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1 **Smouldering to Treat PFAS in Sewage Sludge**

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20 **Abstract**

21 Wastewater treatment plants are accumulation points for per- and polyfluoroalkyl substances  
22 (PFAS) facilitating treatment. This study explores using smouldering combustion to treat PFAS in  
23 sewage sludge. Base case experiments at the laboratory scale (LAB) used dried sludge mixed with  
24 sand. High moisture content (MC) LAB tests, 75% MC sludge by mass, explored impacts of MC on  
25 treatment and supplemented with granular activated carbon (GAC) to achieve sufficient  
26 temperatures for thermal destruction of PFAS. Additional LAB tests explored using calcium oxide  
27 (CaO) to support fluorine mineralization. Further tests performed at an oil-drum scale (DRUM)  
28 assessed scale on PFAS removal. Pre-treatment sludge and post-treatment ash samples from all  
29 tests were analyzed for 12 PFAS (2C-8C). Additional emissions samples were collected from all  
30 LAB tests and analyzed for 12 PFAS and hydrogen fluoride.

31 Smouldering removed all monitored PFAS from DRUM tests, and 4-8 carbon chain length PFAS  
32 from LAB tests. For base case tests, PFOS and PFOA were completely removed from sludge;  
33 however, high content in the emissions (79-94% of total PFAS by mass) shows volatilization  
34 without degradation. Smouldering high MC sludge at ~900 °C (30 g GAC/kg sand) improved PFAS  
35 degradation compared to treatment below 800 °C (<20 g GAC/kg sand). Addition of CaO before  
36 smouldering reduced PFAS content in emissions by 97-99% by mass; with minimal PFAS retained  
37 in the ash and minimal HF production, the fluorine from the PFAS was likely mineralized in the  
38 ash. Co-smouldering with CaO had dual benefits of removing PFAS while minimizing other  
39 hazardous emission by-products.

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41 **Keywords**

42 Smouldering combustion; Sewage sludge; PFAS; Remediation; Wastewater treatment

43 **List of Abbreviations**

44	BDL	Below detection limit
45	CaF <sub>2</sub>	Calcium fluoride
46	CaO	Calcium oxide
47	DI	Deionized water
48	DRUM	Oil-drum reactor scale experiments (0.3 m radius)
49	GAC	Granular activated carbon
50	HF	Hydrofluoric acid
51	H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
52	LAB	Laboratory scale reactor experiments (0.08 m radius)
53	LC-MS/MS	Liquid chromatography with tandem mass spectrometry
54	MC	Moisture content
55	PFAS	Per- and polyfluoroalkyl substances
56	PFBA	Perfluorobutanoic acid
57	PFBS	Perfluorobutanesulfonic acid
58	PFHpA	Perfluoroheptanoic acid
59	PFHpS	Perfluoroheptanesulfonic acid
60	PFHxA	Perfluorohexanoic acid
61	PFHxS	Perfluorohexanesulfonic acid
62	PFPA	Perfluoropropanoic acid
63	PFPeA	Perfluoropentanoic acid
64	PFPeS	Perfluoropentanesulfonic acid
65	PFOA	Perfluorooctanoic acid

66	PFOS	Perfluorooctane sulfonate
67	ppb	Parts per billion
68	TFA	Trifluoroethylene
69	TISAB	Total Ionic Strength Adjustment Buffer
70	USEPA	United States Environmental Protection Agency
71	WWTP	Wastewater treatment plant

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91 **1.0 Introduction**

92 Endocrine disrupting per- and polyfluoroalkyl substances (PFAS) are compounds of concern that  
93 accumulate in sewage sludge and other organic environments (Clarke and Smith, 2011). PFAS are  
94 a group of thousands of chemicals, with the most common being perfluorooctane sulfonate  
95 (PFOS) and perfluorooctanoic acid (PFOA)(Buck et al., 2011). Due to their toxicity and persistence  
96 in the environment, both PFOS and PFOA production have been restricted around the world  
97 (UNEP, 2019; USEPA, 2020). The properties of PFAS, including chemical and thermal stability,  
98 made them useful in a wide range of materials and applications (Kissa, 2001); however, these  
99 same properties also make PFAS widespread in the environment and challenging to remediate.

100 Wastewater treatment plants (WWTPs) are key accumulation points for PFAS, and are therefore  
101 valuable opportunities for intervention technologies (Arvaniti et al., 2014, 2012; Gómez-Canela  
102 et al., 2012; Moodie et al., 2021; Sindiku et al., 2013; Sun et al., 2011; Venkatesan and Halden,  
103 2013; Yan et al., 2012). Sources of PFAS to WWTPs include industrial discharge (Kunacheva et al.,  
104 2011; Washington et al., 2010); landfill leachate (Gallen et al., 2016); and domestic sources (Pan  
105 et al., 2010). Since conventional wastewater treatment methods are ineffective at treating PFAS,  
106 WWTPs tend to be a sink for these compounds (Ahrens et al., 2009). Additionally, WWTPs are  
107 potential sources of PFAS since they can be formed via precursor degradation (Houtz et al., 2018;  
108 Lakshminarasimman et al., 2021; Pan et al., 2010; Sepulvado et al., 2011). Within WWTPs, most  
109 PFAS tends to be concentrated in sewage sludge (Clarke and Smith, 2011; Milinovic et al., 2016;  
110 Zhang et al., 2013). Therefore, sewage sludge management needs to consider the fate of these  
111 compounds. Landfilling sewage sludge can result in PFAS entering the environmental via leachate

112 (Ahrens et al., 2011; Gallen et al., 2016). A common alternative to landfilling sewage sludge is  
113 direct land application as a soil amendment. Land applied sludges can be a significant source of  
114 PFAS contamination to the environment through surface runoff or infiltration (Sepulvado et al.,  
115 2011), or circulation in the environment via plant uptake (Blaine et al., 2013). With increasing  
116 regulations, especially for PFOS and PFOA (USEPA, 2021), there is significant interest in  
117 developing methods to remove and degrade PFAS from sewage sludge. For example, various  
118 thermal treatment methods demonstrate good potential to remove PFAS from sewage sludge  
119 though their application is relatively limited. Current thermal methods being explored include  
120 pyrolysis (Kim et al., 2015; Kundu et al., 2021), hydrothermal treatments (Yu et al., 2020; Zhang  
121 and Liang, 2021), and incineration (Wang et al., 2013). In particular, incineration shows strong  
122 potential destroying contaminants present in sewage sludge (Ross et al., 2018), but it is also  
123 energy intensive and expensive (Werther and Ogada, 1999). Incineration of dried sludge  
124 amended with hydrated lime has been shown to effectively mineralize >70% of fluorine at  
125 treatment temperatures >600°C (Wang et al., 2013). While demonstrating a highly effective  
126 method of treating PFAS contaminated sludge, the long residence times, and the high sludge to  
127 calcium ratio (0.43 g Ca(OH)<sub>2</sub> : 1 g sludge) may make scaling this treatment method challenging  
128 and expensive. Pyrolysis has shown mixed results in its ability to remove PFAS from sewage  
129 sludge, with one study finding insignificant reductions in the biochar following pyrolysis (Kim et  
130 al., 2015), and another study showing effective removal (>90%) of PFOS and PFOA using pyrolysis  
131 at 500°C while sequestering other PFAS in produced biochar by adsorption (Kundu et al., 2021).  
132 Similarly, hydrothermal treatments have also shown mixed results in their ability to treat PFAS.  
133 One study reported that reductions in PFAAs were often coupled with increases in PFAA

