

1       **A preliminary investigation of anaerobically digested municipal sludge cake and**  
2                             **contaminated soil for recycling by pyrolysis.**

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10       **Abstract**

11       This work has investigated the potential of pyrolysis as a recycling solution for two largely  
12       uncharacterised waste streams, anaerobically digested (AD) municipal sludge cake and  
13       brownfield soil (contaminated with oily sludge). Characterisation of emitted organic  
14       compounds from pyrolysis were captured in a solvent (acetone) scrubber and analysed by  
15       GC-MS. Both AD sludge cake and brownfield soil showed considerable promise for 'green-er'  
16       fuels, as a source of syngas (with CO supplementation) and volatile aromatics essential for  
17       fuel quality. However, these waste streams also generated significant amounts of additional  
18       highly toxic pollutants of varying chemistries, further emphasising the importance of using a  
19       trapping approach applicable to a broader range of chemicals. Pleasingly the acetone trap  
20       showed very good efficacy in capturing this breadth of chemistries, supporting its use as an  
21       alternative capture and preparative method, for monitoring volatile and semi-volatile organic  
22       tars

29 **Keywords**

30 Scrubber

31 Pyrolysis/gasification contaminants

32 Tar analysis

33 Gas chromatography-thermal conductivity detection (GC-TCD)

34 Gas chromatography-mass spectrometry (GC-MS)

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## 57 1. Introduction

58 Thermal conversion techniques, such as pyrolysis and gasification, can be used to generate  
59 value-added products from organic waste. During pyrolysis carbon-rich feedstocks are heated  
60 in anoxic environments between 400-700 °C, causing the organic material to decompose and  
61 generate products of a higher heating value (e.g. flammable syngas, bio-oils and bio-chars  
62 (Brownsort, 2009; Mohan et al., 2006; Ok, 2015)). Meanwhile, gasification involves higher  
63 temperatures above >700°C with the addition of controlled amounts of oxidant commonly,  
64 oxygen or steam. This causes partial combustion of the solid and volatile material, thereby  
65 increasing the yield of syngas Syngas is composed of carbon monoxide (CO), hydrogen (H<sub>2</sub>)  
66 and methane (CH<sub>4</sub>), and can be used to generate energy by forming liquid fuels using Fischer-  
67 Tropsch (FT) catalysts (Davis, 2001; Jahangiri et al., 2014; Krylova, 2014). However, syngas  
68 can also contain organic pollutants or 'tars' that consist of linear chain hydrocarbons and  
69 volatile organic compounds (VOCs) such as aromatic, phenolic, and polyaromatic  
70 hydrocarbon (PAH) species (Carpenter et al., 2007; Palma, 2013; Ponzio et al., 2006). Despite  
71 their importance to the calorific value of syngas for energy generation (Hossain and Davies,  
72 2013; Sharma et al., 2012) small VOCs such as benzene, ethylene, and acetylene are  
73 particularly important to monitor as they can cause chemical contamination and catalyst  
74 deactivation at significant monetary cost (Bosmans et al., 2013; Rabou and Drift, 2011).  
75 Similarly, the components of bio-oils can provide economic value as an additional feedstock  
76 for fuels (Unyaphan et al., 2017; Zhang et al., 2019) however, they can also cause mechanical  
77 fouling of equipment if poorly captured. Thus, there remains a need to both capture the  
78 resulting pollution by-products and molecularly characterise the recycling approach, using fit-  
79 for-purpose trapping and measurement processes, prior to the re-use or disposal of 'new'  
80 organic waste. Unfortunately, this can come at significant cost, with VOCs often requiring  
81 specific sampling methods, using sorbents and modified instrumentation, when gas  
82 chromatography-mass spectrometry (GC-MS) analyses are required (Agilent, 2014).  
83 Therefore, a cheap(er) pollutant capture method, such as a solvent trap or 'scrubber' using  
84 methanol, water or isopropanol (Phuphuakrat et al., 2010; Prando et al., 2016), is important

85 for process viability; however, these are often selected specifically to target pollutant classes  
86 common to well-characterised feedstocks such as biomass (pine wood), and are mainly  
87 untested on alternative wastes. Given the drive to recycle more sources of organic waste,  
88 current work has shown an increasing need to capture and monitor for a broader range of  
89 organic pollutants, from an expanding list of largely uninvestigated feedstocks (e.g. municipal  
90 sludge cake and contaminated brownfield soil). Although previous thermal studies on  
91 suitability sewage sludge as a feedstock exist (Gomez-Rico et al., 2008; Mohan et al., 2006;  
92 Oleszczuk et al., 2014; Rosa et al., 2018; Rulkens, 2008), the literature is lacking particularly  
93 with the treatment of AD sludge cake and the analysis of the volatiles organic compounds  
94 emitted in the process. AD sludge cake is the remaining solid material from sewage sludge  
95 treatment. Sewage sludge is treated firstly, by dewatering and centrifugation to form a solid  
96 material (19% dry mass) before it is thermally hydrolysed and anaerobically digested (Gavala  
97 et al., 2003). The undigested solids from this process is further dewatered to produce  
98 anaerobically digested (AD) municipal sludge (Gavala et al., 2003). A recent thermal  
99 gravimetric study on pine wood and anaerobically digested (AD) municipal sludge cake  
100 indicated significant differences in the evolved chemicals of these feedstocks during  
101 thermochemical conversion, with primary losses of sample occurring at 200-400 °C for pine  
102 wood (63.8 %), and 200-500 °C for AD municipal sludge cake (36.5 %) ((Sullivan et al., 2019)).  
103 Although studies on the suitability of sewage sludge as a thermochemical feedstock exist  
104 (Gomez-Rico et al., 2008; Mohan et al., 2006; Oleszczuk et al., 2014; Rosa et al., 2018;  
105 Rulkens, 2008), there is little published literature concerning AD sludge cake and the  
106 pollutants emitted during thermochemical conversion. Similarly, whilst research on brownfield  
107 soil contaminated with coal tar has shown harmful persistent organic pollutants following  
108 pyrolysis (e.g. volatile aromatics, furans and polyaromatic hydrocarbons) (Lara-gonzalo et al.,  
109 2015); (Abdel-Shafy and Mansour, 2016) there is again limited work in characterising oil-  
110 contaminated brownfield soil for land remediation. Therefore, to investigate the breadth of  
111 pollutants anticipated from the thermochemical recycling of these more complex waste  
112 materials, acetone was tested as a low cost scrubber, that offers compatibility with a standard

