measurable influence on the test results.

The emissions of volatile hydrocarbons were estimated using three separate mathematical approaches developed by the USEPA, the UK Environment Agency, and Concawe after adjusting for the elevated vapour pressure and reduced density that would be expected at the 80 °C loading temperature. The resulting emission factor of 10–20 g/tonne was found to be equivalent to a total mass emission of 130–260 kg for a loading duration of 10 hr on a large barge capable of hauling a maximum of 13,000 tonnes of HFO. The fume emission factor during the loading of HFO fuels was found to be 8-fold lower than the factor associated with the barge loading of crude oil and 27-fold lower than the factor for the barge loading of gasoline.

The results of these studies indicated that during the loading of hot commercial HFO on inland waterway barges:

(i) the emissions resulted in low workplace exposures, well below a limit value set by the ACGIH for employees working on-board the barge and even lower for those working onshore at the terminal;
(ii) there was no release of detectable amounts of benzo[a]pyrene;
(iii) there was no mutagenic risk for workers based on testing in a bacterial reversed mutation assay, optimised to detect mutagens that may be present in petroleum substances, on condensates generated from various HFO samples under conditions very similar to operating conditions; and
(iv) there was no substantial contribution to air emissions relative to other types of petroleum hydrocarbon cargos.

Based on the notion that human health risk is a function of both the intrinsic health hazard of a substance and the personal inhalation exposures a worker receives, the testing and analysis conducted as part of this programme indicate that both health hazards and exposures, and therefore health risks, for workers handling commercial grade HFOs during the surveyed barge loading operations did not pose a concern. The studies did not indicate a need for additional control measures on the emissions of hot HFOs during barge loading beyond normal good operational industrial hygiene practices.

1. INTRODUCTION AND OBJECTIVES

Re-classification of heavy fuel oil (HFO) (UN 3082) as an environmentally hazardous substance in 2010 led to the introduction of the requirement that the gas/air mixture shall be returned to shore through a gas recovery or compensation pipe during loading operations. In response to a series of meetings held between UNECE's ADN[1] Safety Committee and FuelsEurope regarding the potential hazards associated with heavy fuel oil (HFO) transport on inland European waterways, Concawe established a working group to investigate the exposures and health risks associated with the transfer of HFO onto inland barges (ECE, 2013). The resulting research programme was aimed at improving the understanding of hazards and exposures to emissions. Although HFO's are known to be CMR (Carcinogenic, Mutagenic or Toxic for Reproduction), the fumes emitted during barge loading had not been not been studied in any detail until this time mainly because of its low volatility. In a previously published occupational exposure study the focus had been put on the dermal exposure route as the main route of concern (Christopher, et al. 2011).

A centrepiece of this research programme was an evaluation of occupational inhalation exposures relative to applicable standards. Other task associated with this research programme included:

1. A description of the family of products to ensure representativeness of test samples
2. Identification and procurement of representative test samples of HFOs that are transported via European inland waterways under UN 3082
3. Development of analytical methodologies to quantify HFO air concentrations during barge loading
4. An estimation of hydrocarbon emissions during barge loading operations
5. An industrial hygiene assessment of work conditions
6. The preparation of a risk assessment report on HFO emissions

The purpose of this report is to summarize the results from these studies and to examine their implications for human health. The focus of this investigation is on those HFOs sold commercially as fuels, including such products as vacuum gas oil, bunker C oil, fuel oil #6, marine fuel oil, and residual fuel oil. The exposure analysis specifically targets those substances with a UN 3082 designation, which implies a flash point greater than 60 °C (ECE, 2011). It does not include primary site-restricted HFOs used as an initial blending stock for preparing the final commercial product.

The primary difference between site-restricted HFOs and those used as fuels is the addition of a cutter stock to achieve the desired viscosity and to improve the fluidization necessary for transfer and combustion. All site-restricted HFOs and fuel products are stored and handled at elevated temperatures to improve their handling. The cutter stock used in a final product can originate from any of several refinery streams depending on availability. Gas oil, kerosene, and other middle distillate fractions represent some of the most commonly used alternatives.

The initial HFO blending stock includes the following site-restricted streams (Concawe, 1998):

- **Long residue**: the residue from the atmospheric distillation of crude oil.
- **Short residue**: the residue from the vacuum distillation of crude oil.
- **Thermal cracker or visbreaker residue**: the residue from thermal cracking processes designed to increase the yield of distillate components from atmospheric and vacuum residues.

[1] Experts on the Regulations annexed to the European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways.

- **Cat cracker slurry oil (clarified oil)**: a heavy fraction from a catalytic cracking operation, a process for the conversion of heavy hydrocarbon fractions into high quality gasoline components.
- **Vacuum gas oil**: a heavy gas oil fraction from the vacuum column.

The composition of HFOs varies widely and depends on refinery configuration, the crude oils being processed, and overall refinery demand for the residues from vacuum distillation and thermal and catalytic cracking processes (Concawe, 1998). A previous exposure study, focussing on dermal exposures, reported compositional data at ppm level (or µg/g) for a series of marker polycyclic aromatic hydrocarbons for blending stock and finished fuels that varied over 2 orders of magnitude (Christopher et al., 2011). Most of the constituents in an unblended HFO possess a high carbon number ranging from C_{20}–C_{98} and are relatively non-volatile. Consequently, most of the constituents have a negligible impact on overall emissions to air (Concawe, 2012b, Kim et al., 2011). However, the addition of the cutter stock to improve handling can have a small but measurable influence on emissions because of its higher vapour pressure. Cutter stocks generally contain hydrocarbons in the C_9–C_{28} range and their use percentage in a final product can vary depending on the specific viscosity needs of the customer (Garaniya et al., 2011). Given the diverse number sources for both the unblended HFO and the cutter stock, the commercial product is compositionally complex and virtually impossible to fully speciate.

Significant concentrations of highly toxic hydrogen sulphide (H_2S) are known to accumulate in headspaces of tanks from decomposition of sulphur-containing compounds and safe handling advice is well established (Concawe, 1998). The hydrocarbon emissions encountered during barge loading may be associated with both the HFO product being loaded as well as any residual vapours arising from the previous cargo. Consequently, some variability is expected in the emissions depending on the volatility of the previous cargo, the length of time since the previous cargo was unloaded, and whether the tanks were degassed prior to reloading with an HFO. In addition, submerged versus splash loading can also have an impact on atmospheric release; however, in the case of the UN 3082 HFOs submerged loading is the only method employed. Submerged loading uses a delivery pipe that extends below the liquid surface to minimize agitation and vapour generation. The submerged loading of an HFO onto a tank barge takes place at a temperature of approximately 80 °C to decrease the viscosity and increase the handling ability of the product. The decreased turbulence that accompanies submerge loading at an elevated temperature will cause any released vapours to accumulate near the liquid surface as a vapour blanket. As a result, a majority of the hydrocarbon vapours may be released during the latter stages of the loading cycle when the head space (i.e. ullage) is less than 3–4.5 meters high.

An indication of the annual number of operations carried out in Europe was obtained by retrieving information coming from the Europe Barge Inspection Scheme (EBIS) which is a system used by all chemical and oil industry company vetting departments. In Europe, there are 1290 tanker barges dedicated to the transport of liquid dangerous goods in bulk. Each barge is EBIS inspected once a year. Based on the EBIS inspection reports issued during the period June 2014-May 2015, 124 different barges were inspected while transporting/carrying UN3082 Fuel Oil product and hence some 10% of the European tanker barge fleet is used to transport HFO. The tonnage of these 124 barges ranged from 1000 to a maximum size of 13317T, with an average of 3900T, as per following distribution:

- 22 barges: Tonnage < 2000T
- 48 barges: Tonnage from 2000T to 4000T
- 34 barges : Tonnage from 4000 to 6000T

- 20 barges: Tonnage > 6000T

It is estimated that the barges carry out some 3000 loading operations annually.

ADN barge construction and cargo handling rules together with industry recommendations under ISGINTT (International Safety Guideline for Inland Waterway Tanker and Terminal) ensure that loading operations are done according to a standard process independent of the terminal or the barge and hence the emissions and exposures are not expected to be influenced by local variation in technical conditions, but only by product and environmental factors, and therefore to be relatively homogeneous.

2. PROJECT OUTLINE

The research programme was performed in stages using expertise from several different organisations. Each stage sought to accomplish a specific set of tasks that were aimed at obtaining a comprehensive picture of the exposures, emissions and hazards associated with volatile hydrocarbons emitted by commercial grade HFOs at a barge loading terminal. The adopted approach was developed and applied previously in health studies for emissions from hot bitumen and has been accepted by the International Agency for Research of Cancer (IARC) for carcinogenicity assessment of bitumen and by the European Chemicals Agency (ECHA) also for chronic toxicity and reproductive toxicity assessment of bitumens.
In essence the programme was performed in the following five phases:

1. Exposure sampling and analytical methods development
2. Vapour condensate generation and characterization
3. Workplace sampling and analysis
4. Mutagenicity testing
5. Emissions estimation

Each of these phases are outlined below and described in more detail in the following sections of this report.

2.1. EXPOSURE SAMPLING AND ANALYTICAL METHODS DEVELOPMENT

A specialised exposure sampling approach was adopted that allowed workplace monitoring for both vapours and aerosols, as can be expected for emissions to ambient air from a hot product. The BIA (Berufsgenossenschaftliches Institut für Arbeitssicherheit) sampling device shown in **Figure 1** was selected. All sampling took place as inland barges were being loaded with a commercial grade HFO. Following sample collection the fume (vapour and mist) samples were analysed for total hydrocarbon content as well as naphthalene and two marker PAHs (pyrene, and benzo[a]pyrene) by gas chromatography.

2.2. VAPOUR CONDENSATE GENERATION AND CHARACTERIZATION

Vapour condensates were generated in the laboratory at a range of temperatures using HFOs that were representative of those used in commerce. The condensates were obtained using the apparatus depicted in **Figure 5** then analytically characterized by measuring boiling point distribution, total fluorescence, and AH content. Naphthalene and a group of 21 PAHs of varying ring size were individually quantitated by gas chromatography/mass spectrometry. These results were compared to those found for the bulk condensate to assess the types of hydrocarbons capable of being released.

2.3. WORKPLACE SAMPLING AND ANALYSIS

Personal and area samples were collected during five barge loading operations at various locations. Both on-board and onshore personnel were monitored as the HFOs were loaded onto barges at temperatures between 72 and 81 °C. Area samples were collected in the vicinity of the exhausts used to expel any vapours from within the barge tanks. Background samples were collected onshore at a site upwind of the barge. Following processing within the laboratory, the extracted samples were analysed for total hydrocarbons and naphthalene, pyrene, and benzo[a]pyrene content as described above. A separate set of worker exposure samples served to characterise the boiling point distribution for comparison with the bulk product.

2.4. HAZARD INFORMATION REFINEMENT BY MUTAGENICITY TESTING

Full assessment of the reprotoxic and carcinogenic potential of emissions from hot HFO according to the the standard OECD guidelines is expected to require four to five years, based on the experience with previous carcinogenicity and current reproductive toxicity studies with bitumen fume condensates. The time requirement to conduct such studies was prohibitive for this route to be pursued under the provisions of the ADN convention. Therefore, a well-validated, short-term alternative is provided by mutagenicity testing which has the additional advantage of not requiring the use of experimental animals. Extensive research, fully published in the peer-reviewed literature, has indicated that standard approaches to mutagenicity testing, such as the methods issued by the OECD, do not work for petroleum substances and in fact run the risk of providing false-negative results. The petroleum industry has therefore developed a modification of the standard bacterial reversed mutation assay (Ames' test) which is optimised to pick up mutagens that may be present in petroleum substances. This assay (the "modified Ames' test") was validated against more than hundred two-year rodent carcinogenicity tests (ASTM, 2010; Blackburn et al., 1986; Blackburn et al., 1996) and shown to be a reliable predictor of the carcinogenic hazard of petroleum substances (regardless the route of exposure). This test was used to examine the genotoxicity of the HFO condensates. The assay was performed at nine plate concentrations of condensate using a single TA 98 strain of *Salmonella typhimurium.* After incubation, the number of revertant colonies was determined and a mutagenicity index was calculated from the slope of the response curve as described in ASTM 1687-10 (ASTM, 2010).

2.5. EMISSIONS ESTIMATION

Several different mathematical approaches were used to calculate an emission factor for total hydrocarbon loss during barge loading of an HFO. Methods developed in the United States and Europe were used to calculate the emissions that would result when an HFO is loaded onto a barge at an elevated temperature. As such, the calculations were able to account for the increased volatility and decreased density that occurs when an HFO is heated to a loading temperature of 80 °C. The final emission factor was used to calculate the total hydrocarbon loss that would result assuming worst case loading conditions.

2.6. INTEGRATION OF INFORMATION TO INFORM RISK ASSESSMENT

In the final evaluation of all information obtained from the project parts, information was suitably combined and interpreted. In particular, in order to inform the carcinogenicity and reproductive toxicity hazard assessment, not only the measured levels of the marker PAHs were compared to available occupational exposure standards, but in addition the total fluorescence readings of the bulk product and released vapour condensate were compared and the mutagenicity results of the various vapour condensate were taken into consideration. All these parameters pointed into the same direction, i.e. that there was no significant health hazard associated with the fumes released during barge loading.

3. MATERIALS AND METHODS

3.1. SAMPLING METHOD

The monitoring programme focused on personal exposure and area concentration measurements for employees working both on and off the barge during actual HFO loading operations. Five separate days of testing were scheduled on barges docked at three fuel terminals located on inland waterways in The Netherlands and Germany. HFO loading generally involved two employees, one located dockside and another aboard the ship. The loading temperature for the five operations ranged from 72–81 °C as shown in **Table 1**. Samples coded red and blue were taken at the same site within a 5-day period, and samples coded pink and green were taken from a single site during a period of several weeks. The sample coded yellow was collected at a third site.

Table 1. Conditions at the HFO barge loading terminals

Survey Code	Terminal Number	Product loading temperature (°C)	Barge size (T)	Loading duration (h)	Date	Local wind speed (m/s)
Red	1	78	4200	6.5	29.08.13	3-6
Blue	1	72	3900	4	04.09.13	2-3
Pink	2	81	13,000	16	21.11.13	3-4
Green	2	81	13,000	12	11.12.13	2-4
Yellow	3	79	1800	1.5	18.10.13	2-3

The employee aboard the ship was responsible for coupling and uncoupling the loading arm used to fill the tanks on the ship. The initial coupling of the loading arm takes place when all valves are in the closed position so there will be minimal opportunities for exposure. Uncoupling takes place after the lines and loading arm are cleared of residual product using nitrogen. The valves are then closed and the lines disconnected; but in some cases there will be a small amount of residual HFO in the lines that is collected in a drip pan. Coupling and uncoupling each required about 20–30 minutes of time, so the opportunity for exposure was limited in duration. Given the semi-volatile nature of HFOs and the tendency to form aerosols at the elevated temperatures required for barge loading, vapours and mists were both collected as part of the exposure programme (Breuer, 1999). A BIA sampling system was used to simultaneously collect vapours and mists. As shown in **Figure 1**, the system uses a special GSP cartridge (Gesamtstaubprobenahme-System) that holds a 37 mm glass fibre filter and 3 g of XAD-2 resin. The flow rate was set to a maximum of 2 L/min through the use of a critical orifice. Sampling pumps were calibrated before and after use to allow the calculation of the total air volume. A photograph of the sample pump and he BIA cassettes is shown in **Figure 2**. Full loading period samples were strived for, but were not always attained in every instance due to operator inactivity or sampling error (pump left running for one of the background samples).

Figure 1 A diagram of the BIA sampler for HFO mist and vapour

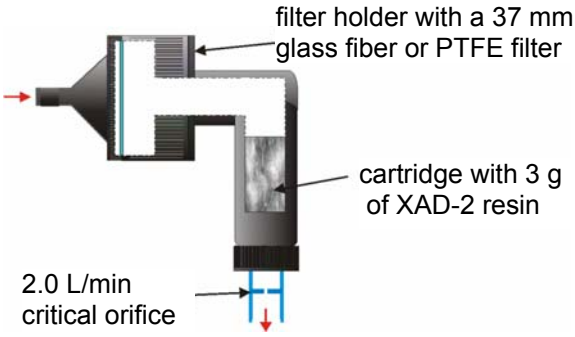


Figure 2 Photographs of BIA cassette and sampling pump calibration device

A - BIA Sampling cassette B - Sampling pump calibration device

Separate samples were collected in parallel for the measurement of total hydrocarbon concentration (THC) and AH levels. Personal air samples were collected in the breathing zones of the on-board and onshore operators and an area sample located near an exhaust vent or hatch used to expel vapours as the tank was being filled. A background sample was also taken at an onshore location upwind of the loading site. The background sample concentrations were subtracted from the personal and area measurements to provide a robust assessment of exposures from the barge loading operation independent of any exposures resulting from emissions at the terminal storage facility. Background hydrocarbon levels ranged from non-quantifiable to 0.015 mg/m^3 for the aerosol samples and non- quantifiable to 0.109 mg/m^3 for the vapour samples. The pictures shown in **Figure 3** depict the placement of the BIA sampling cassettes for the collection of personal, area, and background samples; whereas **Figure 4** shows a heavy fuel oil barge docked at a loading terminal.

Figure 3 Photographs depicting the placement of samplers for THC and AH measurements

A - Personal sampling B - Area sampling C - Background sampling

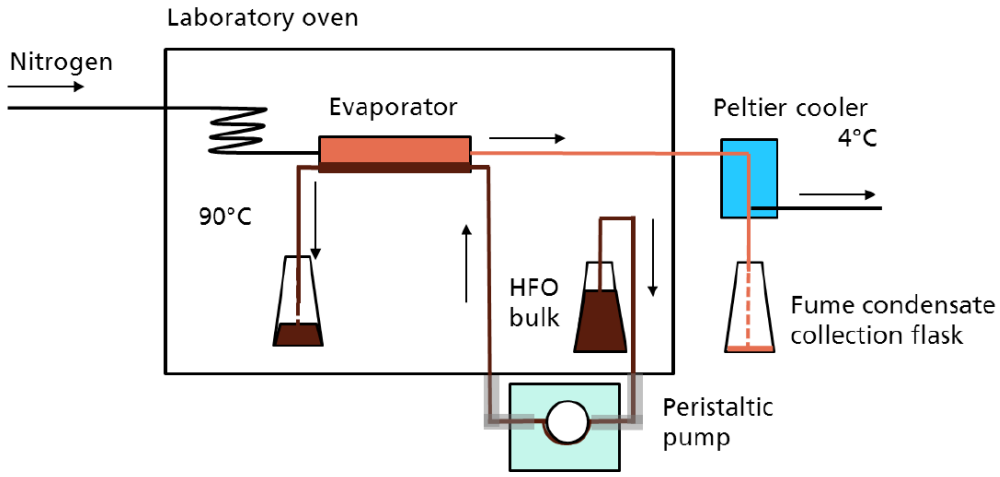
Figure 4 Photograph of a typical barge loading facility

3.2. CONDENSATES

To improve the reliability of inhalation exposure and hazard evaluations with complex petroleum substances, it has been customary to generate fume condensates that capture the volatile fraction that can be readily inhaled or emitted into the air (Kriech et al., 2007). This approach has been used successfully to obtain condensates of emissions from hot bitumen for further detailed analysis in occupational exposure determinations and toxicology assays (Pohlmann et al., 2001). The HFO research programme built off the successful application of these techniques and used a fume condensate to evaluate the nature and magnitude of volatile emissions, exposures, and hazards associated with barge loading. The generation of an HFO condensate provided a representative sample of the volatile emissions that would be expected to occur at the elevated temperatures required for a barge loading operation. A diagrammatic representation of the condensate generator is depicted in **Figure 5**. Condensates were generated at temperatures of 70, 80, and 90 °C. The highest temperature of 90 °C was greater than the temperature encountered during the field study for barge loading and was selected to obtain a worst case estimate of the emissions that could take place during the loading operation. After several analytical characterisations the condensates were used to determine mutagenic potential in a modified reverse mutation assay (ASTM 1687-10). Details concerning the generation and characterization of the condensates are contained within the report placed in **Appendix 1**.

The apparatus was operated by continuously feeding a litre of the bulk HFO sample through an oven that contained an evaporator coil. The flow rate of 300 mL/h was maintained using a peristaltic pump. A pre-heated nitrogen stream of 1 L/min was fed over the surface of an oil layer covering the bottom of the evaporator. Vapours captured by the nitrogen flow were then chilled down to 4 °C in a Peltier cooler, which caused the vaporized compounds to condense and drip into a collection flask.

Figure 5 Diagram of the HFO condensate generator



3.3. SAMPLE ANALYSIS

The personal and areas samples collected in conjunction with this study were analysed for boiling point distribution, fluorescence, vapour and aerosol hydrocarbon levels, and vapour and aerosol AH. Detailed AH measurements were performed on bulk HFO samples and condensates. Full details of the analytical methodologies employed are provided in the full report which is attached as **Appendix 1**.

3.3.1. Boiling point distribution

Boiling point distributions were determined using ASTM method D2887 (ASTM, 1997). This method is capable of providing a simulated distillation of petroleum fractions with boiling point range of 55.5 to 538 °C. A Hewlett-Packard 5890 Series II Plus gas chromatograph equipped with a flame ionization detector was used to determine the boiling point distributions of the condensate, filter, resin, and bulk HFO samples. A split/splitless injector was used in combination with an Agilent 30 m DB-5ms non-polar capillary column (0.32 mm i.d and 0.25 µm film thickness) and a helium carrier gas. The temperature programme included an initial 3 min phase at 40 °C followed by 9 °C/min change up to 120 °C and then an 11 °C/min change up to 320 °C.

The gas chromatograph was calibrated using an ASTM standard n-alkane mixture that was handled in the same manner as the samples. The standard ASTM calibration mixture contains C_5–C_{44} straight chain alkanes at a known concentration. Measurements are accomplished by equating each alkane with a specific boiling point and quantifying the percent contribution of each hydrocarbon peak to the total integrated area under the chromatographic curve. **Table 2** gives the boiling points associated with each alkane found in the chromatogram.

Table 2 Boiling points for the alkanes used for calibration in the BP distribution assay

Alkane Carbon #	Boiling Point (°C)	Boiling Point (°F)	Alkane Carbon #	Boiling Point (°C)	Boiling Point (°F)
5	36	97	25	402	756
6	69	156	26	412	774
7	98	208	27	422	792
8	126	259	28	431	808
9	151	304	29	440	825
10	174	345	30	449	840
11	196	385	31	458	856
12	216	421	32	466	871
13	235	455	33	474	885
14	254	489	34	481	898
15	271	520	35	489	912
16	287	549	36	496	925
17	302	576	37	503	937
18	316	601	38	509	948
19	330	626	39	516	961
20	344	651	40	522	972
21	356	674	41	528	982
22	369	695	42	534	993
23	380	716	43	540	1004
24	391	736	44	545	1013

Bulk HFO samples and condensates were dissolved in dichloromethane prior to injection; whereas the workplace resin and filter samples were extracted with dichloromethane then combined and concentrated prior to analysis. The curve resulting from the boiling point analysis was used to determine a T^{50} value which is the temperature at which 50% of the available volatiles evaporated.

3.3.2. Fluorescence

Ultraviolet fluorescence was employed to measure total 4–6 ring PAHs in the various samples (Kriech et al., 2002, Osborn et al., 2001). This method has been shown to detect both straight and alkylated PAHs at an excitation wavelength of 385 nm and an emission wavelength of 415 nm. In contrast, 2-3 ring PAHs have been shown to be minor fluorescent contributors at the wavelengths employed. Fluorescence intensity was measured using a 1 cm cuvette placed in Shimadzu RF-1501 spectrofluorometer. Bulk and condensate samples were dissolved in cyclohexane prior to analysis. Calibration was accomplished using known concentrations of 9,10-diphenyl-anthracene (DPA) as reference standard. All results were expressed as DPA equivalents for the bulk samples (mg/kg DPAeq) and condensates (mg/L DPAeq).

3.3.3. Total hydrocarbons

Total hydrocarbon (THC) measurements were based on BIA method 6305 (IFA, 1997). The method is based on a Fourier transform infrared spectroscopy determination of the absorption resulting from the stretching of aliphatic CH bonds at wavelengths between 2800 and 3000 cm^{-1}. The method is non-specific and does not differentiate between different classes of hydrocarbons or different congeners within a class. Workplace filter and resin samples were analysed separately following extraction with tetrachloroethene. A Bruker Vector 22 Fourier transform infrared

spectrometer was used for the analysis. The instrument was calibrated using mineral oil (Aldrich No. 16.140-3) since a specific reference standard does not exist for HFOs. Results are reported as mg/m^3 of mineral oil equivalents. The limit of quantitation (LOQ) was 0.05 mg in extract; the corresponding exposure concentration was calculated based on the sampled air volume; results below the limit of quantitation are presented in the Tables as < calculated exposure concentration as per EN 32645.

3.3.4. (Polycyclic) Aromatic Hydrocarbons

Two AH-specific methods were employed depending upon whether workplace samples or bulk/condensates were analysed. The methods differed with respect to the chromatographic conditions used, the types of AHs capable of being examined, and the extraction procedure. Both methods utilized an Agilent Technologies 6890 gas chromatograph with a 6783 B autosampler and a mass selective detector operator operated in the selective ion mode. A split/splitless injector was also used in combination with an Agilent 60 m DB-35ms capillary column (0.25 mm i.d and 0.25 µm film thickness) and helium as the carrier gas. The LOQ of the standard was 10 ng.

3.3.4.1. Bulk products and condensates

For bulk HFO samples and HFO condensates, the concentration of naphthalene and 21 individual PAHs were determined by the GC-MS method of Grimmer (Grimmer et al., 1997). These PAHs included members with ring numbers ranging from 3 to 6 and are listed in **Table 9**. The temperature programme used for chromatographic separation began with an initial temperature of 75 °C, which was increased 15 °C/min up to 200 °C, 5 °C/min up to 280 °C, 10 °C/min up to 300 °C, then finally 10 °C/min up to 340 °C. The bulk fuel oil samples were diluted in toluene and spiked with a deuterated form of each PAH prior to clean-up on a silica gel column.

The silica gel (0.063–0.200 mm) was first conditioned then suspended in cyclohexane and placed into glass columns. The diluted sampled was placed on the column and eluted with 320 ml of cyclohexane. Two fractions of 70 and 250 ml were collected and the first was discarded. The second fraction was reduced in volume to about 10 ml in a rotary evaporator then 2–3 ml of 2-propanol was added before finally concentrating the sample down to about 0.1–1.0 ml depending upon the PAH being analysed.

3.3.4.2. Workplace samples

The aerosol and vapour phase workplace samples were analysed for naphthalene, pyrene, and benzo[a]pyrene. These three AHs provide an indication of the distribution of 2-ring, 4-ring, and 5-ring AHs in the workplace air. The measurement of naphthalene, and benzo[a]pyrene provides an indication of those PAHs with a CMR (Carcinogenic, Mutagenic and Reprotox Substances) classification ranging from C2 (suspected to have CMR potential) for naphthalene to C1B (presumed to have CMR potential) for benzo[a]pyrene (CNRS, 2011).

The temperature programme used for chromatographic separation started at an initial temperature of 75 °C for 1.5 min which was increased 15 °C/min up to 200 °C, 5 °C/min up to 280 °C, then finally 10 °C/min up to 300 °C. The resin and filter samples were extracted with dichloromethane using an ultrasonic bath or reflux condenser respectively. Deuterated naphthalene, pyrene, and benzo[a]pyrene were added to the extracts as internal standards prior to injection and detection in the selective ion mode.

3.4. MUTAGENICITY TESTING

The mutagenicity of nine HFO condensates was evaluated using a modified Ames assay that was optimized to yield highly sensitive indications of genotoxicity for water-insoluble petroleum products (ASTM, 2010). The assay employed *Salmonella typhimurium* strain TA 98 with the *his*D3052/R-factor mutation (R-factor being the plasmid pKM101 which increases error-prone DNA repair) and a series of additional mutations (*uvrB*, *rfa*, *gal*, *chl* and *bio*) since it is the most sensitive to PAH-induced mutations. An extraction with dimethyl sulfoxide (DMSO) was applied to concentrate the polar components present in the test sample (i.e. all aromatic and polyaromatic compounds and some cycloalkanes) and to obtain an aqueous compatible solution that could be applied directly to the agar plates. In addition, this modification of the Ames' test applies hamster instead of rat liver S9 fraction and higher concentrations of NADPH as these modifications were found to increase the sensitivity to mutagenic constituents of petroleum substances significantly whereas the standard mutagenicity assays (i.e. the 'normal' Ames' test, micronucleus tests, chromosomal aberration tests, mouse lymphoma assays) may provide false negative results or ambiguous outcomes (Blackburn et al., 1986; Blackburn et al., 1996). The HFO condensate and DMSO were mixed at a ratio of 1:5 for at least 30 minutes prior to the preparation of five dosing solutions that included the undiluted extract as the highest concentration. A fortified Aroclor 1254-induced hamster liver S-9 fraction was used for metabolic activation. A positive control (Reference Oil 1) was included in each assay, which was extracted with three volumes of DMSO before plate application. The values from the test sample were considered valid if the number revertant colonies from the positive control were at least three times higher than the number observed for the negative DMSO control (solvent control) and the positive control was within the historical control range. The solvent control and the positive control samples produced on average 44 ± 6 (SD) and 138 ± 22 (SD) revertant colonies per plate (n = 15), respectively. Each HFO sample was analysed in triplicate at nine dose levels ranging from 2.5–60 µg/plate. A mutagenicity index (MI) was calculated as the slope of the final dose response curve. If cytotoxicity occurred at higher dose levels, only the initial part of the dose response curve was used to calculate the MI. If the slope of the dose response curve was not statistically significantly different from zero, the MI was reported as zero. The results from the modified Ames assay were considered to be insignificant if the MI was less than 1. Full details of the test method are provided in the full report which is attached as **Appendix 3**.

3.5. EMISSIONS ESTIMATION

Several different approaches can be taken to estimate total hydrocarbon emissions from inland waterway barges. Empirical methods have been published that take advantage of observed relationships between the rate of emission and some physical or chemical characteristics of the petroleum product; however the results obtained using these approaches are unsatisfactory. Other mathematical approaches take advantage of procedures that have been developed by organizations such as the U.S. Environmental Protection Agency (USEPA), the UK Environment Agency (EA), and Concawe (Concawe, 2009, EA, 2007, USEPA, 2008). These three methods were adapted for use with HFOs handled at elevated temperatures by making adjustments for the vapour pressure increase and density decrease that would be encountered. A barge loading scenario was created that allowed use of the emission factors to calculate the mass of volatile hydrocarbons that would be released under worst case conditions. **Table 3** lists the default values used in this loading scenario. Further details on the methodological approach for the emission factor estimation study are provided in **Appendix 4**.

Table 3 Typical barge loading characteristics for a commercial HFO (UN 3082)

Parameter	Value
Capacity of cargo typical barge	3,000–6,000 metric tons - max up to 13,000 metric tons
Number of tanks on a typical barge	10–18 tanks
Loading rate	500–800 tons/hr - max up to 1,000 tons/hr
Loading duration	6–10 hours (rate designed to minimize splash)
Tank hatches	Not opened
Vapour movement	Pushed back into pipes (collector) that run to a single vent that is more than 5 m away from permanent worksites
Size of vent on barge	2 meters high by 15–25 cm in diameter
Location of other vents	Loading arm, loading side of stack (at end of loading, loading arm is sometimes emptied to barge, sometimes to buffer tank on shore with vent to atmosphere 4–6 meters high)
Visible vapour from the vents	None
Temperature of product at storage (max)	80–90 °C (not well controlled)
Temperature during loading (typical)	80 °C
Heating capability on barge	Some barges are equipped with heating
Temperature decrease during transport	1–2 °C/day
Valve operation	2 employees and 8-hour shifts: one crewman and another on land at loading facility. Land operator may supervise more than one barge
Exposure source	Crewman - exposed continuously from barge vent Landsman - only potentially exposed for very short duration (at emptying and disconnecting loading arm)
Equipment	Crewman - standard PPE (overall, shoes, gloves, helmet, goggles, life jacket) Landsman - standard PPE as noted above
H_2S monitoring	Workers wear monitor with alarm; carry evacuation mask

4. RESULTS

4.1. BULK SAMPLES AND CONDENSATES

4.1.1. Boiling point distribution

The boiling point distribution for the five bulk samples collected during the barge exposure survey at the three sites are shown in **Figure 6**. The results are quite similar for four of the five samples with the yellow sample showing a higher percentage of hydrocarbons boiling at temperatures below 425 °C. This difference was also apparent in the fume condensates with the yellow sample showing a noticeably greater amount of higher boiling hydrocarbons (see **Figure 7**). As expected, the T^{50} values for the condensates and bulk samples are very different. The largest difference of 173 °C was observed for the yellow samples where the condensate T^{50} was 402.1 °C and the bulk value was 228.9 °C. The difference observed with the yellow sample indicates that the volatility and opportunity for exposure would be lower with this HFO because the increased boiling point profile indicates a lower overall vapour pressure.

Figure 6 Boiling point distributions for the bulk HFO samples taken from the five barges under study

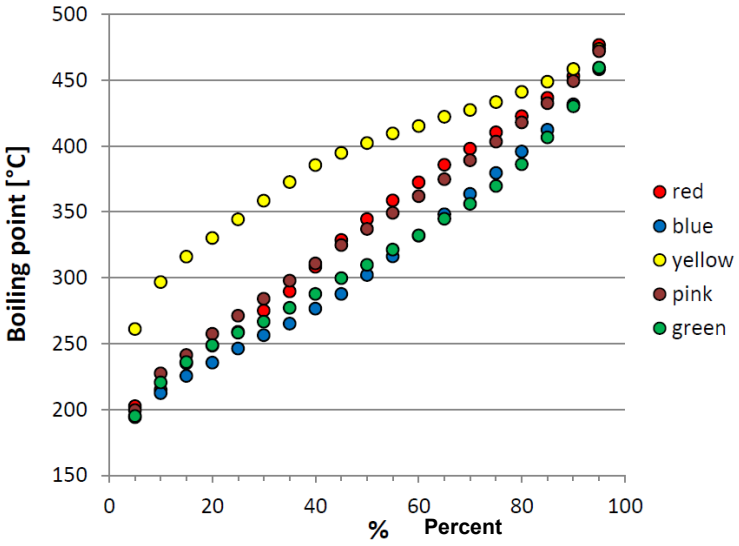
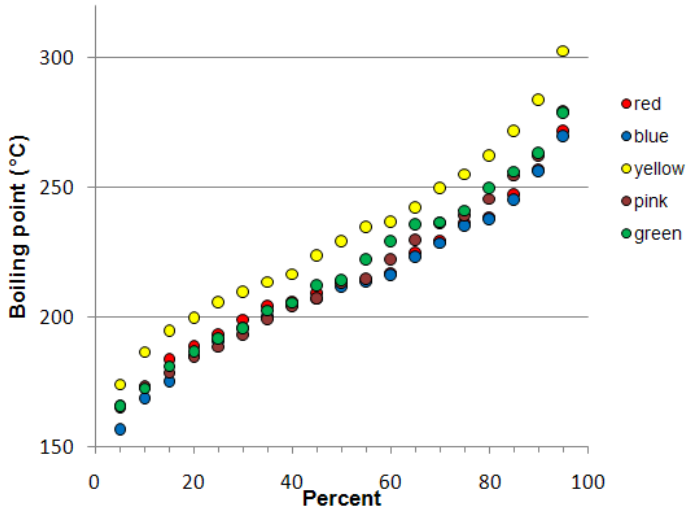


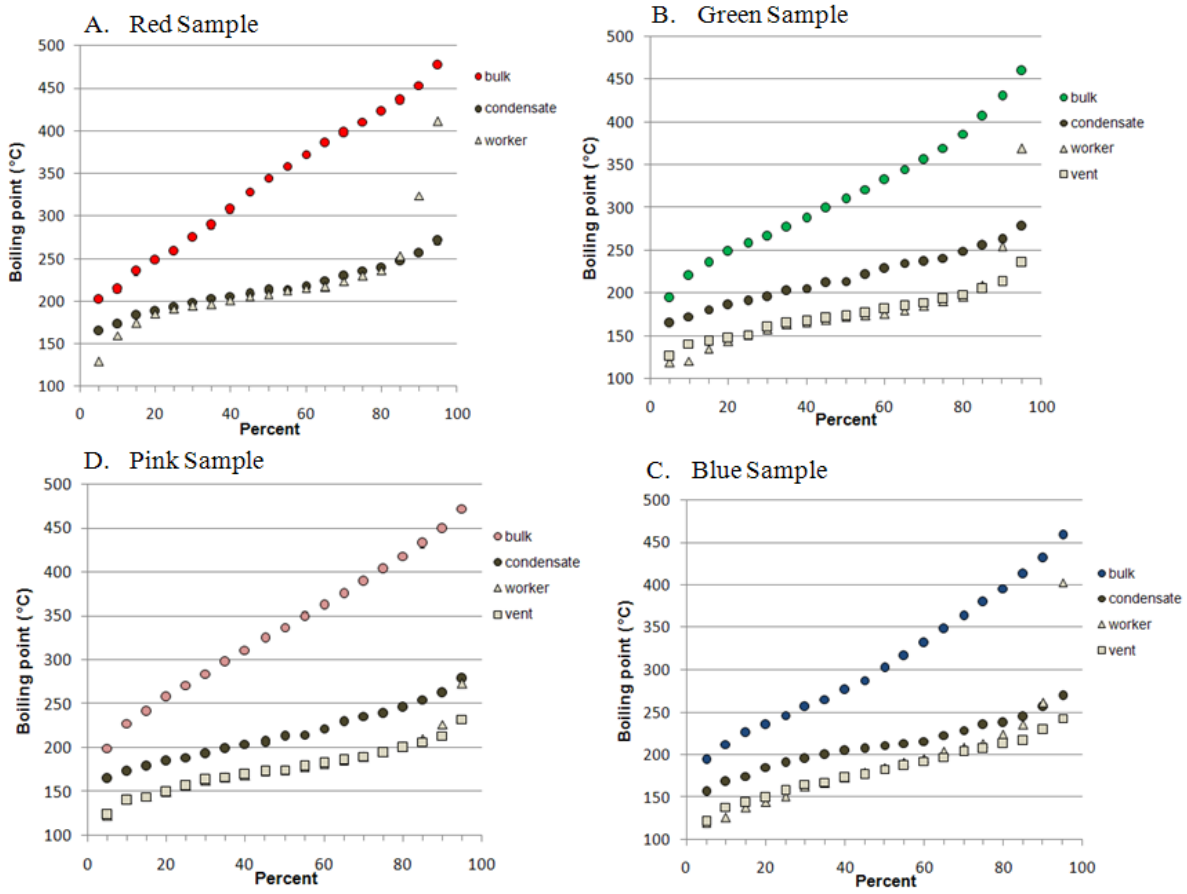
Figure 7 Boiling point distributions of fume condensates collected from the five bulk HFO fuel sample



Further comparative analysis showed that the boiling point distributions of the condensate samples differed noticeably from the personal monitoring samples. Comparisons of the condensates with the personal monitoring samples were possible for 4 of the 5 HFOs examined (insufficient sample volume with the yellow sample), and, as shown in **Figure 8**, some differences can be observed. The boiling point distribution of the red workplace sample was very similar to the condensate except at the lowest and highest 10 % of the distribution. The condensate from the green, blue, and pink samples showed a shift towards higher boiling hydrocarbons relative to the workplace samples, which may have been due to the use of 90 °C as the condensate generation temperature. Unfortunately, a boiling point distribution profile was not available for the yellow personal monitoring sample so a comparison could not be made with the condensate profile. The comparisons for the remaining four samples show that the condensates came reasonably close to replicating the boiling point profile observed with the personal monitoring samples; however, the profiles were not perfectly aligned. Several of the condensates showed a 20–60 °C difference that was evident throughout most of the distribution except the highest 10%, where the worker samples contained a greater amount of higher boiling hydrocarbons than the condensate. These differences in the boiling point distribution profiles indicate that the condensates were not perfectly representative of the chemical characteristics of the vapour mixture that the employees were exposed to during the barge loading operation. However, since the condensates generally contained a greater percentage of those high boiling hydrocarbons of occupational concern, they provided a suitable worst case surrogate of the vapours that could be generated in the workplace environment.

Since the condensate was prepared at a temperature of 90 °C and the HFO temperature on the barges ranged from 72–81 °C, the difference in boiling point distribution for the condensate and personal samples may simply be the result of the volatility differences that would be expected.

Figure 8 Comparison of boiling point distributions for the bulk sample, fume condensate, worker personal ample and vent in four of the five barges examined



4.1.2. Fluorescence

Florescence measurements with the bulk samples and condensates are depicted in **Table 4** for the five HFOs handled during the barge loading operations. The fluorescence intensity of the condensates were 1358–5000 times lower than the bulk sample indicating that a majority of the 4–6 ring PAHs in the bulk sample did not volatilize and did not get captured in the condensate.

Table 4 Fluorescence intensity of bulk fuel samples and condensates

Code	Bulk (mg/kg DPAeq)	Condensate (mg/L DPAeq)	Reduction factor
Red	25900	7.70	3364
Blue	23700	4.74	5000
Yellow	23500	17.3	1358
Pink	24200	7.17	3375
Green	27400	7.53	3639

4.2. PERSONAL AND AREA SAMPLES

4.2.1. Total Hydrocarbons (THC)

Results for the THC measurements yielded some very useful information on the magnitude of exposure for the on-board and onshore workers. The total hydrocarbon exposures of employees working onshore were considerably lower than those working on-board the barge. The surveyed loading durations ranged from 1.5 hours (partial loading) to 16 hours. In occupational hygiene practice it is customary to adjust personal exposure sample results to a reference period of 8 hours, however in this research the actually measured exposure levels during loading are reported, as this is considered more representative for worker exposures independently of the size of vessel being loaded. A comparison of the THC values for both vapours and aerosols presented in **Tables 5** and **6** reveals that the exposure concentrations ranged from about 0.46–16.01 mg/m^3 for on-board workers and 0.15–<0.36 mg/m^3 for those onshore. The average exposure of 6.13 mg/m^3 for the on-board operators is approximately 20-fold higher than the 0.26 mg/m^3 average exposure for those working onshore. These results are not surprising given the closer proximity of the on-board employees to emission sources and the higher hydrocarbon concentrations that are anticipated to be present on the barge. For all but a few of the samples the THC mist levels were below the limit of quantitation. THC background levels did not contribute appreciably to the overall exposures and were non-quantifiable for the aerosol samples and ranged from non-quantifiable to 0.109 mg/m^3 for the vapour samples (**Appendix 1**).

