Exploring PCDD/Fs and potentially toxic elements in sewage sludge during smouldering treatment

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Abstract

Potentially toxic elements (PTEs), persistent organic pollutants, and emerging contaminants make sewage sludge management challenging. There is significant interest in thermal treatment technologies that can destroy these compounds. The most common thermal treatment, incineration, poses risks due to formation and/or release of hazardous substances in process emissions such as polychlorinated dibenzo-\(p\)-dioxins and dibenzofurans (PCDD/Fs) and PTEs. Smouldering has been introduced recently as a potential treatment for managing sewage sludge. Smouldering systems present several advantages over traditional incinerators; however, there are still uncertainties regarding process by-products. This key question was investigated in three laboratory-scale tests (0.08 m radius) and five oil drum-scale tests (0.3 m radius) that were evaluated for PCDD/Fs and PTEs in the mixture before and after treatment as well as in process emissions. Volatile Organic Compounds (VOCs) were also measured. These experiments represent a broad spectrum of conditions to evaluate process emissions, from robust self-sustaining to extinction of smouldering. Robust smouldering had negligible PCDD/Fs in process emissions. Weak smouldering had low levels of PCDD/Fs (emissions factor: \(3.3 \pm 0.3 \mu g\) TEQ/Mg dried sludge destroyed), levels less than uncontrolled emissions from commercial incinerators. Overall, smouldering acted as a sink for PCDD/Fs, as only 0 – 3% of the PCDD/Fs originally present in the sludge were released in the emissions, and >99% of the remainder were destroyed with <1% remaining in post-treatment ash. No evidence was found to support \textit{de novo} synthesis or precursor reactions forming new PCDD/Fs. In addition, 94-100% of all the PTEs analyzed were retained in the post-smouldered material. These results indicate that only minimal emissions treatment for PTEs, PCDD/Fs, and VOCs may be necessary for future sewage sludge smouldering.
systems. These low emissions risks combined with its unique ability to handle high moisture content waste, indicate that smouldering has significant potential as a valuable waste management technique.

**Key words**

Smouldering combustion; Sewage sludge; Potentially toxic elements; PCDD/Fs; Emissions

**List of Abbreviations**

- **BDL**: Below detection limit
- **CEMS**: Continuous emissions monitoring system
- **DI**: Deionized
- **DM**: Dry matter
- **DRUM**: Oil-drum reactor scale experiments (0.3 m radius)
- **GC/MS**: Gas Chromatography/Mass Spectrometry
- **HpCDD**: Heptachlorodibenzo-\(p\)-dioxin
- **HpCDF**: Heptachlorodibenzofuran
- **HxCDD**: Hexachlorodibenzo-\(p\)-dioxin
- **HxCDF**: Hexachlorodibenzofuran
- **ICP-OES**: Inductive Coupled Plasma Optical Emission Spectrometer
- **LAB**: Laboratory scale reactor experiments (0.08 m radius)
- **MC**: Moisture content
- **MSW**: Municipal solid waste
- **OCDD**: Octachlorodibenzo-\(p\)-dioxin
- **OCDF**: Octachlorodibenzofuran
- **PAH**: Polyaromatic hydrocarbon
- **PCDD**: Polychlorinated dibenzo-\(p\)-dioxins
PCDF  Polychlorinated dibenzofurans
PeCDD  Pentachlorodibenzo-\(p\)-dioxin
PeCDF  Pentachlorodibenzofuran
PTE   Potentially toxic element
RPM   Revolutions per minute
TCDD  Tetrachlorodibenzo-\(p\)-dioxin
TCDF  Tetrachlorodibenzofuran
TEF   Toxic equivalency factor
TEQ   Toxic equivalent quantity
USEPA United States Environmental Protection Agency
VOC   Volatile organic compound
WHO   World Health Organization
WWTP  Wastewater treatment plant
XAD   Non-ionic macroreticular resin
1.0 Introduction

Sewage sludge contains high quantities of potentially toxic elements (PTEs) and emerging contaminants including antibiotic resistant bacteria and perfluorinated compounds (Jiwan and Ajah, 2011; Zhou et al., 2019), which have been shown to cause adverse health and environmental impacts (Zhang et al., 2017b). These hazards drive strong interest in thermal conversion techniques that limit their environmental release (Pudasainee et al., 2013; Werther and Ogada, 1999; Zabaniotou and Theofilou, 2008). Incineration is an attractive option for treating sewage sludge due to its ability to destroy organic contaminants (Werther and Ogada, 1999). However, the by-product emissions from sludge incineration often contain hazardous compounds that require additional treatment, particularly polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and PTEs including heavy metals (Fullana et al., 2004; Pudasainee et al., 2013; Shao et al., 2008; Werther and Ogada, 1999).

Recently, smouldering combustion has been demonstrated as a novel sludge treatment technology to reduce energy and carbon demand in wastewater treatment plants (WWTPs) (Rashwan et al., 2016). Smouldering can manage high moisture content (MC) sludge (80-85% MC) with minimal pre-processing, an advantage that fundamentally draws on the slower smouldering combustion time scales compared to those in flaming combustion systems such as incinerators (Torero et al., 2020; Yermán et al., 2015). This key difference allows for more efficient energy transfer in the system. Smouldering-based systems operate in a self-sustaining manner, without the need for supplemental energy after ignition, even in these very high moisture content conditions (Rashwan et al., 2016; Serrano et al., 2020). While smouldering has many advantages
as a low-energy thermal treatment option, the lack of information regarding potential formation of by-products and treatments required to manage them is a barrier to widespread application.

