

1 **Understanding the fate and transport of petroleum hydrocarbons from**  
2 **coal tar within gasholders**

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17 risk

18

1 **Abstract**

2 Coal tars have been identified as posing a threat to human health due to their toxic,  
3 mutagenic and carcinogenic characteristics. Workers involved in former gasholders  
4 decommissioning are potentially exposed to relevant concentrations of volatile and semi-  
5 volatile hydrocarbons upon opening up derelict tanks and during tar excavation/removal.  
6 While information on contaminated sites air-quality and its implications on medium-long  
7 term exposure is available, acute exposure issues associated with the execution of critical  
8 tasks are less understood. Calculations indicated that the concentration of a given  
9 contaminant in the gasholder vapour phase only depends on the coal tar composition,  
10 being only barely affected by the presence of water in the gasholder and the tar  
11 volume/void space ratio. Fugacity modelling suggested that risk-critical compounds such  
12 as benzene, naphthalene and other monocyclic and polycyclic aromatic hydrocarbons  
13 may gather in the gasholder air phase at significant concentrations. Gasholder emissions  
14 were measured on-site and compared with the workplace exposure limits (WELs)  
15 currently in use in UK. While levels for most of the toxic compounds were far lower than  
16 WELs, benzene air-concentrations were found to be above the accepted threshold. In  
17 addition due to the long exposure periods involved in gasholder decommissioning and the  
18 significant contribution given by naphthalene to the total coal tar vapour concentration,  
19 the adoption of a WEL for naphthalene may need to be considered to support operators in  
20 preventing human health risk at the workplace. The Level I fugacity approach used in this  
21 study demonstrated its suitability for applications to sealed environments such as  
22 gasholders and its further refining could provide a useful tool for land remediation risk  
23 assessors.  
24

1 **INTRODUCTION**

2 Manufactured Gasworks plants (MGP) were using underground structures, such as  
3 redundant former gasholders, to collect and store coal tar, a valuable by-product of coal  
4 gasification (Hatheway, 2006). However the conversion to natural gas in the 1960s and  
5 the subsequent decommissioning of the gasworks sites have left numerous underground  
6 structures many of which were backfilled and contain coal tar contaminants. Coal tars are  
7 dense non-aqueous phase liquids (DNAPL) containing hundreds of hydrocarbons  
8 including monocyclic aromatic hydrocarbons such as BTEX compounds (Benzene,  
9 toluene, ethylbenzene and xylenes), as well as polycyclic aromatic hydrocarbons (PAHs)  
10 such as naphthalene and benzo[a]pyrene (Kueper et al, 2003). The relatively high density  
11 and high viscosity of coal tars imply that they may persist in the environment acting as a  
12 source of contamination for soils, sediments, surface and groundwater. In addition coal  
13 tars have been identified as posing a threat to human health due to their toxic, mutagenic  
14 and carcinogenic characteristics (Brown et al., 2006; Kueper, 2003). Due to the constant  
15 need of new land for housing, brownfield remediation has been a fast growing part of the  
16 UK environmental industry in recent years. Recently, remediation activities have been  
17 initiated on various former gasworks sites. Under both the Health and Safety at Work Act  
18 (1974) and the Control of Substances Hazardous to Health (2002), remediation  
19 companies are required to ensure that risks to workers' health are reduced as much as  
20 reasonably possible. Previous exposure assessments at MGP remediation sites have not  
21 shown excessive concentrations of risk-critical compounds within the workplace.  
22 However, peak concentrations on shorter periods of time have been reported to occur  
23 during critical tasks in the proximity of heavily contaminated sites (Foster, 2006; Lingle  
24 et al 2006). In addition, as former gasworks are often frequently located in the vicinity of  
25 residential and public places impacts on external receptors need to be considered.

26         The aim of the present study is to investigate the dependences between the level  
27 of risk-critical compounds found at the workplace, their concentration within the coal tar  
28 and the gasholder specificities. A fugacity approach was used to predict to which extent  
29 coal tar constituents migrate into the vapour phase. To validate the fugacity model, a coal  
30 tar sample collected from an in-filled gasholder under remediation was characterized and  
31 used to set laboratory scale microcosms simulating the gasholder characteristics. On-site

1 measurements of tank emissions were carried out and the results were compared with the  
2 workplace exposure limits (WELs) currently used in the UK.