113 GC-MS set-up (Maštovská and Lehotay, 2004), and a wider dissolution range for alternative  
114 pollutants. For pollutant capture, the scrubber was initially tested using relevant volatile and  
115 semi-volatile standards, followed by application to the thermochemical recycling of these  
116 waste materials; to understand the limitations and benefits of the thermochemical processing  
117 of these feedstocks, further characterisation in terms of nitrogen content and calorific value  
118 was also carried out.

119

## 120 **2. Materials and methods**

### 121 2.1. Standard reference materials

122 Acetone, methanol, 70% nitric acid (all ACS grade), pentane (GC grade), and  
123 triphenylethylene (internal standard, IS) were purchased from Sigma Aldrich (Suffolk, UK).  
124 The standard solutions for creating the calibration graph (QTM PAH mixture 1 and EPA 8040a  
125 phenol calibration mixture) were obtained from Supelco (Suffolk, UK), while those used for  
126 quality control (QC) samples (aromatic mixture 1 (PAHs), phenol mixture 1 and 2 8040a,  
127 volatile aromatic mixture (CLP Volatile mega mix™) and naphthalene-d<sub>8</sub> (IS) were sourced  
128 from Restek (Wycombe, UK). For GC-MS and gas chromatography-thermal conductivity  
129 detection (GC-TCD), ultra-pure helium and argon gases were purchased from Air Products  
130 (Swansea, UK), while high purity nitrogen for pyrolysis was acquired from BOC (Port Talbot,  
131 UK). To test the scrubbers with complex samples, pine wood (purchased from Waters and  
132 Morris in Ammanford, UK), AD municipal sludge cake (sourced from wastewater treatment  
133 plants in South Wales, UK and Accra, Ghana), and soil (10 % contamination with  
134 petrochemical waste from a field site in Rumney, UK) were pyrolysed for syngas production.

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### 136 2.2. Standard (stock) solutions

137 A 10 mg/L VOC and equivalent QC stock solution (for quantitation) were prepared by spiking  
138 the volatile aromatic mixture and a separate batch of CLP Volatile mega mix™, respectively  
139 in acetone. Similarly, 10 mg/L calibration stock solution for SVOCs were prepared using the

140 QTM PAH mixture 1 or EPA 8040a phenol solution along with an appropriate 10 mg/L QC  
141 stock solution for quantitation (see standard reference materials section). The IS solutions  
142 were also prepared in acetone as a 100 mg/L mixture of triphenylethylene and naphthalene-  
143 d<sub>8</sub>.

144

### 145 2.3. Instrumentation

146 Analyses of volatile single-ring aromatics, phenols and polyaromatic hydrocarbons (PAH)  
147 were undertaken using a Trace 1300 and ISQ GC-MS system, operating with Tracefinder  
148 Xcalibur™ software and a TG-5MS column (30 m x 0.25 mm, 0.25 μm) (Thermo Scientific,  
149 Hemel Hempstead, UK). Due to poor column retention and difficulties in differentiating from  
150 low mass fragment ions, simple combustion gases, such as CO, H<sub>2</sub> and CH<sub>4</sub>, were measured  
151 using a Varian micro GC-TCD (Palo Alto, USA). This was operated with two columns using  
152 an argon carrier gas; an 8 m 100 % dimethyl-polysiloxane (CP-SIL 5CB) column (channel 1)  
153 to separate small organics (C3-C6) and a 10 m aluminosilicate molecular sieve column  
154 (Molsieve MSA BF, Varian, Palo Alto, USA) (channel 2) for simple gases (e.g. CO, H<sub>2</sub>, CH<sub>4</sub>).  
155 To generate the syngas, a pyrolysis rig (based on a commercial design) were fabricated in-  
156 house; the latter consisted of a stainless steel (SS) tube (4.7 cm<sup>2</sup> x 70 cm) with a sample  
157 stage, a removable end cap to introduce the feedstock, an inlet valve for nitrogen, and an exit  
158 port for syngas that was connected to (1) an in-line scrubber system (containing acetone) and,  
159 (2) the GC-TCD system for real-time simple gas monitoring. The sample stage was located at  
160 the hottest part of the rig, with operating temperatures monitored here and at the end cap  
161 using two thermocouples. The rig was also fitted with a pressure sensor and a gas safety  
162 dump valve in case of emergencies. The scrubber system comprised of three glass impingers  
163 (max capacity of 250 mL ), connected by a short length (~7-10 cm) of inert high temperature  
164 PTFE tubing; this was maintained at 20 °C by air recirculation to minimise evaporation of the  
165 scrubber solvent, with the PTFE exit-line of the rig to the first impinger fitted at a longer length

166 (~50 cm) to ensure gas cooling (please see the graphical abstract for a simplified schematic  
167 of the rig).

