**Supporting information for:**

Distribution of PAHs, PCBs, and PCDD/Fs in products from the full-scale pyrolysis of diverse contaminated organic waste

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Table S.1. PAH, PCDD/F, and PCB congeners analyzed, the respective number of aromatic rings (PAH) or chlorine atoms (PCDD/F and PCB) and toxic equivalency factors (TEF) analyzed in this study.

|  |  |  |  |
| --- | --- | --- | --- |
| **PAH-16** | **Abbreviation** | **Aromatic rings** | **TEF** |
| Naphthalene | Nap | 2 | 0.001 |
| Acenaphthylene | Acy | 3 | 0.001 |
| Acenaphthene | Ace | 3 | 0.001 |
| Fluorene | Flu | 3 | 0.001 |
| Phenanthrene | Phen | 3 | 0.001 |
| Anthracene | Ant | 3 | 0.01 |
| Fluoranthene | Flt | 4 | 0.001 |
| Pyrene | Pyr | 4 | 0.001 |
| Benz(a)anthracene | B(a)A | 4 | 0.1 |
| Chrysene | Cry | 4 | 0.01 |
| Benzo(b)fluoranthene | B(b)F | 5 | 0.1 |
| Benzo(k)fluoranthene | B(k)F | 5 | 0.1 |
| Benzo(a)pyrene | B(a)P | 5 | 1 |
| Indeno(1,2,3-cd)pyrene | IP | 6 | 0.1 |
| Benzo(ghi)perylene | B(ghi)P | 6 | 0.01 |
| Dibenz(ah)anthracene | DB(ah)A | 5 | 1 |
| **PCDD/F-17** | **Abbreviation** | **Chlorines** | **TEF** |
| 2,3,7,8-Tetrachlorodibenzodioxin | 2,3,7,8-TCDD | 4 | 1 |
| 1,2,3,7,8-Pentachlorodibenzodioxin | 1,2,3,7,8-PeCDD | 5 | 1 |
| 1,2,3,4,7,8-Hexachlorodibenxodioxin | 1,2,3,4,7,8-HxCDD | 6 | 0.1 |
| 1,2,3,6,7,8-Hexachlorodibenxodioxin | 1,2,3,6,7,8-HxCDD | 6 | 0.1 |
| 1,2,3,7,8,9-Hexachlorodibenxodioxin | 1,2,3,7,8,9-HxCDD | 6 | 0.1 |
| 1,2,3,4,6,7,8-Heptachlorodibenxodioxin | 1,2,3,4,6,7,8-HpCDD | 7 | 0.01 |
| Octachlorodibenzodioxin | OCDD | 8 | 0.003 |
| 2,3,7,8-Tetrachlorodibenzofuran | 2,3,7,8-TCDF | 4 | 0.1 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 1,2,3,7,8-PeCDF | 5 | 0.05 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 2,3,4,7,8-PeCDF | 5 | 0.5 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 1,2,3,4,7,8-HxCDF | 6 | 0.1 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 1,2,3,6,7,8-HxCDF | 6 | 0.1 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 1,2,3,7,8,9-HxCDF | 6 | 0.1 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 2,3,4,6,7,8-HxCDF | 6 | 0.1 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 1,2,3,4,6,7,8-HpCDF | 7 | 0.01 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 1,2,3,4,7,8,9-HpCDF | 6 | 0.01 |
| Octachlorodibenzofuran | OCDF | 8 | 0.001 |
| **PCB-7** | **Abbreviation** | **Chlorines** |  |
| 2,4,4'-Trichlorobiphenyl | PCB28 | 3 |  |
| 2,2',5,5'-Tetrachlorobiphenyl | PCB52 | 4 |  |
| 2,2',4,5,5'-Pentachlorobiphenyl | PCB101 | 5 |  |
| 2,2',3,4,4',5'-Hexachlorobiphenyl | PCB138 | 5 |  |
| 2,2',4,4',5,5'-Hexachlorobiphenyl | PCB153 | 6 |  |
| 2,2',3,4,4',5,5'-Heptachlorobiphenyl | PCB180 | 6 |  |
| 2,3',4,4',5-Pentachlorobiphenyl | PCB118 | 7 |  |

Table S.2. Pyrolysis product yields and gas sampling volumes.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Feedstock** | **Pyrolysis temp. (°C)** | **Yield (%)** | | | **Gas sampling volumes** | | | |
| **Biochar** | **Oil** | **Gas** | **V\_gas\_m3** | **V\_gas\_m3kg** | **V\_gas\_m3kg\_propane** | **V\_gas\_m3kg\_feedstock** |
| CWC | 500 | 18 % | 31 % | 52 % | 2.3 | 101.2 | 647.5 | 18.3 |
| 600 | 20 % | 32 % | 49 % | 2.3 | 93.2 | 310.9 | 17.8 |
| 700 | 20 % | 27 % | 53 % | 2.3 | 88.9 | 223.7 | 18.0 |
| 750 | 16 % | 13 % | 71 % |  | 120.1 | 303.5 | 17.8 |
| DSS-1 | 500 | 62 % | 21 % | 17 % | 2.1 | 7.6 | 7.6 | 0.6 |
| 600 | 58 % | 22 % | 20 % | 1.6 | 10.3 | 10.3 | 5.0 |
| 700 | 62 % | 22 % | 16 % | 2.4 | 6.7 | 6.7 | 4.6 |
| 800 | 70 % | 21 % | 10 % |  | 3.8 | 3.8 | 5.0 |
| DSS-2 | 500 | 52 % | 28 % | 20 % | 1.5 | 12.6 | 12.6 | 4.7 |
| 600 | 43 % | 25 % | 32 % | 2.3 | 27.6 | 58.8 | 8.8 |
| 700 | 46 % | 38 % | 16 % | 2.3 | 17.8 | 24.2 | 11.4 |
| 800 | 40 % | 31 % | 29 % | 2.1 | 27.0 | 31.9 | 9.0 |
| FWR | 600 | 35 % | 24 % | 41 % | 2.4 | 37.0 | 44.0 | 12.6 |
| 800 | 35 % | 22 % | 43 % | 2.0 | 41.3 | 55.8 | 14.8 |
| GW | 500 | 31 % | 42 % | 27 % | 2.1 | 22.2 | 42.0 | 6.9 |
| 600 | 32 % | 24 % | 44 % |  | 37.6 | 61.5 | 10.2 |
| 800 | 24 % | 23 % | 54 % | 1.3 | 58.0 | 64.0 | 12.1 |
| LSS | 600 | 57 % | 21 % | 22 % | 2.4 | 16.0 | 20.6 | 0.3 |
| 750 | 49 % | 19 % | 32 % | 2.4 | 78.9 | 294.4 | 32.1 |
| WT | 500 | 30 % | 48 % | 22 % | 1.9 | 17.2 | 26.2 | 2.3 |
| 600 | 27 % | 41 % | 32 % | 2.4 | 29.1 | 44.1 | 6.7 |
| 700 | 21 % | 26 % | 53 % | 1.9 | 66.4 | 91.4 | 12.0 |
| 800 | 18 % | 24 % | 58 % | 1.2 | 73.8 | 79.3 | 12.8 |

