



Report no. 2/20

Additional worker inhalation exposure measurements of heavy fuel oil emissions during barge/truck loading





# Additional worker inhalation exposure measurements of heavy fuel oil emissions during barge/truck loading

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## ABSTRACT

The report details the outcome of a follow-up project of a study initiated by Concawe in 2013, investigating the occupational exposure to emissions from hot Heavy Fuel Oil (HFO) (inhalation exposure to aerosols and vapours) during inland barge loading (Concawe rpt. 1/15R).

In the current follow-up project the objective was to increase the number of measurements for a better representativeness of the exposure assessment used in the Chemical Safety Assessment in the HFO REACH registration dossier. This issue was identified following a comparison of measured exposure data and modelled estimates, as documented in Concawe rpt 13/18.

Inhalation exposure samples (personal and stationary) were collected at four barge loading sites and one truck loading facility on three different occasions, respectively. Total organic matter (TOM) and indicator aromatic hydrocarbons (AH) such as naphthalene and the three polycyclic aromatic hydrocarbons (PAH) phenanthrene, pyrene and benzo[a]pyrene were chosen as parameters to assess the occupational inhalation exposure during inland HFO loading operations.

For the monitored barge loading events, the aerosol-related TOM exposure levels adjusted to 8 hour exposure to account for the variable duration of HFO barge loading and to align with the reference period of the DNEL. These ranged from < 2 to 40  $\mu$ g/m<sup>3</sup>; whereas for the TOM content in the vapour phase, values between 78 and 7,600  $\mu$ g/m<sup>3</sup> were observed. For truck loading, the TOM in the aerosol phase was considerably lower than in the vapour phase (< 42 to 182  $\mu$ g/m<sup>3</sup> and 876 to 21100  $\mu$ g/m<sup>3</sup>, respectively). Naphthalene concentrations varied between 0.2 and 140  $\mu$ g/m<sup>3</sup>. Benzo[a]pyrene was in all personal samples below the limit of quantification and the sum of pyrene, phenanthrene and benzo[a]pyrene ranged between 69 to 678 ng/m<sup>3</sup>. A comparison of monitoring results for barge loading from personal samplers (TOM and naphthalene) for off-shore and on-shore workers reported in Concawe rpt. 1/15R and in the present study, evidenced similar exposure levels.

Measured data collected in the present study were used to refine the Concawe REACH Chemical Safety Assessment for substances in the HFO category.

## **KEYWORDS**

Heavy fuel oil, occupational exposure, inhalation monitoring, chemical safety assessment, barge and truck loading, REACH

## INTERNET

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# SUMMARY

The report details the outcome of a follow-up project of a study initiated by Concawe in 2013, investigating the occupational exposure to emissions from hot Heavy Fuel Oil (HFO) (inhalation exposure to aerosols and vapours) during inland barge loading (Concawe rpt. 1/15R<sup>1</sup>). Six Concawe member companies volunteered to participate in gathering additional inhalation exposure measurement data during inland HFO barge and truck loading.

In the current follow-up project the objective was to increase the number of measurements for a better representativeness of the exposure assessment used in the Chemical Safety Assessment in the HFO REACH registration dossier. This issue was dentified following a comparison of measured exposure data and modelled estimates, as documented in Concawe rpt  $13/18^2$ .

Inhalation exposure samples were collected at four barge loading sites and one truck loading facility on three different occasions, respectively. The sixth site did not carry out any loading during the time window available for the project. The individual sites were anonymized for the project by assigning a colour-code to each site. At each barge loading site the crew member supervising loading on-board and the supporting refinery operator on land were monitored. At the truck loading site the truck driver carrying out loading was monitored. Total organic matter (TOM) and indicator aromatic hydrocarbons (AH) such as naphthalene and the three polycyclic aromatic hydrocarbons (PAH) phenanthrene, pyrene and benzo[a]pyrene were chosen as parameters to assess the occupational inhalation exposure during inland HFO loading operations. The sampling set-up included personal and stationary samplers (close to the source and background). Exposure data obtained from personal samplers were used to calculate 8-hr Time Weighted Average (TWA-8hr) values for the corresponding loading operation, when the sampling time was 2 hours or more. Stationary samples data were used to check background levels, and potential peak measures close to the point of release.

For the monitored barge loading events, the aerosol-related TOM exposure levels adjusted to 8 hour exposure to account for the variable duration of HFO barge loading and to align with the reference period of the DNEL. These ranged from < 2 to 40  $\mu$ g/m<sup>3</sup>; whereas for the TOM content in the vapour phase, values between 78 and 7,600  $\mu$ g/m<sup>3</sup> were observed. For truck loading (n=3 loading events) no TWA-8hr data were calculated as <u>a</u>. the sampling times were below 2 h and <u>b</u>. exposure data related to the unloading of the truck, usually conducted by the same person who is loading the truck (e.g. the driver), could not be collected as part of this study. Similar to the barge loading results, the TOM in the aerosol phase was considerably lower than in the vapour phase (<42 to 182  $\mu$ g/m<sup>3</sup> and 876 to 21100  $\mu$ g/m<sup>3</sup>, respectively).

(P)AH data are reported as the sum of aerosol and vapour phase. Similarly to TOM, only the personal data-sets obtained during HFO inland loading of barges were suitable for the calculation of TWA-8hr values for (P)AH. The monitoring campaigns addressing truck loading did not allow for the calculation of TWA-8hr due to sampling times shorter than 2 h.

Naphthalene concentrations varied between 0.2 and 140  $\mu$ g/m<sup>3</sup>. Benzo[a]pyrene was in all personal samples below the limit of quantification and the sum of pyrene, phenanthrene and benzo[a]pyrene ranged between 69 to 678 ng/m<sup>3</sup>. Naphthalene exposure levels were below the corresponding worker inhalation Derived No Effect Level (DNEL) in the registration dossier, i.e. 25 mg/m<sup>3</sup>.

For phenanthrene, pyrene and benzo[a]pyrene no DNELs are available. The benzo[a]pyrene acceptance level (according to "Begründung zur ERB zu Benzo[a]pyren in BekGS 910" April 2011) is 7 ng/m<sup>3</sup>. For phenanthrene , pyrene and benzo[a]pyrene comparisons can be made based on information available for the OSHA PEL (Occupational Safety & Health Administration

<sup>&</sup>lt;sup>1</sup> Concawe rpt 1/15 (January 2015; revised April 2016) Risk assessment for emission from hot heavy fuel oil during barge loading

<sup>&</sup>lt;sup>2</sup> Concawe rpt. 13/18 (2018) Review of Tier 1 Workplace Exposure Estimates for Petroleum Substances in REACH dossiers



Permissible Exposure Limit) of coal tar pitch volatiles (CTPV<sup>3</sup>) set to 0.2 mg/m<sup>34</sup> for benzenesoluble aerosol, including PAH.

A comparison of monitoring results for barge loading from personal samplers (TOM and naphthalene) for off-shore<sup>5</sup> and on-shore<sup>6</sup> workers reported in Concawe rpt. 1/15R and in the present study, evidenced similar exposure levels.

Measured data collected in the present study were used to refine the Concawe REACH CSA for substances in the HFO category.

<sup>&</sup>lt;sup>3</sup> Definition of CTPV by OSHA: "[...] coal tar pitch volatiles include the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum (excluding asphalt), wood, and other organic matter. Asphalt (CAS 8052-42-4, and CAS 64742-93-4) is not covered under the "coal tar pitch volatiles" standard."

Source: https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1002.

<sup>&</sup>lt;sup>4</sup> <u>https://www.osha.gov/dts/sltc/methods/organic/org058/org058.html</u>. Only 3 of the 5 PAH considered in OSHA method 58 in context of the sum parameter CTPV are included in the calculation of the TWA-8hr, i.e. phenanthrene, pyrene and benzo[a]pyrene.

<sup>&</sup>lt;sup>5</sup> Barge crew member

<sup>&</sup>lt;sup>6</sup> Refinery jetty operator



## 1. INTRODUCTION AND OBJECTIVE

HFOs are classified as carcinogenic substances, and therefore exposure to fumes needs to be adequately controlled. In 2013, Concawe initiated a study investigating the HFO inhalation occupational exposure during inland barge loading (Concawe rpt. 1/15R)<sup>7</sup>. Dermal exposure to HFO had been assessed comprehensively in a previous Concawe-funded project with the Institute of Occupational Medicine (Christopher et al., 2011)<sup>8</sup>.

Workplace monitoring campaigns were conducted at three different barge loading sites as part of the 2013 project providing data on the inhalation exposure of the workers involved. Vapour and aerosol samples were analysed for total hydrocarbon content as well as naphthalene and two marker PAHs (pyrene, and benzo[a]pyrene) by gas chromatography. However, as only 5 data points were monitored, the exposure levels could have been underestimated. This was evidenced in Concawe rpt. 13/18<sup>9</sup> which involved an evaluation of the Concawe REACH Chemical Safety Assessments (CSAs), i.e. comparison of modelled workplace exposure estimates with available measured data for a series of exposure scenarios. Further exposure monitoring work was therefore considered important to produce a more robust estimate. Additionally, recent toxicological review recommended to assess inhalation exposure to emissions from hot HFO as the sum of aerosol and vapour, whereas previously the focus had been on the aerosol component only.

In the current follow-up project, six Concawe member companies volunteered to participate with the aim to collect additional HFO exposure data during barge or truck loading and to provide a more representative dataset for the evaluation of occupational exposure during HFO transfer process from storage tanks to barges and trucks. Inhalation exposure samples were collected at four barge loading sites and one truck loading facility on three different occasions respectively. The sixth site did not carry out any loading during the time window available for the project. At all locations, the HFO was handled at elevated temperature.

<sup>&</sup>lt;sup>7</sup> Concawe Report 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading. Revised version April 2016.

<sup>&</sup>lt;sup>8</sup> Christofer et al. (2011) An Assessment of Dermal Exposure to Heavy Fuel Oil (HFO) in Occupational Settings. Ann. Occup. Hyg., Vol. 55, No. 3, pp. 319-328.

<sup>&</sup>lt;sup>9</sup> Concawe rpt. 13/18 (2018) Review of Tier 1 Workplace Exposure Estimates for Petroleum Substances in REACH dossiers



## 2. WORKPLACE MONITORING - GENERAL APPROACH

The workplace monitoring campaigns were reported on an anonymous basis. As in the preceding project, colour coding was applied, assigning a colour to each participating Concawe member company. A sampling protocol detailing the purpose, requirements, general instructions regarding sample collection and contact details was compiled by Concawe and distributed to the on-site managers of the participating refineries. More details on the tasks during loading can be found in the previous report (Concawe rpt. 1/15R)<sup>10</sup>.

The samples were analysed for total hydrocarbon content (THC), the indicator aromatic hydrocarbons (AH) naphthalene and three polycyclic aromatic hydrocarbons (PAH), namely phenanthrene, pyrene and benzo[a]pyrene. Inhalation exposure to HFO required the measurement of aerosol and vapour phase. A filter (for aerosols) and XAD (for vapour phase) were thefore included in the sample collection train (

Figure 1). As THC and (P)AH cannot be determined from one sample, two identical sampling trains were placed at each sampling position.

All sampling equipment was provided by Fraunhofer ITEM in order to minimize any variations caused by the use of an array of sampling equipment. The GGP-sampler were prepared ready-to use at Fraunhofer ITEM; with filter being placed in the filter holders, XAD being filled in the cartridges and the sampling trains being assembled and closed at the in- and outlet. Each sampling train was wrapped in aluminium foil. Sampling flow rate was adjusted on site by the corresponding occupational hygienist (or professional with adequate knowledge) conducting the sampling. Directly after sampling, the sampling trains were closed at the in- and outlet, packed in aluminium foil and stored at ambient temperature until timely shipment to Fraunhofer ITEM.



*Figure 1.* Sampling train used for collecting HFO related aerosols and vapour phase constituents. Samples were analysed for THC and four selected (P)AH, requiring two identical sampling trains at each sampling location.

<sup>&</sup>lt;sup>10</sup> Concawe Report 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading. Revised version April 2016.



During each sampling campaign involving barge/ship loading two personal samplings (1x on-shore; 1x off-shore), two stationary samplings (1x close to the vent; 1x background) and one field blank were included. In the sampling campaign of truck loading activities, only one personal sampling location (1x truck driver = loading operator), two stationary sampling location (1x close to the vent; 1x background) and one field blank were included. Sampling was conducted by professionals with adequate knowledge in sample collection of airborne substances, aerosol and gases. Three workplace monitoring campaigns were conducted at each participating site and the samples were sent back to Fraunhofer ITEM for analysis.

The same sampling equipment and analytical methods were used as in the initial study<sup>11</sup>. A schematic overview of the general procedure of sample collection and analysis as well as the assigned responsibilities are given in Figure 2.



*Figure 2.* HFO fume related workplace monitoring campaigns - Schematic of the general monitoring procedure.

<sup>&</sup>lt;sup>11</sup> Concawe Report 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading. Revised version April 2016.



## 3. WORKPLACE MONITORING - DATA

The data reports for the workplace monitoring campaigns conducted at the refinery sites of the participating Concawe member companies are attached in **Appendix 2.** 

Exposure data during truck loading (site crimson) are reported separately since the operating conditions differed considerably from barge loading (sites maroon, orange, purple and scarlet). For example the loading time was much shorter during truck loading than for barge loading and the process is taking place in a partly sheltered and roofed location as compared to outdoors. Also, two trucks were loaded via semi-open top loading, whereas barge loading uses a hose bolted to the barge's manifold, as does bottom loading of trucks (one data point). None of the three events monitored included the exposure to HFO fumes during the unloading of the trucks upon delivery to a customer, a task usually conducted by the same person, i.e. the driver. No TWA-8hr exposure data are given due to the sampling time not being representative of an 8h-workshift and because the loading operator may also have been involved in the unloading of the truck, an event that was not monitored in this campaign.

## 3.1. TOTAL HYDROCARBON CONTENT (THC)

The THC data for the four barge loading sampling sites are given in Table 1 and Table 2 for personal and stationary samplers, respectively. The data are not corrected for the respective field blanks. Field blank data were solely used as means to monitor potential substantial contamination of the samples, e.g. during transport. The raw data are reported as mg ME / m<sup>3</sup>, where ME is an abbreviation for Mineral Oil Equivalent. Quantification of the THC content was achieved using mineral oil calibration standards. For the personal samples these values were converted into mg TOM / m<sup>3</sup>, with TOM standing for Total Organic Matter. For this conversion a HFO response factor of 2 was used to take into account the difference in results when calibrating with specific laboratory-generated fume condensates instead of with the standard mineral oil equivalent used in the standardised method<sup>12</sup>. This response factor of 2 is the most conservative value from the previous study<sup>13</sup>, where response factors were determined for five different HFO fume condensates with 2 being the highest and 1.4 being the lowest. This factor was applied to the data presented in Table 1 and Table 3. The resulting TOM data in *Table 1* were used to derive TWA-8hr<sup>14</sup> exposure concentrations (for barge loading only). These ranged from < 2 to 40  $\mu$ g/m<sup>3</sup> for the aerosol phase; whereas for the vapour phase, values between 78 and 7,600  $\mu$ g/m<sup>3</sup> were observed.

For the truck loading events (no TWA-8hr data calculated), similarly to the barge loading results, the TOM in the aerosol phase was considerably lower than in the vapour phase (<42 to 182  $\mu$ g/m<sup>3</sup> and 876 to 21100  $\mu$ g/m<sup>3</sup>, respectively). The truck loading data-set, although very limited, indicates that the loading operator was exposed to a higher HFO concentration during top loading than during bottom loading.

The analytical method had a LOQ of 0.001 mg absolute; corresponding to 0.001 mg/m<sup>3</sup> for an 8 hr sample (sample collection at 2 L/min over a sample duration of 480 min).

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.

<sup>&</sup>lt;sup>12</sup> Gmehling, J., Weidlich, U., Lehmann, E. and Fröhlich, N. (1989): Verfahren zur Berechnung von

<sup>&</sup>lt;sup>13</sup> Concawe Report 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading. Revised version April 2016.

<sup>&</sup>lt;sup>14</sup> Based on the assumption that no other activities are conducted where the worker is exposed to HFO-derived aerosols and vapours.



Site		maroon			orange			purple			scarlet	
event	Α	в	С	Α	В	С	A*	в	С	Α	В	С
rel. humidity [%]	n.i.	92	72	68-93	88-96	68-76	45-55	62-69	70-87	92-94	95-97	74-92
outside temperature [°C]	22	16	20	6	7	6	25	26	21	7	7	3
HFO loading temperature [°C]	79	83	77	80-81	80-81	80-81	76-77	75-76	70	76	83	86
					off-sho	'e						
sampling duration [min]	382	555	520	227	224	226	103	181	467	438	536	634
sampling volume [m <sup>3</sup> ]	0.766	1.12	1.04	0.452	0.448	0.455	0.205	0.364	0.939	0.871	1.09	1.29
filter (aerosol) [mg ME/m³]	0.016	**	0.013	0.018	0.022	0.009	0.044	0.041	0.011	0.001	0.013	0.004
XAD (vapour) [mg ME/m³]	1.55	**	2.33	0.894	0.295	8.07	5.76	2.85	0.540	0.345	0.831	0.556
total [mg ME/m³]	1.57	**	2.35	0.912	0.317	8.08	5.80	2.89	0.551	0.346	0.844	0.560
aerosol-calculated TWA-8h [mg TOM/m³]	0.025	**	0.027	0.017	0.021	0.008	0.019	0.031	0.021	0.002	0.029	0.010
vapour-calculated TWA-8h [mg TOM/m³]	2.47	**	5.05	0.85	0.28	7.60	2.47	2.15	1.05	0.63	1.86	1.47
					on-sho	e						
sampling duration [min]	382	555	520	220	252	226	100	173	487	405	540	616
sampling volume [m <sup>3</sup> ]	0.751	0.777	1.03	0.445	0.469	0.454	0.199	0.346	0.969	0.915	1.1	1.26
filter (aerosol) [mg ME/m³]	0.005	n.d. (< 0.001)	0.018	0.004	0.009	0.002	0.050	0.023	0.009	0.001	0.002	#
XAD (vapour) [mg ME/m³]	0.252	0.601	0.884	0.085	0.209	0.311	0.487	0.191	0.083	1.26	0.180	0.776
total [mg ME/m³]	0.257	0.601 (< 0.602)	0.902	0.089	0.218	0.313	0.538	0.214	0.092	1.26	0.182	0.776
aerosol-calculated TWA-8h [mg TOM/m <sup>3</sup> ]	0.008	n.d. (< 0.002)	0.040	0.004	0.009	0.002	0.021	0.017	0.019	0.002	0.004	#
vapour-calculated TWA-8h [mg TOM/m <sup>3</sup> ]	0.401	1.390	1.915	0.078	0.219	0.293	0.203	0.138	0.168	2.12	0.406	1.99
# - filter cassette missing												
** - Samplers were soaked in	water. Data	a are not repo	orted as res	ults might b	e errorneous	i.						
n.i no information												
NA - not applicable												
BLQ - Below limit of quantifica	ation (numb	oers given in b	orackets inc	licate the LC	DQ).							
n.dnot detected												
* Sampling duration was below	w 2h and t	he sample is	therefore no	ot recomme	nded for the	calculation	of TWA-8hr	values As t	he task is a	repetitive or	ne and only	small

## Table 1. THC data overview (personal samplers) - Barge/ship loading (sites: maroon, orange, purple, scarlet)

\* Sampling duration was below 2h, and the sample is therefore not recommended for the calculation of TWA-8hr values. As the task is a repetitive one and only small variations regarding average exposure during the conduction of the task (HFO loading/transfer) is expected the TWA-8h was calculated.



# Table 2. THC data overview (stationary samplers) - Barge/ship loading (sites: maroon, orange, purple, scarlet)

Site		maroon			orange			purple			scarlet	
event	А	B	С	Α	B	с	Α	B	С	Α	B	С
rel. humidity [%]	n.i.	92	72	68-93	88-96	68-76	45-55	62-69	70-87	92-94	95-97	74-92
outside temperature [°C]	22	92 16	20	6	7	6	40-00 25	26	21	32-34 7	33-37 7	3
HFO loading temperature [°C]	22 79	83	20 77	80-81	7 80-81	80-81	25 76-77	20 75-76	70	76	83	86
	79	03	11	00-01	close to v		70-77	75-70	70	70	03	00
a second base shows they. Facility	00.4		450	001				455	00.4	440	500	500
sampling duration [min]	384	555	450	231	210	227	80	155	321	410	509	592
sampling volume [m <sup>3</sup> ]	0.747	1.12	0.934	0.455	0.414	0.451	0.160	0.313	0.626	0.826	1.02	1.21
filter (aerosol) [mg ME/m³]	0.012	**	***	0.015	0.012	0.011	0.350	0.249	0.026	0.086	**	§
XAD (vapour) [mg ME/m³]	78.1	**	***	59.2	1.86	29.7	758	512	38.2	146	**	§
total [mg ME/m³]	78.1	**	***	59.2	1.87	29.7	758	512	38.3	146	*	§
		· · · · · · · · · · · · · · · · · · ·			backgrou	und						
sampling duration [min]	384	555	460	221	190	258	258	168	464	395	507	595
sampling volume [m3]	0.737	1.19	0.959	0.435	0.378	0.524	0.511	0.336	0.90	0.837	1.02	1.21
filter (aerosol) [mg ME/m³]	0.003	n.d. (< 0.001)	0.015	0.002	0.005	n.d.	0.008	0.006	0.006	0.000	**	0.001
XAD (vapour) [mg ME/m³]	0.141	0.045	0.238	0.009	0.045	0.036	0.106	0.128	0.341	0.067	**	0.215
total [mg ME/m <sup>3</sup> ]	0.144	0.045 (< 0.046)	0.253	0.011	0.050	0.036	0.114	0.134	0.347	0.067	**	0.216
** - Samplers were soaked in	water. Data	a are not repo	rted as res	ults might be	e errorneous							
*** - Sampler was covered in I							ous.					
n.i no information	· ·	, 			J							
BLQ - Below limit of quantifica	ition (numb	ers given in b	rackets ind	licate the LC	)Q).							
n.dnot detected	· ·	Ŭ										
§ - XAD cartridge for "close to	vent " sam	pler was solid	d - due to ov	verload								



## Table 3.THC data overview- Top and bottom truck loading (site crimson)

Site		crimson	
event	A top loading	B top loading	C bottom loading
rel. humidity [%]	77	79	75
outside temperature [°C]	16	14	15
HFO loading temperature [°C]	57-60	59-61	60-63
ре	ersonal sampler - o	perator	
sampling duration [min]	49	38	24
sampling volume [m <sup>3</sup> ]	0.099	0.076	0.048
filter (aerosol) [mg ME/m <sup>3</sup> ]	0.091	0.066	BLQ <sup>15</sup> (< 0.021)
XAD (vapour) [mg ME/m <sup>3</sup> ]	9.18	10.5	0.438
total [mg ME/m³]	9.27	10.6	0.438 (<0.459)
aerosol [mg TOM/m³]	0.182	0.132	BLQ (<0.042)
vapour [mg TOM/m <sup>3</sup> ]	18.4	21.1	0.876
statio	onary sampler - clo	ose to vent	
sampling duration [min]	46	33	22
sampling volume [m <sup>3</sup> ]	0.092	0.066	0.044
filter (aerosol) [mg ME/m <sup>3</sup> ]	0.033	0.015	0.02
XAD (vapour) [mg ME/m <sup>3</sup> ]	0.500	8.03	13.0
total [mg ME/m <sup>3</sup> ]	0.533	8.05	13.0
stati	onary sampler - ba	ckground	
sampling duration [min]	52	74	36
sampling volume [m <sup>3</sup> ]	0.102	0.144	0.07
filter (aerosol) [mg ME/m <sup>3</sup> ]	0.029	BLQ (< 0.007)	BLQ (< 0.014)
XAD (vapour) [mg ME/m <sup>3</sup> ]	0.069	0.132	0.214
total [mg ME/m³]	0.098	0.132 (< 0.139)	0.214 (< 0.228)

 $<sup>^{15}\ \</sup>mathrm{BLQ}$  - Below limit of quantification (numbers given in brackets indicate the LOQ).