## 4 **MATERIALS AND METHODS**

### 5 **Field site and sampling**

6 Coal tar was collected from an underground tank used initially as gasholder and then  
7 converted into a tar storage facility. The gasholder has a diameter of approximately 9  
8 metres and a depth of 4 metres. Its content was a highly viscous semi-solid tarry sludge  
9 with an significant amount of trapped mineral debris. Before remediation of the tank was  
10 undertaken, a bulk 5 kg tar sample was collected to analyse the hydrocarbon content of  
11 the tar matrix and its vapours. The sample was stored one week at 4°C prior to analyses.  
12 VOC emissions were sampled during the third day of remediating the gasholder.  
13 Excavation was still on going and a considerable amount of DNAPL/sludge was present  
14 in the tank. Emissions were sampled (i) inside the gasholder (3 metre depth), (ii) at 10  
15 metres from the border and (iii) off-site (background level). During sampling,  
16 engineering activities were interrupted to minimise emission contribution from vehicle  
17 exhausts. Samples were collected using standard stainless-steel sorbent cartridges,  
18 containing dual packing comprising 50% Tenax TA and 50% Carbotrap (Markes  
19 International Ltd, UK). Air was drawn through the sorbent cartridges using a portable  
20 battery-powered FLEC pump at a controlled flow rate of 50 ml min<sup>-1</sup> for 10 minutes.

### 22 **Chemical analyses**

23 Duplicate tar samples ( $5 \pm 0.05$  g) were chemically dried with 5 g of anhydrous sodium  
24 sulphate. Extraction procedure and gas chromatography-mass spectrometry analysis  
25 conditions have been previously described (Coulon and Delille, 2006).

26 Captured volatiles were analysed using an AutoSystem XL gas chromatograph equipped  
27 with an ATD 400 thermal desorption system and TurboMass mass spectrometer (Perkin  
28 Elmer, Wellesley, MA). Cartridges were desorbed by purging for 2 min at ambient  
29 temperature then for 5 min at 300°C. Volatiles purged from the cartridge were captured  
30 on a cold trap which was initially maintained at 30°C. The trap was then heated to 320 °C  
31 and maintained at that temperature for 5 minutes whilst the effluent was transferred to

1 the gas chromatograph via a heated (180 °C) transfer line coupled directly to a Zebron  
2 ZB624 wall-coated open tubular column (dimensions 30m×0.4mm×0.25mm ID)  
3 (Phenomenex, Torrance, CA). The gas chromatograph oven was maintained at 50 °C for  
4 4 min following injection and the temperature was then raised at 10 °C.min<sup>-1</sup> to 220 °C  
5 and held at this temperature for 9 min. The mass spectrometer was operated using the  
6 full scan mode (range m/z 33 to 350). The resulting mass spectra were combined to form  
7 a total ion chromatogram (TIC) by the GCMS integral software (TuboMass version 4.1).

8

### 9 **Conceptual model definition**

10 A site conceptual model has been developed to identify sources, pathways and receptors  
11 to be considered in the risk assessment. Four phases may be found within the gasholder,  
12 not all of them are necessarily present and volumes vary across a wide range of scenarios:  
13 (1) fill material composed of soil or sediment saturated with tar, (2) DNAPL (coal tar)  
14 may be found at different densities and viscosities. (3) Water may have reached the tank  
15 from rainfall or condensation or been originally present as aqueous liquors or emulsions.  
16 (4) Vapour phase occupying the void space. The relative volumes of the four phases of  
17 the gasholder investigated were as follows: fill material 90 m<sup>3</sup>, DNAPL 60 m<sup>3</sup>, water 35  
18 m<sup>3</sup>, void space 65 m<sup>3</sup>. Since the risk assessment addresses occupational human health and  
19 safety issues, the considered receptors are the workers (healthy subjects between 16 and  
20 60 years) involved with on-site remediation. “Workplace” is defined as the area where  
21 remedial activities (lid removal, digging, loading/piling) are being undertaken i.e. from  
22 the tank border to 10-20 m distance. Workers may be exposed to contaminants through (i)  
23 soil ingestion (ii) inhalation of contaminants present in the gaseous phase or adsorbed  
24 onto fine particles (iii) dermal contact after deposition of soil particles on the cutaneous  
25 surface (Dor, 2005). In this assessment, only the inhalation pathway has been considered.

