Fugitive and Stationary Source Emissions from Coke Plants and Impact on the Local Ambient Air Quality

by

E. Aries, D. Ciaparra, M. J. Schofield, D. R. Anderson, N. Schofield and R. Fisher

Corus Research, Development and Technology, Swinden Technology Centre, Moorgate, Rotherham S60 3AR, UK

Presented by Dr. E. Aries to the Midland Section at Corus Conference Centre, Scunthorpe on the 16th November 2006.

1 Introduction

The steel industry is the leading producer and consumer of coke. It controls about 72% of world coke making capacity, the remaining 28% being controlled by independent producers most of whom use non-recovery coke ovens. In the UK, by-product recovery coke ovens are used in the integrated steel plants operated by Corus UK to provide for the needs of blast furnaces, the latter consuming approximately 85% of the coke production. By-product recovery coke ovens produce waste gases containing organic micro-pollutants including volatile and semi-volatile organic compounds (VOCs and SVOCs) such as benzene and polycyclic aromatic hydrocarbons (PAHs), respectively.

Under a research project in the Research Fund for Coal and Steel Programme, that started in 2004 (ERAMAC-RFCS-CR-03001: *Emissions Reduction through Analysis, Modelling and Control*), the Environment Department of Corus Reseach Development and Technology carried out investigations to characterise fugitive and stationary source releases of VOCs and SVOCs from Dawes Lane Coke Ovens (DLCO, Scunthorpe) and study the impact of the coke oven batteries upon the local ambient air quality. This paper will present details of the sampling and analytical techniques developed by Corus UK to measure the targeted organic pollutants from the most significant fugitive and stationary emission sources of a coke plant. Based on a series of plant measurements, an emissions inventory of VOCs such as benzene, toluene and xylenes, and PAHs such as benzo[a]pyrene is presented. Finally, the results from ambient air measurement carried out in the vicinity of the plant are presented and discussed.

2 Process description and sources of pollution in coke ovens

Metallurgical coke is a porous non-volatile solid, containing about 85% of carbon that is produced by driving off the volatile matter in coal by distillation. The coke product, which contains less than 2% residual volatile matter, is used as a reductant in the blast furnace, while undersize material (coke breeze) is used as a fuel in the iron ore sintering process. The coking, or carbonisation, process takes place in a series of large airtight slot ovens, lined with silica refractory bricks and with doors at each end. A schematic of the process is given in Fig. 1. The coal charge is heated in the absence of air (to prevent combustion) and the crude gas that is released is drawn off and cleaned in an associated by-products recovery plant for further use as a fuel. Typically, the ovens are arranged in batteries of 30 to 70 ovens and are heated via a series of heating flues that are arranged on both sides of each oven. Typically, the oven size is characterised by the door height, which may range from 3.5 m to 9 m (small to jumbo sized ovens).

The coking process begins with charging of coal to the oven using charging cars that transport the coal blend from a series of storage bunkers to the oven to be charged. The coal is carried in a series of hoppers mounted on the charger car and is discharged into the oven by a series of high-rate screw feeders via a set of 4 or 5 charging holes arranged across the top of the oven. Telescopic tubes mounted on the charger car extend downwards to form a seal with each charging hole in order to prevent the fugitive release of charging gases into the atmosphere as a result of the displacement of air inside the oven by the coal charge. Air displaced by the coal and charging fumes is drawn off into the crude gas line by applying suction to the oven during the charging process. After charging, the oven is sealed by replacing the charge hole lids and the coal charge is levelled using a large steel leveller bar to ensure that there is adequate headspace for the crude gas to pass into the gas collection system. The oven lid is further sealed by the application of a water-based luting compound around the periphery of the lid.

Carbonisation is carried out by heating the coal charge to a uniform soak temperature of ~1250°C over a period of 18 to 20 h. When carbonisation is finished, the oven doors are removed and a hydraulic ram is used to push the coke from the oven into a coke guide and collecting car on the opposite side of the oven. After discharge, the incandescent coke is transported to a quench tower where it is rapidly cooled by spraying with water, and subsequently discharged on to a coke wharf.

Each oven is connected to a common crude gas collector main, which runs along the length of the battery, via a series of vertical ascension pipes. Water (flushing liquor) is circulated through the collector main to provide direct cooling of the crude gas and to condense tar from the gas. The gas is cooled further to separate more tar and then the ammonia is scrubbed out of the gas in the ammonia washers and benzol (essentially BTX) is extracted by scrubbing the gas with a wash oil in the benzol plant. The resulting clean gas is used as a fuel for heating of the coke oven batteries and in reheating furnaces and power generation on the works.

The flushing liquor is passed to liquor storage tanks where the tar is allowed to settle and the cooled supernatant liquor is recirculated to the collector main. The flushing liquor condenses tar and water and absorbs ammonia, phenols and other water-soluble substances in the crude gas. Excess flushing liquor is drawn off and purified, prior to discharge, by biological oxidation after first removing ammonia by steam stripping in a free and fixed ammonia still. The tar and benzol are sold off as by-products for further processing.

The potential sources of pollution in coke oven plants have been described in more detail elsewhere [1], but briefly these are:

Fugitive discontinuous emissions caused by technological operations like

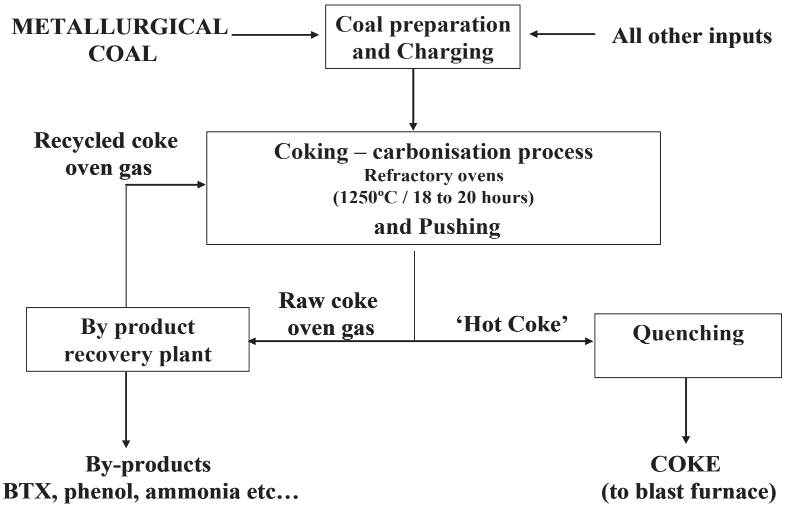
- Coal charging;
- Coke pushing;
- Quenching of hot coke.

Fugitive emissions such as leakages from the coke oven sealing surfaces including

- Oven doors;
- Charging hole lids;
- Ascension pipe covers.

In addition to these, there is a continuous discharge of gases and dusts from the coke oven underfiring stack originating from the combustion process of battery heating system.

Figure 1 Cokemaking using by-product recovery coke ovens



3 Terminology and list of targeted pollutants

3.1 Volatile organic compounds

Volatile organic compounds (VOCs) is a general term that is applied to a wide range of solid or liquid organic compounds that are easily vaporised. Their concentrations in the atmosphere are generally low, but they can exhibit a wide range of effects on the environment. For example, some VOCs exhibit direct toxicity to humans. In particular, benzene is recognised as a genotoxic human carcinogen. Some VOCs are responsible for photochemical smog and ozone formation by interaction with nitrogen oxides in the presence of sunlight, and others with ozone depletion in the upper atmosphere. In the UK, the main atmospheric source of benzene is the combustion and distribution of petrol. In comparison, diesel fuel is a relatively small source of benzene. VOCs are also generated in thermal processes from the steel industry but their emissions are still poorly characterised. In this study, 16 VOCs were targeted (Table 1). Total VOC concentrations will refer to the sum of the individual concentrations of the 16 VOCs listed in Table 1. Total BTEX will refer to the sum of benzene, toluene, ethylbenzene and xylenes (3 isomers) concentrations, whereas total BTX will refer only to the sum of benzene, toluene and xylenes concentrations.

Table 1 A list of the 16 VOCs analysed in fugitive and stationary source coke oven emissions at DLCO.

BTEX
benzene
toluene
ortho-, meta- and para-xylenes
ethylbenzene
Chlorobenzenes isomers
chlorobenzene
1,3-dichlorobenzene
1,2-dichlorobenzene
1,4-dichlorobenzene
1,2,3-trichlorobenzene
1,2,4-trichlorobenzene
Trimethylbenzene isomers
1,3,5-trimethylbenzene
1,2,4-trimethylbenzene
Other targeted species
carbon disulphide (CS_2)
naphthalene

3.2 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) constitute a large group of semi-volatile organic compounds consisting of two or more aromatic rings fused together. Because of their low vapour pressures, some PAHs are present at ambient temperatures in air, both in gaseous form and in association with particles. Lighter PAHs, such as phenanthrene, are found almost exclusively in the gas phase, whereas the heavier ones, such as benzo[a]pyrene B[a]P, are almost totally adsorbed onto particles. In this study, PAHs are classified into three categories according to their molecular weights as follows:

- LM-PAHs - low molecular weight PAHs (range of MW: 128 - 178) comprising two- or three-ringed PAHs such as naphthalene, anthracene, acenaphthylene etc.;
- MM-PAHs - medium molecular weight PAHs (range of MW: 202 - 228) comprising four-ringed PAHs such as chrysene; and,
- HM-PAHs - high molecular weight PAHs (MW > 252) containing five- six- and seven-ringed PAHs such as B[a]P.

Several PAHs are highly carcinogenic or mutagenic, these are listed according to different classifications in Table 2. A group of 16 PAHs has been identified as priority pollutants by the US Environmental Protection Agency (US EPA). The International Agency for Research on Cancer (IARC) has identified a sub-set of six of the US EPA 16 PAHs as probable (Group 2A) or possible human carcinogens (Group 2B).

Table 2 Classification of PAH species

Compound	US EPA 16 PAHs Priority pollutants	IARC Group 2a [1]	IARC Group 2b [2]
Naphthalene	✓		
Acenaphthylene	✓		
Acenaphthene	✓		
Fluorene	✓		
Phenanthrene	✓		
Anthracene	✓		
Fluoranthene	✓		
Pyrene	✓		
Benz[a]anthracene	✓	✓	
Chrysene	✓		
Benzo[b]fluoranthene	✓		✓
Benzo[j]fluoranthene			✓
Benzo[k]fluoranthene	✓		✓
Benzo[a]pyrene	✓	✓	
Dibenzo[a,h]anthracene	✓	✓	
Dibenzo[a,c anthracene			
Benzo[g,h,i]perylene	✓		
Indeno[1,2,3-cd]pyrene	✓		✓
5-methyl chrysene			✓
Dibenzo[a,e]pyrene			✓
Dibenzo[a,h]pyrene			✓
Dibenzo[a,i]pyrene			✓
Dibenzo[a,l]pyrene			✓

[1] Probable human carcinogen

[2] Possibe human carcinogen

To characterise more precisely the carcinogenic potency of PAH mixtures, several toxic equivalency factors (TEFs) have been proposed for PAHs. In particular, Nisbet and Lagoy (1992) compiled a list of TEFs for the 16 US EPA PAHs ^{2}, in which B[a]P was used as a reference compound with a TEF value of 1, whereas the other PAHs with a lower carcinogenic potency were attributed TEF values ranged from 0.001 to 0.1 (Table 3). The B[a]P equivalent concentration (B[a]Peq), which represent a measure of the overall carcinogenic activity of a sample, is calculated by multiplying the concentrations of each of the individual PAH by its respective TEF and by summing the resulting concentrations. This concept is similar to the use of toxic equivalent concentrations for expressing dioxin concentrations in process emissions. However, whereas the dioxin toxic equivalent concentration is commonly used as a measure of the dioxin concentration in waste gas emissions, $B[a]P_{eq}$ is not widely used by environmental regulators. Nevertheless, it is a useful concept for identifying which PAH compounds contribute most to the carcinogenic toxicity of an environmental sample. This is usually done by calculating the percent contribution of each of the 16 US EPA PAHs to the total B[a]Peq concentration. This approach provides a better understanding of the PAH compounds in emissions that are the most significant from a health effect point of view.