## 3.2. SELECTED AROMATIC HYDROCARBONS (AH)

The (P)AH data for the four barge loading sampling sites (maroon, orange, purple and scarlet) are given in *Table 4* and Table 5 for personal and stationary samplers, respectively. The data are not corrected for the respective field blanks. Field blank data were solely used as means to monitor for potential substantial contamination of the samples, e.g. during transport. For the personal samplers TWA-8hr values were calculated for naphthalene and benzo[a]pyrene based on the actual monitoring data. The OSHA method 58<sup>16</sup> covers the sampling and analysis for coal tar pitch volatiles (CTPV), including the five PAHs: phenanthrene, anthracene, pyrene, chrysene and benzo[a]pyrene. In this study only phenanthrene, pyrene and benzo[a]pyrene were considered in the calculation of the TWA 8hr (indicated hereafter as CTPV3<sup>17</sup>) and reported in *Table 4*.

All TWA-8hr inhalation exposure values calculated<sup>18</sup> are shown in *Table 4*. The TWA-8hr for naphthalene varied between 0.2 and 140  $\mu$ g/m<sup>3</sup>. Benzo[a]pyrene was not detected in any of the analysed sample extracts (personal samplers). Calculated TWA-8hr values for CTPV3 ranged between 69 to 678 ng/m<sup>3</sup>.

Results of inhalation exposure during top and bottom truck loading, monitored at site crimson, are reported separately in *Table 6*. Contrary to the TOM data, the exposure to HFO derived (P)AH seemed to be higher during bottom than top truck loading, with naphthalene being the only exception of the four selected AH. Other (P)AH emitting sources (e.g. diesel engine exhaust) at the sampling site might be one explanation for this finding.

<sup>&</sup>lt;sup>16</sup> https://www.osha.gov/dts/sltc/methods/organic/org058/org058.html.

<sup>&</sup>lt;sup>17</sup> Only 3 of the 5 PAH considered in OSHA method 58 for the sum parameter CTPV are included in the calculation of the TWA-8hr, i.e. phenanthrene, pyrene and benzo[a]pyrene, and are therefore denoted as CTPV3 in this report.

<sup>&</sup>lt;sup>18</sup> Based on the assumption that no other activities are conducted where the worker is exposed to HFO-derived fumes.



#### Table 4. (P)AH data overview (personal samplers) - Barge/ship loading (sites: maroon, orange, purple, scarlet)

Site		maroon			orange			purple			scar	let
event	Α	В	С	Α	В	С	A*	B	С	Α	В	С
rel. humidity [%]	n.i.	92	72	68-93	88-96	68-76	45-55	62-69	70-87	92-94	95-97	74-92
outside temperature [°C]	22	16	20	6	7	6	25	26	21	7	7	3
HFO loading temperature [°C]	79	83	77	80-81	80-81	80-81	76-77	75-76	70	76	83	86
					off-s	shore <sup>19</sup>						
sampling duration [min]	382	555	520	227	224	226	103	181	467	438	536	634
sampling volume [m <sup>3</sup> ]	0.756	1.10	1.05	0.454	0.446	0.454	0.208	0.366	0.985	0.879	1.11	1.28
naphthalene [µg/m³]	52.4	**	6.27	15.2	1.95	297	52.0	52.2	3.39	1.05	0.438	6.56
phenanthrene [ng/m <sup>3</sup> ]	183	**	481	166	170	259	356	176	349	303	112	275
pyrene [ng/m <sup>3</sup> ]	35.2	**	32.7	48.8	69.0	30.5	75.1	19.2	38.4	48.2	59.0	54.7
benzo[a]pyrene [ng/m <sup>3</sup> ]	n.d.	**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	(< 3.3)		(< 2.4)	(< 5.5)	(< 5.6)	(< 5.5)	(< 12.0)	(< 6.8)	(< 2.5)	(< 2.8)	(< 2.3)	(< 2.0)
CTPV3 [ng/m <sup>3</sup> ]	218 (< 221)	**	514 (< 516)	215 (< 221)	239 (< 245)	290 (< 296)	431	195	387	351	171	330
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	174 (< 176)	**	557(< 559)	102 (< 105)	112 (< 114)	136 (< 139)	92.5 (<95.1)	73.6 (<80.4)	377 (<380)	320	191	436
naphthalene TWA-8hr [µg/m³]	41.7	**	6.79	7.19	0.911	140	11.2	19.7	3.30	0.958	0.490	8.67
benzo[a]pyrene TWA-8hr [ng/m³]	n.d. (< 2.6)	**	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.4)	n.d. (< 2.6)	n.d. (< 2.5)	n.d. (< 2.6)

n.i. - no information

BLQ - Below limit of quantification (numbers given in brackets indicate the LOQ).

NA - Not applicable

\*\* - Samplers were soaked in water. Data are not reported as results might be erroneous.

n.d. -not detected

CTPV3 - 3 out of 5 Coal Tar Pitch Volatiles, as defined by OSHA: phenanthrene, pyrene and benzo[a]pyrene

\* Sampling duration was below 2h, and the sample is therefore not recommended for the calculation of TWA-8hr values. As the task is a repetitive one and only small variations regarding average exposure during the conduction of the task (HFO loading/transfer) is expected the TWA-8h was calculated.

<sup>&</sup>lt;sup>19</sup> Barge crew member

<sup>9</sup> 



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Table 4. (continued): (P)AH data overview (personal samplers) - Barge/ship loading (sites: maroon, orange, purple, scarlet)

Site		maroon			orange			purple			scarlet	
event	Α	В	С	Α	В	С	A*	В	С	Α	В	С
rel. humidity [%]	n.i.	92	72	68-93	88-96	68-76	45-55	62-69	70-87	92-94	95-97	74-92
outside temperature [°C]	22	16	20	6	7	6	25	26	21	7	7	3
HFO loading temperature [°C]	78.7	82.8	76.8	80-81	80-81	80-81	76-77	75-76	70	76	83	86
				on-sho	ore <sup>20</sup>							
sampling duration [min]	384	555	520	220	252	226	100	173	487	405	539	616
sampling volume [m <sup>3</sup> ]	0.739	1.124	1.05	0.440	0.504	0.453	0.203	0.344	0.959	0.8408	1.0678	1.2474
naphthalene [µg/m³]	4.39	2.69	1.62	0.422	0.408	135	0.868	0.562	0.238	1.81	1.90	1.49
phenanthrene [ng/m³]	189	203	431	145	525	203	375	155	115	317	162	399
pyrene [ng/m <sup>3</sup> ]	34.7	124	41.0	106	197	32.9	118	35.7	51.9	29.5	48.3	129
benzo[a]pyrene [ng/m³]	n.d. (< 3.4)	n.d. (< 2.2)	n.d. (< 2.4)	n.d. (< 5.7)	n.d. (< 5.0)	n.d. (< 5.5)	n.d. (< 12.3)	n.d. (< 7.3)	n.d. (< 2.6)	n.d. (< 3.0)	n.d. (< 2.3)	n.d. (< 2.0)
CTPV3 [ng/m <sup>3</sup> ]	224 (< 227)	327 (<329)	472 (< 474)	251 (< 257)	722 (< 727)	236 (< 242)	493	191	167	346	210	528
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	179 (< 182)	378 (<380)	511 (< 514)	115 (< 118)	379 (< 382)	111 (< 114)	103 (<115)	68.7 (<76.0)	169 (<172)	292	236	678
naphthalene TWA-8hr [µg/m³]	3.51	3.11	1.76	0.193	0.214	63.5	0.181	0.203	0.241	1.53	2.13	1.91
benzo[a]pyrene TWA-8hr [ng/m³]	n.d. (< 2.7)	n.d. (< 2.5)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.5)	n.d. (< 2.6)	n.d. (< 2.6)

n.i. - no information

BLQ - Below limit of quantification (numbers given in brackets indicate the LOQ).

NA - Not applicable

n.d. -not detected

CTPV3 - 3 out of 5 Coal Tar Pitch Volatiles, as defined by OSHA: phenanthrene, pyrene and benzo[a]pyrene

\* Sampling duration was below 2h, and the sample is therefore not recommended for the calculation of TWA-8hr values. As the task is a repetitive one and only small variations regarding average exposure during the conduction of the task (HFO loading/transfer) is expected the TWA-8h was calculated.

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<sup>&</sup>lt;sup>20</sup> Refinery jetty operator



## Table 5. (P)AH data overview (stationary samplers) - Barge/ship loading (sites: maroon, orange, purple, scarlet)

Site		maroon			orange			purple			scarlet	
event	Α	В	С	Α	В	С	Α	В	С	Α	В	С
rel. humidity [%]	n.i.	92	72	68-93	88-96	68-76	45-55	62-69	70-87	92-94	95-97	74-92
outside temperature [°C]	22	16	20	6	7	6	25	26	21	7	7	3
HFO loading temperature [°C]	79	83	77	80-81	80-81	80-81	76-77	75-76	70	76	83	86
				c	lose to vent							
sampling duration [min]	384	555	450	231	210	227	80	155	321	410	509	592
sampling volume [m <sup>3</sup> ]	0.747	1.17	0.925	0.460	0.412	0.459	0.158	0.307	0.632	0.845	1.03	1.18
naphthalene [µg/m³]	4961	**	***	825	19.9	248	25848	9877	214	1525	**	§
phenanthrene [ng/m <sup>3</sup> ]	3041	**	***	316	160	299	52300	23454	476	3485	**	§
pyrene [ng/m <sup>3</sup> ]	82.7	**	***	105	93.4	51.6	645	204	70.2	106	**	§
benzo[a]pyrene [ng/m³]	n.d. (<3.4)	**	***	n.d. (<5.4)	n.d. (<6.1)	n.d. (<5.5)	BLQ (<15.8)	9.19	n.d. (<4.0)	BLQ (<3.0)	**	§
				t	oackground							
sampling duration [min]	384	555	460	221	190	258	258	168	464	395	507	595
sampling volume [m <sup>3</sup> ]	0.780	1.12	0.961	0.437	0.376	0.520	0.506	0.338	0.90	0.784	1.05	1.21
naphthalene [µg/m³]	1.24	1.19	0.582	0.097	0.130	0.372	0.515	1.11	0.141	0.306	**	1.03
phenanthrene [ng/m <sup>3</sup> ]	144	183	511	122	410	220	93.1	150	48.7	307	**	557
pyrene [ng/m <sup>3</sup> ]	56.0	142	45.8	64.1	94.6	21.0	45.8	51.5	15.7	29.4	**	95.9
benzo[a]pyrene [ng/m³]	n. d. (<3.2)	3.17	BLQ (<2.6)	n.d. (<5.7)	n.d. (<6.7)	n.d. (<4.8)	n. d. (<4.9)	n.d. (<7.4)	n.d. (<2.8)	n.d. (<3.2)	**	BLQ (<2.1)

n.i. - no information

<sup>§</sup> - XAD cartridge for "close to vent " sampler was solid - due to overload

\*\* - Samplers were soaked in water. Data are not reported as results might be erroneous.

\*\*\* - Sampler was covered in HFO (on the outside). Data are not reported as results might be erroneous.

BLQ - Below limit of quantification (numbers given in brackets indicate the LOQ).

n.d. -not detected



## Table 6.(P)AH data overview- Top and bottom truck loading (site: crimson)

Site		crimson	
event	A top loading	B top loading	C bottom loading
rel. humidity [%]	77	79	75
outside temperature [°C]	16	14	15
HFO loading temperature [°C]	57,2-59,8	59,2-61,4	59,5-62,6
P	ersonal sampler - ope	erator	
sampling duration [min]	49	38	24
sampling volume [m³]	0.097	0.074	0.047
naphthalene [µg/m³]	183	194	7.59
phenanthrene [ng/m³]	1371	2426	4861
pyrene [ng/m <sup>3</sup> ]	136	286	469
benzo[a]pyrene [ng/m <sup>3</sup> ]	BLQ (< 25.9)	BLQ (< 34.0)	n.d. (< 53.8)
CTPV3 [ng/m <sup>3</sup> ]	1507 (< 1533)	2712 (< 2746)	5329 (< 5383)
stati	onary sampler - close	e to vent	
sampling duration [min]	46	33	22
sampling volume [m <sup>3</sup> ]	0.091	0.065	0.043
naphthalene [µg/m³]	128	102	703
phenanthrene [ng/m³]	610	1830	5222
pyrene [ng/m <sup>3</sup> ]	383	590	822
benzo[a]pyrene [ng/m <sup>3</sup> ]	n. d. (<27.5)	BLQ (<38.8)	n. d. (<58.1)
stat	ionary sampler - bac	kground	
sampling duration [min]	52	74	flow fault
sampling volume [m³]	0.104	0.145	flow fault
naphthalene [µg/m³]	0.595	0.475	-*
phenanthrene [ng/m³]	434	752	-*
pyrene [ng/m <sup>3</sup> ]	116	223	-*
benzo[a]pyrene [ng/m <sup>3</sup> ]	n. d. (<24.2)	n. d. (<17.2)	_*

-\* no samples collected due to flow-fault of pump

BLQ - Below limit of quantification (numbers given in brackets indicate the LOQ).

n.d. -not detected

CTPV3: 3 out of 5 Coal Tar Pitch Volatiles, as defined by OSHA: phenanthrene, pyrene and benzo[a]pyrene)



# 4. CONCLUSION AND DISCUSSION

In total, five workplace monitoring campaigns were conducted, using personal and stationary samplers to gather information on the occupational inhalation exposure to TOM and selected indicator (P)AH during inland HFO loading of barges and/or trucks.

The monitoring of HFO loading of barges showed that the aerosol-related, 8-hour adjusted TOM concentrations ranged from < 2 to 40  $\mu$ g/m<sup>3</sup>; whereas for the TOM content in the vapour phase values between 78 and 7,600  $\mu$ g/m<sup>3</sup> were observed. The campaigns addressing truck loading did not allow for the calculation of TWA-8hr due to sampling times shorter than 2 h. Similar to the barge loading results, the TOM in the aerosol phase was considerably lower than in the vapour phase (<42 to 182  $\mu$ g/m<sup>3</sup> and 876 to 21100  $\mu$ g/m<sup>3</sup>, respectively).

Inhalation exposure to (P)AH during inland HFO loading of barges and/or trucks was investigated on selected indicator substances, namely naphthalene, phenanthrene, pyrene and benzo[a]pyrene. (P)AH data are reported as sum of aerosol and vapour phase. Similarly to TOM, only the personal data-sets obtained during HFO inland loading of barges were suitable for the calculation of TWA-8hr values for (P)AH. The monitoring campaigns addressing truck loading did not allow for the calculation of TWA-8hr due to sampling times shorter than 2 h.

Naphthalene concentrations varied between 0.2 and 140 µg/m<sup>3</sup>. Benzo[a]pyrene was in all personal samples below the limit of quantification and the sum of pyrene, phenanthrene and benzo[a]pyrene ranged between 69 to 678 ng/m<sup>3</sup>. Naphthalene exposure levels were below the corresponding worker inhalation Derived No Effect Level (DNEL) of 25 mg/m<sup>3</sup> in the registration dossier. For phenanthrene, pyrene and benzo[a]pyrene no DNELs are available. The benzo[a]pyrene acceptance level (according to "Begründung zur ERB zu Benzo[a]pyren in BekGS 910" April 2011) is 7 ng/m<sup>3</sup>. For phenanthrene, pyrene and benzo[a]pyrene comparisons can be made based on information available for the OSHA PEL (Occupational Safety & Health Administration Permissible Exposure Limit) of coal tar pitch volatiles (CTPV<sup>21</sup>) set to 0.2 mg/m<sup>3</sup> <sup>22</sup> for benzene-soluble aerosol, including PAH.

Table 7 summarises the results from the personal samplers (THC, 8h TWA-TOM and 8h TWA-naphthalene) for off-shore and on-shore workers from the present study, sorted from the lowest to the highest value according to THC, and the ones reported in Concawe rpt. 1/15R<sup>23</sup>. Overall, measured exposure levels for barge loading in the two studies are similar, with the exception of the two highest values for naphthalene measured in the latter study.

Source: https://www.osha.gov/laws-regs/regulations/standardnumber/1910/1910.1002

<sup>&</sup>lt;sup>21</sup> Definition of CTPV by OSHA: "[...] coal tar pitch volatiles include the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum (excluding asphalt), wood, and other organic matter. Asphalt (CAS 8052-42-4, and CAS 64742-93-4) is not covered under the "coal tar pitch volatiles" standard. "

<sup>&</sup>lt;sup>22</sup> <u>https://www.osha.gov/dts/sltc/methods/organic/org058/org058.html</u>. Only 3 of the 5 PAH considered in OSHA method 58 in context of the sum parameter CTPV are included in the calculation of the TWA-8hr, i.e. phenanthrene, pyrene and benzo[a]pyrene.

<sup>&</sup>lt;sup>23</sup> Concawe Report 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading. Revised version April 2016.



Table 7.Summary of individual monitored exposure data for barge loading (THC, 8h TWA-TOM and 8h<br/>TWA-naphthalene) from the current report and Concawe rpt 1/15R<sup>24</sup>

	Off	-shore worke	ers <sup>25</sup>	On	-shore worke	ers <sup>26</sup>
	тнс	TOM * 8h-TWA	Naphthalen e	тнс	TOM * 8h-TWA	Naphthalen e
	(mg ME /m <sup>3</sup> )	(mg/m <sup>3</sup> )	8h-TWA (µg/m <sup>3</sup> )	(mg ME /m <sup>3</sup> )	(mg/m <sup>3</sup> )	8h-TWA (μg/m <sup>3</sup> )
	0.46		3.7	0.15		0.19
Individual monitoring	0.84		20.6	0.24		2.90
values from Concawe rpt. 1/15R, see Tables	3.16		12	0.28		0.69
5,6,10,11	10.19		90.3	0.36		1.20
5,0,10,11	16.01		199.93			
Arithmetic mean	6.13		65.3	0.26		1.25
Geometric mean	2.88		27.8	0.25		0.82
	0.32	0.30	0.91	0.089	0.08	0.193
	0.35	0.63	0.96	0.092	0.19	0.241
	0.55	1.07	3.30	0.182	0.41	2.13
	0.56	1.48	8.67	0.214	0.16	0.203
Individual monitoring	0.84	1.89	0.49	0.218	0.23	0.214
values from present	0.91	0.87	7.19	0.257	0.41	3.51
report, see Tables 1 and 4	1.57	2.50	41.7	0.313	0.30	63.5
Teport, see Tables Tahu 4	2.35	5.08	6.79	0.538	0.22	0.181
	2.89	2.18	19.7	0.601	1.39	**
	5.8	2.49	11.2	0.776	1.99	1.91
	8.08	7.61	140	0.902	1.96	1.76
	**	**	1.60	1.26	2.12	1.53
Arithmetic mean	2.20	2.37	20.2	0.45	0.79	6.85
Geometric mean	1.26	1.66	6.42	0.33	0.45	0.99

\* Sum of vapour and aerosol

\*\*Data not reported, results might be erroneous (samples soaked in water)

Recent toxicological review recommended to assess inhalation exposure to emissions from hot HFO as the sum of aerosol and vapour, whereas previously the focus had been on the aerosol component only.

As detailed in the previous report (Concawe rpt. 1/15R), there are differences in the composition of the fumes and the bulk HFO substance. The fumes have been found to have no mutagenic effect in the Ames test<sup>27</sup>. The inhalation Derived No Effect Level of 0.18 mg/m<sup>3</sup> used in the current Concawe REACH CSA, based on hazard data from the bulk substance being applied to the skin of the animal, may therefore not be applicable as reference value in case of exposure to HFO fumes.

Measured data collected in the present study were used to refine the Concawe REACH CSA for substances in the HFO category.

<sup>&</sup>lt;sup>24</sup> Concawe Report 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading. Revised version April 2016.

<sup>&</sup>lt;sup>25</sup> Barge crew member

<sup>&</sup>lt;sup>26</sup> Refinery jetty operator

<sup>&</sup>lt;sup>27</sup> Concawe Report 1/15R: Risk assessment for emissions from hot heavy fuel oil during barge loading. Revised version April 2016.



# 5. APPENDIX 1: SAMPLING PROTOCOL FOR HFO VAPOUR AND AEROSOL

## 5.1. PURPOSE

The purpose of this project is to determine the magnitude of personal exposure to Heavy Fuel Oil (HFO) vapour and aerosol during loading of barges, road or rail tankers as part of an update of Concawe HFO REACH dossiers. It builds on earlier work done by Concawe in the context of inland shipping regulations in Europe for which considerable development was required in order to properly characterise and quantify worker exposures. This previous work is comprehensively reported in Concawe Report 1/15R of April 2016. Participants in the current programme are assumed to be familiar with the contents of 1/15R.

As always, member companies participating in this program have been selected on a voluntary basis and are intended to represent a spectrum of geographical locations, cargo specifications, and operating procedures. The overall goal of this sampling and analysis program is to document "representative" HFO inhalation exposures that currently occur at barge and other loading facilities. Because of the specific information needs of REACH dossiers, data on Operational Conditions and Risk Management Measures will be collected.

## 5.2. INTRODUCTION

A recent review of available exposure information commissioned by Concawe for its 2010 REACH Chemical Safety Assessments has highlighted a lack of data for the Contributing Scenarios related to loading of HFO at various types of terminals including on inland waterways. The REACH DNEL for HFO is applicable to aerosol<sup>28</sup> and is very low, thereby limiting the technical possibilities of estimating exposure levels and conclude on chemical safety using desk-top approaches such as exposure modelling. To accomplish this goal both personal and static air samples will need to be collected and analyzed for some HFO constituents, as well as total hydrocarbon matching the DNEL definition, with appropriate separation of aerosol and vapour fractions. Since, multiple sites will be involved in this sampling program, ancillary information will also be needed to ensure comparability and to aid in the final interpretation of the results. Specifically, the following types of supplemental information will also be required:

- The number of staff involved in the loading operation
- The specific activities of people involved in the loading operation
- The positioning of staff in relation to the barge loading emissions
- The duration of the loading operations
- The specific types of personnel protection equipment employed
- The use of vapour recovery or other exposure control devices
- The nature of preceding cargoes on the barge or tanker being loaded and of which vapours may still be present in the hold
- The type of HFO being handled
- Specific details of the sampling and analytical methods employed (i.e. durations, flowrates, and handling procedures)
- The weather conditions during the loading operation, and

• Unusual events during the monitored operation that may have had an impact on the result.

<sup>&</sup>lt;sup>28</sup> DNEL in revised 2020 HFO dossiers is applicable to both aerosol and vapour fraction. Recent toxicological review recommended to assess inhalation exposure to emissions from hot HFO as the sum of aerosol and vapour, whereas previously the focus had been on the aerosol component only.



For the purposes of this study, HFO have been given a definition that is aligned with REACH via CAS numbers. It is understood that the loaded product meets commercial specifications and may contain some constituents, e.g. to aid 'pumpability'. To the degree possible the product information should indicate this.