Release of PCDD/Fs during sludge incineration is a major concern because these compounds are highly toxic and persistent (Fiedler, 2003; Reiner, 2016; Van den Berg et al., 2006; Van Luong et al., 2018). PCDD/F formation is possible from any thermal treatment process with sufficient quantities of carbon, chlorine, oxygen, and metal catalysts (Stanmore, 2004; Zhang et al., 2017a). Several studies have explored the mechanisms of PCDD/F formation during combustion processes (mostly incineration) and consensus is that major formation pathways are: (i) incomplete combustion of existing PCDD/Fs fed to the combustor; (ii) reactions from precursor compounds; and (iii) de novo synthesis from carbon and chlorine (McKay, 2002; Rathna et al., 2018; Stanmore, 2004; Zhang et al., 2017a). Homogeneous, gas-phase reactions with chlorinated organic precursors (e.g., chlorobenzene) can form PCDD/Fs in the combustion chamber at high temperatures (400 - 800°C) (Lopes et al., 2015; Rathna et al., 2018; Vermeulen et al., 2014). However, lower temperature (200 - 400°C) heterogeneous reactions at the gas – solids interface are generally the dominant PCDD/F formation mechanisms in incinerators (Fullana et al., 2004; Stanmore, 2004; Vermeulen et al., 2014; Zhang et al., 2017a). Furthermore, the extent of combustion completeness in incinerators has been shown to affect the release of PCDD/Fs in incinerator emissions, where incomplete combustion favours higher amounts of PCDD/Fs released in the emissions and complete combustion favours lower release of PCDD/Fs (Fiedler, 2003; McKay, 2002). This is partially because products of incomplete combustion (e.g., volatile organic compounds (VOCs)) may promote PCDD/F formation via precursor pathways and, to a lesser extent, de novo synthesis (Tuppurainen et al., 1998). Fluidized bed incinerators
immediately subject sludge to high temperatures (750 – 925°C) at residence times of 2 – 5 seconds (USEPA, 1995a) for complete destruction of PCDD/Fs originally present in the sludge (McKay, 2002). PCDD/Fs in incinerator emissions are typically produced through heterogeneous production pathways in the post-combustion chamber (Altwicker et al., 1992; Vermeulen et al., 2014). Although the PCDD/Fs risks from sludge incineration are well-characterized (Deng et al., 2009; Fytili and Zabaniotou, 2008; Han et al., 2006), they are not well-understood for smouldering systems.

Smouldering systems for sludge often exhibit lower treatment temperatures (400-550 °C) and relatively high fractions of CO/CO₂ (0.05-0.4) (Torero et al., 2020). While these lower temperatures and high CO fractions indicate incomplete combustion, it is not necessarily clear if sludge smouldering systems foster the conditions needed for PCDD/F formation and/or release.

Most applied smouldering systems exhibit efficient heat transfer ahead of smouldering as well as filtration, due to the use of inert porous media – typically coarse grained sand (Torero et al., 2020). As a result, the post-combustion chamber remains near ambient temperature throughout most of smouldering and contains less particulate matter than typical incinerators (Torero et al., 2020); these conditions are not expected to foster PCDD/F formation. These key differences between smouldering systems and incinerators are expected to govern the differences in mechanisms of PCDD/F formation and/or release in these two systems (Yerman, 2016). Therefore, it is not appropriate to extrapolate PCDD/F destruction findings from incinerators to smouldering systems. Instead, this work seeks to evaluate potential PCDD/Fs formation and/or release during smouldering with direct experiments.
Like PCDD/Fs, fate of PTEs during incineration of sewage sludge has been extensively studied (Chanaka Udayanga et al., 2018; Han et al., 2006; Marani et al., 2003; Pudasainee et al., 2013); however, the fundamental differences between incineration and smouldering mean that analogies between these systems are not straightforward. Sewage sludge provides a natural accumulation point for PTEs and during incineration they can be retained in ash or mobilized in the process emissions. The distribution of PTEs during incineration is affected by type of waste and its characteristics; physicochemical properties of the PTEs; reactor type; residence time; and incineration operating conditions such as temperature and airflow rate (Chanaka Udayanga et al., 2018; Nowak et al., 2013; Zhang et al., 2008). These factors likely affect the distribution of PTEs during smouldering treatment. Although smouldered sewage sludge ash is likely safe for landfilling (Feng et al., 2020), more work is still needed to understand compounds being formed and/or released from sewage sludge smouldering, especially within process emissions.

This work aims to improve the understanding of risks associated with smouldering treatment and is the first study to evaluate PCDD/F formation and release from smouldering sewage sludge. The objectives are to evaluate the mechanisms of potential formation and release of PCDD/Fs and VOCs and establish the fate of PTEs from treating sewage sludge with smouldering. To address these goals, smouldering tests were conducted in laboratory and oil-drum sized reactors varying moisture content and sand-to-sludge ratio widely to challenge the system. This approach was used to evaluate potential emissions hazards under a wide range of operating conditions.
2.0 Materials and Methods

2.1. Experimental Set-up and Procedure

Sewage sludge was obtained from Greenway Pollution Control Plant (Greenway) in London, Ontario, Canada. Complete details on wastewater processing and sludge generation at Greenway can be found elsewhere (Rashwan et al., 2016). In these tests, sewage sludge produced from a dewatered slurry of primary and secondary sludge was collected in batches of 40 – 55 kgs ahead of each smouldering test. Virgin sludge was typically collected one day prior to smouldering to allow for experiment set-up and preparation.

Cylindrical reactors fabricated from stainless steel were used for both laboratory experiments (with 0.08 m radius, LAB) and larger scale tests in an oil-drum sized reactor (with 0.3 m radius, DRUM). Well-established smouldering equipment and procedures were used for both the LAB (Rashwan et al., 2016), and DRUM (Fournie et al., 2022; Rashwan et al., 2021a) tests. A basic summary is provided here. Figure 1 illustrates the DRUM reactor set-up and sampling points. The LAB reactor set-up was similar, but it required a scaled-down and simplified sampling approach (Figure S-1 in Supplementary Materials). The reactors were wrapped in 0.051 m thick insulation (LAB: MinWool®, Johns Manville; DRUM: FyreWrap® Elite® Blanket, Unifrax).

The sewage sludge had an average moisture content of 74% and ash content of 1% (both wet mass-basis), determined using USEPA Method 1684 (Tellier, 2001). Eight DRUM and three LAB tests were conducted, summarized in Table 1. DRUM 1 and LAB 1a and 1b used dried sewage sludge (3% MC). This sludge was batch dried in an oven at 105°C until there were no measurable changes in the sludge mass. DRUM 2 and LAB 2 involved sludge as-received (74% MC). DRUM 3
and 5 were similar but used lower sand concentrations. For DRUM 4, the sludge was tumbled in a large mechanical mixer until the moisture content was reduced by 45%. DRUM 6 and 7 were replicates of DRUM 2. DRUM 8 increased sludge content by 1.5x, but otherwise maintained the same conditions as DRUM 2, 6, and 7.