Table 3 Toxic equivalency factors (TEFs) for the 16 priority US EPA PAHs [2]

Compound	TEFs
Naphthalene	0.001
Acenaphthylene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.01
Fluoranthene	0.001
Pyrene	0.001
Benz[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1
Dibenzo[a,h]anthracene	1
Benzo[g,h,i]perylene	0.01
Indeno[1,2,3-cd]pyrene	0.1

A list of all PAH compounds targeted in this study and their respective abbreviations are provided in Table 4.

Table 4 List and abbreviations of targeted PAHs

US EPA 16 PAHs	
Naph	naphthalene
Acy	acenaphthylene
Ace	acenaphthene
Fluor	fluorene
Phen	phenanthrene
Ant	anthracene
Flant	fluoranthene
Pyr	pyrene
B[a]Ant	benz[a]anthracene
Chry + Trip	chrysene + triphenylene
B[b + j]Flant	benz [b + j fluoranthene
B[k]Flant	benz [k fluoranthene
B[a]P	benzo[a]pyrene
IDP	Indeno[1,2,3-cd pyrene
D[a,h + a,c]Ant	dibenzo[a,h + a,c]anthracene
B[g,h,i]Per	benzo[g,h,i perylene
Other PAHs	
MePhen	Methylphenanthrenes
2-PhNaph	2-phenylnaphthalene
DiMePhen	Dimethylphenanthrenes
B[b]Fluor	benzo[b fluorene
B[g,h,i]Flant	benz [g,h,i fluoranthene
B[e]P	benzo[e] pyrene
Per	perylene
Anth	Anthanthrene

4 Materials and Methods

4.1 Sampling and analytical techniques for VOC measurements

The sampling system used by Corus to characterise VOC emissions from coke oven emissions is depicted in Fig. 2. Briefly, the sampling train consisted of a probe attached to a heated sampling line, a heated pump operating at 5 l/min, a gas bleed, a quench impinger, the adsorption tubes and a mass flow controller operating at 50 ml/min, with an accuracy of ±2%. During sampling, all heated components were maintained at 160°C to prevent condensation of moisture. In order to ensure high adsorption efficiency, the hot gas was quenched using an impinger equipped with a cooling system, and the gas temperature was monitored prior to adsorption to ensure that it was below 20ºC throughout the sampling period. In order to retain as wide a range as possible of organic compounds with different chemical affinities, a combination of Carbograph TD, Carbopack X and Spherocarb adsorbent phases was employed (See Figure 3); these adsorption phases are referred to as three-bed tubes. In all cases, a second three-bed tube was also placed after the main tube to act as a backup in case of a breakthrough. Sampling times varied dependent upon the emission source. Typically, sampling times of 15 or 30 minutes were used to monitor for underfiring and door emissions of coke ovens, while sampling times of 30 to 60 minutes were used to monitor for charging hole lid leakages in coke ovens.

Figure 2 Schematic of the sampling device used by Corus UK for the measurement of VOCs from coke oven emission sources

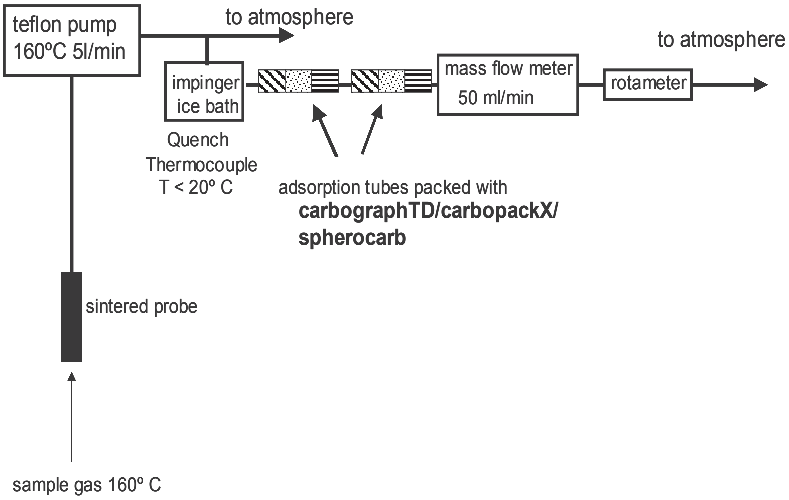
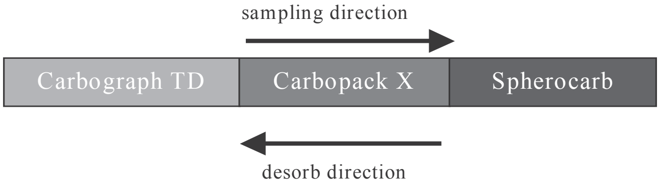


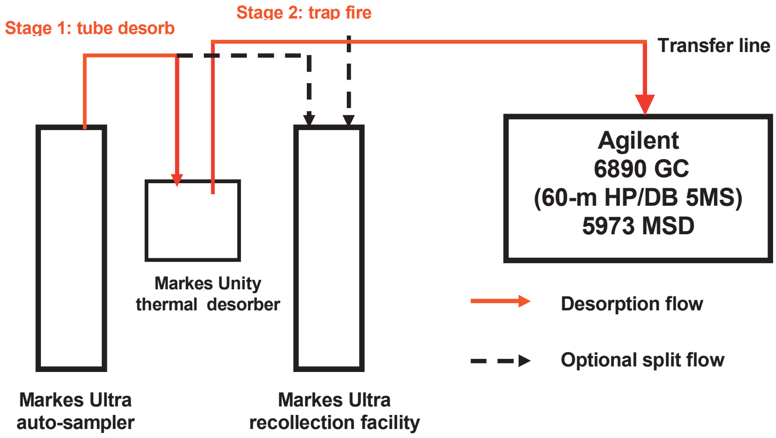
Figure 3 Schematic of a three-bed VOC adsorption tube



Samples were analysed using thermal desorption - gas chromatography - mass spectrometry (TD-GC-MS) for determination of the 16 targeted VOCs (Table 1), using an analytical procedure accredited by the United Kingdom Accreditation Servive (UKAS) to ISO 17025 standard. The analytical system comprised a Markes Unity thermal desorption system coupled to two Markes Ultra multi-tube auto-samplers, an Agilent Model 6890 gas chromatograph (GC) equipped with an Agilent Model 5973 inert mass spectrometer (MS).

Thermal desorption is a two-stage process (Fig. 4). The first stage is tube desorption whereby the VOCs are extracted from the adsorption tubes by heating at 280°C and by applying a reverse flow of carrier gas to focus the compounds desorbed onto a cold trap maintained at -10°C. The second stage is the trap fire whereby the cold trap is heated very rapidly to 300°C. As a result, the VOCs are desorbed from the trap and transferred to the analytical capillary column by the carrier gas stream (helium). As the trap flow (30 ml/min) is much greater than the capillary column flow (1.5 ml/min), a split is necessary. The split flow can be adjusted (typically 1 to 5%), and VOCs in the portion not injected into the GC can be re-collected on a separate three-bed adsorption tube if further analysis of the sample is required. The analytes were separated using a 60 m x 0.25 mm DB-5ms capillary column with 0.25 μm of film thickness, and a mass selective detector (MSD) operating in selected ion monitoring (SIM) mode.

Figure 4 Schematic of the Ultra Unity thermal desorber from Markes International used by Corus UK to analyse VOC emission samples from coke ovens.



4.2 Sampling and analytical techniques for PAH measurements

Samples for PAHs were collected following a UKAS-accredited method (ISO 17025) derived from US EPA Method 23, a method developed for the sampling of dioxins from stationary source emission sources. The sampling train, a Graseby Andersen Manual Stack sampling system (Graseby Andersen, Bedfordshire, UK), was composed of a heated glass-lined sampling probe and filter equipped with a glass fibre filter element and a water-cooled XAD-2 sorbent trap. XAD-2 sorbent traps were prepared and supplied by Hall Analytical Laboratories (Manchester, UK). Samples were collected isokinetically through a heated glass-lined sampling probe. Particulates were collected on a glass fibre filter contained in a heated filter box whilst vapour phase SVOCs were trapped on XAD-2 resin contained in a water-cooled trap. After sampling, the probe liner was washed with acetone, dichloromethane and toluene and the resulting washings were retained for analysis.

Stationary source emission samples (XAD-2 sorbent traps) were extracted with toluene using accelerated solvent extraction (150ºC, 2000 psi) following a UKAS ISO-17025 accredited procedure. After concentration of the total extract, a 10% fraction of the sample was subjected to clean-up to separate PAHs from large amounts of aliphatic and cyclic saturated hydrocarbons prior to GC - MS analyses. 10% fraction of the total extract was applied to a column packed with neutral alumina (Aldrich A1552, super grade, 4 g, activated at 200ºC for at least 16 h). Then the column was washed with 30 ml of *n*-hexane followed by 5 ml of a 20:80 dichloromethane:*n*-hexane mixture to elute the aliphatic fractions. The aromatic fractions were then eluted with 30 ml of dichloromethane.

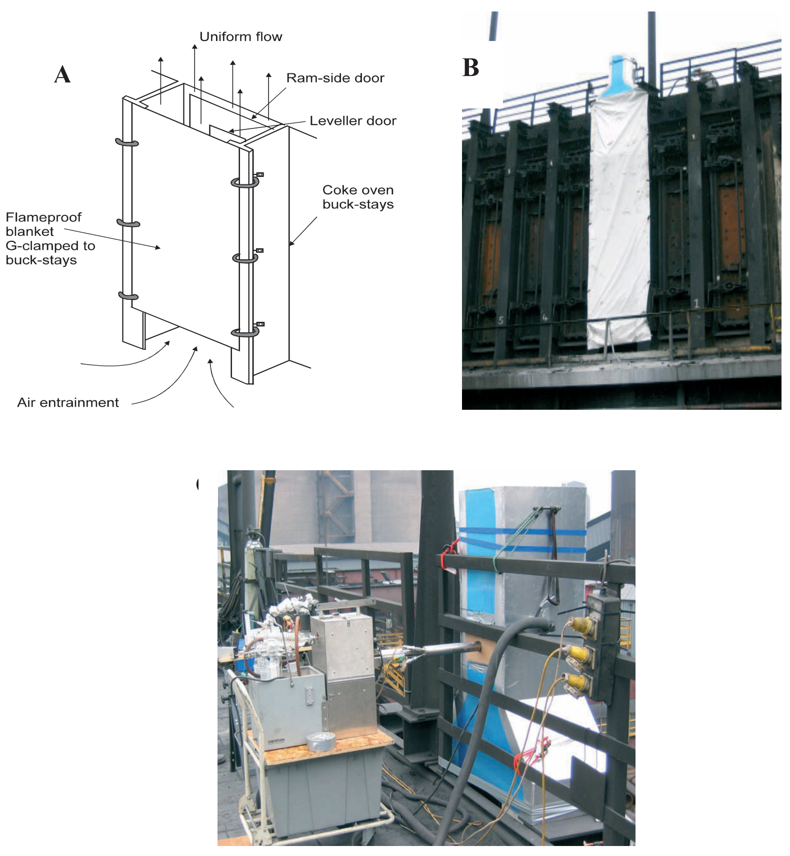
The PAH fractions were analysed using GC-MS in full scan mode for qualitative identifications of PAHs and then re-analysed in SIM mode for quantitation of the different aromatic species. The GC-MS system used was a HP6890 GC coupled to a HP 5973 inert mass selective detector. Injections were performed in splitless mode, with a helium flow rate of 1.0 ml/min, an injector temperature of 270ºC and a DB-5MS (60 m x 0.25 mm x 0.25 μm) capillary column. PAHs were quantified using a set of 8 deuterated PAH internal standards.