134 precursors (Zhang and Liang, 2021), while another showed reductions of ~35-45% PFOS and  
135 ~100% PFOA from sludge at temperatures between 260-350°C with mobilization to produced  
136 biocrude oil noted (Yu et al., 2020). Characterization of gaseous emissions was not included and  
137 PFAS may have been present there, too. Also, these studies used spiked rather than native PFAS;  
138 results with aged PFAS may be different. Ultrasound (Zhang et al., 2022), and acid-microwave  
139 assisted persulfate digestion (Hamid and Li, 2018) have shown to be ineffective to treat PFAS in  
140 sewage sludge; however, these studies do provide valuable information that can help advance  
141 thermal and other treatment technologies. Overall, more work is needed to advance effective  
142 treatment of PFAS in wastewater treatment systems.

143 Smouldering combustion was recently shown to be an effective method of treating PFAS  
144 contaminated soils (Duchesne et al., 2020). Smouldering is a flameless form of burning that  
145 occurs on the surface of a fuel within a porous medium (Torero et al., 2020). This exothermic  
146 reaction produces heat from the heterogenous oxidation of the fuel (i.e., oxygen directly attacks  
147 the fuel surface) (Ohlemiller, 1985). Smouldering has the potential to be self-sustaining with no  
148 additional energy input required after ignition if the oxidation reactions release sufficient energy  
149 to overcome heat losses (Ohlemiller, 1985). Smouldering combustion has been demonstrated to  
150 be an effective, energy efficient remediation strategy for contaminated soils (Gerhard et al.,  
151 2020; Grant et al., 2016; Pironi et al., 2009; Scholes et al., 2015; Switzer et al., 2009), wastewater  
152 sludges (Rashwan et al., 2016), and faeces (Yermán et al., 2015). In this context, the organic  
153 contaminants and/or wastes are the fuel embedded within a soil mixture, and self-sustained  
154 smouldering destroys virtually all of it by oxidation; typically, only inert soil grains (e.g., quartz  
155 sand) and inorganic ash remain after treatment. To treat PFAS contaminated soil, a supplemental



156 fuel was added (i.e., granular activated carbon (GAC)) to achieve sufficient temperature for PFAS  
157 degradation (~900 °C) (Duchesne et al., 2020). While smouldering sewage sludge has been  
158 explored in the context of process optimization (Rashwan et al., 2016), scaling (Feng et al., 2021;  
159 Rashwan et al., 2021a), landfilling potential (Feng et al., 2020), resource recovery potential  
160 (Fournie et al., 2022a), and the behaviour of dioxins and furans (Fournie et al., 2022b), the fate  
161 of PFAS during sewage sludge smouldering is unknown.

162 The aim of this study is to evaluate the use of smouldering to treat PFAS in sewage sludge. This  
163 was done in three phases: (I) evaluating PFAS removal, (II) assessing methods of improving  
164 degradation of PFAS, and (III) exploring the impact of scaling on PFAS removal. Phases I and II  
165 consisted of a series of laboratory smouldering experiments that evaluated PFAS fate in varied  
166 input and operating conditions, including high moisture content sludge, as well as CaO addition,  
167 which has been shown to improve PFAS mineralization during thermal treatment of sewage  
168 sludge (Wang et al., 2013). Finally, Phase III explored how scale impacts PFAS removal. This work  
169 presents the first comprehensive evaluation of PFAS fate during smouldering treatment of  
170 sewage sludge.

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176 **2.0 Materials and Methods**

177 *2.1 Waste collection and preparation:*

178 Sewage sludge was obtained from a wastewater treatment plant in Ontario, Canada. Complete  
179 details on wastewater processing and sludge generation at Greenway can be found elsewhere  
180 (Fournie et al., 2021; Rashwan et al., 2016). The sewage sludge was produced from a dewatered  
181 slurry of primary and secondary sludge and had an average moisture content (MC) of 74.3% on a  
182 wet-mass basis, determined using USEPA Method 1684 (Telliard, 2001). All sewage sludge utilized  
183 for the LAB tests was collected in a single batch (~40 kg) in April 2021 to minimize variability  
184 between tests. Sewage sludge utilized for the DRUM tests was collected in individual batches  
185 (~30 kg) immediately ahead of each test. DRUM tests were performed between February and  
186 June 2018.

187 Sewage sludge storage and preparation followed a modified procedure developed by Rashwan  
188 et al. (2016). Virgin sewage sludge was batch dried in an oven at 105 °C to achieve a MC of <1%.  
189 The samples were dried until there were no measurable changes in sludge mass. To homogenize  
190 the material, the dried sludge was pulverized using an immersion blender and sieved to ensure  
191 all material was <1 cm. The homogenized, dried sludge was then stored in 19 L sealed containers  
192 at 5 °C until use.

193 Preliminary analysis of sewage sludge samples collected between February and June 2018  
194 showed that concentrations of PFOS ranged from 224 – 2230 ng/g and PFOA was below the  
195 detection limit for all samples (Table S1-1, Supplementary Materials, Section S1). The high  
196 variability in sewage sludge PFAS concentrations could be due to temporal changes which has

197 been recently explored (Thompson et al., 2022). The sewage sludge contained similarly high PFOS  
198 compared to treatment studies that have spiked their sewage sludge (Hamid and Li, 2018; Yu et  
199 al., 2020); therefore, the sewage sludge was used without additional PFAS spiking. Furthermore,  
200 not spiking the sludge can improve our understanding of treating PFAS bound within the sludge  
201 matrix.

## 202 *2.2 Smouldering reactor set-up and procedure:*

203 Cylindrical reactors fabricated from stainless steel were used for all laboratory experiments (LAB:  
204 0.08 m radius, 0.008 m<sup>3</sup> volume) and larger scale tests in oil-drum sized reactors (DRUM: 0.3 m  
205 radius, 0.27 m<sup>3</sup> volume). The reactors were wrapped in 0.051 m thick insulation (LAB: MinWool®,  
206 Johns Manville; DRUM: FyreWrap® Elite® Blanket, Unifrax). The reactor set-up and  
207 instrumentation are shown for LAB tests in Figure 1 and DRUM tests in Supplementary Materials,  
208 Section S3.