Table S.3. Total concentration of PAHs, PCDD/Fs and PCBs in feedstock (F) and biochars produced at various temperatures (500-800 ˚C) and European Biochar Certificate (EBC) limit values.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **PAHs (mg/kg)** | | | | | | **PCDD/F (ng/kg)** | | | **PCBs (µg/kg)** | | |
|  | **Temp.** | **∑16 EPA PAH** | **∑16 EPA PAH EBC limit** | **∑8 EFSA PAH** | **∑8 EFSA PAH EBC limit** | **∑17 PCDD/F (TEQ)** | **∑PCDD/F EBC limit** | **∑17 PCDD/F** | **∑7 PCB** | **∑PCB EBC limit** | **∑6 PCB EBC limit** |
| DSS-1 | F | 1.48 ± 0.03 | 6 mg/kg DM  for all EBC  products | 0.52 ± 0.01 | 1 mg/kg DM  (4 mg/kg DM for EBC-BasicMaterials) | 8.3 ± 0.4 | 20 ng/kg I-TEQ OMS | 2011 ± 118 | 21 | 200 µg/kg DM | 10 µg TEQ/kg DM |
| 500 | 18 ± 1 | 3.1 ± 0.09 | n.d. | 2.69 | 1.7 |
| 600 | 22 ± 1 | 1.73 ± 0.07 | n.d. | 2.01 | <LOQ |
| 700 | 7 ± 0.3 | 0.25 ± 0.01 | n.d. | 2.58 | 1.3 |
| 800 | 3.7 ± 0.1 | 0.14 ± 0.01 | n.d. | 0.44 | 0.3 |
| DSS-2 | F | 0.5 ± 0.02 | 0.148 ± 0.004 | 1.78 ± 0.04 | 302 ± 6 | 7.6 ± 0.3 |
| 500 | 37 ± 2 | 2.54 ± 0.08 | 0.03 | 3.31 | 0.6 |
| 600 | 22.9 ± 0.5 | 0.83 ± 0.01 | 0.02 | 2.89 | 0.4 |
| 700 | 5.9 ± 0.5 | 0.17 ± 0.01 | 0.03 | 3.15 | 0.4 |
| 800 | 23 ± 1 | 1.02 ± 0.05 | 0.03 | 2.66 | 0.5 |
| FWR | F | 0.38 ± 0.01 | 0.08 ± 0.004 | 1.18 ± 0.05 | 323 ± 14 | 9.2 ± 0.4 |
| 600 | 9.1 ± 0.5 | 0.22 ± 0.01 | 0.1 | 9.5 |  |
| 800 | 6.7 ± 0.3 | 0.2 ± 0.01 | 0.003 | 0.3 |  |
| LSS | F | 0.98 ± 0.03 | 0.39 ± 0.01 | 3 ± 0.1 | 589 ± 29 | 17 ± 1 |
| 600 | 3.38 ± 0.04 | 0.15 ± 0.01 | n.d. | n.d. | 0.3 |
| 750 | 2.7 ± 0.1 | 0.13 ± 0.01 | n.d. | n.d. | 0.2 |
| WT | F | 5 ± 0.1 | 1.08 ± 0.02 |  |  |  |  |  |  |
| 500 | 2.5 ± 0.1 | 0.16 ± 0.01 |  |  |  |  |  |  |
| 600 | 118 ± 5 | 7.46 ± 0.22 |  |  |  |  |  |  |
| 700 | 21 ± 1 | 0.45 ± 0.01 |  |  |  |  |  |  |
| 800 | 5 ± 0.3 | 0.13 ± 0.01 |  |  |  |  |  |  |
| GW | F | 0.89 ± 0.02 | 0.141 ± 0.005 |  |  |  |  |  |  |
| 500 | 14 ± 1 | 0.54 ± 0.02 |  |  |  |  |  |  |
| 600 | 5 ± 0.2 | 0.31 ± 0.01 |  |  |  |  |  |  |
| 800 | 7.1 ± 0.3 | 0.25 ± 0.01 |  |  |  |  |  |  |
| CWC | F | <LOQ | <LOQ |  |  |  |  |  |  |
| 500 | 9.4 ± 2.5 | 0.39 ± 0.08 |  |  |  |  |  |  |
| 600 | 17 ± 5 | 0.56 ± 0.19 |  |  |  |  |  |  |
| 700 | 6.6 ± 3.4 | 0.23 ± 0.09 |  |  |  |  |  |  |
| 750 | 6.4 ± 0.1 | 0.26 ± 0.02 |  |  |  |  |  |  |