Table 5 Total hydrocarbon exposures for on-board workers*

Site Code	Background conc. (mg/m^3)		Exposure for on-board workers conc. (mg/m^3)		
	Aerosol conc.	Vapour conc.	Aerosol conc.	Vapour conc.	Total conc.
Red	<0.05	<0.05	<0.058	0.841	0.841
Blue	<0.089	< 0.089	<0.123	16.01	16.01
Yellow	<0.124	<0.124	<0.305	0.457	0.457
Pink	<0.056	0.056	<0.073	10.19	10.19
Green	<0.024	0.109	<0.067	3.16	3.16

* background measurements have been subtracted from the monitoring results

Table 6 Total hydrocarbon exposures for onshore workers*

Site Code	Background conc. (mg/m^3)		Exposure for onshore workers conc. (mg/m^3)		
	Aerosol conc.	Vapour conc.	Aerosol conc.	Vapour conc.	Total conc.
Red**					
Blue	<0.089	< 0.089	<0.111	0.239	0.239
Yellow	<0.124	<0.124	<0.208	0.154	0.154
Pink	<0.056	0.056	<0.284	<0.284	<0.284
Green	<0.024	0.109	<0.357	<0.357	<0.357

* background measurements have been subtracted from the monitoring results
** invalid sample result due to sample pump underperformance

Occupational exposure limits (OEL) have not been established within Europe for total hydrocarbons; however, several provinces in Canada as well as the ACGIH have set a limit of 100 mg/m^3 for vapour and aerosol hydrocarbons from No. 2 diesel fuels. Some countries have created an OEL for aliphatic hydrocarbons, but the value is greater than or equal to the value for diesel fuels and does not consider exposure to mists (GESTIS, 2014b). The exposure concentrations observed for workers on-board the barge were well below this occupational exposure limit of 100 mg/m^3. A closer examination of the individual results reveals that the aerosol levels were very low which indicates that the loading operation proceeded at a reasonable rate that did not lead to excessive agitation or the generation of appreciable amounts of hydrocarbon-containing mist. A comparison of the worker aerosol levels with a recently created inhalation DNEL (Derived No Effect Level) of 0.12 mg/m^3 for systemic effects (Concawe, 2012a) for an 8-hour occupational exposure was not possible due to all results being below the limit of quantitation (LOQ) which in some cases was higher than the DNEL; however, in the area samples close to the exhausts (**Table 7**) somewhat lower LOQs were achieved and no aerosol was quantified either. The corresponding acute inhalation DNEL for HFO aerosol has been set at 4700 mg/m^3 for a 15 minute exposure period. A DNEL of 3.5 mg/m^3 has also been established for steam cracked petroleum residues, which are site-restricted HFOs that have not been blended with a cutter stock (GESTIS, 2014a). As such, it is not strictly applicable to the exposure measurements collected in this study. Inhalation DNELs have not been established for the local acute or systemic effects of HFO vapour exposures.

Table 7 Total hydrocarbon concentrations in area sample near exhaust vents*

Site Code	Sample volume (m^3)	Sample time (min)	Background conc. (mg/m^3)		Area sample conc. (mg/m^3)		
			Aerosol conc.	Vapour conc.	Aerosol conc.	Vapour conc.	Total conc.
Red	0.832	330	<0.05	<0.05	<0.06	0.279	0.279
Blue	0.403	212	<0.089	< 0.089	<0.124	78.81	78.81
Yellow	0.167	83	<0.124	<0.124	<0.299	30.71	30.71
Pink	0.969	488	<0.056	0.056	<0.052	35.35	35.35
Green	1.131	565	<0.024	0.109	<0.044	20.93	20.93

* background measurements have been subtracted from the monitoring results

The results for the area sampling near the exhaust vents are shown in **Table 7**. The local air concentration of THC vapours and aerosols ranged from 0.28–78.81 mg/m^3 across the five barges. The lowest and highest concentrations were observed in the red and blue samples. A comparison of these sampling results with those from the personal exposure monitoring failed to reveal any direct relationship, which is not surprising since the placement of area sampling equipment varied considerably across the five barges. In addition, the wind direction relative to the location of the exhaust vent or hatch opening used to discharge the displaced vapours varied for each barge. Despite being located close to the hydrocarbon emission source, the area sampling yielded measurements that were within the 100 mg/m^3 exposure limits for THC. As a result, a worker spending a majority of their time in the vicinity of the exhaust plume would not be exposed to THC levels in excess of the OEL. However, because these measurements were taken outdoors, it is important to consider factors such as wind speed and wind direction, which can have decided impact on the local vapour concentration. Measurements at the loading terminals revealed that the wind speed was relatively constant at about 2–6 m/sec for the monitoring results presented herein. These relatively low wind speeds indicate that the measurements are representative of a worst case scenario and that even lower levels would have been attained if windier conditions existed. Finally, it is noteworthy that the HFO temperatures for the five loading operations were relatively constant and ranged from 72–81 °C, so the sampling results are representative of typical working conditions.

4.2.2. Aromatic hydrocarbon exposures

A second BIA sampling cassette was used for the analysis of naphthalene, pyrene, and benzo[a]pyrene. These three substances were selected because they are representative of the 2-ring, 4-ring, and 5-ring aromatic hydrocarbons that can be found in HFO samples. An analysis of the aromatic hydrocarbon content in fume condensates showed that two of these substances could be found at measurable levels. As shown in **Table 8**, naphthalene and pyrene levels could be found but benzo[a]pyrene was below the detection limits. Because of its higher volatility, the level of naphthalene in the condensates was generally 10 to 20 times higher than in the bulk samples. The level of PAHs possessing 3- or 4-rings was decidedly lower in the condensates than in the bulk samples because of their lower volatility (see **Table 9**).

Table 8 Aromatic hydrocarbon concentration in HFO sample condensates

Aromatic Hydrocarbons	Condensate concentration (µg/g)				
	red	green	pink	blue	yellow
naphthalene	36547	20635	29095	23781	9688
phenanthrene	150	193	175	96.3	228
anthracene	13.5	21.1	18.2	9.2	19.8
fluoranthene	2.6	1.2	1.7	1.1	3.0
pyrene	9.2	5.6	7.0	5.1	11.2
benzo[b]naphtha[2,1-d]thiophene	0.68	0.32	0.44	0.41	2.8
benzo[c]phenanthrene	<0.18	<0.18	<0.18	<0.18	<0.18
benzo[ghi]fluoranthene	<0.18	<0.18	<0.18	<0.18	<0.18
benzo[a]anthracene	0.37	<0.18	0.24	0.26	1.34
cyclopenta[c,d]pyrene	<0.18	<0.18	<0.18	<0.18	<0.18
triphenylene	0.26	<0.18	<0.18	0.20	0.79
chrysene	0.43	0.19	0.28	0.28	1.9
benzo[b]fluoranthene	<0.18	<0.18	<0.18	<0.18	<0.18
benzo[k]fluoranthene	<0.18	<0.18	<0.18	<0.18	<0.18
benzo[j]fluoranthene	<0.18	<0.18	<0.18	<0.18	<0.18
benzo[e]pyrene	<0.18	<0.18	<0.18	<0.18	<0.18
benzo[a]pyrene	<0.18	<0.18	<0.18	<0.18	<0.18
dibenzo[a,h]anthracene	<1.0	<1.0	<1.0	<1.0	<1.0
coronene	<1.0	<1.0	<1.0	<1.0	<1.0
indeno[1,2,3-cd]pyrene	<1.0	<1.0	<1.0	<1.0	<1.0
anthanthrene	<1.0	<1.0	<1.0	<1.0	<1.0
benzo[ghi]perylene	<1.0	<1.0	<1.0	<1.0	<1.0

Table 9 Aromatic hydrocarbon concentration in bulk samples

Aromatic Hydrocarbons	Bulk sample concentration (µg/g)				
	red	green	pink	blue	yellow
naphthalene	2146	2466	149	1990	1422
phenanthrene	669	781	252	710	898
anthracene	83.5	97.3	23.5	83.5	102
fluoranthene	44.8	45.8	14.3	24.9	24.5
pyrene	343	348	61.9	209	194
benzo[b]naphtha[2,1-d]thiophene	177	110	125	28.7	25.3
benzo[c]phenanthrene	18.3	18.1	15.5	<2.5	2.7
benzo[ghi]fluoranthene	n.s.	n.s.	n.s.	<2.5	<2.5
benzo[a]anthracene	147	130	129	13.1	13.8
cyclopenta[c,d]pyrene	7.6	7.6	6	2.9	2.6
triphenylene	52.6	59.6	54	6.1	7
chrysene	178	162	195	15.7	18.5
benzo[b]fluoranthene	35.6	35.5	39.6	3.3	4.2
benzo[k]fluoranthene	10.2	10.2	8.9	<2.5	<2.5
benzo[j]fluoranthene	13.9	12.2	14.3	<2.5	<2.5
benzo[e]pyrene	105	125	55.5	9	11
benzo[a]pyrene	101	96.3	62.5	6.9	8.7
dibenzo[a,h]anthracene	9.6	10.9	9.8	<2.5	<2.5
coronene	8.1	7.4	3.1	3	<2.5
indeno[1,2,3-cd]pyrene	9.1	10.8	6.9	<2.5	<2.5
anthanthrene	25.8	24.7	13	2.5	3.1
benzo[ghi]perylene	91.3	77	18.9	15.7	10.2

n.s.- not specified, peak overlapping

The personal monitoring results for on-board and onshore workers are presented in **Tables 10** and **11** for the vapour samples. The measurements revealed that benz[a]pyrene was below quantitation levels in both the on-board and onshore samples and that pyrene could only be detect in 2 of 5 on-board personal samples at levels of 0.05 and 0.06 µg/m^3. In the German reference document TRGS 910, a tolerance level of 700 ng/m^3 and an acceptance level of 70 ng/m^3 are presented for benz[a]pyrene; all but one of the concentrations calculated to correspond to the LOQ were below the acceptance level (**Tables 10, 11**) benz[a]pyrene). A specific OEL for pyrene does not exist but there is a limit for coal tar pitch volatiles, which has a TWA value of 0.2 mg/m^3 for the sum total of anthracene, benzo[a]pyrene, phenanthrene, acridine, chrysene, and pyrene in the benzene soluble fraction. This value is recognized in the US, Singapore, South Korea, and New Zealand, but a comparable value is not available for Europe (GESTIS, 2014b). A somewhat smaller value of 0.14 mg/m^3 has been promulgated in Ireland. Regardless of the basis for comparison, the pyrene exposures for on-board and onshore personnel were at least 2 orders of magnitude below the OELs of critical concern.

As expected from an examination of the condensate measurements, naphthalene levels were higher than for pyrene or benzo[a]pyrene. Workers on-board the barges displayed personal naphthalene exposure levels up to 0.20 mg/m^3 (199 µg/m^3). Numerous countries within the EU have established an exposure limit of 50–53 mg/m^3 for naphthalene. Austria, France, Italy, Ireland, Sweden, Switzerland, and The Netherlands have established an 8-hr TWA limit of 50 mg/m^3, which is the most

applicable standard for evaluating occupational health risk (GESTIS, 2014b). German reference document TRGS 900 presents an OEL value of 0.5 mg/m^3. Naphthalene aerosol was found at measurable levels in single personal sample for an on-board worker at a value of 0.004 µg/m^3, with the remainder of the samples being below the quantitation limit (**Appendix 1**). The European Commission's Scientific Committee on Occupational Exposure Limits (SCOEL) has deferred establishing an OEL for naphthalene until more information becomes available on its carcinogenic potential (EC, 2010). Based on more recent data, the Health Council of The Netherlands has decided that naphthalene is not classifiable as to its carcinogenic properties since, despite its being a rodent carcinogen, evidence strongly supports the notion that naphthalene is not carcinogenic to humans (Health Council of The Netherlands, 2012; Bailey et al., 2015). The average naphthalene exposure concentration for the five on-board operators was 65.18 µg/m^3, which is more than 700-fold lower than an OEL of 50 mg/m^3 and also well below the German OEL.

Table 10 Aromatic hydrocarbon vapour exposures for on-board workers*

Site Code	Background conc. (µg/m³)			Personal sample conc. (µg/m³)		
	Naphthalene	Pyrene	Benzo[a]pyrene	Naphthalene	Pyrene	Benzo[a]pyrene
Red	0.12	<0.008	<0.008	20.6	<0.012	<0.012
Blue	2.3	0.01	<0.018	199.3	0.05	<0.021
Yellow	0.08	<0.025	<0.025	3.7	<0.061	<0.061
Pink	0.15	<0.011	<0.011	90.3	0.06	<0.015
Green	0.95	<0.007	<0.007	12.0	<0.013	<0.013

* background measurements have been subtracted from the monitoring results

Table 11 Aromatic hydrocarbon vapour exposures for onshore workers*

Site Code	Background conc. (µg/m³)			Personal sample conc. (µg/m³)		
	Naphthalene	Pyrene	Benzo[a]pyrene	Naphthalene	Pyrene	Benzo[a]pyrene
Red	0.12	<0.008	<0.008	5.9	<0.009	<0.009
Blue	2.3	0.01	<0.018	2.9	<0.022	<0.022
Yellow	0.08	<0.025	<0.025	0.19	<0.041	<0.041
Pink	0.15	<0.011	<0.011	0.69	<0.056	<0.056
Green	0.95	<0.007	<0.007	1.2	<0.074	<0.074

* background measurements have been subtracted from the monitoring results

Although the area samples collected in the vicinity of the exhaust vent were higher than those seen for on-board and onshore personal samples, the main difference between the two sample types were restricted to naphthalene. As shown in **Table 12**, the concentrations of naphthalene, pyrene and benzo[a]pyrene in the area samples near exhaust vents were higher than those seen in the personal samples. The naphthalene vapour levels in the area samples rose to as high as 1.5 mg/m^3, exceeding the German reference value for 8 hour exposures, in one barge loading operation ('blue'), yet neither the bulk nor the condensate product showed an elevated naphthalene level (**Tables 8 and 9**). It is worth noting that the area samples were not

representative of personal exposures but intended to be merely source-related samples and as such should not even feature as worst-case exposure samples, as there is no requirement for the crew to spend extended time periods close to the exhaust vents.

Table 12 Aromatic hydrocarbon vapour exposures in background and area samples near exhaust vents*

Site Code	Sample volume (m^3)	Sample time (min)	Background conc. (µg/m^3)			Area sample conc. (µg/m^3)		
			Naphthalene	Pyrene	Benzo[a]pyrene	Naphthalene	Pyrene	Benzo[a]pyrene
Red	0.660	330	0.12	<0.008	<0.008	3.4	<0.015	<0.015
Blue	0.413	212	2.3	0.01	<0.018	1489	0.02	n.a.
Yellow	0.168	83	0.08	<0.025	<0.025	299	<0.06	<0.06
Pink	0.969	482	0.15	<0.011	<0.011	684	0.04	<0.01
Green	1.123	565	0.95	<0.007	<0.007	260	<0.009	<0.009

* background measurements have been subtracted from the monitoring results

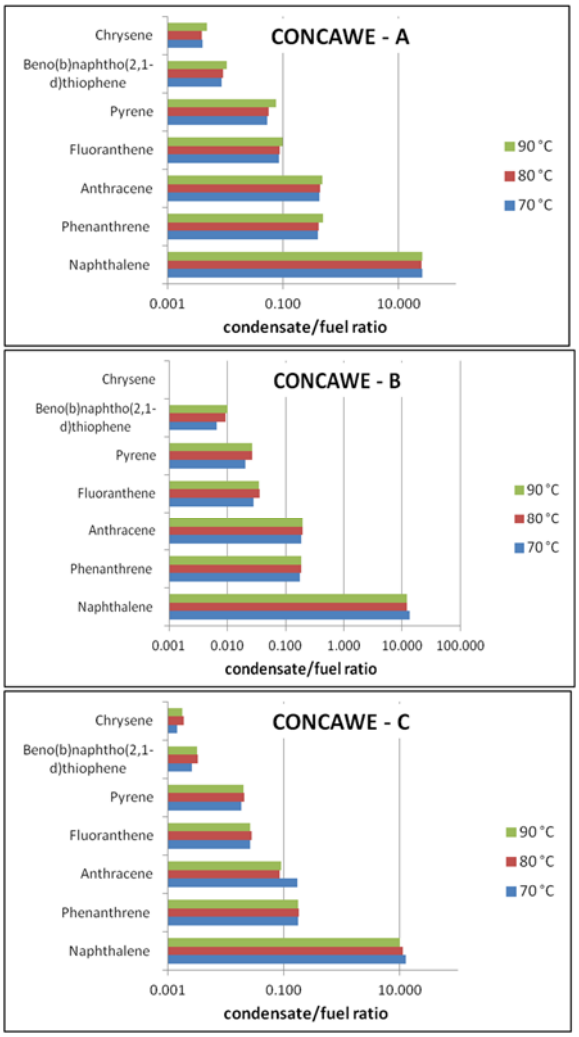
n.a. - not available

Whereas static aerosol sampling occasionally detected the presence of some mist, only 1 in 5 of the on-board samples and none of the onshore samples were above the quantitation limit for any of the three AHs examined (**Appendix 1**). Given the very low levels and the failure to consistently detect measurable aerosol levels, it can be concluded that misting is not occurring to any appreciable degree during the submerged loading of HFOs onto barges.

4.3. MUTAGENICITY TESTING

The results from the first round of testing with condensates generated at 90 °C produced equivocal results with the mutagenicity index ranging from 0.02-9.0 for the five HFO samples. These unexpected findings were ultimately attributed to reproducibility problems with the assay due to false interpretation of the plate readings. Initially, the colonies on the plates were counted with an automated reader which was not properly calibrated for the high concentrations of hamster liver S9 fractions and interpreted the hamster liver preparation erroneously as microcolonies. Therefore, a new round of testing was performed in which the results of the automated plate reader were checked manually. The second round of testing was conducted using a set of three bulk HFO samples collected at the same three loading terminals involved in the exposure study. These new condensate samples were compositionally equivalent to those examined in the first round of testing with similar AH profiles and fluorescence intensities. Condensates were prepared from each bulk sample at temperatures of 70, 80, and 90 °C. The temperatures were selected to cover the range of temperatures that are normally encountered during barge loading. Details regarding the analytical characterization of the nine HFO condensates are presented in **Appendix 2**. This includes measurements of the boiling point distributions, AH content, and total fluorescence. An examination of the AH concentration ratio in the bulk HFO samples and condensate shows that the generation temperature did not appreciably impact the AH content in the condensates (see **Figure 9**).

Figure 9 Comparison of the AH ratio for bulk and condensate samples at the three recovery temperatures



The results of the mutagenicity testing with the nine HFO condensates are presented at **Table 13**. The positive control samples were approximately 3 times higher than the solvent control, which indicated that the test conditions were suitable to yield valid results. In eight of the nine condensates a slight decrease was observed in the number of revertant colonies as the plate concentration increased. The resulting mutagenicity index was less than 1 in each case, indicating negligible mutagenic potential. These results are consistent with the observed decrease in fluorescence of the condensates relative to the bulk samples. The fluorescence of the condensates from samples A, B, and C was generally 2300 to 6500 times lower than the bulk preparation, indicating a sharp reduction the amount of 4- to 6-ring PAHs that were present. Furthermore, these results were corroborated by the results from the PAH analyses of the condensates which showed overall low concentrations of PAH with 4 to 7 rings.

Table 13 Mutagenic response from HFO condensates generated at three temperatures using a modified Ames test (ASTM 1687-10)

Dose (µL/plate)	Mean ± Standard Deviation								
	Sample A-01 (70 °C)	Sample A-02 (80 °C)	Sample A-03 (90 °C)	Sample B-01 (70 °C)	Sample B-02 (80 °C)	Sample B-03 (90 °C)	Sample C-01 (70 °C)*	Sample C-02 (80 °C)	Sample C-03 (90 °C)
positive control	123 ± 19	123 ± 19	123 ± 9	130 ± 38	117 ± 42	160 ± 25	79 ± 15	76 ± 2	83 ± 14
solvent control	29 ± 8	29 ± 8	29 ± 8	41 ± 6	41 ± 7	44 ± 7	34 ± 5	36 ± 3	28 ± 6
2.5	39 ± 13	29 ± 7	48 ± 3	47 ± 11	54 ± 3	44 ± 10	43 ± 6	31 ± 3	41 ± 8
5	46 ± 7	31 ± 6	*	42 ± 17	42 ± 8	57 ± 3	42 ± 11	34 ± 8	31 ± 11
7.5	45 ± 10	34 ± 6	36 ± 5	57 ± 3	43 ± 3	57 ± 13	35 ± 7	33 ± 8	27 ± 8
10	51 ± 6	36 ± 8	184 ± 141	44 ± 2	49 ± 5	50 ± 5	38 ± 12	27 ± 7	29 ± 6
15	36 ± 17	40 ± 12	53 ± 33	50 ± 3	44 ± 6	52 ± 4	32 ± 6	16 ± 6	27 ± 5
30	48 ± 5	55 ± 34	53 ± 17	25 ± 2	23 ± 9	35 ± 4	†	†	†
45	45 ± 6	40 ± 4	42 ± 13	†	†	28 ± 4	†	†	†
52.5	37 ± 3	37 ± 10	39 ± 15	†	†	30 ± 9	57 ± 1	†	†
60	40 ± 8	22 ± 2	18 ± 4	†	†	†	23 ± 4	†	7 ± 4
MI†	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

*all three plates infected
† microcolony formation

4.4. EMISSION ESTIMATION

The emissions of hydrocarbons during the loading of HFO on inland barges were investigated using various approaches that have been advocated by competent authorities from the US and Europe. Empirical, mechanistic and mathematical methods were evaluated to determine their suitability for yielding reliable estimates that were applicable to HFOs meeting the UN 3082 fuel designation. The empirical approaches prove wholly unsuitable since they were unable to account for the differences in vapour pressure and density for HFOs being handled at elevated temperatures. The remaining methods showed some variability but were within an order of magnitude of one another. Two methods from Europe and one from the US were ultimately judged to provide the most reliable estimates, since they were able to compensate for the increased vapour pressure and decreased density of HFO at an assumed average loading temperature of 80 °C. The results in **Table 14** show that the USEPA method yielded the highest emission factors. The UK EA method and the Concawe method yielded factors that were approximately 2 to 4-fold lower, respectively.

Table 14 Comparison of HFO emission factors calculated by different approaches

Method (year)	Emission factor (g/ton)	Comments
USEPA (2008)	22.5 (15.7–29.2)	fully adjusted for elevated HFO loading temperature
Concawe (2009)	4.9 (2.6–6.6)	calculated from a generic formula using adjusted HFO vapour pressure
UK EA (2007)	8.9	correction factors employed for temperature-dependent vapour pressure and density differences

If adjustments are applied to the results from the Concawe and UK EA methods the results from the three methods merge even closer. The adjustment was based on an early Concawe study revealing that emission factor calculations for the barge loading of gasoline did not agree with Differential Absorption Lidar (DIAL) measurements (Concawe, 1995). A differential of 56% was found between the actual and estimated emission factors. Based on these findings, a 50% upward adjustment was made to those estimates that may have underestimated the true emissions. This yielded emission factor estimates ranging from 7.4 to 22.5 g/ton HFO. These are reasonably similar values given the differences in the mathematical approaches. The emission factor for volatile hydrocarbons during the barge loading of an HFO at a temperature of 80 °C is therefore estimated to be in the range of 10-20 g/ton, which is equivalent to a total mass emission of 130-260 kg for a loading duration of 10 hr on a barge capable of hauling a maximum of 13,000 tons of HFO.

5. DISCUSSION

5.1. EXPOSURE ANALYSIS

The preceding analysis shows that the release of volatile hydrocarbons from the loading on inland barges with a commercial HFO as surveyed in this project did not result in personal exposures that exceed the most relevant OEL of 100 mg/m^3. Whereas, the use of cutter stocks containing lower molecular weight hydrocarbons was presumed to cause elevated emissions, these C_9–C_{28} congeners were not released at particularly high levels. This may be due in part to the vapour pressure depression that occurs when they are blended into an HFO residuum from a refinery. Under these circumstances the vapour pressure of each component is essentially reduced as predicted by Raoult's law. Unfortunately, the exact magnitude of the vapour pressure depression cannot be calculated due to the myriad of components in an HFO and the need to know the mole fraction of each component in the mixture. Measurement of personal exposures to total (vapour and aerosol) hydrocarbons did not result in any exposure measurements greater than 16 mg/m^3. As shown in **Table 15**, the safety margin for total hydrocarbon exposures, not corrected for durations other than 8 hours, relative to an OEL of 100 mg/m^3 ranged from 16 to 380.

Table 15 Comparison of personal monitoring measurements with applicable occupational exposure limits.

Metric	Total hydrocarbon*		Naphthalene‡	
	on-board barge	onshore	on-board barge	onshore
avg. conc.(mg/m^3)	6.13	0.26	0.065	0.002
8-hr OEL (mg/m^3)	100	100	50/0.5	50/0.5
safety margin	16	380	770/7.7	25,000/250

* includes both vapour and aerosol measurements
‡ vapour measurements only

Although ADN specifies that the "gas/air mixture shall be returned to shore through a gas recovery or compensation pipe during loading operations", the assumption was made that the emissions could in part exist as aerosol, and therefore a validated exposure monitoring system was adopted that could sample vapour and aerosol simultaneously. The measurement results however indicated that aerosol levels were so low as to be not-quantifiable with this system.

The main class of constituents of HFOs relevant to CMR effects are the aromatics. Concawe report 7/12 indicated a total aromatics content of 42.4% for a typical HFO component (Appendix 4 of CONCAWE, 2012b). It is generally not possible or meaningful to fully speciate this fraction at the molecular level, but it has become customary in health and environmental studies to characterise the aromatics fraction on the basis of analysis of a series of marker PAHs, such as the list proposed by the US Environmental Protection Agency or a slightly different list often used in Germany (Grimmer et al. 1997). Although these marker PAHs are not necessarily ideal representatives since the exact chemical composition of the aromatics fraction is not known, they can be reliably assessed and quantified using standard methods and will

not only be relatively abundant due to their thermodynamic stability, but also have boiling points comparable to their alkylated congeners.

The levels of individual marker PAHs in the bulk product (see **Table 9**) in this study were in the same range as the levels reported in the dermal exposure study for 8 samples of heavy fuel oil or HFO blending components (Table 2 in Christopher et al, 2011), indicating that the surveyed loading operations can be considered representative of HFOs in commerce.

Benzo[a]pyrene poses the greatest toxicological hazard and has been listed has an IARC group 1 carcinogen that is capable of causing cancer in laboratory animals and humans. Benzo[a]pyrene vapour or aerosol was not quantified in a single personal or area measurement on-board or off board the barges, with the limit of quantitation generally below the German acceptance level of 70 ng/m^3. In addition, benzo[a]pyrene vapour or aerosols levels were not found in any of the areas samples collected near the exhaust vents. Taken together, these data indicate that there is a negligible release and exposure to benzo[a]pyrene during the HFO barge loading operations. Likewise, aerosol transport to residential off-site locations beyond the terminal fence line was also judged to be doubtful.

Although pyrene is not considered to be carcinogenic and was categorised by IARC in group 3, which indicates inadequate evidence for inducing human or animal cancer (IARC, 2014), pyrene is considered a good and highly sensitive marker for exposure since, due to its thermodynamic stability, it is in most cases the most abundant PAH in PAH mixtures (Boogaard, 2011). Indeed pyrene was one of the more dominant PAHs in the bulk samples in this study (**Table 9**) and some detectable exposures were recorded for pyrene: quantifiable levels of pyrene were reported for 2 of 10 personal vapour samples, but in none of 10 personal aerosol samples (**Appendix 1, Tables 3.15 and 3.16**). Since air quality guidelines have not been created for this PAH in Europe or North America, these levels cannot be compared to a reference value. There are several PAH-related occupational exposure limits that are applicable to pyrene. The most notable is for coal tar pitch volatiles, which includes several benzene-soluble PAHs in addition to pyrene. A comparison of the highest exposure levels for pyrene with the coal tar pitch OEL of 200 µg/m^3 failed to show any evidence of overexposure or a cause for concern. A similar comparison for naphthalene levels is shown in **Table 15**. Naphthalene was found to be a rodent carcinogen, but the relevance of the available data for humans was questioned and, for that reason, the SCOEL did not derive an OEL for naphthalene in 2010 pending the availability of new data (EC, 2010). Evaluation of all available, including more recent data, strongly supports the view that naphthalene is not carcinogenic to humans (Bailey et al., 2015). The Health Council of The Netherlands reached a similar conclusion and classified naphthalene in category 3 (not classifiable as to its carcinogenicity to human) (Health Council of The Netherlands, 2012). Details are provided in **Appendix 5**.

This study complements a previous occupational exposure study for HFO, which focussed on the dermal exposure route, which was thought to be the main exposure route of concern (Christopher et al., 2011). As in the present study, which focussed on inhalation exposures, the dermal exposures were generally found to be low.

5.2. MUTAGENICITY TESTING

The HFO health and environmental research programme undertaken by Concawe included a hazard component despite the existence of an extensive toxicity database created in conjunction with due diligence activities and voluntary agreements (Concawe, 1998, McKee et al., 2014). Although the *in vitro* mutagenicity of HFO

extracts has previously been determined for many refinery streams, the results are generally limited to site-restricted substances that have not been blended with a cutter stock to produce a commercial fuel. To better characterize the mutagenic potential of fuel-related HFOs, testing was undertaken with condensates prepared from the volatile fraction of three bulk samples collected at barge loading terminals. Condensates were prepared from each of these samples at temperatures of 70 °C, 80 °C, and 90 °C.

Modified Ames' testing showed that all nine condensates produced a minimal change in the number of revertant colonies, yielding a mutagenicity index (MI) less than 0.1. By comparison, a commercial grade heavy fuel No. 6 sample yielded an MI of 24, which is consistent with the presence of high molecular weight (4 to 6 ring) PAHs in this type of sample (McKee et al., 2013). Furthermore, the cut-off value for mutagenicity of lubricant base oils is set at a MI value of 1.0 and for residual aromatic extracts at a MI value of 0.4 (ASTM, 2010; CONCAWE 2012c). Studies have shown that the mutagenicity of stock unblended HFOs in the modified Ames assay is quite variable depending on the source of the residuum. Analysis on separate samples of catalytically cracked clarified slurry oil show that that the MI was appreciably influenced by the percentage of PAHs with 4 to 7 rings (McKee et al., 2013).

Chemical analysis of the nine condensates used in this study showed that naphthalene was by far the most dominant aromatic hydrocarbon with lower amounts of 3- and 4-ring PAHs such phenanthrene, anthracene, and pyrene (see **Appendix 1**). Previous studies have shown that naphthalene is not genotoxic or mutagenic in the Ames assay (Brusick, 2008). Although naphthalene was shown to be a rodent carcinogen, recent insights strongly support the notion that naphthalene does not pose a human carcinogenic hazard (Baily et al., 2015; Health Council of The Netherlands, 2012). Although some 5- and 6-ring PAHs are considered to pose a human carcinogenic risk, the levels of 5- and 6-ring PAHs were below detection limits. Given the PAH distribution profile in the condensates, it can be concluded that the PAHs in the vapour phase do not pose a mutagenic risk and that workers working with HFOs at temperatures up to 90 °C are not in danger from the small amount of vapour being released.

5.3. EMISSIONS ESTIMATION

Contrary to the occupational exposure perspective with focus on AHs, environmental considerations are aimed at total hydrocarbons because of their potential to contribute to ground-level ozone formation and other air quality concerns. After adjusting for deviations in temperature, density, and methodological bias, a worst case total hydrocarbon emission factor of 10–20 g/ton was derived for the volatile hydrocarbons released during the barge loading of an HFO. The upper limit of this range is far below the values observed for other petroleum products such crude oil, gasoline, and petroleum distillates (see **Table 16**). Specific guideline or recommendation for VOC release during the loading or unloading of HFOs from inland waterway barges has not been issued by the European Union. In the absence of such a regulation, fuel distributors have taken extra precautions to ensure that releases are minimized during loading or unloading operation. This includes the use of submerged loading techniques to minimize agitation. Submerged loading employs a delivery pipe that extends below the liquid surface to minimize splatter and mist vapour generation. The initial rate of tank filling is also reduced to prevent excess splashing and agitation that leads to the release of vapours into the air space.

A comparison of the HFO emission factor with those for other petroleum products indicate that HFOs can be loaded onto barges without any concern of excessive

emissions. As shown in **Table 16**, the worst case estimate of hydrocarbon emissions from HFO is 27-fold lower than the factor for gasoline and nearly 8-fold lower than crude oil. In addition, the USEPA endorsed emission factor for the submerge loading of an HFO onto a tank barge is 9.0×10^{-5} lb/1000 gal, which is equivalent to 0.01 g/ton of HFO shipped (USEPA, 2008). This estimate, however, assumes an average temperature during bulk loading of only 16°C (60 °F) which appears to be different from loading practices in the EU on inland waterways where the product is generally heated to improve handling.

To provide some assurance that the emission factors were not underestimated, the values were compared to factors that were roughly calculated from hydrocarbon emission measurements taken in the vicinity of the exhaust vent sites aboard the five barges. As shown in **Table 17**, these measurements yielded emission factors that generally ranged from about 0.02–0.08 g/ton, which is decidedly lower than the 10–20 g/ton estimated to be a worst case value, but reasonably close to the value of 0.01 g/ton adopted by the USEPA. Whereas the emission factors determined from the measurement data are not higher than the calculated estimates, the comparison needs be tempered with the knowledge that the measurements were not perfectly reflective of the concentrations in the exhaust stream. In many cases, the devices used for sample collection were merely located in the vicinity of an exhaust vent without any consideration of variable wind directions.

As a result, the area samples did not always record the hydrocarbon concentrations inside the exhaust plume rising through the vent. Despite these limitations, however, the samples provide a reasonable cross-check of the validity of the emission factor calculations. Overall, the estimated hydrocarbon emissions during the barge loading of an HFO show that the release factor is small and in line with the limited volatility of this product. The results further indicate that loading an HFO onto a 13,000 ton barge over a ten hour period of time would result in a total VOC mass release of 130-260 kg, which is relatively small compared to other sources. These findings are consistent with those of Environment Canada, who concluded that the evaporative fuel losses of VOCs from the storage and transport of HFOs is not a significant source of exposure or release at a production site (Environment Canada, 2013).

Table 16 Published emission factors for barge loading or degassing of fuels or hydrocarbons

Chemical type	UN code	Emission factor (g VOC/ton)	Reference
Gasoline	UN 1203	550	OECD, 2009
Crude oil	UN 1267	137	OECD, 2009
Jet naphtha	UN 1863	200	OECD, 2009
Petroleum distillates	UN 1268	200	CE Delft, 2013
Hydrocarbon liquids	UN 3295	380	CE Delft, 2013
Benzene	UN 1114	220	CE Delft, 2013
Flammable liquids	UN 2398	240	CE Delft, 2013

Table 17 Total hydrocarbon measurements in the vicinity of barge exhaust vent sites and the corresponding emission factors[#†‡]

Site Code	Sample volume (m^3)	Sample time (hr)	Conc. Total hydrocarbon (mg/m^3)	Total Hydrocarbon mass (mg)	Barge loading time (hr)	Barge load rate (m^3/hr)	Volume displacement (m^3)	Emission factor (mg/ton)
Red*	0.832	5.50	0.31	1424	5	922	4610	0.34
Blue	0.403	3.53	78.82	177347	3	750	2250	92.83
Yellow	0.167	1.38	30.75	43047	3.5	400	1400	12.15
Pink	0.969	8.13	35.36	424320	16	750	12000	17.97
Green	1.131	9.42	20.94	188433	12	750	9000	16.43

[#] emission factor calculations assume an HFO density of 1.0 ton/m^3
[†] hydrocarbon levels in aerosol and vapour sample were quantitated separately and summed to arrive at a total
* aerosol level in the red sample was below the detection limit of 0.03 mg/m^3 so the value imputed to be at the LOD
[‡] emission factor = vent concentration x sample time x barge lode rate/load time x load rate

5.4. STUDY STRENGTHS AND LIMITATIONS

The research programme on the barge loading of HFOs is characterized by a number of key strengths that provide a solid basis for future decision making. Notable attributes include its comprehensive nature with personal exposures, atmospheric emissions, and health hazards independently examined and reported upon. The exposure monitoring programme included the use of sampling equipment that allowed the separate collection of aerosols and vapours so the contribution of each type of release could be assessed during the barge loading operations. In addition, state-of-the-science emissions estimation algorithms were developed that allowed the calculation of worst case atmospheric releases of total hydrocarbons during a barge loading scenario. The study also featured the generation of HFO condensates that allowed the mutagenic hazard of the volatile fraction to be determined in a modified Ames assay. Perhaps the greatest the strength of this programme was, however, the wide array of analytical techniques used to characterize, to the extent possible, the hydrocarbon composition of the various HFOs being examined.

Although the programme was well designed and executed, there are several uncertainties and limitations that need to be considered when interpreting the results. First, the number of HFO loading sites and personal samples collected during monitoring campaign was limited, although the compositional variation reported in the literature was also apparent for the HFOs included in the present study, as evidenced by the individual PAH levels in Table 9 which varied over more than an order of magnitude in some cases. This prevented a full statistical analysis of the results relative to applicable occupation exposure limits. This encumbrance was not viewed as a particularly serious problem; however, since observed personal exposure levels were uniformly low, showing little variability across the five operations surveyed. As a result, the inclusion of additional personal exposure samples would not have appreciably changed the magnitude of the exposure margin relative to the OELs. Second, the personal exposure monitoring was confined to the measurement of THC levels and a suite of three aromatic hydrocarbons deemed to be good markers of HFO exposures under actual barge loading conditions. Again, given the low exposure levels, a more refined speciation for individual hydrocarbons would not be expected to yield OEL safety margins that are different from those reported. Third, the BIA sampler employed in the study has been validated in wind speeds up to 4 $m.s^{-1}$ (Kenny et al., 1997), but in one survey of the present study the outdoor wind speed exceeded that value. The type of aerosol expected however would consist of very small droplets due to condensation phenomena which are much less likely to be influenced by high wind speed than large droplets. Finally, the hazard analysis with the mist condensates was restricted to a determination of the mutagenic potential in a modified Ames assay. Although additional testing would have provided greater perspective on the range of possible hazards, the time required for a more complete evaluation would have been prohibitively long. However, the low mutagenicity indices of the fume condensates are corroborated by the low levels of PAH measured in the condensates aa well as by the low levels of fluorescence. In fact, the three independent measurements all indicate the low mutagenic hazard of the fume condensates.

6. CONCLUSIONS

Measurements made in conjunction with this research programme show that naphthalene is the single most abundant aromatic hydrocarbon in the vapour blanket that is emitted during the tank filling process. The concentrations observed in area samples at or near the tank vent revealed maximum total hydrocarbon concentrations of 80 mg/m^3 and maximum naphthalene values of 1.5 mg/m^3 (see **Table 7** and **12**). Taken together, the exposure monitoring data indicated that the workplace controls currently in place to limit contact are sufficient to mitigate any hazards from barge loading of commercial HFOs. These controls together with institutional best practices guidelines for reducing emissions help ensure that unintentional releases and exposures do not occur.

The results of these studies indicated that during the loading of hot commercial HFO on inland waterway barges:

(i) the emissions resulted only in low workplace exposures, well below limit values set by the ACGIH, for employees working on-board the barge and even lower for those working onshore at the terminal;
(ii) there was no release of detectable amounts of benzo[a]pyrene;
(iii) there was no mutagenic risk for employees based on testing in a modified Ames assay using a condensate generated under similar operating conditions; and
(iv) there was no substantial contribution to air emissions relative to other types of petroleum hydrocarbon cargos.

Overall, this analysis indicates that HFO emissions, exposures, and hazards during the surveyed barge loading operations of commercial HFOs, and considered representative for this operation in general, were not excessive or a source of environmental or human health concern. The studies did not indicate a need for additional control measures on the emissions of hot HFOs during barge loading beyond normal good operational practice.

7. REFERENCES

1. ASTM (1997) Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography. D2887-97: American Society of Testing Materials, West Conshohocken, PA

2. ASTM (2010) Standard Test Method for Determining Carcinogenic Potential of Virgin Base Oils in Metalworking Fluids. E1687-10: American Society of Testing Materials, West Conshohocken, PA

3. Bailey, L. A., et al. (2015). "Hypothesis-based weight-of-evidence evaluation and risk assessment for naphthalene carcinogenesis." *Critical Reviews in Toxicology*

4. Blackburn, G. R., et al. (1986). Predicting carcinogenicity of petroleum distillation fractions using a modified Salmonella mutagenicity assay." *Cell Biol Toxicol 2, 63-84*

5. Blackburn, G. R., et al. (1996). "Comparison of biological and chemical predictors of dermal carcinogenicity of petroleum oils." *Polycyclic aromatic compounds 11*, 201-210

6. Boogaard, P.J. Biomonitoring of exposure to polycyclic aromatic hydrocarbons, in: Knudsen LE, Merlo DF (Eds), *Biomarkers and Human Biomonitoring*, Volume 1: Ongoing Programs and Exposures, 2011, Royal Society of Chemistry, Cambridge (ISBN: 9781849732413), UK, pp 338-359

7. Breuer, D. (1999) Measurement of vapour-aerosol mixtures. *J Environ Monitoring 1, 299-305*

8. Brusick, D. (2008) Critical assessment of the genetic toxicity of naphthalene. *Regulatory Toxicology and Pharmacology 51, S37-S42*

9. Christopher, Y. et al. (2011). An Assessment of Dermal Exposure to Heavy Fuel Oil (HFO) in Occupational Settings. *Annals of Occupational Hygiene 55, 319–328*

10. CNRS (2011) European Harmonized Classification and Labelling of Carconogenic, Mutagenic and Reproduction (CMR) Substances According to the Criteria of the CLP Regulation at the Date of the 22nd January 2011. CNRS, Prevention du Risque Chimique, Gif-sur-Yvette, France

11. CONCAWE (1998) Heavy fuel oils. Product Dossier No. 98/109. Brussels: CONCAWE

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

13. CONCAWE (2012a) International Uniform Chemical Information Database (IUCLID) for Heavy Fuel Oil Components. Brussels: CONCAWE

14. CONCAWE (2012b) REACH - Analytical characterisation of petroleum UVCB substances. Report No. 7/12. Brussels: CONCAWE

15. CONCAWE (2012c) Use of the modified Ames test as an indicator of the carcinogenicity of residual aromatic extracts. Report No. 12/12. Brussels: CONCAWE

16. EA (2007) Emission scenario document on transport and storage of chemicals. Bristol, United Kingdom: Environment Agency

17. EC (2010) Recommendations from the Scientific Committee on Occupational Exposure Limits for naphthalene. Brussels, Belgium: European Commission, Employment, Social Affairs, and Inclusion

18. ECE (2011) Carriage of fuel oil, heavy and fuel oil, residual. INF.25. Geneva, Switzerland: Economic Commission for Europe, Inland Transport Committee, Working Party on the Transport of Dangerous Goods

19. ECE (2013) CONCAWE/EUROPIA study on "HFO ADN Emissions and Exposure Assessment". INF.33. Geneva, Switzerland: Economic Commission for Europe, Inland Transport Committee, Working Party on the Transport of Dangerous Goods

20. Environment Canada (2013) Draft Screening Assessment Petroleum Sector Stream Approach, Fuel Oil, No. 4, Fuel Oil, No. 6, Fuel Oil, Residual. Ottawa, Ontario: Health Canada

21. Garaniya, V. et al (2011) Chemical characterization of heavy fuel oil for combustion modeling. Geneva, Switzerland

22. GESTIS (2014a) GESTIS DNEL Database. Sankt Augustin, Germany :Institute for Occupational Safety and Health of the German Social Accident Insurance http://www.dguv.de/ifa/Gefahrstoffdatenbanken/GESTIS-DNEL-Datenbank/index.jsp

23. GESTIS (2014b) GESTIS International Limit Values for Chemical Agents. Sankt Augustin, Germany :Institute for Occupational Safety and Health of the German Social Accident Insurance
http://limitvalue.ifa.dguv.de/Webform_gw.aspx

24. Grimmer, G. et al (1997) Atmospheric emission of polycyclic aromatic hydrocarbons in sampling areas of the German environmental specimen bank. Method for the precise measurement of gaseous and particle-associated polycyclic aromatic hydrocarbons in the sub-nanogram range using deuterated internal standards. *Chemosphere 34, 2213-2226*

25. Health Council of The Netherlands (2012). Naphthalene - Evaluation of the carcinogenicity and genotoxicity. Report 2012/30, The Hague, December 7, 2012

26. IARC (2014) Agents Classified by the IARC Monographs, Volumes 1-109. Lyon: International Agency for Research on Cancer.
http://monographs.iarc.fr/ENG/Classification/ClassificationsGroupOrder.pdf

27. IFA (1997) Measurement of Hazardous Substances - BGIA Arbeitsmappe [BGIA Working Folde], Method 6305: Determination of Exposure to Chemical and Biological Agents. Bielefeld, Germany: Institut fur Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung

28. Kim, E. et al (2011) Compositional characterization of petroleum heavy oils generated from vacuum distillation and catalytic cracking by positive-mode APPI FT-ICR mass spectrometry. *Mass Spectometry Letters 2, 41-44*

29. Kriech, A. J. et al (2002) Evaluation of worker exposure to asphalt paving fumes using traditional and nontraditional techniques. *Aiha Journal 63, 628-635*

30. Kriech, A. J. et al (2007) Generation of bitumen fumes using two fume generation protocols and comparison to worker industrial hygiene exposures. *Journal of Occupational and Environmental Hygiene 4, 6-19*

31. McKee, R. et al (2014) The toxicological effects of heavy fuel oil category substances. *International Journal of Toxicology 33, 95S-109S*

32. McKee, R. et al (2013) Genetic toxicity of high-boiling petroleum substances. *Regulatory Toxicology and Pharmacology 67, S75-S85*

33. Osborn, L. V. et al (2001) Luminescence spectroscopy as a screening tool for the potential carcinogenicity of asphalt fumes. J*ournal of Environmental Monitoring 3, 185-190*

34. Pohlmann, G. et al (2001) Collection of condensate from bitumen vapor for production of atmospheres in inhalation experiments with animals. Gefahrstoffe Reinhaltung der Luft 61:507-509

35. USEPA (2008) AP-42, Fifth Edition. Compilation of Air Pollution Emission Factors, Volume I, Stationary Point and Area Sources. Chapter 5: Petroleum Industry. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC

APPENDIX 1

Final Report

HFO fume collection and analysis

Fraunhofer ITEM
Hannover, Germany

Fraunhofer
ITEM

Final Report – Revised Version

HFO fume collection and analysis

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This report consists of 31 pages.