The key aim of this survey is to obtain industrial hygiene measurements in the field to assess exposures and emissions during inland barge loading operators. Since multiple facilities will be participating in this programme, there will be some degree of measurement variability that will be influenced by the administrative and engineering controls in effect at each site. It is therefore imperative for participants to collect qualitative and quantitative information on the types and effectiveness of these measures to the extent possible. Because exposures may arise as both HFO vapours and aerosols, specialized sampling devices will be provided for efficiently separating and collecting both airborne forms of HFO.

Employee selection and area locations for the exposure monitoring will be determined by appropriate in-house personnel who are knowledgeable about HFO loading operations and the basic principle of industrial hygiene. The final selection of participating facilities will take into account a number of key variables including geographical spread of operating facilities and climatic conditions at the site.

## 5.3. SAMPLING METHODOLOGY

To facilitate consistency, sampling devices will be distributed by a Central Focal Point (CFP) (Fraunhofer Institute for Toxicology and Experimental Medicine) to participating facilities who are members of the Concawe consortium conducting this programme. The CFP will also be responsible for final quantitative analysis of the samples.

Member companies participating in the project need to be certain that the appropriate number of samples is collected for each job type and emission source and that a complete description is provided for each sampling location, job description, and sampling duration (see Annex 2 of Sampling Protocol). In addition, some description of the climatic conditions should be provided as noted in Annex 3 of Sampling Protocol. It is also essential that the cargo loading temperature is measured and recorded to allow an accurate interpretation of the results from the emissions testing.

The final samples will be returned to the CFP where they will be analyzed for naphthalene, phenanthrene, benzo(*a*)pyrene, pyrene, and total hydrocarbon content for exposure and emission determinations. The four P(AH)s (i.e. naphthalene, phenanthrene, benzo(*a*)pyrene and pyrene) will need to be sampled separately from the total hydrocarbon sample. As such, two personal sampling trains will need to run in parallel for each personal and area sample. All exposure measurements will be compared to applicable occupational exposure limits to determine the level of compliance.

#### 5.3.1. Sample number

An important aspect of this programme is to obtain a valid number of exposure measurements that will yield a reliable evaluation airborne concentration of vapour and mist.

Personal samples should be taken on all workers present at the loading area and involved in the loading operation (on the barge as well as on shore).

The personal samples will be paired with the area samples that will be placed at 0.5m of the exhaust stream of the cargo tank vent. In addition, background samples are required, which measure airborne levels not associated with the HFO loading operation. The background sampling should be performed at a location upwind of the barge and the loading arm.

For each sampling campaign, a field blank will be taken along. The field bank accounts for any "contamination" not associated with sampling (e. g. transport).



Companies may conduct monitoring during loading of several representative HFO substances or products. It is imperative, however, that the HFO (product) is sufficiently well described.

## 5.3.2. Sampling Media

The sample collection method has been designed to collect either HFO vapours and aerosol mists, or P(AH). A BIA (Berufsgenossenschaftliches Institut für Arbeitssicherheit) sampling device or equivalent will be used for this purpose. It consists of a 37 mm glass fiber filter holder, cartridge for 3.2 g of XAD-2 resin, and a 2 L/min critical orifice (see diagram below). Further details on the handling, operation, and use of this sampling device are described in Annex 1 of Sampling Protocol. Since HFO vapors/mists cannot be analyzed together with the four P(AH), each sampling site (personal and area) will require the placement of two sampling trains.



The sampling media supplied should be kept sealed in the packaging they are provided in, stored under cool conditions (<20°C), away from potential sources of contamination. The shelf life of the sampling media has not been determined but is expected to be well over a year if contamination is avoided.

## 5.3.3. Sample Pumps

The sampling pumps should be intrinsically safe and comply with the British Approvals Service for Electrical Equipment in Flammable Atmospheres (BASEEFA) or other applicable standard, and/or operated under an appropriate safe system of work. The P(AH) and BIA (i.e. total hydrocarbon) samples will be collected separately using individual pumps. To facilitate collection and ease the burden on employees, the use of a sampling vest / holster capable of holding two standard sized sampling pumps should be considered.

The pumps used should have an accuracy of  $\pm 5\%$  or better, be capable of operating at a flow rate of 2 L/min and be capable of stable operation throughout the sampling period. Sampling times can vary between short-term (10-20 min) through to long-term (4-8 hr), however long-term samples are preferred for comparison to applicable standards.

## 5.3.4. Sampling Package Calibration

Sampling pumps should be calibrated before commencement of, and on completion of, sampling utilising a portable gas flow meter system or other suitable calibration device that is capable of measuring an air flow in the range 0.5-5.0 L/min and accurate to  $\pm 5\%$ . Records should be kept of the calibration results for each pump so any deviation in performance can be detected.



Calibration/certification of the gas flow meter used should be traceable to national standards. Pump flow rates should be checked periodically during the sampling period and in particular if/when a battery pack is changed.

Unused sample units and field blanks used in conjunction with this programme should be protected from contamination by storing in a clean airtight container.

## 5.3.5. Preparation prior to Sampling

Take care not to touch the filter or adsorbent cartridge with contaminated fingers as this may cause contamination which may interfere with subsequent analysis, however there should be no reason to touch, as the sampling devices will be delivered "ready-for-use" and will just need to be removed from their packaging. Disposable, surgical type, gloves are advised to be worn during unpacking.

Before commencing, it should be checked that the filter and XAD cartridge are labelled with an appropriate sample code (see Appendix 1); sampling devices should labelled in advance to avoid contamination. For each sampling location, two samples will have been collected for the separate quantitation of P(AH) and BIA.

All connections for the sampling unit should be hand-tight only. Do not over tighten as this may cause damage to the connections and may compromise the sample.

Sampling pumps must be calibrated in a clean atmosphere with the BIA sampling device included in the sampling train.

#### 5.3.6. Commencement of Sampling

Prior to taking each sample, record the following on the sample collection proforma (Annex 2 of Sampling Protocol):

- Sample numbers for each combination of filter and XAD cartridge.
- Personnel ID (preferably an anonymous code) for the personal samples.
- Date of sampling
- Location of sampling
- Nature of task
- Loading process description (i.e. how the task should be performed in theory, what is described in the site's procedures)

For personal samples, position the sampling head in the breathing zone of the operator being monitored with the sampling unit in a vertical position and fixed securely. Locate the pump on the person in an appropriate position ensuring that any flexible tubing is not restricted in any way.

Area samples should be placed in the exhaust stream at the cargo tank vent, at approximately 0.5m from the vent. Take care not to breathe any vapour/mist.

Background sampling should be performed dockside at a remote location upwind of the barge and the loading arm. Background samples should be collected alongside with the workplace samples (on the same day as the workplace samples and at the same climatic conditions).

Turn sampling pumps on and record:

- Sample start time (hh:mm)
- Initial pump flow rate (L/min)



# 5.3.7. Conclusion of Sampling

At the end of the sampling, turn off the sample pump and record:

- Sample finish time (hh:mm)
- Sampling duration (mins)
- Final pump flow rate (L/min)
- Volume of air sampled (litres)

For each sample the following information is required to describe environmental conditions during the sampling period (see Annex 3 of Sampling Protocol):

- Air temperature (°C)
- Wind speed and direction (m/s)
- Temperature (°C)
- Atmospheric pressure (mm Hg)
- Relative humidity (%)
- Precipitation (mm)
- Cloud cover (octiles)

Draw a simple plot plan and mark locations of operators and sources of product release. Additional information required includes:

- HFO throughput (during sampling period)
- Temperature of loading
- Quantities of HFO loaded
- Configuration of event (position, size, flow rate...)
- Product description
- Any relevant observations, (e.g. control measure)
- Process description / eventual derivations from site's procedures
- Relevant information on additional loaded components to aid 'pumpability'

If allowed, take photographs of tasks to aid descriptions. Immediately after sampling, carefully disconnect the sampling unit from the sample pump and seal with aluminium foil. **DO NOT DISASSEMBLE THE SAMPLING UNITS OR CARTRIDGES**. Place the sealed sampling unit in the cooling box. For details, refer to Annex 1 of Sampling Protocol. In the interim period between sampling and analysis, the samples should be stored in a cool place away from sources of contamination.

## 5.3.8. Blank sample tubes

For each set of samples sent for analysis at least one 'field blank' should be submitted from the same batch. These will be analysed with the appropriate field samples.

For each batch of tubes sent out to participating companies a minimum of two 'field blank' (tandem tubes) samples should be submitted for each 10 field samples submitted.

The field blank tubes will be delivered to member companies participating in the field survey and assembled exactly the same as the actual sample tubes except that the sample unit will



remain sealed when in the field. However, they should be disassembled and sealed along with the field samples.

Samples should be clearly labelled and details entered on the sample submission form (see Annex 2 of Sampling Protocol).

## 5.4. STORAGE AND DESPATCH

UNDER NO CIRCUMSTANCES SHOULD SAMPLE TUBES BE STORED OR DESPATCHED WITH SAMPLES THAT COULD RISK CROSS-CONTAMINATION.

## 5.4.1. Sample Tubes

Sampling units should be despatched by the quickest route available together with a copy of the information requested in the Annexes to this protocol to Fraunhofer. An e-mail should be sent advising the date and method of despatch and numbers of sample tubes including field banks.

## 5.4.2. Bulk Samples

For each barge loading operation examined, a representative bulk sample of 0.5 litres needs to be collected and appropriately stored for shipment to Fraunhofer ITEM. Care should be taken to carefully label and identify the bulk sample so it can be associated with the exposure emission samples. Likewise, the bulk sample should not be shipped in the same container as the monitoring samples to prevent cross contamination of the sampling devices. In fact, it is advisable to dispatch bulk samples and monitoring samples on separate days so that they are not combined during transport using the preferred courier or postal service. The bulk sample should be accompanied by an MSDS (or other documentation) that specifically applies to the HFO being examined.



## Annex 1: Sampling Data for HFO Monitoring Survey

Instructions for sampling and sample transfer

Please use the sampling unit numbers (filter/XAD no) which are listed in the following table to collect samples at the different sites.

- 1. Take BIA and P(AH) sample in parallel, side-by side
- 2. Calibrate each sampling pump prior to sampling
- 3. Sampling and transportation
  - Remove the two caps from the sampling device (sampling head, tube); do not open filled blank cartridges
  - Connect the sampling pump with the sampling device
  - Take all samples at 2 L/min.
  - Disconnect the sampling pump
  - Cap the sampling device and wrap it in aluminium foil
  - Transport to laboratory. Please send the samples to the address below.
  - Please inform the lab by email: <u>Katharina.bluemlein@item.fraunhofer.de;</u> <u>heiko.kock@item.fraunhofer.de</u>
  - Tel: +49 511 5350 215 (Heiko Kock); +49 511 5350 213 (Katharina Bluemlein)

Shipping Address: Fraunhofer ITEM Abteilung: Bio- und Umweltanalytik Nikolai-Fuchs.Str.1 30625 Hannover



# Annex 2: Sampling Documentation Form: Data for HFO Monitoring Survey

Company:.....Location: .....UN number:..... Cargo loading temperature: .....

Date	Sampling Unit <sup>29</sup> Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Initial Pump Flow Rate (I/min)	Final Pump Flow Rate (I/min)	Sample volume (Litres)*
	FB BIA2	Field Blank	-	-	-	-	-	-
	FB PAK2	Field Blank	-	-	-	-	-	-
	BIA 5	Personal 1_L1						
	PAK 5	Personal 1_L1						
	BIA 6	Person 2_L1						
	PAK 6	Person 2_L1						
	BIA 7	Area 1_L1	Close to vent (0.5 m)					
	PAK 8	Area 1_L1	Close to vent (0.5 m)					
	BIA 8	Area 2_L1	Background sample					
	PAK 8	Area 2_L1	Background sample					

Sampled by.....E-mail.....

<sup>&</sup>lt;sup>29</sup> PAK-sampling unit: for (P)AH-determination; BIA-sampling unit for THC-determination



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# Annex 3: Industrial Hygiene Data Report Form

Please make sufficient copies of this sheet to cover all the sampling situations for which samples have been submitted Sample Numbers to which the following information applies

Date	Filter/XAD no.	Company
	BIA 1_L1_P2	Location
	PAC 1_L1_P2	Country

		Start of sampling period	Mid sampling period	End of sampling period
Time	hh:mm	:	:	:
Air temperature	°C			
Wind speed	m/s			
Wind direction				
Atmospheric pressure	mm Hg			
Relative humidity	%			
Precipitation (if available)	mm			
Cloud cover (if available)	*/8			
Additional information				
HFO throughput during sampling	ng			



report no. 2/20

Loading temperature	
Configuration of event	
Product description (name, UN, MSDS)	
Process description	
Product carried in previous load	
Has the tank been de-gassed prior to loading?	
Further relevant observations	

Draw a diagram including locations of operators, area samplers and sources of vapours Include photographs



# Annex 4: Addresses of Contact Points

## Address 1: Fraunhofer

Katharina Blümlein

Fraunhofer Institute for Toxicology and Experimental Medicine ITEM Nikolai-Fuchs-Str. 1 30625 Hannover Germany Tel: +49 511 5350 213 katharina.bluemlein@item.fraunhofer.de

## Address 2: Concawe

Marilena Trantallidi

Boulevard du Souverain 165 B-1160 Brussels Belgium Tel: +32 (0)2 566 91 06 marilena.trantallidi@concawe.eu



# 6. APPENDIX 2. DATA REPORTS

## 6.1. DATA REPORT - TRUCK LOADING SITE "CRIMSON"

## 6.1.1. Introduction and Objective

Heavy fuel oils (HFO) could be transferred at elevated temperatures (between 50 and 70 C) during truck loading, causing vapour emission. Exposure to these vapours is considered an occupational health risk. Concawe initiated a study to shed light on the occupational exposure to HFO derived vapours during truck loading at elevated temperatures.

The exposure atmosphere during truck loading is collected by means of static and personal samplers. The samples will be analysed for:

- Aromatic Hydrocarbons (AH): Naphthalene and the three polycyclic aromatic hydrocarbons (PAH) phenanthrene, pyrene and benzo(a)pyrene as representatives for low and high boiling AH
- Total Hydrocarbon Content (THC): giving an indication on total hydrocarbon concentration as well as on vapour and aerosol phase.

## 6.1.2. Workplace sampling

Workplace samples were collected during truck loading of HFO. The samples were taken with a 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 vapour phase, semivolatile and volatile compounds). Two static samples (close to vent and background) and one personal sample (<u>operator 1</u>: loading operator, see tables) were taken during each truck loading process. In addition to the personal and static sampling units a field blank was carried along at each sampling campaign.

Two sampling units, one intended for (P)AH collection and the second one for THC determination, were always operated in parallel. This was necessary as different filters and XAD grades are required for THC- and (P)AH- sample collection. The THC sampling units were equipped with a 37 mm glass fibre filter (binderless) and an adsorbent cartridge with 3.2 g XAD-2 resin (size 0.5-0.9 mm). The (P)AH sampling units were equipped with a PTFE filter (2  $\mu$ m) and an adsorbent cartridge with 3 g XAD-2 resin (size 0.25-0.84 mm).

Explosion-proof air sampling pumps were attached to the respective sampling units and operated at a flow rate of 2 L/min.

For each sampling campaign, a field blank was taken along. The field bank accounted for any "contamination" not associated with sampling<sup>30</sup> (e.g. transport).

Coded sampling protocols of the individual sampling campaigns are attached in the Appendix 3.

<sup>&</sup>lt;sup>30</sup> No pump attached.



## 6.1.3. Sample analysis

## 6.1.3.1.Total Hydrocarbon Content (THC)

The parameter of THC, based on the BIA method 6305, allows the characterisation of the collected workplace samples in terms of aerosol and vapour phase.

Filter and XAD material were extracted with tetrachloroethene and analysed separately - the filter results providing information on the aerosol phase and the XAD results on the vapour phase. Sample extracts were analysed by IR-spectroscopy (Fourier-Transform-Infrared Spectrometer Vector 22 (Bruker)), measuring the integral absorption of the CH vibrations between 2800-3000 cm<sup>-1</sup>. This method allows the determination of aliphatic CH-groups, but not a differentiation between compound classes. Quantification was achieved using a standard reference mineral oil (Aldrich No. M8410). Results are reported as mineral oil equivalents (ME) in mg/m<sup>3</sup>.

#### 6.1.3.2. Selected Aromatic Hydrocarbon (AH)

All workplace samples are anlaysed for indicator aromatic hydrocarbons such as naphthalene and the three polycyclic aromatic hydrocarbons (PAH) phenanthrene, pyrene and benzo[a]pyrene. Filter and XAD material were extracted with dichloromethane and analysed separately - the filter results providing information on the aerosol phase and the XAD results on the vapour phase. The XAD samples were extracted with 20 mL dichloromethane using an ultrasonic bath. The filter samples were extracted with 200 mL dichloromethane using a reflux condenser. After the addition of internal standard (deuterated AH) and reduction of sample volume, the AH content was determined by gas chromatography - mass spectrometry (GC-MS). The analytes were monitored in Single Ion Monitoring (SIM) mode using the following m/z traces:

- naphthalene (m/z 128) / naphthalene-d<sub>8</sub> (m/z 136),
- phenanthrene (m/z 178) / phenanthrene-d<sub>10</sub> (m/z 188)
- pyrene (m/z 202) / pyrene d<sub>10</sub> (m/z 212),
- benzo[a]pyrene (m/z 252) / benzo[a]pyrene d<sub>12</sub> (m/z 264).

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

#### 6.1.3.3. Grimmer (P)AH - Bulk Material

The refinery provided an aliquot of the HFO-bulk material that was transferred during all three sampling events. The internal Fraunhofer ITEM ID-number A036/17 was assigned to the HFO-bulk material.

The Grimmer (P)AH content of the HFO-bulk material was determined by GC-MS analysis. A sample aliquot was dissolved in toluene. This sample was then spiked with a solution of deuterated reference compounds. Following clean-up on a silica gel column the resulting eluate, which contains the (P)AH, was reduced in volume and the solvent changed from cyclohexane to 2-propanol. The (P)AH content was determined by gas chromatography with mass selective detector (GC/MS, 6890N/5975, Agilent) in SIM mode (Single Ion Monitoring). The (P)AH were quantified by the method of internal standardisation.



## 6.1.4. Results - Sampling Events A to C

In total three sampling events (A; B; and C) were monitored at the site (crimson). The sampling design was always the same, comprising the following sampling positions/locations:

- Area sampler: Close to the vent (approx. 0.5 1.2 m)
- Background sampler: Located in an area with low traffic and working activities
- Personal sampler (loading operator): Worker overseeing the truck loading
- Field blank: Accounting for all non-exposure atmosphere contributions (e. g. transport)

At each position/location to sampling units were placed; one for THC-determination (BIAsampling unit) and one for (P)AH-determination (PAK-sampling unit) (please also see chapter 6.1.2).

#### 6.1.4.1. Process Parameters - site "Crimson"

#### Sampling Event A

Over a time period of 50 min 46,576 kg of HFO were transferred into a truck (top loading) at a product transfer temperature of 57 - 60 C.

The process parameters for the loading event A are summarised in Table 1.

#### Sampling Event B

Over a time period of 40 min 43,064 kg of HFO were transferred into a truck (top loading) at a product transfer temperature of  $59 - 61^{\circ}$ C.

The process parameters for the loading event B are summarised in Table 1.

#### Sampling Event C

Over a time period of 20 min 42,998 kg of HFO were transferred into a truck (bottom loading) at a product transfer temperature of 60 - 63°C.

The process parameters for the loading event C are summarised in Table 1.


Process parameter	Event A (top loading)	Event B (top loading)	Event C (bottom loading)
Outdoor temperature [°C]	16	13.7	14.7
Relative humidity [%]	77	79	75
Loading temperature [°C]	57.2 - 59.8	59.2 - 61.4	59.5 - 62.6
Amount of HFO transferred [kg]	46,576	43,064	42,998

 Table 1. Process parameters: Overview. More detailed information can be found in the coded sampling protocols (Appendix 3)

## 6.1.4.2. Total Hydrocarbon Content (THC) - site "Crimson"

The workplace related THC data (personal samplers) are presented in Table 3. The THC found in the exposure atmosphere close to the vent are shown in Table 4. The findings of the background samplers are also listed in Table 2. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

The data presented in Table 2 to Table 4 were obtained by quantification against a standard mineral oil, hence the values are given in mg ME /  $m^3$ . In the previous study<sup>31</sup>, assessing the workplace exposure to HFO related fumes during barge loading showed, that the standard mineral oil does not give the same IR-response (chapter 6.1.3.1) as the HFO fume condensates. The response factors varied from 1.43 to 2.01, corresponding to a 1.43 to 2.01 lower IR-response of the HFO-fume condensate compared to the standard mineral oil. As a conservative approach, a response factor of 2 was assumed for the THC results obtained for the workplace monitoring campaigns presented in this report, doubling the exposure concentrations (given in mg TOM /  $m^3$ ). The adjusted data for the personal samplers, loading operator, are given in Table 5.

Time-weight-average values (TWA-8h) were not calculated due to 1.) the short sampling time, not being representative for an 8h-workshift of a loading operator and 2.) the missing exposure data during the unloading of the truck, an event that is also contributing to the overall exposure to HFO during an 8h-workshift.

<sup>&</sup>lt;sup>31</sup> Concawe report 1/15R (revised: April 2016): Risk assessment for emissions from hot heavy fuel oil during barge loading.



Table 2.Background - THC data for sampling events A to C. Data presented as mg ME / m³<br/>(ME: mineral-oil equivalent)

	area sampler -	background				
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	16	52	0.102	0.029	0.069	0.098
В	14	74	0.144	BLQ (< 0.007)	0.132	0.132 (< 0.139)
С	14.7	36	0.070	BLQ (< 0.014)	0.214	0.214 (< 0.228)

Table 3.Personal sampler (loading operator) - THC data for sampling events A to C. Data<br/>presented as mg ME / m³ (ME: mineral-oil equivalent)

	personal s	ampler				
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
А	16	49	0.0985	0.091	9.18	9.27
В	14	38	0.076	0.066	10.5	10.6
С	14.7	24	0.048	BLQ (< 0.021)	0.438	0.438 (< 0.459)

Event A and B: top loading; event C: bottom loading

Table 4.Close to the vent - THC data for sampling events A to C. Data presented as mg ME / m³<br/>(ME: mineral-oil equivalent)

	area sampler - o	close to vent				
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	16	46	0.092	0.033	0.500	0.533
В	14	33	0.0655	0.015	8.03	8.05
C	14.7	22	0.044	0.023	13.0	13.0

Event A and B: top loading; event C: bottom loading



Table 5.Personal sampler (loading operator): Adjustment of measured THC exposure data by an<br/>assumed response factor (RF = 2)

	person	al sampler				
event #	sampling duration [min]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]
Α	49	0.091	9.18	2	0.182	18.4
В	38	0.066	10.5	2	0.132	21.1
С	24	BLQ (< 0.021)	0.438	2	BLQ (< 0.042)	0.876

Event A and B: top loading; event C: bottom loading

## 6.1.4.3. Selected Aromatic Hydrocarbon (AH) - site "Crimson"

The workplace related (P)AH data (personal samplers) are presented in Table 7. The (P)AH content found in the exposure atmosphere close to the vent are shown in

Table 8. The findings of the background samplers are also listed in Table 6. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

Personal exposure data (loading operator) varied for the selected (P)AH as follows (please note: naphthalene concentration are given in  $\mu g/m^3$ , whereas phenanthrene and pyrene concentration are reported as  $ng/m^3$ ):

- naphthalene: 7.59 194 μg/m<sup>3</sup>
- phenanthrene: 1371 4861 ng/m<sup>3</sup>
- pyrene: 136 469 ng/m<sup>3</sup>
- benzo[a]pyrene: not detectable or below limit of quantitation.