26

### 27 **Level 1 fugacity calculation**

28 The characteristics of the coal tar sludge were used to parameterise a level I fugacity  
29 model representative of the gasholder environment. The distribution of the contaminants  
30 within the different phases was then modelled under different scenarios. It has been  
31 assumed a sealed gasholder containing four compartments: air (vapour phase), water,

1 DNAPL and soil (fill material). The total mass of contaminant in the tank ( $M$ , mol) is  
 2 given by:

$$3 \quad M = V_{\text{Air}}C_{\text{Air}} + V_{\text{Water}}C_{\text{Water}} + V_{\text{DNAPL}}C_{\text{DNAPL}} + V_{\text{Soil}}C_{\text{Soil}} \quad (1)$$

4 where  $V$  represents volume of each compartment ( $\text{m}^3$ ), and  $C$  represents the  
 5 concentrations of contaminant in each compartment ( $\text{mol m}^{-3}$ ). The relationship between  
 6  $C_{\text{DNAPL}}$ ,  $C_{\text{Air}}$ ,  $C_{\text{Water}}$ ,  $C_{\text{Soil}}$  can be expressed in terms of partition coefficients characterising  
 7 the behaviour of the contaminant within the system. For example, the partition coefficient  
 8 relating the DNAPL and water concentrations is given by:

$$9 \quad C_{\text{DNAPL}} / C_{\text{Water}} = K_{\text{DNAPL/Water}} \quad (2)$$

10 Thus, the total mass of contaminant inside the tank can be expressed as follows:

$$11 \quad M = V_{\text{Air}}[K_{\text{Air/Water}}C_{\text{Water}}] + V_{\text{Water}}[K_{\text{Water/DNAPL}}C_{\text{DNAPL}}, K_{\text{Water/Air}}C_{\text{Air}}] + \\ 12 \quad V_{\text{DNAPL}}[K_{\text{DNAPL/Soil}}C_{\text{Soil}}, K_{\text{DNAPL/Water}}C_{\text{Water}}] + V_{\text{Soil}}[K_{\text{Soil/DNAPL}}C_{\text{DNAPL}}] \quad (3)$$

13 Under the Fugacity approach, the concentration term,  $C$ , is replaced with the fugacity  
 14 term  $Zf$  (Eq.4) where  $Z$  describes the relationship between chemical concentration and  
 15 fugacity ( $f$ ) (Mackay, 2001). The fugacity capacity constants used in the model are shown  
 16 in table 1.

$$17 \quad C = Zf \quad (4)$$

18 In-filled gasholders are sealed environments where each environmental compartment  
 19 considered is expected to be in equilibrium with each other. Thus, fugacity values of each  
 20 compartment are considered as equal (Eq. 5)

$$21 \quad f_{\text{DNAPL}} = f_{\text{S}} = f_{\text{A}} = f_{\text{W}} \quad (5)$$

22 and the equation 3 may be rewritten as:

$$23 \quad M = f[V_{\text{Air}}Z_{\text{Air}} + V_{\text{Water}}Z_{\text{Water}} + V_{\text{DNAPL}}Z_{\text{DNAPL}} + V_{\text{Soil}}Z_{\text{Soil}}] = f \sum V_i Z_i \quad (6)$$

24 The mass of coal tar, soil and water were calculated using literature-derived densities:  
 25 coal tar was assumed to have an average bulk density of  $1.1 \text{ g cm}^{-3}$  (Lee et al., 1992); soil  
 26 was assumed as  $2.4 \text{ g cm}^{-3}$  (Nieman, 2003) and water  $1 \text{ g cm}^{-3}$ . The percent of organic  
 27 carbon of soil was estimated as 0.5% (Nieman, 2003). Thirteen different compounds were  
 28 modelled (BTEX, styrene, 1,2,4-trimethylbenzene, naphthalene, acenaphthylene,

1 acenaphthene, fluorene, phenanthrene and anthracene). Due to their physicochemical  
2 properties (e.g. Henry's law constant, high  $K_{ow}$  and  $K_{oc}$ ), concentrations of PAHs with 4  
3 or more rings were neglected in the air phase as they were expected to be insignificant.

#### 5 **Microcosms experiment**

6 Duplicate microcosms were established in sterile 250 ml vial bottles where volumetric  
7 ratio between each phase was maintained as those found on-site: tar sludge (10%), water  
8 (7%) and air (83%). The sealed void space was created on the top of the bottle using  
9 Teflon foil normally used for VOC sampling bags. VOC samples were collected at  $T_0$   
10 (immediately after preparing the experiment) and after 21 days ( $T_{21}$ ). Between the two  
11 samplings, the microcosms were stored under a fume hood cabinet in darkness at 20°C.