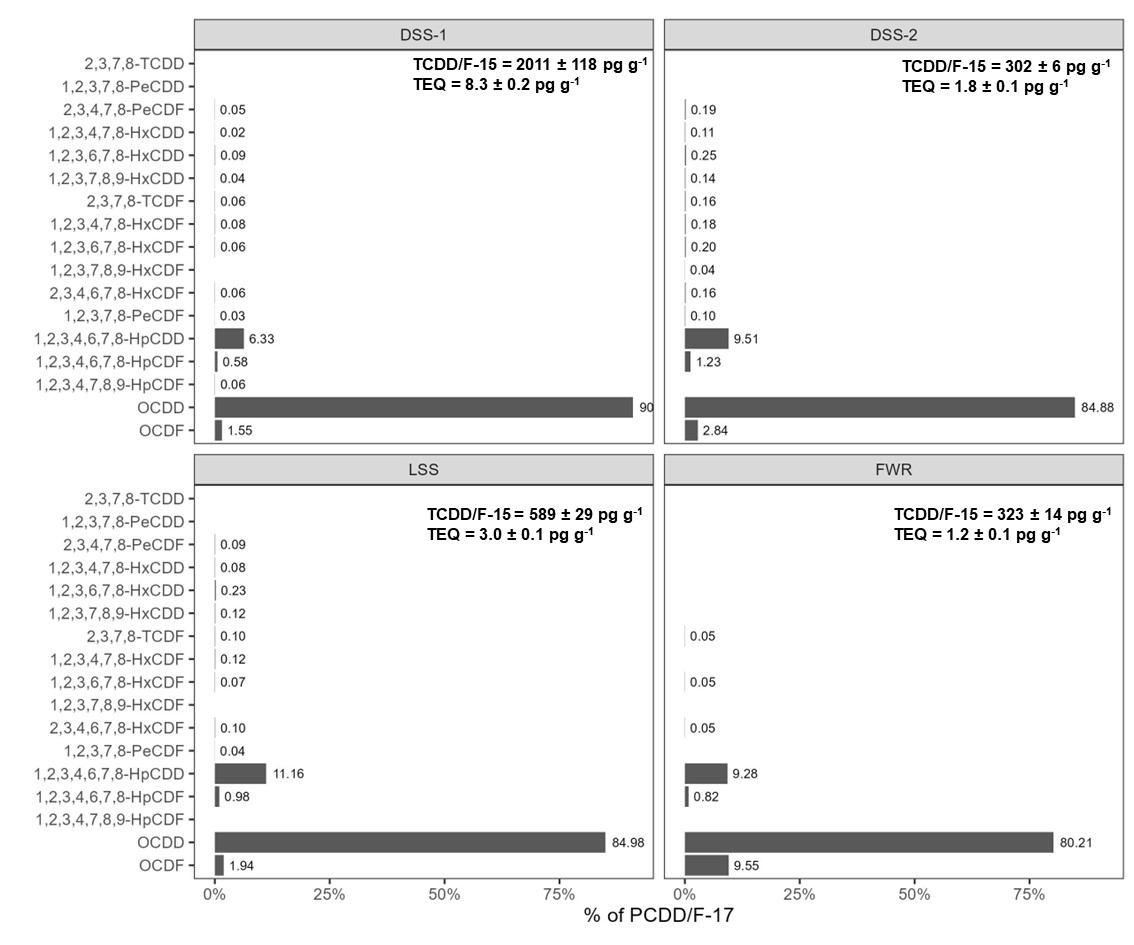


Figure S.1 Total concentration (∑PCDD/F-17, pg g-1), toxic equivalence quotients (TEQ) relative to 2,3,7,8-PCDD, and distribution of dioxins (% of ∑PCDD/F-17) detected in the digested sewage sludges (DSS-1 and DSS-2), limed sewage sludge (LSS), and food waste reject (FWR) prior to pyrolysis, in order of descending TEF.

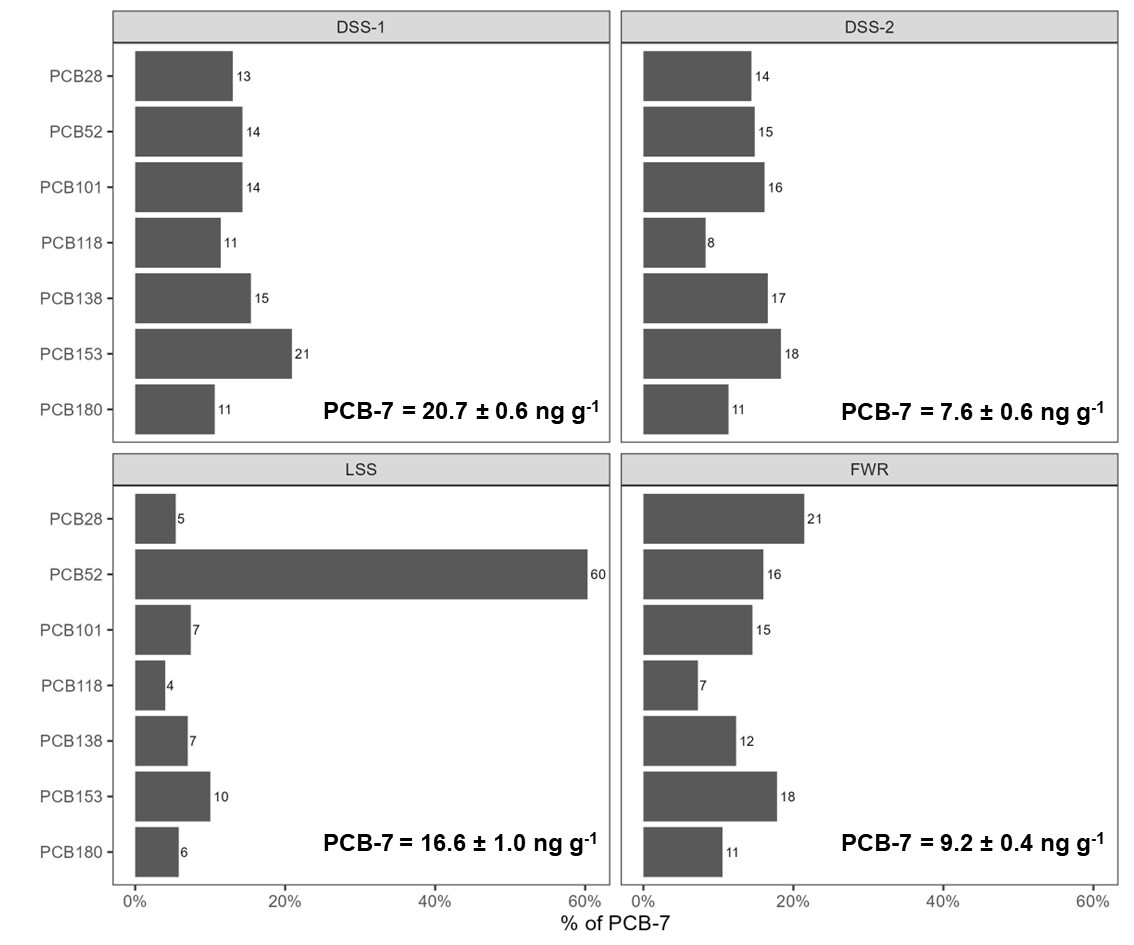
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Figure S.2 Total concentration (ng PCB-7 g-1), and distribution of PCBs (% of PCB-7) detected in the digested sewage sludges (DSS-1 and DSS-2), limed sewage sludge (LSS), and food waste reject (FWR) prior to pyrolysis.

