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Evaluation of solvent for pressurized liquid extraction of PCDD, PCDF, PCN, PCBz, PCPh and PAH in torrefied woody biomass



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ABSTRACT

Biomass torrefaction for sustainable energy production has gained an increasing interest. However, there is a lack of information on the thermal formation of persistent organic pollutants such as dioxins in the torrefied solid product. In this paper, we investigated the applicability of pressurized liquid extraction (PLE) for simultaneous extraction of a number of polychlorinated planar aromatic compounds from torrefied wood. The targeted compounds included polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), benzenes (PCBz), phenols (PCPhs) and PAHs. PLE tests were conducted on torrefied and non-torrefied (i.e. raw) eucalyptus wood chips using 5 single solvents (n-hexane, toluene, dichloromethane, acetone and methanol) and a mixture of n-hexane/toluene (1:1, v/v). The performance of each solvent was evaluated in terms of recoveries of spiked internal standards and the amount of co-extracted sample matrix. High polarity solvents such as methanol and acetone resulted in poor recoveries from torrefied wood for most of the target compounds, probably due to the high co-extraction of thermally degraded lignocellulosic compounds. Raw wood was less solvent-dependent and comparable results were obtained for polar and non-polar solvents. Toluene showed the best performance of the investigated solvents, with average recoveries of $79 \pm 14\%$ and $66 \pm 9\%$ for raw and torrefied wood, respectively. The method was validated using pentachlorophenol-tainted spruce wood chips. The proposed PLE method was compared to the traditional Soxhlet method. Results show that PLE gave equivalent or better extraction for all target compounds.

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1. Introduction

In the transition to a sustainable energy production, there is an increasing need for the use of woody biomass as a replacement of fossil fuels [1]. Raw biomass is widely used as a fuel in various applications, including the production of electrical power and district heating. However, there are a number of challenges when biomass is utilized for coal co-firing due to its relatively low heating value, high moisture content, and susceptibility to microbial degradation. The tenacious fibrous structure makes grinding problematic for pulverization and/or densification processes [2,3]. Logistical management (i.e., transport and storage) of bulk volumes of biomass with low homogeneity is another challenge [4]. One process that could potentially solve all these problems is torrefaction, a thermal pre-treatment method that increases the energy

density of biomass and also improves its properties in other aspects [5,6]. Torrefaction is a mild pyrolysis process operated at temperatures of 200–350 °C and oxygen deficient conditions. In torrefaction, the most reactive fraction of the biomass, i.e. the hemicellulose fraction, is partly decomposed, resulting in a product with increased gross calorific value. Approximately 70–90% of the biomass remains as solid product, i.e. bio-coal. This technology enables the large-scale utilization of woody biomass in existing coal-fired power plants [6].

Many efforts have been made to understand the effects of the torrefaction conditions on the combustion behaviour of torrefied biomass [4,6,7]. However, there is a lack of information on the potential thermal formation of persistent organic pollutants (POPs) in the solid product after torrefaction. One important class of POPs is the dioxins, which commonly refers to two types of chlorinated aromatic compounds: polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF). Their formation involves chloro-organic precursors and/or intermediates such as polychlorobenzenes (PCBz), polychlorophenols (PCPh) and polycyclic aromatic hydrocarbons (PAH) [8]. In addition to PCDD and PCDF,

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polychlorinated naphthalenes (PCN) have recently received increasing attention due to their potential formation in thermochemical processes and similar biological effects as dioxins [9]. A pathway for PCN formation involving PAH precursor has been discussed [10]. A combination of inadequate processing temperature and insufficient oxygen supply has been shown to allow the formation and survival of chlorinated aromatics in the presence of chlorine and metal catalysts [11]. The current POPs studies mostly focus on high temperature processes such as combustion. There has been no publication, to our knowledge, that attempted to quantify POPs concentrations in torrefaction processes. A knowledge gap regarding the occurrence of these compounds and their environmental impact can only be filled when an appropriate analytical method is available.