### 13 **RESULTS AND DISCUSSION**

14 Characterisation of the total petroleum hydrocarbons from the tar sample showed  
15 predominance of aromatic compounds with respect to aliphatic compounds confirming  
16 the coal-based nature of the tar. Concentration and relative abundance of 54 individual  
17 PAHs have been characterised (Table 2). The total PAH concentration was estimated to  
18 be  $49261 \pm 865$  ( $\pm$  SD)  $\text{mg kg}^{-1}$ . The prevalence of lighter PAHs was clearly observed; 2  
19 and 3 rings PAHs represented together more than 80% of the total PAHs, and the latter  
20 accounted for half of the 16 USEPA PAHs. Four rings PAHs represented about 8%  
21 followed by 5 and 6 rings PAHs at 6% and 3%, respectively. The sum of the 16 USEPA  
22 PAHs represented two third (63.6%) of the total PAHs. By far, naphthalene (12448  $\text{mg kg}^{-1}$ )  
23 and phenanthrene (10069  $\text{mg kg}^{-1}$ ) were the most abundant compounds representing  
24 25% and 20%, respectively of the total PAHs. Other 16 USEPA PAHs, such as  
25 acenaphthylene, anthracene, pyrene and benzo[k]fluoranthene were found at relatively  
26 high concentrations ( $> 1300 \text{ mg kg}^{-1}$ ). Benzo[a]pyrene, often used as a reference for  
27 human health risk driver in contaminated soil, is present in smaller amounts (517  $\text{mg kg}^{-1}$ )  
28 <sup>1</sup>). Concentrations of dibenzothiophenes, especially of the mono-alkylated species (5,267  
29  $\text{mg kg}^{-1}$ ,  $>10\%$ ), are higher than the levels reported in the literature (Brown et al, 1999  
30 and 2006; Lee et al, 1992). The abundance of lighter PAHs such as naphthalenes and  
31 phenanthrene/anthracene suggested unweathered characteristics of the coal tar sample.

1 This observation is supported by results of previous studies (Brown et al, 2006; Haeseler,  
2 1999 et al; Sauer et al, 2003) demonstrating that gasholders being sealed environments,  
3 hamper weathering processes of the contaminants.

4 The total VOC concentration representing the sum of 49 volatile/semivolatile  
5 organic compounds was estimated to be 3452 mg m<sup>-3</sup>. Concentrations of the most  
6 dominant compounds are shown in Table 3 (T<sub>0</sub> initial characterisation). These  
7 compounds are also expected to be a source of concern in the workplace. As predicted  
8 from the PAH characterisation, high concentrations of naphthalene were observed (above  
9 150 mg m<sup>-3</sup>). Alkylated monocyclic aromatic compounds and BTEX were also found in  
10 relatively high amounts and BTEX represented more than 20% of the total VOC mixture,  
11 with benzene being determined at an elevated concentration of 88 mg m<sup>-3</sup>. Benzene is  
12 recognised as a carcinogenic compound on the basis of human exposure and naphthalene  
13 is regarded as a possible carcinogen (category 3 carcinogen in CHIP regulations; HSE,  
14 2005). Alkylated monocyclic aromatics such as toluene, ethylbenzene, xylenes, styrene,  
15 trimethylbenzenes are classified as toxic and harmful by the UK (CHIP) and EU health  
16 and safety regulations (HSE, 2005). In addition, nitrogenated compounds were found at  
17 high concentrations (e.g. propionitrile 363.4 mg m<sup>-3</sup>, benzonitrile 285.6 mg m<sup>-3</sup>).  
18 Analyses also identified high concentrations of dimethyl sulphide (250 mg m<sup>-3</sup>),  
19 thiocyanic acid (122.1 mg m<sup>-3</sup>) and halogenated hydrocarbons (difluorochloromethane,  
20 chloromethane). The current UK WEL is as low as 5 mg m<sup>-3</sup> for cyanides, 43 mg m<sup>-3</sup>  
21 difluorochloromethane and 105 mg m<sup>-3</sup> for chloromethane. Thus these compounds may  
22 further increase the hazardous potential of the coal tar emissions from the gasholder.

23 VOC and SVOC measured inside the gasholder, at the workplace and on a  
24 background semi-rural environment are shown in Table 4. When WELs were available  
25 they were displayed together in the table (HSE, 2005). Background concentrations of  
26 risk-critical compounds such as BTEX were < 0.1 or not detected. Gasholder  
27 measurements showed high concentrations of benzene, other monocyclic aromatic  
28 hydrocarbons and naphthalene. About the same relative proportion between these  
29 compounds was found in the workplace measurements. Benzene, toluene and  
30 naphthalene showed concentrations in the workplace of respectively 6.9, 5.2 and 7.7 mg  
31 m<sup>-3</sup>. The benzene concentration is two fold higher than the WEL set by HSE. With the



1 introduction of the EH40/2005 WELs list (HSE, 2005), naphthalene is no longer assigned  
2 a WEL value (previous WEL was 53 and 80 mg m<sup>-3</sup> for long and short term exposure,  
3 respectively). Naphthalene is a possible carcinogen and its concentration in the workplace  
4 should be kept as low as reasonably practicable. However, due to the long exposure  
5 periods involved in gasholder decommissioning and the significant contribution given by  
6 naphthalene to the total coal tar vapour concentration, the adoption of a WEL for  
7 naphthalene may need to be considered to support operators in preventing human health  
8 risk in the workplace.

