Active Creosote Extraction (ACE)

D2.1 Baseline Analysis of Untreated Poles

July 2022

Contents

Executive Summary

Based upon previous work , it has been proven that end of life telegraph poles containing creosote can be treated with high pressure CO2 acting as a supercritical fluid.. At a pressure and temperature above its critical conditions (1078 psi and 31˚C) the gas enters a super-critical phase that has unique properties such that it has the density of a liquid with the mobility of a gas and solvating properties enabling penetration of substrates where contaminants become solubilised.

The recovery of the solvated contaminants is effected through depressurisation causing phase change where the contaminants are recovered and the CO2 gas is discharged and recovered in a closed circuit gas phase. It is anticipated this work will commence during Work Package 4.

It is critical to understand the initial spatial distribution of the creosote within the poles and how that has changed with the weathering processes over tens of years “in the field”. Visual inspection of the radial penetration suggests up to 50% of the wood could be recoverable through pre-treatment by selectively removing the outer layers for treatment.

To explore these opportunities it is important to collect data that is consistent and properly records the physical as well as chemical properties of the contaminant.

Samples taken are duplicated and are tested in house to validate and support the data received from the accredited laboratory and in house analysis can be adapted to allow flexibility in our research as the project progresses.

A set of criteria for the selection of end-of-life utility poles have been developed and utilised, and this has allowed the appropriate initial selection of two poles (known as Pole 100 and 300).

Criteria have also been developed for the appropriate selection of representative samples of the poles, along with analytical methodologies whose development and implementation has establish pre-extraction baseline creosote concentrations.

Analysis of the selected samples has shown some evidence of gravitational effects on Pole 100 where the creosote concentration increased down (top to base) the pole. However, this was not replicated in Pole 300 as the top section had the highest concentration of creosote. Although it must be noted after that, the gravitational effect could be deduced.

Analysis of samples related to increasing horizontal depth led to an overall trend of decreasing creosote concentration towards the centre of the pole, which was clearly shown in Pole 300.

Overall, the same trend was replicated in Pole 100, but in this pole, it also showed the sector with relative depth 5 to 10 cm had a greater creosote concentration than the outer sector.

This trend could be related to the extent of fracturing, which was greater in Pole 100, when compared to Pole 300, which may have allowed creosote migration deeper into the pole, but with limited data, at this stage, it is not possible to highlight a specific trend.

This work has allowed the pre-extraction creosote concentrations to be determined and given an insight into the location of the areas of highest contamination, greater than 1000 mg/kg, as defined in the Waste Acceptance Criteria.

1. Pole And Sample Selection

Creosote Pole Selection Criteria

Redundant creosote poles were selected for use from the National Grid Electricity Distribution depot at Church Village, where they had been delivered to the Depot in various lengths. Figure 1 shows the poles awaiting disposal.

Figure 1. Redundant creosote poles at Church Village

To ensure a sufficient quantity of samples, the creosote poles selected were a minimum length of 6 m and had a 6 m section that had a diameter no greater than 30 cm, as this is the inner diameter of the extraction vessel.

Two creosote poles at the depot fulfilled the criteria and these were recorded as Pole 100 and Pole 300. A third creosote pole was labelled Pole 200; however, it was mistakenly disposed of before it could be collected from the Depot.

Pole 100 (Figure 2), manufactured in 1967, was originated from Cwm Colliery, Beddau (CF38 2PY). Pole 100 had a minimum and maximum diameter of 23 cm and 27 cm, respectively and was 7.2 m in length.

Figure 2. Pole 100.

Pole 300, manufactured in 1962, originated from an unknown source. Pole 300 has a minimum and maximum diameter of 25 cm and 34 cm, respectively and was 12 m in length.

Sample Selection

To ensure the provenance of the samples, the sample sections of the creosote poles were defined and labelled.

The creosote poles were divided into sections, starting at the top with a 15 cm section (Section 1). Directly below Section 1, a 2.5 m section (Section 2) was defined. Directly below Section 2 an additional 15 cm section (Section 3) was defined. This process was repeated until a minimum of two 2.5 m sections and three 15 cm sections were defined.

The 15 cm sections were analysed prior to the commencement of the extraction process to give a baseline concentration value for the creosote quantity at those positions. The 2.5 m sections were used for the supercritical fluid extraction process.

To determine the vertical, top to base, concentration of creosote throughout the poles, samples were taken at Sections 1, 3, 5 and 7 (where applicable).

To determine the horizontal, outer edge to centre, concentration of creosote throughout the poles, three samples were taken at varying horizontal depths, outer edge to centre, at Sections 1, 3, 5 and 7 (where applicable). As the diameter of the sections were approximately 15 cm, each section was subdivided into approximately 5 cm diameter subsections (Figure 3). The outer edge subsection was labelled 1, and represented the depth to 5cm. The middle section, labelled 2, represented a depth of 5 to 10 cm and the inner core section was labelled 3, and represented a depth of 10 cm to the centre.

Figure 3. Vertical sections 1, 3, 5 and 7 (where applicable) were subdivided into three horizontal subsections.

Each 5 cm subsection was labelled with the pole reference number, section reference and subsection reference. For example, 100-1-1 (Pole reference number i.e. 100, section reference number i.e.1,3,5 or 7, and subsection reference number i.e. 1,2 or 3). Therefore the 15 cm Sections 1, 3, 5 and 7 (where applicable) had 3 samples each.

A schematic diagram of the defined sample sections are shown in Figure 4.