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Table of content

1 Introduction 3
1.1 General 3
1.2 Relevant chemical parameters 3
1.3 Tasks of Fraunhofer ITEM 4
2 Material and Methods 4
2.1 Apparatus for fume generation and collection 4
2.2 Workplace sampling 7
2.3 Chemical analysis 8
2.3.1 Boling point distribution 8
2.3.2 Fluorescence 9
2.3.3 Total hydrocarbons 9
2.3.4 (Polycyclic) Aromatic Hydrocarbon ((P)AHs) 10
3 Results 12
3.1 Pre-test for the development of the fume collection method 12
3.2 Sampling events 14
3.2.1 Overview 14
3.2.2 Comparison of workplace, fume condensate and bulk samples 15
3.2.3 Workplace concentrations 26
4 References 30

1 Introduction

1.1 General

Changes to the hazard classification of heavy fuel oils (HFO) resulted in increased ADN requirements for the transport of these substances on European inland waters. In order to improve the knowledge on possible health risks associated with HFO vapor inhalation Concawe has initiated an assessment on HFO emissions during barge loading. Emissions are likely to occur since the products are kept at elevated temperatures between 70°C and 80°C during the entire transportation chain.

The study comprises

- Determination (mass flux and chemical composition) of vapor and aerosol emissions from the vent of the barge during loading
- Assessment of typical exposure of workers during barge loading
- Collection of a sufficient quantity of representative fume condensates generated from the bulk HFO materials in a laboratory set-up under controlled conditions

1.2 Relevant chemical parameters

The following parameters were considered to be relevant for the characterization of workplace atmospheres and the fume collected from HFO samples in the laboratory fume generation apparatus:

1. Boiling point distribution: This parameter provides an overview over the boiling range of the collected material and serves as a parameter to be matched approximately when comparing fumes sampled at the vent of the barge tanks and fumes generated in the laboratory from the same HFO bulk material.

2. Fluorescence at 415 nm: This quantity is an integral chemical indicator for polycyclic aromatic hydrocarbons which are expected to determine the mutagenicity of the material (Kriech et al., 2002, Clar et. Al 2011).

3. Aromatic Hydrocarbons (AHs): Naphtalene and benzo(a)pyrene (+pyrene) as representatives for low and high boiling AHs. In addition, the content of Grimmer-PAHs is measured in HFO bulk samples and condensates.
4. Total hydrocarbons: air samples are analysed for the total hydrocarbon concentration for exposure assessment.

1.3 Tasks of Fraunhofer ITEM

The following tasks had to be carried out by Fraunhofer ITEM

- Participation in exposure assessment: providing filter-XAD sampling trains, performing chemical analysis of loaded sampling cassettes and of HFO bulk samples

- Setting up a laboratory system to simulate vapor emission from the surface of heated HFO in bunkers during filling and transportation as well as to collect the vapor by condensation.

- Generation and collection of fume condensate from the HFO bulk materials comprising those materials investigated in the workplace exposure study

- Chemical characterization of the bulk materials and the fume condensates

2 Material and Methods

2.1 Apparatus for fume generation and collection

A laboratory scale apparatus for collection of millilitre quantities of fume condensates was developed. The system should be able to simulate the conditions of HFO transportation and loading. Fumes had to be generated by evaporation only, splashing and droplet formation from the bulk material had to be avoided. The process temperature was set to 90°C in

order to account for the maximum temperature occurring during the transportation chain of HFO products.

The fume collection scheme is shown in Fig. 2.1. It consists of a laboratory oven heated to 90°C, a peristaltic pump, an evaporation compartment and a Peltier cooler.

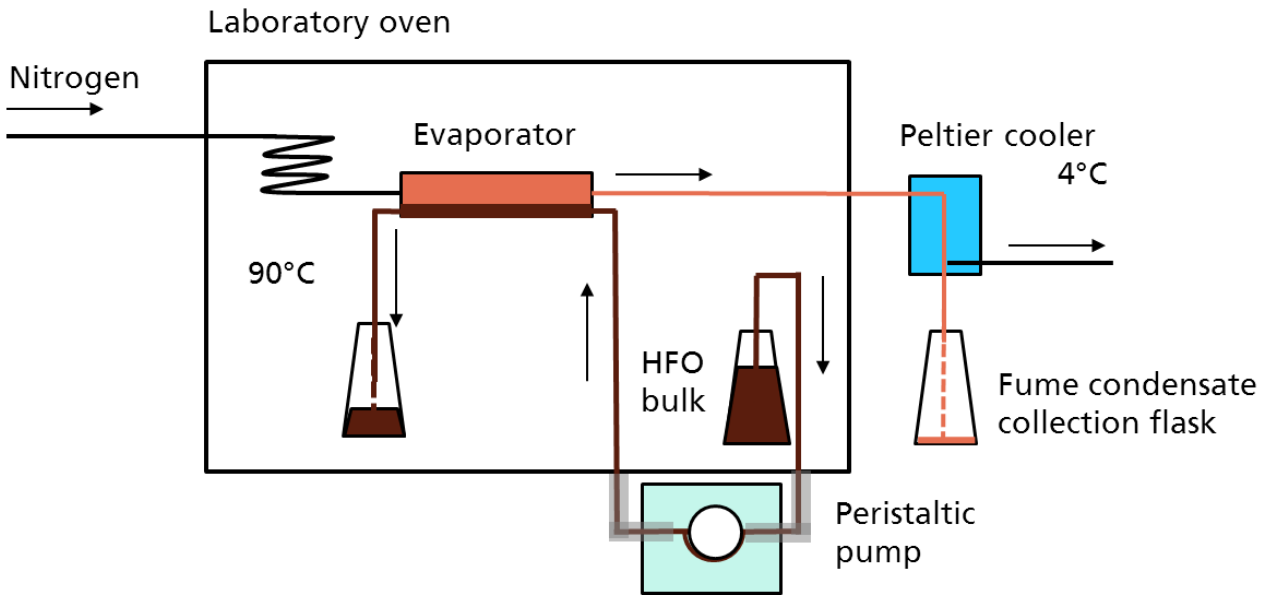

Fig. 2.1: Schematics of the laboratory set-up for fume collection.

A quantity of 1 l of HFO bulk material is heated up to 90° inside the oven. The fuel oil is fed continuously through the evaporator at a flow rate of 300 ml/h using a peristaltic pump and then dumped into a flask. A pre-heated nitrogen stream of 1 L/min is fed over the flat oil layer covering the bottom of the evaporator (layer thickness 3 cm). The vapor containing nitrogen flux is subsequently cooled in a Peltier cooler from 90°C to 4 °C. This causes the vapor compounds to condense and drip into the collection flask.

The evaporator consists of two flat containers with an area of 6x16 cm² and a height of 5 cm which are placed in series. A flow velocity of the nitrogen of 1.4 cm/s is calculated from the height of the gas space above the layer (2 cm) and the gas flow rate of 1 L/min.

The liquid bulk turnover established by the peristaltic pump is 0.3 L/h which corresponds to a mean residence time of approximately 1 h of the bulk material in each of the evaporation containers holding a liquid volume 0.29 L HFO.

The order of magnitude of the evaporation flux density, J_{evap}, [mol/(m²s)] of compounds from the bulk can be estimated by using an empirical evaporation model developed for industrial hygiene purpose for evaporation of substances at temperature, T, from flat surfaces of length L [m] (Gmehlig et al., 1989).

$$J_{evap} = 1.1 \cdot 10^{-2} D^{0.19} \nu^{-0.15} V^{0.96} L^{-0.04} \frac{p_s}{RT}. \qquad \text{Eq. 1}$$

Here, p_s [Pa] and D [m²/s] are the vapor pressure and air diffusivity of the substance; ν [m²/s] and V [m/s] are the viscosity and the velocity of the gas flowing above the surface. It is seen that evaporation is primarily controlled by the vapor pressure of the substances. For multicomponent systems the relative evaporation rates should correspond to the vapor pressure distribution of the compounds which also determines the relative concentrations of the vapor mixture developing above the fuel layer in a real storage tank of the barge.

Prior to the design of the condensate sampling unit two HFO samples (PA and PB that were provided by Concawe) were investigated for their boiling point distributions. The results show that approximately 5 % of the bulk liquid are compounds with boiling point around 200°C. These compounds should dominate the fume mass concentration in the headspace of the storage tanks at 90°C as well as in the laboratory scale evaporation apparatus.

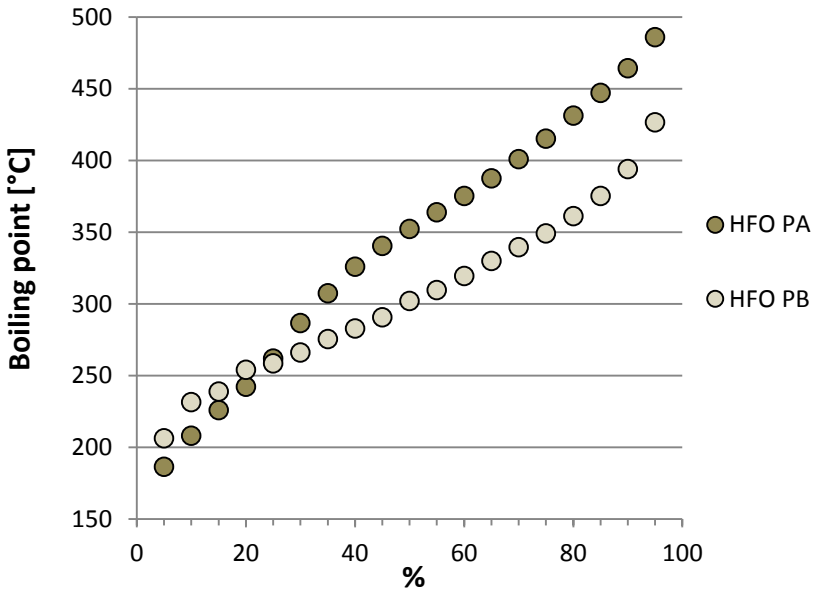

Fig. 2.2: Boiling point distribution of 2 HFO bulk samples (HFO PA and HFO PB)

If dodecane with a boiling point of 208°C is considered as representative for the low boiling fraction of the bulk HFO, Eq. 1 gives an evaporation flux density of $6 \cdot 10^{-5}$ mol/(m²·s) for a surface temperature of 90°C. With the dimensions of the evaporation containers this results in a fume collection rate of 0.9 mL/h. The volumetric turnover rate of the 5% mass fraction of the light boiling compound is 300*0.05 ml/h = 15 mL/h. Thus the light boiling compounds are depleted by 6.7% during the time while the bulk material is in the evaporator.

2.2 Workplace sampling

Workplace samples are collected by employees of the refinery during barge loading of HFOs (UN number 3082). The samples were taken with the German sampler BIA (PGP-System, GGP, closed-face sampler) containing a filter (sampling of aerosol, non- and semivolatile compounds) and an adsorbent cartridge (sampling of vapor phase, semivolatile and volatile compounds). Two static samples (close to vent and background) and two personal samples (operator: offshore, ship, tanker and operator: onshore, loading bridge, oil movement, see tables) are taken during each barge loading process.

Two sampling units always operated in parallel since different filters and XAD grades have to be used for THC and (P)AH collection. For THC determination a 37 mm glass fiber filter (1 µm, binderless) and an adsorbent cartridge with 3 g XAD-2 resign (size 0.5-0.9 mm) is used. For PAH and boiling range distribution a PTFE filter (2 µm) and an adsorbent cartridge with 3 g XAD-2 resign (size 0.25-0.84 mm) is used.

Air sampling explosion proof pumps are used operating at a sampling flow rate of 2 L/min.

The workplace samples are carried out by the industrial hygienist of the sampling site. All sampling units are preloaded with filters and adsorbant, sealed and then shipped to the sampling site.

2.3 Chemical analysis

2.3.1 Boling point distribution

The method is used for analysis of workplaces samples (aerosol and vapor phase), bulk HFOs and HFO condensates.

The boiling point distribution is determined by a method, based on the ASTM standard method D2887-97. The boiling point distribution determined by distillation is simulated by the use of gas chromatography (GC) with flame ionization detector (FID). A non-polar or weakly polar capillary GC column is used to separate the hydrocarbon compounds of the sample extract. The column temperature is raised at a linear rate and the area under the chromatogram is integrated after the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analysis of a known mixture of n-alkanes covering the boiling range expected in the sample. From these data, the boiling range distribution can be calculated.

For analysis of workplace samples, defined aliquots of the dichloromethane extracts from filter and XAD samples (see section AH) are combined, reduced in volume and analyzed with GC-FID using a DB5MS column. The calibration of the boiling points is carried out with an ASTM alkane mixture.

For analysis of bulk products and condensates an aliquot is dissolved in dichloromethane and analysed.

The following instrumental conditions were used:

GC :	HP 5890 Series II Plus
Autosampler:	HP 6890
Injector:	split/splittles (2 µl injection volume)
Carrier gas:	Helium, constant flow (3 ml)
Column:	DB5MS (J&W), 30 m, 0.32 mm i.d., df=0.25 µm
Temperature:	Initial temperature 40 °C, (3 min), 9 °C/min to 120 °C (0.5 min), 11 °C/min to 320 °C, (9.5 min)
Detektor:	FID, 330 °C

2.3.2 Fluorescence

The method (Kriech et al., 2002) is used for characterization of bulk products and condensates. Determination of the UV fluorescence intensity is carried out using diphenylanthracene (DPA) as reference. A known amount of the sample is dissolved in cyclohexane. The fluorescence intensity is measured with a 1 cm cuvette using a Shimadzu spectrofluorometer RF-1501. The excitation wavelength is 385 nm and the emission wavelength 415 nm. Data are given as DPA equivalents in mg/kg (bulk product) and mg/L (condensate).

2.3.3 Total hydrocarbons

This method is used for characterization of workplaces samples (aerosol and vapor phase) and for fuel condensates (BIA response factor determination).

The method is based on an IR determination of aliphatic CH-groups and does not allow a differentiation according to compound classes. Total hydrocarbons are determined by IR analysis measuring the integral absorption of the CH vibrations between 2800-3000 cm^{-1}.

The material collected on filter and on XAD tube is analyzed separately. The samples are extracted with tetrachloroethene and measured using a Fourier-Transform-Infrared Spectrometer Vector 22 (Bruker). Data are calculated relative to a standard reference mineral oil (Aldrich No. 16.140-3). Results are given as mineral equivalents in mg/m³.

Since the composition of the standard reference mineral oil used for calibration differs from the workplace HFOs, the so-called BIA response factor is determined. That means the response of each HFO condensate is compared with the mineral oil standard response.

2.3.4 (Polycyclic) Aromatic Hydrocarbon ((P)AHs)

The method is used for analysis of workplaces samples (aerosol and vapor phase), bulk HFOs and HFO condensates. For the characterization of workplace samples, selected AHs (naphthalene, pyrene, benzo(a)pyrene) were analyzed. For bulk products and condensates, PAHs according to the Grimmer list (Grimmer et al., 1997) and naphthalene were analyzed.

Workplace samples: For analysis of selected AHs, the filter and XAD samples are extracted with dichloromethane. The XAD samples are extracted with 20 ml dichloromethane using an ultrasonic bath. The filter samples are extracted with 200 ml dichloromethane using a reflux condenser. A small aliquot part is used for the determination of the boiling point distribution (see above). The residual solution is analyzed for the AHs after addition of the deuterated AH standards and volume reduction. The analytes are measured by gas chromatography with mass selective detector in SIM mode. The following ions (m/z values) are used for data acquisition and quantification: naphthalene (m/z 128) naphthalene-d_8 (m/z 136), pyrene (m/z 202), pyrene-d_{10} (m/z 212), benzo(a)pyrene (m/z 252), benzo(a)pyrene-d_{12} (m/z 264). The AHs are quantified by the method of internal standardization. Data are given in µg/m³.

Bulk products and condensates: For analysis of Grimmer PAHs and naphthalene in condensate and bulk samples a defined amount of the sample (about 20 mg) is taken (the bulk sample is diluted in 10 ml toluene and 1 ml is used for analysis). The sample is spiked with a solution of deuterated reference compounds.

For silica gel chromatography, silica gel 60 (Merck), 0.063-0.200 mm particle size is conditioned using 12.5 % w/w water. About 40 g silica gel are suspended in cyclohexane and filled into a 25x400 mm glass column. The sample is applied in a small volume of solvent to the silica gel column and eluted with 320 ml of cyclohexane. Two fractions (70 and 250 ml) are collected. The first fraction is rejected. The second fraction is evaporated to about 10 ml. Thereafter, 2-propanol (2-3-ml) is added and the solution reduced in volume to about 1 ml using a TurboVap concentration workstation. The sample is concentrated to about 0.1 ml for the determination of low PAH concentrations and diluted for the determination of naphthalene.
The AHs are measured by gas chromatography with mass selective detector (GC/MS) in SIM mode. The AHs were quantified by the method of internal standardization using the following instrumental conditions:

GC :	Agilent Technologies 6890N
Autosampler:	Agilent Technologies 7683 B
Injector:	split/splittles (1 µl injection volume)
Carrier gas:	Helium, constant flow (1.4 ml)
Column:	DB35MS (J&W), 60 m, 0.25 mm i.d., df=0.25 µm
Temperature:	Initial temperature 75 °C, (0 min), 15 °C/min to 200 °C,
(condensate and bulk)	5 °C/min to 280 °C, 10 °C/min to 300 °C, 10 °C/min to 340 °C
Temperature:	Initial temperature 75 °C, (1.5 min), 15 °C/min to 200 °C,
(workplace samples)	5 °C/min to 280 °C, 10 °C/min to 300 °C (30 min)

Mass spectrometer:	MSD 5975
Ionization:	Electron impact, EI (70 eV)
Source:	230 °C
Transfer line:	280 °C
Quadrupole:	150 °C
Data acquisition:	SIM with 1 mass per component

The analysis included 21 PAHs defined in Grimmer method, and in addition naphthalene. Results are given in µg/g.

As reference standards for calibration the following compounds and [m/z] values of the ions are used for acquisition and quantification:
Naphthalene [128], phenanthrene [178], anthracene [178], fluoranthene [202], pyrene [202], benzo(b)naphtho[2,1-d]thiophene [234], benzo(c)phenanthrene [228], benzo(ghi)-fluoranthene [226], benz(a)anthracene [228], cyclopenta(cd)pyrene [226], triphenylene [228], chrysene [228], benzo(b)fluoranthene [252], benzo(k)fluoranthene [252], benzo(j)fluoranthene [252], benzo(e)pyrene [252], benzo(a)pyrene [252], dibenz(a,h)anthracene [278], coronene [300], indeno(1,2,3-cd)pyrene [276], anthanthrene [276], benzo(ghi)perylene [276].

As internal standards the following compounds and m/z values of the ions are used for acquisition and quantification:
Naphthalene-d_8 [136], phenanthrene-d_{10} [188], anthracene-d_{10} [188], fluoranthene-d_{10} [212], pyrene-d_{10} [212], benz(a)anthracene-d_{12} [240], chrysene-d_{12} [240], benzo(b)fluoranthene-d_{12} [264], benzo(a)pyrene-d_{12} [264], dibenz(a,h)anthracene-d_{14} [292], indeno(1,2,3-cd)pyrene-d_{12} [288], benzo(ghi)perylene-d_{12}[288].

The standards and internal standards were obtained from Dr. Ehrenstorfer, LGC Standards GmbH.

3 Results

3.1 Pre-test for the development of the fume collection method

The fume condensation apparatus was tested using the HFO test sample PA which was delivered by Concawe prior to the field study. One liter of HFO PA was processed in the fume collection apparatus resulting in approximately 3 mL of condensate. The collection was repeated two times. Each collection procedure lasted for about 3 hours resulting in a collection rate of approximately 1 mL/h which is in good agreement with the estimated value.

The boiling point distributions were determined for each sample separately. The results presented in Tab. 3.1 and Fig. 3.1 show a significant shift of the boiling range of the fume

condensate towards lower temperatures when compared with the boiling point distribution of the corresponding HFO bulk material.

The DPA equivalent concentration as determined by fluorescence is a factor of 1600 lower for the fume condensate than for the bulk material (see Tab. 3.2).

Tab. 3.1: Boiling point distribution of HFO PA bulk and lab-generated fumes

Percentage of total mass	Temperature			
	Bulk	Fume 90°C		
		Sample1	Sample 2	Sample 3
5	186.4	158.66	150.82	149.69
10	208	167.47	163.76	160.44
15	225.9	173.15	168.17	166.81
20	242.1	174.81	173.23	172.76
25	261.8	181.05	174.81	174.39
30	286.5	185.28	180.43	178.45
35	307.4	188.56	184.78	181.86
40	325.9	192.67	188.33	185.56
45	340.4	196.05	192.59	189.15
50	352.2	200.70	196.01	192.75
55	363.8	205.63	200.98	196.08
60	375.2	207.79	205.75	201.81
65	387.5	213.34	208.75	205.95
70	400.9	213.90	213.50	209.11
75	415.2	215.97	214.14	213.58
80	431.2	226.69	221.75	215.60
85	447	236.16	232.26	226.61
90	464.3	242.21	239.16	236.24
95	485.9	258.92	256.51	252.02

Tab. 3.2: DPA equivalent concentration in mg/L measured using fluorescence

Bulk	Fume 90°C		
	Sample1	Sample 2	Sample 3
24200	7.00	24.90	11.70
		14.5 ± 9.3	

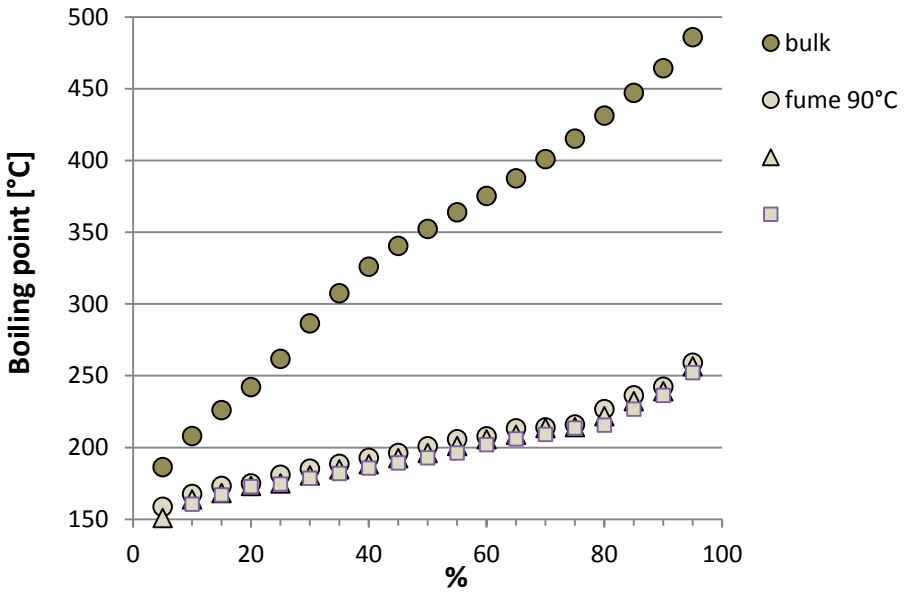

Fig. 3.1: Boiling point distributions of the HFO bulk sample and three samples of the lab-generated fume condensate.

3.2 Sampling events

3.2.1 Overview

Five samplings were carried out. The dates of the sampling actions are listed in Tab. 3.3. Each sampling event is anonymized by a color code.

During the campaigns various personal and area air samples were taken during the loading process of a barge. The personal samples were taken for the load operator working off-shore on the barge. The position of the area samplers was close to vents/manholes of the tank. In addition a second personal sample was taken at an individual working on-shore and a second area sample away from the ship and the local sources for background monitoring. The field measurements were aimed at comparing the properties of the fumes emitted from the tank with the properties of the fumes collected in the laboratory. For this purpose 20 l bulk sample was taken from the loading and shipped to Fraunhofer for fume generation and collection. In addition, information on the exposure level during loading operation had to be gathered.

A sampling protocol was developed prior to carrying out the sampling. At each location at least two personal samplings and two area sampling were mandatory. Two sampling units

were used at each measuring point because different filters and XAD fillings had to be used separately for the AHs and boiling point distribution and the hydrocarbons (total HC).

Tab. 3.3: History and labeling of the field campaigns

Code	Loading temperature °C
Red	78
Blue	72
Yellow	79
Pink	81
Green	81

3.2.2 Comparison of workplace, fume condensate and bulk samples

3.2.2.1 Boiling point distributions

It was decided by the project steering committee to set the evaporation temperature in the laboratory fume generator to 90°C in order to cover all possible loading temperatures during the barge loading process. In reality, the loading temperatures were significantly lower than 90°C as shown in Tab. 3.3. Samples (20 L) were taken from the bulk material during loading and were transferred to Fraunhofer ITEM. These samples were processed in the laboratory fume generator. At the beginning one to two liters of bulk material was pumped through the system without fume sampling. Fume collection was initiated thereafter. Several liters were processed to obtain the quantities of condensates as listed in Tab. 3.4. The table also shows the strong influence of the boiling range of the fuel oil on fume generation. There is a big difference in the T50 values of the boiling point distributions for the bulk HFO material and the fumes generated at 90°C.

Tab. 3.4: Fume condensate and 50%-temperature of the boiling point distribution of the bulk material and the condensate

Code	Quantity of fuel processed [l]	Quantity of fume sampled [ml]	T^{50} bulk [°C]	T^{50} condensate [°C]
Red	5	20	344.6	213.2
Blue	4	35	302.0	211.2
Yellow	6	4	402.1	228.9
Pink	5	20	337.0	212.9
Green	5	20	309.7	213.9

The entire boiling curves of the fuel oils and their corresponding fumes collected in the laboratory at 90°C are shown in Fig. 3.2 and Fig. 3.3. The maximum boiling temperature of the fuels is 480 °C, for the fumes it is 302 °C for the yellow brand, for all others approximately 275 °C. The yellow sample's boiling point distribution differs significantly form the other. Here, the fume collection efficiency is lowest.

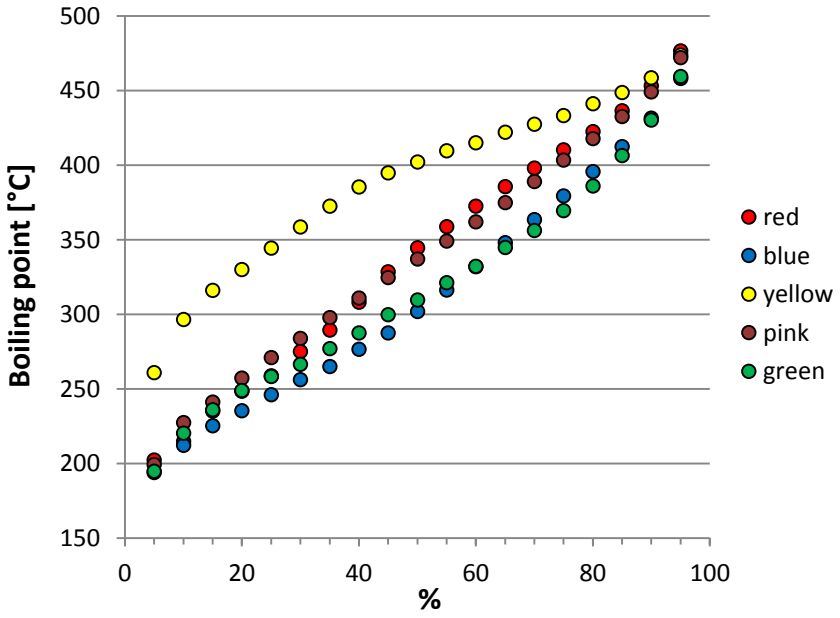

Fig. 3.2: Boiling point distributions of the bulk materials.

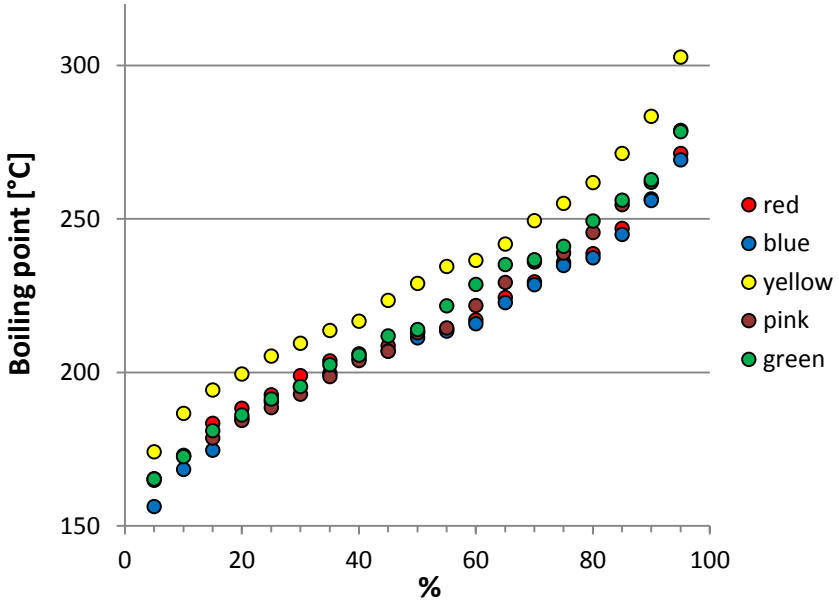

Fig. 3.3: Boiling point distributions of the laboratory generated fumes.

The boiling point distribution of workplace samples, vent samples and fuel condensates are compared in Fig. 3.4- Fig. 3.8. In some cases filter/XAD samples from the field campaigns could not be evaluated for the boiling point distribution because of a very low loading. The general atmospheric background as well as the solvent blank were subtracted from the chromatograms obtained for the workplace samples prior to calculation of the boiling point distribution. Vent and workplace sample compare well. Except for the first sample, the boiling point distributions of the laboratory generated fume condensates are slightly above the vent samples because the laboratory evaporator was operated at 90°C whereas the loading temperatures of the fuels were between 72 and 81 °C. It can probably be assumed that the fuel surface layer in the tank is even at slightly lower temperatures compared to the loading temperature measured in the supply line.

The T^{90}-values of the boiling point distributions are compared in Tab. 3.5. There are differences between the workplace and vent samples in the upper 10%-range of the boiling point distribution. The increased values for the workplace samples stem from an unidentified background which is independent from the overall filter loading determined by the amount of sampled fuel emissions. This can be seen from the raw chromatograms (Fig. 3.9) of a vent sample and the corresponding workplace sample both showing a bimodal structure. The peaks at the high boiling end for both samples are of equal magnitude

whereas the low boiling end of the vent sample is a factor of 10 different due to a much higher mass loading of fuel emission. The origin of the high boiling peaks in the samples could not be identified. It is however quite certain that they are not related to the HFO emissions.

Therefore, it can be assumed that the fuel condensates sampled in the laboratory at 90°C cover the boiling range of emissions occurring at ship loading at all conditions prevailing in reality.

Tab. 3.5: T^{90} –values of the boiling point distributions [°C]

Code	Bulk	Condensate	Vent	Offshore worker
Red	453	257	-	324
Blue	432	260	230	261
Yellow	459	283	229	-
Pink	449	262	213	226
Green	430	262	213	254

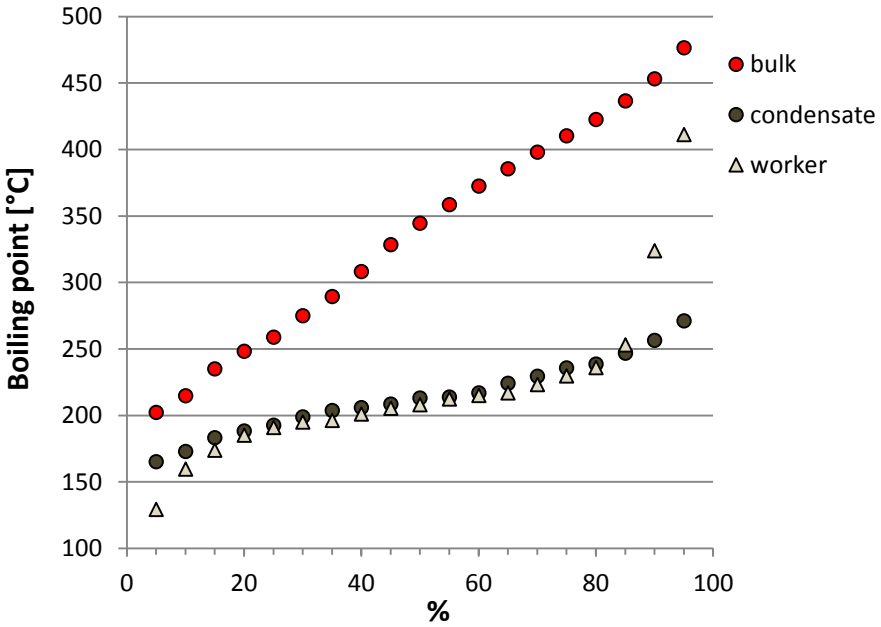

Fig. 3.4: Boiling point distributions of the bulk fuel, the condensate and the field samples (red).

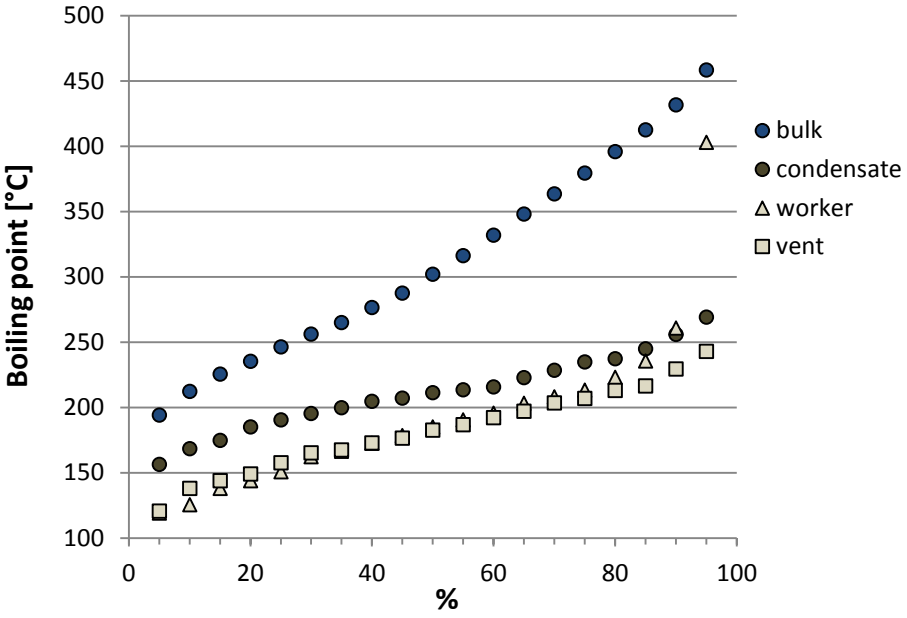

Fig. 3.5: Boiling point distributions of the bulk fuel, the condensate and the field samples (blue).

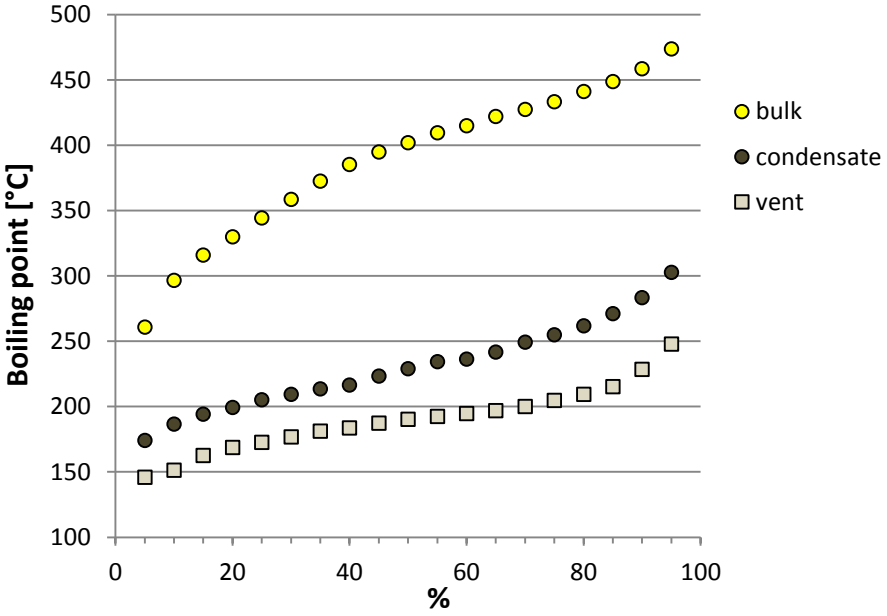

Fig. 3.6: Boiling point distributions of the bulk fuel, the condensate and the field samples (yellow).

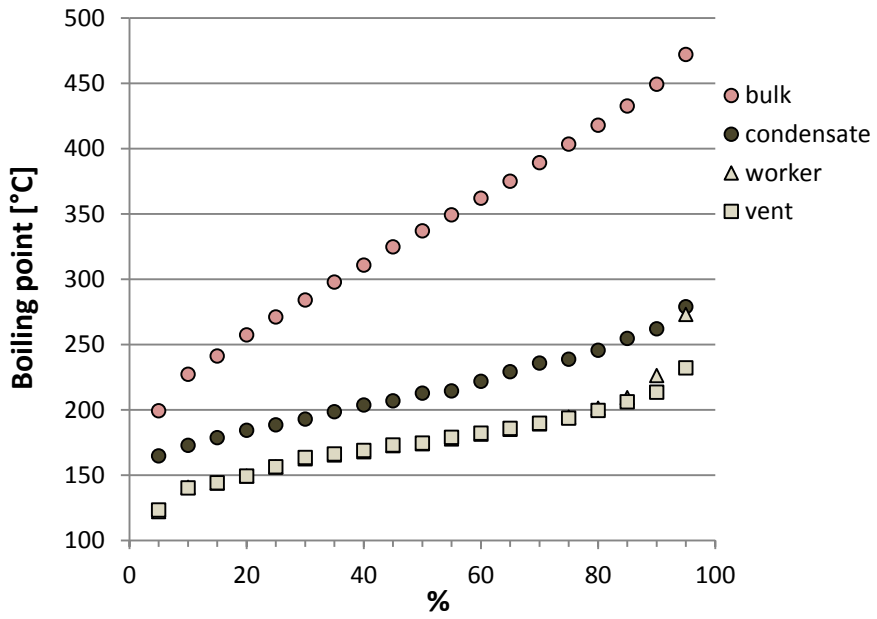

Fig. 3.7: Boiling point distributions of the bulk fuel, the condensate and the field samples (pink).

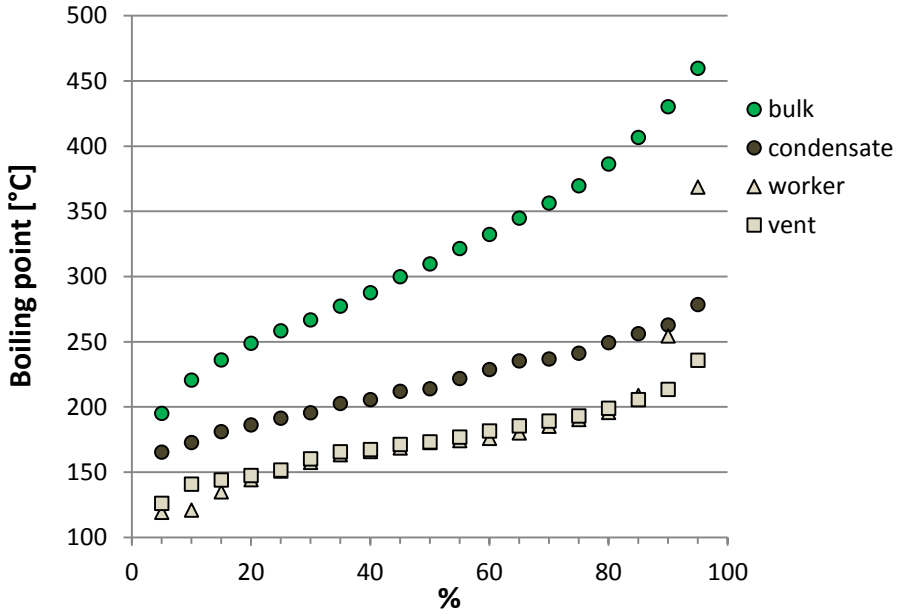

Fig. 3.8: Boiling point distributions of the bulk fuel, the condensate and the field samples (green).