209 Seven LAB and three DRUM tests were conducted, summarized in Table 1. The LAB tests were  
210 separated into two phases. Phase I consisted of three repeat LAB base case tests (I-1, I-2, and I-  
211 3) using dried sewage sludge (MC <1%) mixed with silica sand in a ratio of 6.5:1 sand-to-dried  
212 sludge (g/g). This ratio is higher than what has been used in previous studies smouldering dried  
213 sludge (Fournie et al., 2022a, 2022b; Rashwan et al., 2021a) to increase the fuel loading and  
214 therefore the ability to quantify PFAS products in the emissions and post-treatment materials  
215 (herein referred to as 'ash'). Phase II consisted of four LAB tests: two with higher MC sludge (75%  
216 by mass) combined with GAC (CAS: 7440-44-0, PTI Process Chemicals, 100 mesh size, mean  
217 particle size < 0.15 mm) at 20 g GAC/kg sand (II-1-1) and 30 g GAC/kg sand (II-1-2) and two with

218 CaO (CAS: 1305-788, Carmeuse Lime & Stone) (II-2-1: 5 g CaO/kg sand; II-2-2: 10 g CaO/kg sand).  
219 In the high MC tests, sludge was combined with sand in a ratio of 4.5:1 sand-to-sludge (g/g) on a  
220 wet-mass basis and GAC was added to these higher MC tests to achieve smouldering  
221 temperatures >900 °C by supplementing the low calorific value sludge. These concentrations  
222 were chosen based on previous research involving PFAS-contaminated soils (Duchesne et al.,  
223 2020). The other two tests were similar to the base case, 6.5:1 sand-to-dried sludge, with the  
224 addition of CaO to react with the PFAS in the sludge and mineralize fluorine at treatment  
225 temperatures <900 °C (Wang et al., 2015, 2013). Concentrations were selected to explore how  
226 CaO content impacted mineralization without significantly reducing the fuel bed permeability,  
227 which can deteriorate smouldering performance (Wang et al., 2021). Phase III consisted of three  
228 DRUM tests, the first with dried sludge (III-1), and the other two with high MC sludge (III-2: 72.3%  
229 by mass; III-3: 74.4% by mass). The sand-to-sludge ratios for III-1 and III-2 were 6.5:1, and III-3  
230 was 4.5:1, all on a wet-mass basis. No CaO or GAC was added for these tests.

231 Sludge was mechanically mixed with coarse silica sand (CAS: 14808-60-7,  $1.18 \leq$  mean grain  
232 diameter  $\leq 2.36$  mm, WP #2, K & E) to achieve the target sand-to-sludge ratio (Table 1), and  
233 create a smoulderable mixture (Rashwan et al., 2016). For the higher MC LAB tests (II-1-1 and II-  
234 1-2), water was added to the dried sludge and sand to reconstitute the sludge back to 75% MC  
235 following a method developed by (Rashwan et al., 2016). For the higher MC DRUM tests (III-2 and  
236 III-3), sludge was collected just prior to experimentation and, therefore, did not require any  
237 drying or rewetting prior to treatment. A clean sand cap (~5-10 cm thick) was added on top of  
238 the fuel bed to lower the exiting temperatures when the smouldering front approached the top  
239 of the reactor.

240 Reactors were placed on load cells (LAB: KCC150, Metler Toledo; DRUM: KD1500, Mettler Toledo)  
241 to measure each experiment's fuel destruction rate. Thermocouples (LAB: Type K, 0.0032 m  
242 diameter, Omega Ltd; DRUM: Type K, 0.0064 m diameter; Kelvin Technologies) were installed  
243 along the full height of the reactors to record process temperatures throughout each test. For  
244 the LAB tests, centreline (8 cm) and half-radius (5 cm) thermocouples were installed to better  
245 understand the temperature evolutions throughout the reactor, which has shown to vary more  
246 significantly at smaller scales (Rashwan et al., 2021b).

247 The DRUM test set-up and procedure using convective ignition is described in detail elsewhere  
248 (Fournie et al., 2022a, 2022b; Rashwan, 2020; Rashwan et al., 2021c) and can be found in  
249 Supplementary Materials, Section S3. The LAB test set-up and procedure using conductive  
250 ignition followed established methods (Duchesne et al., 2020; Rashwan et al., 2016), and is  
251 described briefly below (Figure 1).

252 The LAB reactor was ignited using a coiled resistive heater (450 W, 120 V, Watlow Ltd.), with no  
253 air flow. When the first thermocouple reached 200 °C, air was injected into the reactor base at a  
254 Darcy flux of 5.0 cm/s – via a mass flux controller (FMA5400/5500 Series, Omega Ltd.) – for the  
255 remainder of the test until the fuel bed cooled to ambient temperature. Smouldering was  
256 confirmed when the first thermocouple within the fuel bed peaked (3.5 cm from the base). The  
257 heater was then turned off and the airflow supported the self-sustaining smouldering  
258 propagation. The end of each experiment was identified when the smouldering front reached the  
259 end of the fuel bed.

260 *2.3 Emissions and sample collection:*

261 For every experiment, rigorous cleaning procedures were conducted based on (Duchesne et al.,  
262 2020). Ahead of each experiment, all glassware and tubing used in the emissions sampling train  
263 and sample bottles were rinsed three times with deionized (DI) water, isopropanol (CAS 67-63-0,  
264 Fisher Chemical), and methanol (CAS 67-56-1, Fisher Chemical).

265 During experiments, an NDIR infrared gas analyzer measured oxygen, carbon dioxide, and carbon  
266 monoxide data from the LAB tests every two seconds (Model: 7500ZA, Teledyne Analytical  
267 Instruments). Two emissions sampling trains (Figure 1) were used in the LAB tests to subsample  
268 the emissions exiting the reactor for (1) PFAS and (2) hydrofluoric acid (HF). The PFAS sampling  
269 train was adapted from (Duchesne et al., 2020), and the HF sampling train from EPA Method 26  
270 (2019). These methods have been shown to effectively collect PFAS and HF in emissions from LAB  
271 smouldering tests (Duchesne et al., 2020). Each PFAS emissions sample was collected using a  
272 vacuum pump (DOA-P704-AA, Gast) pulling sample at ~3 L/min. The emissions passed through  
273 two sorption tubes containing 50 g GAC aligned in series to prevent PFAS breakthrough and  
274 topped with 1 – 3 g glass wool to secure the GAC. The HF emissions sample was similarly collected  
275 using a vacuum pump pulling sample at ~3 L/min. Emissions from the HF train passed through 4  
276 glass impingers within an ice bath (4.0 °C). Impingers 1 and 4 were empty and impingers 2 and 3  
277 contained 15 mL of 1% H<sub>2</sub>SO<sub>4</sub>. The total volume of emissions sample collected from each sampling  
278 train were quantified using flow totalizers (PFAS train: FMA6616 Series, Omega Ltd.; HF train:  
279 FMA4316 Series, Omega Ltd.). More details on emissions sampling can be found in  
280 Supplementary Materials, Section S2. Leakage of ambient air into each sampling train was  
281 quantified and minimized to <5% (see Supplementary Materials, Section S2 for procedure).

282 Following emissions capture, GAC from each sorption tube was collected in full and stored in  
283 PFAS free polypropylene bottles (VWR®). Additional PFAS samples included the glass wool, tubing  
284 rinse, and sorption tube rinses. The liquid from (1) the first and second impingers, and (2) the  
285 third and fourth impingers were combined into two HF samples. The tubing ahead of the HF  
286 emissions sampling train was rinsed using DI water and the rinse was also collected for analysis.