Quantitative determination of PCDDs and PCDFs in biomass is challenging due to their ultra-trace levels and the highly complex matrix. Methods for the analysis of trace organic pollutants in environmental samples commonly involve Soxhlet extraction of the sample material followed by a multi-step sample clean-up procedure and then instrumental analysis using gas chromatography/mass spectrometry (GC/MS) [12,13]. However, the traditional Soxhlet extraction method is time- and labour-intensive, and requires large amounts of organic solvents. Pressurized liquid extraction (PLE) has been shown to be a promising alternative [14]. It involves extraction with organic solvent at elevated temperature and pressure to enable an exhaustive extraction of the target compounds with relatively short extraction time and low solvent consumption. PLE has been successfully applied to study POPs in a variety of environmental samples including soils, sediments and biota samples [15–18]. PLE has also been used to determine the amount of total extractives in woody biomass [19]. However, the suggested solvents for extraction vary from study to study because as with all other extraction technologies, the extraction efficiency of PLE is matrix-dependent [20].

For the application of PLE on torrefied biomass, one major challenge is the co-extraction of thermally degraded lignocellulosic materials with the target analytes, which, at elevated temperature, become more reactive and soluble in organic solvent. Since the characteristics of torrefied materials differ from those of wood, organic matter in soil, etcetera, due to the decomposition of the polymeric biomass [20] there is a need to develop and optimize PLE procedures for extractives in torrefied biomass. To the best of our knowledge, no attempt has been made to use PLE for the simultaneous extraction of dioxins, dioxin-like compounds, and related precursors (e.g., PCBz, PCPh and PAH) in such samples.

The aim of this study was therefore to develop a PLE method for the simultaneous extraction of PCDD, PCDF, PCN, PCBz, PCPh and PAH from raw and torrefied woody biomass. Of particular interest was the identification of the optimal extraction solvent or solvent mixture. The performance of five solvents frequently used in PLE was evaluated in terms of the recoveries of spiked internal standards and the co-extraction of interfering matrix components. Eucalyptus wood chips (raw and torrefied) were used as the substrates for the extraction tests, and the method was validated using pentachlorophenol-tainted spruce wood chips. The results obtained using the optimized method were compared to those achieved by conventional Soxhlet extraction.

2. Experimental

2.1. Samples

The biomass used for the solvent screening tests were raw and torrefied eucalyptus wood chips (typical length approx. 3 cm). Torrefaction was achieved by treating chips at 300 °C for 16 min

in an oxygen deficient atmosphere in a continuous rotary drum reactor. For the method validation, raw and torrefied pentachlorophenol (PCP)-impregnated spruce chips were used. Impregnation was performed by soaking 2 kg of spruce chips (typical length approx. 3 cm) with 5 g of technical grade pentachlorophenol (Witophen N, Dynamit Nobel) in methanol for 24 h and then applying a vacuum by means of water aspiration to allow the PCP to penetrate into the wood matrix. Torrefaction of the PCP-treated wood was conducted at a set temperature of 270 °C for 50 min in nitrogen using a bench-scale muffle furnace instead of the reactor used for eucalyptus torrefaction, due to the limited amount of spruce chips prepared for the experiment. Because of differences in furnace design and practical issues (e.g. that the muffle furnace had to be heated from room temperature) slightly different temperatures and substantially different treatment times had to be used to obtain the same degree of torrefaction.

Both raw and torrefied wood were ground to a particle size of <1 mm using a cutting-knife mill (Retsch SM 2000, 1 mm mesh) prior to PLE extraction, and were mixed carefully to ensure their homogeneity. A part of the PCP-impregnated samples (raw and torrefied) were further ground to a particle size of <0.5 mm using a ball mill.

