



Waste timber pyrolysis in a medium-scale unit: Emission budgets and biochar quality

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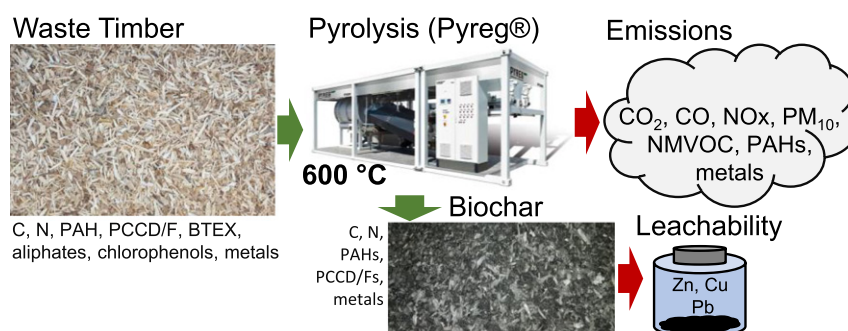
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HIGHLIGHTS

- Pyrolysis of waste timber results in similar emissions to clean wood and leaves.
- Polycyclic aromatic hydrocarbons and metals are enriched in biochar produced from waste timber.
- Polycyclic aromatic hydrocarbons and metals make waste timber biochar unfit for agricultural use.
- Metals in the waste timber biochar have low leachability at neutral pH (<0.1%).
- Pyrolysis should be considered as waste treatment for lightly contaminated organic waste.

GRAPHICAL ABSTRACT



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ABSTRACT

Pyrolysis of organic waste or woody materials yields a stable carbonaceous product that can be mixed into soil and is often termed “biochar”. During pyrolysis carbon-containing gases are emitted, mainly volatile organic carbon species, carbon monoxide and aerosols. In modern pyrolysis units, gases are after-combusted, which reduces emissions substantially. However, emission data for medium- to large-scale pyrolysis units are scant, both regarding gases, aerosols, heavy metals and polycyclic aromatic hydrocarbons (PAH).

Making biochar from lightly contaminated waste timber (WT) is a promising waste handling option as it results in the potential valorization of such residues into e.g. sorbents for contaminant stabilization. For this process to be environmentally sustainable, emissions during the process need to be low and the resulting biochar of sufficient quality. To investigate both issues, we pyrolyzed three batches of WT and one reference batch of clean wood/leaves in a representative medium-scale pyrolysis unit (Pyreg-500, 750 t/year) with after-combustion of the pyrolysis gases, and measured the gas, aerosol, metal and PAH emissions, as well as the characteristics and contamination levels of the resulting biochar, including contaminant leaching.

Mean emission factors for the WT were (g/kg biochar); CO = 7 ± 2 , non-methane volatile organic compounds (NMVOC) = 0.86 ± 0.14 , CH₄ = 0, aerosols (PM₁₀) = 0.6 ± 0.3 , total products of incomplete combustion (PIC) = 9 ± 3 , PAH-16 = $(2.0 \pm 0.2) \cdot 10^{-5}$, As (most abundant metal) = $(2.3 \pm 1.9) \cdot 10^{-3}$ and NO_x =

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0.65 ± 0.10 . There were no significant differences in emission factors between the pyrolysis of WT and the reference respectively, except for PM_{10} , NMVOC, and PAH-16, which were significantly lower for WT than for the clean wood/leaves. The WT biochar did not satisfy premium or basic European Biochar Certificate criteria due to high levels of zinc and PAH. However, leachable metal contents were $<0.1\%$ of total contents. Still, use of the WT-biochar without further improvement or investigation would be limited to ex situ use, not improving soil fertility or in situ remediation.

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1. Introduction

Biochar is produced through pyrolysis of biomass. Due to its high carbon content and stability, it has been advocated as a climate change mitigation technology (Lehmann and Joseph, 2015). An important application of biochar is that it can be used for soil restoration, to improve crop productivity especially in weathered and eroded tropical soils (Jeffery et al., 2017). Another important soil restoration application is the immobilization of soil contaminants, where biochar binds the contaminants so strongly that their leaching to groundwater and uptake in organisms and plants are reduced (Ahmad et al., 2014; Hale et al., 2016).

An important environmental effect of pyrolysis is deleterious emissions during production (Pennise et al., 2001; Sparrevik et al., 2013). Emitted products include methane, carbon monoxide (CO), aerosols ($PM_{2.5}$ or PM_{10}), nitrogen monoxide and dioxide (NO and NO_2 , together NO_x), as well as non-methane volatile organic matter (NMVOC), in addition to hydrogen and micro-pollutants such as heavy metals, metalloids, and polycyclic aromatic hydrocarbons (PAHs) (Pennise et al., 2001). Many of these gases are deleterious to human health, and/or they exacerbate anthropogenic radiative forcing. Most modern pyrolysis units have after-combustion features to avoid emitting these gases and aerosols into the atmosphere, making the production of biochar in modern industrial devices a controlled process with low gas and aerosol emissions and resulting in certifiable high-quality biochar (Peters et al., 2015).

However, published emission factors for gases and aerosols are scant (for the main gases and aerosols) or absent (heavy metals and PAHs), and e.g. life-cycle analyses (LCAs) of modern medium-scale pyrolysis units have been forced to rely on manufacturer's data or estimates from reactor model simulations (Peters et al., 2015).

The majority of research until now has focused on the preparation of biochar from agricultural- and forestry residues (Lehmann and Joseph, 2015), but there are an increasing number of studies looking at other waste fractions as feedstocks for biochar production, a few examples being paper mill effluent (PME) (Devi and Saroha, 2014), sewage sludge (Barry et al., 2019; Kistler et al., 1987) and municipal solid waste (Dong et al., 2015).

Waste timber (WT), a mixture of discarded, lightly-contaminated wood products, such as wood used for construction, furniture and other wooden objects with remains of paint, binding agents and metal, can be a promising feedstock to be valorized into biochar sorbents for the stabilization of soil contaminants (Silvani et al., 2019) or other uses such as a micro-filler for cement (Gupta and Kua, 2019). When using pyrolysis for the handling of contaminated waste for further use as biochar, it is important to assess the potential risk of contaminant content in the biochar (Devi and Saroha, 2014). During pyrolysis, feedstock mass reduction through charring generally leads to an enrichment of metals in the biochar as the majority of the metals are not released through exhaust (Devi and Saroha, 2014; Dong et al., 2015; Kistler et al., 1987). Metals released are a mixture of volatile metal species and metals associated aerosols that escape with the exhaust gasses. Furthermore, a net production of PAHs during pyrolysis is expected due to the nature of the process where aromatic rings are condensed and fused into PAH-like sheet structures (Hajaligol et al., 2001; Mastral and Callén, 2000; Wornat et al., 1987).