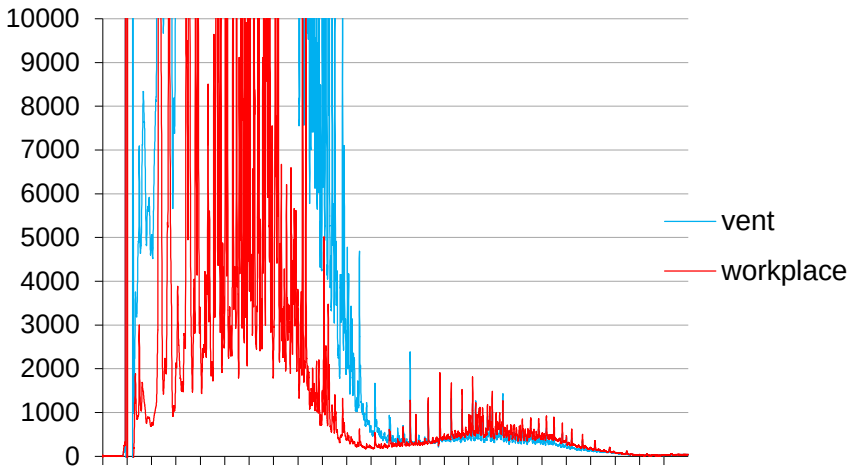

Fig. 3.9: Raw chromatograms of the vent and the workplace sample for the HFO "blue". The vent peaks reach up to 150000.

3.2.2.2 Fluorescence

Fluorescence measurements were carried out for the bulk samples of the HFOs and the corresponding fumes. As shown in

Tab. 3.6 the fluorescence intensity in the laboratory fumes generated from the bulk material is by orders of magnitude lower than the fluorescence of the bulk materials themselves. Field samples were not analyzed for the integrated fluorescence since this would have required an additional sampling train. Clar et al. (2011) point out the correlation between mutagenicity of the sample and the fluorescence intensity. They analyzed condensates of bitumen fumes and obtained values of 30 and 157 mg/kg for condensates collected from the head space in storage tanks of paving and roofing asphalt. The fluorescence intensities of the HFO fume condensates generated in this study are significantly lower than the lowest value of the bitumen fume.

Tab. 3.6: Fluorescence intensities of the bulk and condensate samples

Code	Bulk [mg/Kg DPA eq]	Condensate [mg/l DPA eq]	Reduction factor
Red	25900	7.70	3364
Blue	23700	4.74	5000
Yellow	23500	17.3	1358
Pink	24200	7.17	3375
Green	27400	7.53	3639

3.2.2.3 Aromatic hydrocarbons (AHs)

Results of PAH and naphthalene measurements are given in Tab. 3.7 and 3.8.

Tab. 3.7: PAH and naphthalene concentrations of the bulk samples

AH	Bulk product				
	Red	Blue	Yellow	Pink	Green
	µg/g	µg/g	µg/g	µg/g	µg/g
Naphthalene	2146	2466	149	1990	1422
Phenanthrene	669	781	252	710	898
Anthracene	83.5	97.3	23.5	83.5	102
Fluoranthene	44.8	45.8	14.3	24.9	24.5
Pyrene	343	348	61.9	209	194
Benzo(b)naphtho[2,1-d]thiophene	177	110	125	28.7	25.3
Benzo(c)phenanthrene	18.3	18.1	15.5	< 2.5	2.7
Benzo(g,h,i)fluoranthene	n.s.	n.s.	n.s.	< 2.5	< 2.5
Benz(a)anthracene	147	130	129	13.1	13.8
Cyclopenta(c,d)pyrene	7.6	7.6	6.0	2.9	2.6
Triphenylene	52.6	59.6	54.0	6.1	7.0
Chrysene	178	162	195	15.7	18.5
Benzo(b)fluoranthene	35.6	35.5	39.6	3.3	4.2
Benzo(k)fluoranthene	10.2	10.2	8.9	< 2.5	< 2.5
Benzo(j)fluoranthene	13.9	12.2	14.3	< 2.5	< 2.5
Benzo(e)pyrene	105	125	55.5	9.0	11.0
Benzo(a)pyrene	101	96.3	62.5	6.9	8.7
Dibenz(a,h)anthracene	9.6	10.9	9.8	< 2.5	< 2.5
Coronene	8.1	7.4	3.1	3.0	< 2.5
Indeno(1,2,3-cd)pyrene	9.1	10.8	6.9	< 2.5	< 2.5
Anthanthrene	25.8	24.7	13.0	2.5	3.1
Benzo(g,h,i)perylene	91.3	77.0	18.9	15.7	10.2

n.s. not specified, peak overlapping

Tab. 3.8: PAH and naphthalene concentrations of the condensate samples

AH	Condensate				
	Red	Blue	Yellow	Pink	Green
	µg/g	µg/g	µg/g	µg/g	µg/g
Naphthalene	36547	23781	9688	29095	20635
Phenanthrene	150	96.3	228	175	193
Anthracene	13.5	9.2	19.8	18.2	21.1
Fluoranthene	2.6	1.1	3.0	1.7	1.2
Pyrene	9.2	5.1	11.2	7.0	5.6
Benzo(b)naphtho[2,1-d]thiophene	0.68	0.41	2.8	0.44	0.32
Benzo(c)phenanthrene	< 0.18	< 0.18	< 0.18	< 0.18	< 0.18
Benzo(g,h,i)fluoranthene	< 0.18	< 0.18	< 0.18	< 0.18	< 0.18
Benz(a)anthracene	0.37	0.26	1.34	0.24	< 0.18
Cyclopenta(c,d)pyrene	< 0.18	< 0.18	< 0.18	< 0.18	< 0.18
Triphenylene	0.26	0.20	0.79	< 0.18	< 0.18
Chrysene	0.43	0.28	1.9	0.28	0.19
Benzo(b)fluoranthene	<0.18	<0.18	<0.18	<0.18	<0.18
Benzo(k)fluoranthene	<0.18	<0.18	<0.18	<0.18	<0.18
Benzo(j)fluoranthene	<0.18	<0.18	<0.18	<0.18	<0.18
Benzo(e)pyrene	<0.18	<0.18	<0.18	<0.18	<0.18
Benzo(a)pyrene	<0.18	<0.18	<0.18	<0.18	<0.18
Dibenz(a,h)anthracene	<1.0	< 1.0	< 1.0	< 1.0	< 1.0
Coronene	<1.0	< 1.0	< 1.0	< 1.0	< 1.0
Indeno(1,2,3-cd)pyrene	<1.0	< 1.0	< 1.0	< 1.0	< 1.0
Anthanthrene	<1.0	< 1.0	< 1.0	< 1.0	< 1.0
Benzo(g,h,i)perylene	<1.0	< 1.0	< 1.0	< 1.0	< 1.0

The fume to bulk ratio of the PAHs and naphthalene defined as the ratio of the mass fractions in the fume and the mass fraction in the bulk material is shown in Tab. 3.9 for the AHs which were above detection limit in the laboratory fume for all brands. According to

Eq. 1 this ratio should correlate linearly with the vapor pressure of the AH. The second column of Tab. 3.9 contains the vapor pressure of the AHs at 90°C. The values were taken from the literature (Table 6 of Pankow and Bidleman, 1992). The fume to bulk ratio covers orders of magnitude such as the vapor pressure of the AHs. The light boiling naphtalene is enriched in the fume condensate whereas the crysene is strongly depleted.

Tab. 3.9: Ratio of PAH and naphthalene mass concentrations in the laboratory generated fumes and the corresponding bulk material.

		Fume to bulk ratio of the AH mass fractions				
	P_{vap} [Torr]	Red	Blue	Yellow	Pink	Green
Naphthalene	11.900	17.033	9.644	64.995	14.622	14.515
Phenanthrene	0.132	0.224	0.123	0.904	0.246	0.215
Anthracene	0.129	0.162	0.095	0.844	0.218	0.206
Fluoranthene	0.025	0.058	0.024	0.208	0.070	0.047
Pyrene	0.018	0.027	0.015	0.181	0.033	0.029
Crysene	0.002	0.002	0.002	0.010	0.018	0.010

Fig. 3.10 the data are plotted as function of the vapor pressure. The power law fits carried out for the yellow, red and blue material suggest the linear relationship between vapor pressure and enrichement/depletion of AHs in the fume condensate. The yellow data are located significantly above the other data. This is due to the overall low fume generation rate of the yellow material compared to the other ones as shown in Tab. 3.4. If the data are multiplied by the fume fraction (amount of fume devided by amount of bulk material processed) generated from the different HFO bulks the data points nearly collapse onto a single curve (Fig. 3.11). This means that the transfer of AHs from the bulk to the fume is mainly controlled by the vapor pressure at the storage temperature.

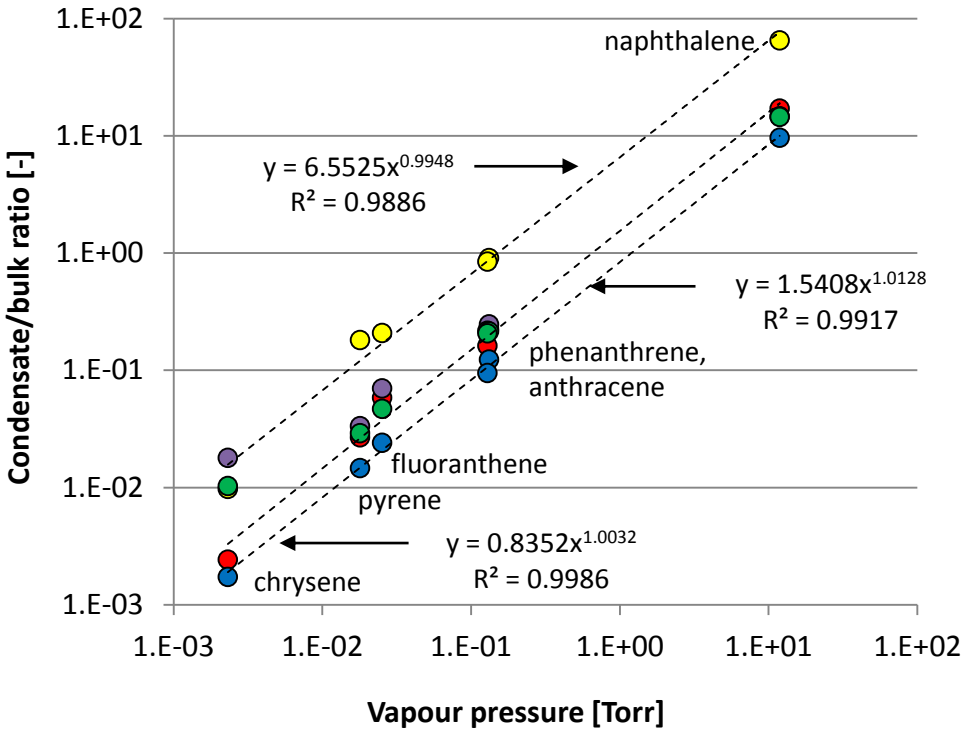

Fig. 3.10: Fume to bulk ratios of PAH and naphthalene mass fractions as function of the vapor pressure.

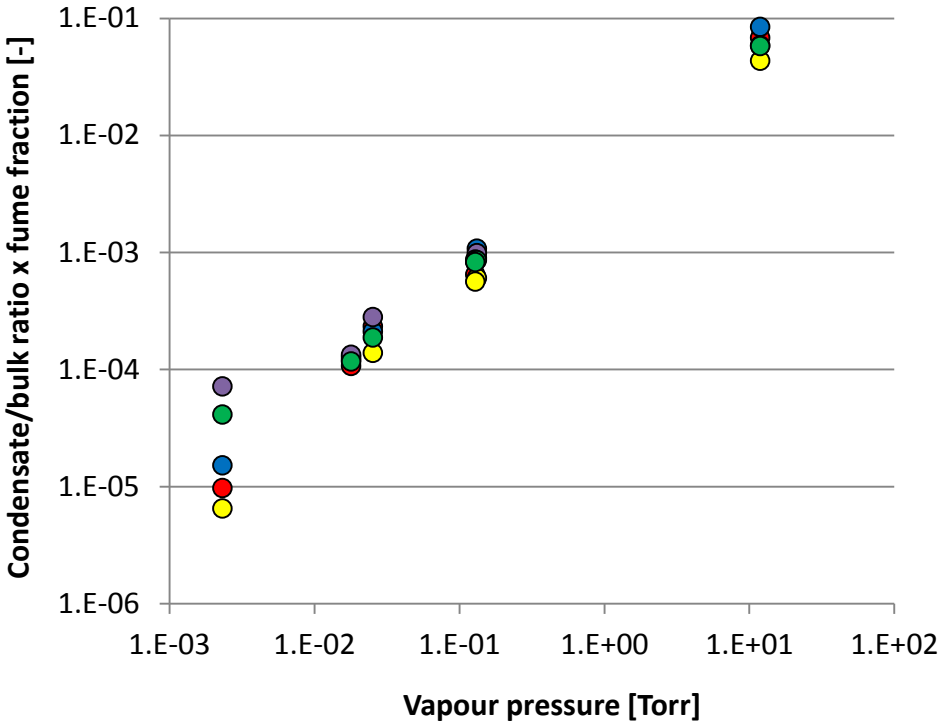

Fig. 3.11: Normalized fume to bulk ratios of PAH and naphthalene mass fractions.

3.2.3 Workplace concentrations

3.2.3.1 Total concentration determined by BIA method

The results are shown in Tab. 3.10 - Tab. 3.13. The concentrations for the aerosol phase (filter) and vapor phase (XAD) are given in mg total hydrocarbon (THC)/m³ mineral oil equivalent. When calibrating the IR extinction with the specific laboratory generated fume condensates instead of with the standard mineral oil equivalent used in the standardized method, a conversion factor is obtained. The values of the conversion factor based on the corresponding fume condensates were: 2.01; 1.83; 1.43; 1.88; 1.92 for the different HFO condensates (red, blue, yellow, pink, green). All data are corrected on field blanks.

In Tab. 3.10 the data of samples collected close to vent are given. The concentrations of total hydrocarbons varied between 0.3-79 mg/m³ for the vapor phase. For the aerosol phase the measured concentrations were < 0.04 mg/m³. The data of personal exposure samples for the ship operators (or offshore workers) are given in Tab. 3.11. The THC concentrations ranged from 0.5-16 mg/m³ (vapor phase) and from <0.005-0.02 mg/m³ (aerosol phase). The results for onshore operators (or loading bridge/oil movement) are shown in Tab. 3.12. In many cases the concentrations were below limit of detection (aerosol phase). For the vapor phase values between 0.03- 0.30 mg/m³ were measured. In summary: exposure is characterized primarily by vapor phase exposure. The personnel working on the barge experienced exposure concentrations that are an order of magnitude above the concentrations of the on-shore workers. Background did not significantly contribute to the overall exposure to hydrocarbon vapors generated from the fuel oil.

Tab. 3.10: Results of samples analyzed by BIA method: samples collected close to vent (static sampling)

Code	Sample volume [m³]	Aerosol (filter) [mg/m³]	Vapor (XAD) [mg/m³]
Red	0.832	<0.06	0.279
Blue	0.403	<0.124	78.811
Yellow	0.167	<0.299	30.712
Pink	0.969	<0.052	35.353
Green	1.131	<0.044	20.932

Tab. 3.11: Results of samples analyzed by BIA method: Workplace samples (operator: offshore, ship, tanker; personal sampling)

Code	Sample volume [m³]	Aerosol (filter) [mg/m³]	Vapor (XAD) [mg/m³]
Red	0.857	<0.058	0.841
Blue	0.407	<0.123	16.005
Yellow	0.164	<0.305	0.457
Pink	0.687	<0.073	10.186
Green	0.750	<0.067	3.159

Tab. 3.12: Results of samples analyzed by BIA method: Workplace samples (operator: onshore, loading bridge, oil movement; personal sampling)

Code	Sample volume [m³]	Aerosol (filter) [mg/m³]	Vapor (XAD) [mg/m³]
Red	1.003	<0.05	0.270
Blue	0.451	<0.111	0.239
Yellow	0.240	<0.208	0.154
Pink	0.176	<0.284	<0.284
Green	0.140	<0.357	<0.357

Tab. 3.13: Results of samples analyzed by BIA method: background sample

Code	Sample volume [m³]	Aerosol (filter) [mg/m³]	Vapor (XAD) [mg/m³]
Red	1.003	<0.05	<0.05
Blue	0.561	<0.089	<0.089
Yellow	0.403	<0.124	<0.124
Pink	0.886	<0.056	0.056
Green	2.049	<0.024	0.109

3.2.3.2 Aromatic hydrocarbons (naphthalene, pyrene, benzo(a)pyrene)

The AHs at the workplace and the vent are dominated by naphthalene as shown in Tab. 3.14 - Tab. 3.17. Data for the aerosol phase (filter) and vapor phase (XAD) are presented as concentrations in µg/m³. All data are corrected on field blanks. In Tab. 3.14 the data of samples collected close to vent are given. The concentrations of naphthalene in the vapor phase samples varied between 3-1489 µg/m³. Pyrene concentrations were < 0.04 µg/m³ and benzo(a)pyrene could not be detected in all samples. The data for the ship operator (or offshore operator) are given in Tab. 3.15. In most samples pyrene and benzo(a)pyrene could not be determined. The naphthalene concentrations in the vapor phase ranged from 3.7-199 µg/m³. For the loading bridge/onshore operators (see Tab. 3.16) the naphthalene concentrations were between 0.2-5.9 µg/m³.

Tab. 3.14: Concentrations of selected AH: samples collected close to vent (static sampling)

Code	Sample volume [m³]	Naphtalene Filter/XAD [µg/m³]*	Pyrene Filter/XAD [µg/m³]*	Benzo (a) pyrene Filter/XAD [µg/m³]*
Red	0.660⁺⁺	<0.015/3.4	<0.015/<0.015	<0.015/<0.015
Blue	0.413	0.04 /1489	<0.02/0.02	<0.02/**
Yellow	0.168	<0.06 /299.1	<0.06/<0.06	<0.06/<0.06
Pink	0.969	0.04 /684.0	<0.01 /0.04	<0.01 /<0.01
Green	1.123	0.35 /260.3	<0.009/<0.009	<0.009/<0.009

*reported values are corrected by field blanks. Field blank values ≤0.01 µg were taken into account with 0.01 µg absolut for naphthalene and pyrene.
⁺⁺ sample unit fixed from sampling operator, n.d. not detectable, (values < 0 after blank correction)

Tab. 3.15: Concentrations of selected AH: Workplace samples (operator: offshore, ship, tanker; personal sampling)

Code	Sample volume [m³]	Naphtalene Filter/XAD [µg/m³]*	Pyrene Filter/XAD [µg/m³]*	Benzo (a) pyrene Filter/XAD [µg/m³]*
Red	0.810	<0.009/20.6	<0.009/<0.009	<0.009/<0.009
Blue	0.473	<0.01/199.3	<0.01/0.05	<0.01/<0.01
Yellow	0.164	<0.061/3.7	<0.061/<0.061	<0.061/<0.061
Pink	0.684	0.004 /90.3	<0.015/0.06	<0.015/<0.015
Green	0.752	<0.013/12.0	<0.013/<0.013	<0.013/<0.013

*reported values are corrected by field blanks. Field blank values ≤0.01 µg were taken into account with 0.01 µg absolut for naphthalene and pyrene.

Tab. 3.16: Concentrations of selected AH: Workplace samples (operator: onshore, loading bridge, oil movement; personal sampling)

Code	Sample volume [m³]	Naphtalene Filter/XAD [µg/m³]*	Pyrene Filter/XAD [µg/m³]*	Benzo (a) pyrene Filter/XAD [µg/m³]*
Red	1.144	<0.009/5.9	<0.009/<0.009	<0.009/<0.009
Blue	0.451	<0.022/2.9	<0.022/<0.022	<0.022/<0.022
Yellow	0.243	<0.041/0.19	<0.041/<0.041	<0.041/<0.041
Pink	0.179	<0.056/0.69	<0.056/<0.056	<0.056/<0.056
Green	0.136	<0.074/1.2	<0.074/<0.074	<0.074/<0.074

*reported values are corrected by field blanks. Field blank values ≤0.01 µg were taken into account with 0.01 µg absolut for naphthalene and pyrene.

Tab. 3.17: Concentrations of selected AH: Background samples (static sampling)

Code	Sample volume [m³]	Naphtalene Filter/XAD [µg/m³]*	Pyrene Filter/XAD [µg/m³]*	Benzo (a) pyrene Filter/XAD [µg/m³]*
Red	1.177	<0.008/0.12	<0.008/<0.008	<0.008/<0.008
Blue	0.561	<0.018/2.3	<0.018/0.01	<0.018/<0.018
Yellow	0.403	<0.025/0.08	<0.025/<0.025	<0.025/<0.025
Pink	0.883	<0.011/0.15	<0.011/<0.011	<0.011/<0.011
Green	1.334	<0.007/0.95	<0.007/<0.007	<0.007/<0.007

*reported values are corrected by field blanks. Field blank values ≤0.01 µg were taken into account with 0.01 µg absolute for naphthalene and pyrene.

4 References

Gmehling, J., Weidlich, U., Lehmann, E. and Fröhlich, N. (1989): Verfahren zur Berechnung von Luftkonzentrationen bei Freisetzung von Stoffen aus flüssigen Produktgemischen. [A method for calculating airborne concentrations of substances when emitted from liquid product mixtures.] *Staub- Reinh*. Luft. 49, 227-230.

Clar, R.C., Burnett, M.D., Parker, C.M., Arp, E.W., Swanson, M.S., Minsavage, G.D., Kriech, J.A., Osborn, L.V., Freemann, J.J., Barter, R.A., Newton, P.E., Beazley, S.L., Stewart, C.W. (2011):Asphalt fume dermal carcinogenicity potential: I. dermal carcinogenicity evaluation of asphalt (bitumen) fume condensates. Regulatory Toxicology and Pharmacology 61, 9–16.

Grimmer, G., Jacob, J, Naujak, K.-W. (1997): Atmospheric emissions of polycyclic aromatic hydrocarbons in sampling areas of the German environmental specimen bank. Method for the precise measurement of gaseous and particle-associated polycyclic aromatic hydrocarbons in the sub nanogram range using deuterated internal standards. Chemosphere, 34: 2213-2226.

Kriech, A.J., Kureka, J.T., Wissel, H.L., Osborn, L.V., Blackburn, G.R. (2002): Evaluation of Worker Exposure to Asphalt Paving Fumes Using Traditional and Nontraditional Techniques, AIHA Journal 63:628–635

Pankow, J.F., Bidleman, T.F. (1992), Interdependence of the slopes and intercepts from log-log-correlations of measured gas-particle partitioning and vapor pressure: Theory and analylsis of available data. Atmospheric Environment Vol. 26A , No. 6, pp. 1071-1080,

APPENDIX 2

Final Report

Phase 2: HFO fume collection and analysis at 70, 80 and 90°C

Fraunhofer ITEM
Hannover, Germany

Fraunhofer
ITEM

Final Report

Phase 2: HFO fume collection and analysis at 70, 80 and 90°C

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This report consists of 19 pages.

March 3, 2015

Table of content

1 Introduction 3

2 Material and Methods 3

2.1 Bulk material 3

2.2 Apparatus for fume generation and collection 3

2.3 Workplace sampling 5

2.4 Chemical analysis 5

3 Results 5

3.1 Comparison of boiling point distributions 5

3.2 Fluorescence 10

3.3 Aromatic hydrocarbons （AHs） 11

1 Introduction

In the initial study "HFO fume collection and analysis" the evaporation temperature in the laboratory fume generator was set to 90 °C in order to cover all possible loading temperatures. The actual loading temperatures recorded in that study, however, were lower than 90 °C, ranging between 72 and 82 °C.

The present additional study addresses this variation by laboratory fume generation at three different temperatures, namely at 70, 80 and 90 °C. As in the previous study the bulk and resulting condensate samples were analysed regarding their boiling point distribution, fluorescence, total hydrocarbon content and aromatic hydrocarbon (AHs) content.

2 Material and Methods

2.1 Bulk material

Three different HFO bulk materials supplied by three different manufactures were subject of investigation in this study. The bulk materials were coded as CONCAWE-A, CONCAWE-B and CONCAWE-C.

2.2 Apparatus for fume generation and collection

A laboratory scale apparatus for collection of millilitre quantities of fume condensates had already been developed in the scope of the initial study "HFO fume collection and analysis". This system generates fumes by evaporation only, avoiding splashing and droplet formation from the bulk material. Fume generation was achieved at three different temperatures: 70; 80 and 90 °C respectively; accounting for possible temperature fluctuations during the transportation chain of HFP products.

The fume collection scheme is shown in **Fig. 2.1.** It consists of a laboratory oven heated to either 70; 80 or 90°C, a peristaltic pump, an evaporation compartment and a Peltier cooler.

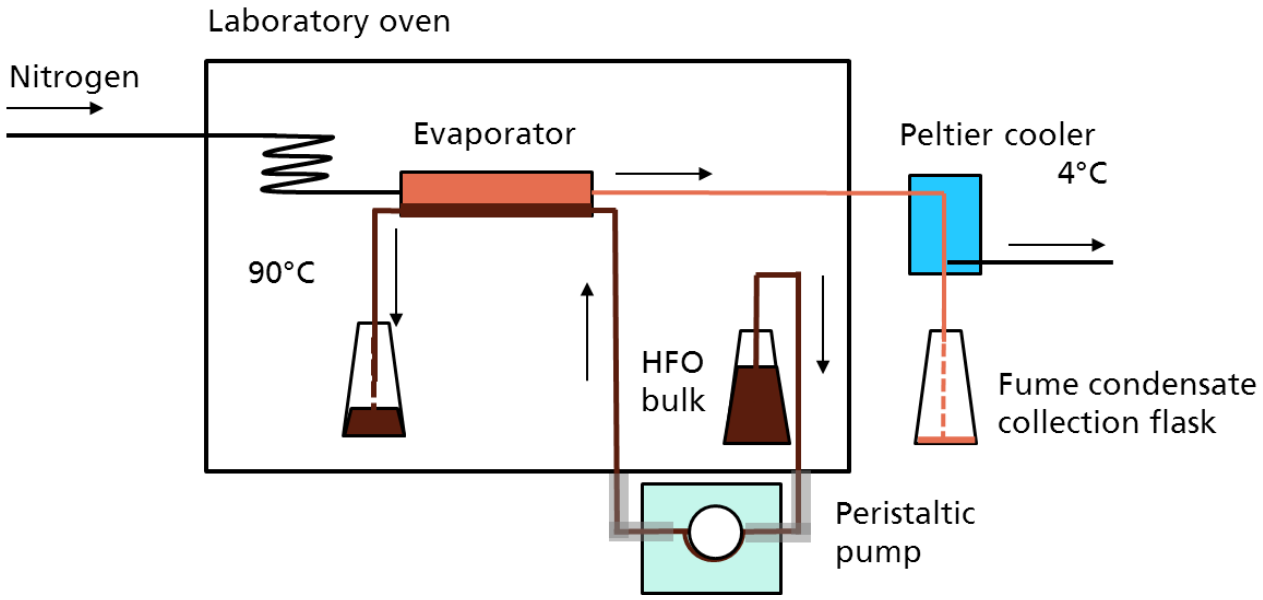

Fig. 2.1: Schematics of the laboratory set-up for fume collection at 90 °C.

A quantity of 1 l of HFO bulk material is heated up to a set temperature (70; 80 or 90°C) inside the oven. The fuel oil is fed continuously through the evaporator at a flow rate of 300 ml/h using a peristaltic pump and then dumped into a flask. A pre-heated nitrogen stream of 1 L/min is fed over the flat oil layer covering the bottom of the evaporator (layer thickness 3 cm). The vapor containing nitrogen flux is subsequently cooled in a Peltier cooler to 4 °C. This causes the vapor compounds to condense and drip into the collection flask.

The evaporator consists of two flat containers with an area of 6x16 cm² and a height of 5 cm which are placed in series. A flow velocity of the nitrogen of 1.4 cm/s is

calculated from the height of the gas space above the layer (2 cm) and the gas flow rate of 1 L/min.

The liquid bulk turnover established by the peristaltic pump is 0.3 L/h which corresponds to a mean residence time of approximately 1 h of the bulk material in each of the evaporation containers holding a liquid volume 0.29 L HFO.

2.3 Workplace sampling

Workplace sampling was not addressed in this study as a comprehensive collection campaign and analysis was already performed in the scope of the study "HFO fume collection and analysis".

2.4 Chemical analysis

Chemical analysis of the HFO bulk and condensate samples comprised:

- Boiling point distribution
- Fluorescence
- Total hydrocarbon
- Polycyclic Aromatic Hydrocarbon (PAHs) and naphthalene.

Details regarding the analytical procedures are described in the final report "HFO fume collection and analysis" in sections 2.3.1 to 2.3.4.

3 Results

3.1 Comparison of boiling point distributions

The boiling point distributions for the bulk materials and the respective condensates were determined. Sampling parameters such as sampling temperatures and durations as well as the resulting sampling rates are detailed in **Tab. 3.1**. The data show that the sampling rates for the materials CONCAWE-B and -C were very similar. For CONCAWE-A on

the other hand the sampling rate was three to four times lower compared to the other two materials.

CONCAWE-A bulk material also differed in respect to its T^{50} value, which was with 407.5 °C considerably higher than the T^{50} values for the other two materials (**Tab. 3.1**). This is also reflected in the corresponding boiling distribution graphs (**Fig. 3.1**). The start and end point of those graphs are for all three materials very similar but for CONCAWE-A the distribution of compounds with boiling points between in 250 to 400 °C is considerably different.

The T^{50} condensate values (**Tab. 3.1**) are comparable for all nine fume condensates. This is also reflected by the individual boiling point distributions shown in **Fig. 3.2** to **3.7.** It is, however, notable that the boiling point distributions for CONCAWE-C differ slightly in all three instances (70; 80 and 90 °C) from the CONCAWE-A and –B condensates in the boiling point range of approx. 214 to 230 °C (**Fig. 3.2 to 3.4**).

The boiling point distributions determined for the three fume condensates of each bulk material demonstrate that the condensate sampling temperature has no impact on the boiling point distribution of the collected condensates (**Fig. 3.5** to **3.7**).

Tab. 3.1: Fume condensate and 50%-temperature of the boiling point distribution of the bulk material and the condensate

Code	Sampling temperature [°C]	Sampling duration [h]	Quantity of fume sampled [ml]	Sampling rate [ml / h]	T^{50} bulk [°C]	T^{50} condensate [°C]
CONCAWE-A	70	14	2.2	0.16	407.5	214.8
	80	5	2.4	0.48		213.8
	90	3	2.8	0.93		213.0
CONCAWE-B	70	14	9.0	0.64	290.2	217.4
	80	5	6.0	1.20		213.3
	90	3	7.5	2.50		213.3
CONCAWE-C	70	14	10.0	0.71	325.1	211.0
	80	5	6.5	1.30		207.8
	90	3.0	8.0	2.67		205.9

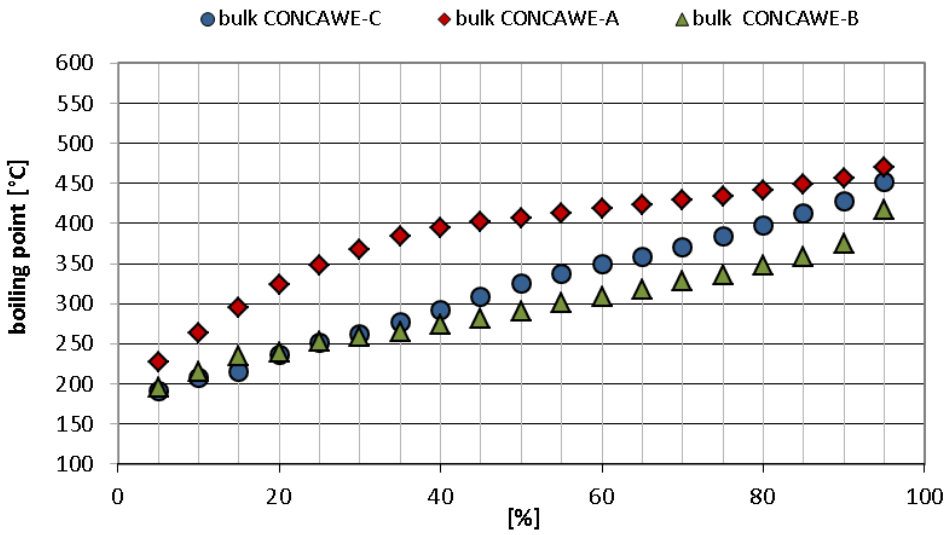

Fig. 3.1: Boiling point distributions of the bulk materials

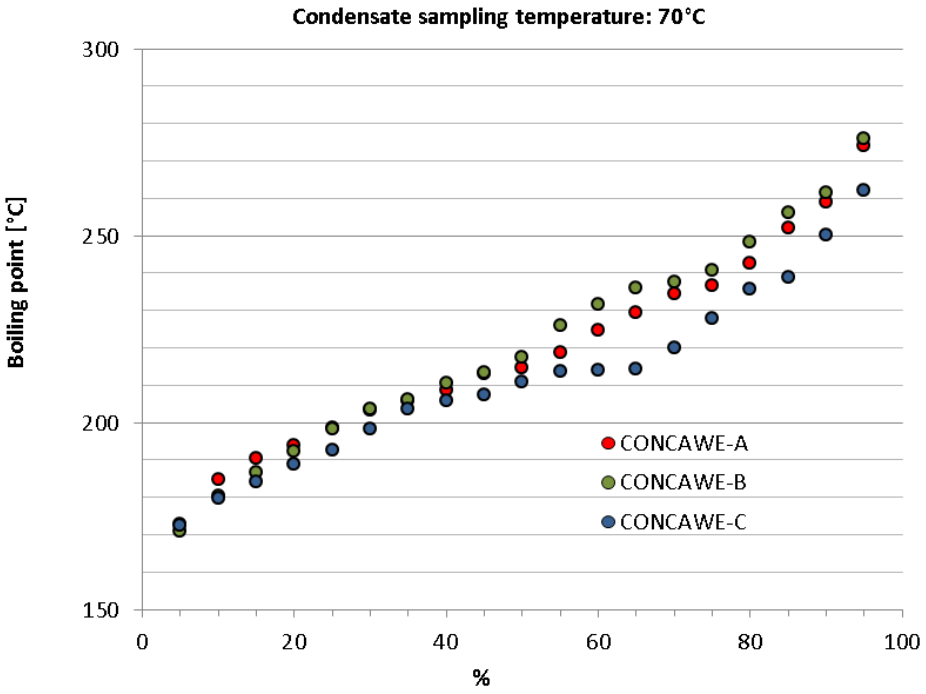

Fig. 3.2: Boiling point distributions of the fumes generated in the laboratory at 70 °C

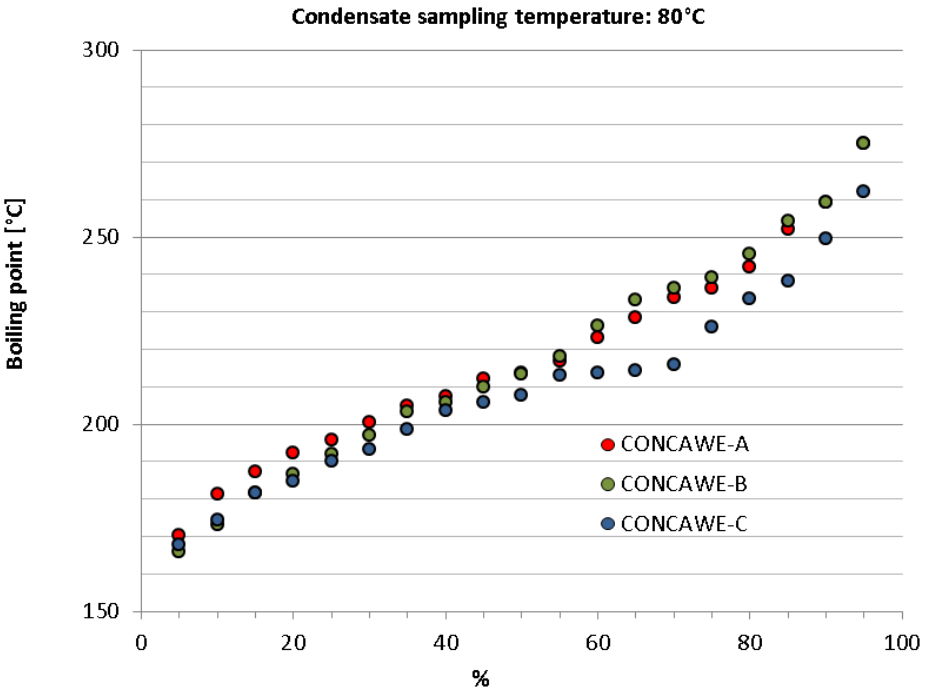

Fig. 3.3: Boiling point distributions of the fumes generated in the laboratory at 80 °C

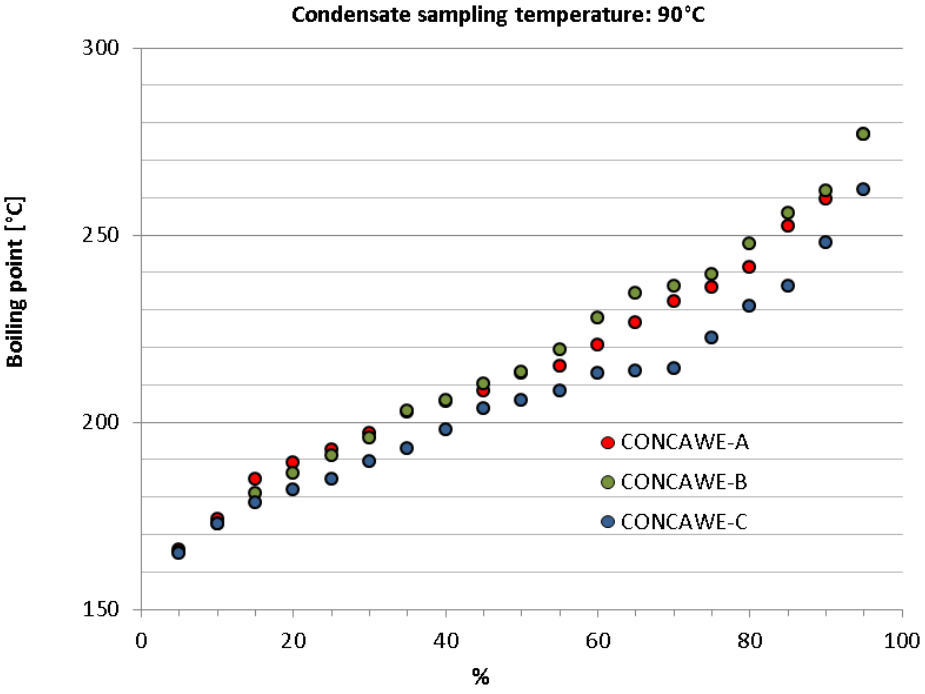

Fig. 3.4: Boiling point distributions of the fumes generated in the laboratory at 90 °C

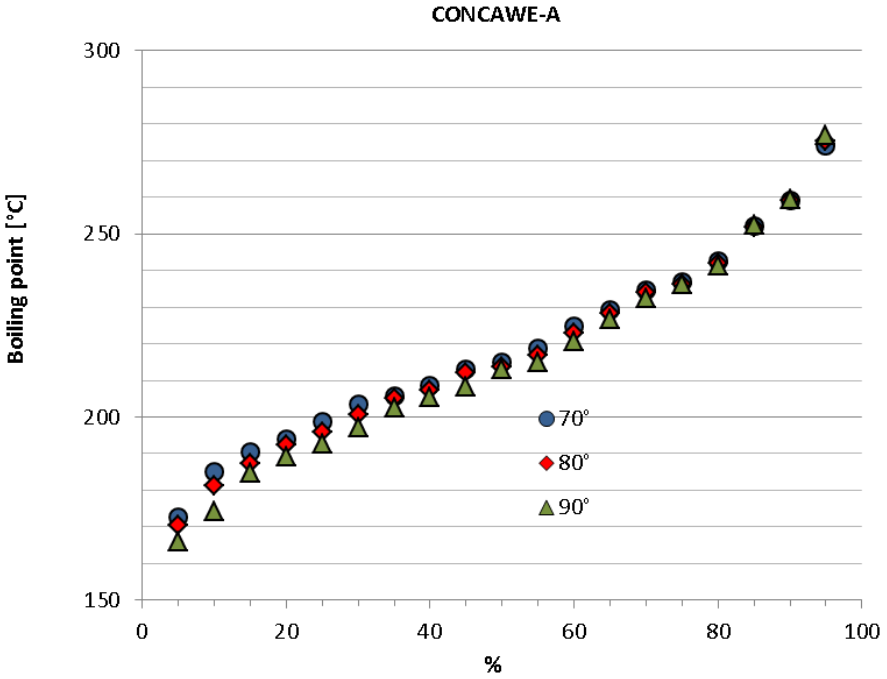

Fig. 3.5: Boiling point distributions of the fumes generated in the laboratory from bulk CONCAWE-A at 70; 80 and 90 °C

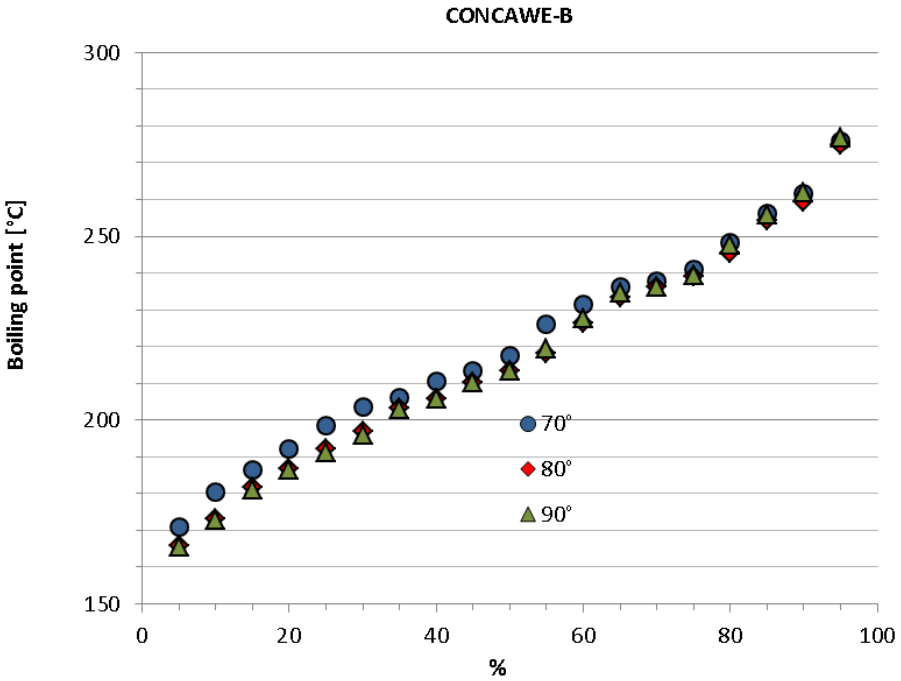

Fig. 3.6: Boiling point distributions of the fumes generated in the laboratory from bulk CONCAWE-B at 70; 80 and 90 °C

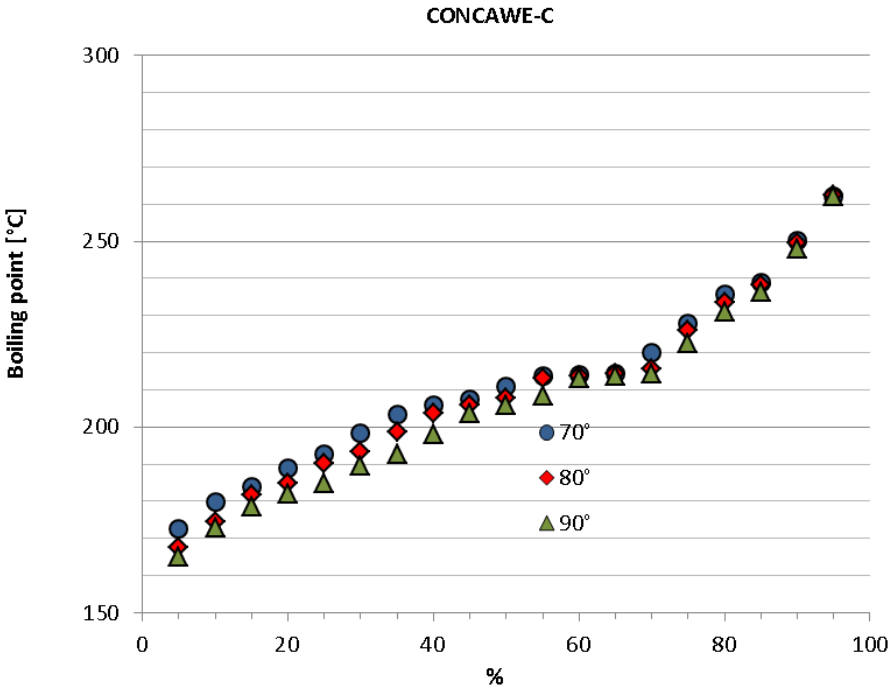

Fig. 3.7: Boiling point distributions of the fumes generated in the laboratory from bulk CONCAWE-C at 70; 80 and 90 °C

3.2 Fluorescence

Fluorescence measurements were carried out for the bulk samples of the HFOs and the corresponding fumes. As shown in **Tab. 3.2** the data demonstrate consistency over the selected temperature range for each HFO product. The fluorescence intensities in the laboratory fumes generated from the bulk material is by orders of magnitude lower than the fluorescence of the bulk materials themselves.