9 Lab-scale microcosm analysis and fugacity level I calculations were used to  
10 predict the partitioning behaviour of the organic compounds from the coal tar. The  
11 presence and residual concentration of PAHs contributing more than 0.5% of the total  
12 PAH concentration in water after 21 days of experiment are shown in Table 5. A clear  
13 prevalence of 2 and 3 ring-PAHs was observed. This finding was predictable as the 2 and  
14 3 ring-PAHs have lower molecular weight and higher solubility than the >3-rings PAHs.  
15 Naphthalenes and indene together accounted for approximately 70% of the mixture of  
16 considered compounds. Theoretical concentrations of 14 PAHs in water calculated  
17 through the fugacity approach were compared with the experimental data as shown in  
18 Figure 1. A good correlation between the calculated and the experimental results for the  
19 14 selected PAHs was observed except for naphthalene where the calculated  
20 concentration (3200 mg m<sup>-3</sup>) was twice as high as the experimental one (1550 mg m<sup>-3</sup>)  
21 (data not shown in Figure 1). This may be due to volatilization of naphthalene from the  
22 water during the sampling procedures.

23 The microcosm air phase characterisation after 21 days of experiment is shown in  
24 Table 3. Overall, higher VOC/SVOC concentrations were observed in the air phase.  
25 Particularly, naphthalene and BTEX concentrations have increased by at least 2 times.  
26 This is probably due to the fact that the three week time period allowed coal tar vapours  
27 to gather at higher amounts within the microcosm air phase. The expected concentration  
28 of naphthalene and BTEX in the air phase according to the fugacity calculation also  
29 showed a good correlation with the experimental data (Table 3). Thus, it was found  
30 appropriate to attempt quantifying the concentration of BTEX in the bulk tar sample by  
31 using the same approach. This was done by changing the known factor in the level I

1 fugacity model and proceeding backwards with the calculation. The results were as  
2 follows: benzene 200 mg kg<sup>-1</sup>, toluene 800 mg kg<sup>-1</sup>, ethylbenzene 2000 mg kg<sup>-1</sup>, o-xylene  
3 1500 mg kg<sup>-1</sup> and p-xylene 1900 mg kg<sup>-1</sup>. These predicted values are in good agreement  
4 with previous studies where BTEX concentration from coal tar within gasholders was  
5 monitored (Brown, 2006; Sauer, 2003; Majoub, 2000).

6 Three scenarios were modelled to evaluate parameters influencing VOC flux from in-  
7 filled tanks: (i) tank almost full with tar (S1); ii) tank almost empty (S2) and (iii) tank  
8 with a profile similar to the investigated gasholder. The air phase concentrations of  
9 BTEX and naphthalene vary only slightly between the three different scenarios  
10 considered (data not shown). Average concentrations of benzene and naphthalene were  
11 estimated to be 360 mg m<sup>-3</sup> and the total average BTEX concentration was approximately  
12 325 mg m<sup>-3</sup>. Due to their low fugacity in the DNAPL phase, concentrations of  
13 acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene did not exceed 1.5  
14 mg m<sup>-3</sup>. This finding suggested that the concentration of contaminant (C<sub>VP</sub>) in the air  
15 phase was dependent and directly proportional to its concentration in the coal tar (C<sub>TAR</sub>),  
16 the source term. Consequently, the following equation was deduced:

$$17 \quad C_{VP} = K * C_{TAR}$$

18 where *K* represented the constant relating C<sub>VP</sub> and C<sub>TAR</sub>. As shown in Table 6, *K* value  
19 decreased with the molecular weight (MW) of the considered compounds. If the coal tar  
20 fingerprint characterisation can be determined before the remediation activities start,  
21 determination of *K* values may provide a valuable tool when predicting vapour emission  
22 concentrations from in-filled tanks. The application of these results to real structures can  
23 support the risk assessment process applicable to the remediation of former MGP.  
24 Following the lid removal, operations may need to be stopped to permit the contaminant  
25 concentrations in the workplace to drop down to safe levels. By using the fugacity  
26 approach, remediation engineers can also predict if such measures will be needed and the  
27 duration of any such interruption period during the remediation activities.