168

#### 169 2.4. Analysis of volatile and semi-volatile organic pollutants

170 Two GC-MS methods were used based on analyte volatility, with each optimised for the  
171 relevant compound suites using a 2.5 µL split-less injection, operating at an inlet temperature  
172 of 300 °C. For VOCs, an oven temperature programme of 40-150 °C at 15 °C/minute (held for  
173 one minute), and 150-300 °C at 25 °C/minute was used, with the transfer line and ion source  
174 temperature set at 300 °C and 250 °C, respectively. Whilst for SVOCs alternative conditions  
175 to accommodate changes in volatility were applied; an oven temperature programme of 40-  
176 250 °C at 20 °C/minute, held for five minutes, 250-300 °C at 20 °C/minute, and, the transfer  
177 line and ion source temperatures of 300 °C and 310 °C, respectively. Data was acquired under  
178 full scan and single ion monitoring (SIM) conditions for the relevant analytes, with the latter  
179 operated as a segmented approach (see Supplementary for details). Compounds within the  
180 scrubbers were identified using the NIST 2.0 database, with reverse and forward match scores  
181 >800 (Vladimir and Sparkman, 2008), and quantified using the nearest eluting IS.

182

#### 183 2.5. Validation of GC-MS Method for VOCs and SVOCs.

184 Prior to application, the method was validated for limit of detection (LOD), accuracy, precision,  
185 lower level of quantitation (LLOQ) and upper limit of quantitation (ULOQ), using two batches  
186 of samples run over separate days. To create and assess the calibration curve each batch  
187 contained a set of calibration standards (250-2000 µg/L and 50-1500 µg/L for SVOC and  
188 VOCs, respectively), five blanks, and five analytical quality controls (AQCs) spiked at 500 µg/L  
189 for VOCs and 1500 µg/L for SVOCs. The LOD for the GC-MS methods was initially calculated  
190 using 3x the standard deviation of the blank signal; however, this can often be misleading with  
191 discrepancies from the manual integration of the signal. Therefore, to confirm the LOD, the  
192 lowest standard with a signal to noise ratio (S/N) >3 was also used. To determine the LLOQ

193 and ULOQ, additional AQC's were analysed at low (50 µg/L for VOCs and 250 µg/L SVOCs)  
194 and high concentrations (1000 µg/L for VOCs and 1500 µg/L for SVOCs), respectively,  
195 whereby the LLOQ was confirmed as the concentration below or near the lowest standard with  
196 acceptable accuracy and precision (see Equations 1 and 2). The acceptance criteria used for  
197 method validation was based on a UKAS approved standard operating procedure (ISO, 2006),  
198 which required an accuracy and precision of ≤20 % for the AQC's at the specified  
199 concentration.

200

$$201 \quad Accuracy (\%) = \frac{(Mean \text{ determined } QC \text{ concentration} - true \text{ } QC \text{ concentration})}{true \text{ } QC \text{ concentration}} \times 100$$

202 Equation 1

203

$$204 \quad Precision (\%) = \frac{standard \text{ deviation of determined } QC \text{ concentration}}{Mean \text{ determined } QC \text{ concentration}} \times 100$$

205 Equation 2

206

## 207 2.6. Pyrolysis of organic feedstock

208 Pine wood, AD municipal sludge cake (both 10 g), and contaminated soil (20 g to ensure  
209 sufficient amounts of VOC and SVOCs) were sieved to <2 mm and heated to >700 °C at 20  
210 °C/minute under nitrogen, in the laboratory-scale test system to mimic slow pyrolysis. Given  
211 the greater anticipated variability of tar content from the raw feedstocks, the scrubber system  
212 comprised of a series of three impingers and each contained a 150 mL of solvent (chosen  
213 from the scrubber evaluation). To assess the usefulness of the target feedstock, the calorific  
214 value (CV) of the material and the producer gas was also determined using a bomb calorimeter  
215 (ISO 1928, "Solid mineral fuels - Determination of gross calorific value by the bomb  
216 calorimetric method; and calculation of net calorific value," 2009) and by the molar fraction  
217 results from the GC-TCD analysis, respectively.

218

219



220 **3. Results and discussion**

221 3.1. Method validation

222 All of the analytes within the VOC methods showed acceptable signal at 1 µg/L for the LOD  
223 and, acceptable precision and accuracy for quantifying over the tested concentration range  
224 (including ULOQ), with 4.08-18.36 %relative standard deviation (%RSD) and -18.6-5.53  
225 %accuracy (see Table 1). As expected, higher LOD values were observed for the less volatile  
226 SVOCs (phenol and PAH standards) but this method also showed acceptable precision and  
227 accuracy for the tested calibration range, with values between 3.24-15.93 %RSD and -9.27-  
228 19.81 %accuracy, respectively (Table 1). Given both protocols met the acceptance criteria for  
229 validation these were then applied for characterising and quantifying compounds observed in  
230 the scrubbers following pyrolysis of the waste samples.

231

232 3.2. Characterisation of AD sludge cake and brownfield soil during pyrolytic waste recycling.