Tab. 3.2: Fluorescence intensities of the bulk and condensate samples

Code	Sampling Temperature [°C]	Bulk [mg/Kg DPA eq]	Condensate [mg/l DPA eq]	Reduction factor
CONCAWE-A	70	24100	8.11	2972
	80		8.64	2789
	90		10.06	2396
CONCAWE-B	70	19500	6.81	2863
	80		6.21	3140
	90		8.30	2349
CONCAWE-C	70	22900	4.45	5146
	80		3.54	6469
	90		3.74	6123

3.3 Aromatic hydrocarbons (AHs)

The results regarding the PAH and naphthalene content in HFO bulk and condensate samples are given in **Tab. 3.3** to **3.6.**

The data obtained for the condensate samples (**Tab. 3.4** to **3.6**) show that the transfer of the AHs from the bulk into the fume phase is not temperature dependent under the conditions detailed above (**chapter 2.2**).

Tab. 3.3: PAH and naphthalene concentrations of the bulk samples

AH	Bulk		
	CONCAWE - A	CONCAWE - B	CONCAWE - C
	µg/g	µg/g	µg/g
Naphthalene	481	1887	7143
Phenanthrene	266	995	889
Anthracene	27.2	121	96.6
Fluoranthene	14.9	30.8	56.9
Pyrene	60.1	145	285
Beno (b) naphtho (2,1-d) thiophene	65.9	23.4	110
Benzo (c) phenanthrene	n. r.	n. r.	n. r.
Benzo (g,h,i) fluoranthene	n. r.	n. r.	n. r.
Benz (a) anthracene	87.2	8.90	100
Cyclopenta (c,d) pyrene	< 1.2	< 1.2	< 1.2
Triphenylene	43.5	3.71	34.4
Chrysene	115	8.69	114
Benzo (b) fluoranthene	27.9	1.46	21.3
Benzo (k) fluoranthene	8.40	< 1.2	6.88
Benzo (j) fluoranthene	7.00	< 1.2	5.62
Benzo (e) pyrene	50.1	4.45	64.3
Benzo (a) pyrene	44.4	4.21	54.8
Dibenz (a,h) anthracene	9.84	< 1.2	6.56
Coronene	5.58	4.03	7.56
Indeno (1,2,3-cd) pyrene	7.21	1.22	6.20
Anthanthrene	13.4	< 3.7	14.3
Benzo (g,h,i) perylene	19.2	6.30	37.4

Tab. 3.4: PAH and naphthalene concentrations of CONCAWE – A condensate samples collected at 70; 80 and 90 °C

	CONCAWE - A		
AH	**70 °C**	**80 °C**	**90 °C**
	µg/g	**µg/g**	**µg/g**
Naphthalene	12501	12258	12400
Phenanthrene	105	111	130
Anthracene	11.5	12.1	13.1
Fluoranthene	1.27	1.31	1.47
Pyrene	3.20	3.42	4.51
Beno (b) naphtho (2,1-d) thiophene	0.56	0.61	0.70
Benzo (c) phenanthrene	< 0.1	< 0.1	< 0.1
Benzo (g,h,i) fluoranthene	< 0.1	< 0.1	< 0.1
Benz (a) anthracene	0.37	0.36	0.43
Cyclopenta (c,d) pyrene	< 0.4	< 0.4	< 0.4
Triphenylene	0.15	0.16	0.18
Chrysene	0.46	0.45	0.55
Benzo (b) fluoranthene	< 0.1	< 1.0	< 1.0
Benzo (k) fluoranthene	< 1.0	< 1.0	< 1.0
Benzo (j) fluoranthene	< 0.4	< 0.4	< 0.4
Benzo (e) pyrene	< 0.4	< 0.4	< 0.4
Benzo (a) pyrene	< 1.0	< 1.0	< 1.0
Dibenz (a,h) anthracene	< 0.4	< 0.4	< 0.4
Coronene	< 1.0	< 1.0	< 1.0
Indeno (1,2,3-cd) pyrene	< 0.4	< 0.4	< 0.4
Anthanthrene	< 0.4	< 0.4	< 0.4
Benzo (g,h,i) perylene	< 0.4	< 0.4	< 0.4

Tab. 3.5: PAH and naphthalene concentrations of CONCAWE – B condensate samples collected at 70; 80 and 90 °C

AH	CONCAWE -B		
	70 °C	80 °C	90 °C
	µg/g	µg/g	µg/g
Naphthalene	25312	22922	22900
Phenanthrene	174	187	185
Anthracene	22.6	23.5	23.8
Fluoranthene	0.86	1.11	1.07
Pyrene	2.99	3.89	3.84
Beno (b) naphtho (2,1-d) thiophene	0.15	0.22	0.24
Benzo (c) phenanthrene	< 0.1	< 0.1	< 0.1
Benzo (g,h,i) fluoranthene	< 0.1	< 0.1	< 0.1
Benz (a) anthracene	< 0.1	0.12	0.12
Cyclopenta (c,d) pyrene	< 0.4	< 0.4	< 0.4
Triphenylene	< 0.1	< 0.4	< 0.4
Chrysene	< 0.1	< 0.1	< 0.1
Benzo (b) fluoranthene	< 0.1	< 1.0	< 1.0
Benzo (k) fluoranthene	< 1.0	< 1.0	< 1.0
Benzo (j) fluoranthene	< 0.4	< 0.4	< 0.4
Benzo (e) pyrene	< 0.4	< 0.4	< 0.4
Benzo (a) pyrene	< 1.0	< 1.0	< 1.0
Dibenz (a,h) anthracene	< 0.4	< 0.4	< 0.4
Coronene	< 1.0	< 1.0	< 1.0
Indeno (1,2,3-cd) pyrene	< 0.4	< 0.4	< 0.4
Anthanthrene	< 0.4	< 0.4	< 0.4
Benzo (g,h,i) perylene	< 0.4	< 0.4	< 0.4

Tab. 3.6: PAH and naphthalene concentrations of CONCAWE – C condensate samples collected at 70; 80 and 90 °C

AH	CONCAWE -C		
	70 °C	**80 °C**	**90 °C**
	µg/g	**µg/g**	**µg/g**
Naphthalene	72456	80725	91646
Phenanthrene	155	163	155
Anthracene	8.79	8.25	16.8
Fluoranthene	1.51	1.58	1.50
Pyrene	5.83	5.92	5.25
Beno (b) naphtho (2,1-d) thiophene	0.36	0.359	0.29
Benzo (c) phenanthrene	< 0.1	< 0.1	< 0.1
Benzo (g,h,i) fluoranthene	< 0.1	< 0.1	< 0.1
Benz (a) anthracene	0.13	0.133	0.17
Cyclopenta (c,d) pyrene	< 0.4	< 0.4	< 0.4
Triphenylene	< 0.4	< 0.4	< 0.4
Chrysene	0.20	0.212	0.17
Benzo (b) fluoranthene	< 1.0	< 1.0	< 1.0
Benzo (k) fluoranthene	< 1.0	< 1.0	< 1.0
Benzo (j) fluoranthene	< 0.4	< 0.4	< 0.4
Benzo (e) pyrene	< 0.4	< 0.4	< 0.4
Benzo (a) pyrene	< 1.0	< 1.0	< 1.0
Dibenz (a,h) anthracene	< 0.4	< 0.4	< 0.4
Coronene	< 1.0	< 1.0	< 1.0
Indeno (1,2,3-cd) pyrene	< 0.4	< 0.4	< 0.4
Anthanthrene	< 0.4	< 0.4	< 0.4
Benzo (g,h,i) perylene	< 0.4	< 0.4	< 0.4

The data presented in **Tab. 3.4** to **3.6** are again diagrammed in **Fig. 3.8** to **3.10.**

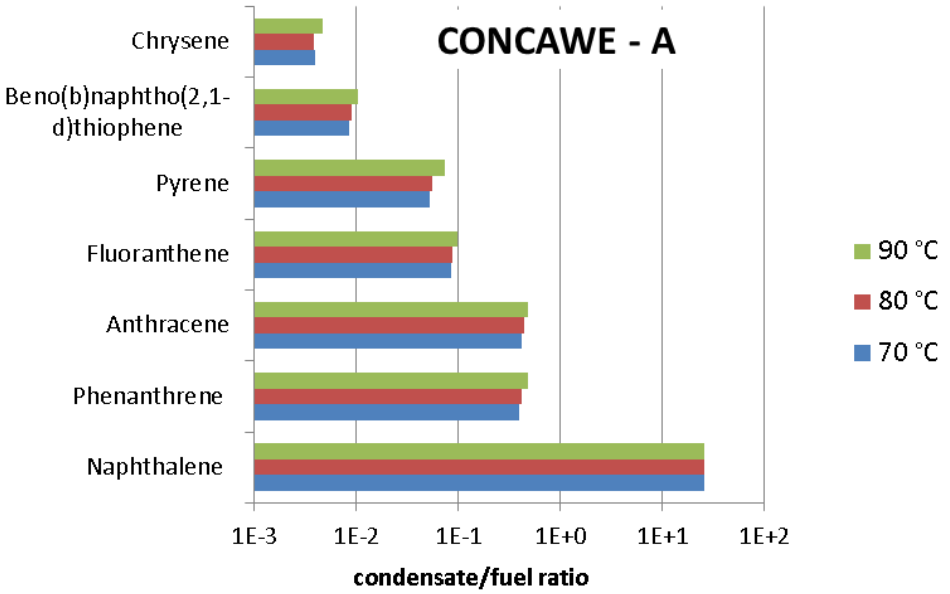

Fig. 3.8: Condensate-to-fuel ratios for selected AHs for HFP condensate CONCAWE-A

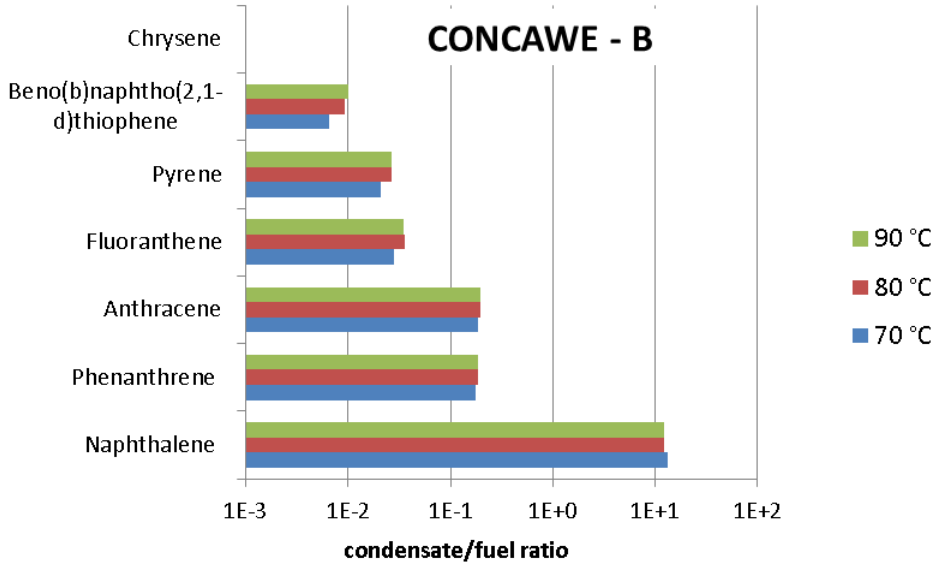

Fig. 3.9: Condensate-to-fuel ratios for selected AHs for HFP condensate CONCAWE-B

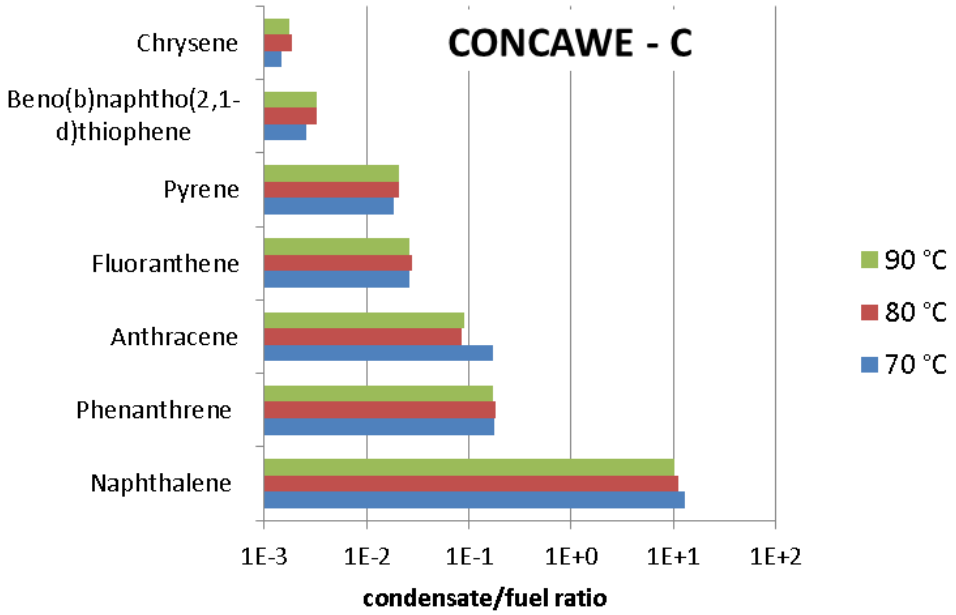

Fig. 3.10: Condensate-to-fuel ratios for selected AHs for HFP condensate CONCAWE-C

In **Fig. 3.11** to **3.13** the condensate-to- fuel ratios of selected AHs are graphically displayed for the three samples at 70; 80 and 90 °C respectively. The condensate-to-fuel ratios observed for CONCAWE-A differ at all three temperature from the other two samples. In all scenarios CONCAWE-A has the highest condensate-to-fuel ratios for the AHs pyrene, fluoranthene, anthracene, phenanthrene and naphthalene. This is most likely linked to the considerably lower condensate sampling rate (**Tab. 3.1** and **Fig. 3.14**) for this HFO product when compared to CONCAWE-B and CONCAWE-C.

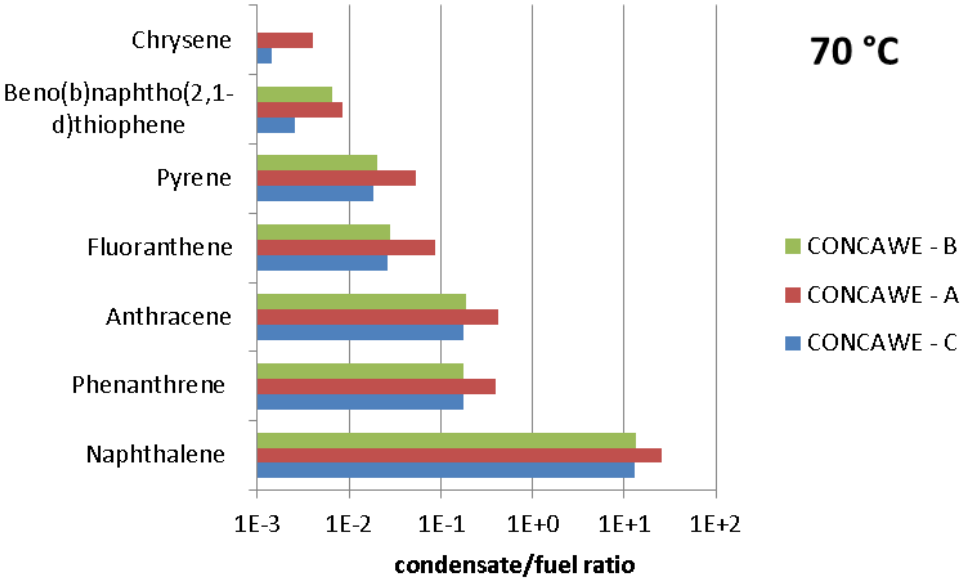

Fig. 3.11: Condensate-to-fuel ratios for selected AHs at 70 °C

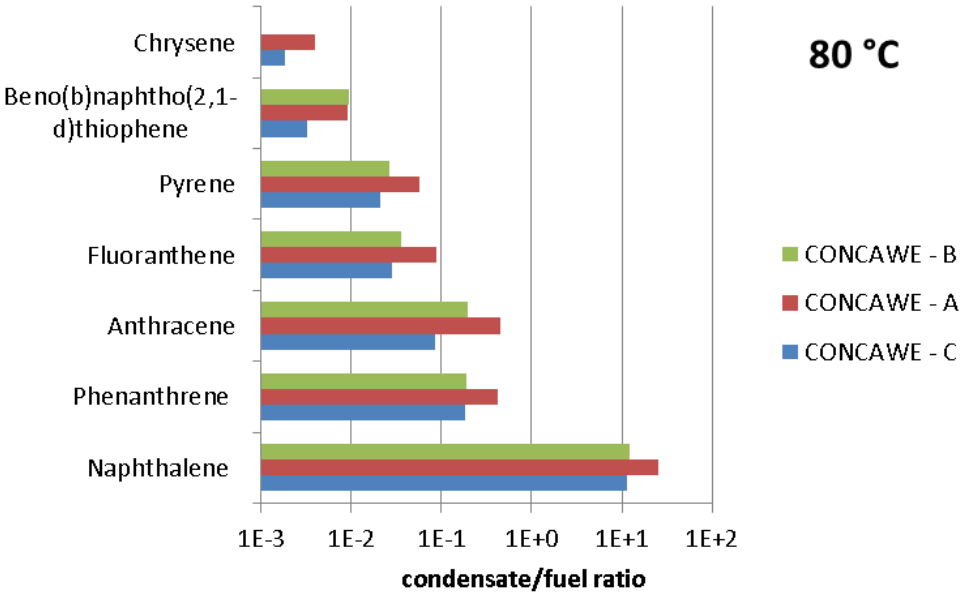

Fig. 3.12: Condensate-to-fuel ratios for selected AHs at 80 °C

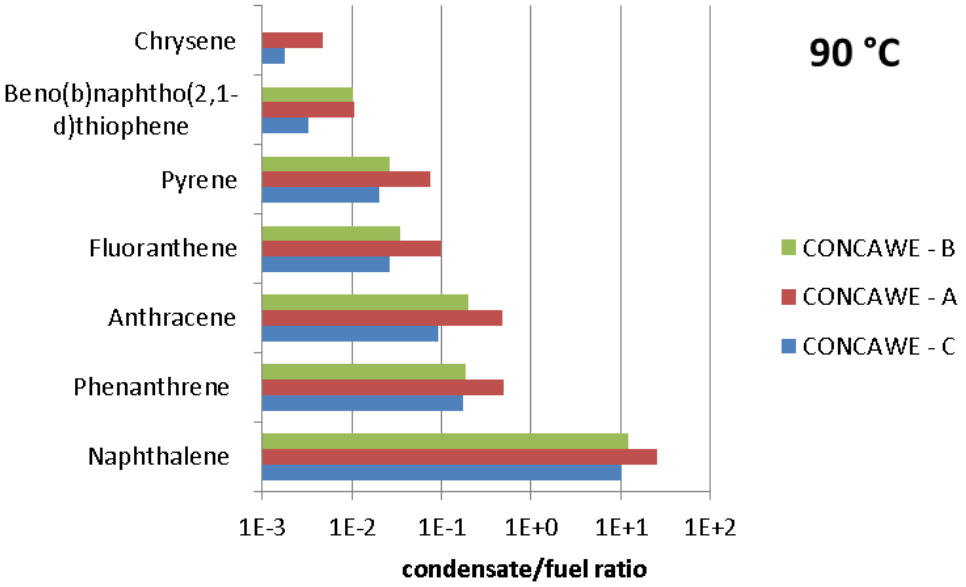

Fig. 3.13: Condensate-to-fuel ratios for selected AHs at 90 °C

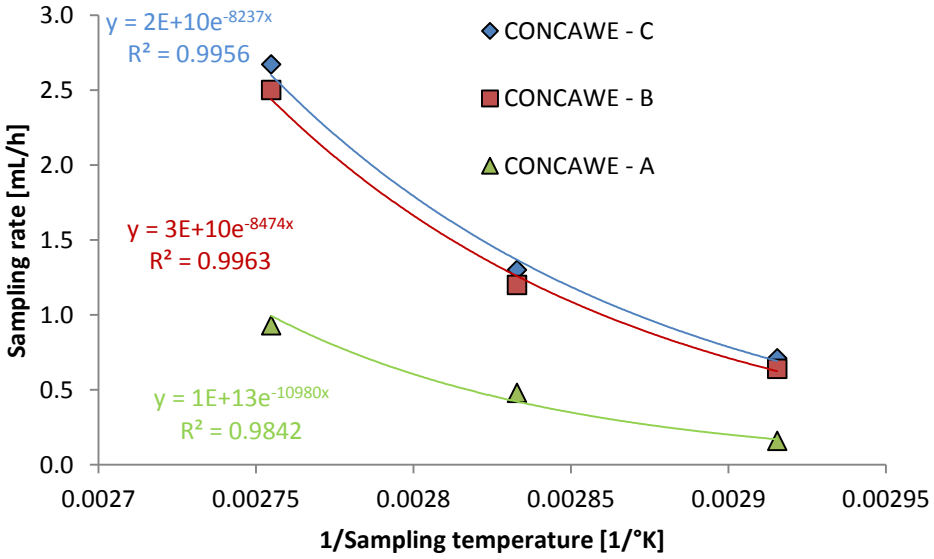

Fig. 3.14: Condensate sampling rates for CONCAWE-A, CONCAWE-B and CONCAWE-C – Arrhenius plot

APPENDIX 3

Evaluation of the Mutagenic Activity of Fume Condensates of Heavy Fuel Oil in the Bacterial Reverse Mutation Test (modified according to ASTM E1687-10)

WIL Research Europe B.V.
‘s-Hertogenbosch, The Netherlands

FINAL REPORT

Study Title

EVALUATION OF THE MUTAGENIC ACTIVITY OF FUME CONDENSATES OF HEAVY FUEL OIL IN THE BACTERIAL REVERSE MUTATION TEST (MODIFIED ACCORDING TO ASTM E1687-10)

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Laboratory Project Identification

Project 506682
Substances 205885, 205886, 205887, 205888, 205889, 205890, 205891, 205892, 205893

1. CONTENTS

1. CONTENTS 2
2. STATEMENT OF GLP COMPLIANCE 5
3. QUALITY ASSURANCE STATEMENT 6
4. SUMMARY 7
5. INTRODUCTION 8
5.1. Preface 8
5.2. Aims of the study 8
5.3. Guidelines 8
5.4. Storage and retention of records and materials 8
6. MATERIALS AND METHODS 9
6.1.1. Test substance information 9
6.1.2. Study specific test substance information 9
6.2. Test substance 205886 9
6.2.1. Test substance information 9
6.2.2. Study specific test substance information 9
6.3. Test substance 205887 9
6.3.1. Test substance information 9
6.3.2. Study specific test substance information 9
6.4. Test substance 205888 10
6.4.1. Test substance information 10
6.4.2. Study specific test substance information 10
6.5. Test substance 205889 10
6.5.1. Test substance information 10
6.5.2. Study specific test substance information 10
6.6. Test substance 205890 10
6.6.1. Test substance information 10
6.6.2. Study specific test substance information 10
6.7. Test substance 205891 11
6.7.1. Test substance information 11
6.7.2. Study specific test substance information 11
6.8. Test substance 205892 11
6.8.1. Test substance information 11
6.8.2. Study specific test substance information 11
6.9. Test substance 205893 11
6.9.1. Test substance information 11
6.9.2. Study specific test substance information 11
6.9.3. Test substance preparation 12
6.10. Reference substances 12
6.10.1. Negative/vehicle control 12
6.10.2. Positive control 12
6.11. Test system 12
6.12. Cell culture 13
6.13. Metabolic activation system 13
6.13.1. Preparation of S9-mix 13
6.14. Study design 13
6.14.1. Colony counting 14
6.15. Electronic data capture 14
6.16. Interpretation 14
6.16.1. Acceptability of the assay 14
6.16.2. Data evaluation 15
6.16.3. List of protocol deviations 15
6.16.4. List of standard operating procedures deviations 15
7. RESULTS 15
8. DISCUSSION AND CONCLUSION 17
9. REFERENCES 18

TABLES

Table 1 Dosing Solutions (µl/plate) 13
Table 2 Dosing Solutions (µl/plate) 14
Table 3 Dosing Solutions (µl/plate) 14
Table 4 Mutagenic response of batch CONCAWE-A-01 (TS 205885) in the *Salmonella typhimurium* reverse mutation assay 19
Table 5 Additional experiment: Mutagenic response of batch CONCAWE-A-01 (TS 205885) in the *Salmonella typhimurium* reverse mutation assay 20
Table 6 Mutagenic response of CONCAWE-A-02 (TS 205886) in the *Salmonella typhimurium* reverse mutation assay 21
Table 7 Additional experiment: Mutagenic response of batch CONCAWE-A-02 (TS 205886) in the *Salmonella typhimurium* reverse mutation assay 22
Table 8 Mutagenic response of CONCAWE-A-03 (TS 205887) in the *Salmonella typhimurium* reverse mutation assay 23
Table 9 Additional experiment: Mutagenic response of batch CONCAWE-A-03 (TS 205887) in the *Salmonella typhimurium* reverse mutation assay 24
Table 10 Mutagenic response of CONCAWE-B-01 (TS 205888) in the *Salmonella typhimurium* reverse mutation assay 25
Table 11 Additional experiment: Mutagenic response of batch CONCAWE-B-01 (TS 205888) in the *Salmonella typhimurium* reverse mutation assay 26
Table 12 Mutagenic response of CONCAWE-B-02 (TS 205889) in the *Salmonella typhimurium* reverse mutation assay 27
Table 13 Additional experiment: Mutagenic response of batch CONCAWE-B-02 (TS 205889) in the *Salmonella typhimurium* reverse mutation assay 28
Table 14 Mutagenic response of CONCAWE-B-03 (TS 205890) in the *Salmonella typhimurium* reverse mutation assay 29
Table 15 Additional experiment: Mutagenic response of batch CONCAWE-B-03 (TS 205890) in the *Salmonella typhimurium* reverse mutation assay 30
Table 16 Mutagenic response of CONCAWE-C-01 (TS 205891) in the *Salmonella typhimurium* reverse mutation assay 31
Table 17 Additional experiment 1: Mutagenic response of CONCAWE-C-01 (TS 205891) in the *Salmonella typhimurium* reverse mutation assay 32
Table 18 Additional experiment 2: Mutagenic response of batch CONCAWE-C-01 (TS 205891) in the *Salmonella typhimurium* reverse mutation assay 33
Table 19 Mutagenic response of CONCAWE-C-02 (TS 205892) in the *Salmonella typhimurium* reverse mutation assay 34
Table 20 Additional experiment: Mutagenic response of batch CONCAWE-C-02 (TS 205892) in the *Salmonella typhimurium* reverse mutation assay 35
Table 21 Mutagenic response of CONCAWE-C-03 (TS 205893) in the *Salmonella typhimurium* reverse mutation assay 36
Table 22 Additional experiment: Mutagenic response of batch CONCAWE-C-03 (TS 205893) in the *Salmonella typhimurium* reverse mutation assay 37

FIGURES

Figure 1 The mutagenicity index of CONCAWE-A-01 (TS 205885) 19
Figure 2 Additional experiment: The mutagenicity index of CONCAWE-A-01 (TS 205885) 20
Figure 3 The mutagenicity index of CONCAWE-A-02 (TS 205886) 21
Figure 4 Additional experiment: The mutagenicity index of CONCAWE-A-02 (TS 205886) 22
Figure 5 The mutagenicity index of CONCAWE-A-03 (TS 205887) 23
Figure 6 Additional experiment: The mutagenicity index of CONCAWE-A-03 (TS 205887) 24
Figure 7 The mutagenicity index of CONCAWE-B-01 (TS 205888) 25
Figure 8 Additional experiment: The mutagenicity index of CONCAWE-B-01 (TS 205888) 26
Figure 9 The mutagenicity index of CONCAWE-B-02 (TS 205889) 27
Figure 10 Additional experiment: The mutagenicity index of CONCAWE-B-02 (TS 205889) 28
Figure 11 The mutagenicity index of CONCAWE-B-03 (TS 205890) 29
Figure 12 Additional experiment: The mutagenicity index of CONCAWE-B-03 (TS 205890) 30
Figure 13 Additional experiment 1: The mutagenicity index of CONCAWE-C-01 (TS 205891) 32
Figure 14 Additional experiment 2: The mutagenicity index of CONCAWE-C-01 (TS 205891) 33

Figure 15 The mutagenicity index of CONCAWE-C-02 (TS 205892).....34
Figure 16 Additional experiment: The mutagenicity index of CONCAWE-C-02 (TS 205892).....35
Figure 17 The mutagenicity index of CONCAWE-C-03 (TS 205893).....36
Figure 18 Additional experiment: The mutagenicity index of CONCAWE-C-03 (TS 205893).....37

APPENDICES

APPENDIX 1 TABLES AND FIGURES 19
APPENDIX 2 SUPPORTING MATERIALS AND METHOD 38

2. STATEMENT OF GLP COMPLIANCE

WIL Research Europe B.V., 's-Hertogenbosch, The Netherlands

The study described in this report has been correctly reported and was conducted in compliance with:

The Organization for Economic Co-operation and Development (OECD) Principles of Good Laboratory Practice (GLP) (as revised in 1997) ENV/MC/CHEM (98) 17.

The sponsor is responsible for all test substance information unless determined by WIL Research Europe B.V.

Purity of the test substances was not indicated for this study. The purity and batch number of the reference oil no.1 (positive control substance) was not indicated.

Analysis of stability, homogeneity and concentration of the test substances under test conditions was not performed as part of this study.

WIL Research Europe B.V.

I.A.J. Verbaan, PhD.
Section Head Discovery

Date: 13 January 2015

C.M. Verspeek-Rip
Study Director

Date: 13 January 2015

3. QUALITY ASSURANCE STATEMENT

WIL Research Europe B.V., 's-Hertogenbosch, The Netherlands

This report was inspected by the WIL Research Europe Quality Assurance Unit to confirm that the methods and results accurately and completely reflect the raw data.

During the on-site process inspections, procedures applicable to this type of study were inspected.

The dates of Quality Assurance inspections are given below.

Project 506682

Type of Inspections	Phase/Process	Start Inspection date	End Inspection date	Reporting date
Study	Protocol	11-Aug-2014	11-Aug-2014	11-Aug-2014
	Test substance preparation	15-Aug-2014	15-Aug-2014	15-Aug-2014
	Protocol Amendment 01	02-Oct-2014	02-Oct-2014	02-Oct-2014
	Protocol Amendment 02	28-Oct-2014	28-Oct-2014	28-Oct-2014
	Protocol Amendment 03	27-Nov-2014	27-Nov-2014	27-Nov-2014
	Protocol Amendment 04	19-Dec-2014	19-Dec-2014	19-Dec-2014
	Report	12-Jan-2015	13-Jan-2015	13-Jan-2015
Process	**Genetic and In Vitro Toxicology**	22-Sep-2014	30-Sep-2014	30-Sep-2014
	Test Substance Handling			
	Exposure			
	Observations/Measurements			
	Specimen Handling			
	Test Substance Receipt	22-Oct-2014	06-Nov-2014	06-Nov-2014
	Test Substance Handling			

The review of the final report was completed on the date of signing this QA statement.

WIL Research Europe B.V.

Quality Assurance

ALISON MORGAN QUALITY ASSURANCE AUDITOR

A. Morgan

Date: 13 January, 2015

4. SUMMARY

Evaluation of the mutagenic activity of fume condensates of Heavy Fuel Oil in the bacterial reverse mutation test (modified according to ASTM E1687-10).

The undiluted extract (60 µl/plate) as well as dilutions containing 52.5, 45, 30, 15 and 7.5 µl extract/plate of the fume condensate of heavy fuel oils: coded as CONCAWE-A-01, CONCAWE-A-02, CONCAWE-A-03, CONCAWE-B-01, CONCAWE-B-02, CONCAWE-B-03, CONCAWE-C-01, CONCAWE-C-02 and CONCAWE-C-03 were tested in the bacterial reverse mutation test with the *Salmonella typhimurium* tester strain TA98. The test was performed in the presence of S9-mix (hamster liver S9 induced by Aroclor 1254). The study was modified to detect the presence of potential dermal carcinogens in virgin base oils used in the formulation of metalworking oils. Due to toxicity of the test compounds, at first an additional experiment was performed with CONCAWE-C-01 (Substance 205891) with the following dose levels: (dilutions of the extract): 2, 5, 7.5, 10, 15, 20 and 30 µl extract/plate. And after that additional experiments were performed with all nine test compounds with the following dose levels: the undiluted extract (60 µl/plate) as well as dilutions containing: 2.5, 5, 7.5, 10, 15, 30, 45 and 52.5 µl extract/plate of the fume condensate of heavy fuel oils.

The study procedures described in this report was based on the most recent ASTM E1687-10 guideline.

The negative control values were within the laboratory historical control data ranges, except for CONCAWE-A-02, CONCAWE-B-02 and CONCAWE-C-02. However, since this value was just without the limit of the range, the validity of the test was considered to be not affected.

The strain-specific positive control values were at least three times the concurrent vehicle control group mean indicating that the test conditions were adequate and that the metabolic activation system functioned properly. Except in the additional experiment with CONCAWE-B-02, CONCAWE-C-01 and C-02, where a 2.1- to 2.9-fold increase was observed.

In all nine extracts of the fume condensate of heavy fuel oils, cytotoxicity, as evidenced by a decrease in the number of revertants, was observed, with the exception of CONCAWE-A-01 in the additional experiment, where no toxic effect was observed.

CONCAWE-C-01 showed a 14-fold increase in the number of revertants at the dose level of 15 µl extract/plate. In an additional experiment the slope of the dose response curve as determined by regression analysis was 2.28. In a second additional experiment to verify this response the mutagenicity Index was 0.37. The increase in colonies observed in the first experiment could not be repeated in the additional experiments and was observed at one dose level only. The mutagenicity Index of 2.28 in the first additional experiment was related to a low mean value of the solvent control (31 revertant colonies) and no dose related increase was observed in the treatment groups, number of revertant colonies ranged from 26 to 49. Therefore these observations were judged as incidental findings and CONCAWE-C-01 is considered to have a high probability of being non-carcinogenic in a mouse skin-painting bio-assay.

The other extracts of the fume condensates of the heavy fuel oils: CONCAWE-A-01, CONCAWE-A-02, CONCAWE-A-03, CONCAWE-B-01, CONCAWE-B-02, CONCAWE-B-03, CONCAWE-C-02 and CONCAWE-C-03 showed mutagenicity indices < 1 in tester strain TA98.

5. INTRODUCTION

5.1. Preface

Sponsor	CONCAWE Boulevard du Souverain 165 1160 Brussels Belgium
Study Monitor	Arlean Rohde
Test Facility	WIL Research Europe B.V. Hambakenwetering 7 5231 DD 's-Hertogenbosch The Netherlands
Study Director	C.M. Verspeek-Rip
Study Plan	Start : 14 August 2014 Completion : 05 December 2014

5.2. Aims of the study

The objective of this study was to evaluate the test substances for their ability to induce reverse mutations in the gene of the histidine-requiring *Salmonella typhimurium* bacterial strain TA98 resulting in histidine-independent *Salmonella typhimurium* strains. The study was modified to detect the presence of potential dermal carcinogens in virgin base oils used in the formulation of metalworking oils.

The traditional Ames plate incorporation test is one of the most commonly performed safety assays in the world, however it has been shown to be generally unsuited to the testing of water-insoluble complex mixtures such as mineral oils. To circumvent poor solubility and other difficulties, this method employs an extraction of the test oil with dimethyl sulfoxide (DMSO) to produce aqueous-compatible solutions which readily interact with the metabolic activation system (S9) and with tester strain TA98.

The study was performed in the presence of a metabolic system (S9-mix: hamster liver S9 induced by Aroclor 1254).

5.3. Guidelines

The study procedures described in this report were based on the following guideline:

ASTM E1687-10 (May 2010): Standard Test Method for Determination Carcinogenic potential of Virgin Base Oils in Metalworking Fluids

5.4. Storage and retention of records and materials

Records and materials pertaining to the study including protocol, raw data and the final report are retained in the WIL Research Europe archives for a period of at least 2 years after finalization of the report. After this period, the sponsor will be contacted to determine how the records and materials should be handled. WIL Research Europe will retain information concerning decisions made.

Due to the relatively small quantity of the test substances no samples have been archived.

6. MATERIALS AND METHODS

6.1. Test substance 205885

6.1.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-A-01
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.1.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminium-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.2. Test substance 205886

6.2.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-A-02
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.2.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.3. Test substance 205887

6.3.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-A-03
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.3.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C,
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.4. Test substance 205888

6.4.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-B-01
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.4.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.5. Test substance 205889

6.5.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-B-02
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.5.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C,
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.6. Test substance 205890

6.6.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-B-03
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.6.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.7. Test substance 205891

6.7.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-C-01
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.7.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.8. Test substance 205892

6.8.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-C-02
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.8.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.9. Test substance 205893

6.9.1. Test substance information

Identification	Fume condensates of Heavy Fuel Oil
Appearance	Brown liquid
Batch	CONCAWE-C-03
Purity/Composition	Not indicated
Test substance storage	In refrigerator (2-8°C) protected from light
Stable under storage conditions until	30 July 2015 (retest date)

6.9.2. Study specific test substance information

Purity/composition correction factor	No correction factor required
Test substance handling	Use amber glassware or wrap container in aluminum-foil
Stability at higher temperatures	Yes, maximum temperature: 25°C
Stability in vehicle	Dimethyl sulfoxide: Not indicated
Solubility in vehicle	Dimethyl sulfoxide: Unknown

6.9.3. Test substance preparation

No correction was made for the purity/composition of the test compounds.

The test substances were extracted with dimethyl sulfoxide (DMSO, Merck, Darmstadt, Germany) prior to testing. Amber-coloured glassware was used when preparing the test solutions. Test substance concentrations were used within 4 hours after preparation.

6.10. Reference substances

6.10.1. Negative/vehicle control

The negative control was DMSO.

6.10.2. Positive control

Name	Reference Oil No.1
Identification number	RS381
Description	Brown viscous liquid (determined at WIL Research Europe)
CAS number	64741-53-3
Batch number	Not indicated
Purity	Not indicated
Expiry Date	21 February 2016 (allocated by WIL Research Europe)
Certified	No
Storage conditions	At room temperature in the dark
Supplier	Petrolabs Inc., Ivyland, PA, USA

6.11. Test system

Test System	*Salmonella typhimurium* bacteria
Rationale	Recommended test system in international guideline (e.g. ASTM).
Source	Trinova Biochem GmbH, Germany (Master culture from Dr. Bruce N. Ames) (TA98: 2006)

The characteristics of the *Salmonella typhimurium* strain are as follows:

Strain	Histidine mutation	Mutation type
TA98	*his*D3052/R-factor*	Frameshift

*: R-factor = plasmid pKM101 (increases error-prone DNA repair)

The tester strain contains the following additional mutations:
rfa : deep rough (defective lipopolysaccharide cellcoat)
gal : mutation in the galactose metabolism
chl : mutation in nitrate reductase
bio : defective biotin synthesis
uvrB : loss of the excision repair system (deletion of the ultraviolet-repair B gene)

Tester strain TA98 was regularly checked to confirm its histidine-requirement, crystal violet sensitivity, ampicillin resistance, UV-sensitivity and the number of spontaneous revertants. Stock cultures of the tester strain are stored in liquid nitrogen (-196°C).

6.12. Cell culture

Preparation of bacterial cultures
Samples of frozen stock cultures of bacteria were transferred into enriched nutrient broth (Oxoid LTD, Hampshire, England) and incubated in a shaking incubator (37°C, 150 spm), until the cultures reached an optical density of 1.0 ± 0.1 at 700 nm (10^9 cells/ml). Freshly grown cultures of each strain were used for a test.

Agar plates
Agar plates (ø 9 cm) contained 25 ml glucose agar medium. Glucose agar medium contained per liter: 18 g purified agar (Merck) in Vogel-Bonner Medium E, 20 g glucose (Fresenius Kabi, Bad Homburg, Germany). The agar plates for the test contained 12.5 µg/plate biotin (Merck) and 15 µg/plate histidine (Acros Organics).

Top agar
Milli-Q water containing 0.6% (w/v) bacteriological agar (Merck) and 0.5% (w/v) sodium chloride (Merck) was heated to dissolve the agar. Samples of 3 ml top agar were transferred into 10 ml glass tubes with metal caps. Top agar tubes were autoclaved for 20 min at 121 ± 3°C.

Environmental conditions
All incubations were carried out in a controlled environment at a temperature of 37.0 ± 1.0°C (actual range 36.0 – 38.7°C). The temperature was continuously monitored throughout the experiment. Due to addition of plates (which were at room temperature) to the incubator or due to opening and closing the incubator door, temporary deviations from the temperature may occur. Based on laboratory historical data these deviations are considered not to affect the study integrity.

6.13. Metabolic activation system

The S9-fraction, Aroclor 1254-induced male Golden Syrian Hamster liver is obtained from Trinova Biochem GmbH, Giessen, Germany.

6.13.1. Preparation of S9-mix

S9-mix was prepared immediately before use and kept on ice. S9-mix contained per 15 ml: 1.5 ml 1 M sodium phosphate buffer pH 7.4; 0.3 ml 0.25 M glucose-6-phosphate (Roche Diagnostics, Mannheim, Germany); 0.6 ml 0.2 M NADP (Randox Laboratories Ltd., Crumlin, United Kingdom); 0.6 ml of a salt solution of 0.2 M $MgCl_2$/0.825 M KCl solution. To 3 ml of S9-mix components 12 ml S9-fraction was added to complete the S9-mix.