4.3 Sampling for fugitive door emissions

At DLCO, trials were undertaken on ram-side and leveller doors to characterise fugitive emissions of both VOCs and SVOCs. The presence of atmospheric and thermal turbulence around the coke oven battery meant that the collection of a representative sample from ram-side and leveller doors was difficult. To overcome this problem, a method of channelling emissions from the whole door and seals was used. A flame retarding blanket was fixed across the outer buckstays of the oven to be measured, leaving a gap at the bottom to assist air entrainment as shown in Fig. 5.

In order to sample the flow stream a chimney or 'top hat' arrangement was designed and access ports were provided to insert sampling probes. A general view of a coke oven door with the blanket and chimney in place is depicted in Fig. 5B, while Fig. 5C shows the arrangement for sampling emissions via the chimney. Immediately after charging and levelling, the blanket and chimney were installed, and sampling for PAHs or VOCs could begin. In most cases, sampling started as soon as possible after the equipment had been installed, typically 30 mins after levelling.

Figure 5 Sampling of fugitive emissions from ram-side and leveller doors at DLCO.



4.4 Sampling for charging hole lid fugitive emissions

As for the ram-side and leveller doors, problems with atmospheric and thermal turbulence meant that emissions needed to be contained and channelled to facilitate the collection of a representative sample from coke oven charging hole lids. Corus UK constructed a metallic artificial stack as shown in Fig. 6. The device was placed over the charging hole lid to collect emissions immediately after coal charging at the beginning of the carbonisation process. Usually, charging hole lids are sealed with a luting compound that is applied by an operator at the beginning of the process. However, for these particular trials, it was decided that charging hole lids would not be luted. As may be seen in Fig. 6, two sampling probes could be inserted in the artificial stack simultaneously for VOCs and PAHs sampling, respectively.

Figure 6 Sampling of fugitive emissions from charging hole lids at DLCO. Sampling for PAHs (left picture) and VOCs (right picture) could be carried out simultaneously.

4.5 Ambient air monitoring

Ambient air samples in the vicinity of DLCO were collected using Graseby Andersen high volume samplers equipped with a polyurethane foam plug (PUFs : 6 cm x 7.6 cm) and a glass fiber filter (Whatman GF/A 110 mm). High volume samplers were typically run at a flow rate of approximately 0.2 m^3/min for a 24-h period, sampling between 250 to 300 m^3 of ambient air.

5 Emission measurements

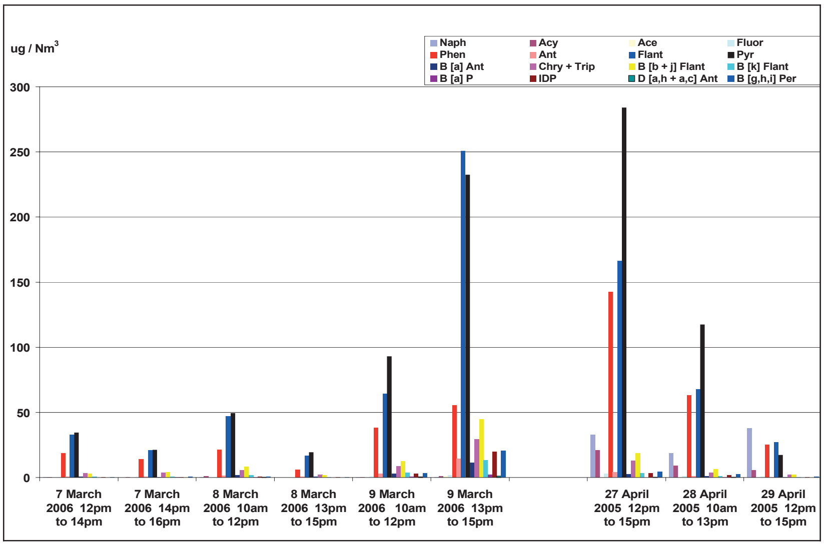
5.1 PAHs in underfiring emissions of DLCO

Two sampling campaigns were carried out, in April 2005 and March 2006, to study PAH emissions from the main underfiring stack of DLCO. In both campaigns, the underfiring stack emissions were monitored on three consecutive days. Typically, sampling times ranged between two and three hours. The results are summarised in Table 5. For each sample, PAH profiles for the 16 US EPA targeted compounds are depicted in Fig. 7.

Table 5 PAH concentrations in underfiring emissions of DLCO

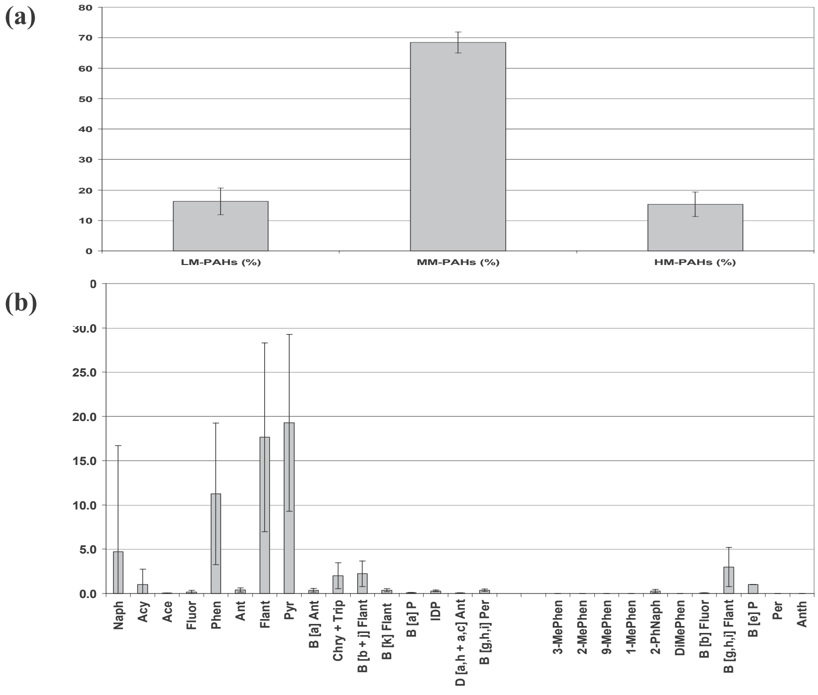
Sample QA Code	**Total US EPA PAHs (μg/Nm^3)**	**Other PAHs (μg/Nm^3)**	**B[a]P (μg/Nm^3)**
March 2006 trial			
TC 396	95.5	8.2	0.08
TC 397	66.3	5.2	0.14
TC 398	139.0	12.4	0.15
TC 399	47.6	4.2	0.07
TC 400	233.8	20.4	0.39
TC 401	699.3	75.9	2.06
April 2005 trial			
TC 061	699.6	45.8	0.11
TC 062	295.0	15.8	0.17
TC 063	120.1	5.0	0.04

Figure 7 16 US EPA PAH profiles in underfiring emissions of DLCO



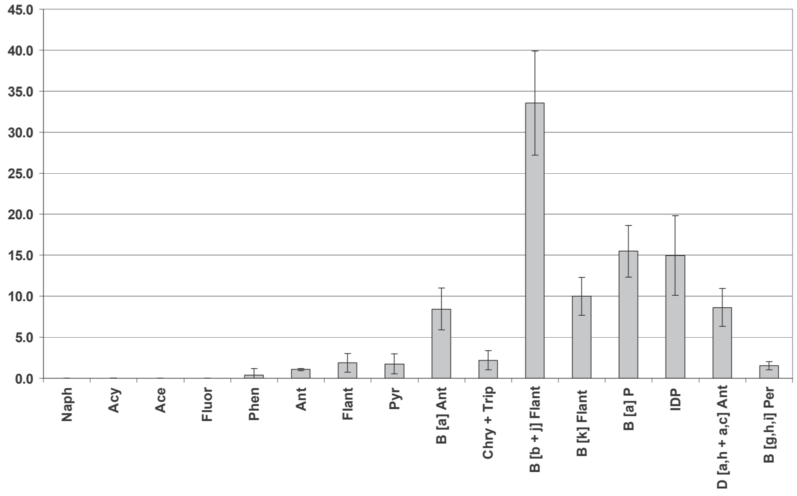
In both trials, PAH emissions appeared to vary significantly from day-to-day, but also within the same day. In March 2006, PAH emissions were significantly higher on the last day of the campaign, particularly with regard to the sample TC401 (Table 5). These variations were also observed in the campaign carried out in April 2005. For instance, high concentrations of PAHs were found for the first sample collected during the campaign (TC061). The composition of the coke oven gas that is burned during the process remains fairly constant. On the other hand, ovens from the batteries were at different stage of the carbonisation process at the time each sample was collected, and each of these ovens could be characterised by different in-leakages. Overall, PAH emissions were dominated by the 16 US EPA PAHs, their concentrations ranged from 47.6 μg/Nm^3 to 699.6 μg/Nm^3 (Table 5). As may be seen from Fig. 8, MM-PAHs contributed almost 70% to the total PAH emissions, with fluoranthene and pyrene being the two most abundant PAHs. For all samples, methylated isomers (ie. methyl- or dimethyl-phenanthrenes) were not detected in underfiring emissions. HM-PAHs contributed between 10 and 20% of the total PAH emissions. Benzo[b+j]fluoranthene, benzo[e]pyrene, and benzo[g,h,i]fluoranthene were the most abundant compounds. For all samples, benzo[a]pyrene was detected at much lower concentrations.

Figure 8 Average contribution (+/- s.d.) of PAH groups to total PAH concentrations and (b) average concentrations of PAHs normalised versus B[e]P (+/- s.d.), in underfiring emissions of DLCO.



In order to characterise more precisely the carcinogenic properties of the PAH underfiring emissions, the concentrations of the most toxic 16 US EPA PAHs were converted into their B[a]P equivalent concentrations (B[a]Peq) using the list of TEFs established by Nisbet and Lagoy (1992)[2]. The % contribution of the 16 US EPA PAHs to the total B[a]Peq is shown in Fig. 9. This approach helps understanding which PAH compounds are the most important to consider from a health effect perspective. The results indicated that the compounds found in higher concentrations in underfiring emissions (i.e. phenanthrene, fluoranthene and pyrene, see Fig. 8B) were not contributing significantly to the overall carcinogenic activity of the emissions. Although high molecular weight PAHs were detected in much lower concentrations, they appeared to be the most important to consider. Particularly, benzo[b+j]fluoranthene were the two compounds contributing the most to the overall toxicity of underfiring emissions (ca. 30 to 40%).

Figure 9 Percent contribution (+/- s.d.) of PAHs to total B[a]Peq in underfiring emissions of DLCO.