2.2. Chemicals

All solvents were of high purity (HPLC grade) and were purchased from Fluka (Buchs, Germany), Merck (Darmstadt, Germany) and Fisher Scientific (Pittsburg, PA, US). Quantification standards, isotopically labeled (¹³C or deuterated) internal standards (IS) and recovery standards were obtained from Wellington Laboratories (Andover, MA, USA). More details of the native and isotopically labeled compounds used in this work are described elsewhere [13].

2.3. Study design

The study was divided into three stages: screening, optimization, and validation (Table 1). In the screening stage, a series of PLE experiments was performed to evaluate the performance of five solvents with different polarities: n-hexane, toluene, dichloromethane (DCM), methanol and acetone. The extraction efficiency of each solvent was examined by comparing the recoveries of spiked IS and the amounts of co-extracted material that were

Table 1

Outline of PLE extraction tests. Both raw and torrefied wood were employed in each trial. Unless otherwise stated, samples were ground to a typical particle size of <1 mm using a cutting mill.

Study stage	Extraction solvent	Wood type	Extraction method	No. of replicates
1: Solvent screening	n-Hexane	Eucalyptus	PLE	2
	Toluene	Eucalyptus	PLE	2
	Dichloromethane	Eucalyptus	PLE	2
	Acetone	Eucalyptus	PLE	2
	Methanol	Eucalyptus	PLE	2
2: Optimization (test of solvent mixture)	Toluene/n-hexane	Eucalyptus	PLE	2
3: Method validation	Toluene	Spruce	PLE	3
	Toluene	Spruce (<0.5 mm)	PLE	3
	Toluene/n-hexane	Spruce	PLE	3
	Toluene	Spruce	Soxhlet	3
	Toluene	Spruce	Soxhlet	3

measured gravimetrically. In the optimization stage, the two best solvents identified during screening were selected as binary solvent mixture. The PLE performance of the binary mixture was compared to that of the two individual solvents. In the validation stage, PLE with the best individual solvent and the binary mixture were evaluated further to validate the method. In addition, the effect of additional sample grinding by ball milling to a particle size of <0.5 mm was evaluated. The performance of PLE was compared to that of a conventional Soxhlet extraction method using toluene as the extraction solvent.

2.4. Sample extraction and cleanup

PLE extraction was performed using an ASE 300 system (Dionex, Sunnyvale, CA) equipped with a 66 mL stainless steel cell. Twelve grams of sample were mixed with 20 g toluene-washed sand (VWR international) and loaded into the cell. The IS were then added and PLE was performed at 160 °C using 3 extraction cycles and a flush volume of 60%. The static time was set at 5 min and the purge time was 90 s. Soxhlet extraction was performed in parallel to obtain reference values. For the Soxhlet extractions, 25 g of sample were mixed with toluene-washed sand (10 g) and loaded in a glass thimble with a porous frit. IS were then added and extraction was performed with toluene (about 400 ml) for 24 h. The extracts were concentrated by rotary vacuum evaporation.

A subsample (10% by mass) was taken from each extract and was used for gravimetric determination of its co-extractive content. A larger subsample (50% by mass) was used for PCDD, PCDF and PCN quantification, and was cleaned up using a multilayer silica column followed by an alumina column and then fractionated using an AX21-carbon column. A smaller subsample (25% by mass) of the concentrated extract was used for PAH, PCPh and PCBz analysis. PCPh was separated from PAH and PCBz by liquid-liquid extraction using a 0.5 M solution of NaOH. The aqueous phase containing PCPh was transferred to another vial, after which the PCPh was acetylated with acetic anhydride and extracted with cyclopentane. The organic phase containing PAH and PCBz was cleaned up using a deactivated SiO₂ column and eluted with cyclopentane. Recovery standards were then added and the volume of solvent was reduced prior to GC/MS analysis. The sample fractionation and cleanup protocols are described in detail elsewhere [13].