6.14. Study design

The test substances and Reference Oil No.1 were extracted in DMSO prior to testing. An 1:5 volume ratio extract of each test substance was used. An 1:3 volume ratio extract of Reference Oil No.1 was used.

The sample were shaken vigorously continuously for a 30 minute period. The samples were centrifuged for 10 minutes to effect phase separation (200 x g). A portion of the lower, DMSO layer, was withdrawn with a pipette and used for testing.

The vehicle control and the reference Oil No.1 were concurrently tested.

The following dose solutions were prepared by diluting the DMSO extract with DMSO to give individual doses deliverable in 60 µl and tested in triplicate, see Table 1.

Table 1 Dosing Solutions (µl/plate)

	0	7.5	15	30	45	52.5	60
µl Extract	0	25	50	100	150	175	200
µl DMSO	200	175	150	100	50	25	0

Since after treatment with CONCAWE-C-01 (Substance 205891) too many dose levels showed a cytotoxic response, an additional experiment was performed with CONCAWE-C-01. The following dose solutions were prepared by diluting the DMSO extract with DMSO to give individual doses deliverable in 60 µl and tested in triplicate (see deviation 2), see Table 2.

Table 2 Dosing Solutions (µl/plate)

	0	2	5	7.5	10	15	20	30
µl Extract	0	7	17	25	33	50	67	100
µl DMSO	200	193	183	175	167	150	133	100

To verify the cytotoxic results obtained in the initial experiment an additional experiment was performed with all nine test compounds. The following dose solutions were prepared by diluting the DMSO extract with DMSO to give individual doses deliverable in 60 µl and tested in triplicate, see Table 3.

Table 3 Dosing Solutions (µl/plate)

	0	2.5	5	7.5	10	15	30	45	52.5	60
µl Extract	0	8	17	25	33	50	100	150	175	200
µl DMSO	200	192	183	175	167	150	100	50	25	0

To sterile tubes, the following items were added and pre-incubated for 20 minutes by 70 rpm at 37°C: 0.5 ml S9-mix, 0.1 ml of a fresh bacterial culture (10^9 cells/ml) of tester strain TA98, 60 µl of each dosing solution. After the pre-incubation period the solutions were added to 3 ml molten top agar (Top agar was melted by heating to 45°C). The ingredients were mixed on a Vortex and the content of the top agar tube was poured onto a selective agar plate. After solidification of the top agar, the plates were inverted and incubated in the dark at 37.0 ± 1.0°C for 48 ± 4h. After this period revertant colonies were counted.

6.14.1. Colony counting

The revertant colonies were counted automatically with the Sorcerer Colony Counter. Plates with sufficient test article precipitate to interfere with automated colony counting were counted manually and evidence of test article precipitate on the plates was recorded. See APPENDIX 2. To determine the toxicity of the test substances, the increase in the size of the microcolonies and the reduction of the revertant colonies were examined. The reduction in the number of revertant colonies has been evaluated by comparing the number of revertant colonies above the dose level with an decrease in the number of revertant. A reduction of 20% or more is considered toxic.

6.15. Electronic data capture

Observations/measurements in the study were recorded electronically using the following programme:

- REES Centron Environmental Monitoring system version SQL 2.0 (REES Scientific, Trenton, NJ, USA).
- Ames study Manager version 1.23 (Perceptive Instruments Ltd., St Edmunds, Suffolk, United Kingdom).

6.16. Interpretation

6.16.1. Acceptability of the assay

The assay is considered acceptable if it meets the following criteria:

a) The negative control data (number of spontaneous revertants per plate) should be within the laboratory historical range for the tester strain: Range 10 – 52, mean value 26, SD 7, n = 679
b) If the DMSO extract of Reference Oil No. 1, diluted 1:3 (one volume of oil plus three volumes of DMSO) reaches, in a dose-responsive manner, at least a three-fold the concurrent control.

6.16.2. Data evaluation

Mutagenic potency is represented by the Mutagenicity Index (MI), the slope of the dose response curve as determined by regression analysis.

Thresholds for interpretation of MI values of Virgin Base Oils in Metalworking Fluids, defined in ASTM E 1687 are as follows:
- Test substances with MI values <1 are considered to have a high probability of being non-carcinogenic in a mouse skin-painting bio-assay.
- Test substances with MI values >1 but <2 may or may not be non-carcinogenic in a mouse skin-painting bio-assay.
- Test substances with MI values >2 are considered to have a high probability of being carcinogenic in a mouse skin-painting bio-assay.

In case a negative Mutagenicity Index is obtained the following is applicable:
- All dose levels with a decrease, due to toxicity in the number of revertant colonies compared to the concurrent solvent control will not be included in the regression analysis.
- A negative mutagenicity Index will be judged as zero.

6.16.3. List of protocol deviations

1. The mean value of the solvent control in the experiment with CONCAWE-A-02, CONCAWE-B-02 and CONCAWE-C-02 was not within the laboratory historical range
   Evaluation: The mean value of 58 was above the limit of the range (52). The mean plate count was just above the limit of the range and clear negative results are observed in all three batches, therefore this deviation in the mean plate count of the solvent control had no effect on the results
2. In the first additional experiment with CONCAWE-C-01, the tested dose levels were 2, 5, 7.5, 10, 15, 20 and 30 µl extract/plate.
   Evaluation: Due to a calculation error the dose range was changed. Since test substances were tested up to the toxic dose level of 30 µl extract/plate, this deviation had no effect on the results.
3. In the additional experiments with CONCAWE-B-02, CONCAWE-C-01 and C-02, the mean plate count of the positive control were not within the acceptability criteria.
   Evaluation: Values of 117, 79 and 76 revertant colonies were not three-fold compared to the concurrent control values of 41, 34 and 36. The purpose of the positive control is as a reference for the test system, where a positive response is required to check if the test system functions correctly. Since the value was more than 2 times greater than the concurrent solvent control values, this deviation in the mean plate count of the positive control had no effect on the results of the study.

The study integrity was not adversely affected by the deviations.

6.16.4. List of standard operating procedures deviations

Any deviations from standard operating procedures were evaluated and filed in the study file. There were no deviations from standard operating procedures that affected the integrity of the study.

7. RESULTS

The undiluted extract (60 extract/plate) as well as dilutions containing 52.5, 45, 30, 15 and 7.5 µl extract/plate of the fume condensate of heavy fuel oils: coded as CONCAWE-A-01, CONCAWE-A-02, CONCAWE-A-03, CONCAWE-B-01, CONCAWE-B-02, CONCAWE-B-03, CONCAWE-C-01, CONCAWE-C-02 and CONCAWE-C-03 were tested in the bacterial reverse mutation test with the *Salmonella typhimurium* tester strain TA98. The test was performed in the presence of S9-mix (hamster liver S9 induced by Aroclor 1254). Due to toxicity of the test compounds, at first an additional experiment was performed with CONCAWE-C-01 (Substance 205891) with the following dose levels (dilutions of the extract): 2, 5, 7.5, 10, 15, 20 and 30 µl extract/plate. And after that additional experiments were performed with all nine test compounds with the undiluted extract (60 µl extract/plate) as well as dilutions containing): 2.5, 5, 7.5, 10, 15, 30, 45 and 52.5 extract/plate of the

fume condensate of heavy fuel oils. All nine test compounds did not precipitate on the plates up to the top dose of 60 µl extract/plate.

CONCAWE-A-01 (TS 205885)
Cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µl extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The Mutagenicity Index is 0.67 (Mutagenicity Index = the slope of the dose response curve as determined by regression analysis). See Table 4 and Figure 1. In the additional experiment, no biologically relevant decrease in the number of revertants was observed up to the top dose of 60 µl extract/plate. The Mutagenicity Index is 0.05. See Table 5 and Figure 2.

CONCAWE-A-02 (TS 205886)
Cytotoxicity, as evidenced by an increase in the size of the microcolonies, was observed at dose levels of 45 µl extract/plate and above. The Mutagenicity Index is 0.12. See Table 6 and Figure 3. In the additional experiment, cytotoxicity, as evidenced by a decrease in the number (compared to the dose level of 30 µl extract/plate), was observed at dose levels of 45 µl extract/plate and above. The Mutagenicity Index is 0.90. See Table 7 and Figure 4.

CONCAWE-A-03 (TS 205887)
Cytotoxicity, as evidenced by an increase in the size of the microcolonies, was observed at dose levels of 45 µl extract/plate and above. The Mutagenicity Index is 0.019. See Table 8 and Figure 5. In the additional experiment, cytotoxicity, as evidenced by a decrease in the number (compared to the dose level of 30 µl extract/plate), was observed at dose levels of 45 µl extract/plate and above. The Mutagenicity Index is 0.78. See Table 9 and Figure 6.

CONCAWE-B-01 (TS 205888)
Cytotoxicity, as evidenced by an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The slope of the dose response curve as determined by regression analysis is -0.13, the Mutagenicity Index will be judged as 0. See Table 10 and Figure 7. In the additional experiment, cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µl extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The Mutagenicity Index is 0.49, See Table 11 and Figure 8.

CONCAWE-B-02 (TS 205889)
Cytotoxicity, as evidenced by an increase in the size of the microcolonies, was observed at dose levels of 45 µl extract/plate and above. The slope of the dose response curve as determined by regression analysis is -0.11, the Mutagenicity Index will be judged as 0. See Table 12 and Figure 9. In the additional experiment, cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µl extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The slope of the dose response curve as determined by regression analysis is -0.02, the Mutagenicity Index will be judged as 0. See Table 13 and Figure 10.

CONCAWE-B-03 (TS 205890)
Cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µg extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The Mutagenicity Index is 0.87. See Table 14 and Figure 11. In the additional experiment, cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µl extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The Mutagenicity Index is 0.52. See Table 15 and Figure 12.

CONCAWE-C-01 (TS 205891)
Due to cytotoxicity, no revertant colonies or microcolonies were observed at 30 extract/plate and above. A 14-fold increase in the number of revertants was observed at 15 µl extract/plate, see Table 16. Since only two analysable dose levels could be judged, no Mutagenicity Index could be determined. In the first additional experiment, cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 7.5 µl extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 10 µl extract/plate and above. The Mutagenicity Index

is 2.28. See Table 17 and Figure 13. In the second additional experiment, toxicity, as evidenced by an increase in the size of the microcolonies, was observed at the dose levels of 30 and 45 µl extract/plate. At dose levels of 52.5 and 60 µl extract/plate no toxicity was observed anymore. The mutagenicity Index is 0.37. See Figure 18 and Figure 14.

CONCAWE-C-02 (TS 205892)
Cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µg extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The slope of the dose response curve as determined by regression analysis is -0.47, the Mutagenicity Index will be judged as 0. See Table 19 and Figure 15. In the additional experiment, cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 7.5 µl extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 10 µl extract/plate and above. The slope of the dose response curve as determined by regression analysis is -0.24, the Mutagenicity Index will be judged as 0. See Table 20 and Figure 16.

CONCAWE-C-03 (TS 205893)
Cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µl extract/plate) or an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The mutagenicity Index is 0.07. See Table 21 and Figure 17. In the additional experiment, cytotoxicity, as evidenced by a decrease in the number of revertants (compared to the dose level of 15 µl extract/plate) or by an increase in the size of the microcolonies, was observed at dose levels of 30 µl extract/plate and above. The slope of the dose response curve as determined by regression analysis is -0.45, the Mutagenicity Index will be judged as 0. See Table 22 and Figure 18.

8. DISCUSSION AND CONCLUSION

The negative control values were within the laboratory historical control data ranges, except for CONCAWE-A-02, CONCAWE-B-02 and CONCAWE-C-02 (see protocol deviation 1). However, since this value was just without the limit of the range, the validity of the test was considered to be not affected.

The strain-specific positive control values were at least three times the concurrent vehicle control group mean indicating that the test conditions were adequate and that the metabolic activation system functioned properly. Except in the additional experiment with CONCAWE-B-02, CONCAWE-C-01 and C-02, where a 2.1- to 2.9-fold increase was observed, see protocol deviation 3.

In all nine extracts of the fume condensate of heavy fuel oils, cytotoxicity, as evidenced by a decrease in the number of revertants, was observed, with the exception of CONCAWE-A-01, A-02 and A-03 in the additional experiment, where no toxic effect was observed.

CONCAWE-C-01 showed a 14-fold increase in the number of revertants at the dose level of 15 µl extract/plate. In an additional experiment the slope of the dose response curve as determined by regression analysis was 2.28. In a second additional experiment to verify this response the mutagenicity Index was 0.37. The increase in colonies observed in the first experiment could not be repeated in the additional experiments and was observed at one dose level only. The mutagenicity Index of 2.28 in the first additional experiment was related to a low mean value of the solvent control (31 revertant colonies) and no dose related increase was observed in the treatment groups, number of revertant colonies ranged from 26 to 49. Therefore these observations were judged as incidental findings and CONCAWE-C-01 is considered to have a high probability of being non-carcinogenic in a mouse skin-painting bio-assay.

The other extracts of the fume condensates of the heavy fuel oils: CONCAWE-A-01, CONCAWE-A-02, CONCAWE-A-03, CONCAWE-B-01, CONCAWE-B-02, CONCAWE-B-03, CONCAWE-C-02 and CONCAWE-C-03 showed mutagenicity indices < 1 in tester strain TA98.

9. REFERENCES

1. Leonardo, J.M., Dornfeld, S.S. and Peak, M.J., 1984, Evaluation of *E. coli* K12 343 \ 13 and derived strains for microbial mutagenicity assays. Mutation Res., 130, 87-95.
2. Ames, B.N., McCann, J. and Yamasaki, E., 1975, Methods for detecting carcinogens and mutagens with the Salmonella/mammalian microsome mutagenicity test, Mutation Res.,31, 347-364.
3. Maron, D.M. and Ames, B.N., 1983, Revised methods for the Salmonella mutagenicity test, Mutation Res., 113, 173-215. Erratum, 1983, Mutation Res., 113, 533.
4. Organisation for Economic Co-operation and Development (OECD), OECD Guidelines for Testing of Chemicals; Guideline no. 471: "Genetic Toxicology: Bacterial Reverse Mutation Test". (adopted July 21, 1997)

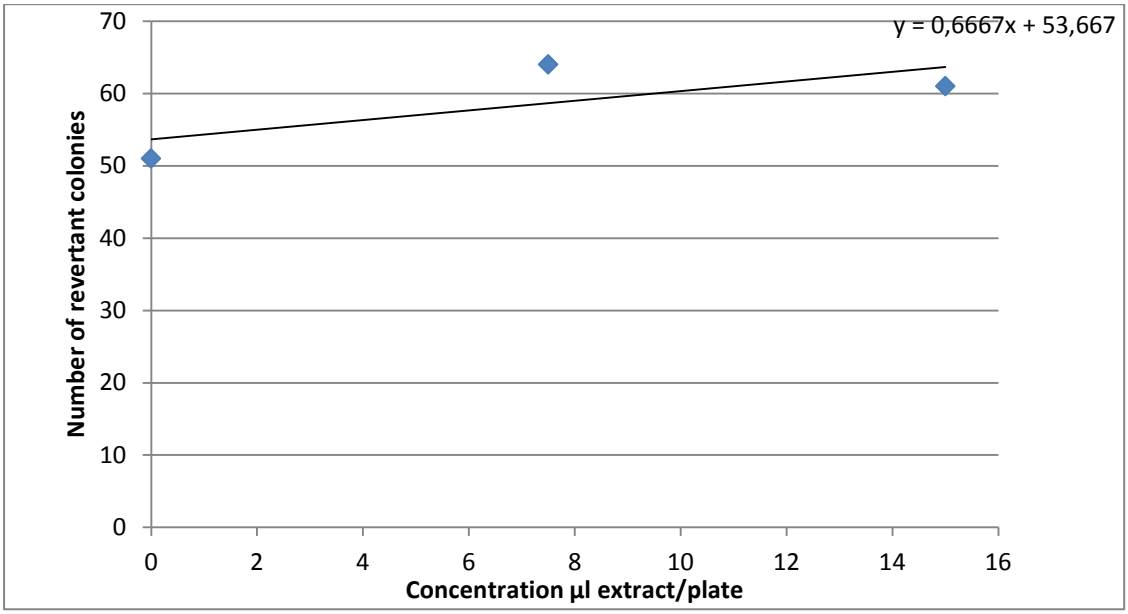
APPENDIX 1 TABLES AND FIGURES

Table 4 Mutagenic response of batch CONCAWE-A-01 (TS 205885) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	188		227		97		171	±	67
solvent control	53		48		53		51	±	3
7.5	75		73		44		64	±	17
15	63		80		41		61	±	20
30	26		30		38		31	±	6
45	MC		MC		MC				
52.5	MC		MC		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies

Figure 1 The mutagenicity index of CONCAWE-A-01 (TS 205885)



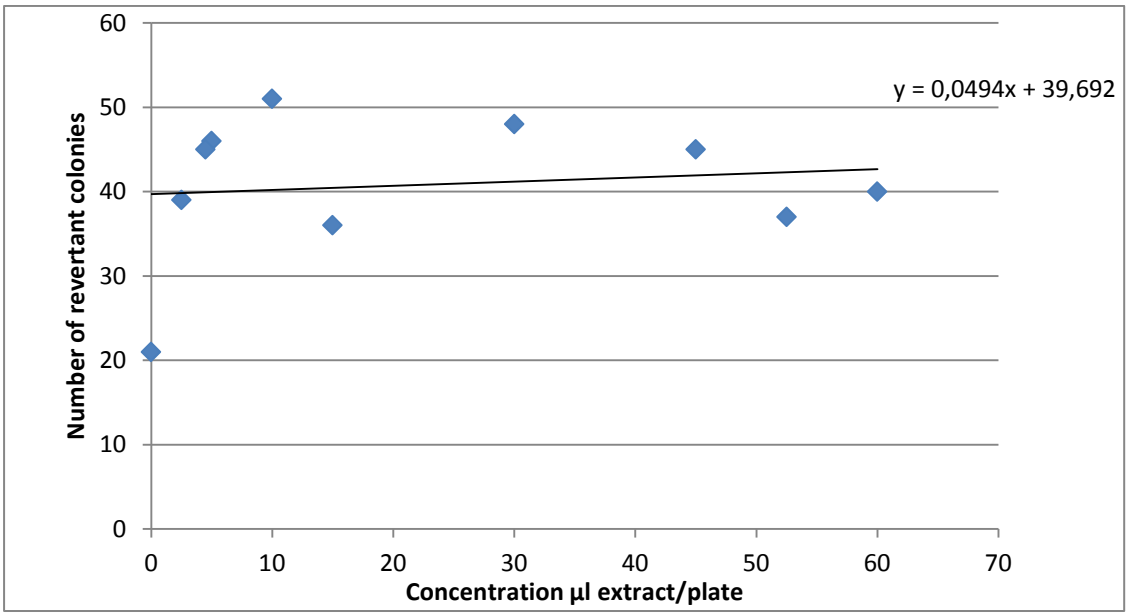
APPENDIX 1 – continued –

Table 5 Additional experiment: Mutagenic response of batch CONCAWE-A-01 (TS 205885) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	i		146		144		145	±	1
solvent control	i		20		21		21	±	1
2.5	52		39		26		39	±	13
5	45		53		39		46	±	7
7.5	41		37		56		45	±	10
10	53		45		56		51	±	6
15	54		33		20		36	±	17
30	44		47		54		48	±	5
45	41		52		41		45	±	6
52.5	37		35		40		37	±	3
60	37	NP	49	NP	34	NP	40	±	8

NP No precipitate
i Plate infected

Figure 2 Additional experiment: The mutagenicity index of CONCAWE-A-01 (TS 205885)



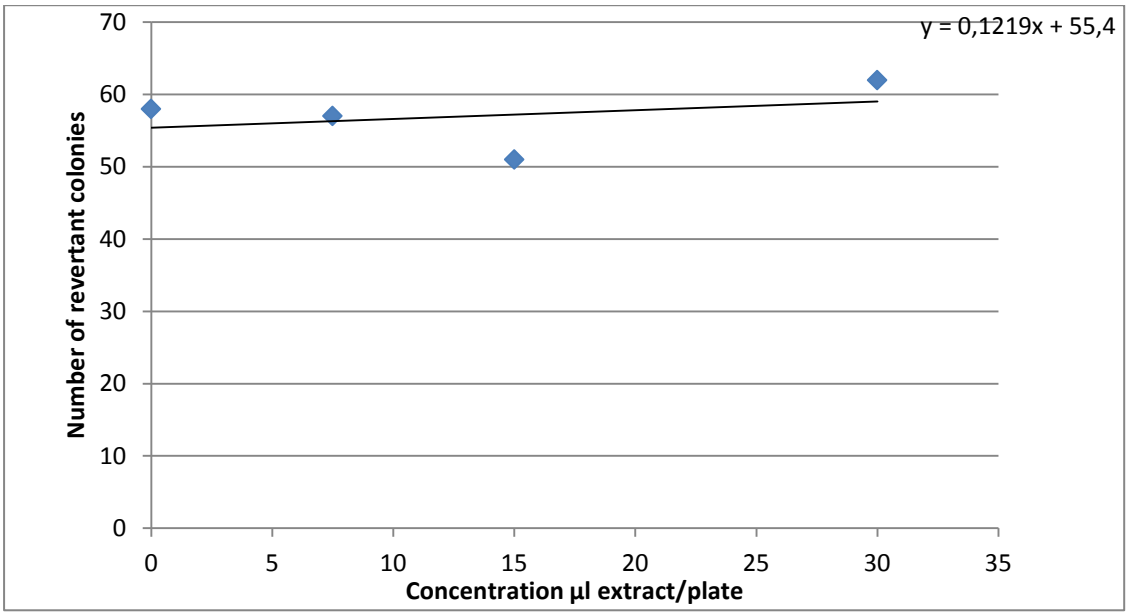
APPENDIX 1 – continued –

Table 6 Mutagenic response of CONCAWE-A-02 (TS 205886) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	165		147		181		180	±	19
	173		212		174				
	184		197		188				
solvent control	51		52		55		58	±	9
	50		53		57				
	71		56		75				
7.5	55		54		63		57	±	5
15	55		39		59		51	±	11
30	58		62		67		62	±	5
45	MC		MC		MC				
52.5	MC		MC		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate

Figure 3 The mutagenicity index of CONCAWE-A-02 (TS 205886)



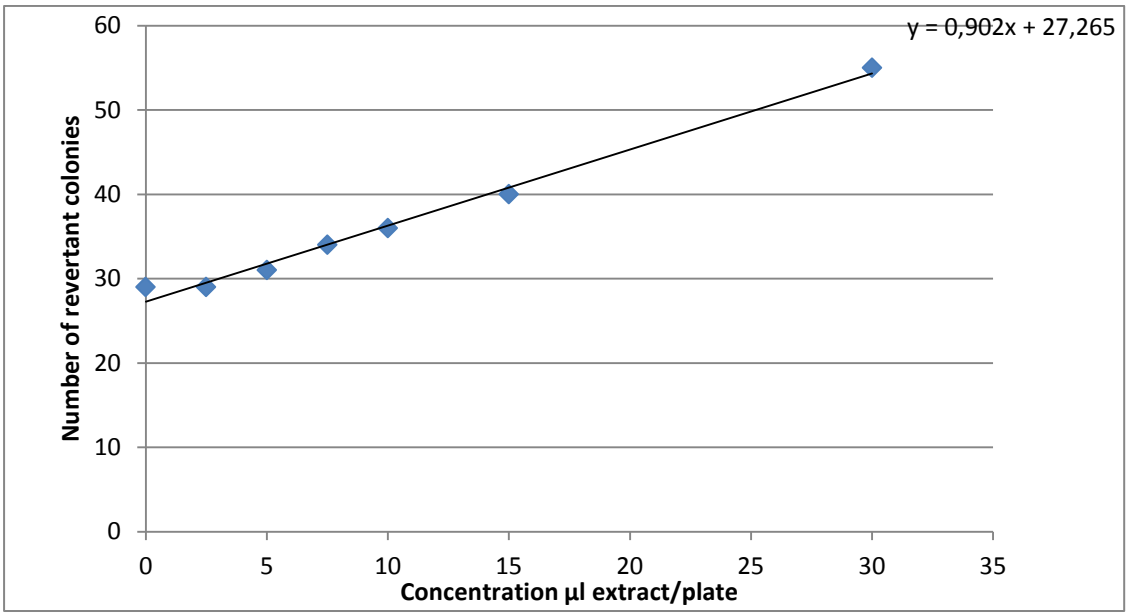
APPENDIX 1 – continued –

Table 7 Additional experiment: Mutagenic response of batch CONCAWE-A-02 (TS 205886) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.											
plate	1		2		3		MEAN			SD		
positive control		i	146		144		145	±		1		
solvent control		i	20		21		21	±		1		
2.5	23		28		36		29	±		7		
5	38		28		28		31	±		6		
7.5	39		27		35		34	±		6		
10	37		44		28		36	±		8		
15	31		36		53		40	±		12		
30	29		42		94		55	±		34		
45	42		37			i	40	±		4		
52.5	27		38		46		37	±		10		
60	24	NP	22	NP	20	NP	22	±		2		

NP No precipitate
i Plate infected

Figure 4 Additional experiment: The mutagenicity index of CONCAWE-A-02 (TS 205886)



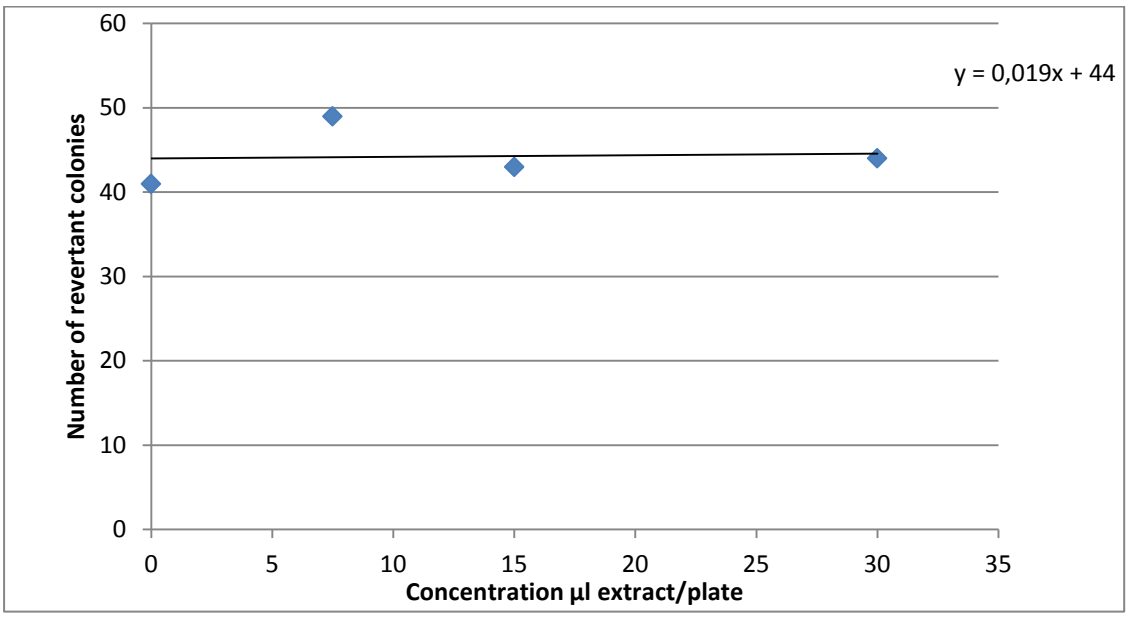
APPENDIX 1 – continued –

Table 8 Mutagenic response of CONCAWE-A-03 (TS 205887) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98 Mean, ± SD.								
plate	1		2		3		MEAN		SD
positive control	188		116		170		151	±	22
	132		147		143				
	152		136		171				
solvent control	31		73		40		41	±	13
	37		46		35				
	38		31		39				
7.5	58		41		48		49	±	9
15	37		43		49		43	±	6
30	49		41		41		44	±	5
45	MC		MC		MC				
52.5	MC		MC		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies

Figure 5 The mutagenicity index of CONCAWE-A-03 (TS 205887)



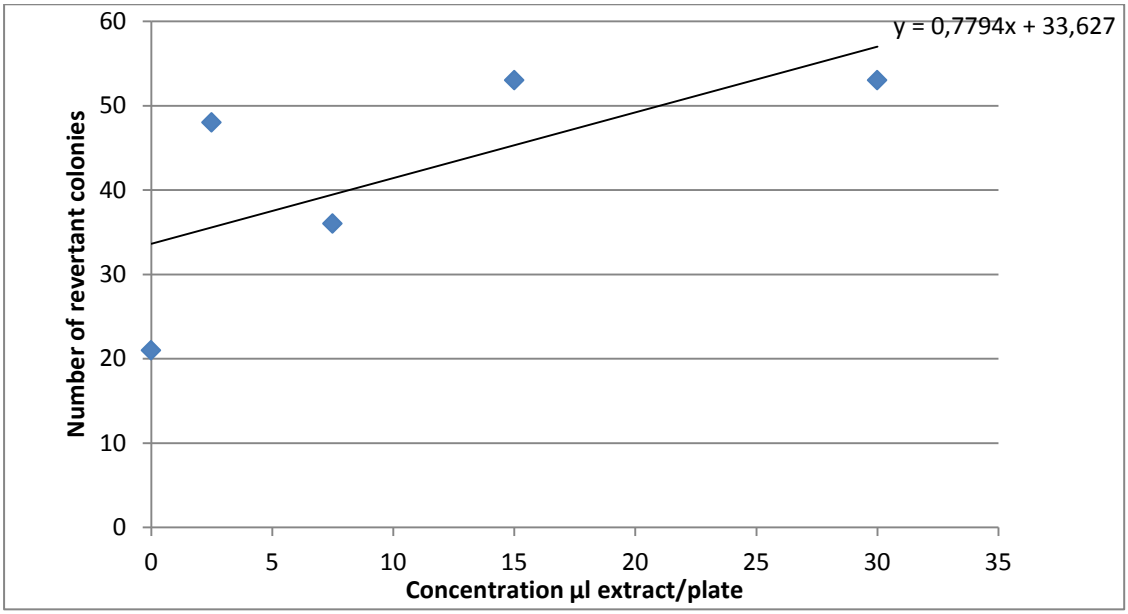
APPENDIX 1 – continued –

Table 9 Additional experiment: Mutagenic response of batch CONCAWE-A-03 (TS 205887) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98 Mean ± SD.										
plate	1		2		3		MEAN		SD		
dose (µg/plate)											
positive control		i	146		144		145	±	1		
solvent control		i	20		21		21	±	1		
2.5		i	46		50		48	±	3		
5		i		i		i		±			
7.5	33		41		33		36	±	5		
10	101		347		103		184	±	141		
15	76		30			i	53	±	33		
30	65		41			i	53	±	17		
45	36		57		33		42	±	13		
52.5	31		56		30		39	±	15		
60		i	15	NP	20	NP	18	±	4		

NP No precipitate
i Plate infected

Figure 6 Additional experiment: The mutagenicity index of CONCAWE-A-03 (TS 205887)



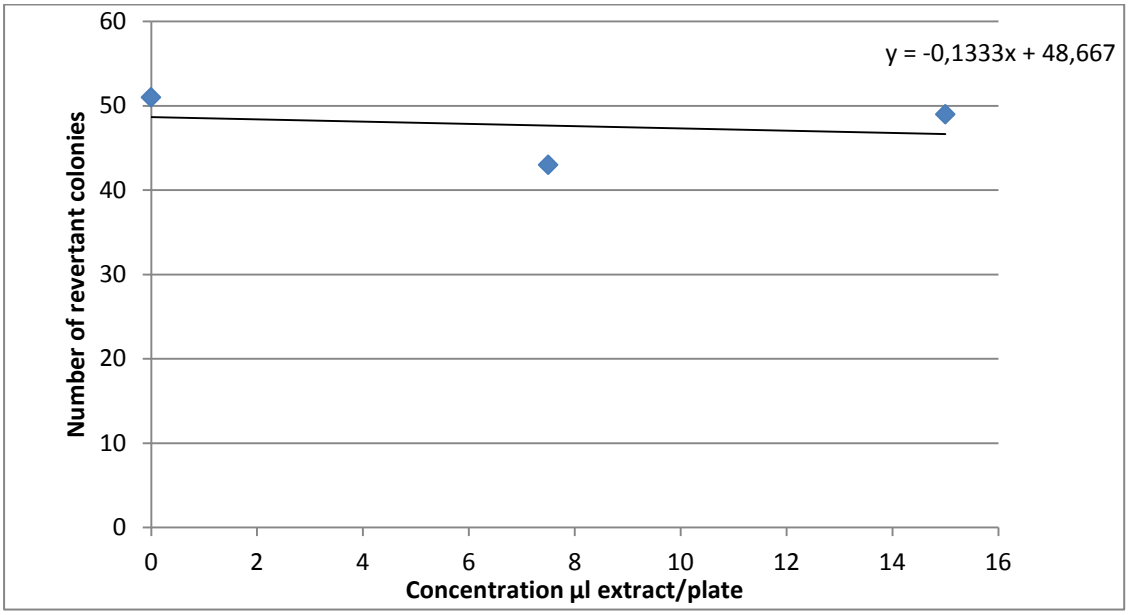
APPENDIX 1 – continued –

Table 10 Mutagenic response of CONCAWE-B-01 (TS 205888) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean, ± SD.				
plate	1	2	3	MEAN	SD
positive control	188	227	97	171 ±	67
solvent control	53	48	53	51 ±	3
7.5	46	42	41	43 ±	3
15	68	48	31	49 ±	19
30	MC	MC	MC		
45	MC	MC	MC		
52.5	MC	MC	MC		
60	MC NP	MC NP	MC NP		

NP No precipitate
MC Microcolonies

Figure 7 The mutagenicity index of CONCAWE-B-01 (TS 205888)



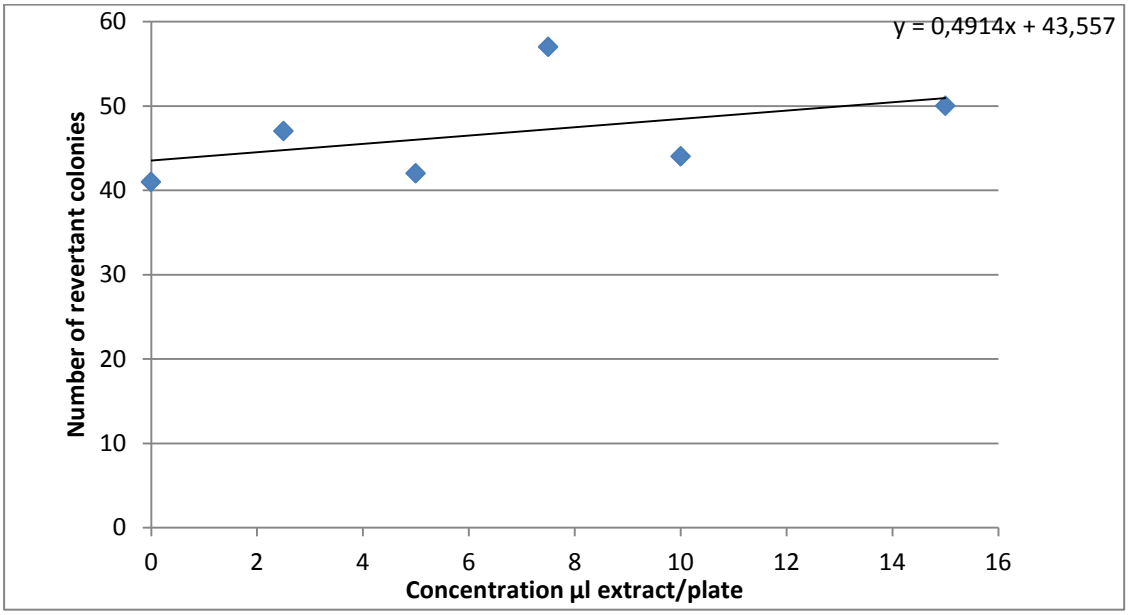
APPENDIX 1 – continued –

Table 11 Additional experiment: Mutagenic response of batch CONCAWE-B-01 (TS 205888) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean, ± SD.								
plate	1		2		3		MEAN		SD
positive control	141		87		161		130	±	38
solvent control	44		45		35		41	±	6
2.5	52		55		35		47	±	11
5	52		52		22		42	±	17
7.5	56		60		54		57	±	3
10	46		42		44		44	±	2
15	48		54		49		50	±	3
30	26		23		MC		25	±	2
45	MC		MC		MC				
52.5	MC		MC		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies

Figure 8 Additional experiment: The mutagenicity index of CONCAWE-B-01 (TS 205888)



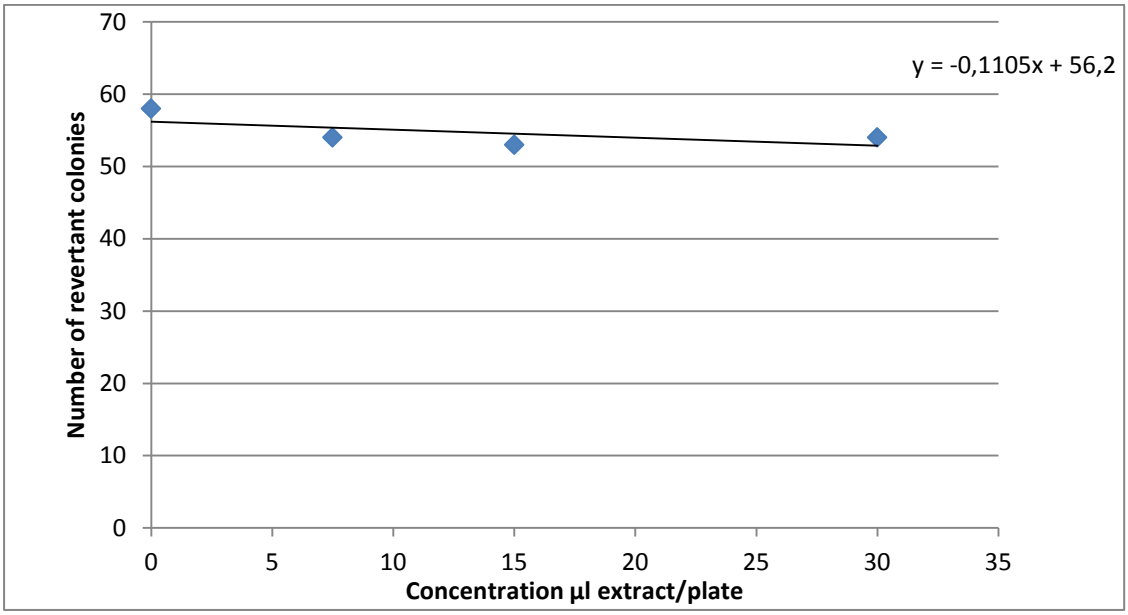
APPENDIX 1 – continued –

Table 12 Mutagenic response of CONCAWE-B-02 (TS 205889) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98 Mean ± SD.				
plate	1	2	3	MEAN	SD
positive control	165	147	181	180 ±	19
	173	212	174		
	184	197	188		
solvent control	51	52	55	58 ±	9
	50	53	57		
	71	56	75		
7.5	60	47	54	54 ±	7
15	57	52	50	53 ±	4
30	87	40	35	54 ±	29
45	MC	MC	MC		
52.5	MC	MC	MC		
60	MC NP	MC NP	MC NP		

NP No precipitate
MC Microcolonies

Figure 9 The mutagenicity index of CONCAWE-B-02 (TS 205889)



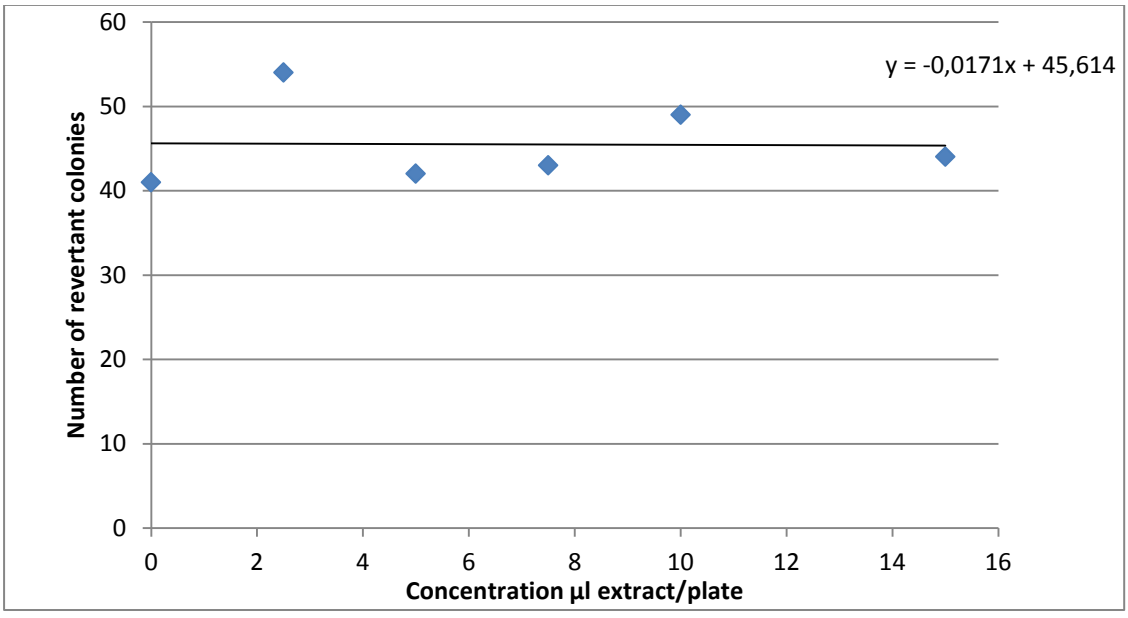
APPENDIX 1 – continued –

Table 13 Additional experiment: Mutagenic response of batch CONCAWE-B-02 (TS 205889) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.			
plate	1	2	3	MEAN SD
positive control	71	125	154	117 ± 42
solvent control	33	44	45	41 ± 7
2.5	57	52	53	54 ± 3
5	34	43	49	42 ± 8
7.5	39	44	45	43 ± 3
10	44	54	48	49 ± 5
15	38	50	45	44 ± 6
30	33	16	19	23 ± 9
45	MC	MC	MC	
52.5	MC	MC	MC	
60	MC NP	MC NP	MC NP	

NP No precipitate
MC Microcolonies

Figure 10 Additional experiment: The mutagenicity index of CONCAWE-B-02 (TS 205889)