287 Representative samples of 100-200 g of post-treatment material (i.e., ash mixed with sand) were  
288 collected from three locations within the reactor, the sand cap (~38 – 48 cm from reactor base),  
289 the top of the fuel bed (~27 – 31 cm from reactor base), and the bottom of the fuel bed (~13 –  
290 20 cm from reactor base) (see Supplementary Materials, Section S2 for sample photos). Samples  
291 were stored in 250 mL jars at 5 °C. Since samples collected at the top and bottom of the fuel bed  
292 had similar concentrations, these values were averaged to approximate the concentration in the  
293 fuel bed following smouldering treatment (herein referred to as ‘ash’). The concentrations in the  
294 sand cap were presented separately (Supplementary Materials, Section S5).

#### 295 *2.4 Emissions and Solids Analyses*

296 Solid samples were extracted with basic methanol (0.1% ammonium hydroxide (CAS: 1336-21-6,  
297 Fisher Scientific) v/v) using 5:1 extractant-to-sample (g/g). Samples were vortexed for 30  
298 seconds, then placed on a shaker table at 30 RPM for 48 hours. Samples were then centrifuged  
299 at 4000 RPM for 10 minutes, and a sub-sample transferred to a PFAS-free HPLC vial for analysis.

300 All PFAS analyses were conducted by the Environmental Sciences Group at the Royal Military  
301 College of Canada. These analyses were completed following a modified EPA 8327 method using  
302 liquid chromatography with tandem mass spectrometry (LC-MS/MS). Full details on the analyses,

303 including quality assurance and quality control can be found in Supplementary Materials, Section  
304 S4.

305 The HF collected in the impinger liquids were analyzed using an ion probe (HQ30d-flexi, Hach).  
306 The analysis followed EPA Method 9214 (1996). Briefly, the probe was calibrated using standards  
307 between 0.5 – 2 mg/L (BDH Chemicals, VWR®). Samples were prepared with 1:1 (v/v) sample-to-  
308 TISAB solution (Supelco, Sigma Aldrich) to neutralize the sample. Samples were analyzed in  
309 triplicates and an internal standard was run between each sample.

310 A combination of X-ray diffractometer (XRD) analysis and Scanning electron microscopy with  
311 energy dispersive X-ray spectroscopy (SEM/EDX) analysis were performed on the post-treatment  
312 ash from I-1, II-2-1, II-2-2, and III-1 tests to evaluate the use of CaO to mineralize fluorine from  
313 the sludge. These analyses were performed by Surface Science Western using a Rigaku SmartLab  
314 XRD, and a Hitachi SU8230 Regulus Ultra High-Resolution Field Emission SEM. Full specifications  
315 of the instrumentation and operating conditions can be found in the Supplementary Materials,  
316 Section S9.



## 317 **3.0 Results and Discussion**

### 318 *3.1. Overview of smouldering experiments*

319 Smouldering destroyed more than 90% of the initial sludge biomass under all experimental conditions, leaving <10% as residual  
320 inorganic ash in the reactor. Peak temperatures ranged between 700 – 926 °C in LAB tests and 461 – 550 °C in DRUM tests (Table 1).

321 Smouldering of dry sewage sludge in base case tests had an average peak centreline temperature of 808 °C ± 65 °C and average  
322 propagation velocity of 0.44 ± 0.13 cm/min (Table 1). The base case tests had the most consistent temperature distributions across  
323 the radius of the reactor (Supplementary Materials, Section S2). Higher MC is a source of heat losses that typically reduces peak  
324 temperatures in the reactor (Fournie et al., 2022a; Rashwan et al., 2021a). These heat losses were offset by the addition of 20 g/kg  
325 GAC (centreline: 746 °C ± 21 °C) and exceeded by the addition of 30g/kg GAC (centreline: 905 °C ± 21 °C) (Phase II; Table 1). Both high  
326 MC/GAC tests had similar average propagation velocities (II-1-1: 0.52 ± 0.13 cm/min; II-1-2: 0.50 ± 0.09 cm/min). This aligns with  
327 previous research exploring the relationship between GAC content and smouldering temperature (Duchesne et al., 2020). The  
328 temperature profiles, sampling times, and heating rates can be found in the Supplementary Materials, Section S2 for LAB tests, and  
329 Section S3 for DRUM tests.

330 Addition of CaO at 5 and 10 g/kg did not alter the smouldering temperature, which remained consistent with base case tests, but it  
331 did impact the propagation velocities (Table 1) and heating rates of the tests (Supplementary Materials, Section S2). Increasing the

332 CaO content in the fuel mixture reduced the propagation velocity from  $0.53 \pm 0.11$  cm/min with 5 g CaO/kg sand to  $0.30 \pm 0.14$  cm/min  
333 with 10 g CaO/kg sand. Additionally, both CaO tests had slower heating rates than all other tests, consistently lower than 125 °C/min  
334 (Supplementary Materials, Section S2). In comparison, the base case and high MC/GAC tests had heating rates between 125 – 300  
335 °C/min. The lower heating rates were likely driven by physical and chemical processes. The addition of CaO may have reduced the  
336 permeability of the fuel mixture. Reductions in permeability have been shown to slow the propagation velocity of smouldering;  
337 however, they should not impact robustness (Wang et al., 2021). Furthermore, although the system is net exothermic, some aspect  
338 of the fluorine mineralization may require energy input. The presence of these additional processes may have slowed energy transfer  
339 to adjacent fuel in the system resulting in decreased heating rates during these tests.

340 The DRUM scale tests (Phase III) had lower treatment temperatures and slower propagation velocities than were observed in any of  
341 the LAB tests. The dry sludge DRUM test, III-1, had average peak centreline temperatures between 534 – 550 °C (Table 1). The two  
342 higher MC DRUM tests (i.e., III-2 and III-3) had average peak centreline temperatures between 461 – 477 °C reflecting the additional  
343 energy to vaporize water ahead of smouldering.

344 For the LAB tests, the average peak half-radius temperatures varied, sometimes significantly, from the average peak centreline  
345 temperatures. These differences in temperatures across the radius of the reactor have important implications for treating PFAS since  
346 high temperatures (>900 °C) are required for effective degradation of these compounds (Duchesne et al., 2020; Mahinroosta and

347 Senevirathna, 2020). Temperature gradients will likely not influence the removal of PFAS from the ash since it has been shown  
348 previously that PFAS volatilize at low temperatures, <400 °C (Crowner et al., 2019; Winchell et al., 2021). However, temperature  
349 gradients will impact degradation, resulting in longer chain compounds in the emissions that would still need to be treated. The  
350 temperature differences across the reactor are likely due to a combination of heterogeneities in the fuel mixtures and heat losses  
351 (Rashwan et al., 2021b). Smouldering sludge at a larger scale – closer to what could be implemented at a WWTP – could minimize  
352 these heat losses and foster more persistent high temperature regions (Rashwan et al., 2021b), and thereby improve treatment.

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370 *3.2. PFAS in virgin sludge and post-treatment solids*

371 Figure 2 outlines the initial concentrations of 12 PFAS in the sewage sludge prior to smouldering compared to the post-treatment  
372 ashes from both LAB and DRUM tests. For all tests, there was complete removal of >3C PFAS from the solids.

