Gallacher, Christopher and Thomas, Russell and Lord, Richard and Kalin, Robert M. and Taylor, Chris (2017) Comprehensive database of Manufactured Gas Plant tars – Part B Aliphatic and aromatic compounds. Rapid Communications in Mass Spectrometry, 31 (15). pp. 1239-1249. ISSN 0951-4198 , http://dx.doi.org/10.1002/rcm.7900

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Comprehensive database of Manufactured Gas Plant tars – Part B Aliphatic and Aromatic compounds

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Abstract

RATIONALE

Coal tars are a mixture of both organic and inorganic compounds and were produced as a by-product from the manufactured gas and coke making industries. The composition of the tar produced varied depending on many factors, these include the temperature of production and the type of retort used. As different production processes produce different tars, a comprehensive database of the compounds present within coal tars from different production processes is a valuable resource. To both understand how their chemical properties differ and what hazards the compounds present within these tars might pose. This study focuses on the aliphatic and aromatic compounds present within a database produced from 16 different tars from 5 different production processes.

METHODS

Samples of coal tar were extracted using accelerated solvent extraction (ASE) and derivatized post extraction using BSTFA with 1% TMCS. The derivatized samples were analysed using two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GCxGC/TOFMS).

RESULTS

A total of 198 individual aliphatic and 951 individual aromatic compounds were detected within 16 tar samples produced by 5 different production processes. The PAH content of coal tars varies greatly depending on the production process used to produce the tars and this is clearly demonstrated within the results. The aliphatic composition of the tars provided an important piece of forensics information that would have otherwise been missed with the detection of petrogenic compounds such as Alkyl Cyclohexanes.

CONCLUSIONS

The aromatic compositions of the tar samples varied greatly between the different production processes investigated used in addition to providing forensic information within the individual production process groups. Alkyl cyclohexanes were detected in all samples from sites known to operate Carbureted Water Gas plants and not detected in those that did not. This suggests petrogenic material may be expected at many UK gaswork sites.

Keywords: GCxGC/TOFMS, Coal Tar, Environmental Forensics

Introduction

Coal tars are primarily dense non-aqueous liquids (DNAPLs) made up of thousands of organic and inorganic compounds, with organic compounds such as polycyclic aromatic hydrocarbons (PAHs) dominating the composition[1]. Coal tar can be produced from a variety of different production sources including manufactured gas and the production of coke. PAHs consist of fused aromatic rings and are persistent within the environment due to the presence of dense π-electrons on both sides of the ring structure[2]. PAHs can be toxic with the level of toxicity varying greatly with the number of fused rings with 4 and 5-ring PAHs have a strong tendency to be carcinogenic and/or mutagenic[3].

Various different manufactured gas production processes were employed over time producing tars with different chemical signatures. For example, the naphtha fraction of Vertical Retort (VR) tars contain relatively more paraffin's than Horizontal Retort (HR) tars and significantly more than Coke Oven (CO) tars[4]. This general rule also applies to paraffins present within the oil fraction, that boil above the naphtha range, with VR tars typically containing 12% of its composition as paraffins while HR and coke oven tars contain 0.9% and 0.3% respectively[4]. The main distinction between coke oven derived coal tars and other tar types is high parent PAH content[5].

The PAH composition of coal tars can vary greatly depending on the tar production process, as well as the feedstock used. For example, the naphthalene content of VR tars is very low making up between 0 and 3% of the total tar[4]. This is not the case in HR or CO tars where naphthalene is generally represent at 7% and 5% respectively of the total composition of the tar[4]. The yields of other PAHs such as anthracene and phenanthrene also follow the same general trend. PAHs can come from either pyrolytic, petrogenic or biogenic sources. PAHs are introduced into the environment through contamination by crude oils, coal and coal tar or various refinery products. They can also occur naturally and are derived from biogenic precursors like terpenes, pigments and steroids[6].

Alkylated PAHs form an important group of compounds that are often ignored in environmental analysis due to difficulties in accurate measurement. The US EPA has created a list of 16 groups of prominent C_1 to C_4 alkyl PAHs derivatives and combined that with the 18 parent PAH's to create the so-called 34 EPA PAHs[7]. Alkylated PAHs can serve as useful indicators for petroleum, coal tar and creosote weathering in the environment. Investigators can use alkyl PAHs to study PAH transport and migration pathways as well as the rate the pollutants degrade[8].

Alkyl PAHs have a large number of possible isomers with alkyl naphthalenes having the lowest possible number of isomers of the parent PAHs. One important point of note is that due to the co-elution of the alkyl PAHs in the GC the EPA34 actually represents several hundred individual alkylated PAH compounds[9]. The use of GCxGC allows for the separation of alkylated PAHs with McGregor et al. 2011[10] reporting the separation of 12 C_2 alkyl naphthalenes into 10 peaks and only 2 pairs of alkyl naphthalenes still co-eluting. The type of column setup used in the GCxGC method is important with normal phase column setups only separating 9 out of a

possible 34 C_3 naphthalene isomers and 14 of the 112 possible C_4 naphthalene isomers, while reserved phase columns setups separate 14 C_3 naphthalene and 20 C_4 naphthalene peaks within the same DNAPL[10].

Alkylated PAHs have been shown to contribute substantially to the toxicity of PAH mixtures, in some cases accounting for 80% of the toxic burden[8]. In crude oil parent PAH's only make up roughly 1% of the total toxic burden with alkyl PAHs making up 99%[9]. In Benthic organisms affected by crude oil contamination only 1.4% of the TU (Toxic units available to benthic organism) is made up of the parent PAHs and the remaining 98.6% is made up by alkyl PAHs[9]. Both historical and many recent studies focus only on the 18 (or 16) parent PAHs and this means that the risks associated with crude oil contaminated sites may be been greatly underestimated. In diesel fuel contaminated sites the parent PAHs account for 2.2% of the composition and 2.7% of the TU. In contrast the PAHs in pyrogenic former manufactured gas plant (FMGP) samples account for 35 to 42% of the total PAH concentrations and TU[9], although this will vary depending on the type of coal tar and the processes that produced it. This suggests that the risks associated with coal tar contaminated sites would also be underestimated when only parent PAHs are used, although to a lesser degree than crude oil contaminated sites.

This study presents the in depth analysis of the aliphatic and aromatic content of 16 tar samples produced by 5 different production processes. A full database of the compounds found within the samples has been published in Gallacher et al., 2017[11].