2.5. GC/MS

Instrumental analysis was carried out using two different GC/MS systems. A GC with a high resolution MS was used for analysis of PCDD, PCDF and PCN. It consisted of a Hewlett-Packard 5890 gas chromatograph (Agilent Technologies, Palo Alto, CA) coupled to an Autospec Ultima mass spectrometer (Waters Corporation, Milford, MA). Separation was performed on a J&W fused silica capillary column DB5-*ms* (60 m × 0.25 mm i.d. × 0.25 μm film thickness). Helium was used as the carrier gas at a constant flow rate of 1 mL min⁻¹. The injector temperature was set to 280 °C. The oven temperature was initially maintained at 190 °C (180 °C for PCN analysis) for 2 min, then increased to 270 °C at 3 °C min⁻¹, and was finally raised to 315 °C at 10 °C min⁻¹. The MS was tuned to a resolution of >10,000 and was operated using electron ionization and selected ion monitoring. Both the transfer line and ion source temperatures were set to 250 °C. A GC low-resolution MS was used for analysis of PCBz, PCPh, and PAH. It consisted of a GC (Hewlett-Packard 5890, Agilent Technologies, Palo Alto, CA) coupled to an Agilent 5975 MSD. Separation was performed on a ZB-SemiVolatile GC column (30 × 0.25 mm i.d. × 0.25 μm film thickness, Zebron). The injector temperature was set to 280 °C. The oven temperature was initially maintained at 80 °C for 2 min, then increased to 180 °C at 10 °C min⁻¹, and was finally raised to

300 °C at 12 °C min⁻¹. The MS was operated in the electron ionization mode using selected ion monitoring. Both the transfer line and ion source temperature were set to 250 °C.

2.6. Quantification

Quantification was performed by the isotope dilution method; the isotopically labeled standards used for each compound group are described elsewhere [13,21]. For each homologue, two of the most intense ions of the molecular ion isotope distribution cluster were monitored. Homologue sums were calculated based on the average response of available native congeners at the specific chlorination level.

3. Results and discussion

3.1. Evaluation of single solvents

The recoveries of the PCDD, PCDF, PCN, PCPh, PCBz and PAH internal standards from raw and torrefied wood using the five different solvents are presented in Fig. 1. The results are expressed as the mean recoveries of the spiked congeners from each compound group. MoCDD was excluded because of its evaporative losses. The recoveries of the spiked IS differ considerably between raw and torrefied wood. For the raw wood, the different solvents yielded fairly similar results, with acceptable recoveries of 50–130% in accordance with EN 1948 standard method [22] for most of spiked congeners. Conversely, for the torrefied wood poor recoveries were observed for most of the compound groups when using methanol (22 ± 3%) and acetone (43 ± 15%) as the extraction solvent. Hexane gave satisfactory results for PCDD, PCDF and PCN but poor recoveries of PAH, PCBz and PCPh. The best results were obtained using toluene, with an average recovery of 66 ± 9% over all spiked compounds. The recoveries of PCPh were highly variable, probably because of interfering compounds present in the final GC/MS analysis solutions or irreproducibility in the derivatization procedure [23].

There were large differences in the co-extractive contents of the extracts obtained using the different solvents, as shown in Table 2. The amount of co-extracted matrix appeared to correlate closely with solvent polarity [24] for the torrefied wood. For example, PLE with methanol, the most polar solvent, released the most co-extractives while PLE with *n*-hexane, the least polar solvent, resulted in the lowest level of matrix dissolution. The chemical compositions of extractives from torrefied biomass are diverse and can be categorized into i.e. sugar and sugar derived compounds, small organic acids, sterols, lignin units and some aromatics [25,26]. Most of these compound classes are better soluble in polar protic solvents than in non-polar solvents, such as *n*-hexane. For raw wood, *n*-hexane extraction released a relatively large quantity of extractives, probably because of the dissolution of lipophilic components (i.e. long-chain aliphatic acids, waxes and sterol esters) [27]. These are expected to have limited thermal stability and may disintegrate during torrefaction.