373 *3.2.1. LAB Experiments (Phase I and Phase II)*

374 In the base case and high MC/GAC tests, TFA (2C) was the primary compound measured in the ash. Traces of PFPA (3C) were also  
375 measured in the ash from one of the base case tests, I-2 (Supplementary Materials, Section S5). Increases of TFA were measured in  
376 the ash during the base case tests (3.1 – 15 ng/g-dry sludge) compared to what was originally present in the dried sludge (0.0 – 8.9  
377 ng/g-dry sludge), which suggests some degradation of larger PFAS during smouldering. Some retention of PFAS, primarily TFA, PFPA,  
378 and/or PFHpS, was observed in the sand cap, likely due to re-condensation (1.6 – 53 ng/g-dry sludge; Supplementary Materials, Section  
379 S5). The high MC tests had the lowest relative temperatures (Supplementary Materials, Section S2) and highest PFAS retentions in the

380 sand cap (II-1-1: 190 ng/g-dry sludge; II-1-2: 110 ng/g-dry sludge). The presence of only TFA in the sand cap of higher GAC test  
381 compared to a distribution of TFA (2C), PFPA (3C), and PFHpS (7C) in the lower GAC test suggests that the higher temperature/energy  
382 smouldering improved degradation of PFAS, breaking down the larger chains into smaller compounds. This same result was found for  
383 smouldering PFAS contaminated soils (Duchesne et al., 2020). Understanding the smouldering conditions under which significant PFAS  
384 degradation is possible for higher moisture content sludge is important because treating higher moisture content sludge can help  
385 reduce energy requirements for dewatering at wastewater treatment plants.

386 Similar to the high MC/GAC tests, both CaO tests only had retention of TFA in the ash (II-2-1: 8.9 ng/g-dry sludge; II-2-2: 19 ng/g-dry  
387 sludge). In addition to TFA, the top sand cap from both CaO tests contained PFCA (Supplementary Materials, Section S5). The top sand  
388 cap retained more total PFAS than remained in the ash for both CaO tests (II-2-1: 47 ng/g-dry sludge; II-2-2: 29 ng/g-dry sludge), likely  
389 reflecting recondensation of PFAS in the top sand cap.

### 390 3.2.2. DRUM Experiments (Phase III)

391 While the LAB tests had some retention of short-chained PFAS in the ash, primarily TFA, the DRUM tests had complete removal of all  
392 PFAS from the ash (Figure 2). The removal was irrespective of the initial PFAS content in the sludge, which varied between sludge  
393 batches collected for each DRUM test (Figure 2). The DRUM tests had lower smouldering front propagation velocities than the LAB  
394 tests (Table 1). The slower front movement means that every location was exposed to elevated treatment temperatures for longer

395 times, which likely facilitated complete removal of all PFAS from the solids. This presents an advantage of smouldering over other  
396 thermal treatment methods for removing PFAS. Smouldering is able to remove and potentially destroy PFAS as the smouldering front  
397 propagates through the fuel bed, as opposed to long residence times which have been required in other studies that do not typically  
398 destroy all PFAS (Hamid and Li, 2018; Wang et al., 2013; Yu et al., 2020; Zhang et al., 2022; Zhang and Liang, 2021).

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### 400 *3.3. PFAS in emissions*

401 Figure 3 outlines the initial contents of 12 PFAS in the sewage sludge prior to smouldering compared to the content measured in the  
402 emissions from the LAB tests.

403 The emissions from the base case tests contained primarily PFOS (4.8 – 440 ng/g-dry sludge) and PFOA (23 – 73 ng/g-dry sludge), both  
404 8C. With complete removal of PFOS from the ash and only somewhat lower PFOS in the emissions compared to the initial content in  
405 the sludge (52 – 907 ng/g-dry sludge), the higher PFOS in the emissions suggests release into the emissions without much degradation.  
406 Emissions under base case smouldering conditions would require further treatment for PFAS. Since low quantities of PFOA were  
407 originally present in the sewage sludge (0.13 – 0.79 ng/g-dry sludge), its elevated presence in the emissions is evidence of formation  
408 during smouldering, possibly through precursors (Zhang and Liang, 2021). Precursor formation of PFOS is also possible and could be

409 another explanation for some of the elevated content in the emissions. Future work could explore PFAS degradation and formation  
410 during smouldering.

411 Both higher MC/GAC tests had similar total PFAS in the emissions (II-1-1: 490 ng/g-dry sludge; II-1-2: 470 ng/g-dry sludge) but the  
412 compounds differed. Of the PFAS analyzed, II-1-1 contained primarily PFOS (430 ng/g-dry sludge; 88%) while II-1-2 comprised primarily  
413 TFA (340 ng/g-dry sludge; 72%), suggesting improved degradation with higher treatment temperatures.

414 The total PFAS content in the emissions from the CaO tests was significantly lower than all other tests (II-2-1: 15 ng/g-dry sludge; II-2-  
415 2: 10 ng/g-dry sludge). The treatment temperatures observed during both CaO tests (centreline: 760 – 880 °C; half-radius: 670 – 810  
416 °C) were likely sufficient to support mineralization of fluorine from PFAS in the presence of adequate calcium (Wang et al., 2013). The  
417 primary PFAS found in the emissions following the CaO tests was TFA (II-2-1: 8.9 ng/g-dry sludge; II-2-2: 7.7 ng/g-dry sludge). The  
418 presence of calcium to mineralize fluorine from PFAS has been shown to prevent the release of short and longer-chained PFAS (>3C)  
419 in emissions (Wang et al., 2013) and reduces the production of secondary fluorinated compounds (Riedel et al., 2021). Higher  
420 concentration of CaO (10 g CaO/kg sand) reduced the total PFAS content in the emissions by 33% (relative to 5 g CaO/kg sand). In  
421 particular, PFOS was not detected in the emissions.

422 With DRUM tests achieving treatment temperatures between 460 – 550 °C (Table 1), we hypothesize that most of the PFAS originally  
423 present in the sludge was released in the emissions with minimal degradation, similar to the LAB base case tests (I-1, I-2, & I-3) and

424 lower concentration GAC test (II-1-1). The only other semi-pilot scale study assessing PFAS treatment of sewage sludge also found  
425 near complete removal of PFAS from the bottom solids via pyrolysis (Zhang and Liang, 2021). Future work could examine the PFAS  
426 emissions by-products from smouldering sludge at larger scales and work to optimize treatment via operating conditions and  
427 amendments (e.g., GAC and/or CaO).

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#### 435 *3.4. Defluorination*

436 Minimal HF was measured in the emissions during the base case tests (1500 – 3800 ng HF/g-dry sludge) and the lower GAC test (II-2-  
437 1: 608 ng HF/g-dry sludge) (Figure 4). The lower relative temperatures (724 – 860 °C), slower heating rates, and lower propagation  
438 velocities likely supported release of longer chained PFAS in the emissions (Figure 3) rather than destroying these compounds.



439 The higher GAC test had the highest production of HF (II-1-2: 43000 ng HF/g-dry sludge), further evidence of improved degradation  
440 during the higher energy/temperature smouldering. Moreover, the faster heating rates (Supplementary Materials, Section S2) and  
441 smouldering propagation (Table 1) may reduce the time for the PFAS to volatilize ahead of being oxidized by the smouldering front. A  
442 faster heating rate may also be favourable to improve degradation when thermal destruction alone is used. Future work could explore  
443 the role of heating rates on PFAS destruction via smouldering.