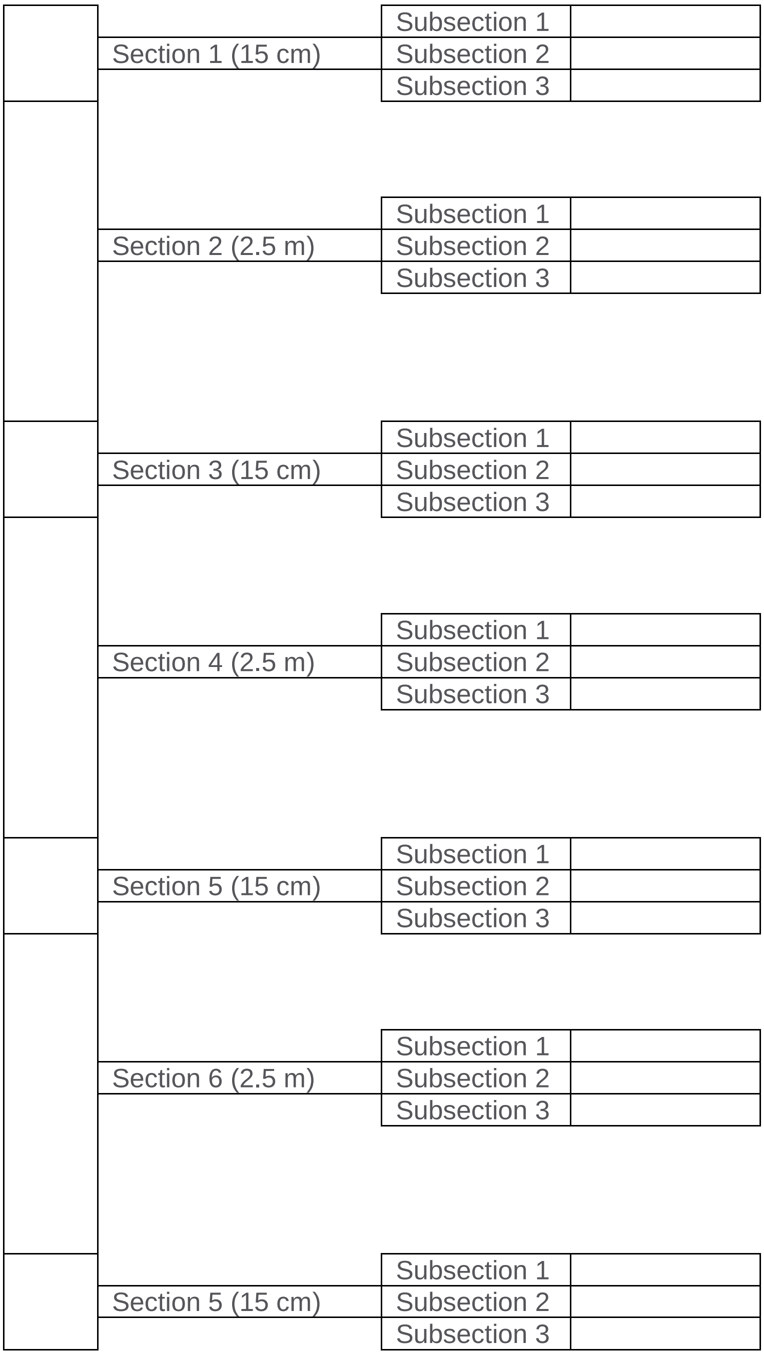


Figure 4. The defined sections of Pole 300.

2. Sample Preparation and Baseline Analysis

Sample Preparation

Sample selection and preparation is fundamentally important and equally as important so to accurately quantify the creosote concentration in the samples. Because it is impracticable to analyse the whole of the pole, samples prepared for analysis must be a random, representative on the whole, and homogeneous.

To achieve this, each of the 15 cm subsections were cut into approximately 1 cm cubes which were then ground into powder using a laboratory grinder as seen in figure 5.

This ensured that each sample was not only well ground, but also well mixed to ensure a true representation was produced, limiting any sample bias. Grinding increases the surface area available to the solvent and therefore increases the efficiency of extraction and solubilisation. The grinder was well cleaned between samples to ensure no cross contamination.

Figure 5. A sample at each preparation stage.

Horizontal fracturing of the poles appeared to allow creosote to migrate deeper into the poles via these imperfections as shown in figure 6. To overcome this issue, a representative sample was taken to avoid areas of creosote migration.

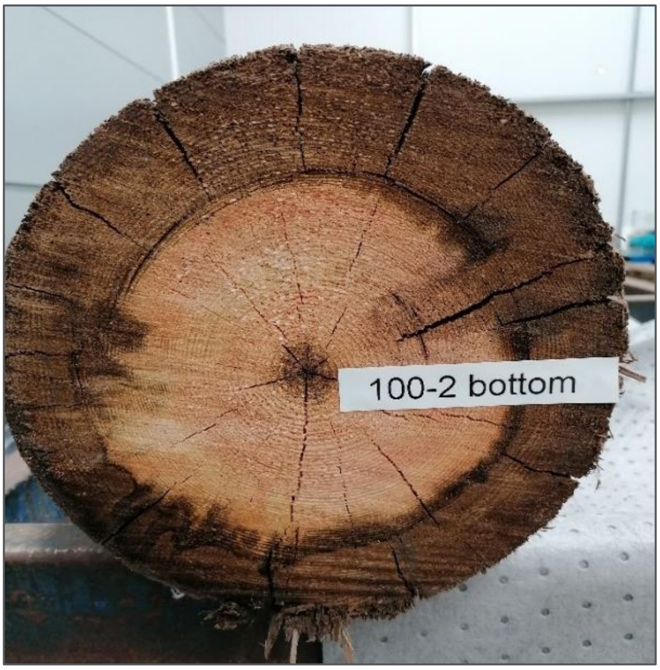


Figure 6. Creosote migration along horizontal fractures.

The samples were ground, mixed, and a random 2.00 gram sample selected and weighed into a 250 cm^3 glass conical flask, using a laboratory balance (±0.01g). 25 cm^3 of tetrachloromethane solvent was added using a 25 cm^3 volumetric pipette (±0.06 cm^3). The flask was then sealed and left for 4 hours, with periodic agitation every 30 minutes before finally undergoing sonication (in an ultrasonic bath) for 8 minutes. The solvent and dissolved creosote was then filtered through a 0.22 micro metre (µm) filter and stored in a sealed sample bottle and a 2 cm^3 chromatography vial.

To ensure the 4 hour extraction time was appropriate to extract all the creosote, a timed set of spectra were completed by infrared spectroscopy using the peak height at 2930 cm^{-1} to quantify the creosote concentration (Figures 7 and 8).