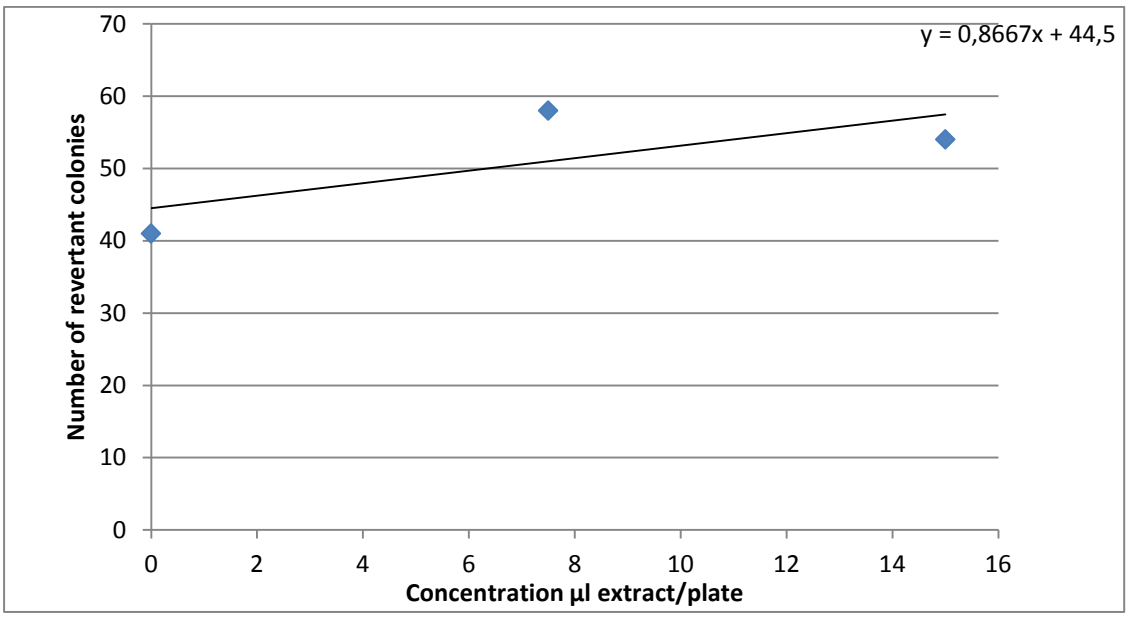
APPENDIX 1 – continued –

Table 14 Mutagenic response of CONCAWE-B-03 (TS 205890) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	188		116		170		151	±	22
	132		147		143				
	152		136		171				
solvent control	31		73		40		41	±	13
	37		46		35				
	38		31		39				
7.5	65		45		64		58	±	11
15	49		60		54		54	±	6
30	15		14		18		16	±	2
45	MC		MC		MC				
52.5	MC		MC		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies

Figure 11 The mutagenicity index of CONCAWE-B-03 (TS 205890)



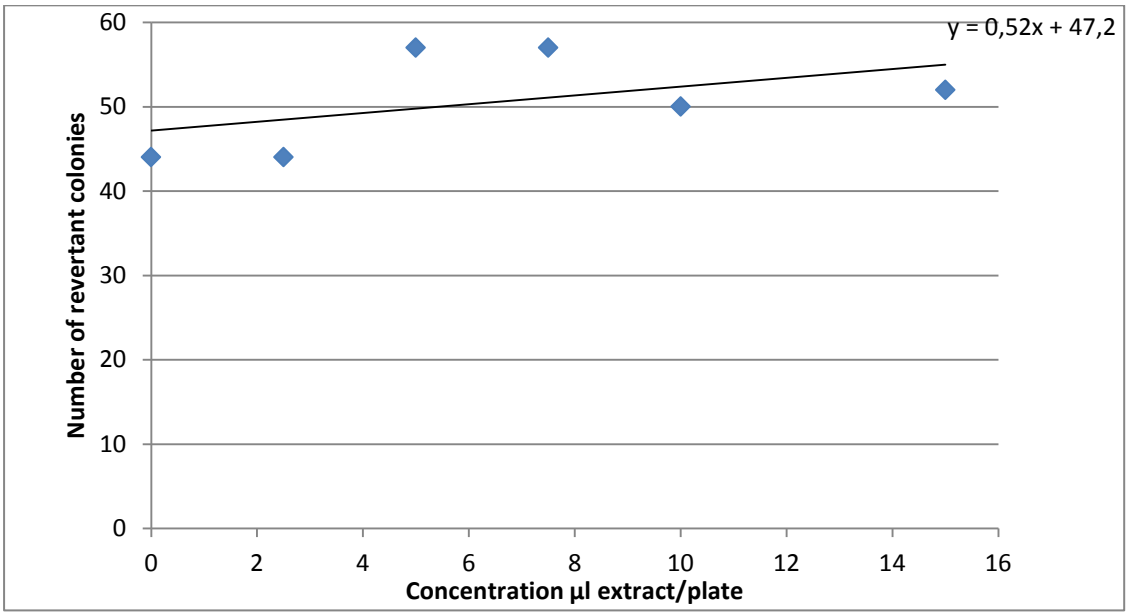
APPENDIX 1 – continued –

Table 15 Additional experiment: Mutagenic response of batch CONCAWE-B-03 (TS 205890) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.				
plate	1	2	3	MEAN	SD
positive control	188	151	141	160 ±	25
solvent control	37	50	46	44 ±	7
2.5	34	54	44	44 ±	10
5	54	57	60	57 ±	3
7.5	50	72	48	57 ±	13
10	46	49	56	50 ±	5
15	48	56	52	52 ±	4
30	34	39	31	35 ±	4
45	MC	25	30	28 ±	4
52.5	23	41	27	30 ±	9
60	MC NP	MC NP	MC NP		

NP No precipitate
MC Microcolonies

Figure 12 Additional experiment: The mutagenicity index of CONCAWE-B-03 (TS 205890)



APPENDIX 1 – continued –

Table 16 Mutagenic response of CONCAWE-C-01 (TS 205891) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	188		227		97		171	±	67
solvent control	53		48		53		51	±	3
7.5	71		50		i		61	±	15
15	650		755		i		703	±	74
30	MC		0		MC				
45	MC		0		0				
52.5	MC		0		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies
i Plate infected

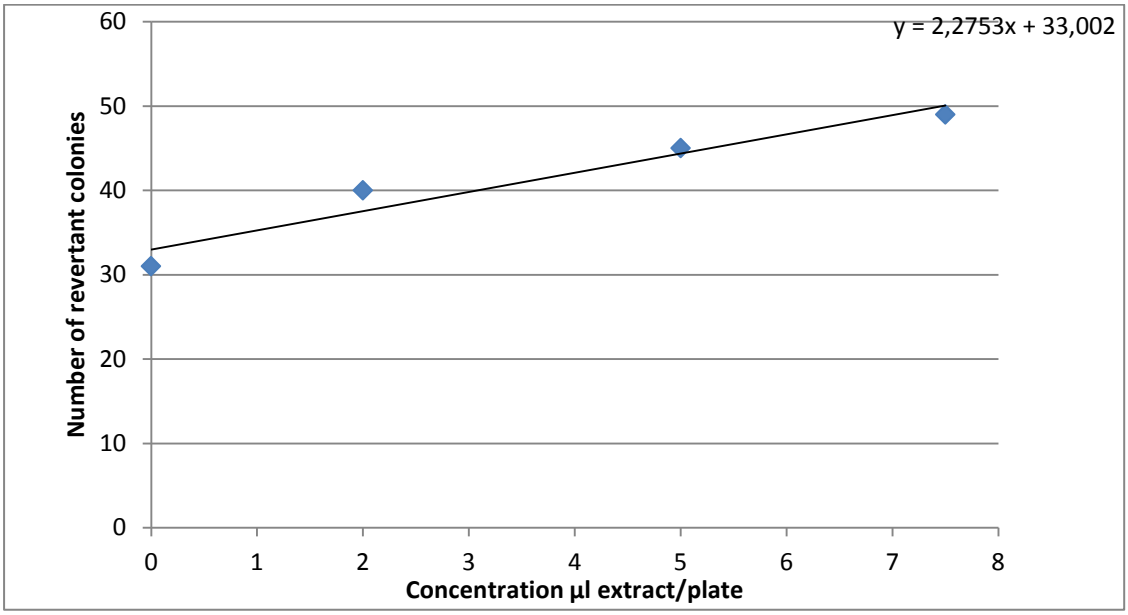
APPENDIX 1 – continued –

Table 17 Additional experiment 1: Mutagenic response of CONCAWE-C-01 (TS 205891) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	131		128		97		119	±	19
solvent control	30		34		28		31	±	3
2	54		29		37		40	±	13
5	54		29		53		45	±	14
7.5	41		41		64		49	±	13
10	34		52		33		40	±	11
15	42		20		37		33	±	12
20	42		14		23		26	±	14
30	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies

Figure 13 Additional experiment 1: The mutagenicity index of CONCAWE-C-01 (TS 205891)



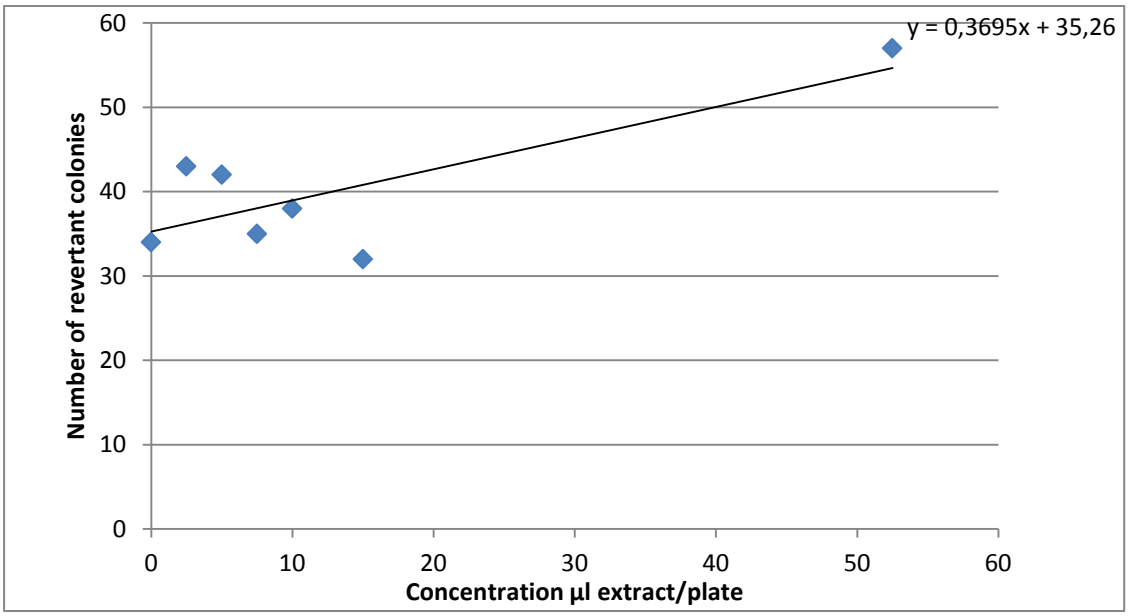
APPENDIX 1 – continued –

Table 18 Additional experiment 2: Mutagenic response of batch CONCAWE-C-01 (TS 205891) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.				
plate	1	2	3	MEAN	SD
positive control	91	84	63	79 ±	15
solvent control	37	29	37	34 ±	5
2.5	39	40	49	43 ±	6
5	37	54	34	42 ±	11
7.5	29	33	42	35 ±	7
10	29	52	33	38 ±	12
15	26	38	31	32 ±	6
30	MC	MC	MC		
45	MC	MC	MC		
52.5	56	MC	57	57 ±	1
60	20	25	MC NP	23 ±	4

NP No precipitate
MC Microcolonies

Figure 14 Additional experiment 2: The mutagenicity index of CONCAWE-C-01 (TS 205891)



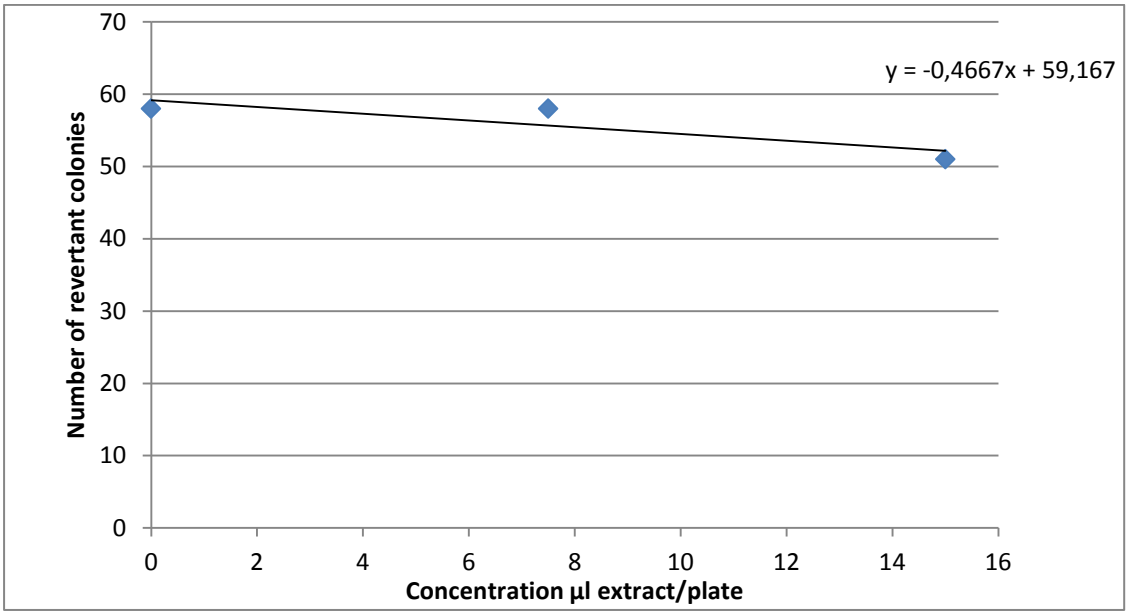
APPENDIX 1 – continued –

Table 19 Mutagenic response of CONCAWE-C-02 (TS 205892) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	165		147		181		180	±	19
	173		212		174				
	184		197		188				
solvent control	51		52		55		58	±	9
	50		53		57				
	71		56		75				
7.5	55		56		62		58	±	4
15	41		51		61		51	±	10
30	16		19		27		21	±	6
45	MC		MC		MC				
52.5	MC		MC		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies

Figure 15 The mutagenicity index of CONCAWE-C-02 (TS 205892)



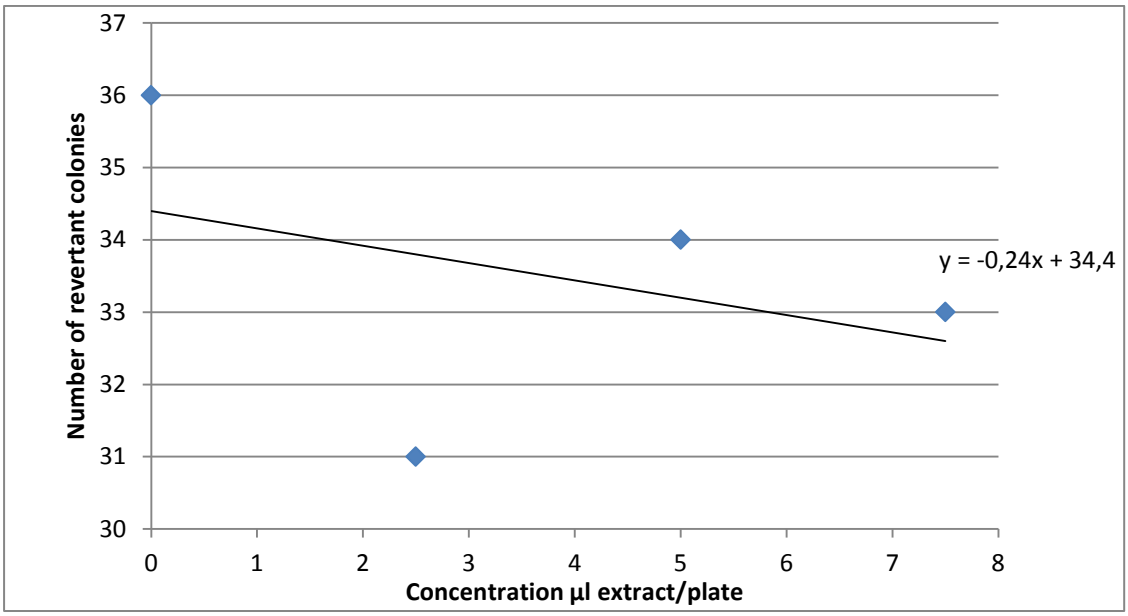
APPENDIX 1 – continued –

Table 20 Additional experiment: Mutagenic response of batch CONCAWE-C-02 (TS 205892) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98 Mean, ± SD.				
plate	1	2	3	MEAN	SD
positive control	75	79	75	76 ±	2
solvent control	36	39	33	36 ±	3
2.5	35	30	29	31 ±	3
5	42	26	34	34 ±	8
7.5	26	31	41	33 ±	8
10	20	26	34	27 ±	7
15	20	19	10	16 ±	6
30	MC	MC MC	MC MC		
45	MC	MC MC	MC MC		
52.5	MC	MC MC	MC MC		
60	MC NP	MC NP	MC NP		

NP No precipitate
MC Microcolonies

Figure 16 Additional experiment: The mutagenicity index of CONCAWE-C-02 (TS 205892)



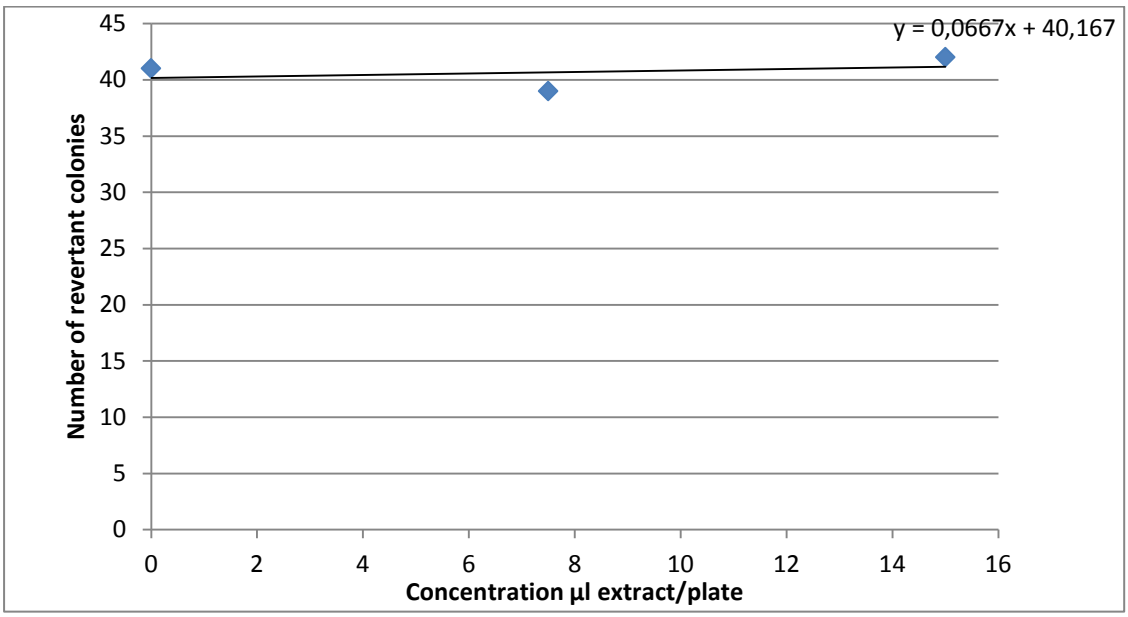
APPENDIX 1 – continued –

Table 21 Mutagenic response of CONCAWE-C-03 (TS 205893) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	188		116		170		151	±	22
	132		147		143				
	152		136		171				
solvent control	31		73		40		41	±	13
	37		46		35				
	38		31		39				
7.5	42		40		35		39	±	4
15	37		45		45		42	±	5
30	4		10		2		5	±	4
45	MC		MC		MC				
52.5	MC		MC		MC				
60	MC	NP	MC	NP	MC	NP			

NP No precipitate
MC Microcolonies

Figure 17 The mutagenicity index of CONCAWE-C-03 (TS 205893)



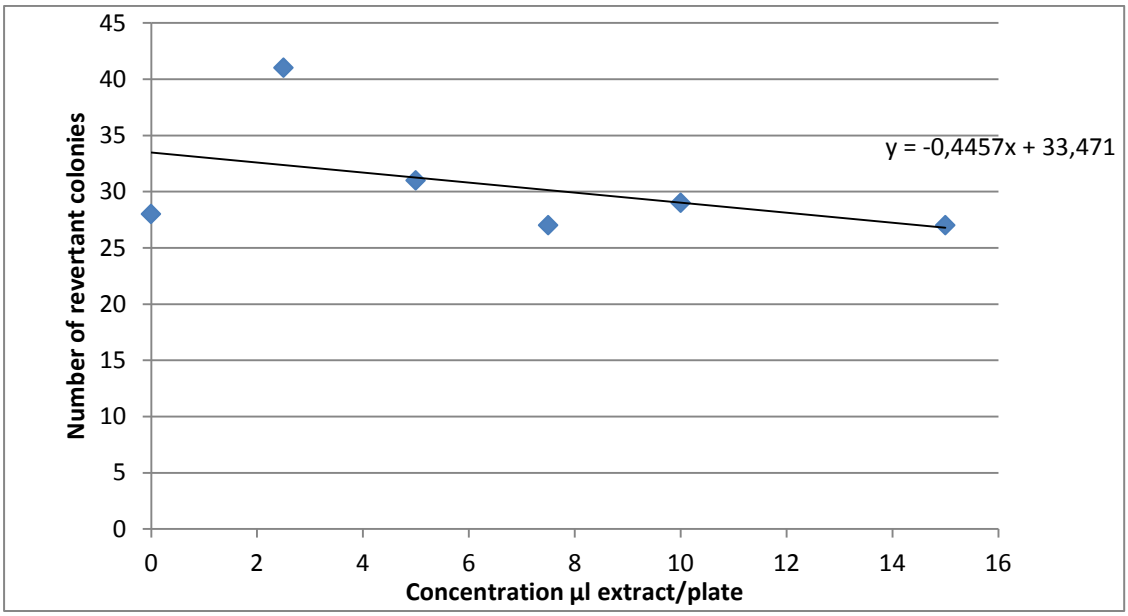
APPENDIX 1 – continued –

Table 22 Additional experiment: Mutagenic response of batch CONCAWE-C-03 (TS 205893) in the *Salmonella typhimurium* reverse mutation assay

Dose µl extract/plate	Number of revertant colonies with *the Salmonella typhimurium* tester strain TA98, Mean ± SD.								
plate	1		2		3		MEAN		SD
positive control	86		67		95		83	±	14
solvent control	34		29		22		28	±	6
2.5	41		34		49		41	±	8
5	23		44		26		31	±	11
7.5	18		33		30		27	±	8
10	30		34		22		29	±	6
15	26		33		23		27	±	5
30	MC		MC		MC				
45	MC		MC		MC				
52.5	MC		MC		MC				
60	7	NP	10	NP	3	NP	7	±	4

NP No precipitate
MC Microcolonies

Figure 18 Additional experiment: The mutagenicity index of CONCAWE-C-03 (TS 205893)



APPENDIX 2 SUPPORTING MATERIALS AND METHOD

Precipitation evaluation

Evidence of test article precipitate on the plates is recorded by addition of the following precipitation definition.

Definition	Characteristics
Slight Precipitate	Distinguished by noticeable precipitate on the plate. However, the precipitate does not influence automated counting of the plate.
Moderate Precipitate	Distinguished by a marked amount of precipitate on the plate, requiring the plate to be hand counted.
Heavy Precipitate	Distinguished by a large amount of precipitate on the plate, making the required hand count difficult.

APPENDIX 4

HFO Emissions during Barge Loading Operations on Inland Waterways – FINAL REPORT

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Philadelphia, USA

Phase I:

HFO Emissions during Barge Loading Operations on Inland Waterways

Contract number: 201305130

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June 11, 2013

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Table of Contents

List of Tables 3

List of Figures 3

Summary 4

Introduction 5

Barge Loading Operations 6

Composition 8

Emission Estimation Techniques 10

A. Empirical 10

B. Mechanistic 11

C. Mathematical 12

Conclusions 18

References 19

Appendix A 23

Appendix B 24

Appendix C 25

List of Tables

Table 1 Total petroleum hydrocarbon (TPH) content of 9 different HFO samples as a function of carbon number 10

Table 2 Vapour pressure of an HFO at multiple temperatures. 14

Table 3 Reported vapour pressure measurements for HFOs at two temperatures. 15

Table 4 Published values for the temperature expansion coefficient of HFO. 16

Table 5 Comparison of HFO emission factors from various sources. 17

List of Figures

Figure 1 Barge loading operation at a petroleum terminal. 6

Figure 2 Barge loading diagram for HFO 7

Figure 3 Loading arm being used to transfer fuel to a waiting barge. 8

Figure 4 Depletion of n-alkanes from two HFOs following controlled weathering experiments. 9

Figure 5 Relationship between vapour pressure and temperature for a marine fuel oil. 13

Figure 6 Comparison of hydrocarbon emission rate using DIAL and published emission factors. 18

Summary

Questions have recently arisen regarding the magnitude of hydrocarbon emissions during the submerge loading of inland waterway barges with commercial heavy fuel oils. Whereas, the loading and transport of some fuels can be associated with measurable releases of hydrocarbons, HFOs are highly viscous products that have a much lower volatility even at the elevated temperatures needed to facilitate transport and handling. The following study was undertaken to estimate the emissions magnitude for HFOs loaded onto tank barges for transport on inland waterways. A variety of empirical, mechanistic, and mathematical approaches were used to estimate an emission factor that could be applied to a standardized loading scenario involving cargo volumes of up to 13,000 metric tonnes and a loading temperature of 80 °C. Since hydrocarbon emissions during loading may be associated with two sources that include residual vapours from the previous cargo (assuming the compartment was not cleaned) as well as the displaced vapors from the HFO being loaded, both sources need to be considered; but the primary concern are the emissions resulting from the HFO.

The survey of available emissions estimations procedures found that empirical methods, based solely on observed associations between vaporization and some physical property of the fuel, were not suitable for use with HFOs given their low volatility. Mechanistic approaches provided a range of useful emission estimates, but the values often failed to adequately account for the elevated vapor pressure (VP) and reduced density (ρ) that HFOs display when heated to the loading temperature of 80 °C. The most robust estimates of hydrocarbon emissions were obtained following adjustment of VP and ρ using published information on the molar heat of vaporization (ΔH_{vap}) and the temperature expansion coefficient (β) for a representative HFO.

Three methods, in particular, were found to yield emission factors that were reasonably similar and of potential value. A standardized mathematical formula proposed by the USEPA for barge loading of fuels such as HFO yielded a value of 22.5±8.8 g/ton of hydrocarbon release. In contrast a generic approach developed by CONCAWE produced a somewhat lower value of 4.9 g/ton, with 95% confidence limits of 2.6-6.6 g/ton. A third value, calculated using factors promulgated by the UK Environment Agency resulted in an intermediate value of 8.9 g/ton. These results were evaluated within the context of reported underestimations of actual hydrocarbon emissions when relying on a calculated emission factor rather than remote sensing measurements. Applying a 50% percent correction factor to the values obtained using European estimation techniques brought them into alignment with values derived using the promulgated USEPA formula. The resulting estimate of hydrocarbon emissions from the barge loading of HFO for inland waterway transport was 10-20 g/ton, which is equivalent to a total mass emission of 130-260 kg for a loading duration of 10 hr on a barge capable of hauling a maximum of 13,000 tons of HFO. These emission estimates are intended to provide a benchmark for evaluating future measurements of hydrocarbon emissions under actual HFO loading conditions for inland tank barges.

Introduction

As a result of recent changes to the classification of heavy fuel oils (HFO), they are now considered to be potentially hazardous substance whose emissions may pose a risk to the environment. Not all HFOs are affected by this designation; only those with a UN 3082 designation and a flash point greater than 60 °C have been targeted for this program. The term heavy fuel oil (HFO) as used in this report refers to a final finished product rather than the refinery streams from which it was made. This distinction is important since the physical and chemical properties of the raw unfinished residuum differ from the blended product that is sold commercially as a fuel. HFOs are generally a mixture of two refinery streams that include the residua from any of several refining processes such as visbreaking, catalytic cracking, and or vacuum distillation, and a cutter stock that is used to achieve the desired characteristics (API, 2011). As such, HFOs are a diverse set of substances with an unknown and variable composition whose chemical and physical properties can fluctuate considerably. Consequently, there is a paucity of high quality data that can be used to develop emission models possessing a high degree of precision.

To better understand the nature and extent of these emissions, CONCAWE has developed a research programme to both estimate and measure hydrocarbon emissions during barge loading operations on inland waterways (ECE, 2013). The following report focuses on the emission estimation portion of this problem using several different empirical and mechanistic approaches to quantitate the vapour release. To facilitate the analysis, a standard barge loading scenario has been developed using representative operating conditions that exist at shipping terminals on European inland waterways (see Appendix B). These conditions have been based on longstanding expertise with the conditions necessary for ensuring health and environmental stewardship at loading and unloading terminals. Further information is provided in the International Safety Guide for Inland Navigation Tank-bargers and Terminals, which contains a detailed description of the health and safety precautions that are advocated for the inland shipping of petroleum products (ISGINTT, 2010).

The most critical variable affecting the estimation of hydrocarbon emissions is vapour pressure, which can vary with temperature. HFOs are often blended from several refinery streams and can include various amounts of aliphatic and aromatic hydrocarbons along with various other heteroatomic organic chemicals. Since HFOs are not defined by their composition but by their process history, physical properties, and conditions of use, detailed chemical analysis is rarely if ever performed. Consequently, estimating the vapour pressure by examining the relative contribution of its constitutive ingredients is not feasible given the thousands of chemicals that may be present.

The emissions that are encountered during a barge loading operation can be influenced by several different factors. These include: i) the presence of any residual organic vapours in "empty" cargo tanks which can be displaced as the HFO is loaded into the holding tanks; ii) the method used to load the holding tank (splash vs. submerged); iii) the volume of cargo being loaded; and iv) the loading temperature size. At room temperature, HFOs are all highly viscous materials with poor flow characteristics; transfer from the terminal to the barge therefore requires the cargo to be heated to reduce the viscosity. The elevated temperature necessitates the application of correction factors to those physical properties (e.g. vapour pressure and density)

that vary as a function of temperature. As a result, emission estimations need to consider the impact that these elevated temperatures will have on the emission rate. Since experimental determinations of emissions during barge loading are not available at this time, estimates need to be performed based on available physical property characteristics.

Barge Loading Operations

The loading of fuel barges that traverse inland waterways takes place at a smaller scale than the loading of larger marine vessels. The terminals where these operations take place may also be appreciably smaller than the larger shipping and receiving terminals designed to handle high volumes of crude oil or gasoline. Figure 1 depicts a typical barge loading operation at a storage terminal located on an inland waterway.

Figure 1 Barge loading operation at a petroleum terminal.
(Source: http://ec.europa.eu/environment/air/pdf/vocloading.pdf)

The emission estimates that follow assume a standardized scenario for loading HFO onto an inland barge. Barges come in many different configurations ranging from very large ocean going vessels to smaller inland ships that can either be self-propelled or tug driven. For the purposes of this project, a barge is considered to be any type of flat-bottomed marine vessel intended for shallow water transport of cargo on inland waterways (NAS, 1987). Further, the vessel type is restricted to tank barges for the transport of petroleum products, rather than dry bulk barges for the transport of dry goods or float barges for moving container goods (see Figure 2).

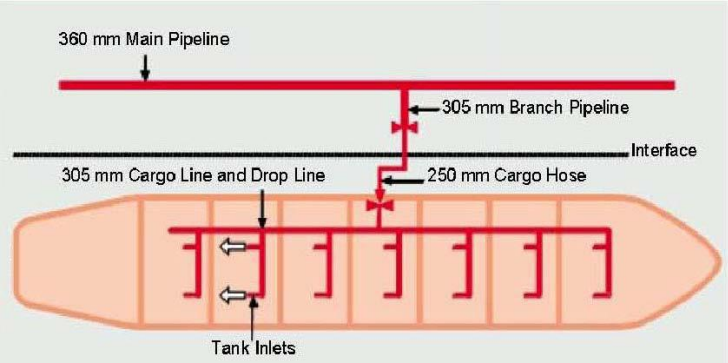

Figure 2 Barge loading diagram for HFO
(Source http://www.isgintt.org/files/Chapter_11en_isgintt_062010.pdf)

The emission estimates that follow were determined for a tank barge used to ferry commercial heavy fuel oil in a semi-liquid state between inland terminals. Tank barges can exist in any number of sizes and configurations depending on their total capacity, which may range from a few thousand tonnes over ten thousand tonnes (see Appendix B). The focus of this report is on self-propelled medium sized tank barges with a capacity of 3000 – 6000 metric tons and a maximum capacity of 13,000 metric tons. Typical dimensions for a vessel with this capacity range as high as 105 m in overall length, 16 m in breath, and 12 m in height. The number of individual loading tanks can be as many as 18 and as few as 10. Typical loading temperatures on such a vessel range from 75 – 85 °C, with 80 °C being the most commonly encountered value. To maintain product quality, HFO is never transported at temperatures greater than 99 °C.

Loading operations are accomplished through the use of a loading arm that facilitates the transfer of HFO from a dockside reservoir to the individual tanks on the barge (see Figure 3). Submerged loading is the method most encountered using a delivery pipe that extends below the surface of the liquid to minimize agitation and vapour generation. As the cargo is loaded vapours generated inside the holding tank are passed into collector pipes that are all attached to a vent riser. A single riser measuring 2 m high by 15-25 cm in diameter is typical for barges carrying an HFO. All hatches remain closed during loading to confine vapour release. The loading rate generally proceeds at 600-800 tons/hr up to a maximum of 1000 tons/hr. Loading duration can vary from 8 to a maximum of 10 hr.

Figure 3 Loading arm being used to transfer fuel to a waiting barge.
(Source http://www.nauticexpo.com/prod/emco-wheaton/marine-loading-arm-for-barges-30696-190729.html)

Composition

The precise composition of HFOs can vary widely with variable quantities high molecular weight olefinic, paraffinic, aromatic, and naphthenic hydrocarbons present together with prescribed amounts of a lower molecular weight cutter stock that is used to achieve the desired physical properties (Holmes and Bullin, 1983). The cutter stock used in a final product can originate from any of several refinery streams depending on availability, with gas oil, kerosene, and other middle distillate fractions representing the most commonly used alternatives. Most of the substances in HFO possess a high carbon number ranging from C_{20}-C_{50} and are relatively non-volatile with a negligible impact on overall emissions (Kim et al., 2011). However, the addition of cutter stocks to many HFO formulations to decrease viscosity and improve handleability can have an appreciable influence on emissions because of their higher vapour pressure. Cutter stocks generally contain hydrocarbons in the in the C_7-C_{20} range and their percent use in the final product can vary depending on the viscosity needs of the customer. In one study of a marine HFO, a cutter stock percentage of 16.2% was determined using GC (Garaniya et al., 2011). The cutter stock was found to contain volatile paraffins and aromatics with a mean molecular weight equivalent to a C_{17} hydrocarbon (i.e. 237 daltons).

Heavy fuel oils also encompasses a variety of substances whose properties are governed by the crude oil source, the method of refining, and type of cutter stock used to achieve the desired viscosity. HFOs go by a variety of names that are often aligned with their intended use. Products such as vacuum gas oil, bunker C oil, fuel oil #6, marine fuel oil, and residual oil are examples of HFOs that are found in commerce. Oftentimes the terms are used synonymously, but there are important differences. HFOs, such as fuel oil #6 or residual fuel oil are recovered after the light oils, gasoline, naphtha, and less viscous fuel oils have been distilled off. The final products are limited to commercial and industrial applications where the fuel can be heated to improve the fluidization necessary for transfer and combustion.

The extremely complex chemical composition of HFOs has limited attempts to characterize the exact chemical composition of HFOs. There have, however, been several semi-quantitative efforts at characterizing the volatile constituents that can contribute to the hydrocarbon emission during a barge loading scenario. In a recent study, using gas chromatography and mass

spectrometry, two representative samples of HFO were weathered under laboratory conditions for several months (Fernández-Varela et al., 2009). Aliquots of unweathered HFO samples were also examined at time 0 to assess the hydrocarbon fingerprint under baseline conditions. These samples showed the presence of C_{10} through C_{40} alkanes with a maximum between C_{20} and C_{24}. Weathering experiments performed for up 101 days showed that alkanes in the C_{10}-C_{17} range underwent the highest degree of depletion in the liquid sample (see Figure 4). These studies agree well with others showing that emissions from HFO samples was dominated by aliphatics with a carbon number less than C_{20} (Wang, 1999).

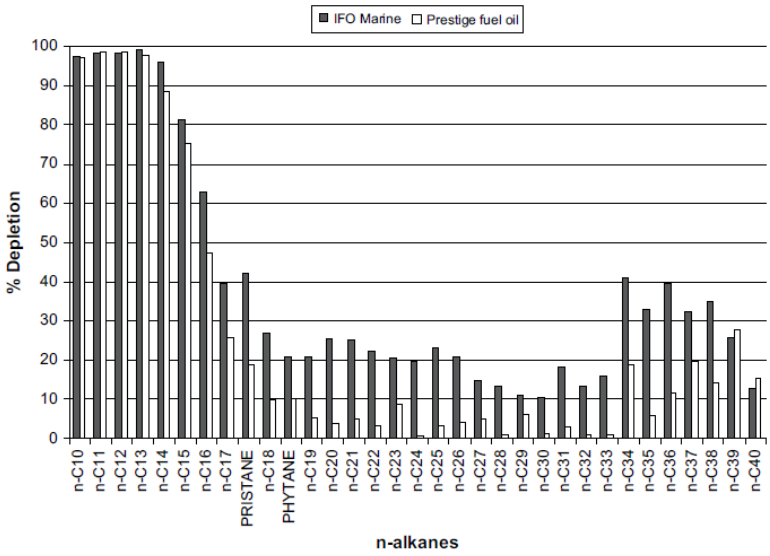

Figure 4 Depletion of n-alkanes from two HFOs following controlled weathering experiments.

Of particular note is a recent CONCAWE-sponsored study that examined the hydrocarbon composition of 9 wide ranging HFO samples collected from five refineries throughout Europe (CONCAWE, 2008). Using two dimensional gas chromatography analyses, the study determined the contribution of different categories to the total hydrocarbon content of each sample. The results, shown in Table 1, indicated that hydrocarbons with a carbon content less than C_{21} constituted 20% or less of the TPH content and that those with a carbon number less than C_{16} were less than 10%. The authors went on to note that the volatility of the different hydrocarbon categories was relatively similar with the distillation temperature of C_{10} alkyl benzenes, naphthenics, iso-paraffins, and paraffins all showing the same approximate values.

Table 1 Total petroleum hydrocarbon (TPH) content of 9 different HFO samples as a function of carbon number

Sample No.	carbon number (%TPH content)		
	total (wt%)	< C_{21} (wt%)	< C_{16} (wt%)
1	97.7	12.5	1.4
2	91.8	3.2	0.4
3	73.7	12.8	3.2
4	77.6	17.4	3.4
5	64.1	19.9	9.7
6	105.0	15.4	3.2
7	82.3	5.7	0.8
8	96.4	17.0	2.8
9	49.0	0.1	<0.1

The compositional information from the CONCAWE-sponsored study may be used to obtain a crude estimate of the emission of volatile substances during a tank loading operation lasting up to 10 hrs. This determination takes advantage of a recent weathering study using an artificial mixture of nine hydrocarbons intended to represent the volatile constituents of an HFO (Zorzetti et al., 2011). The average percent loss of the three C_{10} hydrocarbons (decane, 1,2,3,5-tetramethylbenzene, and naphthalene) in the mixture averaged 36% during ten hours of controlled heating in a chamber operated at a temperature of approximately 25 °C and a flow rate of 11.8 L/min (see Appendix D). Multiplying this average fractional loss with the maximum amount of hydrocarbons with a carbon content < C_{21} (i.e. 20% w/w) from the CONCAWE study yields a very rough estimate of hydrocarbon vapourization equal to 72 g/ton of HFO over a 10 hr period. This value provides a simple baseline emission estimate using readily available experimental information that can be compared to a more detailed estimate of total hydrocarbon emission from terminal loading of all fuel types including at a refinery in the US. Using a USEPA AP-42 emission factor of 3.4 lbs/1000 gallons loaded, McIlvaine calculated an emission factor of 426 g/ton for all types of petroleum fuels including gasoline. This value is approximately 6-fold higher than the value shown above for HFO, which is reasonable given the very rudimentary nature of the calculation.

Emission Estimation Techniques

A. Empirical

Several different approaches can be taken to estimate total hydrocarbon emissions from inland waterway barges. Empirical methods have been developed that take advantage of observed relationships between the rate of emission and some physical or chemical characteristics of the petroleum product. A good example of this approach is a technique developed by Fingas, which takes advantage of the fact that the evaporation of volatiles from petroleum products such as

heavy fuel oils is independent of vapour saturation in the air boundary layer just above the liquid surface (Fingas, 2004). As a result, the calculation is free from the influence of wind speed, liquid turbulence, surface area, film thickness, or scale size. This allowed the development of simple mathematical relationships to describe the degree of evaporation in terms of the distillation percentages measured at 180 °C. The main limitation of this method for HFO is the extremely low volatility of fuel oil products even at elevated temperatures. Consequently, only a very small amount of HFO will distill at 180 °C, which calls into question the reliability of the approach for substances that are at the extremes of the volatility range. Two separate equations were developed, whose use was dependant on the shape of the evaporation curve (i.e. a square root or a logarithmic function). Although extensive testing was performed using a wide variety of crude oils and petroleum products, very few HFOs were examined during model verification (Fingas, 2004). The evaporation rate of a single high viscosity fuel oil was best described using a square root function with the following general form.

$$\%Ev = [0.0254x(\%D) + 0.01x(T-15)] \times \sqrt{t} \qquad (1)$$

Where:
%Ev – percent evaporation (w/w)
%D – percent distillation @ 180 °C
T – temp °C
t – time (min)

Using the loading time and temperature of 600 min and 80 °C, respectively, together with distillation percentage of 0.4 for an HFO, this empirical approach yielded unrealistically high emission rates that were in excess of 150 kg/ton. These results indicate that the low volatility of HFOs severely limits the utility of empirical models such as those formulated above for estimating evaporative emissions under actual use conditions.

B. Mechanistic

Other methods are more mechanistic in nature and take advantage of early API work that measured the emissions during transfer operations at US refineries (API, 1981). These data allowed the USEPA to develop emission factors for a host of refinery operations including the barge loading of fuels ranging from gasoline to HFO. Hydrocarbon emission factors, termed AP42 factors, have been in existence for nearly 50 years and have seen widespread deployment in countries throughout the world (Duprey, 1968). Whereas, AP42 factors were initially aimed at documenting the releases that accompanied refinery manufacturing operations, the 4th edition released in 1985 began to examine the emissions from marine vessel loading as well (USEPA, 1985). These emission factors were developed for a range of petroleum products including residual fuel no. 6 that was loaded onto shallow water barges with a draft of 10-12 ft (USEPA, 2008). The EPA endorsed emission factor for the submerged loading of HFO onto tank barges has a value of 9.0×10^{-5} lb/1000 gal, which is equivalent to 0.01 g/ton of HFO shipped. To calculate a yearly emission rate from this factor some knowledge is needed of the European transport volume on inland waterways. ADN has stated that about 2500 ktons/yr of HFO are transported by barge from German refineries using inland vessels (ECE, 2011). Using a fuel density factor of 890.1 kg/m^3 for liquid fuel oil at a temperature of 60 °F, this shipping rate equates to 27,500 tons/yr of transported HFO and an overall hydrocarbon emission rate of 27,500

tons/yr. This estimate, however, assumes an average temperature during bulk loading of 16°C (60 °F). Since the actual average temperature during loading is expected to be more in the range of 80 °C, the value is highly suspect and likely underestimates the emissions that occur at realistic conditions. A more accurate estimate is possible following a temperature adjustment of the vapour pressure using Clausius-Clapeyron equation (see next section).