444 Based on low HF emissions (3100 – 5800 ng HF/g-dry sludge) and low PFAS in emissions (10 – 15 ng/g-dry sludge), ash (8.9 – 19 ng/g-  
445 dry sludge), and sand cap (27 – 47 ng/g-dry sludge), smouldering with CaO likely mineralized some of the fluorine with the calcium,  
446 forming new compounds that remained sequestered in the ash. This potential mineralization required significantly less calcium  
447 amendment (0.005 – 0.01 g CaO : 1 g sludge for this study) than other studies using calcium amendments (i.e., 0.43 g Ca(OH)<sub>2</sub> : 1 g  
448 sludge (Wang et al., 2013), and 0.037 g Ca(OH)<sub>2</sub> : 1 g sludge (Zhang and Liang, 2021)). Lower calcium requirements make scaling the  
449 process more economically viable. Both elemental and mineral analyses were conducted (Supplementary Materials, Section S9);  
450 however, the concentrations of fluorine and fluorine containing minerals were below the instrument detection limits, likely due to the  
451 low quantity relative to other constituents in the sewage sludge. More work is needed to understand the fate of fluorine during sewage  
452 sludge smouldering and how to optimize treatment, particularly mineralization of fluorine, with calcium amendment and/or GAC.  
453 Smouldering offers key process advantages, effectively treating high MC sludge at lower treatment temperatures (Rashwan et al,  
454 2016; Fournie et al, 2021), while fluorine mineralization has been observed at temperatures as low as 400 °C (Wang et al., 2015, 2013).

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465 **4.0 Conclusion**

466 Smouldering combustion can be used to treat PFAS effectively in high moisture content (MC) sewage sludge with complete removal  
467 of PFAS compounds 4C – 8C. The most effective treatment of PFAS-laden sewage sludge involved the use of calcium oxide (CaO) to  
468 sequester fluorine in the resulting ash. Addition of 5 – 10 mg CaO per kg of dried sludge ahead of smouldering treatment achieved  
469 complete removal of PFAS 4C – 8C without significant PFAS or HF release in emissions. The low ratio of CaO to fuel used in this study  
470 makes scaling the process more economically viable and further optimization is likely possible. In contrast, smouldering of sludge  
471 bulked with only sand volatilized most of the PFAS. Some PFAS recondensed downstream in cooler regions in the reactor and the rest  
472 released via emissions. Supplementing the sludge and sand mixture with higher calorific value fuel (30 g GAC / kg sand) increased the  
473 energy of the system, fostering peak temperatures of ~900 °C, and improved PFAS degradation. Other high calorific value fuels such  
474 as wood chips could achieve similar conditions. While higher energy smouldering supports thermal degradation of PFAS, it also  
475 generates HF emissions, which require further treatment. In contrast, CaO addition achieved similar PFAS 4C – 8C degradation at  
476 temperatures between 670 – 880 °C, which were lower than required to degrade PFAS by other thermal treatments and avoided HF  
477 production. Smouldering with calcium amendment had the dual benefits of removing PFAS without producing other hazardous  
478 emission by-products. Overall, smouldering is a promising, lower energy alternative for treating PFAS in sewage sludge, even  
479 considering high MC sludge. The improved treatment at increasing scale demonstrates high potential for full-scale implementation at  
480 WWTPs.

481 This research explored the mineral phases formed in the ash with calcium and fluorine when a calcium amendment was added to  
482 sewage sludge. As the concentrations of fluorine and fluorine containing compounds were below detection limits of the methods  
483 used, the ultimate fluorine fate after sewage sludge smouldering is still uncertain. Future work could seek to address this question.  
484 Other areas for further investigation include optimizing smouldering treatment of PFAS-laden sewage sludge with calcium  
485 amendments, including high MC sludges, and investigating the long-term stability of mineralized fluorine sequestered in residual  
486 ash. Based on the process improvements noted in this work, calcium amendment may also be beneficial to explore in other sewage  
487 treatment processes for PFAS.

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514 **Supplementary Materials**

515 Supplementary data associated with this article can be found online at:

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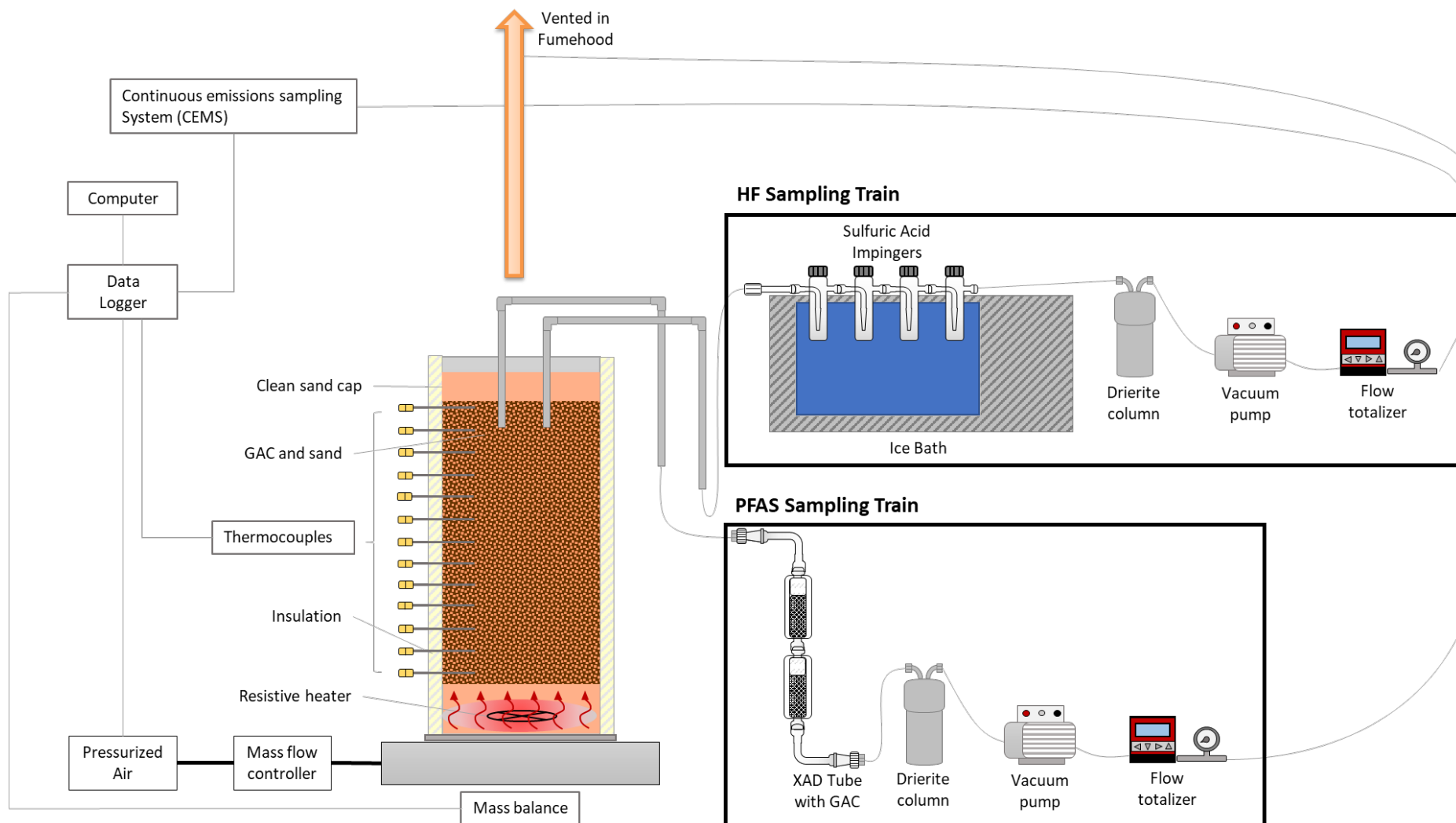
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685 *Figure 1: Experimental set-up and sampling for LAB tests.*