233 Prior to application, the scrubbers and feedstocks were subjected to a programme of  
234 preliminary tests to understand limitations in their performance and suitability for recycling.  
235 Firstly, the capacity of the acetone scrubber to capture organic pollution was determined by  
236 measuring the 'bleed' of organic compounds between the series of scrubbers; this showed  
237 that a typical saturation range for acetone at 20 °C was equivalent to 125-200 g/L of pyrolysed  
238 feedstock, and a series of 3x150 mL scrubbers would be sufficient to capture detectable  
239 organic pollution generated from 10-20 g of feedstock. However, during this work it was noted  
240 that scrubber performance was volume dependent, with a potential loss of performance due  
241 to scrubber evaporation by the syngas. This was therefore tested repeatedly over a 30-40  
242 minute process time to mimic the operation of the rig; pleasingly, despite some evaporative  
243 loss of the scrubber adjacent to the syngas line, this did not exceed 10 %, indicating a sufficient  
244 level of syngas cooling prior to the scrubber system. The largely un-investigated AD municipal  
245 sludge cake and contaminated soil samples were also characterised to understand their  
246 usability for recycling; measurements of inorganic composition, syngas production, CV and tar

247 content were taken as these are thought to differ with feedstock chemistry (and production  
248 method) (Chang et al., 2000; Palma, 2013; Tian et al., 2014; Werner et al., 2014). Interestingly,  
249 despite the common manufacturing method, the pre-pyrolysed Ghanaian AD sludge cake  
250 contained a greater amount of nitrogen (3.5 mg/Kg) and SVOCs (3500 mg/Kg) than that from  
251 the UK (2.5 mg/Kg and 230 mg/Kg, respectively), with the former generating more than double  
252 the amount of harmful nitrogen-containing aromatics following pyrolysis (e.g. to 188.2 mg/L,  
253 see Table 2). To the best of the authors' knowledge, this disparity of AD sludge cake  
254 composition between common production processes has been largely underreported in the  
255 literature and highlights the importance of feedstock (and tar) characterisation. Similarly, this  
256 finding also supports the use of a syngas clean-up that covers a broader range of pollutants,  
257 to minimise the exposure to harmful emissions prior to release/use. To understand the  
258 usefulness of recycling the (waste) feedstocks as an energy source, the syngas composition  
259 and CV were also established; the results again were significant, as they highlighted  
260 differences in syngas production, a variation in organic waste composition and the importance  
261 of material characterisation. Unlike brownfield soil, the syngas generated from AD sludge cake  
262 showed significant potential for thermochemical recycling, with competitive gas ratios to pine  
263 wood; therefore, with CO supplementation, this remains a promising route for 'green' fuel  
264 production due to the significant CV (~25-33%) and lower levels of greenhouse gas (CH<sub>4</sub>)  
265 produced.

266 To provide data indicative of the final process, pine wood (as a well characterised  
267 sample), AD sludge cake and brownfield soil were therefore pyrolysed using the SS rig at  
268 >700 °C and an acetone scrubber. Despite the higher operating temperature of the process  
269 (and lower boiling point of acetone) minimal latent heating and evaporation of the scrubber  
270 was observed, indicating the continued capture of pollutants by solvation. As expected, the  
271 pyrolysis of pine wood showed significant amounts of typical breakdown products and minor  
272 constituents of biomass such as furan derivatives and phenols (Brebú and Vasile, 2010; Kibet  
273 et al., 2012), and terpenoid compounds, respectively. However, the use of acetone also  
274 proved very beneficial in terms of monitoring the volatile emission during the recycling of AD

275 sludge cake as it showed significant capture of highly toxic nitrogen-containing heterocyclic  
276 aromatics (see Table 3). In addition to these pollutants, acetone also captured significant  
277 levels of volatile aromatics desired for fuel production; pleasingly, sludge cake showed  
278 significant promise in generating these 'BTEX' compounds (e.g. benzene, toluene, ethyl  
279 benzene and xylene), with similar levels of observed to pine wood, further supporting the use  
280 of pyrolysis as a viable and valuable recycling solution. Similarly, pyrolysis of oil contaminated  
281 brownfield soil showed significant amounts of single ring aromatic and polyaromatic  
282 hydrocarbons (indicative of the oil content) with very high amounts of benzene and  
283 naphthalene captured in the initial scrubber (see Table 4). Interestingly, the compound profile  
284 observed in the scrubbers post-pyrolysis appear to be the same observed in a prior  
285 characterisation study of the pre-pyrolysed material (raw feedstock). This data is important as  
286 it shows a potential for soil remediation following contamination. Analysis of the post-pyrolysed  
287 soil (vial solvent extractions) showed a decrease of 80.5% of oily sludge contaminant in the  
288 remaining sample. This data is important as it shows potential for contaminated soil  
289 remediation and for recycling this feedstock to generate a source of fuel given the high calorific  
290 value (>30 MJ/kg) of these compounds.

291

### 292 3.3. The recycling of contaminated acetone scrubbers

293 In the interest of meeting the needs of a Circular Economy the remediation of contaminated  
294 acetone for less volatile species was also explored; this was achieved by comparing levels of  
295 VOCs and SVOCs before and after evaporating (and re-condensing) using a distillation  
296 apparatus, at a temperature representing heat that may be sequestered from pyrolysis through  
297 simple heat exchange (e.g. 60 °C). However, given this temperature was significantly lower  
298 than that of pyrolysis (700 °C), it was anticipated that the remediation of the more volatile  
299 BTEX components may be limited due to condensation within the acetone extract. Pleasingly  
300 a colourless liquid was generated following 'scrubber recycling' and most promisingly, SVOCs  
301 were undetectable within the scrubber, with some less volatile BTEX compounds

302 (ethylbenzene, p-xylene and styrene) showing a significant reduction in levels of 67 %, 65.4  
303 %, 82.4 %, respectively (see Supplementary for details). This pilot data therefore, highlights  
304 the potential of acetone as a 'recyclable' capture method for pollution generated via  
305 thermochemical conversion of different feedstocks, aligned with the principles of a Circular  
306 Economy.