Materials and Methods
Samples: See part A
A total of 16 tars samples, coming from 5 different tar production processes, were extracted and analysed. The different processes and sample numbers are listed below:
Low Temperature Horizontal Retort: DNAPL009 (D9L) and DNAPL016 (D16L)
Vertical Retort: DNAPL002-006 (D2-D6V) and DNAPL020 (D20V)
Horizontal Retort: DNAPL007 (D7H), DNAPL008 (D8H), DNAPL010 (D10H) and DNAPL017 (D17H)
Carbureted Water Gas: DNAPL013 (D13C) and DNAPL014 (D14C)
Coke Oven: DNAPL018 (D18CO) and DNAPL019 (D19CO)

Methods:
All solvents used were of analytical grade purchased from Fisher Scientific (Loughborough, U.K.) and D_{10}-phenanthrene, which was used as an injection standard, was purchased from Sigma-Aldrich (Gillingham, U.K.). D_8-naphthalene, D_{10}-fluorene, D_{10}-fluoranthene and D_{10}-pyrene, which were used as recovery standards, was purchased from Sigma-Aldrich (Gillingham, U.K.). An EPA16 PAH mix was purchased from Fisher Scientific (Loughborough, U.K.)

Extraction was performed using an Accelerated Solvent Extraction system (ASE 350 Dionex, Camberley, UK) using 10 mL stainless steel extraction cells. Approximately 0.5g of tar was mixed with an equal amount of diatomaceous earth in a 1:1 ratio. Prior to extraction the samples were spiked a recovery standard. Extraction cells were lined with 2 Dionex glass fibre filter papers and packed with 3g of silica gel 60 deactivated with 10% water. The sample mixture was then loaded into the cells and any residue

was recovered with excess diatomaceous earth. Dichloromethane was used as the extracting solvent for all extractions. ASE was performed at 100°C and 10 MPa, using one dynamic (7 min) and two static (5 min each) extractions. A flush volume of 150% and purge time of 60 s was used. The extracts were concentrated to 1 mL using a Büchi Syncore Analyst (Oldham, U.K). The extracts were then made up to exactly 10 mL using *n*-hexane. A 1 mL aliquot was then transferred to an auto sampler vial prior to analysis and spiked with D$_{10}$-phenanthrene. All samples were derivatized using 100ul of BSTFA with 1% TMCS placed in an oven at 70°C for 1 hour.

GCxGC TOFMS analysis was performed using a Leco Pegasus 4D (St. Joseph, Michigan, USA) time of flight mass spectrometer, connected to an Agilent 7890A (Wilmington, Delaware, USA) gas chromatograph equipped with a LECO thermal modulator. The TOF ion source temperature was 200 °C and the mass range 45 and 500u was scanned at a rate of 200 spectra/second. The detector voltage was set at 1700 V with an electron ionisation energy of 70 eV.

All standards and extracts were analysed with the following primary oven temperature programme: 60°C isotherm for 2 minute, then ramp at 10°C/min to 110°C, then ramp at 3°C/min to 310 °C, and isothermal at 310°C for 15 minutes. The secondary oven and modulator temperatures were programmed at a 10 °C offset relative to the primary oven. The modulation period was 6 seconds with a 1.3 second hot pulse time and a cool time of 1.7 seconds. The injection port temperature was set to 250 °C and set to split injection with a split ratio of 50 and an injection volume of 1μL. Helium was used as the carrier gas, with a flow rate of 1.0 mL/min.

The reversed polarity column set that was used comprised of a mid-polarity TR-50 MS supplied by Thermo Scientific (Hertfordshire, U.K.) (30 m × 0.25 mm i.d. × 0.25 μm film thickness) as the primary column and a non-polar Rtx-5SilMS supplied by Thames Restek (Buckinghamshire, U.K.) (1.5 m × 0.25 mm i.d. m × 0.25 μm film thickness) as the secondary column, connected via a Thames Restek Press-tight connector.

The chromatograms from each sample were processed using Leco ChromaTOF software (Version 4.50.8.0) to search for, identify and align all peaks with a signal-to-noise ratio greater than 10. As it would be impractical to purchase standards of every compound present within the samples any concentration comparisons are relative comparisons of the peak area for each compound adjusted for sample weight and recovery. Only direct like for like compound comparison was performed, as the detector response will remain equivalent.

Results and Discussions

Low Temperature Horizontal Retort (LTHR):
Low Temperature Horizontal Retorts (LTHR) were the first type of retort to be widely used and produced gas from coal operating at temperatures of around 600°C[12]. This relatively low temperature led to a limited degree of decomposition of the organic compounds present within the feedstock coal and therefore the tars produced were more similar in nature to the parent coals from which it was produced.

The aliphatic compositions of the LTHR tars, shown in table 1, are significantly different with sample D9L containing 136 aliphatic compounds, which is the most

aliphatic compounds present in any of the samples present within the database, and sample D16L containing only 37. The relative peaks area of the n-alkanes, *m/z* 57 (10^{-3}), is shown in table 2 and shows that sample D9L contains n-alkanes between C_{11} and C_{32}, whereas sample D16L contains n-alkanes between C_{11} and C_{30}. The concentrations of n-alkanes shared by the LTHR tars are significantly higher in D9L relative to D16L and this is likely down to the fact D9L is in the form of pure DNAPL, whereas D16L is in the form of DNAPL contaminated soil. D16L has also spent a significant amount of time open to the environment and so there is an increased chance of degradation of the n-alkanes. Sample D9L also contains alkyl cyclohexanes between C_4 and C_{14}, shown in table 3, but these compounds are completely absent in sample D16L. This suggests a relationship between the relative concentrations of n-alkanes and the presence of alkyl cyclohexanes within the samples. The large difference in the total number of aliphatic compounds between the samples is down to the presence of a larger number of alkenes in D9L relative to D16L (32:10); the presence of a larger number of branched alkanes in D9L relative to D16L (32:7); and the presence of 36 miscellaneous aliphatics such as alkyl cyclopentenes and alkyl cyclopentadienes within D9L that were not detected in D16L.