The European Biochar Certificate specifies contaminant threshold levels in biochar for agricultural soil improvement (EBC, 2012). These threshold levels are all based on total content in the solid phase. Meanwhile, to give an accurate assessment of risk, bioavailable concentrations should be considered (Reichenberg and Mayer, 2006). The heavy metal content in biochar is highly variable and depends on both feedstock type and pyrolysis process parameters (Beesley et al., 2015), but an elevated biochar pH provides conditions under which most heavy metals have low solubility (Devi and Saroha, 2014; Kistler et al., 1987). However, the high alkalinity in biochar elevating the pH might not last in the long term due to leaching and soil acidity. Bioavailable concentrations of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and dioxins/furans have been reported as negligible in biochars made from a number of different feedstocks (Hale et al., 2012).

As pyrolysis of waste potentially leads to contaminants in both emitted gases and the biochar product, it is important to look at the environmental aspects of the whole pyrolysis process when considering this as a waste treatment option. Therefore, the following research questions were formulated for this study: 1) How are contaminants partitioned between emitted gasses and the biochar product? 2) Does the pyrolysis process decompose/destroy contaminants or lead to more contaminants being produced? 3) What are the leachable/bioavailable content of contaminants in the biochar? Such an understanding of the whole process will provide a more solid basis for assessing the overall environmental impact of pyrolysis as a waste treatment option.

In order to answer these questions, the gas and aerosol emissions of WT pyrolysis in a modern medium-scale unit were investigated and compared to those from a gardening/forestry residue mixture. The quality of the resulting biochars was also evaluated. The pyrolysis unit was fabricated by the company Pyreg and equipped with an after-combustion chamber for oxidation of the pyrolysis gases. The unit can be considered representative for units without electric temperature control, i.e., the pyrolysis energy is used to maintain pyrolysis temperatures $>600^\circ\text{C}$. Gas and particle emissions (CO_2 , CH_4 , CO, NMVOC, aerosols/ PM_{10} , NO_x , metals, PAHs) were determined, as well as biochar characteristics (elemental composition, specific surface area, metal content, PAH content, dioxin content). Thus, this paper is among the first to provide an emission budget, including metals and PAHs, for a medium-scale (750 t/year), modern pyrolysis unit with after-combustion features, using a novel feedstock. In contrast to woody residues from gardening and (agro)forestry, lightly contaminated waste timber is a novel feedstock for biochar generation. This study also provides new insights into how the pyrolysis process affects the contaminant content (metals and organic compounds) in- and leachability (metals) from the WT biochar.

2. Materials and methods

2.1. Pyrolysis

2.1.1. Pyrolysis unit

A Pyreg pyrolysis unit is a medium-sized unit developed for pyrolyzing agricultural waste, green waste and sludge. Pyreg units have been installed at approximately 25 locations, in Austria, China, Germany, Sweden, Switzerland and USA (California). The unit used in this study

was a Pyreg-500, owned by Verora, and located in Edlibach, Switzerland. In this unit, pyrolysis occurs in a cylindrical furnace heated externally by the products of combustion of the pyrolysis gases (Fig. 1). The residual heat is commonly used to dry biomass before pyrolysis but can be diverted for other applications.

2.1.2. Operating principle

The biomass was supplied via a gas-tight feeding mechanism (rotation valve) to the pyrolysis reactor. In the pyrolysis reactor, two screw-shaped conveyors, powered by an electric motor, provided continuous transport through the reactor and assisted in uniform heating of the biomass. The residence time for biomass in the pyrolysis reactor was 20 min. Biomass was pyrolyzed at a temperature of approximately 600 °C. Biochar and pyrolysis gas are not actively separated in this unit. Charred microparticles are however separated from the pyrolysis gas stream in a cyclone (Fig. 1), before the pyrolysis gas is channelled into the combustion chamber and burned by preheated combustion air through flameless oxidation.

2.1.3. Feedstock

Finely shredded waste timber chips from a recycling company in Norway were used as feedstock in the Pyreg unit. Three samples of waste timber chips (WT 1–3), each 2 m³ – approximately 344 kg (d. w.), were pyrolyzed. Waste timber (WT) is a lightly contaminated mix of discarded wood from various businesses (demolition of houses, container rentals, etc.) and wood products from public recycling stations. In practice, it is a mix of pure wood products (such as wood beams, pallets, etc.), and wooden objects such as furniture (Fig. S1). This means that the WT batches consisted of both pure wood, wood fiber and traces of painted wood, in addition to hard board and soft board with various binding agents. No impregnated wood was used. Some of the wood products included in the WT-fraction contain nails or metal plating. Most of these metal products are removed by magnet and manual sorting before chipping, but it is likely that there are some remains of

scrap metal pieces in the feedstock. A test to quantify the amount of scrap metal pieces is described in the SI (section 2). As current sorting processes do not remove all metal pieces from the feedstock however, the WT feedstock should be considered lightly contaminated by metals.

Three parallel samples were taken at random from a pile (>10,000 m³) of waste timber assembled during the month of April 2018. It is assumed that these waste timber samples were representative for a typical mixture of lightly contaminated waste timber handled by a recycling company. However, the authors recognized that there was considerable variation in the origin and properties of each individual wood chip in the batches.

A mixture of clean wood and leaves from gardening waste (both hardwood and softwood; Fig. S1) is the conventional feedstock at the Verora Pyreg plant. A 1 m³ sample of this material (approximately 189 kg d.w.) was run in the Pyreg unit, under the same conditions and with the same measurements as the waste timber samples, to serve as a reference.

For each batch of biomass feedstock about 40 kg of biochar was made in 1.5 to 2 h. Before each sample batch of WT was started, the unit was run with that particular sample for 30–60 min to ascertain that the emissions would not be affected by the previous batch.