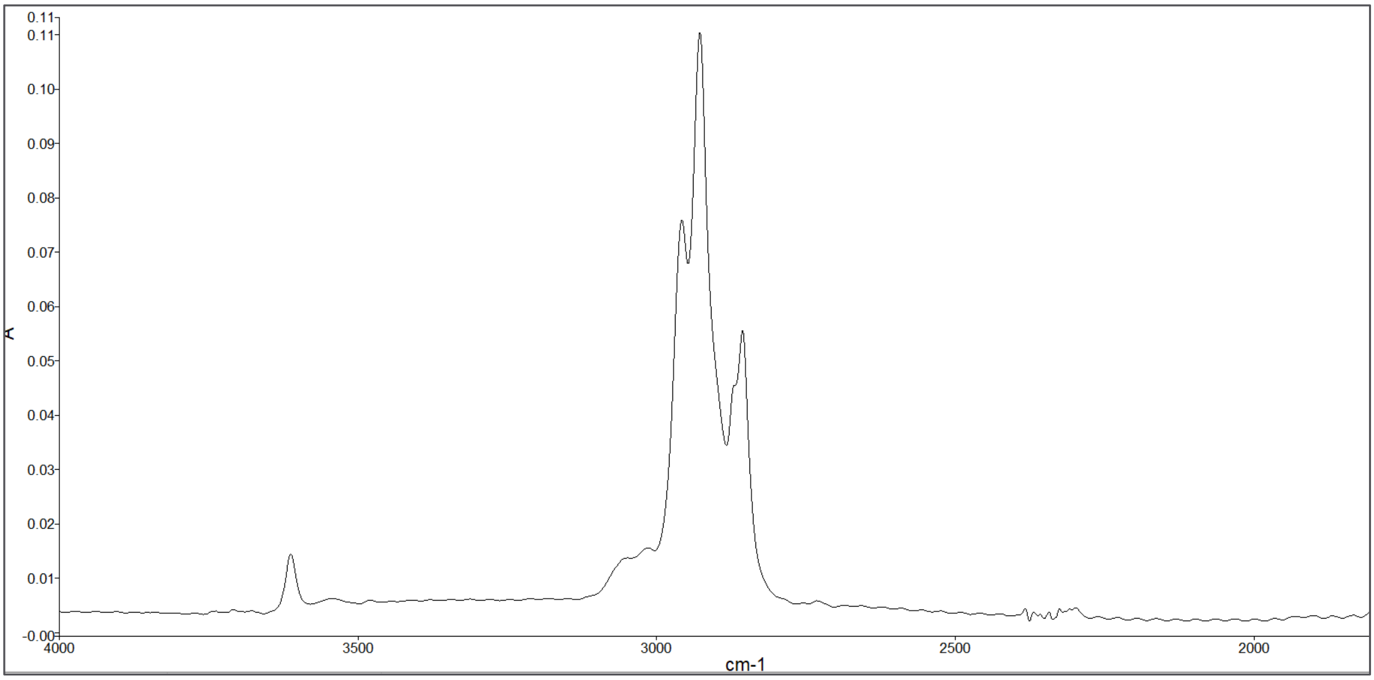


Figure 7. Infrared spectra of Creosote showing most intense peak

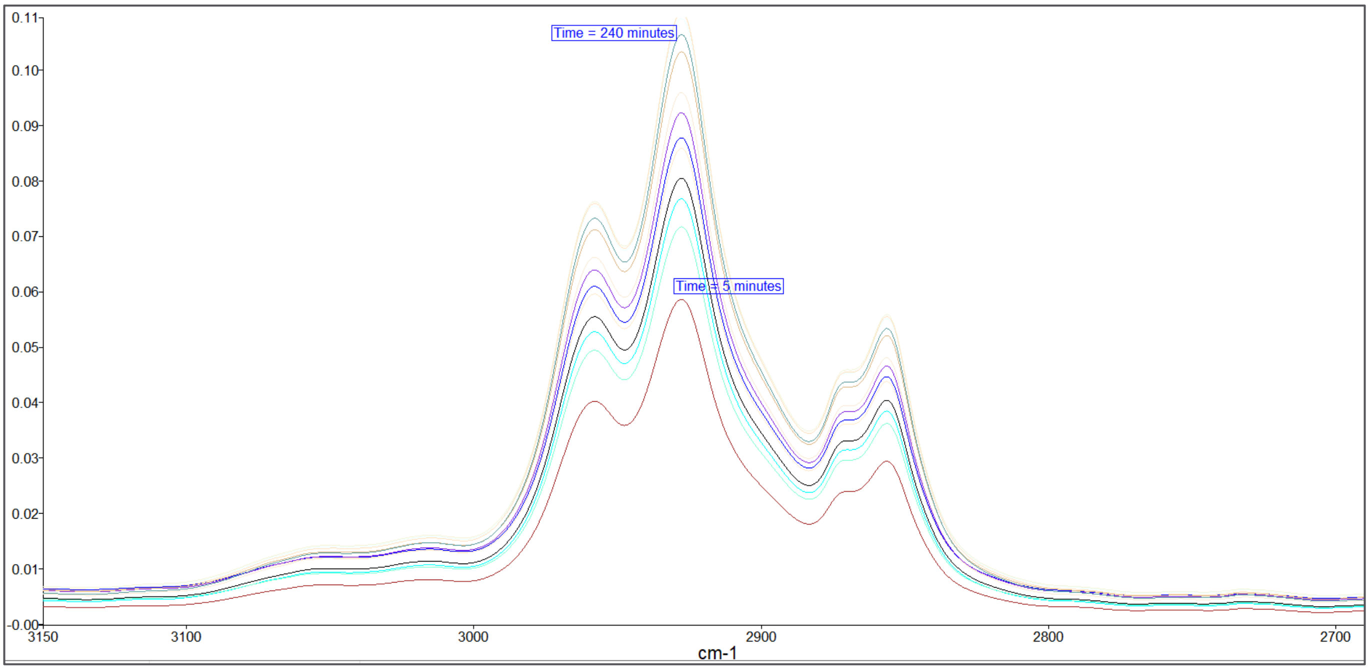


Figure 8. Time lapse spectra of Creosote over 240 minutes.

The solubilisation of creosote from the sample had equilibrated and maximised after 240 minutes.