307

#### 308 **4. Conclusion**

309 Analyte capture using an acetone scrubber and analysis via direct injection GC-MS provides  
310 a simple and effective approach for monitoring and facilitating the recycling of organic waste.  
311 The greater solubility range of acetone has enabled the measurement of a wider breadth of  
312 organic pollutants, essential for de-risking the recycling of 'newer' organic feedstocks such as  
313 oil-contaminated brownfield soil and AD municipal sludge cake. This work has also shown  
314 differences in pollutants generated from materials that have been produced using the same  
315 treatment processes, highlighting the importance of material characterisation prior to  
316 release/re-use of the resulting thermochemical products.

317

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320

#### 321 **Declarations of interest**

322 None.

323

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441 **Tables**

442

443 Table 1: Summary validation data for VOCs and SVOCs showing linearity (coefficient of  
 444 determination,  $R^2$ ), and precision (%Prec) and accuracy (%Acc) of the LLOQ, AQC and ULOQ.  
 445 For the LLOQ, AQC and ULOQ, concentrations were spiked at 50 µg/L, 500 µg/L and 1000  
 446 µg/L VOC protocol and 250 µg/L, 1500 µg/L and 2000 µg/L for the SVOC method, respectively.  
 447 All analytes showed acceptable linearity ( $R^2 \geq 0.99$ ), precision and accuracy at each  
 448 concentration level (<20%).  
 449

Compound	Linearity $R^2$	LLOQ		AQC		ULOQ	
		%Acc	%Prec	%Acc	%Prec	%Acc	%Prec
<b>VOC method</b>							
Benzene	0.9965	3.72	7.61	2.24	12.39	3.18	18.36
Toluene	0.9973	-6.58	16.27	5.53	10.02	1.07	6.01
Ethylbenzene	0.9978	-18.60	4.25	2.89	6.52	3.03	8.43
1,3-dimethylbenzene	0.9984	-18.25	4.08	1.71	6.11	3.54	8.76
P-xylene	0.9983	-15.18	4.52	2.33	6.12	4.09	9.11
Styrene	0.9989	-17.38	4.11	-0.36	7.30	0.47	10.74
1-methy-2-ethylbenzene	0.9989	-17.79	6.30	2.34	6.75	2.77	7.60
1,3-dichlorobenzene	0.9998	-12.66	7.67	0.73	5.90	3.55	8.71
1, 4-dichlorobenzene	0.9998	-11.65	6.95	0.44	5.40	3.70	8.75
1,2-dichlorobenzene	0.9998	-10.61	10.03	1.18	5.89	4.12	8.45
<b>SVOC method</b>							
Napthalene	0.9992	18.00	5.42	-4.70	6.91	0.14	7.78
Acenaphthylene	0.9994	15.03	9.93	-3.26	6.65	0.28	6.38
Acenaphthene	0.9983	12.64	7.58	-3.13	5.66	1.27	6.95
Fluorene	0.9992	14.16	8.52	-3.83	4.50	-0.25	6.71
Phenanthrene	0.9994	15.25	7.46	-3.10	4.35	0.32	5.38
Anthracene	0.9981	19.81	5.58	-5.98	4.94	-2.05	7.69
Fluoranthene	0.9997	8.91	9.81	-3.21	4.59	-1.29	7.06
Pyrene	0.9963	10.11	6.64	-3.48	4.60	-0.74	6.36
Benza(a)anthracene	0.9990	10.98	15.93	-2.15	5.67	-0.73	4.01
Chrysene	0.9963	16.12	9.09	-1.45	5.17	-0.71	3.95
Benza(b)fluoranthene	0.9913	3.18	14.30	-2.64	6.00	-0.22	4.40
Benzo(a)pyrene	0.9932	16.47	10.19	-2.00	6.35	-0.19	3.93
Indeno(123-cd)pyrene	0.9904	15.65	9.98	-2.63	6.87	-0.24	5.11
Dibenza(ah)anthracene	0.9920	14.25	9.53	-1.87	7.32	0.37	3.98
Benzo (ghi) perylene	0.9981	11.15	10.42	-2.18	6.46	-1.02	5.27
Phenol	0.9967	12.33	4.62	-1.74	10.32	3.09	10.93
2-chlorophenol	0.9975	11.76	4.97	-3.71	9.12	0.44	9.45
2-methyl phenol	0.9950	15.77	3.24	-1.51	8.31	0.81	9.24
4-methyl phenol	0.9969	12.70	6.45	-2.58	7.73	0.97	9.31
2-nitro phenol	0.9949	7.29	5.40	-2.75	10.86	-0.94	6.85
2,3-dimethyl phenol	0.9982	6.33	6.44	-1.32	8.84	-2.00	6.76
2,5-dichlorophenol	0.9973	13.82	6.08	-2.01	7.66	-0.46	8.23
2,6-dichlorophenol	0.9997	8.21	6.84	-1.62	7.72	0.07	8.39
4-chloro-3-methylphenol	0.9930	14.44	3.38	-0.77	7.67	1.28	9.71
2,3,6-trichloro phenol	0.9977	8.60	7.67	-4.18	7.16	-1.70	6.34
2,3,5-trichlorophenol	0.9993	5.01	7.76	4.70	10.17	5.48	9.91
4-nitrophenol	1.000	-9.27	14.74	-2.80	8.58	-2.42	7.20
Pentachlorophenol	0.9871	4.96	14.35	0.75	8.33	1.74	8.27

Table 2: Table listing the compounds identified within the scrubbers from the pyrolysis of anaerobically digested sludge cake from a wastewater treatment plant in Ghana at 700 °C. Some of the compounds have been quantified by targeted analysis while those untargeted species have been elucidated by their mass spectrum and semi-quantified in 1 mL aliquot of scrubber (150 mL acetone) by comparing the peak area to an IS. ^targeted compounds, #non-targeted compounds, ND – none detected.