Timeline

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Figure S.3 Total concentration (∑PAH-16 µg g-1), toxic equivalence quotients (TEQ) relative to B(a)P, and distribution of PAHs (% of ∑PAH-16) detected in the digested sewage sludges (DSS-1 and DSS-2), dewatered sewage sludge (DWSS), limed sewage sludge (LSS), food waste reject (FWR), waste timber (WT), garden waste (GW), and wood chips (CWC) prior to pyrolysis.

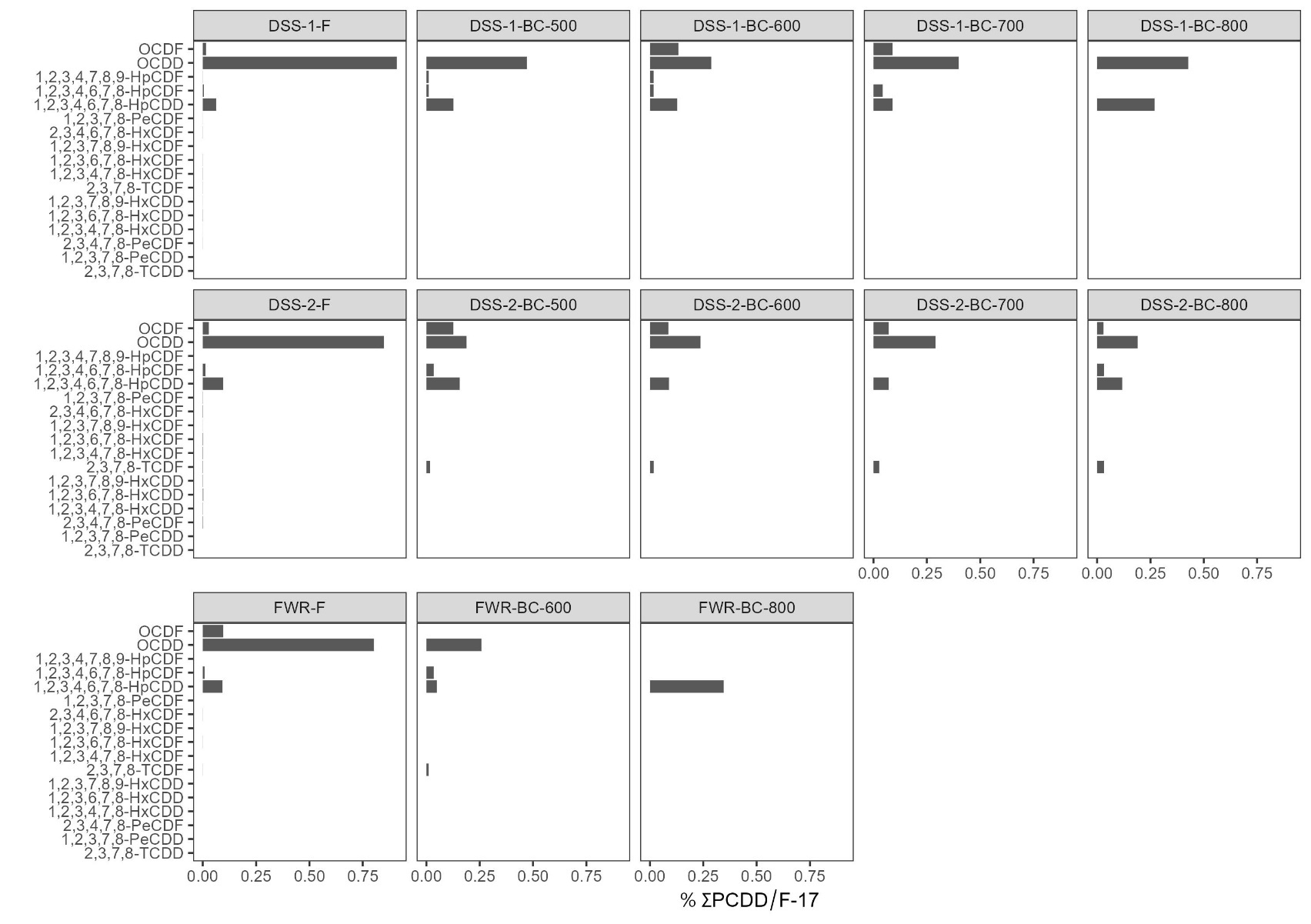


Figure 4 Distribution of PCDD/Fs (% of ∑PCDD/F-17) in the feedstock (F) and biochars (BC) at different temperatures (500-800 ˚C) for the digested sludge 1 (DSS-1), digested sludge 2 (DSS-2), and food waste reject (FWR).