Time-weight-average values (TWA-8h) based on the personal sampler data were not calculated due to 1.) the short sampling time, not being representative for an 8h-workshift of a loading operator and 2.) the missing exposure data during the unloading of the truck, an event that is also contributing to the overall exposure to HFO during an 8h-workshift.



Table 6.Background - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m³], whereas concentrations for all other<br/>analytes are reported as [ng/m³]. Event A and B: top loading; Event C: bottom loading.

	area sampler - background naphthalene			phenanthrene			pyrene			benzo[a]pyrene					
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	16	52	0.1035	0.216	0.379	0.595	BLQ (< 24.2)	434	434 (< 458)	BLQ (< 24.2)	116	116 (< 140)	n. d. (< 24.2)	n. d. (< 24.2)	n. d. (< 24.2)
В	14	74	0.145	0.041	0.434	0.475	BLQ (< 17.2)	752	752 (< 769)	BLQ (< 17.2)	223	223 (< 240)	n. d. (< 17.2)	n. d. (< 17.2)	n. d. (< 17.2)
С	14.7	flow fault	flow fault	-	-	-	-	-	-	-	-	-	-	-	-

n.d. – not detected; BLQ – Below Limit of Quantitation

**Table 7.** Personal sampler (loading operator) - (P)AH data for sampling events A to C. **Note:** Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]. *Event A and B: top loading; Event C: bottom loading.* 

	personal	sampler		naphthalene			phenanthrene		pyrene			benzo[a]pyrene			
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	16	49	0.0965	0.152	183	183	39.7	1332	1371	BLQ (< 25.9)	136	136 (162)	BLQ (< 25.9)	n. d. (< 25.9)	BLQ (< 25.9)
В	14	38	0.0735	0.038	194	194	40.8	2385	2426	BLQ (< 34.0)	286	286 (320)	BLQ (< 34.0)	n. d. (< 34.0)	BLQ (< 34.0)
С	14.7	24	0.0465	BLQ (< 0.054)	7.59	7.59 (< 7.64)	BLQ (< 53.8)	4861	4861 (< 4915)	BLQ (< 53.8)	469	469 (< 523)	n. d. (< 53.8)	n. d. (< 53.8)	n. d. (< 53.8)

n.d. - not detected; BLQ - Below Limit of Quantitation



**Table 8.** Close to vent - (P)AH data for sampling events A to C. **Note:** Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]. *Event A and B: top loading; Event C: bottom loading.* 

	area sampler - close to vent naphthalene			phenanthrene		pyrene			benzo[a]pyrene						
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	16	46	0.091	0.581	127	128	32.1	578	610	BLQ (< 27.5)	383	383 (< 411)	n. d. (< 27.5)	n. d. (< 27.5)	n. d. (< 27.5)
В	14	33	0.0645	BLQ (< 0.039)	102	102	BLQ (< 38.8)	1830	1830 (< 1869)	BLQ (< 38.8)	590	590 (< 629)	BLQ (< 38.8)	n. d. (< 38.8)	BLQ (< 38.8)
С	14.7	22	0.043	1.91	701	703	150	5073	5222	BLQ (< 58.1)	822	822 (< 880)	n. d. (< 58.1)	n. d. (< 58.1)	n. d. (< 58.1)

n.d. – not detected; BLQ – Below Limit of Quantitation



# 6.1.4.4. Grimmer (P)AH - Bulk material - site "Crimson"

The Grimmer (P)AH data for the HFO-bulk material A036/17 (sampling event A; B and C) are presented in Table 9 .

Table 9.	Grimmer	(P)AH:	HFO-bulk	materials	A036/17
Tuble 7.	Grinner	(1)/111		materials	A030/17

	A 036/17
(P)AH - ID	Sampling event A; B and C
	[hā\ā]
Naphthalene	1105
Phenanthrene	1346
Anthracene	152
Fluoranthene	103
Pyrene	582
Benzo[b]naphtho[2,1-d]thiophene	91.8
Benzo[c]phenanthrene	34.3
Benzo[g,h,i]fluoranthene	NA*
Benz[a]anthracene	232
Cyclopenta[c,d]pyrene	22.9
Triphenylene	144
Chrysene	309
Benzo[b]fluoranthene	78.6
Benzo[k]fluoranthene	16.7
Benzo[j]fluoranthene	22.7
Benzo[e]pyrene	179
Benzo[a]pyrene	173
Dibenz[a,h]anthracene	19.2
Coronene	38.7
Indeno[1,2,3-cd]pyrene	18.4
Anthanthrene	51.5
Benzo[g,h,i]perylene	151

NA\* - not applicable, as signals were overlapping



## 6.2. DATA REPORTS - BARGE LOADING SITES "MAROON/ORANGE/PURPLE/SCARLET/MAGENTA"

<u>Note for site Magenta</u>: No samples were collected at site "Magenta" as no loading vessels were available during the scheduled time slot. In order to keep with the proposed timeline the sampling equipment had to be returned to Fraunhofer ITEM.

# 6.2.1. Introduction and Objective

Heavy fuel oil (HFO) could be transferred at elevated temperatures (between 70 and 90 C) during barge/ship loading, causing vapour emission. Exposure to these vapours is considered an occupational health risk. Concawe initiated a study to shed light on the occupational exposure to HFO derived vapours during barge/ship loading at elevated temperatures.

The exposure atmosphere during barge/ship loading is collected by means of static and personal samplers. The samples will be analysed for:

- Aromatic Hydrocarbons (AH): Naphthalene and the three polycyclic aromatic hydrocarbons (PAH) phenanthrene, pyrene and benzo(a)pyrene as representatives for low and high boiling AH
- Total Hydrocarbon Content (THC): giving an indication on total hydrocarbon concentration as well as on vapour and aerosol phase.

# 6.2.2. Workplace sampling

Workplace samples were collected during barge loading of HFO. The samples were taken with a 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 vapour phase, semivolatile and volatile compounds). Two static samples (close to vent and background) and two personal samples (<u>operator 1</u>: offshore, ship, tanker and <u>operator 2</u>: onshore, loading bridge, oil movement, see tables) were taken during each barge loading process. In addition to the personal and static sampling units a field blank was carried along at each sampling campaign.

Two sampling units, one intended for (P)AH collection and the second one for THC determination, were always operated in parallel. This was necessary as different filters and XAD grades are required for THC- and (P)AH- sample collection. The THC sampling units were equipped with a 37 mm glass fibre filter (binderless) and an adsorbent cartridge with 3.2 g XAD-2 resin (size 0.5-0.9 mm). The (P)AH sampling units were equipped with a PTFE filter (2  $\mu$ m) and an adsorbent cartridge with 3 g XAD-2 resin (size 0.25-0.84 mm).

Explosion-proof air sampling pumps were attached to the respective sampling units and operated at a flow rate of 2 L/min.

For each sampling campaign, a field blank was taken along. The field bank accounted for any "contamination" not associated with sampling<sup>32</sup> (e. g. transport).

Coded sampling protocols of the individual sampling campaigns are attached in the Appendix 3.

<sup>&</sup>lt;sup>32</sup> No pump attached.



# 6.2.3. Sample analysis

## 6.2.3.1.Total Hydrocarbon Content (THC)

The parameter of THC, based on the BIA method 6305, allows the characterisation of the collected workplace samples in terms of aerosol and vapour phase.

Filter and XAD material were extracted with tetrachloroethene and analysed separately - the filter results providing information on the aerosol phase and the XAD results on the vapour phase. Sample extracts were analysed by IR-spectroscopy (Fourier-Transform-Infrared Spectrometer Vector 22 (Bruker)), measuring the integral absorption of the CH vibrations between 2800-3000 cm<sup>-1</sup>. This method allows the determination of aliphatic CH-groups, but not a differentiation between compound classes. Quantification was achieved using a standard reference mineral oil (Aldrich No. M8410). Results are reported as mineral oil equivalents (ME) in mg/m<sup>3</sup>.

## 6.2.3.2. Selected Aromatic Hydrocarbon (AH)

All workplace samples are anlaysed for indicator aromatic hydrocarbons such as naphthalene and the polycyclic aromatic hydrocarbons (PAH) phenanthrene, pyrene and benzo[a]pyrene. Filter and XAD material were extracted with dichloromethane and analysed separately - the filter results providing information on the aerosol phase and the XAD results on the vapour phase. The XAD samples were extracted with 20 mL dichloromethane using an ultrasonic bath. The filter samples were extracted with 200 mL dichloromethane using a reflux condenser. After the addition of internal standard (deuterated AH) and reduction of sample volume, the AH content was determined by gas chromatography - mass spectrometry (GC-MS). The analytes were monitored in Single Ion Monitoring (SIM) mode using the following m/z traces:

- naphthalene (m/z 128) / naphthalene-d<sub>8</sub> (m/z 136),
- phenanthrene (m/z 178) / phenanthrene-d<sub>10</sub> (m/z 188)
- pyrene (m/z 202) / pyrene d<sub>10</sub> (m/z 212),
- benzo[a]pyrene (m/z 252) / benzo[a]pyrene d<sub>12</sub> (m/z 264).

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

## 6.2.3.3.Grimmer (P)AH - Bulk Material

The refinery provided aliquots of the HFO-bulk materials that were transferred from the on-shore-site to the barges. Internal Fraunhofer ITEM ID-numbers were assigned to the HFO-bulk materials (Table 10).



Table 10.	HFO-bulk materials: Allocation to sampling event and assigned ID-number	s
for all barge	loading operations	

Sampling site	Sampling event	HFO-bulk material - Fraunhofer ITEM ID
Maroon	А	A071/17
	В	A072/17
	C	A073/17
Orange	А	No material for analysis
	В	No material for analysis
	C	No material for analysis
Purple	А	A020/17
	В	A020/17
	C	A035/17
Scarlet	А	A013/18
	В	A014/18
	C	A016/18

The Grimmer (P)AH content of the HFO-bulk materials was determined by GC-MS analysis. A sample aliquot was dissolved in toluene. This sample was then spiked with a solution of deuterated reference compounds. Following clean-up on a silica gel column the resulting eluate, which contains the (P)AH, was reduced in volume and the solvent changed from cyclohexane to 2-propanol. The PAH content was determined by gas chromatography with mass selective detector (GC/MS, 6890N/5975, Agilent) in SIM mode (Single Ion Monitoring). The (P)AH were quantified by the method of internal standardisation.

For site "Orange", no HFO-bulk material was available for analysis.



# 6.2.4. Results - Sampling Events A to C

In total three sampling events (A; B; and C) were monitored at each barge loading site (maroon, orange, purple, scarlet). The sampling design was always the same, comprising the following sampling positions/locations:

- Area sampler (on board): Close to the vent (approx. 0.5 m)
- Background sampler: Located in an area with low traffic and working activities
- Personal sampler (off-shore): Worker overseeing the barge/ship loading on board of barge/ship
- Personal sampler (on-shore): Worker overseeing the barge/ship loading from the loading bridge
- Field blank: Accounting for all non-exposure atmosphere contributions (e. g. transport)

At each position/location to sampling units were placed; one for THC-determination (BIA-sampling unit) and one for (P)AH-determination (PAK-sampling unit) (see chapter 6.1.2).

## 6.2.4.1. Process Parameters - all barge loading sites

## SITE MAROON

## Sampling Event A

HFO was transferred onto a barge at a product transfer temperature of  $79^{\circ}$ C and a flow rate of  $885 \text{ m}^3/\text{h}$ . Over a time period of approx. 6.5 h air samples were collected - stationary and personal.

## Sampling Event B

HFO was transferred onto a barge at a product transfer temperature of 83  $^{\circ}$ C and a flow rate of 950 m<sup>3</sup>/h. Over a time period of approx. 9.25 h air samples were collected - stationary and personal.

## Sampling Event C

HFO was transferred onto a ship/barge at a product transfer temperature of 77 C and a flow rate of 675 m<sup>3</sup>/h. Over a time period of approx. 7.5 - 8.5 h air samples were collected - stationary and personal.

## SITE ORANGE

## Sampling Event A

Over a time period of 3.5 h 1000 t of HFO were transferred onto the barge at a product transfer temperature of 80 - 81  $^{\circ}$ C. The HFO was transferred at a flow rate of 320 m<sup>3</sup>/h.



**Sampling Event BOver** a time period of 3.5 h HFO<sup>33</sup> was transferred onto the barge at a product transfer temperature of 80 - 81 C. The HFO was transferred at a flow rate of 250 m<sup>3</sup>/h (first 100 m<sup>3</sup>) and 400 m<sup>3</sup>/h (main load).

## Sampling Event C

Over a time period of 4 h HFO<sup>Error! Bookmark not defined.</sup> was transferred onto a barge at a product transfer temperature of 80-81 C. The HFO was transferred at a flow rate of 200 m<sup>3</sup>/h (first 100 m<sup>3</sup>) and 350 m<sup>3</sup>/h (main load).

#### SITE PURPLE

#### Sampling Event A

Over a time period of 2 h 1000 t of HFO were transferred onto the barge at a product transfer temperature of 76 - 77 °C. Not all of the available HFO storage capacities (6000 t) on the barge were used. This rendered the pressure release, caused by air displacement inside the barge storage facility during loading, via the vent system an unlikely event. For the purpose of the workplace monitoring campaign the vent system was therefore opened, allowing the sampling of HFO derived fumes during the sampling event A (please note: the air space might have contained fumes from the previous cargo). The HFO was transferred at a flow rate of 748 m<sup>3</sup>/h (ship's log) to 750 m<sup>3</sup>/h (loading bridge). At the beginning and end of the transfer process, the HFO was pumped at reduced flow rates.

#### Sampling Event B

Over a time period of 3 h 1600 t of HFO were transferred onto the barge at a product transfer temperature of 75 - 76 °C. Not all of the available HFO storage capacities (6000 t) on the barge were used. This rendered the pressure release, caused by air displacement inside the barge storage facility during loading, via the vent system an unlikely event. For the purpose of the workplace monitoring campaign the vent system was therefore opened, allowing the sampling of HFO derived fumes during the sampling event B (please note: the air space might have contained fumes from the previous cargo). The HFO was transferred at a flow rate of 740 - 760 m<sup>3</sup>/h (ship's log) to 760 m<sup>3</sup>/h (loading bridge). At the beginning and end of the transfer process, the HFO was pumped at reduced flow rates.

## Sampling Event C

Over a time period of 8 h 6500 m<sup>3</sup> of HFO were transferred onto a ship at a product transfer temperature of 70 °C. Not all of the available HFO storage capacities (10,981 t) on the ship were used. The vent system was opened during the transfer, allowing the sampling of HFO derived fumes during the sampling event C (please note: the air space might have contained fumes from the previous cargo). The HFO was transferred at a flow rate of 880 - 980 m<sup>3</sup>/h (ship's log) to 760 m<sup>3</sup>/h (loading bridge). At the beginning and end of the transfer process, the HFO was pumped at reduced flow rates.

<sup>&</sup>lt;sup>33</sup> Exact amount not known.



# SITE SCARLET

## Sampling Event A

Over a time period of approx. 10 h HFO was transferred with a throughput of 760 m<sup>3</sup>/h to a barge at a product transfer temperature of 86°C.

## Sampling Event B

Over a time period of approx. 6.5 h HFO was transferred with a throughput of 500 m<sup>3</sup>/h to a barge at a product transfer temperature of 76°C.

## Sampling Event C

Over a time period of approx. 8.5 h HFO was transferred with a throughput of 775 m<sup>3</sup>/h to a barge at a product transfer temperature of 83°C.

The process parameters for the loading events A - C for all barge/ship loading sites are summarised in Table 1. More detailed information can be found in the coded sampling protocols (Appendix 3).

Table 11.	Process parameters: Overview. More detailed information can be found in the coded
	sampling protocols (Appendix 3)

Process parameter	Barge/ship	Event A	Event B	Event C
Outdoor temperature [°C]	Maroon	21.5	15.7 - 17.0	18.2 - 21.0
	Orange	4.4 - 7.3	6.3 - 7.0	5.4 - 6.8
	Purple	24.2 - 25.7	24.3 - 27.2	20.0 - 22.7
	Scarlet	14.5	6.5	6.5
Relative humidity [%]	Maroon	No information (no precipitation)	92 (rain)	71 (no precipitation)
	Orange	67.8 - 92.5	87.5 - 96.3	68.9 - 75.7
	Purple	44.6 - 54.7	62.4 - 68.7	70 - 87
	Scarlet	83	93	96
Loading temperature [°C]	Maroon	78.7	82.8	76.8
	Orange	80 - 81	80 - 81	80 - 81
	Purple	76 - 77	75 - 76	70
	Scarlet	86	76	83
Amount of HFO transferred [t]	Maroon	No information	No information	No information
	Orange	1000	No information	No information



	Purple <sup>34</sup>	1000 / 6000	1600 / 6000	6500 m³ / 10981 t
	Scarlet	No information	No information	No information
HFO transfer rate [m <sup>3</sup> /h]	Maroon <sup>35</sup>	885	950	675
	Orange	320	250 (first 100 m <sup>3</sup> );	200 (first 100 m <sup>3</sup> );
			400 (main load)	350 (main load)
	Purple <sup>36</sup>	748 - 750	740 - 760	880 - 980
	Scarlet	No information	No information	No information

# 6.2.4.2. Total Hydrocarbon Content (THC) - site "Maroon"

The workplace related THC data (personal samplers) are presented Table 3 and Table 14. The THC found in the exposure atmosphere close to the vent are shown in Table 4. The findings of the background samplers are also listed in Table 2. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

The data presented in Table 2 to Table 4 were obtained by quantification against a standard mineral oil, hence the values are given in mg ME /  $m^3$ . In the previous study<sup>37</sup>, assessing the workplace exposure to HFO related fumes during barge loading showed, that the standard mineral oil does not give the same IR-response (chapter 6.1.3.1) as the HFO fume condensates. The response factors varied from 1.43 to 2.01, corresponding to a 1.43 to 2.01 lower IR-response of the HFO-fume condensate compared to the standard mineral oil. As a conservative approach, a response factor of 2 was assumed for the THC results obtained for the workplace monitoring campaigns presented in this report, doubling the exposure concentrations (given in mg TOM /  $m^3$ ). The adjusted data and the resulting time-weight-average values (TWA-8h), for the two personal samplers, on- and off-shore, are given Table 5 and Table 17, respectively.

## Note for site "Maroon":

The sampling conditions (e.g. during rain or sampler positioned too close to the source) introduce an unknown error to the analysis results, that cannot be corrected for. These results are marked accordingly in the respective Tables. In addition, the field blanks showed relatively high THC values.

<sup>&</sup>lt;sup>34</sup> Amount of HFO transferred [t] / loading capacity of ship [t]

<sup>&</sup>lt;sup>35</sup> Rates were reduced at start and end of transfer process

<sup>&</sup>lt;sup>36</sup> Rates were reduced at start and end of transfer process

<sup>&</sup>lt;sup>37</sup> Concawe report 1/15R (revised: April 2016): Risk assessment for emissions from hot heavy fuel oil during barge loading.



# Table 12. Background - THC data for sampling events A to C. Data presented as mg ME / m<sup>3</sup> (ME: mineral-oil equivalent)

	area sampler -	background				
event #	Outdoor temperature [°C]	emperature duration		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	21.8	384	0.737	0.003	0.141	0.144
В	15.7 - 17.0	555	1.189	BLQ (< 0.001)	0.045	0.045 (< 0.046)
C	18.2 - 21.0	460	0.959	0.015	0.238	0.253

BLQ - Below Limit of Quantitation

Table 13.Off-shore personal sampler - THC data for sampling events A to C. Data presented as<br/>mg ME / m³ (ME: mineral-oil equivalent)

	personal sample	er - off-shore	I.			
event #	temperature duration volum		sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	21.8	382	0.766	0.016	1.55	1.57
B*	15.7 - 17.0	555	1.116	*	*	*
C	18.2 - 21.0	520	1.04	0.013	2.33	2.35

\* Sample soaked with water, filter was not wettable with tetrachloroethylene. Data are not reported as results might be erroneous.

Table 14.	On-shore personal sampler - THC data for sampling events A to C. Data presented as
	mg ME / m <sup>3</sup> (ME: mineral-oil equivalent)

	personal sample	er - on-shore				
event #	Outdoor sampling temperature duration [°C] [min]		sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	21.8	382	0.751	0.005	0.252	0.257
В	15.7 - 17.0	555 0.777		BLQ (< 0.001)	0.601	0.601 (< 0.602)
C	18.2 - 21.0	520	1.032	0.018	0.884	0.902

BLQ - Below Limit of Quantitation



Table 15.Close to the vent - THC data for sampling events A to C. Data presented as mg ME / m³<br/>(ME: mineral-oil equivalent)

	area sampler - o	close to vent				
event #	Outdoor sampling temperature duration [°C] [min]		sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	21.8	384	0.747	0.012	78.1	78.1
B*	15.7 - 17.0	555	1.121	*	*	*
C#	18.2 - 21.0	450	0.934	#	#	#

\* Sample soaked with water, filter not wettable with tetrachloroethylene; additionally filter was torn. Data are not reported as results might be erroneous.

<sup>#</sup> The sampling unit was covered with HFO on the outside as well as on the screw threads. Data are not reported as results might be erroneous.



# Table 16. Personal sampler (off-shore): Adjustment of measured THC exposure data by an assumed response factor (RF = 2)

	personal sar	npler - off-shore	•					
event #	sampling filter duration (aerosol) [min] [mg ME/m <sup>3</sup> ] XAD (vapour) [mg ME/m <sup>3</sup> ]		assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA- 8h [mg TOM/m³]	vapour calculated TWA- 8h [mg TOM/m³]	
А	382	0.016	1.55	2	0.031	3.10	0.025	2.47
B*	555	*	*	*	*	*	*	*
C	520	0.013	2.33	2	0.025	4.66	0.027	5.05

\* Sample soaked with water, filter not wettable with tetrachloroethylene. Data are not reported as results might be erroneous.

 Table 17.
 Personal sampler (on-shore): Adjustment of measured THC exposure data by an assumed response factor (RF = 2)

	personal sam	pler - on-shore						
event #	sampling duration [min] filter (aerosol) [mg ME/m³]		XAD (gvapour) [mg ME/m³]	assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA- 8h [mg TOM/m <sup>3</sup> ]	vapour calculated TWA- 8h [mg TOM/m³]
А	382	0.005	0.252	2	0.011	0.503	0.008	0.401
В	555	BLQ (< 0.001)	0.601	2	2 BLQ (< 0.002)		NA (< 0.002)	1.390
С	520	0.018	0.884	2	0.037	1.768	0.040	1.915

BLQ - Below Limit of Quantitation; NA - not applicable





## 6.2.4.3. Selected Aromatic Hydrocarbon (AH) - site "Maroon"

The workplace related (P)AH data (personal samplers) are presented in Table 7 and Table 20. The (P)AH content found in the exposure atmosphere close to the vent are shown in

Table 8. The findings of the background samplers are also listed in Table 6. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

Personal exposure data (on- and offshore) varied for the selected (P)AH as follows (please note: naphthalene concentration are given in  $\mu g/m^3$ , whereas phenanthrene and pyrene concentration are reported as  $ng/m^3$ ):

- naphthalene: 6.27 52.4 µg/m³ (off-shore); 1.62 4.39 µg/m³ (on-shore)
- phenanthrene: 183 492 ng/m<sup>3</sup> (off-shore); 189 434 ng/m<sup>3</sup> (on-shore)
- pyrene: 33.4 35.2 ng/m<sup>3</sup> (off-shore); 34.7 124 ng/m<sup>3</sup> (on-shore)
- benzo[a]pyrene: not detectable (off-shore and on-shore).