## 28 29 **CONCLUSION**

30 In-filled tank remediation activities may be a cause of concern due to the exposure of  
31 workers to the risk-critical compounds present in the coal tar mixture. VOCs and SVOCs

1 may gather at significant amounts within the tank air phase and contribute to acute  
2 exposure levels, especially immediately following the lid removal. The fugacity approach  
3 proved to be a promising tool to predict the concentration of contaminants within the  
4 gasholder air phase. This mainly depends on the coal tar composition regardless the  
5 presence of water within the tank or the different volumetric proportions between  
6 compartments. Risk of not complying with regulatory workplace exposure limits are  
7 mainly linked with the presence of benzene. Due to its carcinogenic profile, values for  
8 benzene are set very low and, as observed in the site-specific exposure assessment, may  
9 be exceeded for critical tasks involving proximity to heavily contaminated structures such  
10 as gasholders. Naphthalene was found to be the most abundant contaminant in the  
11 workplace environment. Protracted exposure to naphthalene vapours should be  
12 considered due to its suspected carcinogenic nature.

13

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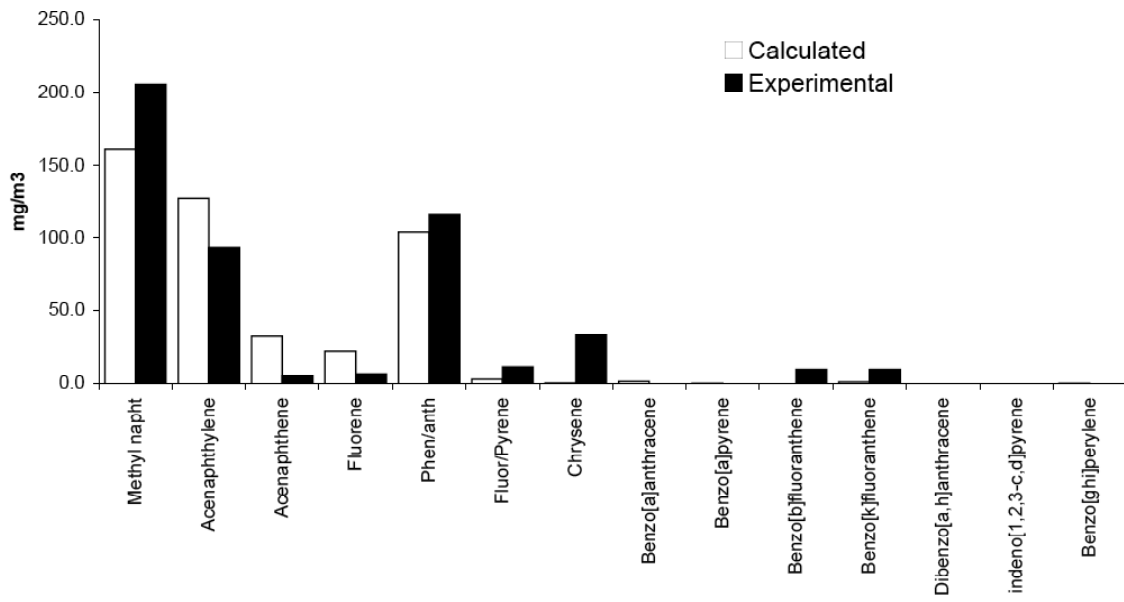
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**Figure 1:** Comparison of measured and predicted concentrations of 14 risk-critical PAHs in the water phase

**Table 1:** Fugacity capacities used in Level I calculation

Compartment	Fugacity capacities (mol m <sup>-3</sup> Pa)	Constant definition
Air	$Z_{\text{AIR}} = 1/RT$	$R = 8.314 \text{ Pa m}^3 \text{ mol}^{-1}\text{K}$ ; $T = \text{K}$ , temperature
Water	$Z_{\text{WATER}} = 1/H$	$H = \text{Henry's law constant (Pa m}^3 \text{ mol}^{-1}\text{)}$
NAPL	$Z_{\text{NAPL}} = K_{\text{ow}} * Z_{\text{WATER}} = K_{\text{ow}}/H$	$K_{\text{ow}} = \text{Octanol-water partition coefficient}$
Soil	$Z_{\text{SOIL}} = Z_{\text{WATER}} * K_d * \rho_s = K_d * \rho_s / H =$ $= K_{\text{oc}} * f_{\text{oc}} * \rho_s / H$	$K_d = \text{Soil-water partition coefficient}$ $K_{\text{oc}} = \text{Organic carbon partition coefficient}$ $f_{\text{oc}} = \text{Soil organic fraction}$ $\rho_s = \text{Soil density}$