The total number of PAHs and Alkyl PAHs present within the LTHR tars, shown in table 1, is very different with sample D9L containing 651 individual compounds and sample D16L containing only 301. Sample D9L contains 198 EPA34 PAHs with sample D16L containing only 136, which is the third lowest number within the database. D9L contains the most individual EPA34 PAHs of the coal gas tars, with only the oil based CWG tars containing more individual compounds. The EPA16 PAH concentrations of all the tar samples are shown in table 4 and clearly show that D9L contains significantly more total EPA16 PAHs, with 66382mg/kg relative to D16Ls 12418mg/kg. The individual concentrations of each of the EPA16 PAHs is higher in D9L relative to D16L with no exception. While the total concentration of EPA16 PAHs is higher within D9L, relative to D16L, it contains the lowest total concentrations of the pure DNAPLs analysed. D16L contains the second lowest of the DNAPL contaminated soils, and water, with only D6V containing lower total concentrations. This suggests that LTHR tars contain a lower level of parent PAHs relative to other tar types and this is likely down to the relatively low temperatures the process used. This may also explain why D9L contains the most EPA34 PAHs of the coal gas tars.

Horizontal Retort (HR):
Advances in horizontal retort technology allowed for increases in operational temperature, which were capable of exceeding $1000^{o}C$[16]. This resulted in a greater degree of thermal decomposition of the organic compounds found within the parent coal, and resulting tar, as well as generating a greater degree of thermal cracking[17].

The aliphatic composition of the horizontal retort tars, shown in table 1, varies widely with sample D8H containing the most aliphatic compounds of the HR tars with 100 and D10H containing the least with 44. Sample D7H contains 55 and sample D17H contains 80 with the relative concentrations of the aliphatics that the samples share varying widely. The relative peak areas of n-alkanes, *m/z* 57 (10^{-3}), is shown in table 2 and shows that sample D8H contains the highest relative concentrations of n-alkanes within the HR tars with n-alkanes ranging between C_{11} and C_{28} with a maximum at C_{12}. The lowest relative concentrations on n-alkanes detected within the

HR tars are present within sample D7H, with n-alkanes ranging from C_{11} to C_{28} with a maximum at C_{12}. Sample D7H also contains the lowest n-alkane concentrations of the pure DNAPL tars analysed. Of the remaining two HR tars D10H contains more n-alkanes between C_{11} and C_{13}, than D17H, whereas D17H contains more n-alkanes between C_{14} and C_{22}. Sample D10H contains n-alkanes ranging between C_{11} and C_{30}, whereas D17H contains n-alkanes ranging between C_{11} and C_{29}. While the relative concentrations of n-alkanes vary widely the same general trend exists with low molecular weight n-alkanes between C_{11} and C_{18} dominating.

The alkyl cyclohexane distributions of the HR tars, shown in table 3, also vary widely. As with the n-alkanes sample D8H contains the most alkyl cyclohexanes in both concentrations and number of compounds with alkyl cyclohexanes ranging between C_4 and C_{15} and a maximum at C_5. Sample D7H also contains the lowest concentrations of alkyl cyclohexanes of the HR tars, although not the smallest number, with alkyl cyclohexanes ranging between C_4 and C_9 with a maximum also at C_5. As with the n-alkanes sample D10H contains more lower molecular weight alkyl cyclohexanes between C_4 and C_7, which is the highest molecular weight alkyl cyclohexane detected within D10H. Sample D17H however contains a wider range of alkyl cylcohexanes, than D10H, between C_4 and C_{13}.

The total number of PAHs and alkyl PAHs present within the HR tars, shown in table 1, varies greatly with sample D8H containing the most compounds with 670. Sample D17H contains the second highest with 579 and sample D7H contains 529. Sample D10H contains the lowest number of compounds with only 334 compounds. The total number of EPA34 PAHs detected within the HR tars follows the same trend as the total number of PAHs, with the exception of D17H which contains the most individual EPA34 PAHs but not the highest number of individual PAHs. The concentration of EPA16 PAHs is shown in table 4 and clearly shows that D8H contains both the highest total concentration of EPA16 PAHs, with 174042mg/kg, and the highest total number of individual PAHs. Sample D17H contains the lowest concentrations of EPA16 PAHs of the HR tars, and the second lowest of the pure DNAPLs analysed. While it contains significantly lower concentrations of EPA16s the relative composition of D17H is more similar to D8H than the other HR tars. The average composition of the HR tars is shown in figure 1 and shows that the greatest degree of variability is present in the relative concentrations of naphthalene and phenanthrene. In both D8H and D17H the most abundant PAH is phenanthrene, whereas in D7H and D10H naphthalene is most abundant. Both the LTHR and HR compositions are very similar suggesting that horizontal retorts produce similar EPA16 compositions, although not similar concentrations, and therefore cannot be used to distinguish horizontal retort tars from each other.

Several compounds appear within the HR tars that do not appear in any other tar type. These compounds include 2 C_3-benzo[x]fluoranthene isomers ($C_{23}H_{18}$) within samples D7H and D8H and 6 and 3 C_4-benzo[x]fluoranthene ($C_{24}H_{20}$) isomers in samples D7H and D8H respectively. It also includes 8 C_3-binaphthalene ($C_{23}H_{20}$) isomers in sample D7H and 11 in sample D8H. Interestingly 4 C_2-dibenzo[a,h]anthracene ($C_{24}H_{18}$) isomers are found in D7H, but not D8H, and 2 C_3-dibenzo[a,h]anthracene ($C_{25}H_{20}$) isomers are found in D8H, but not in D7H. The presence of these high molecular weight alkyl PAHs in the HR tars, that are not present in any other tars suggests, that the high production temperature enriches

concentration of the higher molecular weight compounds, as the lower molecular weight compounds will degrade more readily. This means that while the high molecular weight alkyl PAHs may be presents in relatively low concentrations in the parent material they are enriched as the more easily degradable compounds are destroyed.

Vertical Retort (VR):

In the first decade of the 20th century the Vertical Retort was developed, this rotated the retort by 90[o] from the horizontal and could allow for the continuous production of gas. Although vertical retorts operated at similar temperatures to high temperature horizontal retorts the design of vertical retorts resulted in significantly different tars being produced. This was due to the temperature gradient which existed within a vertical retort (hottest at the base, coolest at the top) and the fact that the tar fog generated could also escape vertically through the coal without degrading on the hot surface of the retort wall. The tar produced was significantly different to both LTHR and HR tars.