An overview of the personal sampler data including the calculated TWA-8hr values for naphthalene, benzo[a]pyrene and coal tar pitch volatiles (CTPV3) is given in

Table 22. The naphthalene TWA-8hr values varied off-shore between 1.6 and 41.7  $\mu$ g/m<sup>3</sup> and on-shore between 1.8 and 3.5  $\mu$ g/m<sup>3</sup>. The TWA-8hr exposure concentration for benzo[a]pyrene was in all cases below 2.7 ng/m<sup>3</sup> and varied between 174 and 569 ng/m<sup>3</sup> for CTPV3.



# Table 18.Background - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m³], whereas concentrations for all other<br/>analytes are reported as [ng/m³]

	area sampler - background				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	21.8	384	0.78	0.0654	1.17	1.24	5.84	138	144	BLQ (< 3.21)	56.0	56.0 (< 59.2)	n. d. (< 3.21)	BLQ (< 3.21)	BLQ (< 3.21)	
В	15.7 - 17.0	555	1.124	0.0037	1.19	1.19	2.29	181	183	BLQ (< 2.22)	142	142 (< 144)	n. d. (< 2.22)	3.17	3.17 (< 5.39)	
С	18.2 - 21.0	460	0.961	0.0185	0.563	0.582	3.20	508	511	BLQ (< 2.60)	45.8	45.8 (< 48.4)	n. d. (< 2.60)	BLQ (< 2.60)	BLQ (< 2.60)	

n. d. - not detected; BLQ - Below Limit of Quantitation

**Table 19.** Off-shore personal sampler - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]

	personal sampler - off-shore				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	21.8	382	0.756	0.0111	52.4	52.4	BLQ (< 3.31)	183	183 (< 186)	BLQ (< 3.31)	35.2	35.2 (< 38.5)	n. d. (< 3.31)	n. d. (< 3.31)	n. d. (< 3.31)	
B*	15.7 - 17.0	555	1.104	*	*	*	*	*	*	*	*	*	*	*	*	
С	18.2 - 21.0	520	1.053	0.0109	6.26	6.27	BLQ (< 2.37)	481	481 (< 483)	BLQ (< 2.37)	32.7	32.7 (< 35.1)	n. d. (< 2.37)	n. d. (< 2.37)	n. d. (< 2.37)	

n. d. - not detected; BLQ - Below Limit of Quantitation

\* Sample soaked with water. Data are not reported as results might be erroneous.



*Table 20.* On-shore personal sampler - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]

	personal sampler - on-shore				naphthalene		phenanthrene		pyrene			benzo[a]pyrene			
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	21.8	384	0.739	0.00672	4.38	4.39	BLQ (< 3.38)	189	189 (< 192)	BLQ (< 3.38)	34.7	34.7 (< 38.1)	n. d. (< 3.38)	n. d. (< 3.38)	n. d. (< 3.38)
В	15.7 - 17.0	555	1.124	0.0029	2.69	2.69	3.59	199	203	4.76	119	124	n. d. (< 2.22)	n. d. (< 2.22)	n. d. (< 2.22)
С	18.2 - 21.0	520	1.05	0.0034	1.62	1.62	BLQ (< 2.38)	431	431 (< 433)	BLQ (< 2.38)	41.0	41.0 (< 43.4)	n. d. (< 2.38)	n. d. (< 2.38)	n. d. (< 2.38)

n. d. - not detected; BLQ - Below Limit of Quantitation

**Table 21.** Close to vent - (P)AH data for sampling events A to C Note: Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]

	area sampler - close to vent				naphthalene		phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	21.8	384	0.747	3.40	4958	4961	62.1	2420	3041	41.4	41.3	82.7	n. d. (< 3.35)	n. d. (< 3.35)	n. d. (< 3.35)
B*	15.7 - 17.0	555	1.174	*	*	*	*	*	*	*	*	*	*	*	*
<b>C</b> <sup>#</sup>	18.2 - 21.0	450	0.925	#	#	#	#	#	#	#	#	#	#	#	#

n. d. - not detected

\* Sample was soaked with water. Data are not reported as results might be erroneous.

<sup>#</sup> The sampling unit was covered with HFO on the outside as well as on the screw threads. Data are not reported as results might be erroneous.



## Table 22. (P)AH data overview (personal sampler)

- <u>For all individual substances:</u> Data reported in brackets are calculated values based on the limit of quantification.
- <u>For the sum parameter of CTPV3</u>: Data reported in brackets consider compounds, which were not detected or present in below their limit of quantification. The corresponding limit of quantification was taken into account in the calculation.

Site		maroon	
event	А	В	C
rel. humidity [%]	n.i.	92	72
outside temperature [°C]	22	16	20
HFO loading temperature [°C]	78.7	82.8	76.8
	off-shore	1	
sampling duration [min]	382	555	520
sampling volume [m <sup>3</sup> ]	0.756	1.104	1.053
naphthalene [µg/m³]	52.4	**	6.27
phenanthrene [ng/m <sup>3</sup> ]	183	**	492
pyrene [ng/m <sup>3</sup> ]	35.2	**	33.4
benzo[a]pyrene [ng/m <sup>3</sup> ]	n.d. (< 3.3)	**	n.d. (< 2.4)
CTPV3 [ng/m <sup>3</sup> ]	218 (< 221)	**	525 (< 527)
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	174 (< 176)	**	569 (< 571)
naphthalene TWA-8hr [µg/m³]	41.7	**	6.79
benzo[a]pyrene TWA-8hr [ng/m³]	n.d. (< 2.6)	**	n.d. (< 2.6)
	on-shore		
sampling duration [min]	384	555	520
sampling volume [m <sup>3</sup> ]	0.739	1.124	1.05
naphthalene [µg/m³]	4.39	2.69	1.62
phenanthrene [ng/m <sup>3</sup> ]	189	203	434
pyrene [ng/m <sup>3</sup> ]	34.7	124	41.9
benzo[a]pyrene [ng/m <sup>3</sup> ]	n.d. (< 3.4)	n.d. (< 2.2)	n.d. (< 2.4)
CTPV3 [ng/m <sup>3</sup> ]	224 (< 227)	327 (<329)	476 (< 478)
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	179 (< 182)	378 (<380)	516 (< 518)
naphthalene TWA-8hr [µg/m³]	3.51	3.11	1.76
benzo[a]pyrene TWA-8hr [ng/m³]	n.d. (< 2.7)	n.d. (< 2.5)	n.d. (< 2.6)

\*\* Samplers soaked in water. Data are not reported as results might be errorneous.

n.d. -not detected

NA - Not applicable

CTPV3 - 3 out of 5 Coal Tar Pitch Volatiles, as defined by OSHA:phenanthrene, pyrene and benzo[a]pyrene NA - Not applicable

# 6.2.4.4.Grimmer (P)AH - Bulk material - site "Maroon"

The Grimmer (P)AH data for the HFO-bulk materials A071/17 (sampling event A); A072/17 (sampling event B) and A073/17 (sampling event C) are presented in Table 9.



Table 23.	Grimmer (P	P)AH: HFO-bulk	materials A071/17	; A072/17 and A073/17
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	A 071/17	A 072/17	A 073/17
(P)AH - ID	Sampling event A	Sampling event B	Sampling event C
-	[µg/g]	[hã\ð]	[µg/g]
Naphthalene	2294	2778	2602
Phenanthrene	539	655	651
Anthracene	89.9	115	129
Fluoranthene	26.7	34.7	33.1
Pyrene	154	177	167
Benzo[b]naphtho[2,1-d]thiophene	35.9	54.2	47.7
Benzo[c]phenanthrene	4.78	7.19	5.70
Benzo[g,h,i]fluoranthene	NA*	NA*	NA*
Benz[a]anthracene	34.8	52.0	43.6
Cyclopenta[c,d]pyrene	3.41	4.36	3.70
Triphenylene	18.9	32.0	24.4
Chrysene	41.5	64.4	51.0
Benzo[b]fluoranthene	8.06	13.2	10.7
Benzo[k]fluoranthene	2.15	3.13	2.62
Benzo[j]fluoranthene	2.82	3.83	3.57
Benzo[e]pyrene	22.1	33.4	26.8
Benzo[a]pyrene	18.8	30.0	24.4
Dibenz[a,h]anthracene	2.54	3.36	2.75
Coronene	3.12	3.35	3.15
Indeno[1,2,3-cd]pyrene	2.46	3.29	2.78
Anthanthrene	4.75	7.28	6.15
Benzo[g,h,i]perylene	10.3	14.9	13.0

NA\* - not applicable, as signals were overlapping



# 6.2.4.5.Total Hydrocarbon Content (THC) - site "Orange"

The workplace related THC data (personal samplers) are presented in Table 35 and Table 146. The THC found in the exposure atmosphere close to the vent are shown in Table 47. The findings of the background samplers are also listed in Table 24. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

The data presented in Table 24 to Table 47 were obtained by quantification against a standard mineral oil, hence the values are given in mg ME /  $m^3$ . In the previous study<sup>38</sup>, assessing the workplace exposure to HFO related fumes during barge loading showed, that the standard mineral oil does not give the same IR-response (chapter 6.1.3.1) as the HFO fume condensates. The response factors varied from 1.43 to 2.01, corresponding to a 1.43 to 2.01 lower IR-response of the HFO-fume condensate compared to the standard mineral oil. As a conservative approach, a response factor of 2 was assumed for the THC results obtained for the workplace monitoring campaigns presented in this report, doubling the exposure concentrations (given in mg TOM /  $m^3$ ). The adjusted data and the resulting time-weight-average values (TWA-8h), for the two personal samplers, on- and off-shore, are given in Table 529 and Table 17 30, respectively.

<sup>&</sup>lt;sup>38</sup> Concawe report 1/15R (revised: April 2016): Risk assessment for emissions from hot heavy fuel oil during barge loading.



Table 244.	Background - THC data for sampling events A to C. Data presented as mg ME / m <sup>3</sup> (ME:
	nineral-oil equivalent)

	area sampler -	background				
event #	ht Outdoor sampling sample temperature duration volume [°C] [min] [m³]		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]	
Α	4.4 - 7.3	221	0.435	0.002	0.009	0.011
В	6.3 - 7.0	190	0.378	0.005	0.045	0.050
C	5.4 - 6.8	258	0.524	n.d. (< 0.002)	0.036	0.036 (< 0.038)

n.d. - not detected

Table 255. Off-shore personal sampler - THC data for sampling events A to C. Data presented asmg ME / m³ (ME: mineral-oil equivalent)

	personal sample	er - off-shore	I				
event #	temperature		sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]	
А	4.4 - 7.3	227	0.452	0.018	0.894	0.912	
В	6.3 - 7.0	224	0.448	0.022	0.295	0.317	
С	5.4 - 6.8	226	0.455	0.009	8.07	8.08	

Table 266.On-shore personal sampler - THC data for sampling events A to C. Data presented as mg<br/>ME / m³ (ME: mineral-oil equivalent)

	personal sample	er - on-shore				
event #	temperature duration volume		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]	
Α	4.4 - 7.3	220	0.445	0.004	0.085	0.089
В	6.3 - 7.0	252	0.469	0.009	0.209	0.218
C	5.4 - 6.8	226	0.454	0.002	0.311	0.313

 Table 277. Close to the vent - THC data for sampling events A to C. Data presented as mg ME / m<sup>3</sup> (ME: mineral-oil equivalent)

	area sampler - o	close to vent					
event #	Outdoor temperature [°C]	sampling sample duration volume [min] [m³]		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]	
А	4.4 - 7.3	231	0.455	0.015	59.2	59.2	
В	6.3 - 7.0	210	0.414	0.012	1.86	1.87	
C	5.4 - 6.8	227	0.451	0.011	29.7	29.7	



	personal sa	mpler - off-shore						
event #	sampling duration [min]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA-8h [mg TOM/m³]	vapour calculated TWA-8h [mg TOM/m³]
Α	227	0.018	0.894	2	0.036	1.79	0.017	0.85
В	224	0.022	0.295	2	0.044	0.59	0.021	0.28
С	226	0.009	8.07	2	0.018	16.1	0.008	7.60

 Table 288.
 Personal sampler (off-shore): Adjustment of measured THC exposure data by an assumed response factor (RF = 2)

 Table 29.
 Personal sampler (on-shore): Adjustment of measured THC exposure data by an assumed response factor (RF = 2)

	personal sa	ampler - on-shore						
event #	sampling duration [min]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA-8h [mg TOM/m³]	vapour calculated TWA-8h [mg TOM/m³]
Α	220	0.004	0.085	2	0.008	0.170	0.004	0.078
В	252	0.009	0.209	2	0.018	0.418	0.009	0.219
С	226	0.002	0.311	2	0.004	0.622	0.002	0.293



## 6.2.4.6. Selected Aromatic Hydrocarbon (AH) - site "Orange"

The workplace related (P)AH data (personal samplers) are presented in Table 71 and Table 202. The (P)AH content found in the exposure atmosphere close to the vent are shown in

Table 8. The findings of the background samplers are also listed in Table 60. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

Personal exposure data (on- and offshore) varied for the selected (P)AH as follows (please note: naphthalene concentration are given in  $\mu g/m^3$ , whereas phenanthrene and pyrene concentration are reported as  $ng/m^3$ ):

- naphthalene: 1.95 297 μg/m³ (off-shore); 0.408 135 μg/m³ (on-shore)
- phenanthrene: 166 259 ng/m<sup>3</sup> (off-shore); 115 525 ng/m<sup>3</sup> (on-shore)
- pyrene: 30.5 69.0 ng/m<sup>3</sup> (off-shore); 32.9 197 ng/m<sup>3</sup> (on-shore)
- benzo[a]pyrene: not detectable (off-shore and on-shore).

An overview of the personal sampler data including the calculated TWA-8hr values for naphthalene, benzo[a]pyrene and coal tar pitch volatiles (CTPV3) is given in Table 334. The naphthalene TWA-8hr values varied off-shore between 0.911 and 140  $\mu$ g/m<sup>3</sup> and on-shore between 0.193 and 63.5  $\mu$ g/m<sup>3</sup>. The TWA-8hr exposure concentration for benzo[a]pyrene was in all cases below 2.6 ng/m<sup>3</sup> and varied between 102 and 379 ng/m<sup>3</sup> for CTPV3.



*Table 290.* Background - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]

	area sampler - background				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	4.4 - 7.3	221	0.437	0.015	0.082	0.097	6.82	115	122	BLQ (< 5.7)	64.1	64.1 (< 69.8)	n.d. (< 5.7)	n.d. (< 5.7)	n.d. (< 5.7)	
В	6.3 - 7.0	190	0.376	0.009	0.121	0.130	BLQ (< 6.65)	410	410 (< 417)	BLQ (< 6.65)	94.6	94.6 (< 101)	n.d. (< 6.65)	n.d. (< 6.65)	n.d. (< 6.65)	
С	5.4 - 6.8	258	0.520	0.253	0.119	0.372	16.4	204	220	BLQ (< 4.81)	21.0	21.0 (< 25.8)	n.d. (< 4.81)	n.d. (< 4.81)	n.d. (< 4.81)	

n.d. - not detected; BLQ - Below Limit of Quantitation

*Table 301.* Off-shore personal sampler - - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]

	personal sampler - off-shore				naphthalene			enanthre	ne	pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	4.4 - 7.3	227	0.454	0.007	15.2	15.2	BLQ (< 5.51)	166	166 (< 172)	BLQ (< 5.51)	48.8	48.8 (< 54.3)	n.d. (< 5.51)	n.d. (< 5.51)	n.d. (< 5.51)
В	6.3 - 7.0	224	0.446	BLQ (< 0.006)	1.95	1.95 (< 1.96)	6.91	163	170	7.00	62.0	69.0	n.d. (< 5.61)	n.d. (< 5.61)	n.d. (< 5.61)
С	5.4 - 6.8	226	0.454	0.015	297	297	5.4	254	259	BLQ (< 5.51)	30.5	30.5 (< 36.0)	n.d. (< 5.51)	n.d. (< 5.51)	n.d. (< 5.51)

n.d. - not detected; BLQ - Below Limit of Quantitation



	personal sampler - on-shore				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	4.4 - 7.3	220	0.440	0.008	0.413	0.422	BLQ (< 5.68)	145	145 (< 151)	BLQ (< 5.68)	106	106 (< 112)	n.d. (< 5.68)	n.d. (< 5.68)	n.d. (< 5.68)	
В	6.3 - 7.0	252	0.504	0.007	0.401	0.408	BLQ (< 4.96)	525	525 (< 530)	BLQ (< 4.96)	197	197 (< 202)	n.d. (< 4.96)	n.d. (< 4.96)	n.d. (< 4.96)	
С	5.4 - 6.8	226	0.453	0.095	135	135	7.22	196	203	BLQ (< 5.52)	32.9	32.9 (< 38.4)	n.d. (< 5.52)	n.d. (< 5.52)	n.d. (< 5.52)	

*Table 312.* On-shore personal sampler - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]

n.d. - not detected; BLQ - Below Limit of Quantitation

Table 323.Close to vent - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m³], whereas concentrations for all other<br/>analytes are reported as [ng/m³]

	area sampler - close to vent				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	4.4 - 7.3	231	0.460	0.162	825	825	12.2	304	316	BLQ (< 5.44)	105	105 (< 110)	n.d. (< 5.44)	n.d. (< 5.44)	n.d. (< 5.44)	
В	6.3 - 7.0	210	0.412	0.009	19.9	19.9	BLQ (< 6.07)	160	160 (< 166)	BLQ (< 6.07)	93.4	93.4 (< 99.5)	n.d. (< 6.07)	n.d. (< 6.07)	n.d. (< 6.07)	
С	5.4 - 6.8	227	0.459	0.148	248	248	14.7	284	299	BLQ (< 5.45)	51.6	51.6 (< 57.1)	n.d. (< 5.45)	n.d. (< 5.45)	n.d. (< 5.45)	

n.d. - not detected; BLQ - Below Limit of Quantitation



# Table 334. (P)AH data overview (personal samplers)

- For all individual substances: Data reported in brackets are calculated values based on the limit of quantification.
- <u>For the sum parameter of CTPV3:</u> Data reported in brackets consider compounds, which were not detected or present in below their limit of quantification. The corresponding limit of quantification was taken into account in the calculation.

Site		orange									
event	Α	R	с								
rel. humidity [%]	67,8-92,5	87,5-96,3	68,-75,7								
outside temperature [°C]	6	7	6								
HFO loading temperature [°C]	80-81	80-81	80-81								
		00-01	00-01								
	off-shore										
sampling duration [min]	227	224	226								
sampling volume [m <sup>3</sup> ]	0.454	0.446	0.454								
naphthalene [µg/m³]	15.2	1.95	297								
phenanthrene [ng/m <sup>3</sup> ]	166	170	259								
pyrene [ng/m <sup>3</sup> ]	48.8	69.0	30.5								
benzo[a]pyrene [ng/m <sup>3</sup> ]	n.d. (< 5.51)	n.d. (< 5.61)	n.d. (< 5.51)								
CTPV3 [ng/m <sup>3</sup> ]	215 (< 221)	239 (< 245)	290 (< 296)								
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	102 (< 105)	112 (< 114)	136 (< 139)								
naphthalene TWA-8hr [µg/m³]	7.19	0.911	140								
benzo[a]pyrene TWA-8hr [ng/m³]	n.d. (< 2.61)	n.d. (< 2.62)	n.d. (< 2.60)								
	on-shore										
sampling duration [min]	220	252	226								
sampling volume [m <sup>3</sup> ]	0.440	0.504	0.453								
naphthalene [µg/m³]	0.422	0.408	135								
phenanthrene [ng/m <sup>3</sup> ]	145	525	203								
pyrene [ng/m <sup>3</sup> ]	106	197	32.9								
benzo[a]pyrene [ng/m <sup>3</sup> ]	n.d. (< 5.68)	n.d. (< 4.96)	n.d. (< 5.52)								
CTPV3 [ng/m <sup>3</sup> ]	251 (< 257)	722 (< 727)	236 (< 242)								
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	115 (< 118)	379 (< 382)	111 (< 114)								
naphthalene TWA-8hr [µg/m³]	0.193	0.214	63.5								
benzo[a]pyrene TWA-8hr [ng/m <sup>3</sup> ]	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)								

n.d. -not detected

CTPV3 - 3 out of 5 Coal Tar Pitch Volatiles, as defined by OSHA: phenanthrene, pyrene and benzo[a]pyrene



## 6.2.4.7.Total Hydrocarbon Content (THC) - site "Purple"

The workplace related THC data (personal samplers) are presented in 36 and Table 1437. The THC found in the exposure atmosphere close to the vent are shown in Table 438. The findings of the background samplers are also listed in 35. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

The data presented in Table 25 to Table 438 were obtained by quantification against a standard mineral oil, hence the values are given in mg ME /  $m^3$ . In the previous study<sup>39</sup>, assessing the workplace exposure to HFO related fumes during barge loading showed, that the standard mineral oil does not give the same IR-response (chapter 6.1.3.1) as the HFO fume condensates. The response factors varied from 1.43 to 2.01, corresponding to a 1.43 to 2.01 lower IR-response of the HFO-fume condensate compared to the standard mineral oil. As a conservative approach, a response factor of 2 was assumed for the THC results obtained for the workplace monitoring campaigns presented in this report, doubling the exposure concentrations (given in mg TOM /  $m^3$ ). The adjusted data and the resulting time-weight-average values (TWA-8h), for the two personal samplers, on- and off-shore, are given in Table 50 and Table 17 39, respectively.

<sup>&</sup>lt;sup>39</sup> Concawe report 1/15R (revised: April 2016): Risk assessment for emissions from hot heavy fuel oil during barge loading.



Table 345. Background - THC data for sampling events A to C. Data presented as I	ng ME / m <sup>3</sup> (ME:
mineral-oil equivalent)	

	area sampler -	background				
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
А	24.2 - 25.7	258	0.511	0.008	0.106	0.114
В	24.3 - 27.2	168	0.336	0.006	0.128	0.134
С	20 - 22.7	464	0.900	0.006	0.341	0.347

Table 356.Off-shore personal sampler - THC data for sampling events A to C. Data presented as<br/>mg ME / m³ (ME: mineral-oil equivalent)

	personal sample	er - off-shore	1			
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	24.2 - 25.7	103	0.205	0.044	5.76	5.80
В	24.3 - 27.2	181	0.364	0.041	2.85	2.89
C	20.2 - 22.6	467	0.939	0.011	0.540	0.55

Table 37.On-shore personal sampler - THC data for sampling events A to C. Data presented as mg<br/>ME / m³ (ME: mineral-oil equivalent)

	personal sample	er - on-shore				
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
А	24.2 - 25.7	100	0.199	0.050	0.487	0.538
В	24.3 - 27.2	173	0.346	0.023	0.191	0.214
С	20.2 - 22.6	487	0.969	0.009	0.083	0.092

Table 38.Close to the vent - THC data for sampling events A to C. Data presented as mg ME / m³<br/>(ME: mineral-oil equivalent)

	area sampler - o	close to vent				
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
А	24.2 - 25.7	80	0.160	0.350	758	758
В	24.3 - 27.2	155	0.313	0.249	512	512
C	20.2 - 22.6	321	0.626	0.026	38.2	38.3



## Table 39.Personal sampler (off-shore): Adjustment of measured THC exposure date [mg ME/m³] by an assumed response factor (RF = 2)

	personal sample	er - off-shore						
event #	sampling duration [min]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA-8h [mg TOM/m³]	vapour calculated TWA-8h [mg TOM/m³]
А	103	0.044	5.76	2	0.088	11.5	0.019*	2.47*
В	181	0.041	2.85	2	0.082	5.70	0.031	2.15
С	467	0.011	0.540	2	0.021	1.08	0.021	1.05

\* Sampling duration was below 2 h, and the sample is therefore not recommended for the calculation of TWA-8hr values. As the task is a repetitive one and only small variations regarding average exposure during the conduction of this task (HFO loading/transfer) is expected, the TWA-8hr was calculated.