**Table 2:** PAH fingerprint characterisation of the coal tar sample from the gasholder

Aromatic hydrocarbons	Ring Nb	Conc. (mg kg <sup>-1</sup> )*	Composition (%)	Aromatic hydrocarbons	Ring Nb	Conc. (mg kg <sup>-1</sup> )*	Composition (%)
Naphthalene	2	12448 (146)	25.30	Benzo[k]fluoranthene	4	1259 (16)	2.60
Indene	2	1371 (14)	2.80	Benzo[a]anthracene	4	655 (22)	1.30
Acenaphthylene	2	1362 (7)	2.80	C1-Fluoran/Pyr	4	234 (25)	0.50
C1-napht	2	1068 (5)	2.20	Fluoranthene	4	231 (9)	0.50
1'1'Biphenyl	2	343 (14)	0.70	Chrysene	4	133 (4)	0.30
C4-Napht	2	278 (20)	0.60	Benzo[c]phenanthrene	4	80 (13)	0.20
Acenaphthene	2	245 (4)	0.50	Benzo[b]naphthofuran	4	110 (13)	0.20
C2-Napht	2	149 (4)	0.30	Benzo[b]naphtho-thiophene	4	68 (22)	0.10
C3-Napht	2	100 (8)	0.20	C1-Chrysene	4	67 (6)	0.10
Phenanthrene	3	10069 (118)	20.40	Benzo[c]carbazole	4	53 (20)	0.10
C1-Dibenzo	3	5267 (71)	10.70	C2-Fluoran/Pyr	4	38 (6)	0.10
Anthracene	3	2364 (39)	4.80	Benzo[a]pyrene	5	517 (4)	1.10
C3-Dibenzo	3	1915 (21)	3.90	Indeno[1,2,3-c,d] fluoranthene	5	462 (11)	0.90
C1-Phen/Anth	3	981 (15)	2.00	Perylene	5	308 (4)	0.60
Dibenzofuran	3	941 (12)	1.90	Benzo[J]fluoranthene	5	217 (32)	0.40
C2-Dibenzo	3	675 (19)	1.40	Benzo[ghi]perylene	5	157 (31)	0.30
Carbazol	3	382 (25)	0.80	Benzo[b]chrysene	5	71 (20)	0.10
Fluorene	3	306 (5)	0.60	Dibenzo[a,h] anthracene	5	57 (14)	0.10
C3-Phen/Anth	3	176 (19)	0.40	C1-Perylene	5	27 (9)	0.10
Dibenzothiophene	3	166 (10)	0.30	Benzo[ghi]perylene	6	425 (12)	0.90
C2-Phen/Anth	3	161 (6)	0.30	Dibenzo(DEF,MNO) chrysene	6	245 (14)	0.50
C1-Fluorene	3	145 (8)	0.30	Indeno[1,2,3-c,d] pyrene	6	81 (11)	0.20
C2-Fluorene	3	96 (3)	0.20	Dibenzo[a,l]pyrene	6	71 (16)	0.10
C3-Fluorene	3	66 (9)	0.10	Dibenzo[a,h]pyrene	6	70 (18)	0.10
Pyrene	4	2154 (30)	4.40	Dibenzo[a,i]pyrene	6	65 (14)	0.10

\*\* average concentration of duplicate samples. Standard deviation is shown in parentheses. C1 to C3 represent carbon number of alkyl groups in alkylated PAH homologues