2.1.4. Pyrolysis process temperatures

Temperatures measured at the inner wall of Reactors 1 and 2 were 503 ± 33 °C during the runs of waste timber samples (WT 1–3), and 477 ± 18 °C during the runs of the reference sample. The temperature at the centre of the reactors is likely higher, as the temperature in the cyclone with no external heating, was 700–800 °C. Considering the cyclone temperature (700–800 °C) and pyrolysis gas temperature (≈500 °C), it is likely that the pyrolysis temperature was >600 °C. Incineration of the pyrolysis gases occurred at temperatures >1000 °C (1023 ± 19 °C for WT, 1096 ± 15 °C for the reference). After heating the Pyreg® reactor, the temperature of the exhaust gases was 500–600 °C. The change in temperatures in the different compartments of the

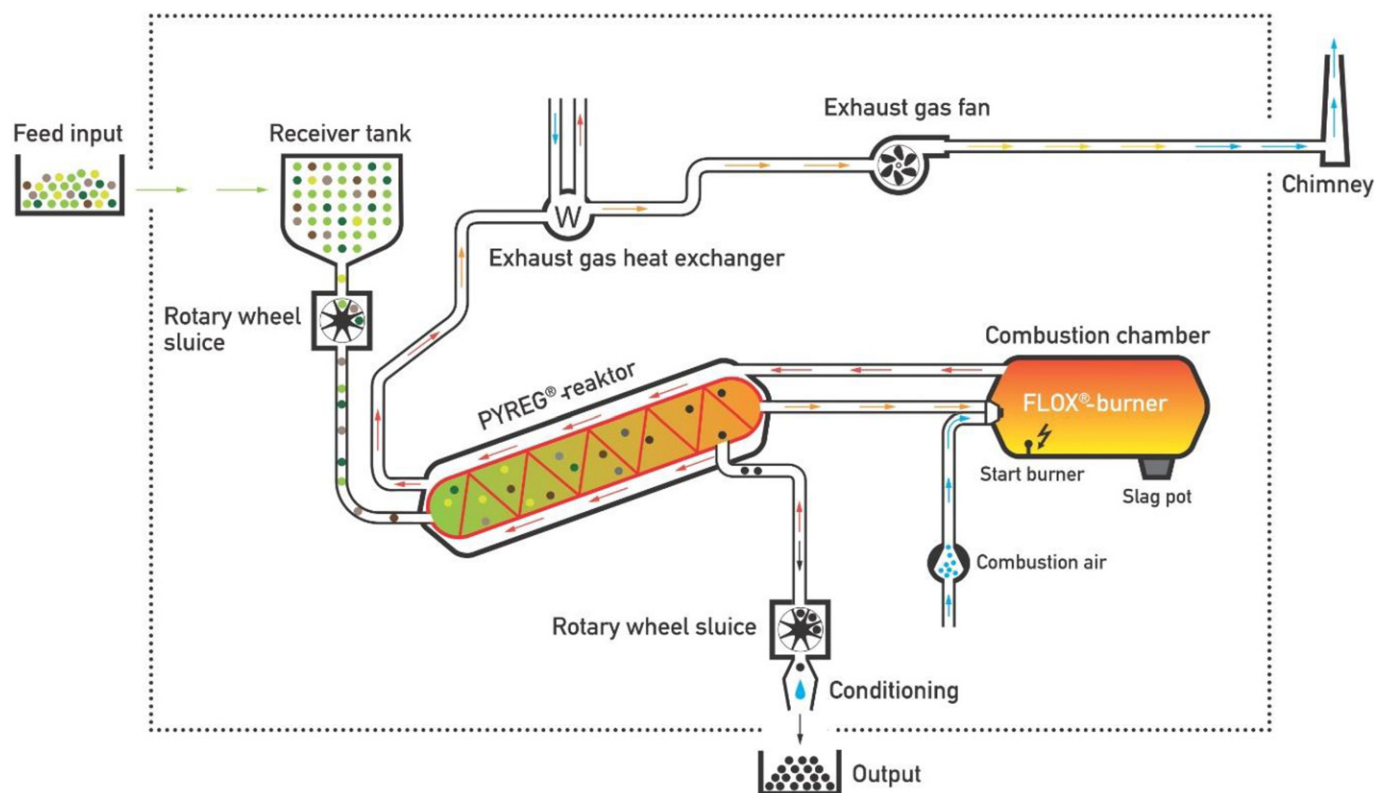


Fig. 1. The principle of the Pyreg-500 unit: The pyrolysis occurs in a cylindrical furnace (PYREG® reactor) heated externally by the products by flameless combustion of the pyrolysis gases in the combustion chamber (FLOX®-burner). An exhaust gas heat exchanger transfers residual heat to external use.

Pyreg unit during the pyrolysis cycles is demonstrated for the all four samples in Fig. S2.

2.2. Feedstock characterization

2.2.1. Moisture content

Moisture in the feedstock was measured by weighing before and after drying overnight at 110 °C. The waste timber contained 8.6% moisture, whereas the reference wood/leaves batch contained 20.9% moisture.

2.2.2. Elemental composition

Subsamples of the air-dried and sieved samples were dried at 60 °C to determine dry matter content and then milled prior to determination of total carbon (C) and total nitrogen (N) by dry combustion (EC12, C determinator, Leco Corporation) (Nelson and Sommers, 1982) and the Dumas method (TruSpec, CHN analyzer, Leco Corporation) (Bremmer and Mulvaney, 1982), respectively. The carbon content in the feedstock samples was used to establish a carbon balance during carbonization to calculate emission factors.

2.2.3. Contaminant concentrations

The WT samples were per definition not contaminated but were screened for traces of a wide range of contaminants in order to document the absence or presence of unknown contamination. All analyses of contaminants in the WT feedstock was done in triplicates according to accredited methods. Metals (As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sn, V and Zn) were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES) according to standard ISO 11885. Volatile organic compounds (VOCs) in the form of benzene, toluene, ethylbenzene and xylenes (BTEX), aliphates with carbon chain lengths C5–C10, chlorobenzenes (mono-, di-, tri-, tetra-, penta- and hexachlorobenzenes) and chlorinated solvents (dichloromethane, 1,2-dichloroethane, 1,2-dichloropropane, trichloromethane, tetrachloromethane, trichloroethanes, trichloroethene, tetrachloroethene and vinyl chloride) in the biochar were all analyzed using gas chromatography mass spectroscopy (GC–MS) in accordance with standard ISO 15009. Chlorophenols (2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dichlorophenol; 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- and 3,4,5-trichlorophenol, 2,3,4,5- and 2,3,4,6-tetrachlorophenol and pentachlorophenol) were also analyzed using GC–MS, but according to standard ISO 14154. Aliphates with carbon chain lengths C₁₀–C₃₅ were determined using gas chromatography with a flame ionization detector (GC–FID) using method EN 14039. Chlorinated pesticides (17 pcs, see Table S3 for full list), were measured using gas chromatography with electron capture detection (GC–ECD) by US-EPA method 8081.