The aliphatic composition of the vertical retort tars, shown in table 1, varies greatly, even within the 5 samples from the same site, with sample D20V containing the most individual compound with 126. Sample D2V contains only 24 aliphatics; D3V contains 56, D4V contains 105; D5V contains 93; and D6V contains 70. The relative peak areas of the n-alkanes, *m/z* 57 (10^{-3}), is shown in table 2 and clearly shows that D20V contains the highest relative concentration and the most individual n-alkanes of the VR tars ranging between C_{11} and C_{34} with a maximum at C_{14}. D20V is the only pure DNAPL VR tar analysed and so would be expected to contain higher concentrations of n-alkanes than D2V to D6V, as these are DNAPL contaminated soils. Despite the fact that samples D2V to D6V come from the same sample site they contain significantly different n-alkane compositions with D2V containing the least n-alkanes ranging between C_{11} and C_{18} with a maximum at C_{12}. Sample D2V comes from a different part of the site and this may explain the lower concentrations of n-alkanes present within the sample, compared to the D3V to D6V. Samples D3V, D4V and D5V came from the same tar tank and have similar numbers of n-alkanes, although not concentrations. Sample D3V contains n-alkanes ranging between C_{11} and C_{28} with a maximum also at C_{12} and both samples D4V and D5V contains n-alkanes ranging between C_{11} and C_{30} with a maximum also at C_{12}, Sample D6V contains n-alkanes ranging between C_{11} and C_{33} with a maximum at C_{14} and was taken from a borehole down gradient of the tar tank from which samples D3V to D5V were obtained.

In all cases as the molecular weight of the n-alkanes increases the relative difference in the concentrations found in D20V increases relative to the other VR samples. While samples D2-D6V have different relative concentrations of n-alkanes, and different total number of compounds, the trends within the samples are similar with low molecular weight n-alkanes between C_{11} and C_{17} dominating and those alkanes above C_{17} being present in only relatively minor levels. This is not the case in sample D20V that has significant n-alkanes between C_{11} and C_{30} following a decreasing trend from C_{14} and with the n-alkanes above C_{31} being present in only minor concentrations. This suggests that the tars from these two sites (D2-D6V and D20V) have significantly different compositions, at least in the context of aliphatics. This also extends to the alkyl cyclohexanes, shown in table 3, as while sample D4V has the

widest range (C_4-C_{16}) with a maximum at C_6 sample D20V contains the highest concentrations within the shared compounds (C_4-C_{14}) with a maximum also at C_6. The alkyl cyclohexane concentrations also vary greatly within sample D2-D6V with sample D4V containing significantly higher concentrations than the other tar samples from the same site, including those taken from the same tar tank. Sample D20V is the only sample in the database to contain C_{24}-C_{29} alkenes and the only samples with n-alkanes ranging between C_{11} and C_{34}. Sample D20V is also the only sample within the database that contains n-alkanes between C_{11} and C_{34} and samples D6V and D20V are the only samples containing the C_{33} n-alkanes.

The average EPA16 composition of the Vertical Retort tars is shown in figure 1 and shows that the VR samples have extremely varied EPA16 PAH compositions, with the greatest degree of variability in the percentage of the composition that comes from naphthalene. Samples D2V to D6V come from the same sample site whereas sample D20V came from a completely different site and has a significantly different EPA16 PAH composition. The EPA16 PAH % composition of sample D20V is also shown in figure 1 and shows a signature that is dominated by phenanthrene, which makes up 31.4% of the overall EPA16 PAH composition. The EPA16 PAH % composition of samples D2-D5V, shown in figure 1, is similar with naphthalene dominating, as well as large proportions of phenanthrene and acenaphthylene. As a general trend as the relative proportion of naphthalene increases from sample D2 to D5V (22.2% to 30.7%), the proportions of phenanthrene decreases (15.8% to 12.6%) and the proportions of acenaphthylene also decreases (16.6% to 8.9%). The EPA16 PAH % composition of sample D6V is also shown in figure 1 and shows a very different signature to the other samples on the site (D2-D5V) and a signature that is more similar to D20V with phenanthrene dominating.

The significant differences between sample D6V and the other samples from the same site may suggest that sample D6V is more highly degraded than the other samples and this is further suggested by the relative concentrations of the EPA16 PAHs found within the samples. Sample D6V has the lowest concentrations of EPA16 PAHs, shown in table 4, found within the VR samples with a large bias towards lower concentrations of naphthalene and acenaphthylene and a much smaller difference between higher molecular weight PAHs such as benzo[a]pyrene. This suggests that sample D6V's EPA16 PAH compositional signature has been lost due to degradation of the sample. This is highly likely as the sample was taken from a borehole down gradient of the tar tank. Samples D3V to D5V were taken from within the tar tank itself. Sample D20V contains significantly higher concentrations of EPA16 PAHs relative to the other VR tars, as it is a pure DNAPL. The higher concentrations of EPA16 PAHs and the fact the sample is a pure DNAPL this suggests that the EPA16 PAH composition graph for sample D20V may be more indicative of a pure VR tar than the other VR tar samples. It should be noted however that the statistical analysis used in McGregor et al., 2012[5] is still capable of discriminating these tars as VR tars but this method uses 156 compounds within the statistical analysis rather than just the EPA16, which is often solely used alone for forensic analysis.

The total number of PAHs and Alkyl PAHs present within the VR tar samples, shown in table 1, varies greatly. While sample D20V is pure DNAPL and contains the highest concentrations of PAHs within the VR tars it does not contain the most individual PAHs with D4 containing 604 individual PAHs relative to 573 present

wtihin D20V. Sample D4V also contains the most EPA34 PAHs with 188. The remaining VR tar samples contain less PAHs than D20V. The PAH compositions of the VR samples also gives an important piece of forensic information as VR tars should contain less naphthalene (0-3% of the total tar) relative to HR (7%) and CO (5%) tars[4]. This is the case for samples D20V and D6V but not for the VR tars D2-D5V. This could suggest that the naphthalene present within samples D2-D5V may have come from a source other than the VR tar, which is possible due to the complex history of the site. This also suggests that while the VR tars D2-D5V may contain elements from other tar types the statistical analysis developed in McGregor et al., 2012[5] is still able to discriminate them as being VR tars.

Coke Oven tars (CO):
Coke oven tars are the only form of coal tar that is still produced within the UK with the temperature of the coke oven determining the overall composition of the tar produced. Coke ovens operating at low temperatures (<700°C) produced phenolic and PANH compounds[18] whereas coke ovens operating at high temperatures (>700°C) produced tars with high PAH content. Metallurgical coke is produced between 900°C and 1095°C[18] with both coke oven tars falling within this range. D18CO however was produced by a more modern, efficient and higher temperature coke oven, built in the 1970s, relative to oven that produced D190CO, built in the 1930s.