**Table 3:** Characterisation of the VOC content of the coal tar.

VOC/SVOC	T <sub>0</sub> (mg m <sup>-3</sup> )	T <sub>21</sub> measured by TDGCMS (mg m <sup>-3</sup> )	T <sub>21</sub> predicted by fugacity model (mg m <sup>-3</sup> )
Propionitrile	363 (51)	-	-
Benzonitrile	285 (12)	-	-
Benzene, 1-propynyl-	278 (9)	542 (19)	-
Difluorochloromethane	269 (12)	-	-
Dimethyl sulfide	254 (10)	-	-
Naphthalene	155 (6)	374 (22)	360
Benzene, 1-methyl-3-nitro-	194 (6)	-	-
Toluene	156 (2)	460 (30)	456
p-Xylene	148 (7)	418 (24)	400
Benzene, 1,4-dimethyl-2-nitro-	142 (1)	-	-
o-Xylene	139 (2)	260 (14)	257
Chloromethane	138 (8)	-	-
Styrene	111 (4)	-	-
Indene	108 (6)	-	-
Ethylbenzene	108 (3)	515 (19)	510
Benzene	88 (0.8)	348 (10)	310
Benzene, 1,2,3-trimethyl-	43 (0.9)	71 (9)	-
Isoquinoline	31 (0.2)	164 (12)	-
Benzofuran	24 (0.2)	82 (8)	-
Biphenylene	24 (0.2)	-	-
Benzene, 1-ethyl-2-methyl-	23 (0.3)	-	-
Benzene, 1,3-dimethyl-	12 (0.1)	-	-
Naphthalene, 2-methyl-	3.7 (0.07)	-	-
Pyridine	3.2 (0.05)	166 (12)	-
Phenol	2.7 (0.05)	1.9 (0.2)	-
Benzofuran, 3-methyl-	1.5 (0.5)	1.0 (0.4)	-
Thiophene, 3-methyl-	0.9 (0.07)	13 (2)	-
Thiophene	0.8 (0.03)	170 (10)	-
Benzonitrile	0.3 (0.08)	428 (73)	-
Indole	-	168 (28)	-
Benzene, 1,2,3,5-tetramethyl-	-	4.6 (1.3)	-

Standard deviation is indicated in parentheses



**Table 4:** VOC and SVOC measured inside the gasholder, at the workplace and off-site (background). When available, WEL is indicated (HSE, 2005).

All values are in mg m <sup>-3</sup>					
Compounds	Background	Tank	Workplace	WELs 8h	WELs 15min*
Acenaphthylene	n.d.	1.7	1.3	-	-
Benzaldehyde	0.0	0.2	0.1	-	-
Benzene **	0.2	39.5	6.9	3.25	
Benzene, 1,3,5-trimethyl-	n.d.	28.5	0.3	125	-
Benzofuran	n.d.	5.1	0.3	-	-
Benzonitrile	n.d.	0.9	0.1	-	-
Dibenzofuran	n.d.	0.3	0.2	-	-
Ethylbenzene	0.1	2.0	0.6	441	552
Indene	n.d.	25.4	2.7	48	72
Naphthalene	n.d.	87.7	7.7	-	-
Naphthalene, 1,2-dimethyl-	n.d.	37.2	0.1	-	-
o-Xylene	n.d.	4.3	0.8	220	441
Phenol **	0.1	4.1	0.4	7.8	-
p-Xylene	n.d.	16.5	0.5	220	441
Pyridine	n.d.	1.5	n.d.	16	33
Styrene	n.d.	4.5	0.6	430	1080
Toluene	n.d.	33.6	5.2	191	574
Acetic acid, methoxy-	0.4	n.d.	0.8	616	770
Benzene, 1-ethyl-4-methyl-	n.d.	n.d.	0.1	-	-
Benzene, 1-propynyl-	n.d.	n.d.	2.7	-	-
Biphenylene	n.d.	n.d.	1.3	-	-
Cyclohexane	n.d.	n.d.	0.4	350	1050
Naphthalene, 1-methyl-	n.d.	n.d.	0.1	-	-

n.d. not detected; \*HSE recommends, when short-term (15 min) exposure limits are not provided to multiply the long term WEL by a factor of 3. \*\*WEL for benzene and phenol are provided in ppm, these were converted in mg m<sup>-3</sup>

**Table 5:** Characterisation of the PAH content in the water phase after 21 days of experiment. Compounds contributing less than 0.5% are not shown.

PAHs	Concentration ( $\mu\text{g l}^{-1}$ )	Composition (%)
Naphthalene	1550.8	37.6
Indene	1106.3	26.8
C1-napht	402.1	9.7
C3-napht	147.2	3.6
Fluoranthene	113.9	1.0
Dibenzothiophene	103.3	1.8
Acenaphthylene	93.6	2.3
Anthracene	79.4	1.4
1'1'Biphenyl	72.2	1.8
C2-napht	50.6	1.2
Dibenzofuran	21.6	0.5

**Table 6:** Values of the compound specific constant  $K$  for the 13 risk-critical compounds

Compound	$K$ ( $\text{kg m}^{-3}$ )	Compound	$K$ ( $\text{kg m}^{-3}$ )
Benzene	1.84	Naphthalene	0.03
Toluene	0.56	Acenaphthylene	5.45E-04
Ethylbenzene	0.26	Acenaphthene	0.01
m/p-Xylenes	0.21	Fluorene	2.31E-04
o-Xylene	0.17	Phenanthrene	6.31E-05
Styrene	0.07	Anthracene	5.49E-05
1,2,4-Trimethylbenzene	0.07		