In each test, the specified mass of sludge was mixed with coarse silica sand (Bell & Mackenzie Number 12; $1.180 \leq \text{mean grain diameter} \leq 2.000$ mm; porosity ($\phi$) = 0.37; bulk density $([1 - \phi] \rho_s) = 1670$ kg m$^{-3}$; 0.04 – 0.4% MC) to achieve the specified sand-to-sludge ratio (Table 1) in a mechanical drum mixer (Rashwan et al., 2016). All experiments were packed carefully into the reactor to minimize packing heterogeneities; however, the mixtures in DRUM 3 and 5 were slightly more densely packed than the other high MC experiments, which contributed to poor smouldering performance. A clean sand cap (2.5-5 cm thick) was added on top of sand/sludge mixtures in all LAB and DRUM tests to lower the exiting emissions temperatures for safety purposes.

The reactors were placed on load cells (KCC150 (LAB) and KD1500 (DRUM), Mettler Toledo) to measure mass loss during smouldering. Thermocouples (Type K 0.0032 m diameter Omega Ltd (LAB); 0.0064 m diameter Kelvin Technologies (DRUM)) were installed along the full height of the reactors to record process temperatures throughout each test. Air was injected into the base of the reactors and was operated using a mass flux controller (FMA5400/5500 Series, Omega Ltd. (LAB); 8290B045PDB67 ASCO Numatics (DRUM)). The base of the reactor was then heated via a convective heater (F074719 2 kW SureHeat® JET (LAB); F074736 36 kW SureHeat® MAX (DRUM), Osram Sylvania) until ignition, which was identified when the first thermocouple in the
sand/sludge mixture peaked (i.e., 0.02 and 0.06 m up the column in the LAB and DRUM experiments, respectively). Following ignition, the heater was turned off and air flow was maintained to support self-sustaining smouldering. The end of each experiment was identified when the smouldering front reached the end of the sand/sludge mixture in the reactor.

Representative samples, 19 – 100L per DRUM test, of the post-treatment material (i.e., ash mixed with silica sand) were collected in 19 L buckets that aimed to capture heterogeneities throughout the reactor. Post-treatment materials were then separated into sand and ash fractions as defined by grain sizes greater than and less than 0.25 mm, respectively.

PCDD/Fs were measured in emissions in LAB 1a, 1b, and 2 and DRUM 1, 2, 3, and 4 to explore release behaviour under a range of experimental conditions including scaling and varying sludge MC. Repeat LAB and DRUM tests evaluated how variable performance influences PCDD/F release. Energy efficiency improves with increasing scale (Rashwan et al., 2021b); however, non-uniform air flux also increases (Rashwan et al., 2021a), both of which influence smouldering performance. VOCs were measured in the emissions from DRUM 3 and 5. Both DRUM 3 and 5 were more densely packed than other tests which resulted in weak smouldering; therefore, the VOCs measured during these tests are representative of the maximum VOCs that would likely be released during non-robust smouldering. Elemental analyses were performed on the virgin sludge and remaining ash from DRUM 1, 2, 6, 7, and 8, all of which had complete destruction of smoulderable fuel, thereby contained only inert, inorganic ash.
2.2 Emissions Monitoring

Continuous emissions monitoring systems (CEMS) measured oxygen, carbon dioxide, and carbon monoxide data from the LAB tests every two seconds (MGA3000C, ADC), and methane, carbon dioxide, carbon monoxide, and total hydrocarbons from the DRUM tests every five seconds (ABB Ltd.). The locations of all emissions sampling points for DRUM tests are shown in Figure 1, and LAB tests in Figure S1-1.

The PCDD/F emissions sampling train was constructed based on USEPA Method 23, modified following Wallbaum et al. (1995). An XAD tube containing XAD-2 resin (Sigma-Alderich, USA) was used to capture PCDD/Fs within the emissions. A cold-water condenser ahead of the XAD tube was used to rapidly cool the emissions. In the LAB tests, a single emissions sample was collected from the reactor (Supplementary Materials, Section S1). In the DRUM tests, emission samples were collected at two locations along the experimental system: (i) just above the fixed bed, and (ii) at the exhaust of the onsite emissions treatment system (Figure 1). The two emissions sampling locations were used to analyze PCDD/Fs that may have been produced/released during smouldering and verify the effectiveness of the emissions treatment system. A flow meter ahead of the LAB and DRUM reactor sampling train was used to measure air flow through the sampling system and adjust valves to maintain constant flow throughout the sampling period. Oxygen content was measured immediately after the reactor sampling trains (LAB: MGA3000C, ADC; DRUM: Landtec GEM2000 portable gas analyzer). The duration of the PCDD/F emissions sampling was recorded from when the pump was turned on, thereby diverting a fraction of the emissions from the reactor outlet through the PCDD/F sampling train, until the pump was turned
off. The timing and duration of PCDD/F sampling varied between tests to predominantly capture PCDD/F emissions away from initial- and end-effects (Table 1). The condensate that accumulated during emissions sampling was collected from the condenser and analyzed with the XAD-2 resin.

An evacuated Summa® canister (ALS Canada Ltd.) was used to collect emissions samples from DRUM 3 and 5. The canister was connected to the reactor hood directly above the PCDD/F sampling train (Figure 1). A flow controller was used to collect the emissions samples at a constant rate throughout each test. Sampling occurred for 270 min for DRUM 3, and 200 min for DRUM 5 (due to less smoulderable material in this test), as the smouldering front progressed up the reactor. The emissions samples were analyzed benzene, benzyl chloride, chlorobenzene, 1,2-dichlorobenzene, 1,3- dichlorobenzene, 1,4- dichlorobenzene, ethylbenzene, 4-ethyltoluene, styrene, toluene, 1,2,4-trichlorobenzene, 1,2,4- trichlorobenzene, 1,3,5- trichlorobenzene, o-xylene, m&p-xylene by ALS using Gas Chromatography/Mass Spectrometry (GC/MS) complying with USEPA Method T0-15, i.e., as recommended by the National Environmental Protection (Air Toxics) Measure (USEPA, 1999).