Table 40. Personal sampler (on-shore): Adjustment of measured THC exposure date [mg ME/m<sup>3</sup>] by an assumed response factor (RF = 2)

	personal sampl	er - on-shore						
event #	sampling duration [min]	filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA-8h [mg TOM/m³]	vapour calculated TWA-8h [mg TOM/m³]
А	100	0.050	0.487	2	0.101	0.975	0.021*	0.203*
В	173	0.023	0.191	2	0.046	0.382	0.017	0.138
С	487	0.009	0.083	2	0.019	0.165	0.019	0.168

\* Sampling duration was below 2 h, and the sample is therefore not recommended for the calculation of TWA-8hr values. As the task is a repetitive one and only small variations regarding average exposure during the conduction of this task (HFO loading/transfer) is expected, the TWA-8hr was calculated.



## 6.2.4.8. Selected Aromatic Hydrocarbon (AH) - site "Purple"

The workplace related (P)AH data (personal samplers) are presented in Table 72 and Table 203. The (P)AH content found in the exposure atmosphere close to the vent are shown in

Table 84. The findings of the background samplers are also listed in Table 61. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

Personal exposure data (on- and offshore) varied for the selected (P)AH as follows (please note: naphthalene concentration are given in  $\mu g/m^3$ , whereas phenanthrene and pyrene concentration are reported as  $ng/m^3$ ):

- naphthalene: 3.39 52.2 µg/m³ (off-shore); 0.238 0.868 µg/m³ (on-shore)
- phenanthrene: 176 356 ng/m<sup>3</sup> (off-shore); 115 375 ng/m<sup>3</sup> (on-shore)
- pyrene: 19.2 79.0 ng/m<sup>3</sup> (off-shore); 35.7 118 ng/m<sup>3</sup> (on-shore)
- benzo[a]pyrene:not detectable (off-shore and on-shore).

On overview of the personal sampler data including the calculated TWA-8hr values for naphthalene, benzo[a]pyrene and coal tar pitch volatiles (CTPV3) is given in Table 405. The naphthalene TWA-8hr values varied off-shore between 3.3 and 19.7  $\mu$ g/m<sup>3</sup> and on-shore between 0.181 and 0.241  $\mu$ g/m<sup>3</sup>. The TWA-8hr exposure concentration for benzo[a]pyrene was in all cases below 2.5 ng/m<sup>3</sup> and varied between 73.6 and 377 ng/m<sup>3</sup> for CTPV3.



Table 361.Background - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m³], whereas concentrations for all other<br/>analytes are reported as [ng/m³]

area sampler - background				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	24.2 - 25.7	258	0.506	0.00723	0.508	0.515	BLQ (< 4.9)	93.1	93.1 (<98.0)	BLQ (< 4.9)	45.8	45.8 (< 50.7)	n.d. (< 4.9)	n.d. (< 4.9)	n.d. (< 4.9)
В	24.3 - 27.2	168	0.338	0.0503	1.06	1.11	BLQ (< 7.4)	150	150 (< 157)	BLQ (< 7.4)	51.5	51.5 (< 58.9)	n.d. (< 7.4)	n.d. (< 7.4)	n.d. (< 7.4)
С	20 - 22.7	464	0.900	0.0105	0.130	0.141	BLQ (< 2.8)	48.7	48.7 (< 51.5)	BLQ (< 2.8)	15.7	15.7 (< 18.5)	n.d. (< 2.8)	n.d. (< 2.8)	n.d. (< 2.8)

n.d. - not detected; BLQ - Below Limit of Quantitation

**Table 372.** Off-shore personal sampler - - (P)AH data for sampling events A to C. **Note:** Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>]

	personal sampler - off-shore				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	24.2 - 25.7	103	0.208	0.0792	51.9	52.0	16.3	340	356	BLQ (< 12.0)	75.1	75.1 (< 87.1	n.d. (< 12.0)	n.d. (< 12.0)	n.d. (< 12.0)	
В	24.3 - 27.2	181	0.366	0.0159	52.2	52.2	BLQ (< 6.8)	176	176 (< 183)	BLQ (< 6.8)	19.2	19.2 (< 26.0)	n.d. (< 6.8)	n.d. (< 6.8)	n.d. (< 6.8)	
С	20.2 - 22.6	467	0.985	0.0037	3.39	3.39	6.55	342	349	BLQ (< 2.5)	38.4	38.4 (< 40.9)	n.d. (< 2.5)	n.d. (< 2.5)	n.d. (< 2.5)	

n.d. - not detected; BLQ - Below Limit of Quantitation



Table 383.On-shore personal sampler - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m³], whereas concentrations<br/>for all other analytes are reported as [ng/m³]

	personal sampler - on-shore				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	24.2 - 25.7	100	0.203	0.0254	0.843	0.868	BLQ (< 12.3)	375	375 (< 387)	BLQ (< 12.3)	118	118 (< 130)	n.d. (< 12.3)	n.d. (< 12.3)	n.d. (< 12.3)	
В	24.3 - 27.2	173	0.344	0.00744	0.555	0.562	BLQ (< 7.3)	155	155 (< 162)	BLQ (< 7.3)	35.7	35.7 (< 43.0)	n.d. (< 7.3)	n.d. (< 7.3)	n.d. (< 7.3)	
С	20.2 - 22.6	487	0.959	BLQ (< 0.003)	0.238	0.238 (< 0.241)	2.62	112	115	BLQ (< 2.6)	51.9	51.9 (< 54.5)	n.d. (< 2.6)	n.d. (< 2.6)	n.d. (< 2.6)	

n.d. - not detected; BLQ - Below Limit of Quantitation

Table 394.Close to vent - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m³], whereas concentrations for all other<br/>analytes are reported as [ng/m³]

area sampler - close to vent				n	aphthalen	e	phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]
А	24.2 - 25.7	80	0.158	2.18	25846	25848	920	51380	52300	253	392	645	BLQ (< 15.8)	n.d. (< 15.8)	BLQ (< 15.8)
В	24.3 - 27.2	155	0.307	0.388	9877	9877	132	23323	23455	BLQ (< 8.1)	204	204 (< 212)	9.19	n.d. (< 8.1)	9.19 (< 17.3)
С	20.2 - 22.6	321	0.632	0.220	214	214	27.4	449	476	BLQ (< 4.0)	70.2	70.2 (< 74.2)	n.d. (< 4.0)	n.d. (< 4.0)	n.d. (< 4.0)

n.d. - not detected; BLQ - Below Limit of Quantitation



## Table 405. (P)AH data overview (personal samplers)

- <u>For all individual substances:</u> Data reported in brackets are calculated values based on the limit of quantification.
- <u>For the sum parameter of CTPV3:</u> Data reported in brackets consider compounds, which were not detected or present below their limit of quantification. The corresponding limit of quantification was taken into account in the calculation.

overt	Α	В	С
event		-	-
rel. humidity [%]	44.6-54.7	62,4-68,7	70-87
outside temperature [°C]	25	26	21
HFO loading temperature [°C]	76-77	75-76	70
	off-shore		
sampling duration [min]	103	181	467
sampling volume [m <sup>3</sup> ]	0.208	0.366	0.985
naphthalene [µg/m³]	52.0	52.2	3.39
phenanthrene [ng/m <sup>3</sup> ]	356	176	349
pyrene [ng/m <sup>3</sup> ]	75.1	19.2	38.4
benzo[a]pyrene [ng/m³]	n.d. (< 12.0)	n.d. (< 6.8)	n.d. (< 2.5)
CTPV3 [ng/m <sup>3</sup> ]	431 (< 443)	195 (< 202)	387 (< 390)
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	92.5* (< 95.1)*	73.6 (< 80.4)	377 (< 380)
naphthalene TWA-8hr [µg/m³]	11.2*	19.7	3.30
benzo[a]pyrene TWA-8hr [ng/m <sup>3</sup> ]	n.d. (< 2.6)*	n.d. (< 2.6)	n.d. (< 2.4)
	on-shore		
sampling duration [min]	100	173	487
sampling volume [m <sup>3</sup> ]	0.203	0.344	0.959
naphthalene [µg/m³]	0.868	0.562	0.238
phenanthrene [ng/m³]	375	155	115
pyrene [ng/m <sup>3</sup> ]	118	35.7	51.9
benzo[a]pyrene [ng/m³]	n.d. (< 12.3)	n.d. (< 7.3)	n.d. (< 2.6)
CTPV3 [ng/m <sup>3</sup> ]	493 (< 505)	191 (< 198)	167 (< 170)
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	103* (< 115)*	68.7 (< 76.0)	169 (< 172)
naphthalene TWA-8hr [µg/m³]	0.181*	0.203	0.241
benzo[a]pyrene TWA-8hr [ng/m <sup>3</sup> ]	n.d. (< 2.6)*	n.d. (< 2.6)	n.d. (< 2.6)

n.d. -not detected

CTPV3 - 3 out of 5 Coal Tar Pitch Volatiles, as defined by OSHA: phenanthrene, pyrene and benzo[a]pyrene \* Sampling duration was below 2 h, and the sample is therefore not recommended for the calculation of TWA-8hr values. As the task is a repetitive one and only small variations regarding average exposure during the conduction of this task (HFO loading/transfer) is expected, the TWA-8hr was calculated.



# 6.2.4.9. Grimmer (P)AH - Bulk material - site "Purple"

The Grimmer (P)AH data for the HFO-bulk materials A020/17 (sampling event A and B) and A035/17 (sampling event C) are presented in Table 96.

Table 416. Grimmer (P)AH: HFO-bulk materials A020/17 and A035/17

	A 020/17	A 035/17
(P)AH - ID	Sampling event A and B	Sampling event C
	[µg/g]	[µg/g]
Naphthalene	170	313
Phenanthrene	196	310
Anthracene	28.8	41.1
Fluoranthene	15.9	20.6
Pyrene	68.5	90.1
Benzo[b]naphtho[2,1-d]thiophene	69.2	91.1
Benzo[c]phenanthrene	7.12	9.64
Benzo[g,h,i]fluoranthene	NA*	NA*
Benz[a]anthracene	80.2	102
Cyclopenta[c,d]pyrene	10.7	8.85
Triphenylene	44.5	57.8
Chrysene	107	129
Benzo[b]fluoranthene	53.6	56.1
Benzo[k]fluoranthene	9.54	9.63
Benzo[j]fluoranthene	16.7	16.5
Benzo[e]pyrene	79.0	83.1
Benzo[a]pyrene	71.1	73.1
Dibenz[a,h]anthracene	13.5	11.4
Coronene	7.93	6.20
Indeno[1,2,3-cd]pyrene	9.75	8.63
Anthanthrene	19.4	17.0
Benzo[g,h,i]perylene	31.7	26.5

NA\* - not applicable, as signals were overlapping


#### 6.2.4.10.Total Hydrocarbon Content (THC) - site "Scarlet"

The workplace related THC data (personal samplers) are presented in Table 348 and Table 49. The THC found in the exposure atmosphere close to the vent are shown in Table 40. The findings of the background samplers are listed in Table 247. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

The data presented in Table 247 to Table 503 were obtained by quantification against a standard mineral oil, hence the values are given in mg ME /  $m^3$ . In the previous study<sup>40</sup>, assessing the workplace exposure to HFO related fumes during barge loading showed, that the standard mineral oil does not give the same IR-response (chapter 6.1.3.1) as the HFO fume condensates. The response factors varied from 1.43 to 2.01, corresponding to a 1.43 to 2.01 lower IR-response of the HFO-fume condensate compared to the standard mineral oil. As a conservative approach, a response factor of 2 was assumed for the THC results obtained for the workplace monitoring campaigns presented in this report, doubling the exposure concentrations (given in mg TOM /  $m^3$ ). The adjusted data and the resulting time-weight-average values (TWA-8h) for the two personal samplers, off- and on-shore, are given in Table 51 and Table 522.

<sup>&</sup>lt;sup>40</sup> Concawe report 1/15R (revised: April 2016): Risk assessment for emissions from hot heavy fuel oil during barge loading.



Table 47.	Background - THC data for sampling events A to C. Data presented as mg ME / m <sup>3</sup> (ME:
	mineral-oil equivalent)

	area sampler -	background				
event #	Outdoor temperature [°C]	sampling sample duration volume [min] [m³]		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
А	6.0-6.9	395	0.8366	n.d. (< 0.001)	0.067	0.067 (< 0.068)
В	5-8	507	1.0211	*	*	*
С	2-4	595	1.214	0.001	0.215	0.216

n.d. - not detected; \* - Filter and XAD were wet.

**Table 48.** Off-shore personal sampler - THC data for sampling events A to C. Data presented as mg ME / m<sup>3</sup> (ME: mineral-oil equivalent)

	personal sample	er - off-shore				
event #	Outdoor temperature [°C]	rature duration volume		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	6.0-6.9	438	0.8707	0.001	0.345	0.346
В	5-8	536	1.0918	0.013	0.831	0.844
C	2-4	634	1.287	0.004	0.556	0.560

Table 49.On-shore personal sampler - THC data for sampling events A to C. Data presented as<br/>mg ME / m³ (ME: mineral-oil equivalent)

	personal sample	er - on-shore				
event #	Outdoor temperature [°C]	temperature duration volume [°C] [min] [m³]		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	6.0-6.9	405	0.9153	0.001	1.258	1.259
В	5-8	5-8 540 1.1		0.002	0.180	0.182
C	2-4	616	1.2566	#	0.776	Min. 0.776

# - filter cassette missing

Table 50.Close to vent - THC data for sampling events A to C. Data presented as mg ME/m³ (ME:<br/>mineral-oil equivalent)

	area sampler - c	lose to vent				
event #	Outdoor temperature [°C]	perature duration volume		filter (aerosol) [mg ME/m³]	XAD (vapour) [mg ME/m³]	total [mg ME/m³]
Α	6.0-6.9	410	0.826	0.086	145.6	145.7
B*	5-8	509	1.0233	*	*	*
<b>C</b> <sup>#</sup>	2-4	592	1.2106	#	#	#

\* - filter and XAD were wet; # - XAD was soaked with HFO fumes. Overload of sampler. Data are not reported as results might be erroneous.



### Table 51.Personal sampler (off-shore): Adjustment of measured THC exposure data by an assumed response factor (RF = 2)

	personal sa	mpler - off-shore						
event #	sampling duration [min]	duration [mg ME/m <sup>3</sup> ] [mg ME/m <sup>3</sup> ]		assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA-8h [mg TOM/m³]	vapour calculated TWA-8h [mg TOM/m³]
Α	438	0.001	0.345	2	0.002	0.69	0.002	0.63
В	536	0.013	0.831	2	0.026	1.66	0.029	1.86
С	634	0.004	0.556	2	0.008	1.11	0.010	1.47

 Table 52.
 Personal sampler (on-shore): Adjustment of measured THC exposure data by an assumed response factor (RF = 2)

	personal sa	mpler - on-shore						
event #	sampling duration [min]	luration [min] [mg ME/m <sup>3</sup> ] [mg ME/m <sup>3</sup> ]		assumed response factor	aerosol [mg TOM/m³]	vapour [mg TOM/m³]	aerosol calculated TWA-8h [mg TOM/m³]	vapour calculated TWA-8h [mg TOM/m³]
Α	405	0.001	1.258	2	0.002	2.515	0.002	2.122
В	540	0.002 0.180 2		2	0.004	0.361	0.004	0.406
С	616	616 # 0.776		2	#	1.552	#	Min. 1.991

# - filter cassette missing



#### 6.2.4.11. Selected Aromatic Hydrocarbon (AH) - site "Scarlet"

The workplace related (P)AH data (personal samplers) are presented in Table 754 and Table 5555. The (P)AH content found in the exposure atmosphere close to the vent are shown in Table 5656. The findings of the background samplers are also listed in Table 63. The data were not corrected by the respective field blanks, as the field blank samplers were not subjected to an air flow. Field blank data merely served as monitoring controls for the sampling campaign and subsequent sample analysis.

Personal exposure data (loading operator) varied for the selected (P)AH as follows (please note: naphthalene concentration are given in  $\mu g/m^3$ , whereas phenanthrene and pyrene concentration are reported as  $ng/m^3$ ):

- naphthalene: 7.59 194 µg/m<sup>3</sup>
- phenanthrene: 1371 4861 ng/m<sup>3</sup>
- pyrene: 136 469 ng/m<sup>3</sup>
- benzo[a]pyrene: not detectable or below limit of quantitation.

On overview of the personal sampler data including the calculated TWA-8hr values for naphthalene, benzo[a]pyrene and coal tar pitch volatiles (CTPV3) is given in Table 57. The naphthalene TWA-8hr values varied off-shore between 0.49 and 8.67  $\mu$ g/m<sup>3</sup> and on-shore between 1.53 and 2.13  $\mu$ g/m<sup>3</sup>. The TWA-8hr exposure concentration for benzo[a]pyrene was in all cases below 2.6 ng/m<sup>3</sup> and varied between 191 and 436 ng/m<sup>3</sup> for CTPV3.



*Table 53.* Background - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>].

	area sampler - background				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	6.0-6.9	395	0.7837	0.023	0.283	0.306	BLQ (< 3.19)	307	307 (< 310)	BLQ (< 3.19)	29.4	29.4 (< 32.6)	n.d. (< 3.19)	n.d. (< 3.19)	n.d. (< 3.19)	
B*	5-8	507	1.0503	*	*	*	*	*	*	*	*	*	*	*	*	
С	2-4	595	1.208	0.025	1.00	1.03	BLQ (< 2.07)	557	557 (< 559)	BLQ (< 2.07)	95.9	95.9 (< 98)	n.d. (< 2.07)	BLQ (< 2.07)	BLQ (< 2.07)	

n.d. - not detected; BLQ - Below Limit of Quantitation; \*- Filter and XAD were soaked with water. Data are not reported as results might be erroneous.

**Table 424.** Off-shore personal sampler - (P)AH data for sampling events A to C. **Note:** Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>].

	personal sampler - off-shore				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	6.0-6.9	438	0.8791	0.007	1.04	1.05	BLQ (< 2.84)	303	303 (< 306)	BLQ (< 2.84)	48.2	48.2 (< 51.0)	n.d. (< 2.84)	n.d. (< 2.84)	n.d. (< 2.84)	
В	5-8	536	1.1087	0.023	0.415	0.438	BLQ (< 2.26)	112	112 (< 114)	BLQ (< 2.26)	59.0	59.0 (< 61.3)	n.d. (< 2.26)	n.d. (< 2.26)	n.d. (< 2.26)	
С	2-4	634	1.2775	0.007	6.55	6.56	2.07	273	275	3.71	51.0	54.7	n.d. (< 1.96)	n.d. (< 1.96)	n.d. (< 1.96)	

n.d. - not detected; BLQ - Below Limit of Quantitation



Table 55.	On-shore personal sampler - (P)AH data for sampling events A to C. Note: Data for naphthalene are given in [µg/m <sup>3</sup> ], whereas concentrations
	for all other analytes are reported as [ng/m³].

	personal sampler - on-shore				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	6.0-6.9	405	0.8408	0.007	1.80	1.81	BLQ (< 2.97)	317	317 (< 320)	BLQ (< 2.97)	29.5	29.5 (< 32.5)	n.d. (< 2.97)	n.d. (< 2.97)	n.d. (< 2.97)	
В	5-8	539	1.0678	0.003	1.90	1.90	BLQ (< 2.34)	162	162 (< 164)	BLQ (< 2.34)	48.3	48.3 (< 50.5)	n.d. (< 2.34)	n.d. (< 2.34)	n.d. (< 2.34)	
С	2-4	616	1.2474	0.018	1.47	1.49	4.18	395	399	7.89	121	129	n.d. (< 2.0)	n.d. (< 2.0)	n.d. (< 2.0)	

n.d. - not detected; BLQ - Below Limit of Quantitation

*Table 56.* Close to vent - (P)AH data for sampling events A to C. **Note:** Data for naphthalene are given in [µg/m<sup>3</sup>], whereas concentrations for all other analytes are reported as [ng/m<sup>3</sup>].

	area sampler - close to vent				naphthalene			phenanthrene			pyrene			benzo[a]pyrene		
event #	Outdoor temperature [°C]	sampling duration [min]	sample volume [m³]	filter [µg/m³]	XAD [µg/m³]	total [µg/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	filter [ng/m³]	XAD [ng/m³]	total [ng/m³]	
А	6.0-6.9	410	0.8454	0.229	1525	1525	23.8	3461	3485	26.1	80.3	106	BLQ (< 2.96)	BLQ (< 2.96)	BLQ (< 2.96)	
B*	5-8	509	1.0338	*	*	*	*	*	*	*	*	*	*	*	*	
C**	2-4	592	1.184	**	**	**	**	**	**	**	**	**	**	**	**	

n.d. - not detected; BLQ - Below Limit of Quantitation

\*- Filter and XAD were soaked with water. Data are not reported as results might be erroneous.

\*\* - XAD was soaked with HFO fumes. Overload of sampler. Data are not reported as results might be erroneous.



#### Table 57.(P)AH data overview (personal samplers)

- <u>For all individual substances:</u> Data reported in brackets are calculated values based on the limit of quantification.
- <u>For the sum parameter of CTPV3:</u> Data reported in brackets consider compounds, which were not detected or present below their limit of quantification. The corresponding limit of quantification was taken into account in the calculation.

Site		scarlet							
event	Α	В	С						
rel. humidity [%]	92-94	95-97	74-92						
outside temperature [°C]	6.5	6.5	3						
HFO loading temperature [°C]	76	83	86						
off-shore									
sampling duration [min]	438	536	634						
sampling volume [m <sup>3</sup> ]	0.8791	1.1087	1.2775						
naphthalene [µg/m³]	1.05	0.438	6.56						
phenanthrene [ng/m <sup>3</sup> ]	303	112	275						
pyrene [ng/m <sup>3</sup> ]	48.2	59.0	54.7						
benzo[a]pyrene [ng/m³]	n.d. (< 2.84)	n.d. (< 2.26)	n.d. (< 1.96)						
CTPV3 [ng/m <sup>3</sup> ]	351 (< 354)	171 (< 173)	330 (< 332)						
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	320 (< 295)	191 (< 194)	436 (< 439)						
naphthalene TWA-8hr [µg/m³]	0.958	0.490	8.67						
benzo[a]pyrene TWA-8hr [ng/m³]	n.d. (< 2.59)	n.d. (< 2.52)	n.d. (< 2.59)						
	on-shore								
sampling duration [min]	405	539	616						
sampling volume [m <sup>3</sup> ]	0.8408	1.0678	1.2474						
naphthalene [µg/m³]	1.81	1.90	1.49						
phenanthrene [ng/m <sup>3</sup> ]	317	162	399						
pyrene [ng/m <sup>3</sup> ]	29.5	48.3	129						
benzo[a]pyrene [ng/m³]	n.d. (< 2.97)	n.d. (< 2.34)	n.d. (< 2.00)						
CTPV3 [ng/m <sup>3</sup> ]	346 (< 349)	210 (< 212)	528 (< 530)						
CTPV3 TWA-8hr [ng/m <sup>3</sup> ]	292 (< 295)	236 (< 238)	678 (< 680)						
naphthalene TWA-8hr [µg/m³]	1.53	2.13	1.91						
benzo[a]pyrene TWA-8hr [ng/m³]	n.d. (< 2.51)	n.d. (< 2.63)	n.d. (< 2.57)						

n.d. -not detected

CTPV3: 3 out of 5 Coal Tar Pitch Volatiles, as defined by OSHA: phenanthrene, pyrene and benzo[a]pyrene



#### 6.2.4.12. Grimmer (P)AH - Bulk material - site "Scarlet"

The Grimmer (P)AH data for the HFO-bulk materials A013/18; A014/18 and A016/18 (sampling event A; B and C) are presented in Table 958.