The poor extraction of spiked compounds from torrefied wood by polar solvents could be related to the high amount of co-extracted material in the resulting extracts, as shown in Table 2. During torrefaction, most of the hemicellulose and some of the cellulose and lignin in the wood are decomposed into smaller polymers [6,28]. Based on the principle that “like dissolves like”, this material may be more soluble in polar solvents with high hydrogen bonding capability (e.g., acetone and methanol) than in non-polar solvents such as hexane. As a result, the polar solvent extracts would have higher contents of co-extractives, which may affect subsequent analyses. This is especially true for methanol. It was

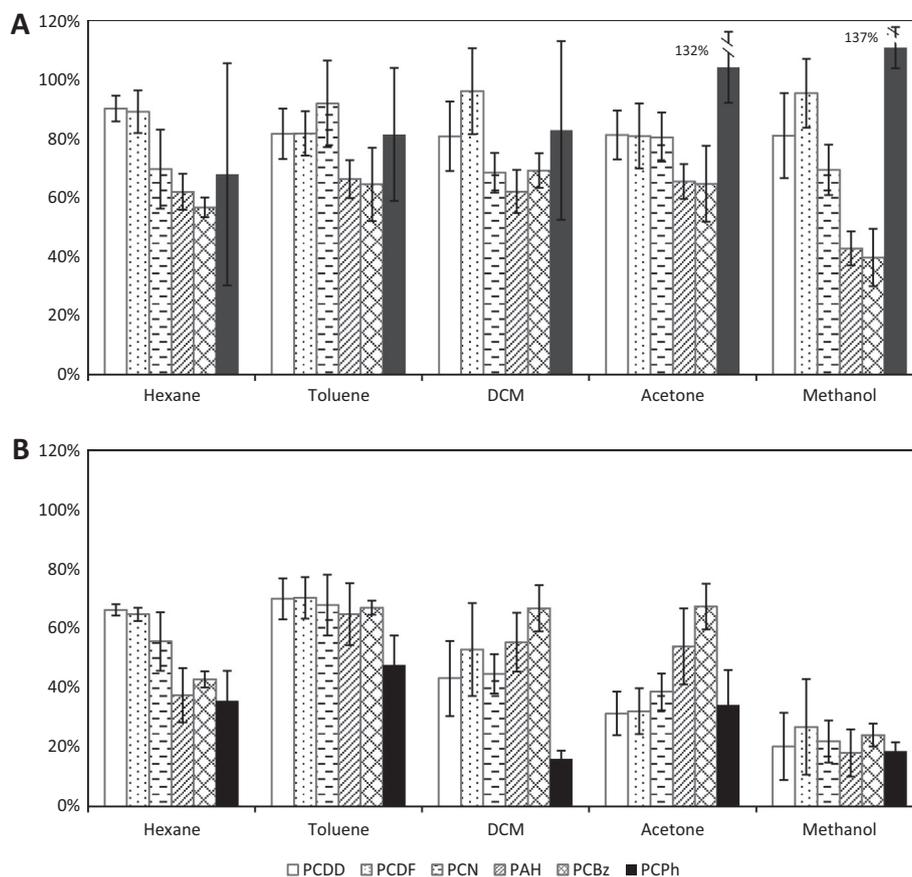


Fig. 1. Recoveries of PCDD, PCDF, PCN, PAH, PCBz and PCPh from raw (A) and torrefied wood (B) using five different extraction solvents. Error bars represent ± 1 standard deviations. DCM: dichloromethane.

Table 2
Matrix co-extractive contents of different PLE extracts.