The EPA promulgated emission factor for HFO contrasts with the value proposed by the California Air Resources Board (CARB). The CARB factor was used to create an emissions inventory for terminals located in state of California during the year 1976 (CARB, 1981). The emission factor of 0.3 lb/1000 gal took into consideration prior cargos and residual vapours that remain in the tanks when they are not cleaned. Although the emission factor specifically applies to a residual fuel oil, few details are provided regarding the loading temperature or the type of marine vessel that was examined. The factor equates to an emission of 37.6 g/ton of HFO loaded onto a ship or barge, which is more than 3 orders of magnitude greater than the value proposed by the USEPA. Lewis also proposed an emission factor to be used in conjunction with a life cycle analysis for the production of fuels such as diesel, gasoline, liquefied petroleum gas, kerosene, compressed natural gas (CNG), rapeseed methyl ester and HFO (Lewis, 1997). A generic factor of 4.35 x 10-4 g/Cj was proposed for the terminal loading of HFO onto an unspecified type of vessel. This value, expressed in terms of energy output (i.e. gigajoules) can be equated to HFO mass using a conversion factor of 42.84 Gj/ton for an HFO with unknown characteristics. The resulting emission factor of 1.7 g/ton is intermediate between the values championed by the USEPA and CARB. In each of these instances, however, there has been no correction for the elevated vapour pressure or decreased density that accompanies the loading of HFO at an elevated temperature.

C. Mathematical

In Europe, the UK Environment Agency offers a more reasonable mathematical approach for estimating hydrocarbon emissions from the barge loading of any chemical substance with a known vapour pressure and density (EA, 2007). The approach is based on recommendations published by the Institute of Petroleum (IP), which advocated use of their protocol for satisfying VOC emission reporting requirements under the European Monitoring and Evaluation Programme (EMEP) and other UNECE initiatives (IP, 2000). The UK adaptation of the IP protocol utilizes the following formula for an inland barge that has been cleaned beforehand.

$$E_{HFO} = \frac{1.29 \times M_{HFO} \times VP_{HFO}}{RHO_{HFO} \times 1x10^5} \qquad (2)$$

Where:
E_{HFO} – emissions per loading event (kg)
M_{HFO} – mass of HFO loaded onto barge (kg)
VP_{HFO} – HFO vapour pressure at loading temperature (Pa)
RHO_{HFO} – HFO density at loading temperature (kg/m^3)

This approach is highly dependent upon having an accurate measure of vapour pressure and density at the temperature of interest (i.e 80 °C); but most published values for HFO are given at temperatures that are either much higher or much lower. A similar situation arises with the basic

formula that the USEPA encourages users to employ when the supplied emission factors are not applicable.

$$L_L = \frac{12.46 \times S \times P_{HFO} \times M_{HFO}}{T} \qquad (3)$$

Where:
L_L – loading loss per 1000 gallons of liquid loaded (lb/1000 gal)
S – saturation factor for submerged loading onto barges (0.5 dimensionless)
P_{HFO} – true vapour pressure for HFO (psia)
M_{HFO} – vapour molecular weight for HFO (lb/lb-mole)
T – temperature for bulk loaded liquids (°R)

To use these methods, a mathematical adjustment is needed to correct for the temperatures that exist on a barge during the loading of HFO. The vapour pressure of HFO at the 80 °C (176 (°K) loading temperature can be determined using the Clausius-Clapeyron equation (see equation 4), which estimates the vapour pressure at any temperature assuming that measurements are available at another known temperature (Jones, 2010). This adjustment is made possible by the fact that the shape of vapour phase diagram for most liquids, including HFO, has a similar curvi-linear shape (see figure 5).

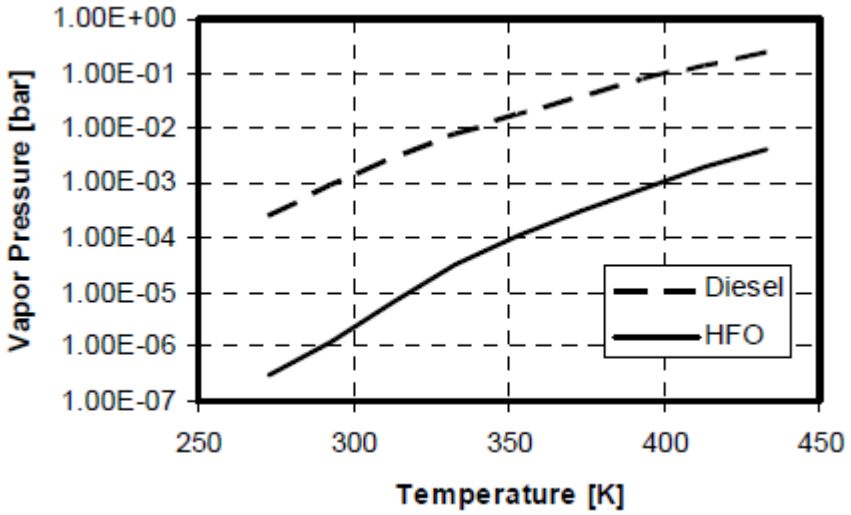

Figure 5 Relationship between vapour pressure and temperature for a marine fuel oil. (Source: Kyriakides et al., 2006)

Although, the Clausius-Clapeyron equation is intended for use with pure liquids it also provides a reasonably good approximation for petroleum mixtures (Jones, 2010).

$$P_2 = P_1 \times \exp[-\Delta H_{vap}/R \times (1/T_1 - 1/T_2)] \qquad (4)$$

Where:
P_2 – the vapour pressure of interest (Pa)
T_2 – the corresponding temperature at the vapour pressure of interest (°K)
P_1 – the vapour pressure at another known temperature (Pa)

T_1 – the temperature for the secondary vapour pressure measurement (°K)
R – gas constant (8.3145 J/mol/°K)
ΔH_{vap} – molar heat of vapourization (J/mol)

The key to solving the Clausius-Clapeyron equation is finding a suitable value for the molar heat of vapourization, which is defined as the amount of heat required to volatilize 1 mol of a liquid. ΔH_{vap} may either be measured in a calorimeter or calculated if vapour pressure measurements are available at a minimum of two temperatures. Although the vapour pressure of many HFOs has been measured, the values are typically confined to a single temperature or they are associated with an HFO that is not representative of the product shipped at inland terminals. As such, published vapour pressure determinations using accepted methodologies can show considerable variability with values of < 0.13 to 2.0 kPa at 20 °C reported by some groups (API, 2011). The USEPA has released vapour pressure determination for residual fuel oil no.6 (see Table 2), but the values are suspiciously low when compared to those from more authoritative sources (USEPA, 2008).

Table 2 Vapour pressure of an HFO at multiple temperatures.

Vapour Pressure (Units)	**Residual Oil No. 6**						
	VP@40 °F (277.6 °K)	**VP@50 °F (283.2 °K)**	**VP@60 °F (288.7 °K)**	**VP@70 °F (294.3 °K)**	**VP@80 °F (299.8 °K)**	**VP@90 °F (305.4 °K)**	**VP@100 °F (310.9 °K)**
psi	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
Pa	0.1379	0.2068	0.2758	0.4137	0.6205	0.8963	1.3100
kPa	0.00014	0.00021	0.00028	0.00041	0.00062	0.00090	0.00131

Source: http://www.epa.gov/ttn/chief/ap42/ch07/final/c07s01.pdf (USEPA, 2008)

Two published values of ΔH_{vap} were located in the literature, but both were associated with an HFO that is not representative of the fuel oils that are sold as final products. The first value of 232 kJ/kg may only apply to the cutter stock that was used to prepare a residual fuel oil for use in combustion experiments (Goldsworthy, 2006). A second, appreciably higher, value of 636 kJ/kg is reportedly associated with a marine fuel oil with a reasonable density of 953.7 kg/m^3, but there are valid concerns about its accuracy given its very high magnitude (Kyriakides et al., 2006). Another approach to determining ΔH_{vap} relies on a rearranged version of the Clausius-Clapeyron equation that requires reliable vapour pressure measurements at a minimum of two temperatures (see equation 5). The vapour pressure of HFOs can vary widely as a result of the broad range of formulation possibilities that exist. CONCAWE and API have both made attempts at characterizing the vapor pressure for the HFOs produced within a refinery or sold commercially (CONCAWE, 2010; API, 2011). The API vapour pressure extremes are generally limited to a compilation of reported values from a small number of MSDSs for products distributed in the United States. The CONCAWE summary of vapour pressure data on the other hand is far more comprehensive and focuses on HFOs that are produced at European refineries.

$$\Delta H_{vap} = [-R \times \ln(P_1/P_2)]/(1/T_1 - 1/T_2) \qquad (5)$$

A first attempt at using the vapour pressure data published by the USEPA (see Table 2) yielded an ΔH_{vap} value of 121.3 kJ/kg when assuming an average HFO molecular weight of 400 daltons (USEPA, 2006). Although the USEPA data were associated with a residual fuel oil #6, the reported vapour pressure values are again suspiciously high and patently untenable. A reasonable approximation of ΔH_{vap} was obtained, however, using reported vapour pressure measurements from the recent CONCAWE compendium of physical property information for HFOs (CONCAWE, 2010). Of the three HFO products with measured results at two temperatures, the results for a residual fuel oil sample (CAS 68476-33-5) were judged to be the most relevant (see table 3). The flash point for sample 3 was above flashpoint cutoff for a UN 3082 designation which is consistent with the overall flashpoint range for residual fuel oils. The flash point for HFOs with the same CAS no. was 70-168 °C, which encompasses the 60 °C cutoff. Using the vapour pressure values at 120 and 150 °C, a final average ΔH_{vap} value of 10.4 kJ/kg was determined for the two residual fuel oil samples. Substituting this value into the Clausius-Clapeyron equation as depicted in equation 4 yielded an average vapour pressure of 657 Pa (1.45 psi) at 80 °C (353.2 °K) when P_1 was assigned a value of 727 or 791 Pa @ 120 °C (393.2 °K).

Table 3 Reported vapour pressure measurements for HFOs at two temperatures.

Sample No.	**CAS No.**	**Flash Point (°C)**	**VP @ 120 °C (kPa)**	**VP @ 150 °C (kPa)**	**ΔH_{vap} (kJ/kg)**	**Description**
1	64741-45-3	NA	0.090	0.097	---	tower residue
2	64741-81-7	NA	0.024	0.063	---	heavy petroleum distillate
3	68476-33-5	88-109	0.727	0.800	11.0	residual fuel oil
4	68476-33-5	NA	0.791	0.861	9.8	residual fuel oil

NA – not available
Source: Compilation of selected physical-chemical properties for petroleum substances (CONCAWE, 2010)

The estimated ΔH_{vap} value was used together with several other parameters to calculate the hydrocarbon emissions resulting from the barge loading of residual fuel oil. Two parameters, in particular, provided the remaining information necessary to carry out the final calculation. The saturation factor (S) adjusts for the degree of air saturation that occurs as the tank is filled and possesses a value of 0.5 for submerge loading of inland barges (USEPA, 2008). In addition, a vapour molecular weight of 190 lb/lb-mole for residual fuel oil no. 6 was listed for use in equation 3 by the USEPA. By this approach, the final temperature adjusted emission factor for barge loading of a commercial fuel oil at 80 °C was 22.5 g/ton. The USEPA indicates that the accuracy of this calculation is ± 30%, which gives an emission factor ranging from 15.7 to 29.2 g/ton (see Table 5). For a barge capable of loading a maximum of 13,000 tons of HFO, the predicted hydrocarbon emissions would range from 204-380 kg. Since HFO is submerge-loaded into a tank barge, the released vapours tend to accumulate near the liquid surface. It would be expected that the major of the hydrocarbon vapours would be released in the latter stages of the loading cycle when the head space (i.e. ullage) is less than 10-15 feet high.

The validity of the estimate using USEPA sanctioned equations was corroborated with the method developed by the UKs Environment Agency (see equation 2). A realistic application of this approach requires the determination of a temperature adjusted density value to correct for the elevated temperatures at loading. Equation 6 provides a method for correcting liquid density that is dependent on a value for the temperature expansion coefficient (Jones, 2010).

$$\rho_1 = \rho_0/(1+\beta(T_1-T_0) \qquad (6)$$

Where:
ρ_1 – the density of interest (g/cm^3)
T_1 – the corresponding temperature at the vapour pressure of interest (°C)
P_0 – the density at another known temperature (g/cm^3)
T_0 – the temperature for the secondary density measurement (°C)
β – temperature expansion coefficient (°C^{-1})

The temperature expansion coefficient (β), also known as a volume correction factor, is an important conversion factor that allows customers to calculate the mass of shipped fuel oil at a standard temperature. As such, values for β are available from a several engineering web sites that focus on petroleum products. The temperature expansion coefficients for various HFOs show a surprising consistency across product types. A cursory evaluation of published values produced values ranging from 0.00064-0.0008 °C^{-1}. More robust measures of β may be available, but they are contained in proprietary tables from standard setting organizations that restrict distribution to organizational members and sponsors. An average β value of 0.0007 was used along density limits cited by CONCAWE for residual fuel oil sample no. 3 listed in Table 3 (CONCAWE, 2010). These limits of 0.988 and 0.995 g/cm^3 @ 15 °C yielded an average HFO density of 0.948 g/cm^3 @ 80 °C. The average density decrease for a change in HFO temperature from 15 °C to 80 °C was 4.4%.

Table 4 Published values for the temperature expansion coefficient of HFO.

Description	**Temperature Expansion Coefficient (°C^{-1})**	**Source**	**Website**
heavy fuel oil	0.00068	Akwaugh	http://www.akwaugh.com/info1.htm
gas oil	0.00080	Esso	http://www.jonesoil.ie/fs/doc/misc-datasheets/gasoil.pdf
bunker oil	0.00064	Bright Hub Engineering	http://www.brighthubengineering.com/marine-engines-machinery/35476-bunkering-operations-precautions-and-corrections/

The emission estimates using the USEPA methods were compared to the value calculated using CONCAWE's modification of the approach developed by the Institute of Petroleum (IP, 2000; CONCAWE, 2009). CONCAWE proposed using an emission factor of 7.45 g/m^3/kPa for the generic loading of barges with a product having a known vapour pressure. This value yielded an emission factor of 4.9 g/ton when using a temperature adjusted vapour pressure of 0.624 kPa @ 80 °C. This value, while lower than the USEPA, is not unreasonable and covers the range of

plausible estimates. The most recent version of EMEP/EEA Emissions Inventory Guidebook has mostly adopted the CONCAWE emission factor for barge loading and assigned a value of 7 $g/m^3/kPa$, but went further and assigned 95% confidence limits of 4 $g/m^3/kPa$ and 10 $g/m^3/kPa$ to this value (EMEP, 2009). The corresponding temperature adjusted limits for HFO loading result in emission factors ranging from 2.6 to 6.6 g/ton, which suggests relatively little variability and a high degree of reliability in the CONCAWE estimates. Using the preceding temperature adjusted vapour pressure and density values, hydrocarbon emission estimates were also calculated using the UK Environment Agency approach described in equation 2 (EA, 2007). This equation, which was also derived from the analysis performed by the Institute of Petroleum, considers the role of both vapor pressure and density on the final emissions estimate. The emission factor relied on values for M_{HFO} (13,000,000 kg), VP_{HFO} (657.5 Pa), and RHO_{HFO} (947.8 kg/m^3) and was determined to be 8.9 g/ton, which was intermediate between the USEPA and CONCAWE-derived factors.

Table 5 Comparison of HFO emission factors from various sources.

Source (year)	Hydrocarbon emission factors for barge loading		Comments
	lb/1000 gal	g/ton	
Cal EPA (1989)	0.3	37.9	marine vessel loading of residual fuel oil
Lewis (1997)		1.7	originally stated as 0.04 g/Gj (gigajoule); HFO energy output is 42.84 Gj/ton
AP42 (2008)	0.00009	0.01	residual fuel oil No. 6 loaded onto inland barge
Zorzetti et al. (2011)		72	based on evaporation of C10 model hydrocarbons
USEPA (2008)[A]		**22.5 (15.7-29.2)**	fully adjusted for elevated HFO loading temperature
CONCAWE (2009)[A]		**4.9 (2.6-6.6)**	calculated from generic formula using adjusted vapour pressure for an HFO cargo
EA (2007)		**8.9**	temperature correction factors employed for vapour pressure and density

[A] Range of HFO emissions factor calculated using information from available sources. Bold type: estimates judged to be the most reliable.

Further refinement of these estimates to a range that has practical value requires an evaluation of past validation studies focusing on refinery operations. Recent criticism has been levied against the use of emission factors to estimate emissions from refinery operations because they purportedly underestimate hydrocarbon releases when compared to actual measurements that relied on Differential Absorption Lidar (DIAL) or other remote sensing devices for quantitation (Cuclis, 2012). These direct measurement methodologies have purportedly yielded VOC emission values that were 5-10-fold higher than the estimates obtained using AP42 emission factors. The difference between the two approaches were attributed to the ideal operating conditions that are often assumed to exist when using emission factors and the less than ideal situations that often exist on site. CONCAWE performed a similar evaluation that focused on the emissions differential for barge loading operations using factors promulgated by API (i.e.

API 2517 and API 2517 addendum); however the emission factors employed were for a volatile fuel (i.e. gasoline) rather than a non-volatile HFOs (CONCAWE, 1995). The results shown in Figure 6 show that the emission rate of hydrocarbons using the DIAL direct measurement method was 56% greater than the values using API emission factors. These data suggest that published emission factors are reasonably robust and that the deviations between measured and predicted emissions occur when the values are applied to the large number of sources that can be found within a petroleum refinery.

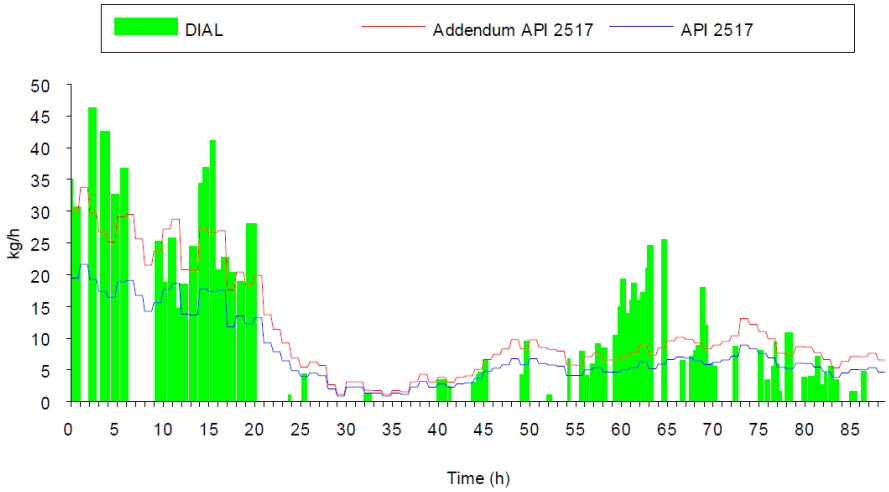

Figure 6 Comparison of hydrocarbon emission rate using DIAL and published emission factors. Source: http://193.219.133.6/aaa/Tipk/tipk/4_kiti%20GPGB/46.pdf (CONCAWE, 1995)

Taking these differences into consideration, the range of hydrocarbon emission factors for the submerge loading of HFOs onto inland barges is estimated to range from 10-20 g/ton. These limits take into consideration the loading temperature of 80 °C, the range of estimates from the three most feasible approaches (see Table 5), and the application of 50% correction factor to low end estimates that employed the CONCAWE and UK EA procedures. For a barge with maximum capacity of 13,000 tons the emission of hydrocarbons is estimated to range from 130 to 260 kg and the average rate of release over the 10-hr loading period is predicted to be 13 to 26 kg/hr.

Conclusions

The emissions of hydrocarbons during the loading of HFO on inland barges were investigated using various approaches that have been advocated by knowledgeable authorities from the US and Europe. Empirical, mechanistic, and mathematical methods were evaluated to determine their suitability for yielding a reliable estimate applicable to HFOs meeting the UN 3082 fuel designation. The techniques showed considerable variability with the empirical approaches being wholly unsuitable and the mechanistic approaches yielding values that could not account for the volatility and density changes that occur at elevated loading temperatures. Two methods from Europe and one from the US were ultimately judged to provide the most reliable estimates, since they were able to compensate for the increased vapour pressure and decreased density of HFO at the actual average loading temperature of 80 °C. Considering the results from all three methods and following adjustment for purported underestimations using emission factors instead

of actual measurements, a final emission factor of 10-20 g/ton was determined. This factor may be used to calculate an emission rate under any barge loading scenario where the total mass of HFO loaded and the total loading time are known.

References

ABS (1984). Notes on Heavy Fuel Oil. American Bureau of Shipping. Houston, TX. http://www.eagle.org/eagleExternalPortalWEB/ShowProperty/BEA%20Repository/Rules&Guides/Current/31_HeavyFuelOil/Pub31_HeavyFuelOil

AEA (1997). Fuel and Energy Production Emission Factors. Methodologies for Estimating Air Pollutant Emissions from Transport. Report 18797001\FINAL\2. AEA Technologies. Harwell, England. http://www.inrets.fr/ur/lte/cost319/MEETdeliverable20.pdf

API (1981). Atmospheric Hydrocarbon Emissions from Marine Vessel Transfer Operations. Pub. No. 2514A, 2nd edition. American Petroleum Institute. Washington, DC.

API (2011). Heavy Fuel Oils Category, Analysis and Hazard Characterization. American Petroleum Institute. Washington, DC. http://www.epa.gov/hpv/pubs/summaries/heavyfos/c15368hc.pdf

Balu, S. (2011). Bunkering Operations: Precautions, Checklists, Calculations & Corrections Explained. Bright Hyb Engineering. Troy, NY. http://www.brighthubengineering.com/marine-engines-machinery/35476-bunkering-operations-precautions-and-corrections/

CARB (1981). Inventory of Emissions from Marine Operations within the California Coastal Waters. ARB-A6-208-30. California Air Resources Board, Sacramento, CA. http://www.arb.ca.gov/research/apr/past/a6-208-30a.pdf

CONCAWE (2008). CONCAWE Risk Assessment Project: Detailed Compositional Analysis of Heavy Fuel Oil (HFO) Samples. Report GS.08.50772. Shell Global Solutions. Chester, England.

CONCAWE (2009). Air Pollutant Emission Estimation Methods for E-PRTR Reporting by Refineries, 2009 Edition. Conservation of Clean Air and Water in Europe. Brussels, Belgium. http://www.csb.gov.tr/db/ippceng/icerikbelge/icerikbelge1195.pdf

CONCAWE (2010). Compilation of Selected Physico-chemical Properties of Petroleum Substances. Conservation of Clean Air and Water in Europe. Brussels, Belgium.

CONCAWE (1995). VOC Emissions from External Floating Roof Tanks: Comparison of Remote Measurements by Laser with Calculation Methods. Report No. 85/52. Conservation of Clean Air and Water in Europe. Brussels, Belgium. http://193.219.133.6/aaa/Tipk/tipk/4_kiti%20GPGB/46.pdf

CONCAWE (date unknown). Category Justification for Petroleum Substances. Heavy Fuel Oil Components. Conservation of Clean Air and Water in Europe. Brussels, Belgium.

Cuclis (2012). Why emission factors don't work at refineries and what to do about it. 20th International Emission Inventory Conference, August 13-16. Tampa, FL. http://www.epa.gov/ttnchie1/conference/ei20/session7/acuclis.pdf

Duprey, R.L. (1968). Compilation of Air Pollutant Emission Factors. Pub. No. 999-AP-42. U.S. Department of Health, Education and Welfare, National Center for Air Pollution Control. Durham, NC. http://www.epa.gov/ttn/chief/ap42/oldeditions/1st_edition/ap42_phs_1968.pdf

EA (2007). Emission Scenario Document on Transport and Storage of Chemicals. Environment Agency. Bristol, United Kingdom. http://a0768b4a8a31e106d8b0-50dc802554eb38a24458b98ff72d550b.r19.cf3.rackcdn.com/scho0407bmlk-e-e.pdf

ECE (2011). Heavy Fuel Oil. Report INF.12. Economic Commission for Europe, Inland Transportaton Committee, Working Party on the Transport of Dangerous Goods. Bern Switzerland. http://www.unece.org/fileadmin/DAM/trans/doc/2011/dgwp15ac1/ECE-TRANS-WP.15-AC1-11-BE-inf12e.pdf

ECE (2013). CONCAWE/EUROPIA Study on HFO AND Emissions and Exposure Assessment. Report INF.33. Economic Commission for Europe, Inland Transportaton Committee, Working Party on the Transport of Dangerous Goods. Bern Switzerland. http://www.unece.org/fileadmin/DAM/trans/doc/2013/dgwp15ac2/WP15-AC2-22-inf33e.pdf

EMEP (2009). EMEP/EEA Emission Inventory Guidebook. Part B Sectorial Guidance Chapters, Chapter 1. Fuels. European Environment Agency. Copenhagen, Denmark. http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009/part-b-sectoral-guidance-chapters/1-energy/1-b-fugitives/1-b-2-a-v-distribution-of-oil-products.pdf/view

EU (2001). Measures to Reduce Emissions of VOCs during Loading and Unloading of Ships in the EU. Report AEAT/ENV/R/0469 Issue 2. European Union. Brussels, Belgium. http://ec.europa.eu/environment/air/pdf/vocloading.pdf

Fernández-Varela, R., Andrade, J.M., Muniategui, D., Prada, D., and Ramírez-Villalobos, F. (2009). The comparison of two heavy fuel oils in composition and weathering pattern, based on IR, GC-FID and GC-MS analysis: Application to the Prestige wreackage. *Water Research* **43**, 1015-1026.

Fingas, M.F. (1996). The Evaporation of Crude Oil and Petroleum Products. Doctoral Thesis. McGill University. Montreal, Canada. http://digitool.library.mcgill.ca/R/?func=dbin-jump-full&object_id=40119&local_base=GEN01-MCG02

Fingas, M.F. (1999). The evaporation of oil spills: Development and implementation of new prediction methodology. International Oil Spill Conference Proceedings, March 8-11. Seattle, WA. http://ioscproceedings.org/doi/pdf/10.7901/2169-3358-1999-1-281

Fingas, M.F. (2004). Modeling evaporation using models that are not boundary-layer regulated. *Journal of Hazardous Materials* **107**, 27-36.

Garaniya, V., McWilliam, D., and Goldswory, L. (2011) Chemical characterization of heavy fuel oil for combustion modeling. Proceedings of the World Engineers Convention 2011 (WEC2011), September 4-9. Geneva, Switzerland. http://ecite.utas.edu.au/75960

Holmes, J.W. and Bullin, J.A. (1983). Fuel oil compatibility probed. *Hydrocarbon Processing*, **Sept.**, 101-103. http://www.bre.com/portals/0/technicalarticles/Fuel%20Oil%20Compatibility%20Probed.pdf

IEA (2005). Energy Statistics Manual. International Energy Agency. Paris, France. http://www.iea.org/stats/docs/statistics_manual.pdf

IP (2000). Protocol for the Estimation of VOC Emissions from Petroleum Refineries and Gasoline Marketing Operations. The Institute of Petroleum. London, United Kingdom.

ISGINTT (2010). International Safety Guide for Inland Navigation Tank-barges and Terminals. *C*hapter 22, Management of the Tanker and Terminal Interface, 1st edition. Oil Companies International Marine Forum, Central Comission for the Navigation of the Rhine. Strasbourg, France. http://www.isgintt.org/files/isgintt062010_en.pdf

Jones, J.C. (2010). Products of refinery residue. In: Hydrocarbons: Physical Properties and their Relevance to Utilisation. J.C. Jones & Ventus Publishing ApS. Aberdeen, United Kingdom. http://kosalmath.files.wordpress.com/2010/08/hydrocarbons.pdf

Kim E., No, M., Koh, J., and Kim, S. (2011) Compositional characterization of petroleum heavy oils generated from vacuum distillation and catalytic cracking by positive-mode APPI FT-ICR mass spectrometry. *Mass Spectrometry Letters* **2**, 41-44. http://www.ibc7.org/msl/data_file/submission/V.2N.2/V2.N2.19.pdf

Kyriakides, N., Chryssakis, C., and Kaiktsis, L. (2009). Influence of heavy fuel properties on spray atmomization for marine diesel engine applications. SAE Technical Paper Series 2009-01-1858, SAE Powertrain, Fuels & Lubricants, Florence, Italy. http://www.ntua.gr/marinelive/marinecfd/Publications/2009-01-1858.pdf

Lewis, C.A. (1997). Fuel and Energy production Emission Factors. MEET Project: Methodologies for Estimating Air Pollutant Emissions from Transport. Task No. 3.4, Deliverable No. 20. Report No. R112. European Commission, Brussels, Belgium. http://www.inrets.fr/ur/lte/cost319/MEETdeliverable20.pdf

McIlvaine Refinery Process Air Emissons (date unknown). The McIlvaine Company. Northfield, IL. http://www.mcilvainecompany.com/brochures/refinery_process.htm

NAS (1987). Controlling Hydrocarbon Emissions from Tank Vessel Loading. National Academy of Sciene, Committee on Control and Recovery of Hydrocarbon Vapors from Ships and Barges. National Academy Press. Washington, DC. (http://www.nap.edu/catalog/1133.html)

TCEQ (2010). Barge Emission Estimates. Report ERG No.: 0262.03.002. The Texas Commission on environmental Quality. Austin, TX.

http://www.tceq.texas.gov/assets/public/implementation/air/am/contracts/reports/ei/5820783985FY1002-20100831-ergi-barge_emission_estimates.pdf

USEPA (2006). AP 42, Fifth Edition Compilation of Air Pollution Emission Factors, Volume I, Stationary Point and Area Sources, Chapter 7: Liquid Storage Tanks. U.S. Environmental Protection Agency, Office of Air Quality Planning & Standards. Research Triangle Park, NC. http://www.epa.gov/ttn/chief/ap42/ch07/final/c07s01.pdf

USEPA (2008). AP 42, Fifth Edition Compilation of Air Pollution Emission Factors, Volume I, Stationary Point and Area Sources, Chapter 5: Petroleum Industry. U.S. Environmental Protection Agency, Office of Air Quality Planning & Standards. Research Triangle Park, NC. http://www.epa.gov/ttn/chief/ap42/ch05/final/c05s02.pdf

Zorzetti, B.M., Shaver, J.M., and Harynuk, J.J. (2011). Estimation of the age of a weathered mixture of volatile organic compounds. *Analytica Chimica Acta* **694**, 31-37.

Appendix A

Typical Barge Loading Operations for HFO (UN 3082) on an Inland Waterway

Parameter	Value
Capacity of cargo typical barge	3,000–6,000 metric tons - max up to 13,000 metric tons
Number of tanks on a typical barge	10–18 tanks
Loading rate	500–800 tons/hr - max up to 1,000 tons/hr
Loading duration	6–10 hours (rate designed to minimize splash)
Tank hatches	Not opened
Vapour movement	Pushed back into pipes (collector) that run to a single vent that is more than 5 m away from permanent worksites
Size of vent on barge	2 meters high by 15–25 cm in diameter
Location of other vents	Loading arm, loading side of stack (at end of loading, loading arm is sometimes emptied to barge, sometimes to buffer tank on shore with vent to atmosphere 4–6 meters high)
Visible vapour from the vents	None
Temperature of product at storage (max)	80–90 °C (not well controlled)
Temperature during loading (typical)	80 °C
Heating capability on barge	Some barges are equipped with heating
Temperature decrease during transport	1–2 °C/day
Valve operation	2 employees and 8-hour shifts: one crewman and another on land at loading facility. Land operator may supervise more than one barge
Exposure source	Crewman - exposed continuously from barge vent Landsman - only potentially exposed for very short duration (at emptying and disconnecting loading arm)
Equipment	Crewman - standard PPE (overall, shoes, gloves, helmet, goggles, life jacket) Landsman - standard PPE as noted above
H_2S monitoring	Workers wear monitor with alarm; carry evacuation mask

Appendix B

Key Consideration in a Barge Loading Safety Checklist

A safety checklist should be made in writing between the Responsible Crew Member and the Terminal Representative covering the following:

- Tanker's name, berth, date and time.
- Names of tanker and shore representatives.
- Cargo distribution on arrival and departure.
- The following information on each product:
  - Quantity.
  - Shore tank(s) to be filled.
  - Tanker's cargo tank(s) to be discharged.
  - Lines to be used tanker/shore.
  - Cargo transfer rate.
  - Operating pressure.
  - Maximum allowable pressure.
  - Temperature limits.
  - Venting systems.
  - Sampling procedures.
- Restrictions necessary because of:
  - Electrostatic properties.
  - Use of automatic shutdown valves.

The discharge plan should include details and expected timing of the following:
The sequence in which the tanker's cargo tanks are to be discharged, taking account of:
Tanker and shore tank change over.
Avoidance of contamination of cargo.
Pipeline clearing for discharge.
Tank cleaning.
Other movements or operations which may affect flow rates.
Trim and freeboard of the tanker.
The need to ensure that permitted stresses will not be exceeded.
Ballasting operations.
Efficient stripping and discharging last of cargo's drainings.

- The initial and maximum discharge rates, having regard to:

The specification of the cargo to be discharged.
The arrangements and capacity of the tanker's cargo lines, shore pipelines and tanks.
The maximum allowable pressure and flow rate in the tanker/shore hoses or arms.
Precautions to avoid accumulation of static electricity.
Any other limitations.

- Bunkering or storing operations.
- Emergency stop procedure.

Appendix C

Percentage loss of C_6-C_{10} hydrocarbons in artificial weathering experiments (Zorzetti et al., 2011).

Weathering time (min)	Sample Code	Benzene	2,2,4-trimethylpentane	Heptane	Toluene	m-Xylene	Nonane	Decane	1,2,3,5-tetramethylbenzene	Naphthalene
1	SA-1	0.091	0.0828	0.0728	0.1279	0.1325	0.0985	0.1132	0.1683	0.0971
1	SA-1	0.0862	0.0815	0.0701	0.1213	0.1274	0.1068	0.1307	0.1625	0.0955
1	SA-1	0.0889	0.085	0.0724	0.1273	0.1307	0.0988	0.1114	0.1727	0.0977
1	SB-1	0.0877	0.0825	0.071	0.1236	0.1295	0.108	0.1298	0.158	0.0926
1	SB-1	0.099	0.087	0.0733	0.1292	0.1275	0.0968	0.1038	0.1762	0.0944
1	SB-1	0.0855	0.081	0.0706	0.126	0.1302	0.0973	0.1119	0.1792	0.1023
1	SC-1	0.0859	0.0772	0.0669	0.1229	0.1316	0.1022	0.1247	0.1689	0.1009
1	SC-1	0.0805	0.0766	0.0672	0.1219	0.1317	0.0983	0.1147	0.1862	0.1065
1	SC-1	0.0821	0.0763	0.0666	0.1191	0.1287	0.0946	0.1111	0.1947	0.1116
1	SD-1	0.0687	0.0762	0.0656	0.1173	0.1339	0.1032	0.1169	0.1956	0.108
1	SD-1	0.076	0.0725	0.0627	0.1147	0.1289	0.1066	0.1336	0.1783	0.1068
1	SD-1	0.0708	0.0713	0.0613	0.1122	0.1276	0.1005	0.1222	0.2004	0.1164
Average		0.0835	0.0792	0.0684	0.1220	0.1300	0.1010	0.1187	0.1784	0.1025
600	SA-11	0.0352	0.0626	0.0554	0.1101	0.1428	0.1233	0.1523	0.1871	0.1104
600	SA-11	0.0354	0.0623	0.0554	0.1123	0.145	0.1139	0.134	0.2043	0.1183
600	SA-11	0.0353	0.0624	0.0548	0.1129	0.1454	0.1117	0.1334	0.2066	0.1187
600	SB-11	0.0325	0.0593	0.0524	0.109	0.1441	0.1103	0.1343	0.215	0.1228
600	SB-11	0.037	0.0638	0.0558	0.1123	0.1453	0.1121	0.1283	0.2158	0.1132
600	SB-11	0.0392	0.0628	0.0557	0.1114	0.1411	0.1213	0.1503	0.1877	0.1098
600	SC-11	0.0013	0.0104	0.0104	0.0414	0.1305	0.1316	0.1956	0.2779	0.1695
600	SC-11	0.0011	0.0119	0.0112	0.0447	0.1397	0.1295	0.1735	0.2968	0.1666
600	SC-11	0.0012	0.0119	0.0111	0.0457	0.1417	0.1296	0.1746	0.2899	0.167
600	SD-11	0.0018	0.0165	0.0157	0.0573	0.1458	0.1266	0.1686	0.2757	0.1657
600	SD-11	0.0016	0.0157	0.0149	0.0542	0.1409	0.1239	0.1688	0.2844	0.169
600	SD-11	0.0014	0.0141	0.0137	0.0472	0.1344	0.1265	0.183	0.2761	0.1716
Average		0.0186	0.0378	0.0339	0.0799	0.1414	0.1217	0.1581	0.2431	0.1419
Percent Loss		-77.75%	-52.24%	-50.46%	-34.50%	8.75%	20.53%	**33.20%**[A]	**36.26%**[A]	**38.45%**[A]

[A] Three C_{10} hydrocarbons yielded an average percentage loss of 36.0%..

APPENDIX 5

Human Carcinogenicity of Naphthalene

The U.S. National Toxicology Program (NTP) published results of chronic naphthalene inhalation bioassays in male and female F344/N rats, and male and female B6C3F1 mice (NTP, 1992; NTP, 2000). In the rat studies, increased incidences of two forms of nasal tumours were observed, specifically rare and highly malignant olfactory epithelial neuroblastomas in both sexes, and respiratory epithelial adenomas in males. In the mouse studies, an increased incidence of benign lung adenomas was observed in females. Based on those findings and supporting information, several authorities classified naphthalene as to its carcinogenicity. In 2002 IARC concluded that there is sufficient evidence in experimental animals for the carcinogenicity of naphthalene but inadequate evidence in humans for the carcinogenicity of naphthalene and consequently classified it as *possibly carcinogenic to humans* (Group 2B) (IARC, 2002). In 2003, the European Union issued the Risk Assessment Report on naphthalene under the EU Existing Substances Regulation, classifying naphthalene as a Category 3 carcinogen (EC, 2003)[1]. This implies that naphthalene was considered to cause concern for humans owing to *possible carcinogenic effects* but in respect of which the available information is not adequate for making a satisfactory assessment. There is some evidence from appropriate animal studies but available data were insufficient to place the substance in Category 2. In the USA, the National Toxicology Program listed naphthalene as a chemical “reasonably anticipated to be carcinogenic” in its 11 Report on Carcinogens (NTP, 2004).

Since the publication of the original NTP bioassays and the subsequent carcinogenicity classifications by several authoritative bodies, considerable research has been conducted to elucidate the mode of action (MoA) for the findings in rodents and their relevance to humans. Overall, the results across species and tissues are consistent with a threshold naphthalene MoA in rat nose and mouse lung that involves high-dose GSH depletion, followed by cytotoxicity, chronic inflammation, regenerative hyperplasia and tumor formation and suggests that low metabolism in human respiratory tissue is consistent with little to no toxicity or carcinogenic risk at typical naphthalene environmental exposures.

These research findings and the NTP bioassay findings are summarized in Bailey et al. (2016). Some of the key findings are as follows:

- The NTP mouse and rat bioassays were conducted at naphthalene concentrations chosen based on physical-chemical properties, rather than range-finding studies. These concentrations exceeded Maximum Tolerated Dose (MTD) at all exposure levels in both species, confounding study interpretation.
- The NTP studies found that inhalation exposure to naphthalene elicited benign lung bronchiolar adenomas in mice. In the rat, naphthalene elicited nasal respiratory epithelial adenomas and olfactory epithelial neuroblastomas.
- Tumours confined to specific epithelial tissues of respiratory tract directly exposed to naphthalene vapours, suggesting a very specific and local MoA.

[1] Category 3 as defined in the EU Dangerous Substance Directive (DSD) is equivalent to Category 2 under the current CLP and GSH.

- In both rats and mice there is widespread cytotoxicity and inflammation at all doses evaluated in the tissues where tumours occur. By contrast, tissues beyond these epithelial tissues do not show such cytotoxicity and hyperplasia, and they do not have tumours. Taken together, this and other evidence strongly suggests a causal role (necessary but not sufficient role) for site-specific GSH depletion and cytotoxicity in the MoA, and suggests a nonlinear dose-response or practical threshold for carcinogenic hazard.
- There is concentrated and localized metabolic activity towards naphthalene in the nasal and lung tissues where toxicity occurs, indicative of a role for site-specific metabolism in naphthalene carcinogenicity. The balance and types of specific cytochrome P450s and other enzymes responsible for naphthalene activation and detoxification ultimately determines the potential to cause injury, and this balance likely varies across tissues and species. The rate of naphthalene oxidation is considerably slower in primate nasal and lung tissue, relative to that measured in rats and mice.
- The majority of genotoxicity studies has yielded negative results, with the only positive results occurring at already cytotoxic concentrations. These findings across multiple studies are most supportive of either a cytotoxic, or combined cytotoxic/genotoxic MoA. Further, if genotoxicity from naphthalene metabolites is involved in the MoA, it is only at high concentrations, which is not consistent with an initiating genotoxic/mutagenic event and again is more supportive of a nonlinear dose-response or practical threshold.
- Nasal tumours are rare in humans, such that if naphthalene exposure could cause tumours in nasal epithelium this would likely have been identified in by case reports in naphthalene-exposed occupational workers.

Under CLP naphthalene is still classified H351 (Carcinogenic Cat. 2), however, the evidence as outlined above strongly supports a cytotoxic threshold MoA in rodents and little risk for human respiratory cancer at typical and occupational exposure levels. In its most recent evaluation, The Health Council of the Netherlands has already advised that naphthalene should be considered as not classifiable (Health Council of the Netherlands, 2012).

References:

Bailey LA, Nascarella MA, Kerper LE, Rhomberg LR (2016). Hypothesis-based weight-of-evidence evaluation and risk assessment for naphthalene carcinogenesis. *Crit Rev Toxicol* **46(1)** 1-42

EC (2003). European Communities. European Union Risk Assessment Report. Naphthalene, (CAS No. 91-20-3; EINECS). Luxembourg.

Health Council of the Netherlands (2012). Naphthalene - Evaluation of the carcinogenicity and genotoxicity. Subcommittee on the Classification of Carcinogenic Substances of the Dutch Expert Committee on Occupational Safety (DECOS). Publication no. 2012/30, The Hague, The Netherlands: Health Council of the Netherlands.

IARC. 2002. Naphthalene. In Traditional Herbal Medicines, Some Mycotoxins, Naphthalene and Styrene. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, vol. 82. Lyon, France: International Agency for Research on Cancer. pp. 367-435.

NTP. 1992. Toxicology and Carcinogenesis Studies of Naphthalene (CAS No. 91-20-3) in B6C3F1 Mice (Inhalation Studies). Technical Report Series no. 410. Research Triangle Park, NC: National Toxicology Program.

NTP. 2000. Toxicology and Carcinogenesis Studies of Naphthalene (CAS No. 91-20-3) in F344/N Rats (Inhalation Studies). Technical Report Series no. 500. Research Triangle Park, NC: National Toxicology Program.

NTP. 2004. Eleventh Report on Carcinogens - Naphthalene, Department of Health and Human Services. Research Triangle Park, NC: National Toxicology Program.

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