Both CO tar samples contain a relatively small number of aliphatic compounds with D18CO containing only 2 aliphatics and D19CO containing only 9. Sample D18CO contains the C_{11} and C_{12} n-alkane whereas D19CO contains n-alkanes between C_{11} and C_{17} as well as a single n-alkene (C_{10}) and a single branched alkane (C_{14}). Since the samples are both of freshly produced coke oven tar and therefore should not contain any petrogenic contamination any aliphatics present within the sample were either produced during the breakdown of the coal within the coke oven to produce coke or were present within the original parent material. It should be noted that sample D19CO was produced from a lower temperature coke oven than D18CO and contains relatively more aliphatics, which suggests the lower temperature may result in the production of or lessen the destruction of aliphatics within the tar produced. Sample D19CO contains more of the C_{11} n-alkane and C_{12} n-alkane, shown in table 2, relative to D18CO. When the whole database is considered the concentrations of aliphatic compounds within the CO tars are the lowest of any tar type. The low aliphatic content is expected, as only 0.3% of the oil fraction that boils above Naphtha should be present as paraffins (alkanes) within coke oven tars[4]. The low aliphatic content is likely down to the destruction of n-alkanes during the long production process of the coke, which is significantly longer than that of manufactured gas.

Both samples contain a similar number of PAHs and Alkyl PAHs with D18CO containing 359 and D19CO containing 387. The difference in the total number of PAH compounds is mostly down to D19CO containing slightly more alkyl PAHs (D18CO:D19CO) such as C_3-naphthalene (5:11) and C_3-phenanthrene/anthracene (9:13). This trend reverses for the higher molecular weight alkyl PAHs such as C_1-benzo[x]fluoranthene (14:11) and C_1-benzo[g,h,i]perylene (11:7). Both coke oven samples contain no alkylated benzenes above C_4 and no alkylated indenes or indanes above C_2. The % composition of EPA16 PAHs is shown in figure 1 showing that Phenanthrene is the dominant PAH. The relative compositions of the EPA16 PAHs in

the samples is similar with the exception of acenaphthylene and Phenanthrene. Sample D18CO contains only 8.0% acenaphthylene, whereas sample D19CO contains 14.1% and sampled D18CO contains only 17.0% phenanthrene and D19CO contains 19.9%. The coke oven tars do generally have a unique EPA16 PAH signature relative to the other tars in the database as they have the lowest relative percentage of naphthalene. Sample D18CO also contains 124 EPA34 PAHs and sample D19CO contains 141.

The relative concentrations of EPA16 PAHs, shown in table 4, in the sample is important from a forensics standpoint as higher temperature coke ovens are associated with having higher PAH contents[15]. This can be clearly seen in the concentrations of EPA16 PAHs as sample D18CO, the higher temperature coke oven, contains significantly more EPA16 PAHs overall, than sample D19CO. Sample D18CO also contains higher relative concentrations of all of the EPA16 PAHs with the exception of acenaphthylene. The remaining EPA16 PAHs are present in higher concentrations with the smallest difference in the concentrations of acenaphthene and the largest being benzo[g,h,i]perylene. When the database is taken as a whole sample D18CO contains the highest total combined concentration of the EPA16 PAHs with D19CO containing the 3rd most, with marginally less than D8H. Sample D18CO also contains the highest absolute abundances of the majority of the EPA16 PAHs with the exceptions of naphthalene (D7H), acenaphthylene (D19CO), acenaphthene (D20V, D7H, D8H, D10H, D17H, D13C, D14C), indeno[123-c,d]pyrene (D8H, D7H), benzo[g,h,i]perylene (D8H, D7H) and dibenzo[a,h]anthracene (D8H, D7H, D10H, D17H, D20V, D9L, D14C). In general this suggests that coke oven tars have a greater parent PAH content relative to coal tars produced from gas manufacturing processes. The results also suggest that higher operational temperatures result in increased parent PAH concentrations as while both CO tar samples are high temperature coke oven tars, as they are metallurgical coke, the oven that produced D18CO is more modern and operates at a higher temperature. This suggests that even within coke ovens that would be considered to be the same vastly different tar compositions can still be produced.

Carbureted Water Gas (CWG):
The Carbureted Water Gas process was an adaptation of the water gas process, where steam was passed over a hot carbon source (usually coke), with a spray of oil introduced to the hot gas produced in order to improve its calorific value[19]. Since the water gas process did not generate significant amounts of tar[18] then the tar produced by the CWG process is dominated by the feedstock oil used, with a degree of temperature dependent alteration as the process operated between 650°C and 700°C[18].

The aliphatic compositions of the two CWG tars are significantly different with sample D14C containing 128 aliphatic compounds and D13C containing only 85. There is also a significant difference in the relative concentrations of the compounds that the samples share. Sample D14C contains n-alkanes between C_{11} and C_{29}, whereas sample D13C contains n-alkanes between C_{11} and C_{24}. The relative peak area of the n-alkanes, *m/z* 57 (10^{-3}), shown in table 2 clearly shows that D14C contains significantly higher concentrations of n-alkanes than D13C, which is down to the fact D14C is a pure DNAPL and D13C is a tar contaminated ground water sample. D14C contains the most significant concentrations of n-alkanes within the database, with the highest relative concentrations of the n-alkanes ranging between C_{11} and C_{20}.

This is likely down to the fact it is an oil based rather than coal based tar, with even D14C containing significant concentrations of n-alkanes compared to pure coal gasification DNAPLS.

Alkyl cyclohexanes are commonly associated with petrogenic contamination[14] and are present within both of the CWG samples with D14C containing between C_4 and C_{14} and D13C containing between C_4 and C_{12}. As with the n-alkanes the relative concentrations of the alkyl cyclohexanes, shown in table 3, are significantly higher in sample D14C over D13C. While the relative concentrations of the compounds are very different the overall distributions of the alkyl cyclohexanes in the samples are again similar. This suggests that both CWG plants produced tars with very similar aliphatic distributions. Several other samples contain significant concentrations of alkyl cyclohexanes including D8H, D20V and D9L. A general trend is present within both the concentrations of n-alkanes present within a sample and the concentrations of alkyl cyclohexanes, which may suggest the level of petrogenic material present with the tar samples. The results suggest that D8H, D9L, D20V and several other samples may contain significant amounts of petrogenic material. The only samples not containing alkyl cyclohexanes are both the CO tars and sample D16L. Both the CO tars were taken on the day of production and therefore should not contain any petrogenic material. Sample D16L contains extremely low concentrations of n-alkanes and so it is possible that alkyl cyclohexanes are present but are not detectable. It should also be noted that sample D16L is the only sample site known to not contain a CWG plant. All of the remaining coal tars were taken from sites that operated both coal gas manufacturing plants and a CWG plant and it is highly likely that CWG tar would have been mixed into the coal tars produced at these locations, as CWG tar had little resale value and so would be used to bulk out the more lucrative coal tars.