	Snyder polarity index ^a	Raw wood		Torrefied wood	
		Extractives (% w/w)	RSD (%)	Extractives (% w/w)	RSD (%)
n-Hexane	0.1	0.75	7.4	0.08	10.5
Toluene	2.4	0.32	9.3	0.32	6.3
Dichloromethane	3.1	0.16	9.4	0.25	2.2
Acetone	5.1	0.77	3.1	0.99	4.9
Methanol	6.6	2.35	14.6	1.92	18.4

^a Snyder and Kirkland [24].

observed in our study that the methanol extraction resulted in high viscosity residue upon solvent removal. This dense and gelatinous concentrate was difficult to re-dissolve and transfer to the cleanup columns. As such, some of the analytes may not have been transferred to the cleanup columns or may have been encapsulated in the residue, leading to losses of target compounds. Similarly, encapsulation of contaminants in the wood matrix may explain the overall lower recoveries obtained for torrefied wood (Fig. 1B) as compared to raw wood (Fig. 1A).

In summary, our results show that polar solvents with hydrogen-bonding potential are not suitable for pressurized liquid extraction of POPs from torrefied wood. In addition, the aromatic solvent toluene performed better than n-hexane at extracting planar polynuclear aromatic compounds from torrefied wood. It is well known that such compounds have a high affinity to activated carbon and other carbonaceous materials such as torrefied wood [29]. This affinity may be due to π - π interactions in the case of

PAHs or charge-transfer complexation in the case of halogenated aromatics. Toluene is aromatic and can disrupt these strong analyte-matrix interactions more efficiently than n-hexane, which can only form weaker dispersive interactions with the target analytes. Matrix effects thus influence the sorption of both analytes and co-extractives, and both factors must be considered when selecting a PLE solvent. This is especially important for the torrefied material due to the generally low IS recoveries compared to those of raw materials, regardless the polarities of solvents employed.

3.2. Evaluation of a solvent mixture (toluene/n-hexane, 1:1)

Although single solvent extraction is currently the most common choice for PLE, there have been many attempts to find solvent mixtures that perform better than individual solvents. Combinations of polar and nonpolar solvents including acetone/toluene and acetone/n-hexane have proven to be effective for sample extraction in environmental analysis [30,31]. Our screening experiments revealed that polar solvents with hydrogen-bonding potential extracted large quantities of interfering materials, so binary mixtures featuring acetone were not investigated. Instead, a mixture of n-hexane and toluene (1:1) was tested in hope of achieving a similar extraction efficiency to that for toluene alone while releasing less co-extracted material than either of the individual solvents. The extraction efficiencies of the n-hexane/toluene mixture were within the acceptable range (50–130%) and statistically equivalent to those for toluene (Student's *t*-test at $\alpha = 0.05$) for all analytes in both raw and torrefied wood samples, with the exception of PCDF and PCBz in the torrefied