To ensure that all measurements were independent of previous experiments, background samples were taken while injecting hot air (50 – 60°C) through the empty DRUM and LAB setups to quantify the background concentration of PCDD/Fs. Background concentrations were all below detection limits.

All LAB tests were performed in fume hoods that collected the emissions exiting the reactor into a centralized collection system. Emissions exiting the DRUM reactors were passed through an onsite treatment system prior to release from a stack. The custom treatment system (Newterra
Ltd) consisted of two granular activated carbon vessels (820 and 75 kg, respectively), followed by a vessel with impregnated potassium permanganate media (with 150 kg of material).
Figure 1: Experimental set-up and sampling for DRUM tests.
Table 1: Summary of smouldering experiments

<table>
<thead>
<tr>
<th>Test</th>
<th>Sludge Properties</th>
<th>Sand: Sludge</th>
<th>Sludge Added</th>
<th>Sand Added</th>
<th>Bulk Density</th>
<th>Air Flux</th>
<th>Peak Temperature</th>
<th>Propagation Velocity</th>
<th>Other Analyses Performed</th>
<th>Comments</th>
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<td>MC (wet mass %)</td>
<td>Ash (dry mass %)</td>
<td>(g/g)</td>
<td>(kg)</td>
<td>(kg/m³)</td>
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<td></td>
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<tr>
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<td>3.2</td>
<td>29</td>
<td>24:1</td>
<td>0.52</td>
<td>12</td>
<td>1600</td>
<td>5.0</td>
<td>520</td>
<td>0.53</td>
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<td>24:1</td>
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<td>6.3</td>
<td>1500</td>
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<td>1100</td>
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<td>1200</td>
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<td>PTEs</td>
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</table>

1 The total sand to fuel mass ratio is presented, although the MC (%) and Ash (%) varied between tests
2 Ignited at a higher air flux
2.3. Elemental Analysis and Mass Balance Calculations

Total contents of aluminum, cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead, and zinc in the virgin sewage sludge, virgin sand, and post-treatment ash and sand were determined with inductively coupled plasma, optical emission spectroscopy, and mass spectrometry (ICP-OES). These elements were selected because they are currently monitored at WWTPs. Triplicate samples of solids were extracted by microwave assisted acid digestion following USEPA Method 3051A (Element, 2007).

Experimental data was used to determine the distribution of mass of each element within the reactor pre- and post-smouldering. Masses of sand and sewage sludge added into the systems was carefully tracked during mixing, packing, and unpacking. The mass of post-treatment ash generated was determined based on the quantity of sewage sludge added to the system and the mass removed during smouldering as measured by the load cell. Due to the nature of a fixed bed reactor, the sand matrix is conserved with no losses during treatment (Yermán et al., 2015).

The total masses of sand and ash size fractions were extrapolated based on sieve analysis from 6 subsamples taken from each test (Supplementary Materials, Section S2). The total quantity of each element was similarly extrapolated for each size fraction and compared to the total quantities originally in virgin sewage sludge and sand. Differences were assumed as losses via volatilization.

2.3. Dioxin and Furan Analysis
A modified QuEChERS method (Haimovici et al., 2016) was used to extract the aliquot from the XAD-2 and condensate samples for PCDD/Fs analysis by Gas Chromatography/High-Resolution Mass Spectrometry (GC/HRMS). All analyses were performed at the mass spectrometry laboratory, Ministry of Environment, Conservation, and Parks, Toronto, ON. The measured masses of the 17 most toxic PCDD/F congeners (i.e., the PCDD/Fs containing chlorine atoms in the 2,3,7,8 positions on the benzene rings) (Reiner, 2016) were converted into concentrations in the emissions based on measurements from a downstream flow totalizer (see Supplementary Materials, Section S3 for full method and calculations).

PCDD/F emissions concentrations were normalized to account for sampling volume, reactor scale, air flux into the reactor, bulk density of the sludge and sand mixture, MC of the fuel, ash content, sand-to-sludge mass ratio, smouldering propagation velocity, and the temperatures and pressures of the air entering and leaving the reactor (Supplementary Materials, Section S4). The emission factors were then determined according to USEPA (1995b) as the mass of PCDD/F toxic equivalent quantity (TEQ) per mass of dry sewage sludge destroyed (see Supplementary Materials, Section S4 for full method and calculations).

According to the Canadian Council of Ministers of the Environment Environmental Compliance Approval (ECA), the allowable maximum concentration of PCDD/Fs in the undiluted flue gas, emitted from sewage sludge incinerator stacks is 80 pg/m³ TEQ corrected to 11% O₂ at a reference temperature and pressure of 25°C and 101.3 kPa, respectively. To compare the PCDD/F concentrations to regulatory standards, experimental values were corrected to these reference conditions (see Supplementary Materials, Section S3 for full calculations).
3.0 Results and Discussion

3.1. Smouldering Behaviour

Smouldering destroyed more than 90% of the initial sludge biomass, leaving 1-10% as residual inorganic ash in the reactor. Peak temperatures ranged between 450 – 600°C in LAB tests and 325 – 550°C in DRUM tests (Table 1).

The evolution of three dominant smouldering burn patterns observed in the experiments are shown in Figure 2 (adapted from Rashwan et al., 2021). In robust smouldering, the smouldering front is well distributed in the cross-sectional area of the reactor and remains that way as the front propagates through the material. Robust smouldering, with minimal crust/unburned sections, was observed in LAB 1a and 1b and DRUM 1 and 4 (Figure 2A). Internal and external factors can reduce smouldering robustness. Heat losses at reactor walls (i.e., edge effects) inhibit smouldering at the walls while smouldering remains robust at the center of the reactor. These edge effects were observed as pyrolyzed crusts near the reactor walls after treatment in DRUM 2, and 6–8 (Figure 2B). In these tests, wall temperatures were less than 200 °C, thereby indicating that the material did not completely smoulder near the wall (Supplementary Materials, Section S2). Heterogeneities can further inhibit smouldering by inducing channeling and other irregularities in the porous media. Weak smouldering was observed in LAB 2, and DRUM 3 and 5. With extinction conditions near the reactor wall and non-uniform flow field, both driven by heat losses, large fractions in these experiments remained unburned (Rashwan, 2020; Rashwan et al., 2021c). These weak smouldering conditions led to non-self-sustaining conditions in LAB 2, evident with declining temperatures along the centreline until extinction halfway up the fuel pack.
(Supplementary Materials, Section S2), and borderline-self-sustaining conditions in DRUM 3 and 5, with declining peak temperatures but no quenching (Supplementary Materials, Section S3). Therefore, these experiments represent a broad spectrum of conditions to evaluate process emissions, from robust self-sustaining to extinction of smouldering.
Figure 2: Summary of the different burn patterns observed in the experiments. Times 1 to 4 show smouldering front propagation, where Time 1 shows ignition at the reactor base, Time 2 shows when the front propagated part-way up the column, Time 3 shows when the smouldering front is approaching the top of the contaminant pack, and Time 4 shows the approximate post-treatment burn patterns. A. represents tests with no/minimal crust, B. shows pyrolyzed/unburned crust due to edge effects, and C. shows significant crust formation and large, unburned regions.
3.2. Fate of Potentially Toxic Elements (PTEs)