Both CWG tar samples contain a large number of PAHs with sample D13C containing 657 and sample D14C 729. This means that sample D14C contains the most individual PAHs of any sample in the database with sample D13C containing the 3rd most, slightly behind sample D8H that contains 671. Sample D14C contains the largest number of EPA34 PAHs within the database with a total of 202, with D13C containing the 2nd most with 200. The average EPA 16 composition of the CWG tars, shown in figure 1, shows that the EPA16 compositions are dominated by naphthalene and phenanthrene. The EPA16 PAH concentrations of the CWG tars, shown in table 4, show that D14C contains significantly higher concentrations of PAHs than D13C, which is again expected as D14C is a pure DNAPL and D13C is a contaminated ground water sample. Naphthalene is the most abundant PAH present within D13C, with phenanthrene the most abundant PAH in D14C. The concentrations of naphthalene present within the original tar that sample D13C came from were likely even more significant as naphthalene is the most water soluble of the EPA16 PAHs and so a larger percentage will have been lost into the groundwater. This suggests that the EPA16 compositions and absolute concentrations of the original CWG tars would have been significantly different and this is likely due to a difference in the feedstock oils used to produce the tars.

Diagnostic Ratios:
Various diagnostic ratios have been applied to tars and tar contaminated samples, a selection of which are shown in table 5, in order to give information about the potential source and manufacture processes used to produce the tars[20,21,22]. The ratios

of phenanthrene to anthracene (Phe/Ant) and fluoranthene to pyrene (Flt/Pyr) can be used to distinguish between different sources of PAH contaminated with a Phe/Ant ratio of <10 showing that a sample is pyrogenic in nature[21]. The phenanthrene to anthracene ratio of all the tar samples is <10, including the CWG tars. The ratio of phenanthrene to anthracene should not be used alone however[21] and when combined with the ratio of Flt/Pyr the CWG tars fall within the petrogenic rather than pyrogenic range, 0.6 to 0.8[22], which would make sense as they are derived from oil based feedstocks rather than coal and are not pyrolysed during the CWG process. The fluoranthene to pyrene ratio of the remaining tars fall within the range of pyrogenic material, 1.0 to 1.4 or higher[22], with the exceptions of D2V, D3V, D4V and D5V. Both D2V and D3V fall within the range expected of lower temperature processes such as CWG tars, whereas D4V and D5V fall between the two diagnostic ratio regions. This further suggests the complex site history of the samples from the site that produced sampled D2V to D6V and may be explained by the presence of petrogenic material, such as alkyl cyclohexanes.

The ratios of anthracene/anthracene+phenanthrene (Ant/(Ant+Phe), flouranthene/fluoranthene+pyrene (Flt/Flt+Pyr) and benzo[a]anthrancene/benzo[a]anthracene+chrysene (BaA/(BaA +Pyr) should be >0.1, >0.5 and >0.35 respectively[20]. A flouranthene/fluoranthene+pyrene ratio of <0.5 has previously been reported for samples D2V to D5V and may be due to the presence of a gas reforming plant on the site[20]. This was found to be the case again with samples D2V to D5V falling below 0.5 as well as both of the CWG tars, which is an oil based process. Both the Ant/(Ant+Phe) and BaA/(BaA+Pyr) ratios fall within the expected ranges for all the samples with the Ant/(Ant+Phe) ratios >0.1 and BaA/(BaA+Pyr) ratios >0.35 for all of the sample regardless of the production process used to produce them.

Conclusion

The results of the study showed that different tar production processes produce tars with distinctly different aromatic and aliphatic contents, with the use of GCxGC/TOFMS allows for the detection of a large number of compounds with tars that would otherwise likely be missed. The analytical method was capable of detecting 951 individual aromatic and 198 individual aliphatic compounds providing important forensic information about the samples. For example the detection of alkyl cyclohexanes, an indicator of petrogenic material, within tars that were not produced using petroleum. Alkyl cyclohexanes were detected within all samples from sites that contained a CWG plant and not detected in those that did not. This suggests that the presence of alkyl cyclohexanes may be expected on many UK gaswork sites as CWG plants were often added in order to meet peak demands with the tars produced by the CWG process having little value if sold.

The results clearly showed that a wide range of aliphatic and aromatic compounds can be detected within coal tars, even within those produced from the same retort type. The coke oven tar samples are of particular importance as they were both produced from the same feedstock coal and on the same day, although within different coke ovens. Both of the coke ovens used produced metallurgical coke and therefore would be considered high temperature coke ovens, however the more modern coke oven that produced D18CO operated at a higher temperature than that which produced D19CO. This higher temperature resulted in distinct changes within the tars produced with a

significant enrichment of parent PAHs alongside simultaneous loss of alkylated PAHs. The lower temperature present with D19CO also resulted in a higher aliphatic content, although this content is minor compared to other tar types. This could also extend to other tar types as while for example horizontal retorts are separated into LTHR and HR types the HR type tars could still have been produced at very different temperatures with different plants often operating at different temperatures and efficiencies. This means that both the temperature of the retort and the retort type may play an important role in the compositions of the tars produced even by the same retort types.

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Sample	Aliphatic	PAH total	EPA34 total	Tar Type
D2V	24	424	144	SD
D3V	56	488	157	SD
D4V	105	604	188	SD
D5V	93	477	165	SD
D6V	70	442	160	SD
D20V	126	573	182	D
D7H	55	529	188	D
D8H	100	670	192	D
D10H	44	334	135	D
D17H	80	579	197	D
D9L	136	651	198	D
D16L	37	301	136	SD
D13C	85	657	200	WD
D14C	128	729	202	D
D18CO	2	359	125	D
D19CO	9	387	140	D

Table 1 – Aliphatic and aromatic number of compounds

Figure 1 – Percentage EPA16 PAH compositions of tars. LTHR – Low Temperature Horiztonal Retort, HR – Horizontal Retort, CWG – Carbureted Water Gas, VR – Vertical Retort, CO – Coke Oven.