Anaerobically digested sludge cake (Ghana)	Compound name	Scrubber concentration (mg/L)		
		1	2	3
Volatile aromatic compounds <sup>^</sup>	Benzene	8.00	19.47	ND
	Toluene	22.10	44.18	ND
	Ethylbenzene	4.91	2.13	ND
	p-xylene	2.75	0.87	ND
	Styrene	4.49	0.80	ND
	1,3-dimethylbenzene	2.95	0.60	ND
Phenolic compounds <sup>^</sup>	Phenol	5.20	ND	ND
	4-methylphenol	2.27	ND	ND
	2-methylphenol	22.49	ND	ND
	2,3-dimethylphenol	3.13	ND	ND
Nitrogen containing compounds (LOD <0.1 mg/L) <sup>#</sup>	N-isopropyl cyclohexamine			
	2-ethylamino methyl cyclohexanone	5.47	2.07	ND
	2,2,6,6-tetramethyl-4-piperidinone	37.61	19.19	ND
		26.91	30.49	ND
	n-cyclohexylacrylamide	1.53	1.47	ND
	n-cyclohexyl-propanamide	13.62	13.73	ND
	1-butyl-2,5 dimethyl-1H-pyrrol	6.33	2.33	ND
	1,2,2,5-tetramethyl-3-piperidinone	7.47	4.73	ND
		4.80	ND	ND
	Indole	4.87	ND	ND
	7-methyl indolizine	5.53	ND	ND
Glutamic acid dibutyl ester				
<b>Estimated total tar content (mg/L)</b>		<b>192.43</b>	<b>142.06</b>	<b>&lt;0.100</b>
<b>Mass of tar (mg)</b>		<b>28.86</b>	<b>21.31</b>	<b>&lt;0.015</b>

Table 3: Table listing the compounds identified within the scrubbers from the pyrolysis of UK anaerobically digested (AD) sludge cake at 700 °C. Some of the compounds have been quantified by targeted analysis while those untargeted species have been elucidated by their mass spectrum and semi-quantified in 1 mL aliquot of scrubber (150 mL acetone) by comparing the peak area to an IS. ^targeted compounds, #non-targeted compounds, ND – none detected.

Anaerobically digested sludge cake (UK)	Compound name	Scrubber concentration (mg/L)		
		1	2	3
Volatile aromatic compounds <sup>^</sup>	Benzene	6.50	0.38	ND
	Toluene	32.40	0.75	ND
	Ethylbenzene	6.50	0.22	ND
	o-xylene	15.31	0.13	ND
	p-xylene	2.00	ND	ND
	styrene	11.40	0.15	ND
	1,3-dimethylbenzene	1.72	ND	ND
	1-methyl-2-ethylbenzene	0.66	ND	ND
Polycyclic aromatic compounds <sup>^</sup>	Naphthalene	5.00	0.36	ND
	Acenaphthylene	0.74	0.15	ND
	Phenanthrene	1.30	0.24	ND
	Anthracene	0.30	ND	ND
	Fluoranthene	0.21	0.01	ND
	Pyrene	0.30	ND	ND
	Benzo (b) fluoranthene	0.11	ND	ND
	Benzo (a) anthracene	0.11	ND	ND
Phenolic compounds <sup>^</sup>	Phenol	4.60	0.89	ND
	4-methylphenol	2.40	0.43	ND
	2-methylphenol	6.50	0.83	ND
	2,3-dimethylphenol	6.50	0.60	ND
Nitrogen containing compounds (LOD <0.1 mg/L) <sup>#</sup>	N-isopropyl cyclohexamine	3.93	ND	ND
	2-ethylaminomethyl cyclohexanone	22.52	2.26	ND
	N-cyclohexylpropanamide	18.31	1.73	ND
	n-cyclohexylacrylamide	3.88	ND	ND
	2,2,6,6-tetramethyl-4-piperidinone	19.09	0.54	ND
	1,2,2,5-tetramethyl-3-piperidinone	7.52	2.05	ND
	3-hydroxy-1-isopropyl-2-methyl-4(1H)-pyridinone	1.29	ND	ND
	5-pentyl-1-H-1,2,4-triazol amine	0.83	ND	ND
	5-hexyl-1-H-1,2,4-triazol amine	1.13	ND	ND
<b>Estimated total tar content (mg/L)</b>		<b>183.06</b>	<b>11.72</b>	<b>&lt;0.100</b>
<b>Mass of tar (mg)</b>		<b>27.46</b>	<b>1.76</b>	<b>&lt;0.015</b>

Table 4: Table listing the compounds identified within the scrubbers from the pyrolysis of oil-contaminated brownfield soil at 700 °C. Some of the compounds have been quantified by targeted analysis while untargeted species have been elucidated by their mass spectrum and semi-quantified in 1 mL aliquot of scrubber (150 mL acetone) by comparing the peak area to an IS. ^targeted compounds, #non-targeted compounds, ND – none detected.