5.2 PAHs in fugitive door emissions of DLCO

Two sampling campaigns were carried out, in September 2004 and November 2005, to characterise PAHs in fugitive door emissions of DLCO. Fugitive emissions were measured from ram-side and leveller doors. Details of the samples collected during the two trials are summarised in Table 6. Ovens exhibiting BCRA leakage grades of 0, 2 and 3 were investigated. Typically, ovens exhibiting a low BCRA leakage grade (ie. grade 0) were sampled during three hours, whereas ovens exhibiting a relatively high BCRA grade (grade 2 or 3) were sampled for an hour.

Table 6 Details of the sampling campaigns carried out by Corus to characterise fugitive door emissions of DLCO.

Oven N. / Sample QA code	**Sampling date/time**	**BCRA grade**
November 2005		
Oven 1 / TC 404	15 Nov 2005 / 11h52 to 14h57	0
Oven 3 / TC 405	16 Nov 2005 / 10h30 to 13h26	0
Oven 2 / TC 406	17 Nov 2005 / 12h57 to 13h59	3
Oven 2 / TC 407	17 Nov 2005 / 14h22 to 15h24	3
Oven 2 / TC 408	17 Nov 2005 / 15h49 to 16h51	2
Oven 1 / TC 390	22 Nov 2005 / 09h46 to 10h49	2
Oven 1 / TC 391	22 Nov 2005 / 11h05 to 12h07	2
Oven 1 / TC 392	22 Nov 2005 / 12h20 to 13h23	2
Oven 4 / TC 393	24 Nov 2005 / 12h30 to 15h34	0
September 2004		
Oven 3 / TB 853	30 June 2004 / 3-h sample	0
Oven 5 / TB 854	01 July 2004 / 3-h sample	0
Oven 4 / TB 855	02 July 2004 / 3-h sample	0

The results are summarised in Table 7. Data showed that the range of emissions observed for a given BCRA leakage grade was relatively important. For instance, total US EPA PAH concentrations for ovens exhibiting a BCRA leakage grade 0 ranged from 18 to 575 μg/m^3 and from 4212 to 8217 μg/m^3 for ovens exhibiting BCRA grades 2 and 3, respectively. As may be seen from Table 7, emissions from ovens that were classified grade 3 appeared to be lower than emissions from ovens classified grade 2 indicating that it would be difficult to establish any type of correlation between the emission concentrations of PAHs and the BCRA grade leakages.

Table 7 PAH concentrations in fugitive door emission of DLCO.

Oven N. / QA Code	**BCRA grade**	**Total US EPA PAHs (μg/Nm^3)**	**Other PAHs (μg/Nm^3)**	**B[a]P (μg/Nm^3)**
November 2005				
Oven 1 / TC 404	0	575	165	21
Oven 3 / TC 405	0	18	8.4	0.11
Oven 2 / TC 406	3	4548	1265	220
Oven 2 / TC 407	3	3736	982	196
Oven 2 / TC 408	2	7553	1533	350
Oven 1 / TC 390	2	8217	7458	515
Oven 1 / TC 391	2	4212	1835	410
Oven 1 / TC 392	2	8199	2940	711
Oven 4 / TC 393	0	20	9	0.21
September 2004				
Oven 3 / TB 853	0	275	169	2.1
Oven 5 / TB 854	0	289	315	3.1
Oven 4 / TB 855	0	306	243	3.4

Typical PAH profiles are depicted in Fig. 10. These were dominated by LM-PAHs (2- and 3-ring compounds), particularly phenanthrene and its methyl-substituted analogues. The variability in the data appeared to be significantly higher for LM-PAHs, most probably due to their higher volatility. MM-PAHs

(4-ring compounds) were dominated by fluoranthene, pyrene and chrysene. In comparison, HM-PAHs were found at much lower concentrations in fugitive emissions, but their contribution to the overall toxicity of the emissions was very significant. As may be seen from Fig. 11, benzo [a] pyrene contributed almost 60% to the total B[a]Peq, followed by dibenzo[a,h + a,c]anthracene (ca. 13%) and benz[a]anthracene (ca. 10%).

Figure 10 Average contribution (+/- s.d.) of PAH groups to total PAH concentrations and (b) average concentrations of PAHs normalised versus B[e]P (+/- s.d.), in fugitive door emissions of DL CO.

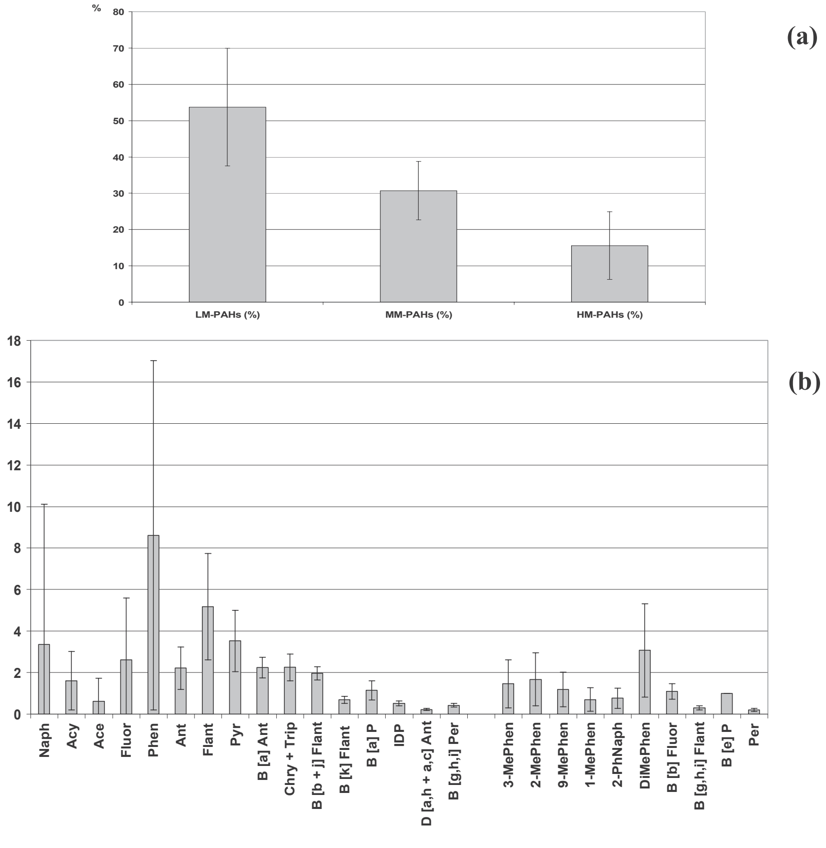
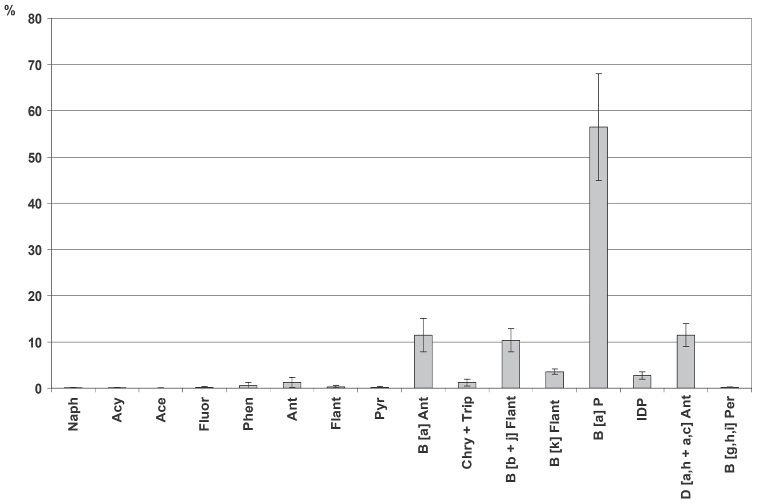


Figure 11 Percent contribution (+/- s.d.) of PAHs to total B[a]Peq in fugitive door emissions of DLCO.



5.3 PAHs in charging hole lid emissions of DLCO

A sampling campaign was carried out in March 2006 to characterise PAHs in fugitive lid emissions at DLCO. Charging hole lids exhibiting BCRA leakage grades of 0 and 1 were investigated. Fugitive emissions were monitored during the carbonisation process immediately after coal charging. The results are summarised in Table 8. Total PAH emissions for charging hole lids with a BCRA leakage grade of 1 were very consistent and typically within the range 26 to 32 mg/m^3. However, relatively different values were observed for the two charging hole lids investigated exhibiting a BCRA leakage grade of 0. For these lids, total PAH emissions ranged from 1.7 to 13.5 mg/m^3.

Table 8 PAH concentrations in fugitive charging hole lid emission of DLCO

Sample QA code	BCRA grade	Total US EPA PAHs (µg/Nm^3)	Total Other PAHs (µg/Nm^3)	B[a]P (µg/Nm^3)
TC 417	0	1707	445	31
TC 422	0	13459	4088	679
TC 418	1	28938	10320	2257
TC 419	1	30710	9368	1874
TC 420	1	31957	13194	1395
TC 421	1	26490	6513	986

Typical PAH profiles are depicted in Fig. 12. As previously described for fugitive door emissions, charging hole lid emissions were dominated by LM-PAHs (ca. 50%) and MM-PAHs (ca. 30%) (Fig. 12a). LM-PAHs, such as phenanthrene and its methyl-substituted analogues, and MM-PAHs such as fluoranthene, pyrene or chrysene were predominant (Fig. 12b). Benzo[a]pyrene contributed almost 60% to the total B[a]Peq, followed by benz [a] anthracene, dibenzo[a,h]anthracene and benzo[b+j]fluoranthene, contributing individually about 10% to the total B[a]Peq (Fig. 12c). These data appeared to be very comparable with the fugitive emissions characterised previously from the doors of DLCO (Fig. 11).

Figure 12 (see next page) (a) Average contribution (+/- s.d.) of PAH groups to total PAH concentrations, (b) average concentrations (+/- s.d.) of PAHs normalised versus B[e]P and (c) percent contribution (+/- s.d.) of the 16 US EPA PAHs to total B[a]Peq, in charging hole lid emissions of DLCO.