n-Alkane	D2V	D3V	D4V	D5V	D6V	D20V	D7H	D8H	D10H	D17H	D9L	D16L	D13C	D14C	D18CO	C19CO
C11	436	534	1403	731	329	1852	329	4046	1570	654	5804	59	1248	6398	8	22
C12	490	538	1812	907	426	3319	444	6497	1628	904	6620	65	1840	11563	7	30
C13	416	437	1752	810	501	3602	310	5822	1366	1037	5300	76	1833	14873	ND	35
C14	315	336	1380	698	422	3454	245	4168	831	1150	3496	61	1672	14136	ND	28
C15	271	292	1126	334	327	3005	190	3050	291	1140	2427	49	1562	11810	ND	<LOQ
C16	189	190	802	428	254	2440	140	2144	301	855	1751	56	1066	8427	ND	9
C17	47	91	527	311	170	2252	75	1810	243	700	1309	28	598	6767	ND	2
C18	436	87	190	13	156	2017	94	1408	168	404	1320	38	447	4608	ND	ND
C19	ND	26	275	91	114	1822	69	721	115	329	1015	48	262	2943	ND	ND
C20	ND	<LOQ	222	89	35	1624	34	263	<LOQ	99	1058	26	102	1856	ND	ND
C21	ND	<LOQ	184	104	52	1514	14	449	95	190	963	9	93	1109	ND	ND
C22	ND	14	72	81	69	1311	6	153	32	143	836	20	33	536	ND	ND
C23	ND	3	89	8	41	735	30	159	41	39	770	7	12	296	ND	ND
C24	ND	<LOQ	103	16	6	919	31	165	42	84	583	1	11	182	ND	ND
C25	ND	<LOQ	27	15	21	992	8	51	13	28	563	8	ND	67	ND	ND
C26	ND	<LOQ	86	13	30	774	13	58	<LOQ	45	422	3	ND	13	ND	ND
C27	ND	2	59	13	15	607	10	25	<LOQ	52	341	<LOQ	ND	46	ND	ND
C28	ND	<LOQ	12	<LOQ	12	382	5	11	<LOQ	13	126	<LOQ	ND	15	ND	ND
C29	ND	ND	25	<LOQ	3	344	ND	ND	<LOQ	12	51	<LOQ	ND	3	ND	ND
C30	ND	ND	10	3	8	116	ND	ND	<LOQ	ND	107	2	ND	ND	ND	ND
C31	ND	ND	ND	ND	<LOQ	29	ND	ND	ND	ND	15	ND	ND	ND	ND	ND
C32	ND	ND	ND	ND	<LOQ	50	ND	ND	ND	ND	28	ND	ND	ND	ND	ND
C33	ND	ND	ND	ND	<LOQ	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C34	ND	ND	ND	ND	ND	13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 2 - n-Alkane peak areas m/z 57 adjusted for sample weight and internal standard response (10^{-3}) ND = not detected

C no	D2V	D3V	D4V	D5V	D6V	D20V	D7H	D8H	D10H	D17H	D9L	D16L	D13C	D14C	D18CO	C19CO
C4	43	69	293	131	48	416	40	802	368	147	1043	ND	295	522	ND	ND
C5	71	103	297	212	40	366	75	1292	460	194	1285	ND	381	1392	ND	ND
C6	40	52	325	105	71	475	44	688	232	120	622	ND	194	1195	ND	ND
C7	13	37	194	81	44	365	25	588	115	97	548	ND	144	1133	ND	ND
C8	ND	26	213	26	27	314	10	223	ND	89	249	ND	94	839	ND	ND
C9	ND	14	96	24	9	219	4	155	ND	71	164	ND	60	399	ND	ND
C10	ND	ND	11	16	5	65	ND	104	ND	32	51	ND	14	201	ND	ND
C11	ND	ND	34	10	<LOQ	57	ND	64	ND	21	63	ND	15	124	ND	ND
C12	ND	ND	16	4	3	57	ND	23	ND	<LOQ	31	ND	8	126	ND	ND
C13	ND	ND	9	ND	<LOQ	11	ND	17	ND	2	15	ND	ND	15	ND	ND
C14	ND	ND	3	ND	ND	28	ND	4	ND	ND	43	ND	ND	11	ND	ND
C15	ND	ND	2	ND	ND	ND	ND	3	ND	ND	ND	ND	ND	ND	ND	ND
C16	ND	ND	<LOQ	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 3 – Alkyl cyclohexane peak area m/z 83 adjusted for sample weight and internal standard response (10^{-3}) ND = not detected, <LOQ = less than limit of quantification

Compound	D2V	D3V	D4V	D5V	D6V	D20V*	D7H*	D8H*	D10H*	D17H*	D9L*	D16L	D13C	D14C*	D18CO*	C19CO*
Naphthalene	4289	4806	6811	3839	626	6284	26321	16581	24789	11402	9292	2702	7534	22147	24753	14073
Acenaphthylene	3211	3412	2621	1118	621	2143	6911	11178	4282	4105	3599	743	3664	15800	21204	23254
Acenaphthene	378	404	384	230	197	3211	1121	2069	951	1129	931	172	1271	2570	1058	885
Fluorene	1348	1401	1501	700	543	5071	6321	9980	4527	3940	3421	531	2451	11663	17726	10968
Phenanthrene	3055	2981	3613	1578	1320	26899	18306	25669	16908	12718	9080	1979	4977	24854	45190	32779
Anthracene	780	816	1021	483	419	3031	7639	9358	4145	2888	2789	642	1115	5475	17849	10218
Flouranthene	680	704	1277	581	681	11241	14049	17072	10696	7774	6811	923	953	7218	25627	15957
Pyrene	1083	1105	1385	625	656	9011	10741	13348	7787	6449	4689	715	1176	8686	21807	11161
Benzo[a]Anthracene	434	452	628	316	370	3501	5493	6106	3455	2315	2157	466	420	2597	13130	7278
Chrysene	397	411	535	296	340	3021	4618	4833	2852	2088	1778	418	384	2175	10088	5187
Benzo[b]Fluoranthene	357	360	622	319	441	4026	5520	6389	4515	2824	2741	395	322	2030	15684	7875
Benzo[k]Fluoranthene	267	281	417	240	290	2333	3601	3597	2453	1706	1580	278	404	1328	7791	4110
Benzo[a]Pyrene	594	607	850	421	516	5568	7301	8516	5670	3687	3064	475	510	3711	17029	8561
Indeno[123-c,d]pyrene	915	931	1327	632	786	9017	11833	13821	9181	5948	4932	719	773	5987	11398	5151
Benzo[g,h,i]Perylene	1118	1129	1656	738	943	11878	15607	18264	12093	7794	6439	852	920	2856	12569	5394
Dibenzo[a,h]anthracene	422	435	728	380	484	4719	6678	7261	5629	3603	3079	408	370	2985	2888	1736
Total EPA16 PAH	19327	20234	25374	12498	9233	110954	152058	174042	119932	80369	66382	12418	27244	122081	265790	164585