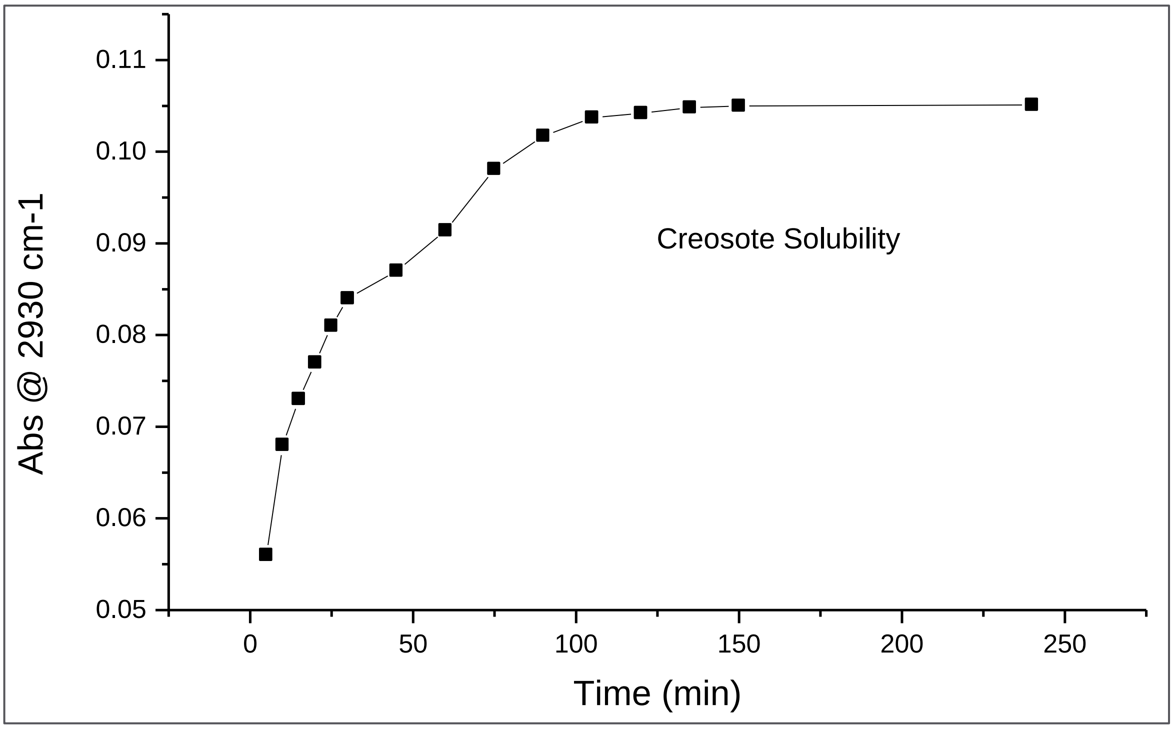


Figure 9. Intensity of Infrared Abs @ 2930 cm^{-1} (Creosote concentration) with time.

To ensure the creosote had been extracted a second extraction procedure was conducted on a previously extracted sample. The result of which showed a concentration level less than 6 mg/kg.

Sample Analysis

Samples from each of the 15 cm sections were prepared and internally analysed as well as externally analysed by Milton, Treharne and Davies. Analysis of the samples externally had a return time of approximately 2 to 3 weeks, so to allow the rapid monitoring that was going to be required, internal analysis was also undertaken.

All samples were ground and homogenized in house, these were then subdivided into 2 identical samples to allow comparison between the two analytical streams.

External analysis

All Polycyclic Aromatic Hydrocarbons (PAH) were extracted using Dichloromethane and Hexane (organic solvents) and analysed using Gas Chromatography-Mass Spectrometry (GC-MS).

Total Petroleum Hydrocarbons (TPH) were extracted using Hexane and the Aliphatic (straight chain) and Aromatic (ring structure) hydrocarbons separated and individually analysed using Gas Chromatography-Flame Ionisation Detector (GC-FID). All results were presented without associated error levels.

In-House analysis

Several in-house analytical techniques were used to analyse the creosote (PAH) content.

High Performance Liquid Chromatography (HPLC) & Gas Chromatography-Mass Spectrometry (GC-MS)

Figure 10, HPLC, and figure 11, GC-MS, show the individual compounds in creosote, quantitation of these individual components, and more importantly their total quantitation. This is achieved by integrating the area of each peak. The total area is then directly related to the total concentration.

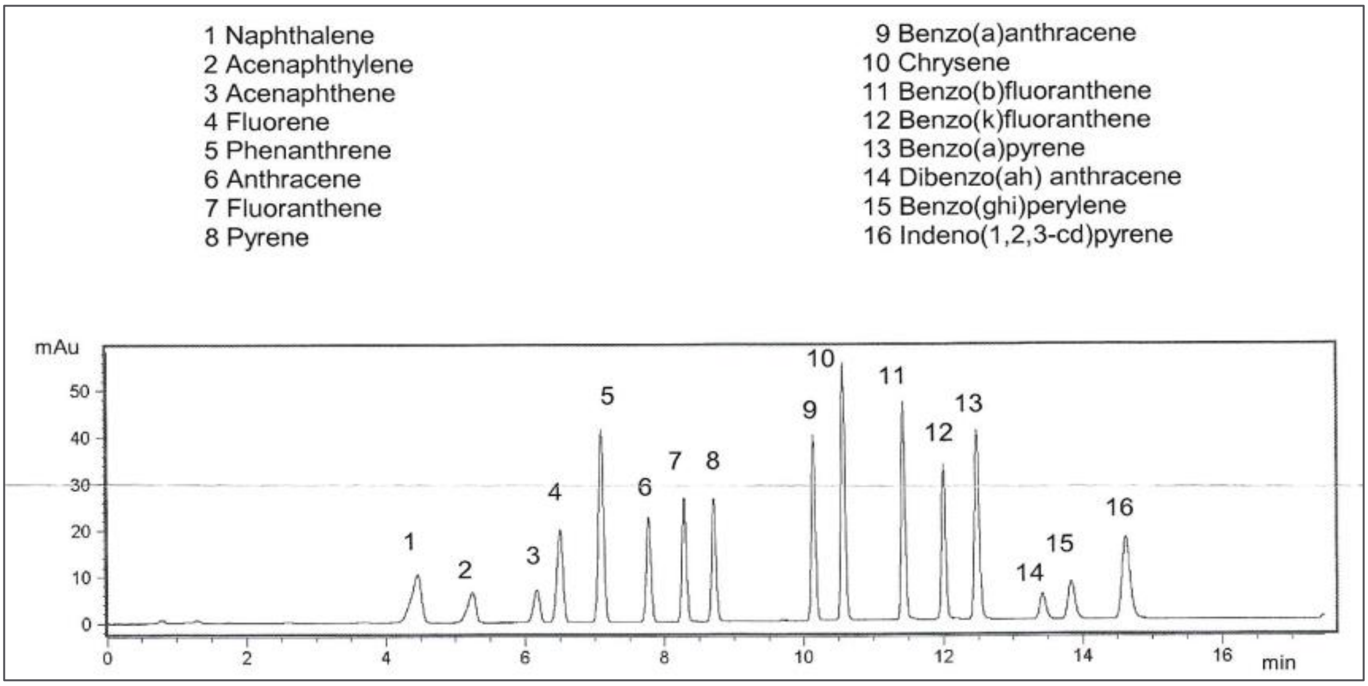


Figure 10. HPLC display of PAHs under analysis, individual PAHs shown above.