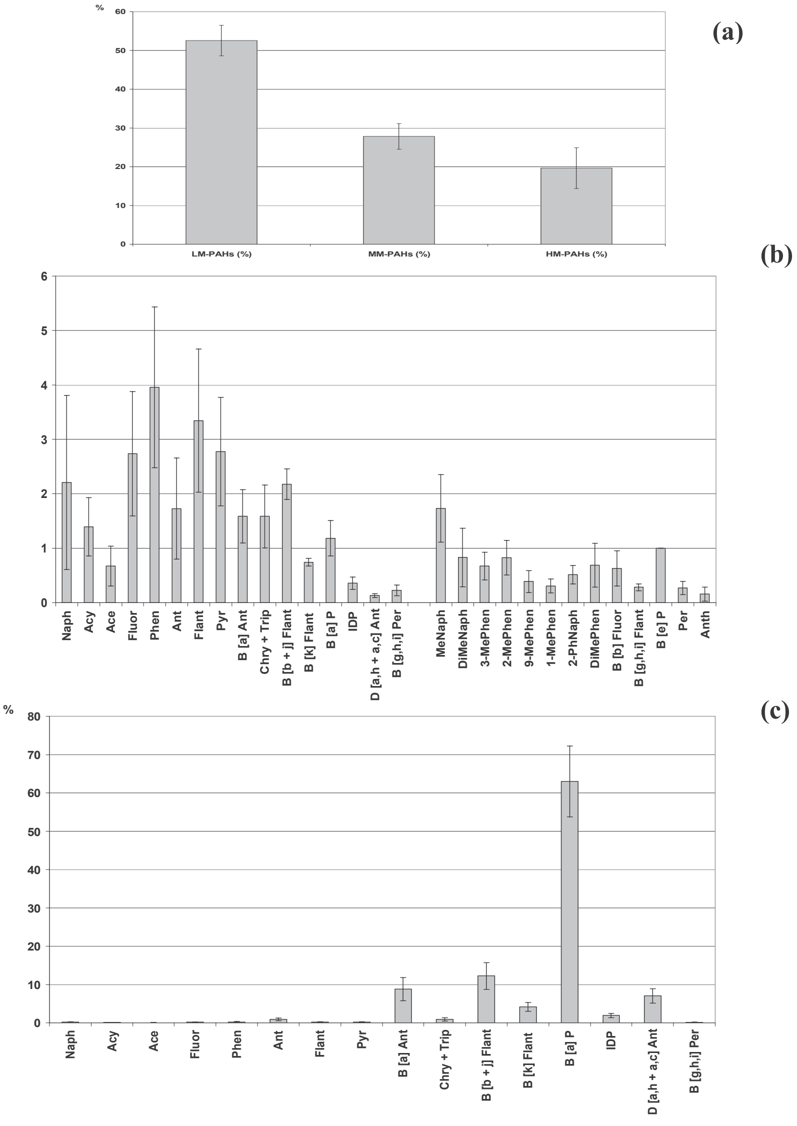

(a)
%
60
50
40
30
20
10
0
LM-PAHs (%)
MM-PAHs (%)
HM-PAHs (%)
(b)
6
5
4
3
2
1
0
Naph
Acy
Ace
Fluor
Phen
Ant
Flant
Pyr
B [a] Ant
Chry + Trip
B [b + j] Flant
B [k] Flant
B [a] P
IDP
D [a,h + a,c] Ant
B [g,h,i] Per
MeNaph
DiMeNaph
3-MePhen
2-MePhen
9-MePhen
1-MePhen
2-PhNaph
DiMePhen
B [b] Fluor
B [g,h,i] Flant
B [e] P
Per
Anth
(c)
%
80
70
60
50
40
30
20
10
0
Naph
Acy
Ace
Fluor
Phen
Ant
Flant
Pyr
B [a] Ant
Chry + Trip
B [b + j] Flant
B [k] Flant
B [a] P
IDP
D [a,h + a,c] Ant
B [g,h,i] Per

Figure 12

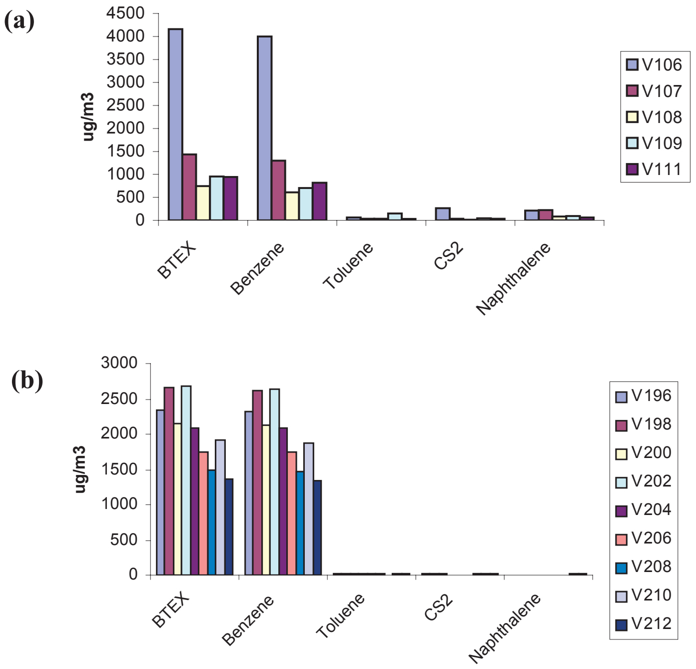
5.4 VOCs in underfiring emissions of DLCO

Two sampling campaigns were undertaken at DLCO to determine the concentrations of speciated VOCs in underfiring emissions. Five samples were collected during the first campaign that took place in April 2005 and nine samples during the second campaign in March 2006. In both cases, samples were collected consecutively on the same day. Sampling times varied between 15 and 30 min, the stack was therefore monitored over a total period of 4 h in March 2006. The results are summarised in Table 9, while VOC profiles are depicted in Fig. 13. For the April 2005 campaign, the average BTEX emission was 1649 μg/m^3. Emissions appeared to vary from sample-to-sample, especially for V106, which exhibited high VOC concentrations in comparison to the other samples. For the March 2006 campaign, the average BTEX concentration was 2047 μg/m^3, ranging from 1361 μg/m^3 (V212) to 2672 μg/m^3 (V202). The main contributor to VOC emissions was benzene. For instance, the benzene contribution to total targeted VOCs in March 2006 campaign was almost 97% of VOCs emitted. Typically, naphthalene and carbon disulphide were found at very low concentrations.

Table 9. VOC concentrations in underfiring emissions of DLCO.

	Total targeted VOCs ($\mu g/Nm^3$)	BTEX ($\mu g/Nm^3$)	Benzene ($\mu g/Nm^3$)
28-Apr-2005			
V106	4759	4161	3999
V107	1809	1437	1302
V108	980	748	611
V109	1201	955	705
V111	1135	944	819
13-Mar-2006			
V196	2381	2345	2317
V198	2691	2653	2627
V200	2173	2148	2128
V202	2699	2672	2647
V204	2123	2096	2078
V206	1774	1752	1735
V208	1519	1493	1477
V210	1963	1908	1876
V212	1423	1361	1336

Figure 13 Emission profiles of selected VOCs in underfiring emissions of DLCO in (a) April 2005 and (b) March 2006 sampling trials.



5.5 VOCs in fugitive door emissions of DLCO

A sampling campaign was carried out in November 2005 at DLCO to determine the concentrations of speciated VOCs in fugitive door emissions. Over a five-day period, twenty-two samples were collected from four different ovens exhibiting various BCRA leakage grades (0, 2 and 3). Sampling was carried out at different times after the ovens were charged to investigate the evolution of VOC fugitive emissions with time.

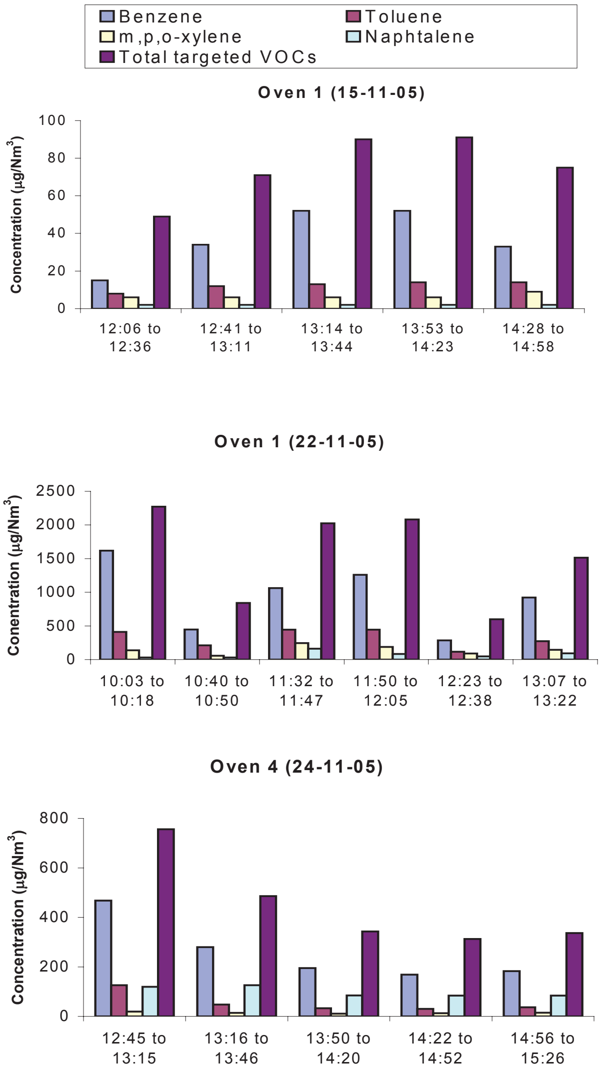
Table 10 summarises the VOC data obtained for the sampling trial carried out in November 2005 at DLCO. The overall mean concentration of the 16 speciated VOCs was 654 µg/Nm^3. BTEX concentrations ranged from 30 µg/Nm^3 (V160) to 2186 µg/Nm^3 (V176). Although concentrations of benzene and toluene varied significantly between samples, their contributions to the total VOC concentrations were relatively similar from one day to another and at different sampling times on a same day. Benzene was the compound that exhibited the highest contribution to total targeted VOCs with an average contribution of 57 %. The contributions of toluene, naphthalene and m, p, o-xylenes to the total VOC concentrations were 17 %, 9 % and 7 %, respectively. Other targeted VOCs were either not detected or similar to blank levels. Overall, ovens exhibiting BCRA leakage grades of 2 and 3 exhibited significantly higher VOC emissions than ovens with a BCRA leakage grade of 0, apart from the oven 4 on the last sampling day. It is difficult to explain why oven 4 (BCRA rating 0) was characterised by similar VOC concentrations to that of oven 2, which exhibited a much higher BCRA rating (2 - 3). As a consequence, no linear correlation was found between BCRA leakage grades and total VOC emissions.

Fig. 14 shows the evolution of BTX, naphthalene and total targeted VOC concentrations as a function of the time, starting immediately after coal charging for selected ovens. Typically, it appeared that VOC emissions increased at the beginning of the carbonisation process and decreased later in the cycle for most ovens.

Table 10 VOC concentrations in fugitive door emissions of DLCO.

	BCRA Rating	Total VOCs (μg/Nm^3)	BTEX (μg/Nm^3)	Benzene (μg/Nm^3)
		15-11-2005 / Oven 1		
V160	0	49	30	15
V161	0	71	53	34
V162	0	90	72	52
V163	0	91	73	52
V164	0	75	57	33
		16-11-2005 / Oven 3		
V168	0	295	261	197
V169	0	213	177	113
V170	0	309	265	195
		17-11-2005 / Oven 2		
V172	3	513	451	266
V173	2	607	559	425
V174	2	505	455	336
		22-11-2005 / Oven 1		
V176	2	2270	2186	1618
V177	2	844	732	449
V178	2	2025	1789	1061
V179	2	2082	1925	1259
V180	2	599	508	285
V181	2	1512	1360	922
		24-11-2005 / Oven 4		
V183	0	757	617	468
V184	0	486	344	280
V185	0	343	241	195
V186	0	313	213	169
V187	0	337	237	183

Figure 14 Evolution of the concentrations of selected VOCs in coke oven fugitive door emissions at DLCO, immediately after coal charging.



6 Ambient air measurements

6.1 Monitoring for PAHs in ambient air in the vicinity of DLCO

In total, three sampling campaigns were carried out at DLCO. Details of the samples collected are summarised in Table 11. Both in July 2004 and April 2005, a sampling site situated less than 200 m from the coke oven batteries and in a predominant downwind direction was selected. This sampling site was designated 'downwind location'. A map of the sampling positions around DLCO is provided in Fig. 15. In November 2005, three sampling locations were selected and monitored simultaneously. One sampler was at the 'downwind location', monitored in the two previous trials. The second sampling position was located near the by-product plant at an upwind location and was designated 'upwind location'. Finally, a downwind sampling site situated further away from the coke plant (ca. 1500 m) and near the steelworks boundary was selected for the study and was designated 'site boundary' (Fig. 15).

Table 11 Ambient air samples collected in the vicinity of DLCO for the characterisation of PAHs in the ambient air.