Table 4– EPA16 PAH concentrations of database tars (mg/kg)

Sample	Phe/Ant	Flt/Pyr	Flt/(Flt+Pyr)	Ant/(Ant+Phe)	BaA/(BaA+Chr)
D2V	3.92	0.63	0.39	0.20	0.52
D3V	3.65	0.64	0.39	0.21	0.52
D4V	3.54	0.92	0.48	0.22	0.54
D5V	3.27	0.93	0.48	0.23	0.52
D6V	3.15	1.04	0.51	0.24	0.52
D20V	8.87	1.25	0.56	0.10	0.54
D7H	2.40	1.31	0.57	0.29	0.54
D8H	2.74	1.28	0.56	0.27	0.56
D10H	4.08	1.37	0.58	0.20	0.55
D17H	4.40	1.21	0.55	0.19	0.53
D9L	3.26	1.45	0.59	0.23	0.55
D16L	3.08	1.29	0.56	0.24	0.53
D13C	4.46	0.81	0.45	0.18	0.52
D14C	4.54	0.83	0.45	0.18	0.54
D18CO	2.53	1.18	0.54	0.28	0.57
C19CO	3.21	1.43	0.59	0.24	0.58

Table 5 – Select PAH diagnostic ratios

Supplementary information: Site History

DNAPL001-006 (D2-D6) samples were taken from the same site that manufactured gas between 1836 and 1971. The site had manufactured gas from a wide range of process from low temperature horizontal retorts, high temperature horizontal retort and later vertical retort. D2 was taken from a borehole near a gasholder on the southern boundary of the site. D3, D4 and D5 were taken directly from a former tar tank on the opposite side of the site. This tar tank had been built at the same time as the vertical retort plant had been constructed. D6 was taken from a borehole located near to the tar tank containing samples D3, D4 and D5. All of the samples were produced by the Vertical Retort process. D2, D3 and D6 are Sandy soil samples heavily contaminated with tar. D4 and 005 are both waterlogged soils that are heavily contaminated with tar.

The site initially operated simple horizontal retorts until the gasworks it was redeveloped in 1878 and expanded in 1912 to include five continuous vertical retort beds. This was further extended in the 1920's with the addition of an additional five continuous vertical retorts. From the early 1930's until 1952 the plant remained at capacity, with various improvements to increase efficiency, such as the addition of two water gas plants. The site was expanded again in 1952 with the construction of a purification plant, additional vertical retorts and the development of a storage area for primary flash distillate (a type of light petroleum distillate). A CWG plant and microsimplex oil gasification plant operated on the site and so there is the potential for traces of CWG and oil gas tar within the samples.

DNAPL007 (D7) was taken from a site that operated between 1856 and 1969 and initially produced low temperature horizontal retort gas. However, this later switched to higher temperature horizontal retort gas and the tar sample came from this process rather than the earlier LTHR process. The sample is in the form of pure DNAPL taken at the base of an underground gasholder tank during a remediation project in 2009.

DNAPL008 (D8) was collected from a FMGP, which operated between 1856 and 1971 and may contain traces of CWG tar as the site produced CWG in the later stages of its operation. The majority of the tar would have been produced by the HR process and this was shown in the statistical analysis of the tars (McGregor et al., 2012). The sample is in the form of pure DNAPL in water. The tar sample was taken from a former 250,000 gallon tank associated with the horizontal retort house and was taken from a skimmer pump, which was being used to empty the tar tanks during a remediation process

DNAPL009 (D9) was obtained from a site that ceased production in 1953, with an unknown initial operation date, the site was manufacturing gas using a vertical retorts when it closed, but could also have produced horizontal retort, likely a LTHR, or carbureted water gas. The CWG plant was commissioned in 1902, with vertical retorts being constructed in 1913 and 1931. Statistical analysis showed the samples to have been derived from the LTHR process (McGregor et al., 2012). The sample is in the form of pure DNAPL in water and was taken from inside a former tar well during a remediation process. The sample was taken within a clean glass laboratory sample of 250ml.

DNAPL010 (D10) was obtained from a FMGP, which operated between 1849 and 1981 and mainly operated horizontal retorts, originally using LTHR and later switching to producers fired HR process circa 1890's. The tar samples were collected from a circular concrete tar tank known to be associated with the later HR process. The sample is in the form of pure DNAPL in water. The site also operated a CWG plant so it is possible that CWG tar may also be present within the sample.

DNAPL013 (D13) operated from 1885 until the 1970's, the site manufactured gas using horizontal retort until 1939, taking a bulk gas supply from another source. It did continue to maintain and use its CWG plan to supply peak demand. . The sample of liquid NAPL was removed from a groundwater NAPL plume beneath the site by a skimmer pump.

DNAPL014 (D14) was taken from the same site as DNAPL017 and was taken from an infilled former gasholder and later a tar emulsion storage tank, used for the storage of NAPL emulsions produced by the CWG process and was present in the form of pure DNAPL. This sample was obtained from a remediation system, which used total fluids pumping

DNAPL016 (D16) was obtained from a FMGP which operated between 1854 and 1946 and was a typical small country town FMGP site. The site is known to have operated hand charged directly fired horizontal retorts which would have produced a tar with low temperature characteristics (LTHR), which was shown in the statistical analysis (McGregor et al., 2012). The sample was recovered from the core barrel of a pioneer rotary drilling rig and is in the form of a tar saturated soil.

DNAP017 (D17) and was taken from the same site as DNAPL014 (D14) from a site which operated from 1868 to 1976. The site operated HR, Coke ovens, CWG, gas reforming plant and a by-products works. The samples were obtained from an area of the site where both the CWG and HR had operated. D17 was taken from a tar tank that would have been associated with the HR process.

DNAPL018 (D18) and DNAPL019 (D19) were taken from coke ovens that were still in operation at a steelworks. Both samples were taken on the day of coke production with D18 coming from an oven that has been in operation since the 1970's. D19 was taken from a coke oven that has been in operation since the 1930's. Both samples are in the form of pure DNAPL. The coals used in the manufacture of these tars was a blend of up to 12 non British imported crushed coals.

DNAPL020 (D20) operated from 1885 and ceased production in 1975. The site initially used horizontal retorts until the 1920s before then operating a Vertical retort plant and CWG plant. The coal tar sample was derived from the VR process. The sample is in the form of pure DNAPL taken from a site drain. The site also operated a CWG plant so CWG tar may be present in trace amounts.