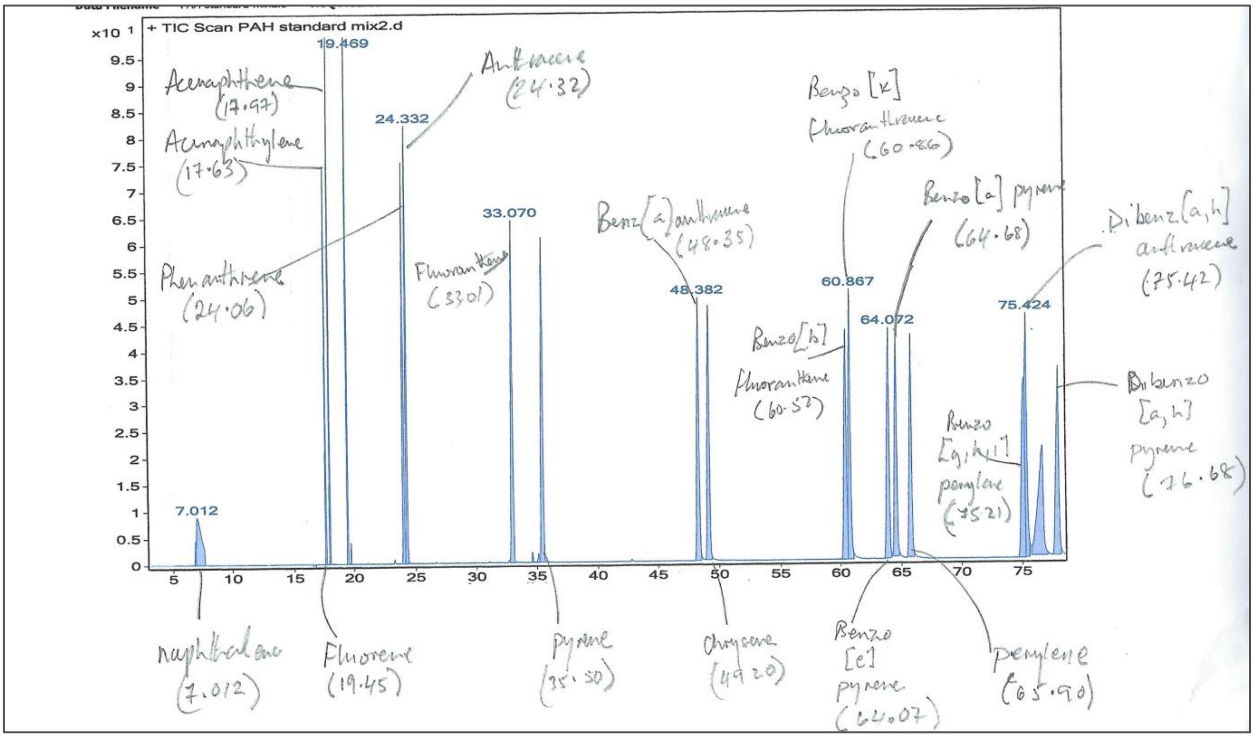


Figure 11. GC-MS display of PAHs under analysis.

Infrared Spectroscopy (IR)

The same can be achieved with Infrared spectroscopy, shown in figure 12 where either the height of a selected peak or its area is directly related to its concentration (Lambert -Beer Law).

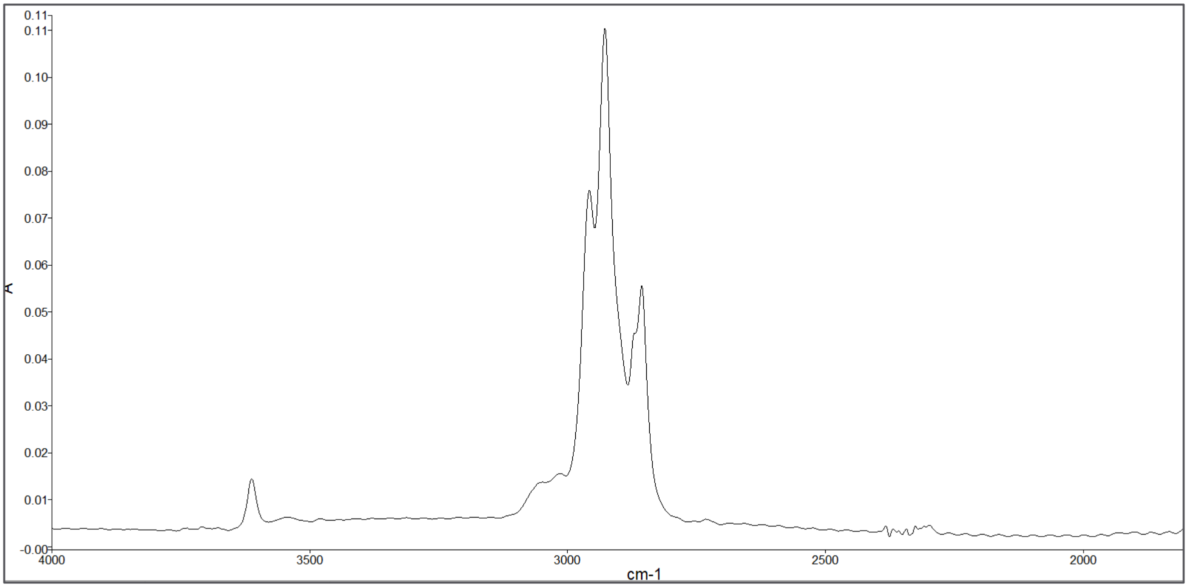


Figure 12. Infrared Spectrum of Creosote.

Chromatography allows the individual components to be quantified, while IR only allows the total concentration of creosote to be determined as there is no separation of the components.

IR is the quickest, and easiest technique to use. Samples only take minutes to be analysed. Chromatographic methods take longer, generally 20-40 minutes for HPLC and 40 to 90 minutes for GC-MS.

Standard Material for Quantitation

Quantitation relies on a comparison of the unknown sample with a standard representative material, the closer the match to the sample under comparison, generally the smaller the errors in the results. Generally, it is not feasible to obtain the same standard material as the unknown under analysis, so in this case, a very acceptable standard PAH calibration solution was used for analysis.