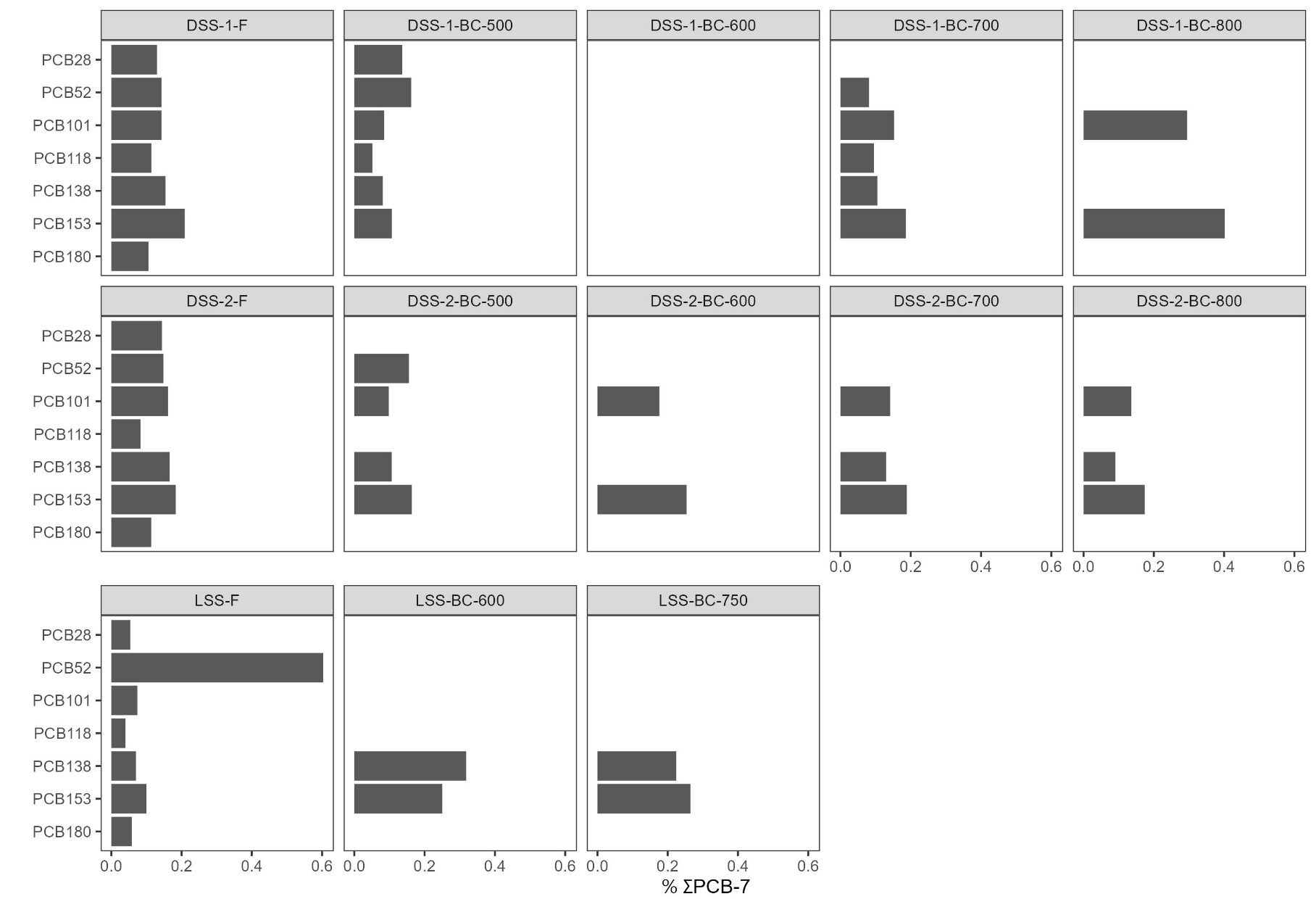


Figure S.5 Distribution of PCBs (% of ∑PCB-7) in the feedstock (F) and biochars (BC) at different temperatures (500-800 ˚C) for the digested sludge 1 (DSS-1), digested sludge 2 (DSS-2), and limed sludge feedstocks (LSS).

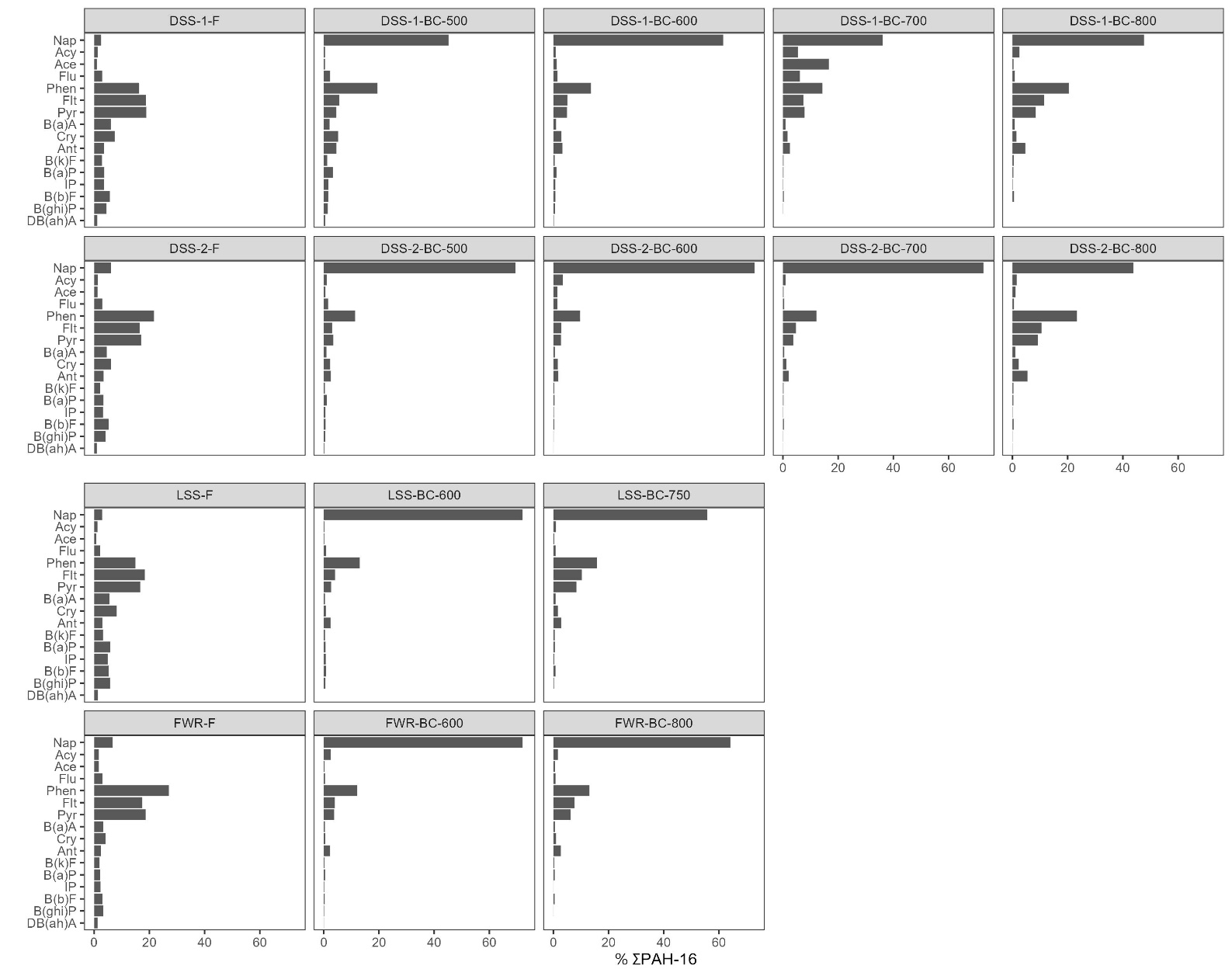


Figure S.6 Distribution of PAHs (% of ∑PAH-16) in the feedstock (F) and biochars (BC) at different temperatures (500-800 ˚C) for the sewage sludge and food waste reject samples.