Oil contaminated brown field soil	Compound name	Scrubber concentration (mg/L)		
		1	2	3
Volatile aromatic compounds^	Benzene	184.00	1.80	ND
	Toluene	73.28	0.36	ND
	Ethylbenzene	5.16	0.08	ND
	Styrene	24.92	0.03	ND
	p-Xylene	8.52	0.19	ND
	m-Xylene	5.92	0.09	ND
Phenolic compounds^	Phenol	2.50	ND	ND
Targeted* and non-targeted polyaromatic compounds	Naphthalene*	169.61	4.13	ND
	2-methylnaphthalene	2.12	0.74	ND
	1-methylnaphthalene	11.71	0.42	ND
	Biphenyl	8.40	0.33	ND
	1, 6-dimethylnaphthalene	5.79	0.22	ND
	1, 7-dimethylnaphthalene	9.36	0.37	ND
	2-ethenylnaphthalene	4.24	0.02	ND
	Acenaphthylene*	27.6	1.02	ND
	Acenaphthylene derivatives	5.46	0.21	ND
	Phenylene	4.43	ND	ND
	Fluorene*	14.22	0.04	ND
	Dibenzothiophene	4.15	0.55	ND
	Phenanthrene*	67.60	0.23	ND
	2-methylanthracene	11.20	2.39	ND
	8,9-dihydro-4-cyclopenta (def) - phenanthrene	9.14	0.40	ND
	Anthracene*	16.23	0.43	ND
	2-phenylnaphthalene	4.92	0.64	ND
	Fluoranthene*	20.41	0.22	ND
	Pyrene*	27.62	0.73	ND
	Benz(a)anthracene*	8.00	0.94	ND
	Chrysene*	8.20	0.33	ND
	Benzo (a) pyrene*	3.54	0.32	ND
	Benz (b) fluoranthene*	5.47	0.32	ND
Indeno (123-cd) pyrene*	1.20	0.26	ND	
Dibenza (ah) anthracene*	0.36	0.04	ND	
Benzo (ghi) perylene*	1.52	ND	ND	
<b>Estimated total tar content (mg/L)</b>		<b>756.80</b>	<b>17.85</b>	<b>&lt;0.10</b>
<b>Mass of tar (mg)</b>		<b>113.52</b>	<b>2.68</b>	<b>0.015</b>

## Supplementary

Table S1: Table detailing the mass scan parameters used for quantitation of volatile and semi-volatile compounds.

Compound	Full mass scan ( <i>m/z</i> )	Retention time (minutes)	SIM scan ( <i>m/z</i> )
<b>Volatile</b>			
Benzene and Toluene	50-350	2.00-3.80	78, 91
Ethyl benzene		3.80-4.55	91
Xylene and Styrene		4.55-4.80	91, 104
Benzene (1-methyl 2-ethyl)		4.80-5.70	105
Dichlorobenzene		5.70-6.50	146
D8-Napthalene, Trichlorobenzene		6.50-16.33	136, 179
<b>Semi-volatile</b>			
Chrysene and Benzo (a) anthracene	50-450	14.00-20.00	228
Indeno (1,2,3 cd)-pyrene, Dibenzo (ab) anthracene, Benzo (ghi) perylene		20.00-24.00	276, 278

Table S2: Table detailing the typical chemical composition and energy content of the pyrolysis feedstocks and products generated. The lipid and semi-volatile composition of feedstocks were determined by pentane extraction and GC-MS full scan using spiked internal standards for semi-quantification. The nitrogen content for solid material was determined by standard Kjeldahl method. The total energy content of feedstocks was determined by bomb calorimetry and the syngas derived from pyrolysis of the feedstocks was calculated by from the GC-TCD analysis of the permanent gases calculated based on molar percentage.

Sample	Lipid/semi-volatile composition in feedstock		Mass of nitrogen content (mg/Kg)	Calorific value		Syngas composition Mol %			
	Source	Mass (mg/Kg)		Feedstock (MJ/Kg)	Syngas (MJ/m <sup>3</sup> )	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>
Pine wood	Terpenoids	195.84	N/A	18.67	6.34	45.3	1.98	<0.1	2.71
UK AD sludge cake	Lipids and dietary fats	230.13	2.5	12.15	3.04	22.6	1.1	<0.1	<0.1
Ghana AD sludge cake	Sterols	3500	3.5	18.00	6.41	45.5	7.58	3.35	<0.1
Brown field soil	10% mass contaminated with PAHs	equiv. 2500	N/A (Kjeldahl)	7.02	0.725	3.3	<0.1	<0.1	<0.1

Table S3: Table listing the compounds identified within the scrubbers from the pyrolysis of pine wood at 700 °C. Targeted compounds have been quantified while untargeted species have been elucidated by their mass spectrum and semi-quantified in 1 mL aliquot of scrubber (150 mL acetone) by comparing the peak area to an IS. ^targeted compounds, #non-targeted compounds, ND – none detected.

Pine wood	Compounds identified	Scrubber concentration (mg/L)		
		1	2	3
Volatile aromatic compounds <sup>^</sup>	Benzene	31.71	ND	ND
	Toluene	25.60	0.16	ND
	Ethylbenzene	9.03	0.18	ND
	1,3-dimethylbenzene	5.50	ND	ND
	Styrene	3.00	ND	ND
	P-xylene	2.74	ND	ND
Polycyclic aromatic compounds <sup>^</sup>	Naphthalene	2.70	0.70	ND
	Acenaphthylene	0.46	0.13	ND
	Phenanthrene	0.41	ND	ND
	Anthracene	0.18	ND	ND
	Fluorene	0.21	0.15	ND
Phenolic compounds <sup>^</sup>	Phenol	10.98	1.90	ND
	4-methylphenol	5.79	1.52	ND
	2-methylphenol	6.84	1.01	ND
	2,3-dimethylphenol	7.40	1.00	ND
	4-chloro-3-methylphenol	3.02	0.52	ND
Non-Targeted Other (LOD 0.05 mg/L) <sup>#</sup>	2-Furancarboxylic acid	5.70	2.05	ND
	2-Furanmethanol	7.30	2.79	ND
	2-Furanone	6.28	1.99	ND
	2-Cyclopenten-1-one	7.11	2.76	ND
	Carbanicacic-phenyl ester	9.23	4.11	ND
	3-methylcyclopentane	10.06	3.43	ND
	Benzyl alcohol	4.47	1.98	ND
	2-methoxyphenol	20.86	10.35	ND
	Cresol	31.06	27.57	ND
	6-methyl-4-pyrimidinol	21.75	ND	ND
	4-ethyl-2-hydroxy-cyclopentene-1-one	5.21	5.29	ND
	Salicyl alcohol	6.32	3.65	ND
	p-ethylguaicol	16.20	3.21	ND
	4-ethenyl-2-methoxyphenol	16.20	5.06	ND
	Isoeugenol	32.00	11.91	ND
	Anhydro-D-mannosan	150.12	5.74	ND
	Conifyl aldehyde	10.78	2.15	ND
	Arabinose	6.35	0.67	ND
	Dehydroabietic acid	0.10	ND	ND
	Methyldehydroabietate	0.060	ND	ND
Retene	0.067	ND	ND	
<b>Estimated total tar content (mg/L)</b>		482.80	101.98	<0.100
<b>Total mass of tar (mg)</b>		72.42	15.30	<0.015