For internal analysis comparisons, as well as using a standard PAH solution, a creosote sample was obtained from Burt, Boulton and Haywood Ltd (BBH) of Newport (NP20 2WA), producers of creosote-impregnated poles. This was used to produce additional calibration graphs by both Infrared spectroscopy and HPLC.

As the exact details of the external PAH calibration solution are unknown the relationship between the external results and the in-house results for the same wood samples must be determined.

To this end, both Infrared and HPLC were used, with GC-MS being used to profile the extraction samples to ensure all components are being extracted equally.

Infrared Quantification

Using the creosote standard obtained from BBH, a series of standard solutions were prepared and analysed, as detailed previously. Infrared spectroscopy is the quickest method of analysis and will be used to predict extraction efficiency before the samples are externally quantified.

Figures 13 and 14 show the baseline concentration values for the two utility poles analysed, Pole 100 and 300. Figure 13 gives the relationship between the mass of creosote dissolved in 25 cm3 tetrachloromethane and its absorbance at 2930 cm-1.

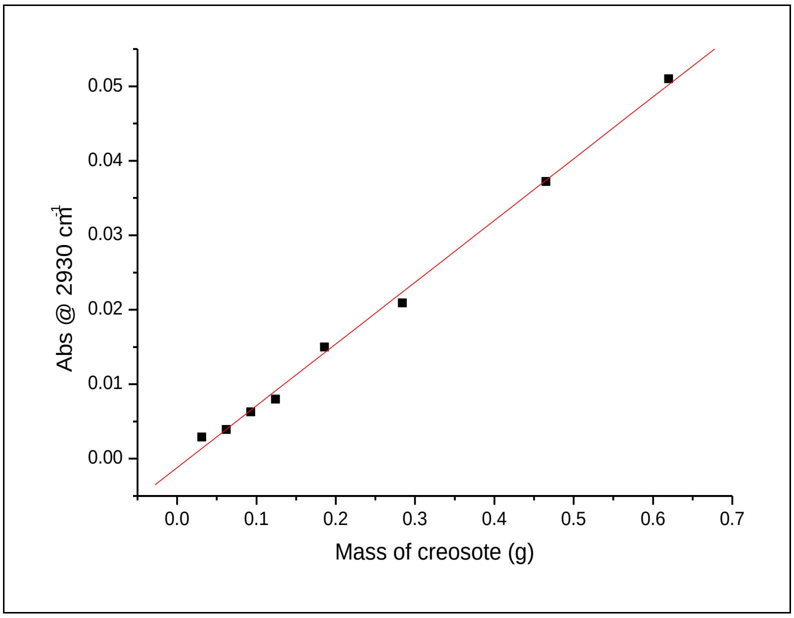


Figure 12. Infrared calibration graph.

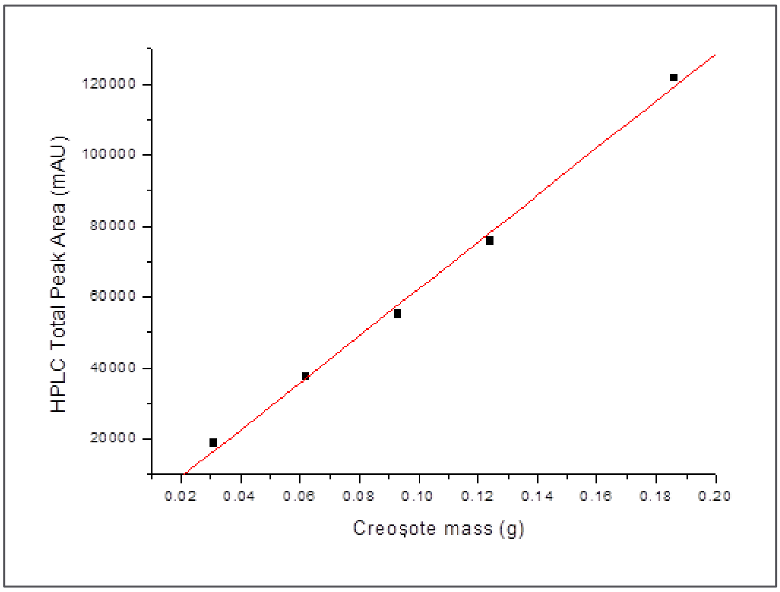


Figure 13. HPLC calibration graph.

3. Result and Conclusions

All results shown have been externally quantified and verified. The sample analysis results have been summarised for both Pole 100 and Pole 300 in Figures 14 and 15.

Laboratory sample analysis results are enclosed within the Appendix (Ref. A).

Baseline Waste Classification

Classification of the waste has been conducted in line with "Guidance on the classification and assessment of waste (1st Edition v1.2.GB) Technical Guidance WM3".

We have selected the most appropriate codes from the EWC List (European Waste Catalogue) and will confirm with the Regulator their acceptance and preference:

07	WASTES FROM ORGANIC CHEMICAL PROCESSES
07 04	wastes from the MFSU of organic plant protection products (except 02 01 08 and 02 01 09), wood preserving agents (except 03 02) and other biocides
07 04 13*	solid wastes containing dangerous substances
20	MUNICIPAL WASTES (HOUSEHOLD WASTE AND SIMILAR COMMERCIAL, INDUSTRIAL AND INSTITUTIONAL WASTES) INCLUDING SEPARATELY COLLECTED FRACTIONS
20 01	separately collected fractions (except 15 01)
20 01 37*	wood containing dangerous substances

With reference to document WM3 pages A3 to A6 give an "Introduction on how to use the list of waste

Page A7 gives a description of the waste (07)

Page A16 to page A17 gives further subdivision on waste 07 (07 04 13) as shown in table

Pages A38 to A39 give the description for Code 20

Source data for the Creosote components has been derived from the Material Safety Data Sheet (MSDS) and we have selected Carcinogenic HP7 as the primary risk driver and Hazard Statement H350 as the most stringent threshold at 0.1%. However, there are a number of idiosyncrasies around this level that will need clarification/agreement with the

Regulator. Currently the target for this project is to reduce the total concentration of PAHs (creosote) to below the 1000 mg/kg.