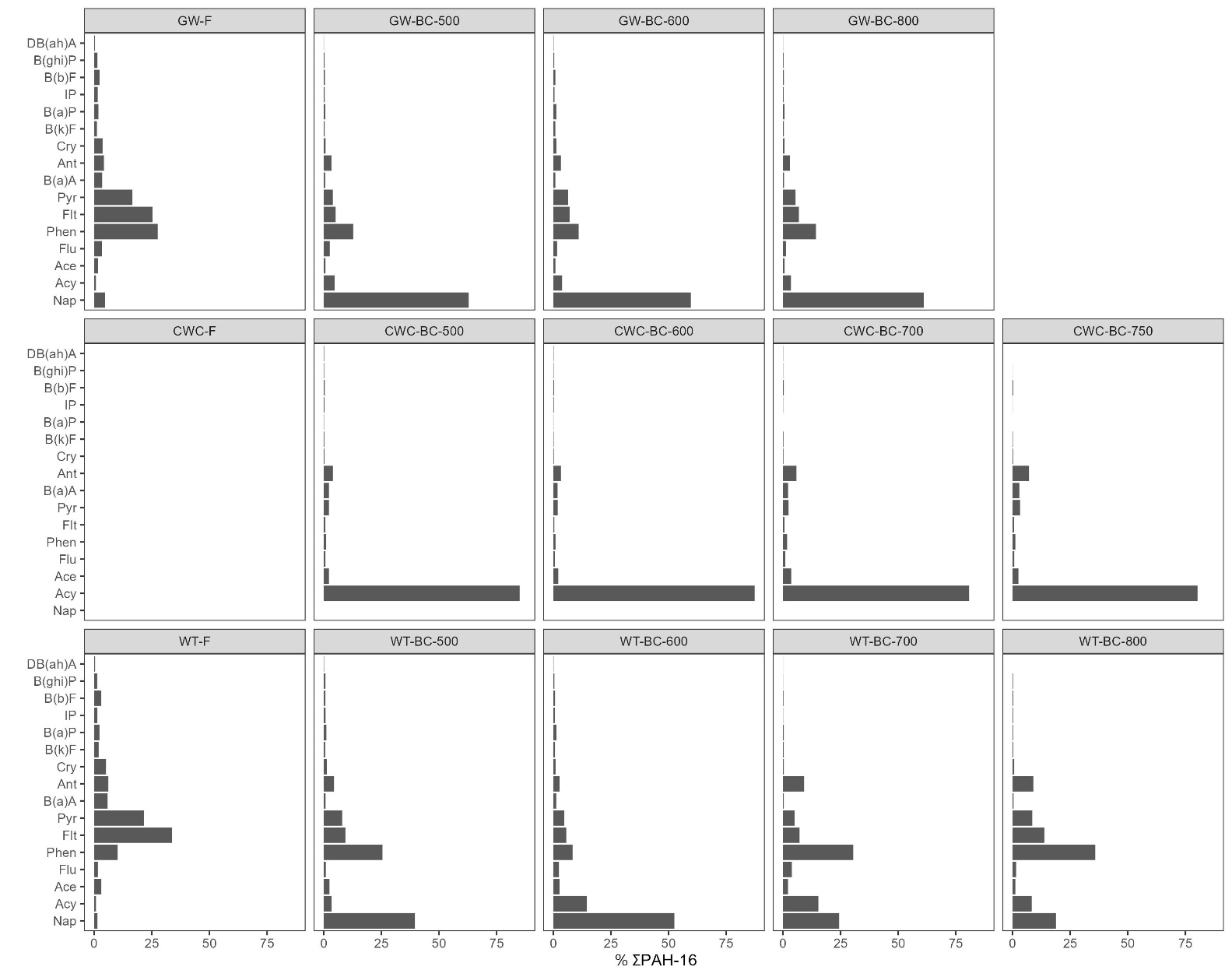


Figure S.7 Distribution of PAHs (% of ∑PAH-16) in the feedstock (F) and biochars (BC) at different temperatures (500-800 ˚C) for the wood-based samples

Table S.4 Total concentration of each pollutant class (PCDD/Fs, PAHs, and PCBs) in feedstock (F) and biochars. The feedstocks were measured standard deviations were conducted in triplicate measurements (n=3). (you have this in the main MS now.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **FWR** | | | **DSS-1** | | | | | **DSS-2** | | | | | **LSS** | | |
|  | **F** | **600** | **800** | **F** | **500** | **600** | **700** | **800** | **F** | **500** | **600** | **700** | **800** | **F** | **600** | **750** |
| **∑PAH**  **(mg kg-1)** | 323 ± 14 | 9.5 | 0.30 | 2011 ± 118 | 2.7 | 2.0 | 2.6 | 0.44 | 302 ± 6 | 3.3 | 2.9 | 3.2 | 2.7 | 58 ± 29 | n.d. | n.d. |
| **∑PCDD/F-17**  **(ng TEQ kg-1)** | 1.2 ± 0.1 | 0.1 | 0.003 | 8.3 ± 0.2 | 0.01 | 0.01 | 0.01 | 0.003 | 1.8 ± 0.1 | 0.03 | 0.02 | 0.03 | 0.03 | 3.0 ± 0.1 | n.d. | n.d. |
| **∑PCB-7**  **(µg kg-1)** | 9.2 ± 0.4 | n.d. | n.d. | 21 ± 1 | 1.70 | <LOQ | 1.3 | 0.26 | 7.6 ± 1 | 0.64 | 0.39 | 0.39 | 0.53 | 17 ± 1 | 0.25 | 0.24 |

Table S.5 PAHs and sum PAH-16 in CWC and DSS-1 condensate at different temperatures (mg kg-1). Add tables for PCDD/Fs and PCBs too