2.3. Emission measurements

2.3.1. Gas emissions

Effluent gas from the Pyreg unit was analyzed for carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), non-methane volatile organic carbon (NMVOC), nitric oxides (NO_x) and particulate matter (≤10 µm, PM₁₀). Total suspended particles (TSP) were derived from PM₁₀ as described by Sparrevik et al. (2015), to give a measure for aerosol content in the effluent gas. Total products of incomplete combustion (PIC) were calculated by summarizing the contents of CO, CH₄, NMVOC and TSP (PM₁₀). During the 1.5 to 2 h run-time of each batch, 6 to 10 gas emission measurements were conducted for CO, CO₂, CH₄, NMVOC, NO_x and PM₁₀. All measurements were done at the exhaust pipe of the Pyreg unit, the only outlet for gases and aerosols.

CO was measured using a Kane 255 KIT flue gas analyzer with a detection limit of 1 ppm and a maximum concentration of 20,000 ppm. CO₂, NO_x, CH₄ and NMVOC were measured using a Microdetector II 6460, which has an infrared sensor with detection limit 0.1% for CO₂ and CH₄, a photoionization detector (PID) with detection limit

0.1 ppm for NMVOC, and an electrochemical sensor for NO. The measured NO-value was converted by the instrument to NO_x by assuming that 97% of NO_x is NO (conversion factor 1.03) (Sparrevik et al., 2015). The PID was calibrated before use with an isobutene standard. PM₁₀ was measured with a Thermo Scientific pdr-1500 instrument, which has a photometric detector with a detection limit of 0.1 µg/m³. In order to convert the measured PM₁₀ mass units to molar ratios, it was assumed that all particles consisted of elementary carbon. Furthermore, it was assumed that TSP contains 70% PM₁₀ (Schikowski et al., 2005), and thus a conversion factor of 1.4 was used to calculate TSP from measured PM₁₀.

2.3.2. Metal and PAH emissions

PAH and metals in the emitted gasses were sampled using a low volume air sampler operated at a rate of 2 m³/h and equipped with exact measurement of total air flow. In this sampler, particles are collected on a pre-washed glass fiber filter (GFF, 0.45 µm) and gas phase PAH in a pre-washed polyurethane foam (PUF). Particles on the GFF were analysed for metals (As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Mo, Pb, Sn, V and Zn) by digesting the whole filter with HNO₃ in an Ultraclave from Milestone at 260 °C. After digestion the sample was diluted and analysed for metals using an Agilent Triple QQQ 8800 ICP-MS with a reaction-collision cell. PAHs in particles collected on GFF and PUF was extracted using accelerated solvent extraction (ASE) with toluene, clean up in a silica column and the extracts then analysed using GC–MS–MS according to ISO 12884. Deuterated internal standards were used (Naphthalene-D8; Acenaphthene-D10; Phenanthrene-D10; Fluoranthene-D10; Benz(a)pyrene-D12; Dibenzo(ah)anthracene-D14). Total PAH concentrations in emitted gases were reported as the sum of the particulate and gas phase concentrations.

For metals and PAHs one measurement integrated over the whole time interval was done for each sample batch, because detection limits did not allow more frequent measurements. All measurements were done at the exhaust pipe of the Pyreg unit, the only outlet for gases and aerosols.

2.3.3. Data analysis

Emission factors were calculated using the carbon balance approach (Bailis et al., 2003; Cornelissen et al., 2016; Pennise et al., 2001; Sparrevik et al., 2015). This method circumvents the need to register the absolute mass of gases emitted in order to calculate emitted quantities of each gas per mass of feedstock. A carbon balance was set up between the biomass going into the process and the biochar coming out. Then the net molar component-to-CO₂ emission ratios were calculated and used to derive the emission factors in g per kg biochar produced. More details can be found in Cornelissen et al. (2016) and Sparrevik et al. (2015).

Standard deviations and standard errors of the mean were calculated with regard to the propagation of errors. For the emission factors however, standard deviations were simplified to reflect only the variance within the calculated factors.

A Tukey Honestly Significant Difference (HSD) test was used to test for effects of sample type on gas emission concentrations (CO₂, CO, CH₄, NMVOC, NO_x, and PM₁₀). The emission concentrations for the three samples (WT 1–3) and the reference were compared. For all tests, differences with *p*-values < 0.05 were considered significant.

2.4. Biochar characterization

2.4.1. Yield and general properties

To establish accurate mass balances for the yield calculations, smaller subsamples of each of the WT samples and the reference sample (about 10 kg d.w.) were run in only one of the two parallel pyrolysis chambers, for 10 min. Moisture content was determined in the same way as for the feedstock. The WT biochar had a water content of 33%, while the reference biochar contained 28% water. The biomass feeding

rate and biochar output rate were determined by weighing the masses 3 times, each time with 10 min for scale equilibration. Carbon and nitrogen were determined using the same method as for the feedstock.

A range of other biochar properties were determined for the WT according to the described standard from EBC (2012).

2.4.2. Contaminant content

All biochar samples were analysed in triplicates. Carbon content in the biochars was measured on 100-mg samples using the same methods as for the WT feedstock. The biochars were analysed for 16 individual PAHs by 36-h exhaustive toluene Soxhlet extraction according to published procedures (Hale et al., 2012; Hilber et al., 2012). The same deuterated internal standards as for the GFF and PUF analysis were used. PCDD/Fs (17 congeners) were extracted with toluene (ASE) and cleaned up using mixed silica columns (acid, neutral and basic) and aluminium oxide column, before being analysed with HR-MS according to standard EN 16190. Seventeen ^{13}C -labelled internal standards were used (1 for each congener). Surface area and pore volume were done by N_2 adsorption at 77 K according to the method described by Kwon and Pignatello (2005). Metals (As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sn, V and Zn) in biochar were measured using ICP-OES according to standard ISO 11885. Aliphates ($\text{C}_5\text{--C}_{35}$), BTEX, chlorobenzenes, chlorinated solvents, chlorophenols and chlorinated pesticides were analysed by ALS Laboratory Group Norway AS using the same accredited methods as described for the feedstock.