Vertical Creosote Variation

The Total PAH values of samples representing subsections 100-1-1, 100-3-1 and 100-5-1 (outmost subsections of Pole 100) are 3340 mg/kg, 4530 mg/kg and 5890 mg/kg, respectively. The values increase down (top to base) the pole which suggests gravity draws the creosote down the pole resulted in higher creosote values at the base.

The Total PAH values of the samples representing subsections 300-1-1, 300-3-1, 300-5-1 and 300-7-1 (outmost subsections of Pole 300) are 5570 mg/kg, 1740 mg/kg, 2290 mg/kg and 4860 mg/kg, respectively. These values do not follow the same trend as the one described in Pole 100. The high value of 300-7-1 (4860 mg/kg) may well be due to the fact that it was below ground and so protected from environmental effects.

Horizontal Creosote Variation

Subsections 100-1-1, 100-1-2 and 100-1-3, each horizontally deeper into the pole, the concentration of creosote in the sector covering 5 to 10 cm in depth, has a higher concentration than the outer sector, approximately 150%. The same pattern is seen with subsections 100-5-1, 100-5-2 and 100-5-3 where there is an approximately 110% value for 100-5-2 compared with 100-5-1.

Subsections 100-3-1, 100-3-2 and 100-3-3 do not show this same trend. The common trend in all sectors is that the inner sectors 100-1-3, 100-3-3 and 100-5-3 all have significantly lower creosote concentrations than all others, which would be expected.

Comparing the subsections with those detailed above there is a common trend in all that the creosote concentration decreases towards the centre of the pole.

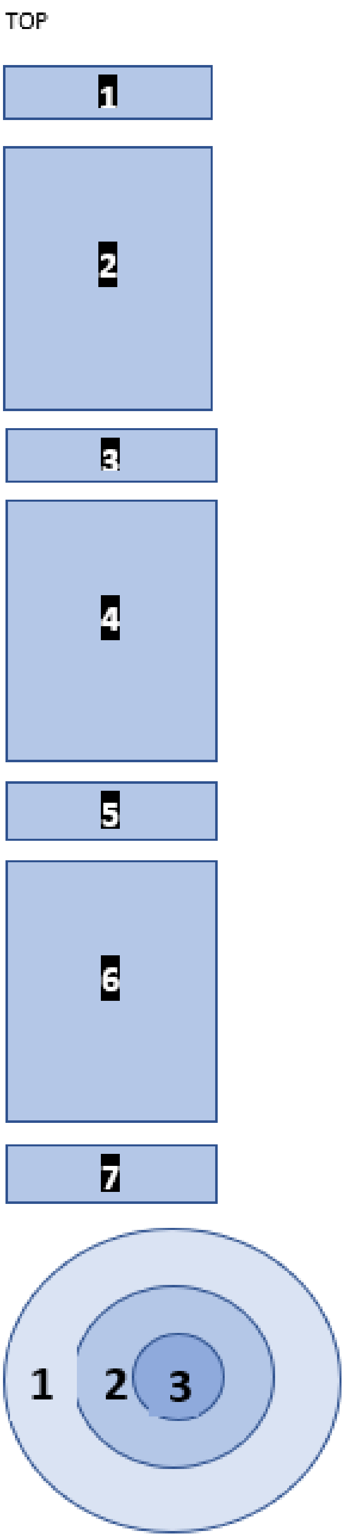
An additional observation to make for pole 300 is that all the inner sections, depth of 5 cm to the centre, are below the concentration levels required.

Conclusion

Only the most inner sector of Pole 100 is below 1000 mg/kg threshold, and in conclusion it would be expected that pole 100 will require a longer extraction period to Pole 300.

Knowing the concentrations (both individually speciated and total) for the PAHs in the pre-extracted utility poles will allow the determination of the extraction efficiency for the different methods of extraction to be employed.

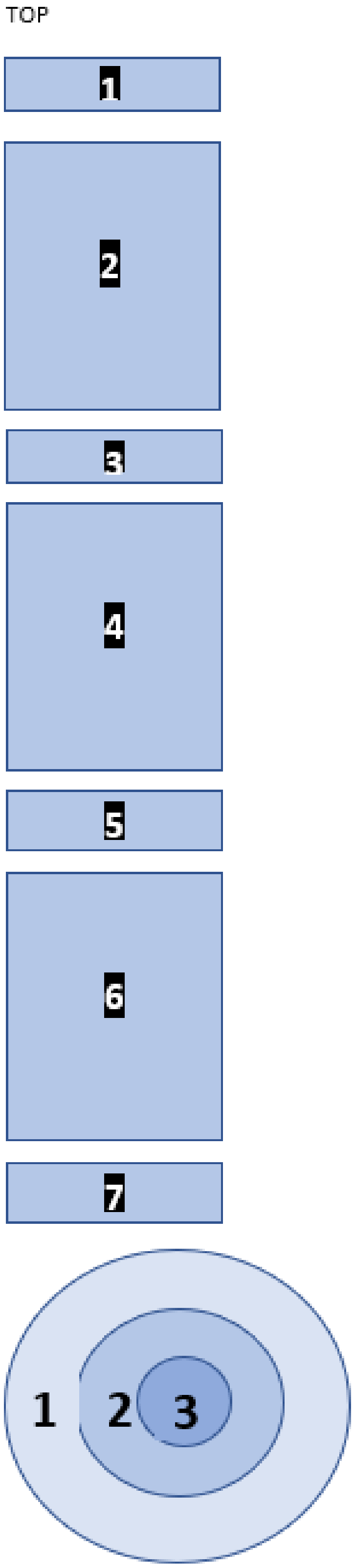
Concentration trends of the poles, both vertically and horizontally, are unclear at this point because of the small data set. More poles would need to be analysed before any definitive conclusions can be upheld, but there is a limit placed (by Natural Resources Wales) on the number of poles we can store, and therefore analyse, at a time.



Pole Identifying Number	100
Date of manufacture	1967
Length	7.2 on receipt
Minimum diameter	23 cm
Maximum diameter	27 cm
Site location	Cwm Colliery

Location	Concentration (mg/kg)
1-1	3340
1-2	5040
1-3	202
2	
3-1	4530
3-2	1220
3-3	353
4	
5-1	5890
5-2	6350
5-3	320
6	
7-1	N/A
7-2	N/A
7-3	N/A

Figure 14. Pole 100 results.



ole Identifying Number	300
Date of manufacture	1962
Length	12 m
Minimum diameter	25 cm
Maximum diameter	34 cm
Site location	Unknown

Location	Concentration (mg/kg)
1-1	5570
1-2	542
1-3	246
2	
3-1	1740
3-2	366
3-3	24
4	
5-1	2290
5-2	61
5-3	7
6	
7-1	4860
7-2	444
7-3	7.82

Figure 15. Pole 300 results.