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **CWC** | | | | | | **DSS-1** | | |
|  | **500** | | **600** | **700** | **750** | | **600** | **700** | **800** |
| Naphthalene | 886 | 1130 | 1880 | 1690 | 361 | 3499 | 2190 | 2010 | 1390 |
| Acenaphthylene | 1560 | 2313 | 4260 | 4740 | 1160 | 5456 | 257 | 219 | 169 |
| Acenaphthene | 62.4 | 84.7 | 152 | 123 | 16.1 | 155 | 73 | 44 | 29.8 |
| Fluorene | 312 | 460 | 859 | 694 | 127 | 1403 | 470 | 303 | 223 |
| Phenanthrene | 178 | 224 | 480 | 456 | 118 | 1300 | 558 | 395 | 297 |
| Anthracene | 56.9 | 73 | 155 | 148 | 38.8 | 464 | 191 | 141 | 98.7 |
| Fluoranthene | 51.6 | 62.3 | 143 | 138 | 43.9 | 425 | 126 | 98.1 | 76.4 |
| Pyrene | 47.7 | 57.6 | 120 | 118 | 39.7 | 390 | 129 | 95.9 | 74 |
| Benz(a)anthracene | 22.6 | 28.1 | 55.2 | 47.1 | 19.1 | 162 | 96.1 | 73.6 | 56.9 |
| Chrysene | 19 | 24.1 | 47.1 | 40.2 | 20.9 | 135 | 145 | 127 | 82.9 |
| Benzo(b)fluoranthene | 8.25 | 9.82 | 22.8 | 18.2 | 11.1 | 60.9 | 26.8 | 22.1 | 17.7 |
| Benzo(k)fluoranthene | 6.65 | 7.44 | 18.4 | 14.6 | 9.61 | 46.9 | 14.4 | 12.1 | 8.65 |
| Benzo(a)pyrene | 15.5 | 18 | 41.2 | 34 | 19.6 | 121 | 36.2 | 28.9 | 22.5 |
| Indeno(1,2,3-cd)pyrene | 5.24 | 5.76 | 14.2 | 11.1 | 7.91 | 51.5 | 13.1 | 10.3 | 8.19 |
| Benzo(ghi)perylene | 3.87 | 4.14 | 10.3 | 8.89 | 7.58 | 40.3 | 9.15 | 7.03 | 5.41 |
| Dibenz(ah)anthracene | 1.64 | 1.94 | 4.42 | 3.41 | 2.17 | 12 | 5.91 | 3.89 | 2.98 |
| **Phase separation** | very low tar | much tar | very low tar | very low tar | very low tar | much tar | none | none | none |
| **∑PAH-16 (mg kg-1)** | **3237** | **4504** | **8263** | **8285** | **2002** | **13722** | **4341** | **3591** | **2563** |

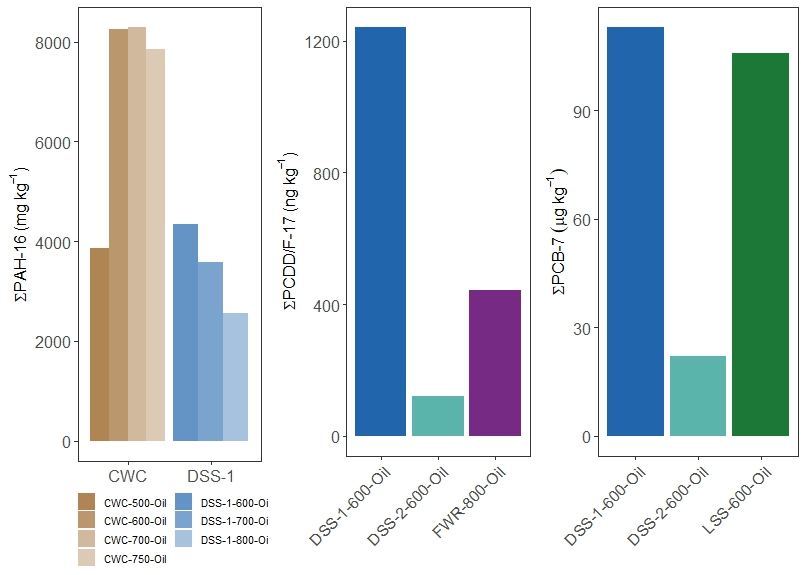


Figure S.1 Pollutant concentration in pyrolysis oil.