686 *Table 1: Summary of smouldering experiments*

Experiment	Experimental Conditions						Results	
	Moisture Content	Sand/Sludge	GAC Concentration	CaO Added	Pack Height	Air Flux	Average Centreline Peak Temperature ± S.E. <sup>a</sup>	Smouldering Velocity ± S.E. <sup>a</sup>
	(%)	(g/g)	(g GAC/kg sand)	(g CaO/kg sand)	(cm)	(cm/s)	(°C)	(cm/min)
PHASE I: LAB Base case								
I-1	0	6.5 <sup>b</sup>	-	-	31.1	5.0	856 ± 34	0.44 ± 0.07
I-2	0	6.5 <sup>b</sup>	-	-	34.3	5.0	737 ± 37	0.42 ± 0.08
I-3	0	6.5 <sup>b</sup>	-	-	34.9	5.0	831 ± 41	0.46 ± 0.08
PHASE II: LAB High MC and Amendments								
II-1-1	75 <sup>c</sup>	4.5 <sup>d</sup>	20	-	29.2	5.0	746 ± 21	0.52 ± 0.13
II-1-2	75 <sup>c</sup>	4.5 <sup>d</sup>	30	-	29.2	5.0	905 ± 21	0.50 ± 0.09
II-2-2	0	6.5 <sup>b</sup>	-	5	28.6	5.0	818 ± 57	0.53 ± 0.11
II-2-1	0	6.5 <sup>b</sup>	-	10	29.2	5.0	824 ± 54	0.30 ± 0.14
PHASE III: DRUM								
III-1	3.2	6.5 <sup>d</sup> (25.5 <sup>b</sup> )	-	-	53.5	5.0	542 ± 7.7	0.34 ± 0.04
III-2	72.3 <sup>e</sup>	6.5 <sup>d</sup>	-	-	61.6	5.0	473 ± 1.7	0.23 ± 0.01
III-3	74.4 <sup>e</sup>	4.5 <sup>d</sup>	-	-	61.9	5.0	469 ± 7.8	0.23 ± 0.03

687 <sup>a</sup> Standard error calculated as  $\frac{\sigma}{\sqrt{n}}$

688 <sup>b</sup> Measured on a dry-mass basis

689 <sup>c</sup> Moisture content of virgin sludge after drying and rehydrating

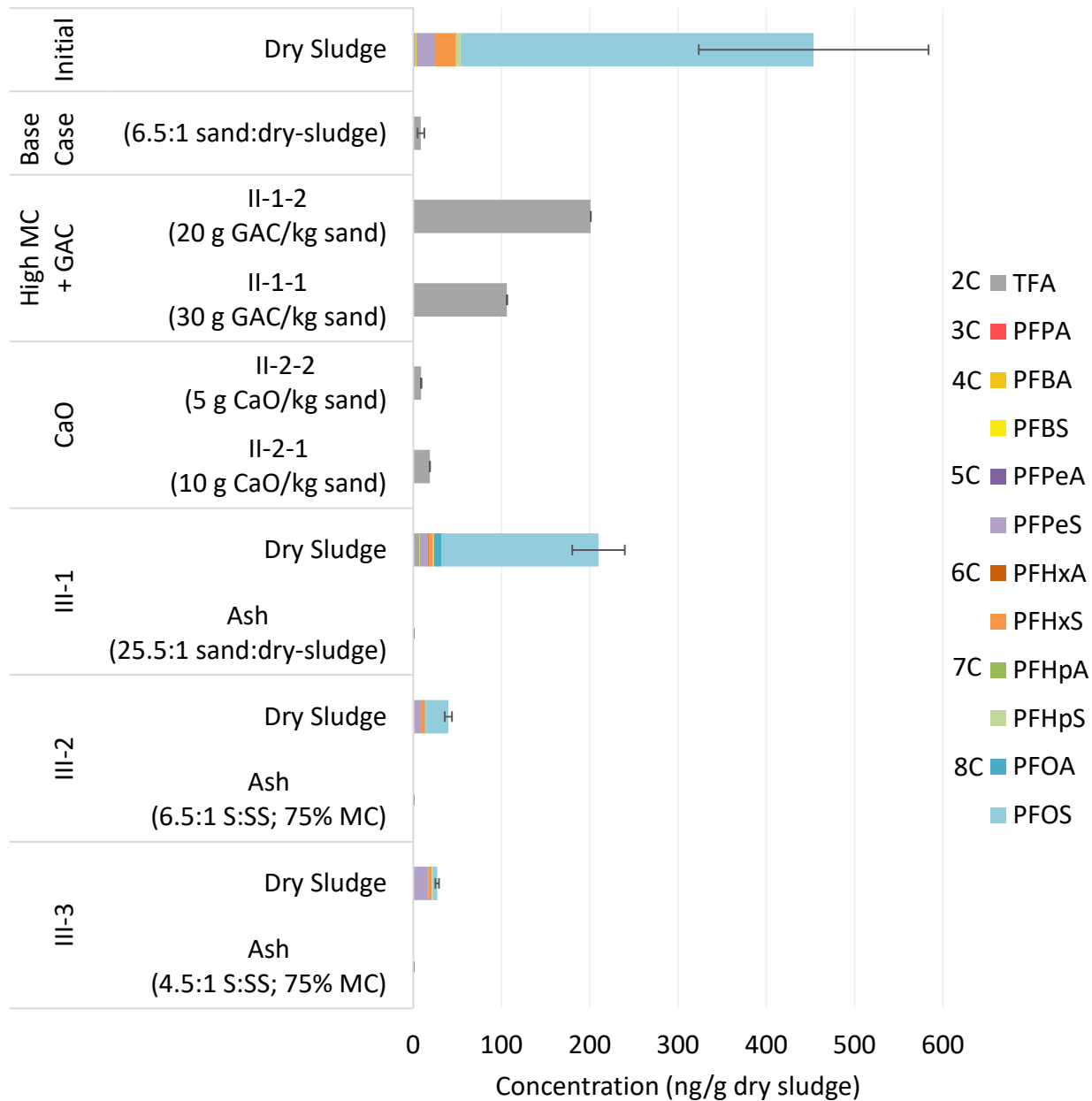
690 <sup>d</sup> Measured on a wet-mass basis

691 <sup>e</sup> Moisture content of virgin sludge, no drying occurred for these tests