Sampling date	QA code	Volume collected (m^3)
Downwind location		
30/06/2004	TB 874	246
01/07/2004	TB 875	258
02/07/2004	TB 876	525
25/04/2005	TC 056	252
26/04/2005	TC 057	230
27/04/2005	TC 058	227
28/04/2005	TC 059	222
15/11/2005	TC 335	255
16/11/2005	TC 339	290
Upwind location		
14/11/2005	TC 333	331
15/11/2005	TC 336	311
16/11/2005	TC 340	358
Site boundary		
14/11/2005	TC 334	283
15/11/2005	TC 338	265
16/11/2005	TC 341	322

Figure 15 Ambient air monitoring of PAHs at DLCO. Two sampling positions were selected in the close vicinity of the plant (downwind and upwind locations). A sampling site was situated further away from the plant (ca. 1500 m) at a downwind position near the steelworks boundary.

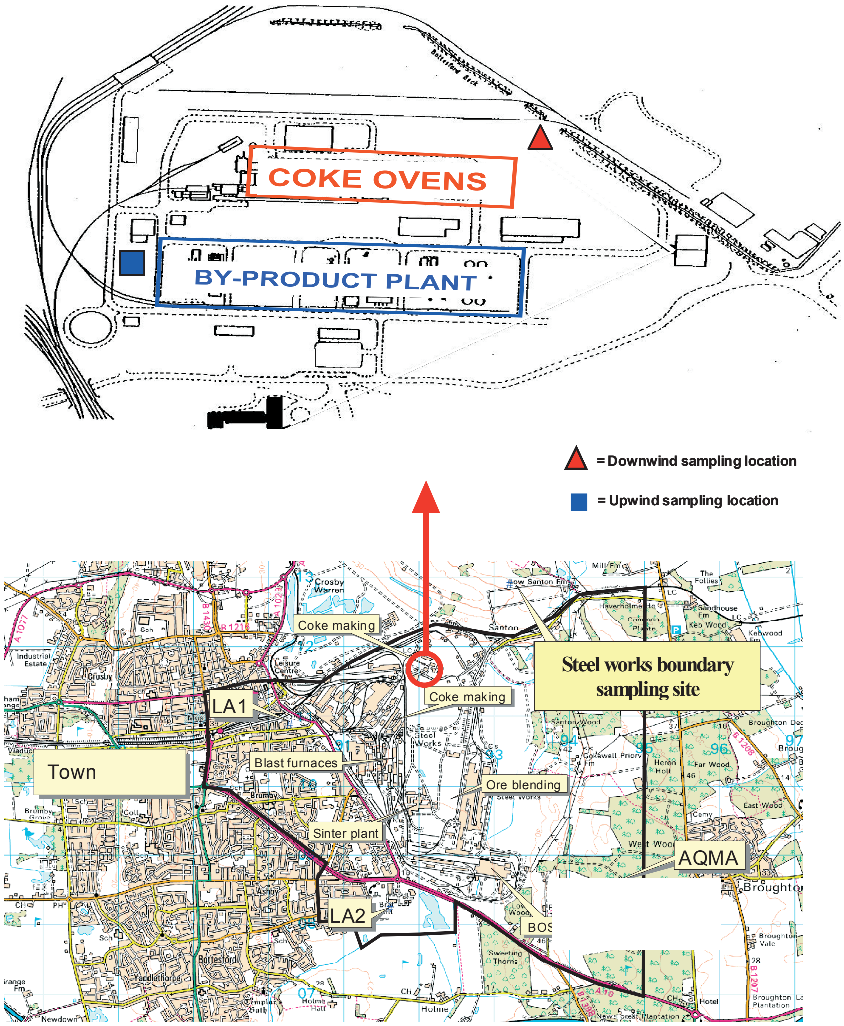
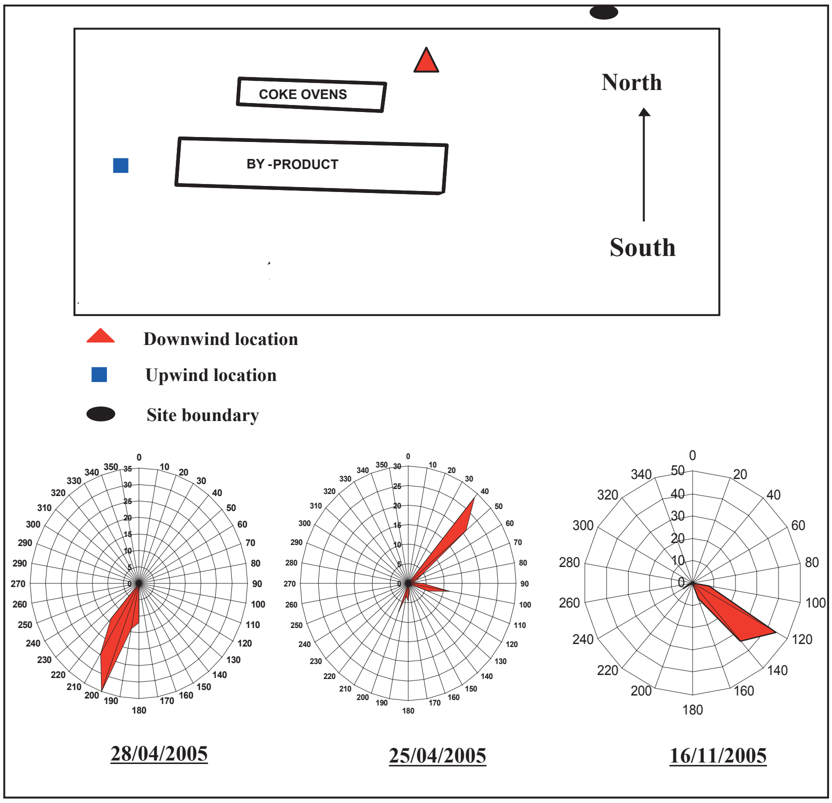


Table 12 summarises the weather data (% wind directions, average wind speed and ambient temperatures) during the three ambient air monitoring campaigns carried out at DLCO. Fig. 16 illustrates, using wind roses, the predominant wind directions for selected days of the sampling campaigns. Over the sampling period, average wind speed and temperatures remained fairly constant. Typically, wind speed ranged from 12.0 to 20.5 km/h on most days, apart on the 16th November 2005 when very low wind speeds were recorded (ie. 2.5 km/h). Temperatures ranged from 6.5°C to 16°C. With regard to wind directions, significant differences were observed. Typically, the predominant wind directions at DLCO is orientated from the south-west towards the north -east (within a sector 180° - 230°). As may be seen from Table 12, such wind directions were observed predominantly on the 30th June 2004, on the 26, 27 and 28th April 2005, and on the 15th November 2005. However, opposite wind directions were observed particularly on the 25th April and the 14th November 2005. Finally, wind directions predominantly from the west towards the east were recorded on the 1st July 2004, whereas wind directions from the south-east towards the north-west were predominant on the 16th November 2005.

Table 12 Percent wind directions, average temperatures and wind speed at DLCO for the PAH ambient air monitoring campaigns.

	Percent of wind directions						
Sampling Date	0 - 50°	50° - 90°	90° - 140°	140° - 180°	180° - 230°	230°- 270°	270° - 360°
30/06/2004	-	-	-	-	66.0	27.0	7.0
01/07/2004	-	-	-	-	4.2	86.8	9.0
02/07/2004	-	-	-	-	53.5	43.7	2.8
25/04/2005	28.7	29.5	23.5	2.6	15.7	-	-
26/04/2005	1.3	2.0	11.8	6.9	77.3	0.7	-
27/04/2005	-	-	20.9	11.5	66.9	0.7	-
28/04/2005	-	-	-	0.7	99.3	-	-
14/11/2005	-	48.2	29.3	1.5	6.2	14.8	-
15/11/2005	-	-	12.5	2.4	82.5	2.6	-
16/11/2005	-	-	92.5	7.5	-	-	-

Figure 16 Examples of predominant wind directions at DLCO during selected days of the PAH ambient air monitoring campaigns.



28/04/2005

25/04/2005

16/11/2005

PAH concentrations for the ambient air monitoring campaigns are summarised in Table 13. At the downwind sampling site, total PAH concentrations ranged from 78 to 4312 ng/Nm^3 (Total US EPA 16 PAHs), whereas B[a]P concentrations ranged from 2.0 to 123.6 ng/Nm^3. In good agreement with the weather data, the lowest PAH concentrations were recorded on the 25th April 2005 (B[a]P = 3.5 ng/Nm^3) when wind directions were orientated predominantly from the downwind location towards the coke ovens (north-east – south-west direction), but also on the 16th November 2005 (B[a]P = 2.0 ng/Nm^3) when wind directions were mostly from the south-east towards the north-west (Fig. 16). For all other days, the wind was always orientated from the coke ovens towards the downwind location (i.e. within a sector 180° - 270°) resulting in relatively high concentrations of B[a]P in the ambient air (ie. 22.9 to 123.6 ng/Nm^3). These concentrations can be considered as typical of those that may be observed immediately downwind of a coke oven battery. With regard to the upwind sampling site, significantly lower concentrations of PAHs were determined. For instance, B[a]P concentrations were between 0.9 and 2.2 ng/Nm^3. This can be explained by the fact that no wind directions within a sector 0 to 60° were detected between the 14th and the 16th November 2005. Such wind directions would have put this sampling site downwind from the coke ovens. Therefore, concentrations determined at this site can be considered as typical background concentrations in the immediate vicinity of a coke oven battery at an upwind location. Finally, the lowest PAH concentrations were determined at the site boundary. B[a]P concentrations ranged from 0.02 to 0.8 ng/Nm^3. The highest PAH concentrations were recorded on the 14th November 2005 when the site boundary sampler was predominantly downwind from the coke ovens, however B[a]P concentration did not exceed 1 ng/Nm^3 (ca. 0.8 ng/Nm^3, Table 13). In good agreement with the weather data, the lowest concentrations were determined at the boundary site on the 16th

November 2005 when wind directions were mostly orientated from the south-east towards the north-west (Fig. 16).

Table 13 Ambient air concentrations of PAHs in the vicinity of DLCO and at a sampling location situated close to the steelworks boundary.

Sampling date	Total US EPA 16 PAHs ng / Nm^3	B[a]P ng / Nm^3
Downwind location		
30/06/2004	3984	109.7
01/07/2004	3067	72.5
02/07/2004	2244	63.0
25/04/2005	78	3.5
26/04/2005	1646	49.9
27/04/2005	974	22.9
28/04/2005	1981	53.0
15/11/2005	4312	123.6
16/11/2005	217	2.0
Upwind location		
14/11/2005	220	2.2
15/11/2005	209	1.6
16/11/2005	74	0.9
Site boundary		
14/11/2005	214	0.8
15/11/2005	51	0.4
16/11/2005	1.4	0.02

In July 2003, the European Commission presented its proposal for a Directive relating to PAHs in ambient air [3]. This proposed

Directive will be the fourth 'Daughter' Directive of the Air Quality Framework Directive (96/62/EC) **[4]**. Instead of limit values, a 'target value' has been proposed for B[a]P (as an indicator of PAHs). For B[a]P, the target value proposed by the commission is 1.0 ng B[a]P/m^3, annual mean, which should be attained 'as far as possible and without entailing excessive costs', by the 1st of January 2010.