Table 2 presents a mass balance of elemental retention and volatilization during smouldering. The ash and sand fractions comprised ~2% and ~98% of the total post-treatment material mass, respectively. However, both fractions retained roughly equal amounts of PTEs, i.e., the ash retained 33 to 77 (± 15%) of PTEs, while the sand retained 28 to 78 (± 5%) of PTEs. Because dry sieving did not completely separate ash and sand, some ash was likely retained in the sand fraction (i.e., due to physical attachment). The high retention of some elements in the sand may be due to this retained ash, compounded because of the large relative mass of sand. In addition, some PTEs may have condensed on the sand during smouldering treatment.

Table 2 shows that, following smouldering treatment, most PTEs were retained within the reactor. Retentions of cadmium, chromium, copper, lead, nickel, and zinc were all ~100% (Table 2). In comparison, losses of 60-100% of cadmium, 30-50% of lead, and 20% of chromium, copper, nickel, and zinc are commonly observed during sewage sludge incineration (Zhang et al., 2008). Compared to incineration, the lower treatment temperatures during smouldering likely limited volatilization of these PTEs so they remained in the ash and were not released in the emissions. For example, from the 2018 National Pollutant Release Inventory Report (which summarizes elemental release from WWTPs through sludge incineration in London, Canada), one large WWTP reported losses of: 9 kg of cadmium, 76 kg of lead, 2.7 tonnes of zinc, and 4.1 tonnes of total particulate matter (City of London, 2019). Considering the initial elemental concentrations in the sludge and the annual quantity processed by this WWTP, elemental losses in incinerator emissions equate to ~38% of cadmium, ~6% of lead, and ~22% of zinc originally in the sludge.
(Supplementary Materials, Section S5). In comparison, smouldering treatment retained 85 to 111 (± 16%) of all PTEs within post-treatment ash and sand (Table 2).

Low release of PTEs during smouldering relative to incineration is likely due to: (i) lower air flow rates; (ii) use of fixed beds instead of fluidized beds; (iii) lower smouldering temperatures; and (iv) less particulate release. These process differences likely reduce the potential for volatilized PTEs in the emissions.
<table>
<thead>
<tr>
<th>Element</th>
<th>Average Elemental Concentration (mg/kg-dry matter) ± SE (^a)</th>
<th>Mass Balance (% total content) ± SE (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sludge Post-Treatment</td>
<td>Sand (^b)</td>
</tr>
<tr>
<td>Al</td>
<td>8100 ± 300</td>
<td>260 ± 90</td>
</tr>
<tr>
<td>Cd</td>
<td>2 ± 0.2</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Co</td>
<td>2.9 ± 0.4</td>
<td>0.11 ± 0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>100 ± 8</td>
<td>3.7 ± 1</td>
</tr>
<tr>
<td>Cu</td>
<td>500 ± 30</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>Fe</td>
<td>40000 ± 4000</td>
<td>830 ± 200</td>
</tr>
<tr>
<td>Mg</td>
<td>4400 ± 400</td>
<td>58 ± 14</td>
</tr>
<tr>
<td>Mn</td>
<td>240 ± 20</td>
<td>4.3 ± 4</td>
</tr>
<tr>
<td>Mo</td>
<td>13 ± 2</td>
<td>0.21 ± 0.03</td>
</tr>
<tr>
<td>Ni</td>
<td>41 ± 5</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>Pb</td>
<td>60 ± 14</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>680 ± 70</td>
<td>15 ± 40</td>
</tr>
</tbody>
</table>

\(^a\) Standard error calculated as \(\sigma/\sqrt{n}\)

\(^b\) Post-treatment sand (> #60 sieve size)

\(^c\) Mostly post-treatment ash (< #200 sieve size)

\(^d\) Content in post-treatment ash was determined from ash (< #200 sieve) and mixed sand fines and ash (i.e., between the #200 and #60 sieve sizes)

\(^e\) The standard error was calculated from the uncertainties from each calculation added in quadrature
3.3. PCDD/F Formation and Release

3.3.1. PCDD/F Results from LAB and DRUM Tests

Smouldering removed >99% of 1234678-HpCDD, >99.9% of OCDF and OCDD, and ~100% of all other PCDD/F compounds initially present in the sewage sludge. Table 3 summarizes the quantities of PCDD/Fs released in the combustion gases from the LAB and DRUM tests, and Figure 3 presents the quantities normalized per mass of sludge destroyed.

Four DRUM tests were monitored for PCDD/Fs. No PCDD/Fs were detected in the emissions from either DRUM 2 or DRUM 4, both of which were sampled during robust smouldering conditions. DRUM 1, which was sampled near the end of smouldering and captured end-effects, and DRUM 3, which exhibited less robust smouldering, released small concentrations: 45 and 48 pg TEQ /m$^3$ PCDD/Fs, respectively. These small PCDD/F concentrations in DRUM 1 and 3 were comparable to the LAB experiments, where LAB 1a and 1b released 26 - 35 pg TEQ /m$^3$ PCDD/Fs, and LAB 2 released 3.9 pg TEQ /m$^3$ PCDD/Fs (Table 3). All LAB and DRUM tests that had measurable PCDD/Fs in the emissions released some 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDD, and OCDD (Table 3). LAB 1a also released 1,2,3,6,7,8-HxCDD, which was also measured in DRUM 3, along with 1,2,3,4,6,7,8-HpCDF, OCDF, 1,2,3,4,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD, which were not detected in any other experiment.