2.4.3. Enrichment factors

Enrichment factors for metals in biochars were calculated as the ratio between a metal in the biochar and the feedstock, as shown in Eq. (1):

$$E_f = C_{\text{metal, biochar}} / C_{\text{metal, feedstock}} \quad (1)$$

where E_f is enrichment factor, $C_{\text{metal, biochar}}$ the concentration of a metal in biochar and $C_{\text{metal, feedstock}}$ the concentration of the same metal in the feedstock.

2.4.4. Leaching tests

Leachable content of metals and anions was estimated using a batch leaching test with a liquid to solid ratio (L/S) equal to 10, in accordance with CEN EN 12457. Eluates were filtrated using a GFF (0.45 μm) before analysis. Metals in the eluates were determined according to methods ISO 17294-1,2(mod), ISO 11885(mod) and ISO 17852. Anions in the

eluates were analysed by ion chromatography using methods ISO10304-1 and NS-EN 16192 and dissolved organic carbon (DOC) by infrared spectrometry (IR) according to methods NS-EN 1484 and NS-EN 16192. pH in the eluates was measured by potentiometry according to ISO 10523.

3. Results and discussion

3.1. Feedstock composition

The chipped waste timber samples and pure mixed wood (reference) both contained about 50% total carbon, as was expected for biomass from temperate/boreal trees (Thomas and Martin, 2012) (Table 1). The higher nitrogen (N) concentration in the waste timber (2%) compared to the mixed wood reference (1%) was unexpected, as the reference contained more leaves, which are known to have higher N-concentrations than wood (Nordin et al., 2001). The difference could be a result of additives in the waste timber and/or the use of heavily fertilized young trees for the industrial wood production, as N has been shown to be accumulated in fertilized trees (Nordin et al., 2001). The C/N ratios were around 25 for the waste timber and 60 for mixed biomass.

Few organic contaminants were detected in the WT samples (Table 1 and S3), with the exception of $\Sigma\text{PAH-16}$ (0.9 ± 0.7 mg/kg). Traces of tri-, tetra- and pentachlorophenols (<1 mg/kg) were detected in all three WT samples, in addition to the chlorinated pesticide Lindane ($\gamma\text{-HCH}$, 0.05 ± 0.05 mg/kg) in the WT 2 sample. No polychlorinated biphenyls (PCBs), chlorinated benzenes, phthalates, brominated flame retardants or organic solvents were detected. The PAH content of the reference (3.5 mg/kg) was somewhat higher than that of the WT samples, possibly due to dust deposited on leaves and bark (e.g. dust from traffic). Aliphate content ($\text{C}_{16}\text{--C}_{35}$) was detected in the WT samples (884 ± 420 mg/kg), but this is most likely natural oil and tar in the wood material since the aliphate content ($\text{C}_{16}\text{--C}_{35}$) of the mixed wood reference was three times higher (3060 mg/kg).

In terms of contaminants, the heavy metal content (As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sn, V and Zn) were more pronounced than the organic compounds (Table 1 and S3) – most heavy metals except Hg, Mo and Sn were detected in the WT samples. Among the detected metals, Zn showed the highest concentration (153 ± 388 mg/kg). The heavy metal concentrations were also higher in the WT samples than the reference for all detected metals except V.

Table 1

Selected parameters from the screening of the waste timber feedstock samples (WT 1–3): Total carbon (%), total nitrogen (%), heavy metals (mg/kg) and organic contaminants (mg/kg). Data for the reference sample also shown.

Parameter	Unit	WT 1	WT 2	WT 3	WT (mean)	Reference
Total C	%	49.0	48.6	48.8	48.8 ± 2	49.9
Total N	%	2.07	2.36	2.24	2.2 ± 0.1	0.96
C/N ratio	–	27.6	24.1	25.5	26 ± 2	60.5
As (arsenic)	mg/kg	14 ± 19	25 ± 37	13 ± 8	17 ± 42	<1.00
Pb (lead)	mg/kg	17 ± 4	7 ± 1	9 ± 3	11 ± 6	2
Cd (cadmium)	mg/kg	0.13 ± 0.08	0.23 ± 0.09	0.10 ± 0.05	0.2 ± 0.1	<0.10
Cu (copper)	mg/kg	18 ± 11	30 ± 22	13 ± 11	20 ± 27	4.6
Co (cobalt)	mg/kg	2 ± 2	1.1 ± 0.3	1.2 ± 0.9	1 ± 2	0.17
Cr (Chromium)	mg/kg	13 ± 12	30 ± 40	12 ± 11	18 ± 43	0.94
Ni (nickel)	mg/kg	<1.0	0.7 ± 0.3	0.9 ± 0.6	0.7 ± 0.7	<1.0
Zn (zinc)	mg/kg	300 ± 385	96 ± 51	64 ± 10	153 ± 388	26
V (vanadium)	mg/kg	0.2 ± 0.2	0.12 ± 0.07	0.4 ± 0.2	0.2 ± 0.3	0.7
$\Sigma\text{PAH-16}$	mg/kg	0.8 ± 0.4	0.7 ± 0.3	1.1 ± 0.5	0.9 ± 0.7	3.5
2,4,6-Trichlorophenol	mg/kg	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.02	<0.020
2,3,4,6-Tetrachlorophenol	mg/kg	0.7 ± 0.9	1 ± 2	0.4 ± 0.4	0.8 ± 1.8	<0.020
Pentachlorophenol	mg/kg	1 ± 1	1.3 ± 0.9	0.5 ± 0.3	1 ± 2	<0.020
$\gamma\text{-HCH}$ (lindane)	mg/kg	<0.010	0.05 ± 0.05	<0.010	<0.05	<0.010
Aliphates ($\text{C}_{16}\text{--C}_{35}$)	mg/kg	875 ± 155	951 ± 364	825 ± 141	884 ± 420	3060