Appendix A – Sample Analysis Results

Sample Reference		100-1-1	100-1-2	100-1-3	100-3-1	100-3-2	100-3-3
Speciated PAHs							
Naphthalene	mg/kg	< 0.05	110	63	21	65	79
Acenaphthylene	mg/kg	18	29	1.8	29	11	2.5
Acenaphthene	mg/kg	50	420	19	200	120	31
Fluorene	mg/kg	39	440	17	150	120	25
Phenanthrene	mg/kg	170	1200	35	490	360	68
Anthracene	mg/kg	220	480	11	270	100	22
Fluoranthene	mg/kg	1000	1000	24	1100	200	54
Pyrene	mg/kg	910	790	20	1100	140	41
Benzo(a)anthracene	mg/kg	340	220	4.5	430	37	12
Chrysene	mg/kg	210	160	3	270	27	7.9
Benzo(b)fluoranthene	mg/kg	140	86	1.5	160	9.8	3.5
Benzo(k)fluoranthene	mg/kg	64	42	0.81	88	7.5	2.9
Benzo(a)pyrene	mg/kg	89	60	1.1	110	7	3
Indeno(1,2,3-cd)pyrene	mg/kg	19	10	< 0.05	23	2.2	0.63
Dibenz(a,h)anthracene	mg/kg	5.4	3	< 0.05	7.6	< 0.05	< 0.05
Benzo(ghi)perylene	mg/kg	20	9.9	< 0.05	26	1.7	0.64
Total PAH							
Speciated Total EPA-16 PAHs	mg/kg	3340	5040	202	4530	1220	353

Sample Reference		100-5-1	100-5-2	100-5-3	300-1-1	300-1-2	300-1-3

Speciated PAHs

Naphthalene	mg/kg	71	250	50	160	65	79
Acenaphthylene	mg/kg	38	46	3.2	65	8.1	2.5
Acenaphthene	mg/kg	440	640	37	1400	130	60
Fluorene	mg/kg	340	670	33	1300	130	46
Phenanthrene	mg/kg	950	1400	82	1100	82	23
Anthracene	mg/kg	460	710	23	470	42	9.7
Fluoranthene	mg/kg	1300	1100	41	440	34	11
Pyrene	mg/kg	1100	880	33	360	29	8.5
Benzo(a)anthracene	mg/kg	430	260	7	100	7.9	2.9
Chrysene	mg/kg	300	160	4.6	64	5.7	1.2
Benzo(b)fluoranthene	mg/kg	180	100	2.2	38	2.8	0.66
Benzo(k)fluoranthene	mg/kg	93	46	1.3	17	1.1	0.44
Benzo(a)pyrene	mg/kg	120	69	1.4	27	2.1	0.57
Indeno(1,2,3-cd)pyrene	mg/kg	29	13	0.45	5.3	0.37	< 0.05
Dibenz(a,h)anthracene	mg/kg	8.6	3.5	< 0.05	< 0.05	< 0.05	< 0.05
Benzo(ghi)perylene	mg/kg	30	14	0.34	8.7	0.65	< 0.05

Total PAH

Speciated Total EPA-16 PAHs	mg/kg	5890	6350	320	5570	542	246

Sample Reference		300-3-1	300-3-2	300-3-3	300-5-1	300-5-2	300-5-3

Speciated PAHs

Naphthalene	mg/kg	92	73	16	120	28	3.7
Acenaphthylene	mg/kg	< 0.05	3.7	< 0.05	50	< 0.05	< 0.05
Acenaphthene	mg/kg	380	79	3.9	460	12	1.7
Fluorene	mg/kg	370	83	2	510	12	0.99
Phenanthrene	mg/kg	330	57	0.94	390	5.3	0.41
Anthracene	mg/kg	150	21	0.33	200	1.8	< 0.05
Fluoranthene	mg/kg	170	19	0.34	240	1.3	< 0.05
Pyrene	mg/kg	140	16	0.26	200	1	< 0.05
Benzo(a)anthracene	mg/kg	40	6.2	< 0.05	49	< 0.05	< 0.05
Chrysene	mg/kg	29	2.7	< 0.05	33	< 0.05	< 0.05
Benzo(b)fluoranthene	mg/kg	15	1.4	< 0.05	17	< 0.05	< 0.05
Benzo(k)fluoranthene	mg/kg	4.9	0.88	< 0.05	5.9	< 0.05	< 0.05
Benzo(a)pyrene	mg/kg	8.9	1.2	< 0.05	11	< 0.05	< 0.05
Indeno(1,2,3-cd)pyrene	mg/kg	2.4	0.22	< 0.05	2.4	< 0.05	< 0.05
Dibenz(a,h)anthracene	mg/kg	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Benzo(ghi)perylene	mg/kg	3.5	0.39	< 0.05	3.3	< 0.05	< 0.05

Total PAH

Speciated Total EPA-16 PAHs	mg/kg	1740	366	23.6	2290	61.2	6.79

Sample Reference		300-7-1	300-7-2	300-7-3

Speciated PAHs

Naphthalene	mg/kg	440	74	4.8
Acenaphthylene	mg/kg	73	6.4	< 0.05
Acenaphthene	mg/kg	1100	110	1.2
Fluorene	mg/kg	1100	96	0.87
Phenanthrene	mg/kg	940	73	0.75
Anthracene	mg/kg	340	29	0.22
Fluoranthene	mg/kg	370	24	< 0.05
Pyrene	mg/kg	300	23	< 0.05
Benzo(a)anthracene	mg/kg	89	5	< 0.05
Chrysene	mg/kg	52	2.6	< 0.05
Benzo(b)fluoranthene	mg/kg	28	1.1	< 0.05
Benzo(k)fluoranthene	mg/kg	13	1.2	< 0.05
Benzo(a)pyrene	mg/kg	20	0.99	< 0.05
Indeno(1,2,3-cd)pyrene	mg/kg	3.7	0.3	< 0.05
Dibenz(a,h)anthracene	mg/kg	< 0.05	< 0.05	< 0.05
Benzo(ghi)perylene	mg/kg	5.5	0.47	< 0.05

Total PAH

Speciated Total EPA-16 PAHs	mg/kg	4860	444	7.82