All measured PCDD/F values were exceptionally low. After correcting the reactor emissions to 11% oxygen (Table 3), the concentrations from the DRUM tests were 105 pg TEQ /m$^3$ PCDD/Fs from DRUM 1, 145 pg TEQ /m$^3$ PCDD/Fs from DRUM 3. The corrected concentrations from the LAB tests were slightly lower, with 70 pg TEQ /m$^3$ PCDD/Fs from LAB 1a, 63 pg TEQ /m$^3$ PCDD/Fs
from LAB 1b, and 18 pg TEQ /m$^3$ PCDD/Fs from LAB 2. Therefore, the PCDD/F release from all LAB tests were below the standard 80 pg TEQ /m$^3$ ECA requirement for exhaust stack release. While the PCDD/F release from the DRUM tests were slightly higher than the ECA requirement, after passing through the onsite emissions treatment system, all emissions from every experiment fully complied with the ECA and most tests had no detectable stack release (Supplementary Materials, Section S3).

After smouldering, only three PCDD/F compounds were detected in the post-treatment ash from DRUM 1: OCDF, OCDD, and 1234678-HpCDD (Supplementary Materials, Section S3). These measurements were all above the detection limit but below the calibrated range. The ash contained ~1.27 pg/g 1234678-HpCDD, ~0.24 pg/g OCDF, and ~5.09 pg/g OCDD.

The normalized PCDD/F release amounts in Figure 3 accounted for variable experimental conditions across the LAB and DRUM scale tests. These results show that most experiments released similar amounts of common PCDD/Fs. In addition, the LAB tests generally exhibited slightly lower PCDD/F release than the DRUM tests, except for OCDD released from LAB 2. Figure 3 also includes hypothetical release values if all PCDD/Fs initially present in the sludge were released.

3.2.2. Interpretation of Results

The PCDD/F emission factors determined in this study for sewage sludge smouldering at the Drum scale under robust conditions (0 µg TEQ /Mg dried sludge destroyed), LAB scale (0.88 ± 0.2 µg TEQ /Mg dried sludge destroyed), and DRUM scale under weaker conditions (3.3 ± 0.3 µg TEQ /Mg dried sludge destroyed) are lower than averaged uncontrolled emissions from commercial
incinerators (4650 µg I-TEQ/Mg sludge destroyed; range: 465 – 465000 µg I-TEQ/Mg sludge destroyed (Nielsen et al., 2019)). In weaker conditions, smouldering sewage sludge releases lower levels of PCDD/Fs than robust incineration; however, the mechanisms leading to PCDD/Fs in the emissions are hypothesized to be different than those in incinerators (see Section 3.2.3.). Of the dioxins measured, the two lowest toxicity congeners, OCDD and 1,2,3,4,6,7,8-HpCDD, comprised most of the released PCDD/F compounds from both LAB and DRUM tests. OCDD comprised 69 – 90% of LAB and 55 – 58% of DRUM PCDD/F emissions by mass; 1,2,3,4,6,7,8-HpCDD comprised 9 – 26% of LAB and 24 – 32% of DRUM PCDD/F emissions by mass. The most toxic congener released from any smouldering experiment was 2,3,7,8-TCDF (TEF of 0.1), which contributed < 5% of the PCDD/F mass in the LAB tests, and < 10% PCDD/F mass in DRUM tests.

The two laboratory repeats, LAB 1a and 1b, both of which were characterized as having robust smouldering throughout the test, had very similar PCDD/F results indicating good repeatability. Comparatively, LAB 2 was characterized as non-robust since it fostered non-self-sustaining smouldering, which was evident from the large crust formation and declining temperatures (Supplementary Materials, Section S1). This experiment released less PCDD/Fs than LAB 1a and 1b, even under weaker conditions, which could be due to less overall material smouldered during LAB 2. Overall, a very small quantity of PCDD/Fs (consistently below the ECA regulations) were released during each LAB test, irrespective of smouldering performance. The quantities were similar to the PCDD/Fs measured in the emissions from DRUM tests during less robust smouldering conditions (i.e., DRUM 1 and 3).
For the larger scale repeat of LAB 1a and 1b, i.e., DRUM 1, the PCDD/F sample may have captured end-effects when the smouldering front reached the end of the fuel bed (Figure 2). Similar to the behaviour of other condensable compounds in applied smouldering systems, PCDD/Fs may be released ahead of the smouldering front and retained by the porous media (i.e., sand) through (i) recondensation onto the cooler sand grains and/or (ii) physical filtration (e.g., if the PCDD/Fs are sorbed on unburned particulate material). If recondensation occurs, then some accumulated PCDD/Fs could be released when the smouldering front reached the end of the fuel bed, which has been demonstrated for other condensable compounds in smouldering systems (Kinsman, 2015; Martins et al., 2010; Rashwan et al., 2021b; Yermán et al., 2015). The total unburned hydrocarbons measured in the emissions from DRUM 2, 3, and 4 supports this recondensation hypothesis, as the total hydrocarbons relative to the CO\(_2\) fraction increased throughout smouldering propagation (Supplementary Materials, Section S2). Therefore, this data indicates that condensable hydrocarbons, sometimes including PCDD/Fs, likely accumulated in the cool region ahead of the smouldering front and were released from the system when the temperatures rose as the smouldering front approached the end of the system, i.e., similar to a common distillation column. All other tests were not timed to capture this end-effect (Supplementary Materials, Sections S1 and S2).

Under weaker smouldering conditions, the PCDD/Fs measured from DRUM 3 were generally similar to those measured when the smouldering front exited the fuel pack in DRUM 1. However, the weaker smouldering in DRUM 3 released additional PCDD/Fs that were not measured during stronger smouldering (i.e., DRUM 2 and 4) or when the front exited the column (DRUM 1). This may be because this experiment did not facilitate the high temperatures and residence times to
destroy these PCDD/Fs, and instead released them in the emissions; Section 3.2.3. discusses this hypothesized pathway in more detail.