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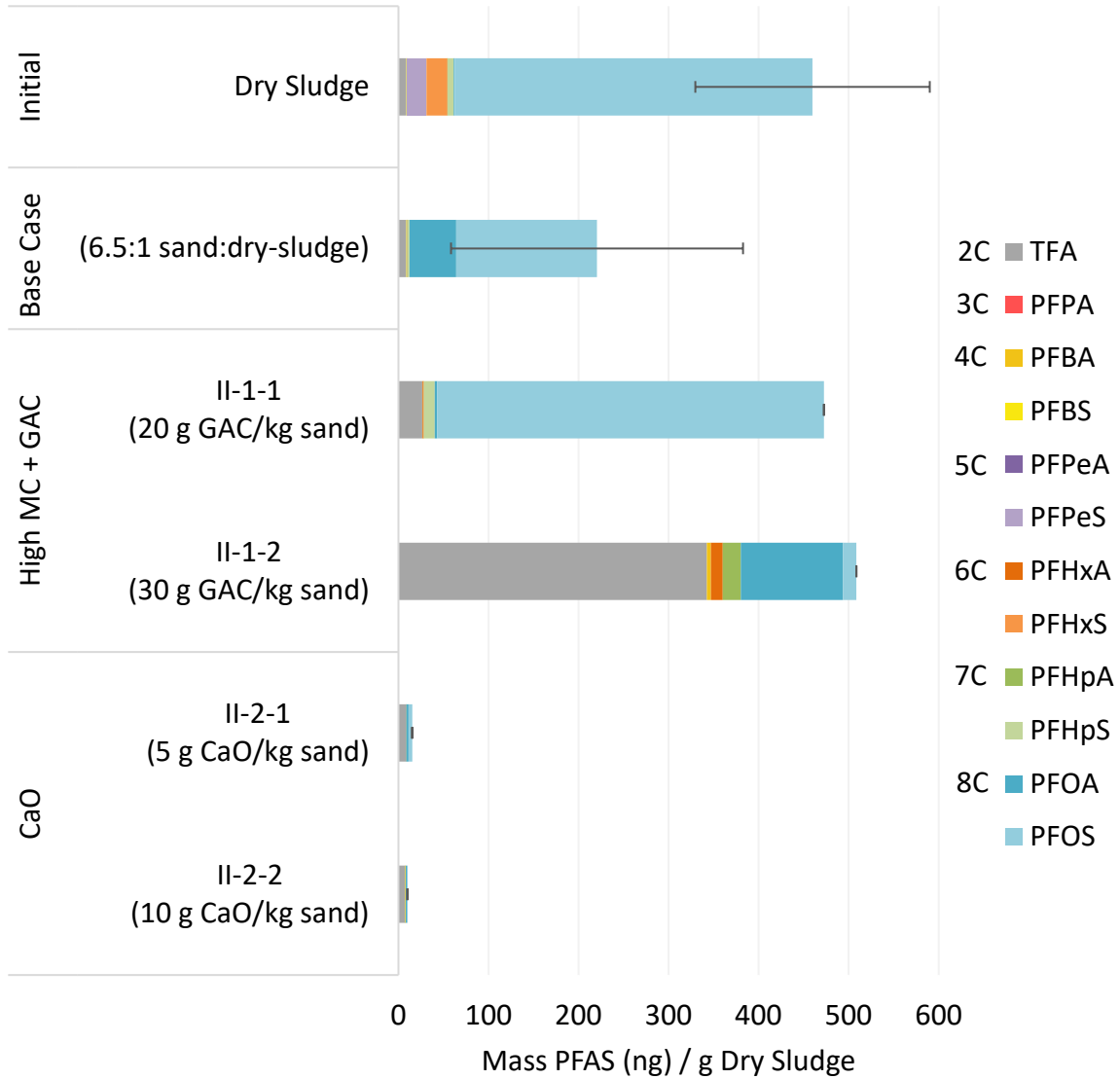
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696 *Figure 2: Content of 12 PFAS originally present in sludges and post-treatment solids following*  
 697 *smouldering treatment from a) LAB Phase I: base cases and Phase II: high MC (75%) and GAC, and*  
 698 *CaO tests, and b) DRUM Phase III. Error bars represent standard error of the cumulative PFAS*  
 699 *concentration determined from replicate samples.*

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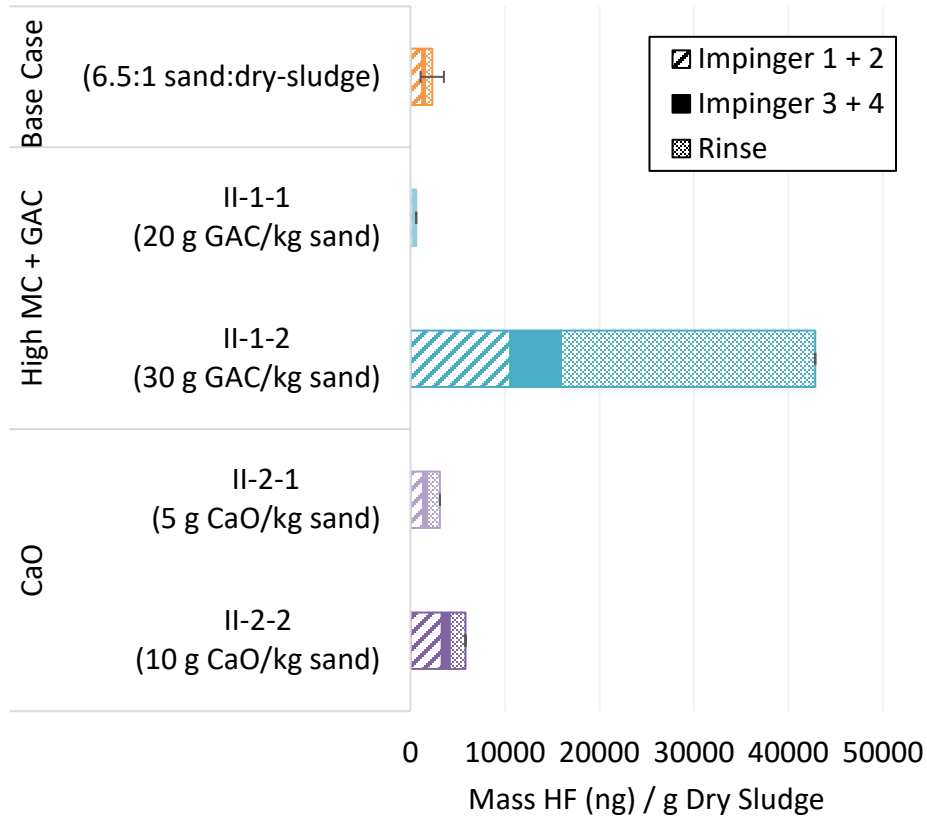
704 *Figure 3: Content of 12 PFAS in the emissions during smouldering compared to the content*  
 705 *originally present in the dried sludge. The content in the emissions has been normalized to account*  
 706 *for differences between the experiments.*

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712 *Figure 4: HF content measured in the emissions from each laboratory smouldering experiment.*  
 713 *The contents collected from two sections of the glassware sampling train and additionally the*  
 714 *glassware rinse have been presented separately. The contents in the emissions have been*  
 715 *normalized to account for differences between the experiments.*

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