Results from this study show that the target value proposed at the EU-level for B[a]P on an annual average basis will probably be very difficult to meet for DLCO (in the immediate vicinity of the coke oven battery). These data are in good agreement with a study carried out by another coke-making research organisation at two different coke plants in Germany. Their study showed, using mathematical spread models, that the 1 ng/m^3 target value for B[a]P would only be met and complied with at a distance of approximately 1200 to 1700 m away from the coke oven batteries **[5]**. This study also compared the ambient air concentrations of B[a]P in the vicinity of old and new coke plants. B[a]P concentrations in ambient air samples collected 800 m away from a very recent coke plant (10 years old) ranged between 2 ng/m^3 and 5 ng/m^3, whereas B[a]P annual mean concentrations for an older coke plant (35 - 40 years old), based on the analysis of ambient air samples collected 250 m away from the plant, were in the range 20 ng/m^3 to 35 ng/m^3. For this particular plant, B[a]P values as high as 130 ng/m^3 were observed depending on the predominant wind directions. These values are in good agreement with the concentration determined in the present study at DLCO, which was commissioned in 1979.

7 Emissions inventory

DLCO comprise three batteries of 25 ovens (5.3 m oven doors; 75 ovens in total) that are heated by standard underfiring techniques. The coal charging is sequential: the ovens are charged and pushed on a noughts and fives schedule. Each oven has a nominal carbonisation time of 18 h 11 min (allowing 99 ovens to be pushed in a 24 h period). On average, 686 ovens are pushed per week. In 2005, the coke oven batteries produced 595,470 t of dry wharf coke for use in blast furnace operation.

For underfiring emissions, annual mass releases and emission factors of PAHs and VOCs were calculated using the dry waste gas emission flow rate of the stack (i.e. 24.2 Nm^3/s) and the 2005 annual production of dry wharf coke by DLCO.

With regard to fugitive emissions, calculations were made to estimate annual mass releases and emission factors of VOCs and PAHs for door and charging hole lid emissions. Leakage surveys were carried out over a six-month period for pusher, leveller doors and charging hole lids. An independent inspector recorded BCRA leakage grades during short-time observations (15 minutes), on 24 days chosen randomly during the 6-month period. Results of the survey are summarised in Table 14, and showed that the occurrence of leakage grades higher than 0 was relatively rare at DLCO. On average, only 5 pusher doors, almost no leveller doors and 9 charging hole lids were characterised by a BCRA leakage grade of 1. For pusher doors, BCRA grades 0, 1 and 2 respectively represented 93%, 6.8% and 0.1% of the leaks. Only 0.3% of the leveller door leakages were classified as a grade 1, while the rest were grade 0 leaks. With regard to charging hole lid leakages, 97% were classified as a grade 0 and only 2.9% as a grade 1.

Table 14 Survey of BCRA leakage grades by an independent inspector for charging hole lids, pusher and leveller doors at DLCO during a 6-month period.

	N. of ovens leaking per day and per BCRA grade											
Date	Pusher doors (75 doors in total)				Leveller doors (75 doors in total)				Charging hole lids (300 in total)			
BCRA grade	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
06.01.06	5								0			
13.01.06	2								15			
20.01.06	3	1							30			
25.01.06	1								14			
17.02.06	4								11			
24.02.06	2								25			
03.03.06	4								0			
09.03.06	5								6			
16.03.06	1				2				15			
22.03.06	5				1				50			
30.03.06	5								0			
05.04.06	5								4			
15.04.06	6								2			
21.04.06	6								5			
28.04.06	7								5			
05.05.06	9	1							6			
11.05.06	12								1			
19.05.06	5								0			
25.05.06	4				1				5			
02.06.06	7								2			
09.06.06	4								9			
15.06.06	6								2			
21.06.06	6								0			
29.06.06	3								5			
08.07.06	7								11			
11.07.06	8								0			
Average	5.1	0.1			0.2				8.6			
Ratio (%)	6.8	0.13			0.3				2.9			

Since only ovens with grades 0, 2 or 3 were investigated during the two sampling campaigns carried out in this study (See Table 7), annual mass release calculations for ovens exhibiting a BCRA grade of 1 had to be made using emission concentrations of grade 2 ovens. For this reason, the emissions inventory data reported in this study for DLCO are expected to be overestimated. Fugitive emissions were only measured for pusher and leveller doors. Therefore, any emission from a coke-side door would be assumed equal to the emission from a pusher door of similar BCRA grade.

No significant difference was witnessed between the temperature and velocity of waste gases from doors with leakage grades 2 and 0. Therefore, an average velocity, mean value of the velocity measurements taken at the top of the artificial chimney, was used to calculate mass emission rates (2500 m^3/h).

Calculations were made to estimate annual mass releases and emission factors for VOCs and PAHs for the charging hole lid emissions of DLCO. Only charging hole lids exhibiting BCRA leakage grades of 0 and 1 were considered for calculations since no leakages with grades higher than 1 were observed during the leakage survey (Table 14). It appeared that each lid was luted by a coke oven worker almost immediately after coal charging, at the beginning of the carbonisation process. Once the lid was luted, there were virtually no more fugitive emissions from the charging hole lid. Considering that charging hole lids were typically luted within 10 minutes of the start of the carbonisation process at DLCO, a leaking time of 10 minutes per carbonisation cycle was used to estimate annual mass releases of VOCs and PAHs.

Tables 15 and 16 summarise emission factors and annual mass releases of PAHs and B[a]P, respectively, for fugitive and stationary source emissions of DLCO. The data were compared to previous results reported in several European studies carried out between 1990 and 2006.

The most significant source of PAHs from the coke ovens appeared to be fugitive door emissions. Annual mass releases of total US EPA PAHs and B[a]P were estimated to be 1580 kg/annum and 59 kg/annum at DLCO, respectively. The estimated emission factors were 2.65 g/tonne of coke of total US EPA PAHs and 100 mg/tonne of coke of B[a]P. As may be seen from Table 15, emission factors for DLCO were well within the emission factors previously reported for old and new coke plants both in France [6], and in Germany [7].

In comparison, charging hole lid fugitive emissions were significantly lower. At DLCO, emission factors and annual mass releases were calculated assuming that charging hole lids were leaking only 10 minutes during a carbonisation cycle. Annual mass releases of total PAHs and B[a]P were 2.4 kg/annum and 74 g/annum, respectively, for DLCO. As may be seen from Tables 15 and 16, there appeared to be significant differences between the data reported in the literature and the data reported in this study. This can be attributed to the fact that in previous studies, annual mass releases were estimated considering that charging hole lids would leak in an identical manner over the complete duration of the carbonisation process.

With regard to stationary source emissions, PAH emissions from the main underfiring stack of DLCO were determined. It was estimated that mean annual mass releases of PAHs were 203 kg/annum, whereas B[a]P emissions represented only 273 g/annum. These values were also significantly lower than fugitive door emissions.

Table 17 summarises emission factors and annual mass releases of VOCs, benzene and BTEX for fugitive and stationary source emissions of DLCO. These data are compared to previous results reported in several European studies carried out between 1990 and 2006.

As may be seen from Table 17, no data from the literature could be found concerning VOC underfiring emissions from any European coke plant. But, the results obtained in this study indicated that underfiring emissions were a significant source of VOCs at DLCO, followed by fugitive door emissions. Annual mass releases from the underfiring stack of DLCO for total VOCs, BTEX and benzene were 1.6 tonnes/annum, 1.5 tonnes/annum and 1.4 tonnes/annum, respectively. For benzene, this corresponded to an emission factor of 2.4 g/tonne of coke for the underfiring stack of DLCO, whereas an emission factor of 1.1 g /tonne of coke was found for fugitive door emissions.

The research carried out allowed the pollutants released in the most significant coke making emissions to be identified, as well as highlighting the priorities for improved pollution control. With regard to coke oven batteries, fugitive door leakages were the most significant source of VOC and PAH emissions to atmosphere, efforts should be focused on controlling those emissions. For UK coking plants, the PPC permits (pollution prevention and control regulations) specify limits that shall be achieved for door and top leakage. Typically, door and lid leakage control factors of 98% and 99%, respectively, are specified for UK coke plants. Good maintenance is imperative in order to meet such tight regulations and to prolong battery life as far as possible. If the maintenance of the coke plant is carried out thoroughly, it has been shown in the past that these limits can be achieved, as reported for example at a UK coke plant that averaged 99.7 % of oven top leakage control and 99.4% of door leakage control in the 1990s [11].

As a general rule, the limits specified above can be achieved if the following measures are carried out consistently:

- Improvement of oven door and frame seals (flexible sealing doors);

- Door and frame seal cleaning in each cycle (using high-pressure water-jet);

- Sealing of ascension pipe (water-sealed ascension pipes);

- Maintenance of free gas flow in the coke oven (good leveling of the charged coal);

- Need to consider door frame casting as integral part of door sealing system, replacing them when tolerances go beyond the permissible limit;

- Employee training for inspection, adjustment, repair and replacement of coke oven doors and door frames;

- Regular cleaning and maintenance of all sealing surfaces of each door and door frame.

Table 15. Emission factors and estimated annual mass releases of total PAHs (US EPA 16) for DLCO and selected European Coke plants.

Emissions	Study	Annual mass releases[a] (kg/annum)	Emission factors[a] (mg/tonne of coke)
Fugitive door	***DLCO (2005)***		
	Range	1338 - 2731	2247 - 4585
	Mean	**1580**	**2653**
	Klein, 1990[b]		
	Mean	-	**83** (6 m door, new plant) **28** (7 m door, new plant) **3760** (old plant)
	Eisenhut, 1990[c]		
	Mean	-	**9** (new plant, good condition) **3715** (old plant, bad condition)
Charging hole lid	***Dawes Lane Coke Ovens (2005)***	*(10 min leakage time)*	
	Range	2.2 - 2.6	3.6 - 4.5
	Mean	**2.4**	**4.0**
	Eisenhut, 1990[c]		
	Mean	-	**118** (new plant, good condition) **3268** (old plant, bad condition)
Underfiring	***Dawes Lane Coke Ovens (2005)***		
	Range	36 - 534	61 - 896
	Mean	**203**	**341**

[a] For DLCO, mass emissions and emission factors were calculated using the 2005 coke production (595,470 t of dry wharf coke produced).

[b] Klein, F., 1990. Recherche communautaire sur la pollution par les HAPs en cokerie. In proceedings of the information days organised by the commission of the European communities. 20-21 November, pp 235 – 243. [6]

[c] Eisenhut, 1990. Coking plant environment in West Germany. Coke making International, Vol 1, pp. 74-77. [7]

Table 16. Emission factors and estimated annual mass releases of B[a]P for DL CO and selected European coke plants.

Emissions	**Study**	**Annual mass releases[a] (kg/annum)**	**Emission factors[a] (mg/tonne of coke)**
Fugitive door	***DLCO (2005)***		
	Range	6.6 – 114	11 – 190
	Mean	**59.4**	**100**
	***Klein,** 1990[b]*		
	Mean	-	**10** (6 m door, new plant) **2.7** (7 m door, new plant) **180** (old plant)
	Eisenhut, 1990[c]		
	Mean	-	**56** (Rigid hammer knife sealing) **0.3 to 15** (Flexible door sealing, ie. Membranes)
	EC coke, 1993[d]		
	Range	-	4.4 – 44
	Hein et al., 1996[e]		
	Mean	-	**0.89** (Modern plant : 'Kaiserstuhl')

Table 16 (continued). Emission factors and estimated annual mass releases of B[a]P for DLCO and selected European coke plants.