In DRUM 2 and 4, the PCDD/Fs were sampled soon after self-sustaining smouldering was achieved and during robust smouldering (sample timing and temperature histories are presented in Supplementary Materials, Section S2). Therefore, these PCDD/F measurements demonstrate that very small amounts of PCDD/Fs were likely released during robust smouldering and recondensed locally, and a small amount of recondensed PCDD/Fs were likely released as an end-effect, as hypothesized in DRUM 1.

The normalized PCDD/F results in Figure 3 provide further insight into the conditions that influence PCDD/F release during smouldering. Interestingly, after accounting for all experimental and operational differences between LAB and DRUM tests, the PCDD/F results align more closely than in Table 3. While smaller LAB scale experiments exhibited slightly higher smouldering propagation velocities (Table 1), heating rates (Supplementary Materials, Section S1 and S2), and peak temperatures (Table 1) than the larger DRUM scale experiments, the characteristic smouldering behaviour in these two systems was similar. This similar system behaviour corresponds to similar PCDD/Fs released per mass of sludge smouldered (Figure 3), which demonstrates that PCDD/F released during sewage sludge smouldering may not be sensitive to changes in operational conditions (e.g., reactor scale or air flux). This is an important finding, as it demonstrates that the risk from PCDD/Fs may be low in commercial scale smouldering reactors for sewage sludge treatment.
Table 3: Summary of PCDD/F release in combustion gases from DRUM and LAB tests

<table>
<thead>
<tr>
<th>Congener</th>
<th>TEF¹</th>
<th>LAB 1a</th>
<th>LAB 1b</th>
<th>LAB 2</th>
<th>DRUM 1</th>
<th>DRUM 2</th>
<th>DRUM 3</th>
<th>DRUM 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>2378-TCDF</td>
<td>0.1</td>
<td>91</td>
<td>170</td>
<td>20</td>
<td>340</td>
<td>B.D.L.</td>
<td>120</td>
<td>B.D.L.</td>
</tr>
<tr>
<td>1234678-HpCDD</td>
<td>0.01</td>
<td>710</td>
<td>900</td>
<td>150</td>
<td>1100</td>
<td>B.D.L.</td>
<td>800</td>
<td>B.D.L.</td>
</tr>
<tr>
<td>OCDD</td>
<td>0.0003</td>
<td>2100</td>
<td>2400</td>
<td>1400</td>
<td>2000</td>
<td>B.D.L.</td>
<td>1900</td>
<td>B.D.L.</td>
</tr>
<tr>
<td>Total Mass Concentration ³ pg / m³</td>
<td>3100</td>
<td>3500</td>
<td>1600</td>
<td>3400</td>
<td>3400</td>
<td>0</td>
<td>3400</td>
<td>0</td>
</tr>
<tr>
<td>Total TEQ Concentration ⁴ pg TEQ / m³</td>
<td>35</td>
<td>26</td>
<td>3.9</td>
<td>45</td>
<td>48</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Oxygen content ⁵ %</td>
<td>16</td>
<td>17</td>
<td>19</td>
<td>18</td>
<td>16</td>
<td>16</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Oxygen correction factor ⁶</td>
<td>-</td>
<td>2.0</td>
<td>2.4</td>
<td>4.7</td>
<td>3.2</td>
<td>1.9</td>
<td>2.2</td>
<td>2.5</td>
</tr>
<tr>
<td>TEQ Concentration (corrected to O₂) ⁷ pg TEQ / m³</td>
<td>70</td>
<td>62</td>
<td>18</td>
<td>150</td>
<td>0</td>
<td>110</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

¹ Toxic equivalency factors (USEPA, 2010)
2 Below the detection limit (B.D.L.), where these limits are summarized in the Supplementary Materials
3 Sum of the PCDD/F mass measured in the emissions normalized per unit volume of emissions analyzed
4 Total mass concentration considering the TEQs of the PCDD/Fs measured
5 Measured immediately after the sampling train
6 Calculated according to the Canadian Council of Ministers of the Environment (1989) equation: Concentration (at 11% O₂) = Concentration × [20.9 − 11.0/20.9 − ]
7 TEQ concentration of PCDD/Fs in emissions normalized to 11% oxygen content
Figure 3: PCDD/F measured in the emissions from LAB and DRUM tests normalized per mass of dry fuel destroyed. The solid columns present the emissions results on the primary axis. DRUM tests 2 and 4 are not presented since both had no detection of any PCDD/F compound. The outlined columns show the upper and lower range of PCDD/F content in the virgin sewage sludge normalized per mass of dry fuel; thereby assuming the approximate maximum rates if all PCDD/Fs initially present in the sludge were released.
3.2.3. Pathways of PCDD/F Release

The sludge used in this study contained quantifiable amounts of 14 out of the 17 most toxic PCDD/F congeners. Figure 3 shows the PCDD/Fs originally present in the virgin sewage sludge normalized to the MC and range of ash contents typically observed in the sewage sludge (i.e., 22 – 29%). This illustrates a range of hypothetical maximum values if all PCDD/Fs initially present in the sludge were released. All the normalized PCDD/F releases from the DRUM and LAB experiments are lower than this hypothetical range. Moreover, all PCDD/F compounds released in the emissions were present in the virgin sludge, even the unique compounds released from DRUM 3 during weak smouldering. The mass fractions of PCDD/F congeners within the sludge are shown in Figure 4. The mass fractions also suggest that the measured compounds are being released rather than created, because they align with the distribution observed in the emissions, i.e., OCDD comprises the largest PCDD/F mass fraction at 86%, followed by 1,2,3,4,6,7,8-HpCDD at 7% (Supplementary Materials, Section S2).

Because the temperatures during smouldering treatment evolve in space in time, the sludge is heated from ambient temperature to peak smouldering temperatures at heating rates between 50-200 °C min⁻¹. Therefore, the PCDD/Fs originally present in the sludge may have transformed or changed phase due to the lower heating rates and transported out of the reactor instead of being completely destroyed. The drying, pre-heating, and pyrolysis zones (Figure 2) within a smouldering reactor provide the low-temperature conditions that may facilitate the release of PCDD/Fs originally present in the virgin sewage sludge. While most of these PCDD/Fs likely
recondense within the sand-sludge matrix ahead of the smouldering front, some may be released with the emissions.