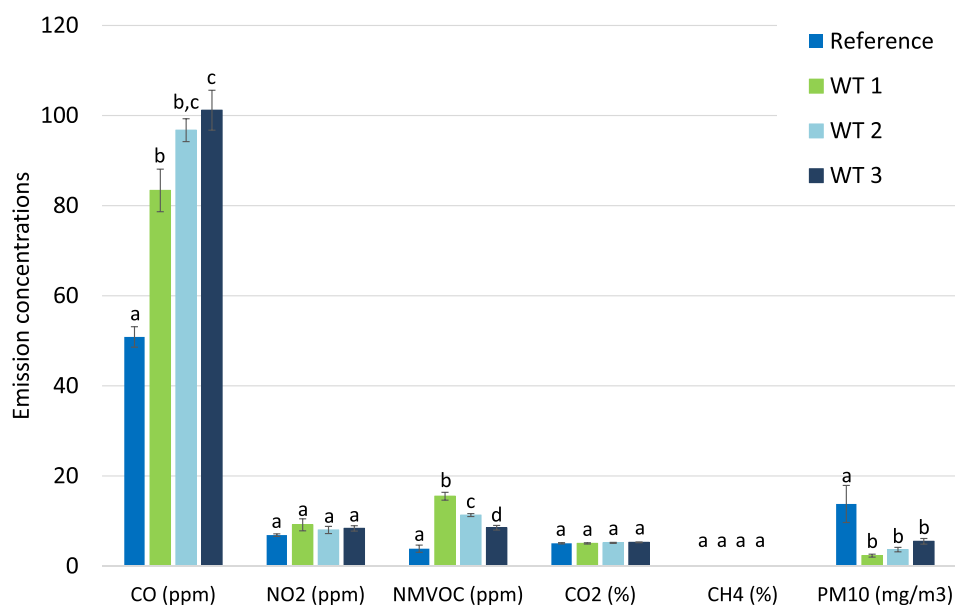


Fig. 2. Emission concentrations of CO (ppm), NO₂ (ppm), NMVOC (ppm), CO₂ (%) and PM₁₀ (mg/m³) during the pyrolysis of waste timber (WT 1–3) and a clean wood mixture (Reference). Concentrations shown as average of 8–12 measurements \pm standard error of the mean (SEM). Letters (a–c) indicate significant differences (Tukey HSD-test, $p < 0.05$).

3.2. Emissions during pyrolysis

3.2.1. Gas emissions

The gas emissions from the Pyreg unit were dominated by CO (Fig. 2), as has been observed for other pyrolysis techniques under tropical conditions (Cornelissen et al., 2016; Pennise et al., 2001; Sparrevik et al., 2015). CO emission concentrations were significantly higher for the WT (80–100 ppm) than for the reference (50 ppm). Methane emission concentrations were below detection limit (0.05%) for all samples, which signifies efficient post-combustion of the pyrolysis gasses (Sparrevik et al., 2015). NMVOC emission concentrations were significantly higher for WT (10–20 ppm) than for the reference (3 ppm). However, the opposite trend was seen for PM₁₀, with the reference (12 mg/m³) showing significantly higher emissions than the WT (2–8 mg/m³). This can be explained by the reference sample containing not only wood, like the WT, but also a fair amount of leaves, as it has

been shown that leaves increase the aerosol emissions during pyrolysis (Sparrevik et al., 2015).

The emission factors (Fig. 3) showed the same trends as the emission concentrations (Fig. 2) and were about ten times lower than the emission factors for pyrolysis of shrubbery under tropical conditions, using a low tech “Kon Tiki” flame curtain kiln – see Fig. S3 and Cornelissen et al. (2016). NMVOC emission factors were also about 5 times lower in this study than in a study by Greenberg et al. (2006), where leaves and shrubbery were pyrolyzed at 300 °C under laboratory conditions.

The emissions of CO and NO_x from a pyrolysis unit with a combustion chamber can be optimized for individual feedstocks according to Sehn and Gerber (2007), who studied the release of CO and NO_x as a function of the air to fuel ratio (AFR) during the combustion of pyrolysis gasses. At AFR = 1 there is exactly enough O₂ for the complete combustion of pyrolysis gases to CO₂. An AFR < 1 will give incomplete

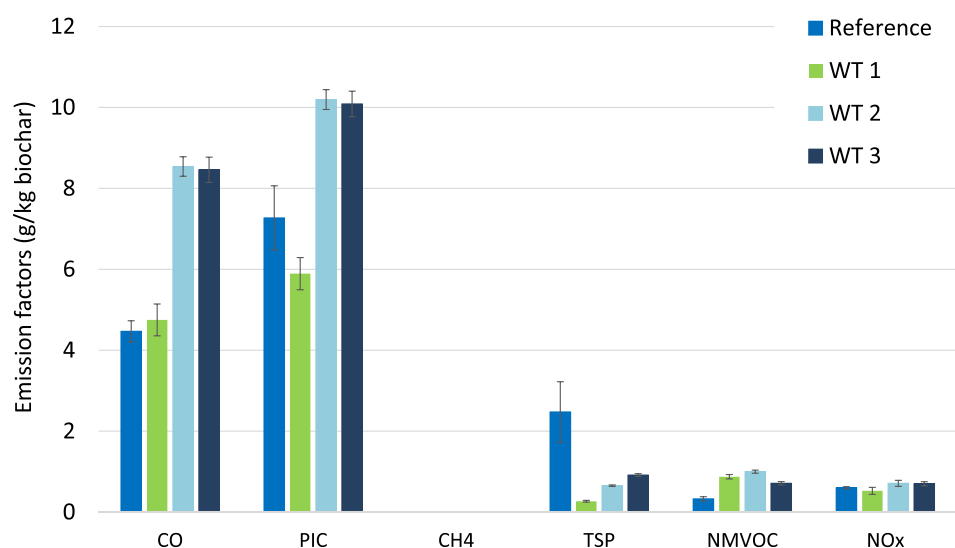


Fig. 3. Emission factors (g/kg biochar) for CO, PIC, CH₄, TSP, NMVOC and NO_x from pyrolysis of waste timber (WT 1–3) and a clean wood mixture (Reference). Factors shown as mean of 8–12 measurements \pm SEM.

combustion and thus more CO emissions. Therefore, the AFR should be >1 to minimize the emissions of CO. At high temperatures (1100 °C) combined with a high AFR however, NO_x emissions will increase. For wood pellets, which can be compared to the WT feedstock in this study, a relatively high AFR is required (>1.10) (Sehn and Gerber, 2007). This relation could explain the higher CO and lower NO_x emissions recorded in this study compared to other Pyreg units across Europe, as a lower AFR of (approximately 1.01) was used in this study compared to the other Pyreg units that were operated at AFR = 1.03. It is thus expected that the CO emissions from the pyrolysis of WT can be reduced by using a higher AFR (e.g. 1.03–1.05).