Emissions	**Study**	**Annual mass releases[a] (kg/annum)**	**Emission factors[a] (mg/tonne of coke)**
Charging hole lid	***DLCO (2005)***	(10 min leakage time)	
	Range	0.011 – 0.138	0.019 – 0.232
	Mean	**0.074**	**0.13**
	Eisenhut, 1990[c]		
	Mean	-	**2.9** (new plant, good condition) **267** (old plant, bad condition)
	EC coke, 1993[d]		
	Range	-	8.9 - 14.8
	Hein et al., 1996[e]		
	Mean	-	**8.91** (old plant) **0.15** (Modern plant : 'Kaiserstuhl')
Underfiring	***DLCO (2005)***		
	Range	0.03 - 1.58	0.06 - 2.64
	Mean	**0.273**	**0.46**

[a] For DLCO, mass emissions and emission factors were calculated using t the 2005 coke production (595,470 t of dry wharf coke produced).

[b] Klein, F., 1990. Recherche communautaire sur la pollution par les HAPs en cokerie. In proceedings of the information days
organised by the commission of the European communities. 20-21 November, pp 235 – 243. [6]

[c] Eisenhut, 1990. Coking plant environment in West Germany. Coke making International, Vol 1, pp. 74-77. [7]

[d] EC coke, 1993. European Commission (DG XI/A/3). Technical notes on the best available technologies to reduce emissions of pollutants into air from coking plants. [8]

[e] Hein et al., 1996. Environmental protection and occupational health and safety for next century coke oven plants. In proceedings of the Conference 'Steel and the Environment in the 21st Century'. April 2-3, pp. 23-30. [9]

Table 17. Emission factors and estimated annual mass releases of VOCs for DLC O and selected European coke plants.

Emissions	**Study**	**Annual mass releases**[a] **(kg/annum)**	**Emission factors**[a] **(mg/tonne of coke)**
Fugitive door	***DLCO (2005)***		
	BTEX		
	Range	189 - 2323	317 - 3902
	Mean	**835**	**1560**
	Benzene		
	Range	103 – 1753	174 - 2945
	Mean	**669**	**1123**
	Thomas, *1990*[b]		
	Mean (benzene)	-	**13000** (old coke plant) **800** (new coke plant)
	Eisenhut, 1990[c]		
	Range (benzene)	-	8000 to 14000 (Rigid hammer knife sealing) 200 to 300 (Flexible door sealing, ie. membranes)
	EC coke, 1993[d]		
	Range (benzene)	-	200 - 14000
	Hein et al., 1996[e]		
	Mean (benzene)	-	**90** (Modern plant : 'Kaiserstuhl')

Table 17 (continued). Emission factors and estimated annual mass releases of VOCs for DLCO and selected European coke plants.

Emissions	**Study**	**Annual mass releases[a] (kg/annum)**	**Emission factors[a] (mg/tonne of coke)**
Charging hole lid	***DLCO (2005)***	(10 min leakage time)	
	BTEX		
	Range	0.35 - 0.38	0.58 - 0.64
	Mean	**0.36**	**0.61**
	Benzene		
	Range	0.29 - 0.31	0.49 - 0.52
	Mean	**0.30**	**0.50**
Charging hole lid	***Thomas, 1990[b]***		
	Mean (benzene)	**-**	**25000** (old plant)
	Eisenhut, 1990[c]		
	Mean (benzene)	-	**800** (new plant, good condition) **267** (old plant, bad condition)
	EC coke, 1993[d]		
	Range (benzene)	-	800 - 8000
	Hein et al., 1996[e]		
	Mean (benzene)	-	**800** (old plant) **0.09** (Modern plant : 'Kaiserstuhl')

Table 17 (continued). Emission factors and estimated annual mass releases of VOCs for DLCO and selected European coke plants.

Emissions	Study	Annual mass releases[a] (kg/annum)	Emission factors[a] (mg/tonne of coke)
Underfiring	***DLCO (2005)***		
	Total VOCs		
	Range	748 - 3632	1265 - 6100
	Mean	**1563**	**2624**
	BTEX		
	Range	571 - 3176	958 - 5333
	Mean	**1461**	**2454**
	Benzene		
	Range	466 - 3052	783 -5126
	Mean	**1408**	**2365**

[a] For DLCO, mass emissions and emission factors were calculated using t the 2005 coke production (595,470 t of dry wharf coke produced).

[b] Thomas, F., 1990. Joint investigation into the measurement of BTX in and around coke works. In proceedings of the information days organised by the commission of the European communities. 20-21 November, pp 222 - 234. 10

[c] Eisenhut, 1990. Coking plant environment in West Germany. Coke making International, Vol 1, pp. 74-77. 7

[d] EC coke, 1993. European Commission (DG XI/A/3). Technical notes on the best available technologies to reduce emissions of pollutants into air from coking plants. 8

[e] Hein et al., 1996. Environmental protection and occupational health and safety for next century coke oven plants. In proceedings of the Conference 'Steel and the Environment in the 21st Century'. April 2-3, pp. 23-30. 9

8 Conclusions

VOCs (essentially benzene, toluene and xylenes) and PAHs (including benzo[a] pyrene) have been characterised in fugitive and stationary source emissions as well as in the ambient air of DLCO (Scunthorpe Works, Corus UK).

With regard to PAH emission measurements, the sampling campaigns undertaken showed that a clear distinction should be made between stationary source and fugitive emission releases from coke plants. Indeed, underfiring emissions appeared to be significantly different from any other type of fugitive emission releases. For underfiring emissions, a very distinctive PAH pattern was observed where a limited number of compounds was identified. Typically, MM-PAHs such as fluoranthene and pyrene were the most abundant compounds, no methylated PAHs were detected, and HM-PAHs such as benzo[a]pyrene were found at very low concentrations. On the contrary, a more diverse PAH pattern was identified for fugitive releases (including doors and charging hole lids). For all fugitive releases, PAH profiles were dominated by LM-PAHs (ie. naphthalene, phenanthrene and their methylated products), followed by MM-PAHs (ie. fluoranthene, pyrene), and to a lesser extent by HM-PAHs (benzo[a]pyrene). As a consequence, the carcinogenic activities of underfiring and fugitive releases were very different. For fugitive emissions, B[a]P was the PAH contributing most to the overall toxicity of the emissions (ca. 60%), whereas benzo[b and k]fluoranthene were the two compounds contributing most to the toxicity of underfiring emissions (ca. 40%).

Ambient air measurement campaigns for PAHs were carried out in the vicinity of DLCO. The studies indicated that the target value of 1 ng/m^3 proposed at the EU-level for B[a]P on an annual average basis will probably be very difficult to meet for DLCO, and for most European steelworks, in the immediate vicinity of cokemaking operations.

With regard to VOC emission measurements, the sampling campaigns undertaken indicated that BTX and naphthalene were the most abundant compounds in both stationary source and fugitive emission releases from coke plants. The analytical methods employed permitted the screening for other volatile organic pollutants such as carbon disulphide or chlorobenzene isomers, but these were below the limit of detection in coke oven emissions. Typically, benzene was the compound contributing the most to the total BTX concentration, particularly for underfiring emissions (ca. 75% to 97%). For fugitive emissions (including doors and charging hole lids), the VOC profiles obtained indicated that benzene contributed the most to the total VOC concentration (ca. 60% to 70%), followed by naphthalene and toluene each contributing between 10 to 20% of total VOC, and xylenes (ca. 5% to 10%).

Emission measurement data were used to develop an emissions inventory for DLCO. Annual mass releases and emission factors for PAHs (including B[a]P) and VOCs (including benzene) were estimated for underfiring emissions and typical coke oven fugitive releases (door and charging hole lid leakages). Estimates were made using plant production data and results from independent surveys carried out to determine the coke oven door and charging hole lid BCRA grade leakages.

The most significant source of PAHs from coke ovens appeared to be the fugitive door emissions. For instance, annual mass releases of B[a]P were estimated to be 59 kg/annum, corresponding to emission factors of 100 mg/tonne of coke. For other cokemaking operations, annual mass releases and emission factors of B[a]P were very low in comparison. For instance, B[a]P emission factors of 0.46 mg/tonne of coke and 0.13 mg/tonne of coke were found for underfiring and charging hole lid emissions at DLCO.

With regard to VOCs, the results obtained in this study indicated that underfiring emissions was the most significant source of VOCs (mostly benzene) at DLCO (excluding the by-product plant), followed by fugitive door emissions. Benzene emission factors were 2.4 g/tonne of coke and 1.1 g /tonne of coke for underfiring and fugitive door emissions, respectively.

The research carried out allowed the pollutants released in the most significant coke making emissions to be identified, as well as highlighting the priorities for improved pollution control. With regard to coke oven batteries, fugitive door leakages were the most significant source of PAH emissions to atmosphere, and efforts should be focused on controlling those emissions. Good maintenance is imperative to meet such regulations and to prolong battery life as far as possible. If the maintenance of the coke plant is carried out thoroughly, it has been shown in the past that such limits can be achieved consistently.

As a general rule, to achieve PPC limits for door and lid leakages, the following measures are important:

- Improvement of oven door and frame seals (flexible sealing doors) ;
- Door and frame seal cleaning in each cycle (with high-pressure water-jet) ;
- Sealing of ascension pipe (water-sealed ascension pipes) ;
- Maintainence of free gas flow in the coke oven (good levelling of the charged coal);
- Need to consider door frame casting as integral part of door sealing system, replacing them when tolerances go beyond the permissible limit ;
- Employee training for inspection, adjustment, repair and replacement of coke oven doors and door frames ;
- Regular cleaning and maintenance of all sealing surfaces of each door and door frame.

It is also possible for coke plants to achieve these limits with capital investment in several ways, such as the use of new technology in hoods and ventilation control, or operation and maintenance schemes using various kinds of sealants for coke oven doors.

8 References

1. Fisher, R., 2001. Sources, measurement and control of fugitive emissions in the cokemaking process. The Coke Oven Manager's Year Book, 87 - 105.
2. Nisbet, C., and Lagoy, P., 1992. Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). Regulatory Toxicology Pharmacology 16, 290-300.
3. COM (2003) 423 final, 16.7.2003.
4. OJ L 296, 21, 11. 1996.
5. Hein, M., Huhn, F., Sippel, M., 2003. Influence of coke plant on ambient air quality against the background of new legal regulations in the European Union. In proceedings of the Third International Conference on Science and Technology of Iron-Making. Dusseldorf, Germany (16-20th June), pp 582-587.
6. Klein, F., 1990. Recherche communautaire sur la pollution par les HAPs en cokerie. In proceedings of the information days organised by the commission of the European communities. 20-21 November, pp 235 - 243.
7. Eisenhut, 1990. Coking plant environment in West Germany. Coke making International, Vol 1, pp. 74-77.
8. EC coke, 1993. European Commission (DG XI/A/3). Technical notes on the best available technologies to reduce emissions of pollutants into air from coking plants.

9. Hein et al., 1996. Environmental protection and occupational health and safety for next century coke oven plants. In proceedings of the Conference 'Steel and the Environment in the 21st Century'. April 2-3, pp. 23-30.
10. Thomas, F., 1990. Joint investigation into the measurement of BTX in and around coke works. In proceedings of the information days organised by the commission of the European communities. 20-21 November, pp 222 – 234.
11. Carr, J.H., 1991. British Steel's Redcar Coke Ovens, a total quality performance. The Year Book of the Coke Oven Managers Association, pp. 94-106.

9 Acknowledgements

We thank Dr. R.B. Smith for supporting the work described in this paper. The authors would like to thank the European Commission for funding this work under the Programme of the Research Fund for Coal and Steel (ERAMAC project RFCS-CR-03001). We would like to thank all the people who were involved in the sampling campaigns and the analyses, and particularly Mrs S. Richardson, S.S. Baker, D. Wadsworth and Miss A. Horne. Finally, we thank L.G. Brimacombe and Dr P.D.E Brooks for helpful comments in preparing the manuscript.