Table 58.Grimmer (P)AH: HFO-bulk materials A013/18; A014/18 and A016/18

	A 013/18	A 014/18	A 016/18
PAH - ID	Sampling event A	Sampling event B	Sampling event C
	[µg/g]	[µg/g]	[µg/g]
Naphthalene	965	945	1052
Phenanthrene	602	626	668
Anthracene	100	95.4	99.3
Fluoranthene	38.5	28.5	31.7
Pyrene	217	182	194
Benzo[b]naphtho[2,1-d]thiophene	89.4	65.7	72.1
Benzo[c]phenanthrene	12.5	7.83	9.42
Benzo[g,h,i]fluoranthene	NA*	NA*	NA*
Benz[a]anthracene	83.2	46.6	57.8
Cyclopenta[c,d]pyrene	5.57	3.41	3.86
Triphenylene	42.4	26.5	35.8
Chrysene	89.6	61.2	76.2
Benzo[b]fluoranthene	25.0	18.7	20.3
Benzo[k]fluoranthene	4.79	3.95	4.02
Benzo[j]fluoranthene	8.28	5.56	5.73
Benzo[e]pyrene	64.9	46.3	52.3
Benzo[a]pyrene	57.2	46.1	52.9
Dibenz[a,h]anthracene	5.77	4.61	4.68
Coronene	9.10	6.82	5.85
Indeno[1,2,3-cd]pyrene	6.00	4.91	4.84
Anthanthrene	12.8	11.9	14.0
Benzo[g,h,i]perylene	61.5	46.0	42.6

NA\* - not applicable, as signals were overlapping



## 7. APPENDIX 3. CODED SAMPLING PROTOCOLS OF INDIVIDUAL SAMPLING CAMPAIGNS

### 7.1. SITE "CRIMSON"

### CODED WORKPLACE MONITORING PROTOCOL - EVENT A (CRIMSON)

Sampling Documentation Form - Data for HFO Monitoring Survey - Tank truck top loading

Company: Crimson Location: Crimson UN number: 1202 / CAS No. 68476-33-5 Cargo loading temperature: 57.2 - 59.8 °C

Date	Sampling Unit <sup>41</sup> Filter/XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event A	FB BIA2	Field Blank	-							
Event A	FB PAK2	Field Blank	-							
Event A	BIA 5	Personal 1	Loading operator	8:38	9:27	49	2.02	2.00	2.01	98.5
Event A	PAK 5	Personal 1	Loading operator	8:38	9:27	49	2.00	1.94	1.97	96.5
	BIA 6	Person 2		not	a 2 <sup>nd</sup> persor	vipvolvod				
	PAK 6	Person 2			a z <sup>as</sup> persor	i ilivolveu				
Event A	BIA 7	Area 1	Close to vent (1.2 m)	8:38	9:24	46	2.00	1.99	2.00	92
Event A	PAK 7	Area 1	Close to vent (1.2 m)	8:38	9:24	46	1.99	1.96	1.98	91
Event A	BIA 8	Area 2	Background sample, 40 m upwind	8:41	9:33	52	1.98	1.94	1.96	102
Event A	PAK 8	Area 2	Background sample, 40 m upwind	8:41	9:33	52	2.01	1.96	1.99	103.5

<sup>&</sup>lt;sup>41</sup> PAK-sampling unit: for (P)AH-determination; BIA-sampling unit for THC-determination



Date	All sample (n) media 5 till 7					
Event A	BIA n_Xn					
Event A	PAK n_Xn					

Company: crimson

Location: crimson

BIA 5 / PAK 5 (loading operator, P1) BIA 7 / PAK 7 (close to vent) BIA 8 / PAK 8 (background area)		Start of sampling period	Mid of sampling period	End of sampling period
Time	hh:mm	/	10:00	/
Air temperature	°C	/	16	/
Wind speed	m/s	/	4	/
Wind direction		/	south	/
Atmospheric pressure	hPa	/	996.6	/
Relative humidity	%	/	77	/
Precipitation		/	without	/
Cloud cover	*/8	/	7/8	/
<ul> <li>/ = no data recorded</li> <li>Additional information</li> <li>HFO throughput during sampling</li> <li>Loading temperature</li> </ul>	46576 kg 57.2 - 59.8 °(	c		
Configuration of event	See attachme			
Product description (name, UN, MSDS)	UN 1202 CAS No. 684	·		
Process description	Tank truck up	oloading (top load	ling)	
Has the tank been de-gassed prior to loading?	no			
Last material prior to loading	/			
Further relevant observations	/			
Additional information	~ 5 min with	out exposure when	n moving the tru	ıck



#### CODED WORKPLACE MONITORING PROTOCOL - EVENT B (CRIMSON)

### Sampling Documentation Form - Data for HFO Monitoring Survey - Tank truck top loading

Company: Crimson Location: Crimson UN number: 1202 / CAS No. 68476-33-5 Cargo loading temperature: 59.2 - 61.4 °C

Date	Sampling Unit <sup>42</sup> Filter/XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)			
Event B	FB BIA3	Field Blank	-										
Event B	FB PAK3	Field Blank	-										
Event B	BIA 9	Personal 1	Loading operator	10:04	10:42	38		2.00		76			
Event B	РАК 9	Personal 1	Loading operator	10:04	10:42	38		1.94		73.5			
Event B	BIA 10	Person 2		not a 2 <sup>nd</sup> person involved									
Event B	PAK 10	Person 2				not a z	z <sup>as</sup> person inv	olved					
Event B	BIA 11	Area 1	Close to vent (1.2 m)	10:07	10:40	33		1.99		65.5			
Event B	PAK 11	Area 1	Close to vent (1.2 m)	10:07	10:40	33		1.96		64.5			
Event B	BIA 12	Area 2	Background sample, 40 m upwind	9:35	10:49	74		1.94		144			
Event B	PAK 12*	Area 2	Background sample, 40 m upwind*	9:35	10:49	74		1.96		145			

\* Sample contaminated due to broken sampler - sampler felt to pieces which felt to ground

<sup>42</sup> PAK-sampling unit: for (P)AH-determination; BIA-sampling unit for THC-determination



Date	All sample (n) media 5 till 7
Event B	BIA n_Xn
Event B	PAK n_Xn

Company: crimson

Location: crimson

BIA 9 / PAK 9 (loading operator, P1) BIA 11 / PAK 11 (close to vent) BIA 12 / PAK 12 (background area)		Start of sampling period	Mid of sampling period	End of sampling period			
Time	hh:mm	/	/	10:50			
Air temperature	°C	/	/	14			
Wind speed	m/s	/	/	5			
Wind direction		/	/	East (80°)			
Atmospheric pressure	hPa	/	/	895.3			
Relative humidity	%	/	/	79			
Precipitation		/	/	without			
Cloud cover	*/8	/	/	5/8			
<ul> <li>/ = no data recorded</li> <li>Additional information</li> <li>HFO throughput during sampling</li> </ul>	43064 kg						
Loading temperature	59.2 - 61.4°C						
Configuration of event	See attachme	ents/photos					
Product description (name, UN, MSDS)	UN 1202 (MSI CAS No. 6847						
Process description	Tank truck up	oloading (top load	ling)				
Has the tank been de-gassed prior to loading?	no						
Last material prior to loading	/						
Further relevant observations	/						
Additional information							



### CODED WORKPLACE MONITORING PROTOCOL - EVENT C (CRIMSON)

Sampling Documentation Form - Data for HFO Monitoring Survey - Tank truck bottom loading

Company: Crimson Location: Crimson UN number: 1202 / CAS 68476-33-5 Cargo loading temperature: 59.5 - 62.6 °C

Date	Sampling Unit <sup>43</sup> Filter/XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event C	FB BIA4	Field Blank	-							
Event C	FB PAK4	Field Blank	-							
Event C	BIA 13	Personal 1	Loading operator	16:17	16:41	24		2.00		48
Event C	PAK 13	Personal 1	Loading operator	16:17	16:41	24		1.94		46.5
Event C	BIA 14	Person 2		not a	2nd porcon	involved				
Event C	PAK 14	Person 2		not a	2 <sup>nd</sup> person	mvotved				
Event C	BIA 15*	Area 1	Close to vent (1.2 m)	16:18	16:40	22		1.99		44
Event C	PAK 15*	Area 1	Close to vent (1.2 m)	16:18	16:40	22		1.96		43
Event C	BIA 16	Area 2	Background sample, 40 m upwind	16:06	16:42	36		1.94		70
Event C	PAK 16	Area 2	Background sample, 40 m upwind*	16:06	/		Flow fault			

\* Use sampler 15 only for measurements at the vent system due to prior (not full removable) contamination (outside)

<sup>&</sup>lt;sup>43</sup> PAK-sampling unit: for (P)AH-determination; BIA-sampling unit for THC-determination



Date	All sample (n) media 5 till 7
Event C	BIA n_Xn
Event C	PAK n_Xn

Company: crimson

Location: crimson

BIA 13 / PAK 13 (loading operator, P1) BIA 15 / PAK 15 (close to vent) BIA 16 / PAK 16 (background area)	)	Start of sampling period	Mid of sampling period	End of sampling period
Time	hh:mm	/	16:30	/
Air temperature	°C	/	14.7	/
Wind speed	m/s	/	3	/
Wind direction		/	North (20°)	/
Atmospheric pressure	hPa	/	086.1	/
Relative humidity	%	/	75	/
Precipitation		/	without	/
Cloud cover	*/8	/	8/8	/
Additional information HFO throughput during sampling Loading temperature	42998 kg 59.5 - 62.6°C			
Configuration of event	See attachme	ents/photos		
Product description (name, UN, MSDS)	UN 1202 (MS CAS 68476-33	DS attached) 3-5		
Process description	Tank truck u	ploading (bottom	n loading)	
Has the tank been de-gassed prior to loading?	no			
Last material prior to loading	/			
Further relevant observations	/			
Additional information				





### 7.2. SITE "MAROON"

### CODED WORKPLACE MONITORING PROTOCOL - EVENT A (MAROON)

Sampling Documentation Form - Data for HFO Monitoring Survey - ShipCompany: Maroon Location: MaroonUN number: 3082CAS No. 68476-33-5Cargo loading temperature: 78.7 °C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event A	FB BIA 2	Field Blank								
Event A	FB PAK 2	Field Blank								
Event A	BIA 5	Person 1	ship operator	9.28	15.50	382	2.06	1.95		766
Event A	PAK 5	Person 1	ship operator	9.28	15.50	382	1.99	1.97		756
Event A	BIA 6	Person 2	landside loading operator (loading bridge)	9.28	15.50	382	2.02	1.91		751
Event A	PAK 6	Person 2	landside loading operator (loading bridge)	9.28	15.52	384	2.08	1.77		739
Event A	BIA 7	Area 1	Close to vent (< 0.5m)	9.28	15.52	384	2.03	1.86		747
Event A	PAK 7	Area 1	Close to vent (< 0.5m)	9.28	15.52	384	1.93	1.96		747
Event A	BIA 8	Area 2	Background sample	9.28	15.52	384	2.02	1.82		737
Event A	PAK 8	Area 2	Background sample	9.28	15.52	384	2.03	2.03		780



Date	All sample (n) media 5 to 7
Event A	BIA n_Xn
Event A	PAK n_Xn

Company: maroon

Location: maroon

		Start of sampling period	Mid of sampling period	End of sampling period	
Time	hh:mm	09.28		15.52	
Air temperature	°C	21.5		21.5	
Wind speed	m/s	13		15	
Wind direction		West		West	
Atmospheric pressure	hPa	1009.0		1009.7	
Relative humidity	%				
Precipitation		None		None	
Cloud cover	*/8	Partly cloud		Heavy cloud	
Additional information					
HFO throughput during sampling	885 m3/h				
Loading temperature	78.7				
Configuration of event	See photo				
Product description (name, UN, MSDS)	UN 3082 CAS No. 684	176-33-5			
Process description	See photo				
Has the tank been de-gassed prior to loading?	No No				
Last material prior to loading	UN 3082				
Further relevant observations					
Additional information					



Date	sample media
Event A	BIA 8 Area 2
Event A	PAK 8 Area 2

Company: maroon Location: maroon Country:

Same conditions as all samples

background sample (area 2)		Start sampling period	of	Mid sampling period	of	End sampling period	of
Time	hh:mm						
Air temperature	°C						
Wind speed	m/s						
Wind direction							
Atmospheric pressure	hPa						
Relative humidity	%						
Precipitation							
Cloud cover	*/8						
Additional information							



#### CODED WORKPLACE MONITORING PROTOCOL - EVENT B (MAROON)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

Location: Maroon

UN number: 3082 / CAS No. 68476-33-5

Cargo loading temperature: 82.8°C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event B	FB BIA 3	Field Blank		13.15	22.30					
Event B	FB PAK 3	Field Blank		13.15	22.30					
Event B	BIA 9	Person 1	ship operator	13.15	22.30	555	2.01	Fault	2.01	1116
Event B	PAK 9	Person 1	ship operator	13.15	22.30	555	2.00	1.98	1.99	1105
Event B	BIA 10	Person 2	landside loading operator (loading bridge)	13.15	22.30	555	1.63	1.17	1.40	777
Event B	PAK 10	Person 2	landside loading operator (loading bridge)	13.15	22.30	555	2.01	2.04	2.03	1124
Event B	BIA 11	Area 1	Close to vent (< 0.5m)	13.15	22.30	555	2.00	2.04	2.02	1121
Event B	PAK 11	Area 1	Close to vent (< 0.5m)	13.15	22.30	555	2.00	2.23	2.12	1174
Event B	BIA 12	Area 2	Background sample	13.15	22.30	555	2.00	2.29	2.14	1189
Event B	PAK 12	Area 2	Background sample	13.15	22.30	555	2.05	2.00	2.02	1124



Date	All sample (n) media 9 to 12
Event B	BIA n_Xn
Event B	PAK n_Xn

Company: maroon

Location: maroon

		Start of sampling period	Mid of sampling period	End of sampling period		
Time	hh:mm	13.15	not registerd	22.30		
Air temperature	°C	17.0		15.7		
Wind speed	m/s	1		1.5		
Wind direction		W-NW		Z -ZW		
Atmospheric pressure	hPa	1008		1010		
Relative humidity	%	92		92		
Precipitation		Rain		rain		
Cloud cover	*/8	Heavy cloud		Heavy cloud		
Additional information						
HFO throughput during sampling	950 m3/h					
Loading temperature	82.8					
Configuration of event	See photo					
Product description (name, UN, MSDS)	UN 3082 CAS No. 684	76-33-5				
Process description	See photo					
Has the tank been de-gassed prior to loading?	to No					
Last material prior to loading						
Further relevant observations						
Additional information						



Date	sample media
Event B	BIA 12 Area 2
Event B	PAK 12 Area 2

Company: maroon Location: maroon Country:

Same as all samples

background sample (area 2)		Start of sampling period	Mid of sampling period	End of sampling period
Time	hh:mm			
Air temperature	°C			
Wind speed	m/s			
Wind direction				
Atmospheric pressure	hPa			
Relative humidity	%			
Precipitation				
Cloud cover	*/8			
Additional information				



#### CODED WORKPLACE MONITORING PROTOCOL - EVENT C (MAROON)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

Company: Maroon Location: Maroon

UN number: 3082 / CAS No. 68476-33-5

Cargo loading temperature: 76.8 °C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event C	FB BIA 4	Field Blank								
Event C	FB PAK 4	Field Blank								
Event C	BIA 13	Person 1	ship operator	10.20	19.00	520	2.02	1.98	2.00	1040
Event C	PAK 13	Person 1	ship operator	10.20	19.00	520	2.05	2.00	2.025	1053
Event C	BIA 14	Person 2	landside loading operator (loading bridge)	10.20	19.00	520	2.00	1.97	1.985	1032
Event C	PAK 14	Person 2	landside loading operator (loading bridge)	10.20	19.00	520	2.09	1.95	2.02	1050
Event C	BIA 15	Area 1	Close to vent (< 0.5m)	10.20	17.50	450	2.10	2.05	2.075	934
Event C	PAK 15	Area 1	Close to vent (< 0.5m)	10.20	17.50	450	2.02	2.09	2.055	925
Event C	BIA 16	Area 2	Background sample	10.20	18.00	460	2.10	2.07	2.085	959
Event C	PAK 16	Area 2	Background sample	10.20	18.00	460	1.96	2.22	2.09	961



Date	All sample (n) media 13 to 15
Event C	BIA n_Xn
Event C	PAK n_Xn

Company: maroon

Location: maroon Country:

		Start of sampling period	Mid of sampling period	End of sampling period
Time	hh:mm	10.20	14.30	19.00
Air temperature	°C	18.2	20.0	21.0
Wind speed	m/s	0.3	5	6-7
Wind direction		Ν	W/SW	W/SW
Atmospheric pressure	hPa	1019.0		
Relative humidity	%	71		
Precipitation		NONE	NONE	NONE
Cloud cover	*/8	moderate cloud	moderate cloud	moderate cloud
Additional information				
HFO throughput during sampling	675 m3/uur			
Loading temperature	76.8 °C			
Configuration of event	See photo			
Product description (name, UN, MSDS)	UN 3082 CAS No. 684	76-33-5		
Process description	See photo			
Has the tank been de-gassed prior to loading?	No			
Last material prior to loading				
Further relevant observations				
Additional information				



Date	sample media					
Event C	BIA 16 Area 2					
Event C	PAK 16 Area 2					
	Same as all					

samples

Company: maroon Location: maroon Country:

background sample (area 2)		Start sampling period	of	Mid sampling period	of	End sampling period	of
Time	hh:mm						
Air temperature	°C						
Wind speed	m/s						
Wind direction							
Atmospheric pressure	hPa						
Relative humidity	%						
Precipitation							
Cloud cover	*/8						
Additional information							



### 7.3. SITE "ORANGE"

CODED WORKPLACE MONITORING PROTOCOL - EVENT A (ORANGE)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

Company: Orange

Location: **Orange** UN number: **3082** 

Cargo loading temperature: 80-81°C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Mid Flow Rate (L/min	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event A	FB BIA 2	Field Blank									
Event A	FB PAK 2	Field Blank									
Event A	BIA 5	Person 1	Landside loading operator (loading bridge); static outside**	15:30	19:10*	220	2.02	2.03	2.02	2.02	445
Event A	PAK 5	Person 1	Landside loading operator (loading bridge); static outside**	15:30	19:10*	220	1.99	1.98	2.03	2.00	440
Event A	BIA 6	Person 2	Ship operator	15:26	19:13*	227	2.00	1.99	1.98	1.99	452
Event A	PAK 6	Person 2	Ship operator	15:26	19:13*	227	2.01	1.98	2.01	2.00	454
Event A	BIA 7	Area 1	Close to vent (< 0.5m)	15:20	19:11*	231	2.00	1.94	1.97	1.97	455
Event A	PAK 7	Area 1	Close to vent (< 0.5m)	15:20	19:11*	231	2.00	1.96	2.02	1.99	460
Event A	BIA 8	Area 2	Background sample (harbour entrance region)	15:43	19:24*	221	1.98	1.93	2.00	1.97	435
Event A	PAK 8	Area 2	Background sample (harbour entrance region)	15:43	19:24*	221	1.99	1.94	2.00	1.98	437

\* Sampling stopped - heavy rain\*\* No loading bridge operator involved, process full automatically controlled during loading operation



Date	All sample media
Event A	BIA 5-8
Event A	PAK 5-8

Company: Orange

Location: Orange Country:

		Start of sampling period	Mid of sampling period	End of sampling period		
Time	hh:mm	15:00	18.00	20:00		
Air temperature	°C	7.3	6.3	4.4		
Wind speed	m/s	7.0 (squally)	4.6 (squally)	1.8		
Wind direction		SW	SW	SW		
Atmospheric pressure	hPa	989	990	990		
Relative humidity	%	67.8	78.9	92.5		
Precipitation		none	none	none		
Cloud cover	*/8	6/8	6/8	dark		
Additional information						
HFO throughput during sampling	320 m <sup>3</sup> /h (loa	ading bridge log)				
Loading temperature	80-81°C					
Configuration of event	See attachme	ents/photos not a	llowed			
Product description (name, UN, MSDS)	UN 3082 (HFC	0)				
Process description	HFO loading					
Has the tank been de-gassed prior to loading?	No - not allow	wed without prote	ection systems			
Last material prior to loading	HCGO					
Further relevant observations	<u> </u>	monitored fro only (1000 / 2000	om 15:20 (t)	till 19:13;		
	Further loading activities in the surrounding harbour (ships) and refinery area.					
Additional information	Background sample (harbour entrance region) without loading impact (upwind side)					



### CODED WORKPLACE MONITORING PROTOCOL - EVENT B (ORANGE)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

Company: Orange

Location: **Orange** UN number: **3082** 

Cargo loading temperature: 80-81°C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Mid Flow Rate (L/min	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event B	FB BIA 3	Field Blank									
Event B	FB PAK 3	Field Blank									
Event B	BIA 9	Person 1	Landside - loading bridge; static inside office*	16:43	20:55	252	2.00	1.83	1.75	1.86	469
Event B	PAK 9	Person 1	Landside - loading bridge; static inside office*	16:43	20:55	252	2.00	1.98	2.03	2.00	504
Event B	BIA 10	Person 2	Ship operator	17:23	21:07	224	2.02	/	1.98	2.00	448
Event B	PAK 10	Person 2	Ship operator	17:23	21:07	224	2.02	/	1.95	1.99	446
Event B	BIA 11	Area 1	Close to vent (< 0.5m)	17:28	20:58	210	2.01	1.94	1.95	1.97	414
Event B	PAK 11	Area 1	Close to vent (< 0.5m)	17:28	20:58	210	2.02	1.95	1.92	1.96	412
Event B	BIA 12	Area 2	Background sample (harbour entrance region)	18:15	21:25	190	1.99	/	1.99	1.99	378
Event B	PAK 12	Area 2	Background sample (harbour entrance region)	18:15	21:25	190	1.99	/	1.97	1.98	376

\* No loading bridge operator involved, process full automatically controlled during loading operation



Date	All sample media
Event B	BIA 9-12
Event B	PAK 9-12

Company: Orange

Location: Orange

		Start of sampling period	Mid of sampling period	End of sampling period			
Time	hh:mm	18:00	19.30	21:00			
Air temperature	°C	7.0	6.8	6.3			
Wind speed	m/s	3.2 (squally)	4.1 (squally)	4.8 (squally)			
Wind direction		SW	SW	SW			
Atmospheric pressure	hPa	994	995	995			
Relative humidity	%	96.3	91.9	87.5			
Precipitation		none	none	none			
Cloud cover	*/8	1/8	dark	dark			
Additional information							
HFO throughput during sampling	250 400 m <sup>3</sup> /h (ma		(first loading bridge	100 m <sup>3</sup> ) log			
Loading temperature	80-81°C						
Configuration of event	See attachme	ents/photos not a	llowed				
Product description (name, UN, MSDS)	UN 3082						
Process description	HFO loading						
Has the tank been de-gassed prior to loading?	No - not allo	wed without prot	ection systems				
Last material prior to loading	No informati	on available					
Further relevant observations	Loading monitored from 16:43 till 21:07; part loading only; process full automatically controlled during loading operation						
Additional information	Further loading activities in the surrounding harbour (ships) and refinery area.						
	Background sample (harbour entrance region) without loading impact (upwind side)						