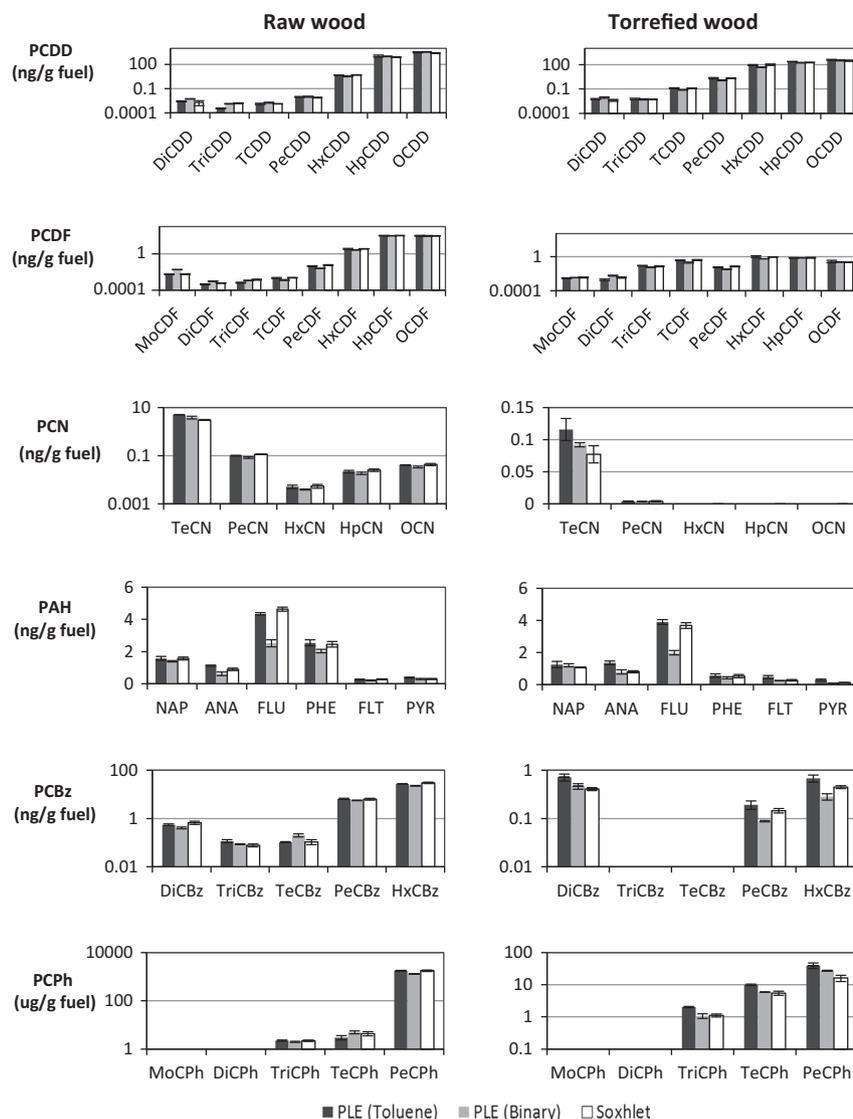


Fig. 2. Yields of PCDD, PCDF, PCN, PAH, PCBz and PCPh from raw and torrefied spruce wood (PCP-tainted). The three extraction types were PLE using toluene, PLE using n-hexane/toluene (binary mixture) and Soxhlet extraction using toluene. Error bars represent ± 1 SD. Individual PAHs are referred to by the following abbreviations: naphthalene (NAP), acenaphthylene (ANA), fluorene (FLU), phenanthrene (PHE), fluoranthene (FLT), and pyrene (PYR).

wood sample, which had a slightly improved recovery using the binary solvent ($75 \pm 7\%$ for PCDFs and $72 \pm 5\%$ for PCBz) compared to using toluene ($70 \pm 6\%$ for PCDFs and $67 \pm 2\%$ for PCBz). It was therefore concluded that the binary mixture gave similar extraction efficiency to that achieved with toluene alone, at least for the spiked IS. The co-extractive content of the n-hexane/toluene extract from the torrefied wood sample was also lower ($0.24 \pm 0.03\%$) than that achieved using toluene alone ($0.32 \pm 0.02\%$). This may partly explain the better results achieved with the binary mixture.

3.3. Validation

The performance of PLE with toluene and n-hexane/toluene (1:1) was evaluated using 'raw' and torrefied PCP-tainted spruce wood. Technical PCP normally contains relatively large quantities of impurities including PCDDs and PCDFs [32], and has been widely used as a wood preservative. Impregnation of spruce chips with technical PCP aimed to ensure that the torrefied material would contain measurable quantities of PCDDs and PCDFs so that the

developed PLE method could be validated against low, intermediate and high levels of the target analytes in a single sample [33].