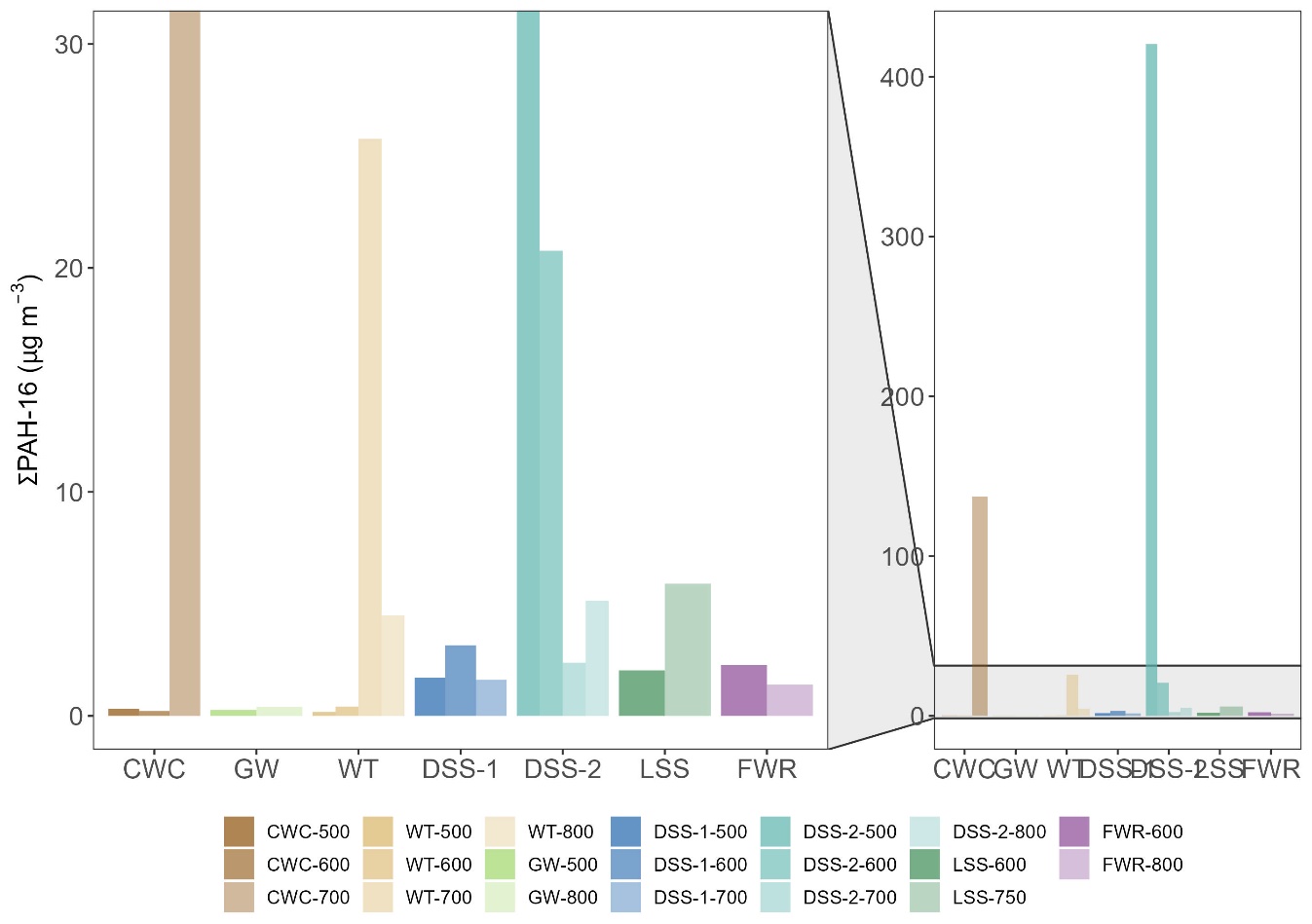


Figure S. 2 Pollutant concentration in exhaust

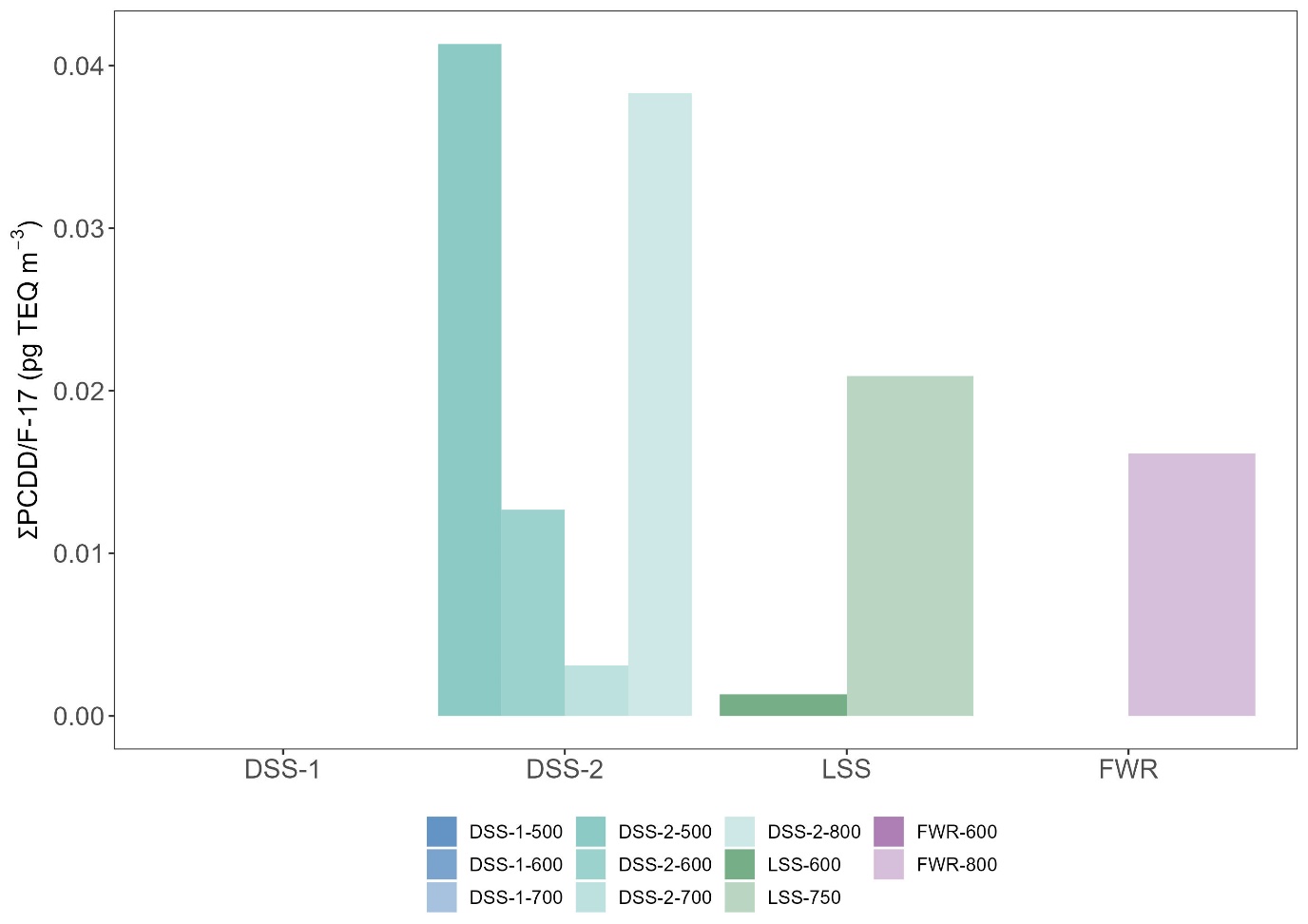


Table S.6 Chloride (Cl) content in feedstocks.

|  |  |
| --- | --- |
| **feedstock** | **Cl (g/kg)** |
| DSS-1 | 0.24 ± 0.01 |
| DSS-2 | 0.33 ± 0.08 |
| FWR | 2.57 ± 0.15 |
| GW | <LOD |
| LSS | 0.02 ± 0.03 |
| WT | 0.01 ± 0.01 |
| GW | <LOD |

Table S.7. Concentration of pollutants in pyrolysis oil.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Feedstock** | **Pyr.**  **temp. ˚C** | **pollutant class** | **source** | **yield** | **Conc. (total)** | **Conc. (TEQ)** | **Conc. (yield corrected)** | **n() congeners detected** |
| CWC | 500 | PAH-16  (mg/kg) | wood | 0.31 | 3871±571 | 28±1.9 | 1191±176 | 16 |
| 600 | 0.32 | 8263 | 67 | 2627 | 16 |
| 700 | 0.27 | 8285 | 56 | 2204 | 16 |
| 750 | 0.13 | 7862±3990 | 107±73 | 1012±514 | 16 |
| DSS-1 | 600 | sludge | 0.22 | 4341 | 64 | 946 | 16 |
| 700 | 0.22 | 3591 | 51 | 801 | 16 |
| 800 | 0.21 | 2563 | 39 | 530 | 16 |
| DSS-1 | 600 | PCDD/F-17 (ng/kg) | sludge | 0.22 | 1241 | 50 | 270 | 15 |
| DSS-2 | 600 | 0.25 | 120 | 1.8 | 30 | 5 |
| FWR | 800 | reject | 0.22 | 442 | 16 | 99 | 9 |
| DSS-1 | 600 | PCB-7  (µg/kg) | sludge | 0.22 | 113 |  | 25 | 7 |
| DSS-2 | 600 | 0.25 | 22 |  | 5 | 7 |
| LSS | 600 | 0.21 | 106 |  | 22 | 7 |