### CODED WORKPLACE MONITORING PROTOCOL - EVENT C (ORANGE)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

Company: Orange Lo

Location: **Orange** UN number: **3082** 

Cargo loading temperature: 80-81 °C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min )	Mid Flow Rate (L/min	Final Flow Rate (L/min )	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event C	FB BIA 4	Field Blank									
Event C	FB PAK 4	Field Blank									
Event C	BIA 13	Person 1	Landside - loading bridge; static inside office*	9:56	13:42	226	2.02	2.00	2.01	2.01	454
Event C	PAK 13	Person 1	Landside - loading bridge; static inside office*	9:56	13:42	226	2.02	1.92	2.07	2.00	453
Event C	BIA 14	Person 2	Ship operator	9:52	13:38	226	2.02	1.98	2.04	2.01	455
Event C	PAK 14	Person 2	Ship operator	9:52	13:38	226	2.01	1.99	2.03	2.01	454
Event C	BIA 15	Area 1	Close to vent (< 0.5m)	9:54	13:41	227	2.00	1.95	2.01	1.99	451
Event C	PAK 15	Area 1	Close to vent (< 0.5m)	9:54	13:41	227	2.04	2.01	2.02	2.02	459
Event C	BIA 16	Area 2	Background sample (harbour entrance region)	10:06	14:24	258	2.02	/	2.04	2.03	524
Event C	PAK 16	Area 2	Background sample (harbour entrance region)	10:06	14:24	258	2.01	/	2.02	2.02	520

\* No loading bridge operator involved, process full automatically controlled during loading operation



Date	All sample media
Event C	BIA 13-16
Event C	PAK 13-16

Company: Orange

Location: Orange

		Start of sampling period	Mid of sampling period	End of sampling period		
Time	hh:mm	10:00	12:00	14:30		
Air temperature	°C	5.4	5.78	6.8		
Wind speed	m/s	5.6 (squally)	3.1 (squally)	1.5 (squally)		
Wind direction		SW	SW	SW		
Atmospheric pressure	hPa	1002	1002	1002		
Relative humidity	%	75.7	72.0	68.9		
Precipitation		none	light drizzle	none		
Cloud cover	*/8	6/8	8/8	7/8		
Additional information						
HFO throughput during sampling	200 350 m³/h (ma		(first 1 loading bridge	100 m <sup>3</sup> )		
Loading temperature	80-81°C					
Configuration of event	See attachme	ents/photos not a	llowed			
Product description (name, UN, MSDS)	HFO, UN 308	2				
Process description	HFO loading					
Has the tank been de-gassed prior to loading?	No - not allow	wed without prot	ection systems			
Last material prior to loading	No information	on available				
Further relevant observations	Loading monitored from 9:52 till 13:38; part loading only (total load: 1439 m <sup>3</sup> ); process full automatically controlled during loading operation					
Additional information	Further loading activities in the surrounding harbour (ships) and refinery area.					
	Background sample (harbour entrance region) without loading impact (upwind side)					



### 7.4. SITE "PURPLE"

CODED WORKPLACE MONITORING PROTOCOL - EVENT A (PURPLE)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

Company: Purple

Location: Purple

UN number: 3082 / CAS No. 68476-33-5 Cargo loading temperature: 76-77 °C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event A	FB BIA 2	Field Blank								
Event A	FB PAK 2	Field Blank								
Event A	BIA 5	Person 1	ship operator*	15:09	16:52	103	2.01	1.97	1.99	205
Event A	PAK 5	Person 1	ship operator*	15:09	16:52	103	2.04	2.00	2.02	208
Event A	BIA 6	Person 2	landside loading operator (loading bridge)	15:02	16:42	100	2.00	1.98	1.99	199
Event A	PAK 6	Person 2	landside loading operator (loading bridge)	15:02	16:42	100	2.05	2.00	2.03	203
Event A	BIA 7	Area 1	Close to vent (< 0.5m)	15:12	16:32	80	2.02	1.98	2.00	160
Event A	PAK 7	Area 1	Close to vent (< 0.5m)	15:12	16:32	80	1.98	1.96	1.97	158
Event A	BIA 8	Area 2	Background sample (entrance region)	13:16	17:34	258	2.00	1.96	1.98	511
Event A	PAK 8	Area 2	Background sample (entrance region)	13:16	17:34	258	1.98	1.94	1.96	506

\* HFO pump-ship disconnection work included



Date	All sample (n) media 5 till 7
Event A	BIA n_Xn
Event A	PAK n_Xn

Company: Purple

Location: Purple

Person 1 and 2 area 1(loading bridge / ship*: 16:00)		Start of sampling period	Mid of sampling period	End of sampling period			
Time	hh:mm	14:45	15:30/16:00*	16:30			
Air temperature	°C	25.6	25.3/25.0*	25.0			
Wind speed	m/s	2-5 (squally)	0.5-1 / 1-5*	1-5 (squally)			
Wind direction		SW	SW / SW*	SW			
Atmospheric pressure	hPa	1019	1019/1019*	1019			
Relative humidity	%	52.7	51.3/48.0*	46.9			
Precipitation		none	None/none*	none			
Cloud cover	*/8	2/8	2/8 / 2/8*	1/8			
Additional information							
HFO throughput during sampling	750 m <sup>3</sup> /h (bridge) - 748 m <sup>3</sup> /h (ships log); loading starts and ends with reduced flow rates						
Loading temperature	76-77°C						
Configuration of event	See attachme	ents/photos					
Product description	UN 3082 (HFC	0)					
(name, UN, MSDS)	CAS No. 684	76-33-5					
Process description	HFO loading	at bridge					
Has the tank been de-gassed prior to loading?	No - not allow	wed without prote	ection systems				
Last material prior to loading	comparable H	HFO with increase	ed sulphur conte	nt			
Further relevant observations	actual loading took place from 14:50 till 16:30; part loading only (1000 / 6000 t)						
Additional information	no further loading activities in the surrounding harbour (ships) and refinery area (vessels on road or railway) vent system (ship, tank 3) only opened on request for monitoring measurements (not necessary during part loading operation).						



Date	sample media
Event A	BIA 8
Event A	PAK 8

Company: Purple Location: Purple Country:

background sample (entrance	Start of sampling period	Mid of sampling period	End of sampling period			
Time	hh:mm	13:16	/	17:34		
Air temperature	°C	25.7	/	24.2		
Wind speed	m/s	0.5-1.0	/	0.5-2		
Wind direction		SW	/	SW		
Atmospheric pressure	hPa	1019	/	1019		
Relative humidity	%	54.7	/	44.6		
Precipitation		none	/	none		
Cloud cover	*/8	4/8	/	1/8		
Additional information	widely protected area with low traffic and other working activities surrounding					

/ = no data recorded



#### CODED WORKPLACE MONITORING PROTOCOL - EVENT B (PURPLE)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

Company: Purple

Location: Purple

UN number: 3082 / CAS No. 68476-33-5

Cargo loading temperature: **75-76** °C

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event B	FB BIA 2	Field Blank								
Event B	FB PAK 2	Field Blank								
Event B	BIA 5	Person 1	ship operator*	14:35	17:36	181	1.97	2.04	2.01	364
Event B	PAK 5	Person 1	ship operator*	14:35	17:36	181	2.03	2.01	2.02	366
Event B	BIA 6	Person 2	landside loading operator (loading bridge)	14:45	17:38	173	1.96	2.04	2.00	346
Event B	PAK 6	Person 2	landside loading operator (loading bridge)	14:45	17:38	173	1.97	2.01	1.99	344
Event B	BIA 7	Area 1	Close to vent (< 0.5m)**	14:57	17:32	155	2.00	2.04	2.02	313
Event B	PAK 7	Area 1	Close to vent (< 0.5m)**	14:57	17:32	155	1.96	2.00	1.98	307
Event B	BIA 8	Area 2	Background sample (entrance region)	15:29	18:17	168	2.02	1.98	2.00	336
Event B	PAK 8	Area 2	Background sample (entrance region)	15:29	18:17	168	2.03	1.99	2.01	338

\* HFO pump-ship connection and disconnection work included \*\* visible HFO splashing out of the aerating flap at the end of the loading operation



Date	All sample (n) media 5 till 7
Event B	BIA n_Xn
Event B	PAK n_Xn

Company: Purple

Location: Purple

Person 1 and 2 area 1(loading bridge/ship* 17:00)		Start of sampling period	Mid of sampling period	End of sampling period			
Time	hh:mm	15:00	16:30/17:00*	17:45			
Air temperature	°C	24.3	27.2 / 26.5*	25.9			
Wind speed	m/s	0.5 - 1.5	1-2 / 1-2.5*	1 - 2.5			
Wind direction		SO	SO / SO*	SO			
Atmospheric pressure	hPa	1008	1007/1007*	1007			
Relative humidity	%	64.4	62.4 / 63.9	68.7			
Precipitation		none	none/none*	none			
Cloud cover	*/8	1/8	1/8 / 1/8*	7/8			
Additional information							
HFO throughput during sampling	760 m <sup>3</sup> /h (bridge) - 740- 760 m <sup>3</sup> /h (ships log); loading starts and ends with reduced flow rates						
Loading temperature	75-76°C						
Configuration of event	See attachme	nents/photos					
Product description	UN 3082 (HFO)						
(name, UN, MSDS)	CAS No. 684	76-33-5					
Process description	HFO loading	at bridge					
Has the tank been de-gassed prior to loading?	No - not allowed without protection systems						
Last material prior to loading	UN 3082 (HFO)						
Further relevant observations	actual loading took place from 14:50 till 17:30; part loading only (1600 / 6000 t)						
	no further loading activities in the surrounding harbour (ships) and refinery area (vessels on road or railway)						
Additional information	vent system (ship, tank 1) only opened on request for monitoring measurements (not necessary during part loading operation).						



Date	sample media
Event B	BIA 8
Event B	PAK 8

Company: Purple Location: Purple Country:

background sample (entrance	Start of sampling period	Mid of sampling period	End of sampling period			
Time	hh:mm	15:30	/	18:30		
Air temperature	°C	25.1	/	27.7		
Wind speed	m/s	0-1*	/	0-1*		
Wind direction		SO	/	SO		
Atmospheric pressure	hPa	1008	/	1007		
Relative humidity	%	63.8	/	65.0		
Precipitation		none	/	none		
Cloud cover	*/8	1/8	/	8/8		
Additional information	tion widely protected area with low traffic and other work activities surrounding					

/ = no data recorded

\* slipstream zone



### CODED WORKPLACE MONITORING PROTOCOL - EVENT C (PURPLE)

Sampling Documentation Form - Data for HFO Monitoring Survey - Ship

## Company: Purple Location: Purple UN number: 3082 / CAS No. 68476-33-5 Cargo loading temperature: 70 °C

[Sampling campaign was run over night]

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total Time (min)	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Mean Flow Rate (L/min)	Total Sample Volume (L)
Event C	FB BIA 2	Field Blank								
Event C	FB PAK 2	Field Blank								
Event C	BIA 5	Person 1	ship operator	21:31	05:19	467	2.03	1.98	2.01	939
Event C	PAK 5	Person 1	ship operator	21:31	05:19	467	1.98	2.23	2.11	985
Event C	BIA 6	Person 2	landside loading operator (loading bridge)	21:07	05:16	487	2.01	1.97	1.99	969
Event C	PAK 6	Person 2	landside loading operator (loading bridge)	21:07	05:16	487	1.97	1.96	1.97	959
Event C	BIA 7	Area 1	Close to vent (< 0.5m)**	21:44	23:04	80	1.97			
Event C				01:24	05:27	241		1.92		
Event C						321			1.95	626
Event C	PAK 7	Area 1	Close to vent (< 0.5m)**	21:44	23:04	80	2.00			
Event C				01:24	05:27	241		1.94		


Event C						321			1.97	632
Event C	BIA 8	Area 2	Background sample (entrance region)**	20:12	22:56	164	1.94	1.95		
Event C				01:13	06:13	300		1.94		
Event C						464			1.94	900
Event C	PAK 8	Area 2	Background sample (entrance region)**	20:12	22:56	164	2.02	2.00		
Event C				01:13	06:13	300		1.80*		
Event C						464			1.94	900

\* Sampler head got damaged at 01:30am when the flow rate was checked.

\*\* Sampling campaign was interrupted for BIA/PAK 7 and 8 due to rain at 11pm. After the rain had stopped sampling was continued at approx. 1am.

Additional information:

 Start loading:
 9:30pm (Day 1)

 End of loading:
 0:10pm (Day 2)

 Total load:
 11,392 m³ / 10,981 t



Date	All sample (n) media 5 till 7	Company: Purple
Event C	BIA n_Xn	Location: Purple
Event C	PAK n_Xn	Country:

Person 1 and 2 readings were taken on board of ship		Start of sampling period	Mid of sampling period	End of sampling period	
Time	hh:m	22:00	01:24	05:30	
Air temperature	°C	22.6	20.7	20.2	
Wind speed	m/s	0.5 - 1.0	1.5 - 2.5	0.5 - 1.0	
Wind direction		WSW	WSW	SW	
Atmospheric pressure	hPa	1005	1005	1005	
Relative humidity	%	84	77	70	
Precipitation		Light drizzle	none	none	
Cloud cover	*/8	Not visible	Not visible	Not visible	
Additional information	-				
HFO throughput during sampling		980 m <sup>3</sup> /h (bridge g starts and ends	, ,	low rates	
Loading temperature	70°C				
Configuration of event	See at	tachments/photo	os		
Product description	UN 308	32 (HFO)			
(name, UN, MSDS)	CAS N	0. 68476-33-5			
Process description	HFO lo	ading at bridge			
Has the tank been de-gassed prior to loading?	No - no	ot allowed witho	ut protection sy	vstems	
Last material prior to loading	Low su	ılphur VGO			
Further relevant observations	Actual loading took place from 09:30pm and still ongoing when workplace monitoring equipment was taken down (6500m <sup>3</sup> total transfer)				
Additional information		r loading activi downwind of sh		rounding harbour	



Date	sample media	Company: Purple
Event C	BIA 8	Location: Purple
Event C	PAK 8	Country:

background sample (entrance regio	on; area 2)	Start of sampling period	Mid of sampling period	End of sampling period		
Time	hh:mm	22:10	01:30	06:15		
Air temperature	°C	22.7	21	20		
Wind speed	m/s	0.5 - 1.0	0.5	1.0 - 1.5		
Wind direction		WSW	WSW	SW		
Atmospheric pressure	hPa	1005	1005	1005		
Relative humidity	%	85	73	87		
Precipitation		Light drizzle	none	none		
Cloud cover	*/8	Not visible	Not visible	6/8		
Additional information	Widely protected area with low traffic and other working activities surrounding					



#### 7.5. SITE "SCARLET"

#### CODED WORKPLACE MONITORING PROTOCOL - EVENT A (SCARLET)

Company:\_Scarlet\_\_\_\_ Location:\_\_\_\_ UN Number:\_\_3082 / CAS No. 68476-33-5\_\_\_\_ Cargo loading temperature:\_\_76°C\_\_\_\_\_

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total sampling time [min]	Final Pump Flow Rate (l/min)	Sample volume (Litres)*
Event A	FB BIA4	Field Blank	-	-	-		-	-
Event A	FB PAK4	Field Blank	-	-	-		-	-
Event A	BIA 13	Personal 1	Ship	7.13	14.31	438	1.988	870.7
Event A	PAK 13	Personal 1	Ship	7.13	14.31	438	2.007	879.1
Event A	BIA 14	Person 2	Quay jetty 43	7.17	14.02	405	2.260	915.3
Event A	PAK 14	Person 2	Quay jetty 34	7.17	14.02	405	2.076	840.8
Event A	BIA 15	Area 1	Close to vent (0.5 m)	7.35	14.25	410	2.015	826.2
Event A	PAK 15	Area 1	Close to vent (0.5 m)	7.35	14.25	410	2.062	845.4
Event A	BIA 16	Area 2	Background sample	7.42	14.17	395	2.118	836.6
Event A	PAK 16	Area 2	Background sample	7.42	14.17	395	1.984	783.7

Due to malfunction of calibrator, only end flow is observed



## Sample Numbers to which the following information applies

Date	Sampling Unit	Company:Scarlet	
Event A	all	Country:	
		Location:	

Meteorological data		St	art	Mid	End
Meteorological data				of sampling pe	riod
Time	hh:mm	8.00		11.30	13.30
Air temp.	°C	6.9		6.5	6.0
Wind speed	m/s	6		5	5
Wind direction		Е		ESE	E
Atmospheric pressure	hPa	999		1001	1003
Relative humidity	%	94		92	93
Precipitation		-		-	Drizzle
Cloud cover	*/8	8/8		8/8	8/8
Additional information					
HFO throughput during sa	mpling		500 r	m³/h	
Loading temperature			76°C		
Product description (name	e, UN, MSDS)		UN 3	082	
			CAS No.		i la
Process description			Load	Loading barge	
Product carried in previous loading			Same	2	
Has the tank been de-gass	ed prior to loadi	ng?	No		
Further relevant observat	ions				



#### CODED WORKPLACE MONITORING PROTOCOL - EVENT B (SCARLET)

Company:\_\_\_\_\_Scarlet\_\_\_ Location:\_\_\_\_\_\_ UN Number:\_<u>3082 / CAS No. 68476-33-5\_\_\_\_\_</u> Cargo loading temperature:\_\_83°\_\_\_\_\_

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total sampling time [min]	Initial Pump Flow Rate (l/min)	Final Pump Flow Rate (l/min)	Sample volume (Litres)*
Event B	FB BIA2	Field Blank	-	-	-		-	-	-
Event B	FB PAK2	Field Blank	-	-	-		-	-	-
Event B	BIA 5	Personal 1	Ship	22.43	07.39	536	2.050	2.024	1091.8
Event B	PAK 5	Personal 1	Ship	22.43	07.39	536	2.073	2.064	1108.7
Event B	BIA 6	Person 2	Quay jetty 32	22.42	07.42	540	2.042	2.044	1103.2
Event B	PAK 6	Person 2	Quay jetty 32	22.42	07.41	539	1.993	1.969	1067.8
Event B	BIA 7	Area 1	Close to vent (0.5 m)	23.08	07.37	509	2.026	1.995	1023.3
Event B	PAK 7	Area 1	Close to vent (0.5 m)	23.08	07.37	509	2.025	2.037	1033.8
Event B	BIA 8	Area 2	Background sample	23.17	07.44	507	2.026	2.002	1021.1
Event B	PAK 8	Area 2	Background sample	23.17	07.44	507	2.086	2.057	1050.3

At end of measurement period deck mate did make some samples near loading point. On jetty 32 vapours was clearly smelled. Some trouble and leakages when disconnecting hose.

Sample 1 (BIA 5) showed 0000 in the display at the end. Pump was turned on but not sure if it run well. Flow check afterwards was ok



Sample Numbers to which the following information applies

Date	Sampling Unit
Event B	All inc background

Company: \_\_\_\_Scarlet\_ Country: \_\_\_\_\_

\_\_\_\_

\_\_\_\_

Location:

Meteorological data		St	art	Mid	End	
meteorological data				of sampling per	riod	
Time	hh:mm	22.15	22.15		7.00	
Air temp.	°C	8		5	6	
Wind speed	m/s	3		2	3	
Wind direction		SE (120	<b>ॲ</b> )	NW (340°)	NW (290°)	
Atmospheric pressure	hPa	1001		1003	1005	
Relative humidity	%	95		97	97	
Precipitation		-		Rain	-	
Cloud cover	*/8	8/8		8/8	?	
Additional information						
HFO throughput during sa	mpling		775	m³/h		
Loading temperature			83°0	2		
Product description (name	e, UN, MSDS)		UN3	JN3082		
			CAS No. 68476			
Process description			Loading from 1230			
Product carried in previous loading			Same type			
Has the tank been de-gass	ed prior to loadi	ng?	No			
Further relevant observat	ions					



#### CODED WORKPLACE MONITORING PROTOCOL - EVENT C (SCARLET)

Company:\_\_\_\_Scarlet\_\_\_\_\_ Location:\_\_\_\_\_ UN Number:\_\_\_3082\_/ CAS No. 68476-33-5\_\_\_ Cargo loading temperature:\_\_\_82°C\_\_\_\_\_

Date	Sampling Unit Filter / XAD	Personnel ID	Job/Task	Start Time	Stop Time	Total sampling time [min]	Initial Pump Flow Rate (l/min)	Final Pump Flow Rate (l/min)	Sample volume (Litres)*
Event C	FB BIA3	Field Blank	-	-	-		-	-	-
Event C	FB PAK3	Field Blank	-	-	-		-	-	-
Event C	BIA 9	Personal 1	Quay	8:59	19:15	616	2.04	2.04	1256.6
Event C	PAK 9	Personal 1	Quay	8:59	19:15	616	2.02	2.03	1247.4
Event C	BIA 10	Person 2	Ship	8:56	19:30	634	2.01	2.05	1287
Event C	PAK 10	Person 2	ship	8:56	19:30	634	2.00	2.03	1277.5
Event C	BIA 11	Area 1	Close to vent (0.5 m)	9:44	19:36	592	2.01	2.08	1210.6
Event C	PAK 11	Area 1	Close to vent (0.5 m)	9:44	19:36	592	2.00	2.00	1184
Event C	BIA 12	Area 2	Background sample	9:28	19:23	595	2.01	2.07	1213.8
Event C	PAK 12	Area 2	Background sample	9:28	19:23	595	2.00	2.06	1207.9



Sample Numbers to which the following information applies

Date	Sampling Unit
Event C	BIA/PAK 9-11

Company: \_Scarlet\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_

Location: \_ \_\_

Country:

Meteorological data		Star	t	Mid	End
			of sampling period		
Time	hh:mm	9:30		14:30	19:45
Air temp.	°C	13		16	15
Wind speed	m/s	4		4	2
Wind direction		180°		210°	<b>290</b> °
Atmospheric pressure	hPa	1012		1010	1009
Relative humidity	%	92		74	84
Precipitation		-		-	-
Cloud cover	*/8	6/8		8/8	8/8
Additional information					
HFO throughput during sampling			760 m³/hr		
Loading temperature			86°C		
Product description (name, UN, MSDS)			UN 3082		
			CAS No. 68476-33-5		
Process description			Loading barge		
Product carried in previous loading			Same		
Has the tank been de-gassed prior to loading?			No		
Further relevant observations			Loading started 11 <sup>h</sup> 05 <sup>m</sup>		
Personnel on ship did deck tour every 20 minutes after start of loading					



# 8. GLOSSARY

AH	Aromatic Hydrocarbon
BLQ	Below Limit of Quantification
CSA	Chemical Safety Assessment
CTPV	Coal Tar Pitch Volatiles
CTPV3	3 of the 5 PAH, i.e. phenanthrene, pyrene and benzo[a]pyrene, considered in OSHA method 58
DNEL	Derived No Effect Level
ECHA	The European Chemicals Agency
HFO	Heavy Fuel Oil
LOQ	Limit of Quantification
ME	Mineral Oil Equivalent
OEL	Occupational Exposure Limit
OSHA	Occupational Safety & Health Administration
P(AH)	Polycyclic (Aromatic Hydrocarbons)
PEL	Permissible Exposure Limit
ТНС	Total Hydrocarbon
ТОМ	Total Organic Matter
TWA-8hr	Time Weighted Average over 8 hours



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- Heiko Kock
- Mechthild Raabe
- Ute Sänger

Members of the participating refineries and workers being monitored.



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