3.2.2. Metal and PAH emissions

Concentrations of metals in exhaust from the Pyreg unit during pyrolysis of WT were highest for As (24 ± 19 µg/m³) and Cr (19 ± 8 µg/m³). For most of the metals, except As and Sn, emission concentrations for WT were lower than those for the clean wood reference (Table 2). This was the opposite of the trend seen for feedstock concentrations (see Table S3). Ba and Zn emission concentrations could not be quantified due to high blank values in the GFF. There are few reported studies on the emissions of metals during pyrolysis, with the exception of studies focusing on alkali- and alkaline earth metals (Long et al., 2012; Olsson et al., 1997). Volatilization of heavy metals has been the focus of some studies of the pyrolysis of waste materials (Devi and Saroha, 2014; Dong et al., 2015; Helsen and Van den Bulck, 2000; Kistler et al., 1987), however, in these studies emissions were measured indirectly through mass balance estimates between feedstock and biochar. This approach will be discussed in Section 3.3.3.

Emission concentrations of PAHs during the pyrolysis of WT (Table 2) were highest for naphthalene (82 ± 25 ng/m³), acenaphthene (10 ± 8 ng/m³), phenanthrene (34 ± 16 ng/m³), fluoranthene (16 ± 4 ng/m³) and chrysene (9 ± 2 ng/m³). About half (53 ± 12%) of the released PAHs were in the gas phase and the majority of this fraction was

made up by the smaller 2-ringed naphthalene and 3-ringed acenaphthylene, fluorene and phenanthrene. The larger PAHs (4–6 rings) were mainly associated with the emitted particles (Table 2). The emission concentrations of PAHs were generally lower for the WT samples (ΣPAH-16 = 177 ± 28 ng/m³) than those for the reference sample (ΣPAH-16 = 398 ng/m³). The difference was almost entirely made up by higher concentrations of phenanthrene, fluoranthene, chrysene and benzo(b)fluoranthene of which the gas phase fractions were low (25, 18, 9 and 14%, respectively). This means that the higher PAH emission concentrations from the reference sample were mostly related to particle bound PAHs, corroborating with the reference sample also having a higher aerosol emission (PM₁₀) than the WT samples (Fig. 2).

The emission factors for metals and PAHs per ton biochar mirrored the trends seen for the emission concentrations, as it was As and Cr that gave the largest emissions per mass biochar, with 2.35 g/t (As) and 1.9 g/t (Cr) of biochar produced (Table 2). This is based on a gas emission rate of approximately 1200 m³/h and a biochar production rate of 25 kg/h. An average Pyreg 500 unit produces up to 2000 t/yr. If 2000 t of biochar are produced within a year this would mean a total As-release of 4.7 kg, Cr of 3.8 kg, Pb of 1.04 kg and ΣPAH-16 of 0.04 kg.

3.3. Biochar

3.3.1. Yield and general properties

The average biochar yield for the three WT samples was 26 ± 4% (see Table 3 and S4). A similar yield of 25% was recorded for the reference sample. This means that the mass of the feedstock is reduced into about a fourth of its original mass and is as expected from other studies of similar feedstocks (Cornelissen et al., 2016; Lehmann and Joseph, 2015). The carbon content of the WT biochar (81 ± 1%) was relatively high compared to the threshold quality criteria of >50% in the EBC (2012). Considering the feedstock carbon content of 49 ± 2%, this means that 44 ± 7% of the feedstock carbon was captured in the WT

Table 2

Concentrations of selected metals (ng/m³) from particles- and PAHs in both gas and particles in the exhaust from the pyrolysis of waste timber (WT 1–3) and the pure wood mixture (Reference). Mean concentration of the WT samples shown (mean ± st.dev). Gas phase fraction (%) shown for PAHs. Calculated emission factors (g/t of biochar) for WT shown for both metals and PAHs.

Element	Emission concentrations					WT – gas phase fraction (%)	WT – emission factors (g/t)
	WT 1	WT 2	WT 3	WT mean	Reference		
Metals (µg/m ³ , particles)							
Arsenic (As)	1.9	29.8	39.1	24 ± 19	35	–	2.35
Cadmium (Cd)	0.1	1.4	1.5	1.0 ± 0.8	5.4	–	0.1
Chromium (Cr)	9.9	20.3	26.5	19 ± 8	96	–	1.9
Copper (Cu)	0.7	3.5	5.6	3.3 ± 2.5	20	–	0.33
Lead (Pb)	1.6	4.9	9.2	5 ± 4	10.8	–	0.52
Mercury (Hg)	0.1	0.4	0.8	0.4 ± 0.3	1.4	–	0.042
Molybdenum (Mo)	0.3	2.1	2.2	1.5 ± 1.1	5.7	–	–
Nickel (Ni)	1.1	5.4	5.1	3.9 ± 2.4	18	–	0.4
Tin (Sn)	0.1	0.2	0.4	0.2 ± 0.2	0.3	–	–
PAH (ng/m ³ , particles + gas phase)							
Naphtalene	83.7	106.0	55.7	82 ± 25	35.1	78 ± 10	0.0092
Acenaphtylene	10.9	3.5	4.2	6 ± 4	3.0	87 ± 18	0.0068
Acenaphtene	3.3	9.0	18.6	10 ± 8	12.2	0 ± 0	0.0011
Fluorene	9.4	5.1	7.7	7 ± 2	10.0	72 ± 16	0.0008
Phenanthrene	50.6	19.5	32.0	34 ± 16	81.9	25 ± 11	0.0038
Anthracene	4.1	0.5	0.0	2 ± 2	0.0	0 ± 0	0.0002
Fluoranthene	20.7	12.1	14.6	16 ± 4	73.3	18 ± 14	0.0018
Pyrene	7.5	2.4	1.7	4 ± 3	9.4	21 ± 3	0.0004
Benzo(a)anthracene	1.4	1.5	0.7	1.2 ± 0.4	5.1	0 ± 0	0.0001
Chrysene	9.7	7.2	9.7	9 ± 2	86.4	9 ± 18	0.0010
Benzo(b)fluoranthene	4.3	3.8	6.0	5 ± 1	66.2	14 ± 18	0.0005
Benzo(k)fluoranthene	0.6	0.8	1.0	0.8 ± 0.2	8.4	0 ± 0	0.0001
Benzo(a)pyrene	0.6	0.7	0.0	0.4 ± 0.4	1.0	0 ± 0	0.00005
Indeno(1,2,3-cd)pyrene	0.0	0.5	0.0	0.2 ± 0.3	2.9	0 ± 0	0.00002
Benzo(ghi)perylene	n.d.	n.d.	n.d.	n.d.	2.0	0 ± 0	–
Dibenzo(ah)anthrasene	n.d.	n.d.	n.d.	n.d.	0.9	0 ± 0	–
ΣPAH-16	207	173	152	177 ± 28	398	43 ± 22	0.020

Table 3
Biochar yield and contaminants of concern in biochar from waste timber (WT 1–3) and pure wood mixture (Reference), compared to threshold values for premium and basic quality biochar according to the European Biochar Certificate (EBC).