Table S4: Table describing the compounds identified in the acetone pooled scrubber before and after acetone remediation.

	Compounds identified	Scrubber concentration (mg/L)	
		Pre-recycling	Recycled
<b>VOC Targeted</b>	Benzene	10.84	9.17
	Toluene	9.86	8.19
	Ethylbenzene	1.37	0.46
	P-xylene	0.78	0.27
	Styrene	2.56	0.45
	<b>Total</b>	<b>25.41</b>	<b>18.54</b>
	<b>SVOC Targeted</b>	Phenol	3.89
2-methylphenol		2.0	ND
4-methylphenol		2.62	ND
2,3-dimethylphenol		2.23	ND
Naphthalene		0.60	ND
4-chlorophenol		0.70	ND
Phenanthrene		0.35	ND
<b>Total</b>		<b>12.39</b>	<b>&lt;0.01</b>
<b>Non-targeted</b>	2-propyl-1-pentanol methyl ether	1.09	ND
	N-cyclohexyl propanamide	6.21	ND
	2,2,6,6 Tetramethy-4-piperidinone	2.41	ND
	Cresol	8.69	ND
	2, 5-dimethoxytoluene	1.19	ND
	Isoegenol	1.37	ND
	Andro D-mannosan	3.00	ND
	<b>Total</b>	<b>23.96</b>	<b>&lt;0.100</b>

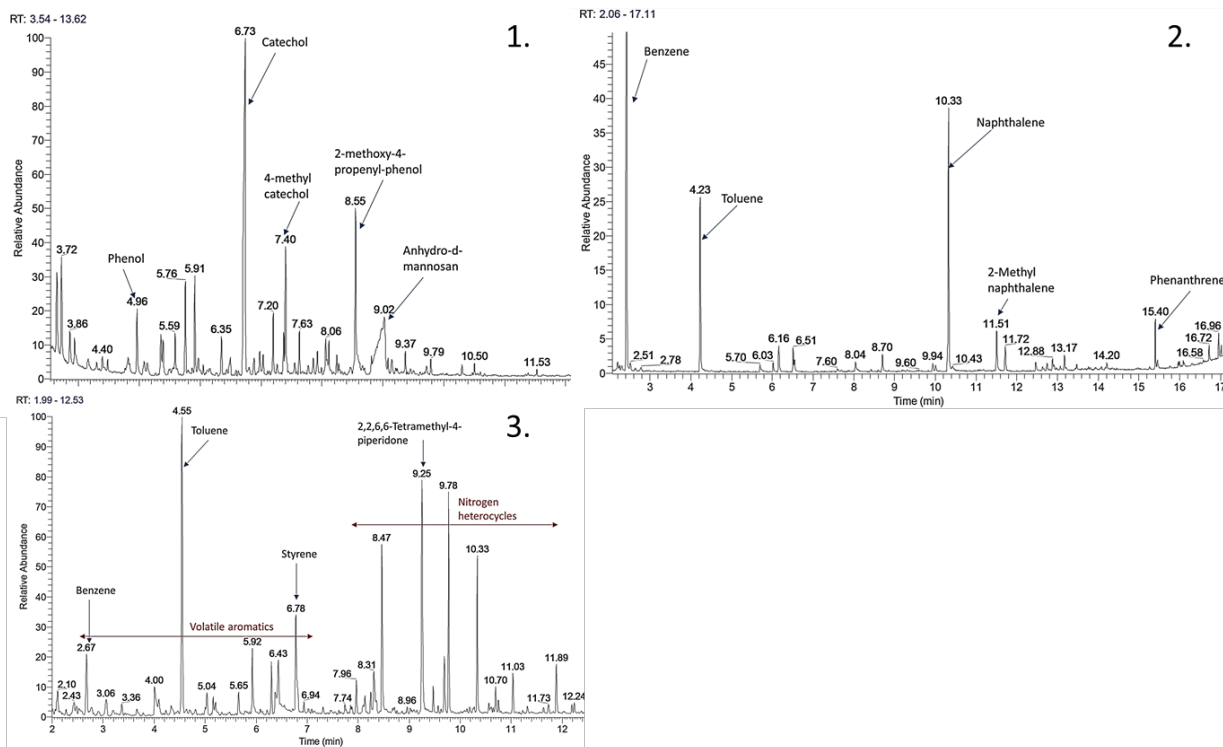


Figure S1: Shows the total ion chromatogram of scrubber 1 showing volatile and semi-volatile organic compounds captured during the thermal treatment (pyrolysis) of pine wood (1.), brown field soil contaminated with oily sludge (2.) and UK AD sludge cake (3.). The main components of each spectra were identified from NIST 2.0 library search.