Non-uniform conditions (both in the flow field and reactions due to heat losses) within the fixed bed may produce localized zones of lower temperatures, typically at the reactor edges, that result in air channeling (Figure 2B/C). With the smouldering front moving unevenly through the waste pack, some regions will be subjected to extended low-temperature conditions and may be bypassed by the smouldering front (i.e., unburned areas). Therefore, non-uniform conditions during weak smouldering may result in higher quantities of PCDD/Fs released in emissions relative to stronger smouldering conditions. Furthermore, during weaker smouldering conditions (e.g., DRUM 3), the unburned sludge would likely still contain some amount of the original PCDD/Fs. Comparatively, during robust smouldering, the PCDD/Fs that are not released from the sludge are almost completely destroyed (>99% of all compounds; Supplementary Materials, Section S3). Non-uniform conditions may be overcome by (1) improving the homogeneity of the fuel permeability (Solinger et al., 2020), such as through improved packing procedures, and (2) by decreasing the ratio between radial and axial heat transfer time scales (e.g., by decreasing the injected air flux) (Rashwan et al., 2021a). However, based on the emission factors for smouldering sewage sludge (Section 3.2.2.), even with the presence of non-uniform conditions, emission risks for PCDD/Fs are low compared to uncontrolled commercial incinerators.
Figure 4: Mass fractions of the 17 PCDD/F congeners found in the emissions from DRUM and LAB tests compared to the virgin sewage sludge.

3.2.4. Pathways of Formation

During non-robust smouldering conditions, products of incomplete combustion (e.g., VOCs) are more likely to form. VOCs, particularly benzenes and chlorinated benzenes, were quantified to provide some insight into potential PCDD/F formation via precursor pathways. The concentrations of benzene-type aromatic VOCs within the combustion gases of DRUM 3 and 5 are shown in Figure 5. Since DRUM 5 and DRUM 3 supported weak smouldering that resulted in large quantities of unburned and pyrolyzed sludge, the VOCs produced during these tests provides a conservative estimate of precursors present in the emissions during non-robust conditions. Overall, few benzene-type aromatic VOCs were observed in the combustion gases, and the trends are relatively consistent between experiments. The highest concentration of aromatic VOCs was released from DRUM 3, 27,500 µg/m³ of benzene, followed by 12,800 and
11,900 µg/m³ of styrene and toluene, respectively. These compounds were also released from DRUM 5, but to lesser extents, i.e., 8,800 µg/m³ of benzene, 5,600 µg/m³ of styrene, and 10,100 µg/m³ of toluene. Chlorobenzene, which is a known precursor of PCDD/Fs, was not present in detectable concentrations for DRUM 3 and relatively minor concentrations for DRUM 5 (254 µg/m³). Additionally, all isomers of dichlorobenzene, and 1,2,4-trichlorobenzene were below detection limits for both tests. Therefore, even under weak combustion conditions, smouldering does not produce significant quantities of PCDD/F precursor compounds, making this an unlikely pathway of formation.

*De novo* synthesis accounts for significantly less PCDD/F formation in typical incinerators than precursor pathways (Tame et al., 2007), and the same is likely true for smouldering. The chemistry, low process air fluxes, and filtration offered by the porous media minimize particulate matter and soot release in the emissions from smouldering systems (Torero et al., 2020). Therefore, *de novo* reactions, which occur on the surfaces of solid carbon in the combustion gases (e.g., soot; (Stanmore, 2004)), are probably negligible in sludge smouldering systems. However, more work is needed to better understand *de novo* reactions in smouldering systems.

Furthermore, the emissions temperatures directly above the fuel bed (between ~4 – 37 cm above pack for LAB tests and 40 – 60 cm DRUM tests) do not generally correspond to the range for optimal heterogeneous reactions (i.e., 200-400°C; Rathna et al., 2018) until after the smouldering front reaches the end of the fuel pack (see Supplementary Materials, Sections S2 and S3). These optimal temperatures are only achieved in the emissions following robust smouldering (e.g., LAB 1a and 1b, and DRUM 1 and 4) where robust smouldering would destroy any precursor
compounds that could potentially form PCDD/Fs in the post-combustion region. During weaker smouldering (e.g., LAB 2, and DRUM 3), the emissions temperatures did not achieve this optimal range, even though PCDD/Fs were detected. This result further suggests that PCDD/Fs measured were released, not formed.

PCDD/F formation may be possible from heterogeneous pathways in smouldering, much like incineration; however, results from this study were not able to identify de novo synthesis or precursor formation mechanisms despite smouldering in a wide range of operating conditions. More work needs to be done to fully understand the mechanisms governing the risks of PCDD/F formation in smouldering systems. If the formation mechanisms are possible, the most likely opportunity to capture them is as part of end effects (i.e., when the smouldering front reaches the end of the reactor). Future research could better characterize and quantify PCDD/Fs and other compounds during end-effects but this work needs to be designed with the transient nature of this region in mind. From these experiments, evidence on PCDD/F release points to mobilization of PCDD/Fs contained in the initial sludge.
Figure 5: Concentrations of aromatic VOCs in the combustion gases from DRUM 3 and 5 during sewage sludge smouldering. Compounds below the detection limits have been labeled as ‘BDL’.

4.0 Conclusion

Smouldering provides an economic and energy efficient technique for thermally treating sewage sludge and reducing hazardous by-product formation. Smouldering combustion destroys sludge and concentrates potentially toxic elements (PTEs) within a relatively small volume of post-treatment ash.

In terms of emissions by-products, smouldering acted as a sink for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), i.e., only 0 – 3% of the originally present PCDD/Fs were released in the emissions and >99% of the remainder were destroyed. Less than 1% of originally present PCDD/Fs remained in the post-treatment ash with the PTEs. This release of PCDD/Fs was relatively insensitive to operational conditions, including reactor scale and applied air flux.
However, due to recondensation, more PCDD/Fs may have been released as an end-effect when
the smouldering front reached the end of the reactor. Further research into understanding the
PCDD/F release dynamics may facilitate selective application of emissions management
measures when needed, instead of continuously. In all cases, because the quantity of PCDD/Fs
released were near the allowable limit for stack emissions in Canada, minimal emissions
treatment would be required, thereby simplifying industrial application of smouldering
treatment for sewage sludge.

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