The PLE results were compared to those obtained by the Soxhlet method, as shown in Fig. 2. The concentrations of PCDD, PCDF, PCN, PCBz, and PCPh are presented as homologue sums, and six representative PAHs were selected for analysis from the 16 prioritized by the US EPA. The results obtained with toluene and the binary mixture were comparable for most of the PCDD and PCDF. However, toluene provided higher yields of TeCN, fluorene, fluoranthene, pyrene, and most of the PCBzs and PCPhs in the torrefied wood samples. The difference in performance between toluene and the binary mixture was less pronounced for the raw wood sample. Statistically significant differences (Student's *t*-test, $\alpha = 0.05$) were only found for fluorene, acenaphthylene and phenanthrene; in all three cases, toluene provided a higher yield. This difference may indicate that the analyte-matrix interactions in torrefied wood are stronger than in raw wood, and that toluene is more efficient at disrupting these interactions. The IS recoveries were also better for toluene (PCBz $103 \pm 8\%$, PCDF $89 \pm 13\%$, PCDD $84 \pm 3\%$, PCN

108 ± 15%) than for the binary mixture (PCBz 102 ± 6%, PCDF 80 ± 13%, PCDD 67 ± 3%, PCN 95 ± 12%). We therefore conclude that toluene is the preferred PLE solvent for our application.

It is noteworthy that the binary solvent mixture extracted PCBz and PCDF better than toluene in the initial solvent evaluation study, whilst the opposite was true in the validation study. However, the differences in extraction efficiency between the two extraction systems were small in both cases. In addition, slightly different samples were used in the two studies (see Section 2.1 for details).

The proposed PLE method exhibited excellent precision, with relative standard deviations (RSD%) below 20% for all compounds. Repeated extraction of the same sample released <0.5% of the amounts found after the first extraction (based on the total concentration of each group of compounds), suggesting that the proposed method is exhaustive. The results for the ball-milled samples (<0.5 mm) were virtually identical to those for the cutting-knife milled samples (<1 mm), suggesting that extra grinding was unnecessary. The PLE method using toluene performed similarly to the traditional Soxhlet method for PCDD and PCDF and better for PCN, PAH, PCBz and PCPh.

A comparison of the PCDD and PCDF levels before and after torrefaction showed that highly chlorinated PCDDs and PCDFs including OCDD, HpCDD, OCDF and HpCDF were lower in the torrefied product than the raw material. Conversely, the concentrations of PCDDs and PCDFs with relatively low degrees of chlorination such as TriCDF, TeCDF, TeCDD and PeCDD were higher in the torrefied product. A similar trend was observed in a study on the pyrolysis of contaminated waste wood [33]. They suggested that decomposition of higher chlorinated PCDD and PCDF, and/or formation of less chlorinated PCDD and PCDF might be responsible for the observed results. Further discussion on the formation and/or removal of PCDDs and PCDFs during torrefaction is beyond the scope of this study.

4. Conclusion

Simultaneous determination of multiple POPs in environmental samples has long been challenging due to their ultra-trace levels, the highly complex matrices, and the wide range of target chemicals. For the application of PLE on torrefied wood, one additional difficulty is the co-extraction of thermally decomposed lignocellulosic materials as interference for POPs quantification, which has not been addressed before. In this study, we demonstrated the feasibility of using PLE for simultaneous extraction of PAH and five groups of chlorinated planar aromatic compounds (PCDD, PCDF, PCN, PCBz, PCPh) in torrefied woody biomass. The choice of solvent for PLE is critical because the extraction efficiency depends on the nature of the biomass matrix as well as the properties of the target analytes. Solvents with high polarity give rise to high amount of interfering co-extractives from the thermally degraded lignocellulosic biomass, while non-polar solvents such as hexane do not efficiently extract the target analytes from torrefied wood. Toluene proved to be the optimal solvent for this application because it provided adequate extraction of the target analytes and limited extraction of the matrix. Our results demonstrate that PLE with an appropriate extraction solvent provides a reliable extraction and enable simultaneous quantification of PAH and several chlorinated planar aromatic compounds in thermally treated woody biomass. Torrefaction is an emerging alternative in biomass thermal refining, and could possibly be introduced as the initial step in all thermochemical processes. The provided information in this paper could be beneficial for monitoring organic pollutants in the process of not only torrefaction but also pyrolysis and gasification.

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