Compound	Unit	WT 1 biochar	WT 2 biochar	WT 3 biochar	WT biochar average	Reference biochar	Threshold – premium quality biochar	Threshold – basic quality biochar
Biochar yield	%	30.9	23.7	24.4	26 ± 4	25.2	–	–
Metals								
As (arsenic)	mg/kg	3.6 ± 0.5	5 ± 7	2.0 ± 0.6	4 ± 7	–	<13	<13
Pb (lead)	mg/kg	90 ± 23	129 ± 64	140 ± 29	120 ± 70	5 ± 6	<120	<150
Cd (cadmium)	mg/kg	0.25 ± 0.08	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	<0.2	<1.0	<1.5
Cu (copper)	mg/kg	100 ± 124	28 ± 20	31 ± 14	50 ± 130	25 ± 11	<100	<100
Cr (chromium)	mg/kg	3 ± 1	5 ± 4	2.9 ± 0.7	4 ± 4	11 ± 12	<80	<90
Hg (mercury)	mg/kg	<0.20	<0.20	<0.20	<0.20	<0.07	<1	<1
Ni (nickel)	mg/kg	2.3 ± 0.7	1.7 ± 0.5	3 ± 1	2 ± 1	5 ± 3	<30	<50
Zn (zinc)	mg/kg	1397 ± 311	2771 ± 2759	2173 ± 476	2100 ± 2800	99 ± 50	<400	<400
PAHs								
Naphthalene	mg/kg	7.5	5.9	4.7	6.0 ± 1.4	0.7	–	–
Fluorene	mg/kg	0.2	1.0	0.2	0.5 ± 0.5	n.d.	–	–
Phenanthrene	mg/kg	3.0	5.6	1.5	3.4 ± 2.1	0.13	–	–
Anthracene	mg/kg	0.7	1.5	0.6	0.9 ± 0.5	0.03	–	–
Fluoranthene	mg/kg	2.1	1.2	0.2	1.2 ± 1.0	0.04	–	–
Pyrene	mg/kg	1.5	0.7	0.3	0.8 ± 0.6	0.05	–	–
Benzo(a)anthracene	mg/kg	0.6	0.2	n.d.	0.4 ± 0.3	0.02	–	–
Chrysene	mg/kg	0.6	0.2	n.d.	0.4 ± 0.3	0.02	–	–
ΣPAH-16	mg/kg	16.7	16.5	8.8	14 ± 5	1.3	<4	<12
PCDD/Fs								
2378-TCDD	ng/kg	0.22	0.30	0.33	0.28 ± 0.06	–	–	–
12378-PeCDD	ng/kg	0.74	0.79	0.91	0.81 ± 0.09	–	–	–
123478-HxCDD	ng/kg	0.29	0.31	0.37	0.32 ± 0.04	–	–	–
123678-HxCDD	ng/kg	1.31	1.24	1.27	1.27 ± 0.04	–	–	–
123789-HxCDD	ng/kg	1.20	1.23	1.50	1.3 ± 0.2	–	–	–
1234678-HpCDD	ng/kg	6.30	6.39	5.26	6.0 ± 0.6	–	–	–
OCDD	ng/kg	8.54	8.74	4.80	7 ± 2	–	–	–
Sum TEQ	ng/kg	1.33	1.46	1.62	1.5 ± 0.2	0.90	<20	–

biochar. Other biochar properties according to EBC (2012) are shown in Table S5 but are not relevant to this study and will therefore not be discussed here.

3.3.2. Organic contaminant decomposition and production

A contaminant screening of the biochar produced from the pyrolysis of WT revealed that the only organic contaminants detected were PAHs and dioxins (Table 3), suggesting that the other organic contaminants detected in the feedstock material (Table 1), such as chlorophenols and chlorinated pesticides, were decomposed or transformed through pyrolysis at about 600 °C. Traces of β-HCH (0.16 mg/kg) were detected in one of the triplicate analysis of the WT2 biochar, but it is assumed that this is an outlier – a possible result of sample contamination. To the authors knowledge there are few to no studies in the literature that in detail explore the fate of organic contaminants other than PAHs and PCDD/Fs following the pyrolysis of an organic waste material. The indications from this study are promising for pyrolysis as a treatment option for such wastes, but this topic must be explored further, especially for waste fractions with higher organic contaminant contents, and the potential decomposition of some compounds has to be weighed against the potential formation of other compounds such as PAHs and PCDD/Fs (Hale et al., 2012).

PAH-content in the WT biochar was dominated by the lighter 2-ringed naphthalene (6.0 ± 1.4 mg/kg–42.9% of ΣPAH-16) and 3-ringed phenanthrene (3.4 ± 2.1 mg/kg–24.3% of ΣPAH-16). The ΣPAH-16 content (14 ± 5 mg/kg) was in the range of concentrations reported in other studies (Brown et al., 2006; Hale et al., 2012; Singh et al., 2010; Zhurinsk et al., 2005). With an average concentration of 0.9 ± 0.4 mg/kg ΣPAH-16 in the feedstock, 14 ± 0.4 mg/kg in the resulting biochar and an additional 0.02 mg/kg in emitted exhaust, considering a biochar yield of 26%, there was a net production of approximately 10.6 mg ΣPAH-16 per kg biochar. The majority of these PAHs (99.9%) remained in the biochar, with only a minor amount being emitted through the exhaust.

Hale et al. (2012) compared PAH-contents across biochars produced with 0.5-, 1-, 3- and 8-h residence time, and showed that a shorter pyrolysis time can result in a higher PAH production. Thus, the relatively short residence time for feedstock in the pyrolysis reactor of the Pyreg unit (approx. 20 min) likely contributed to raising the PAH content of the biochar. With regards to pyrolysis temperature, it has been reported that both lower (Hale et al., 2012) and higher (Sharma and Hajaligol, 2003) temperatures favour PAH production.

The authors did not expect to find PCDD/Fs in any of the wood products that made up the WT-mixture, so the feedstock was not screened for dioxin content. Dioxin formation, as a result of pyrolysis, has not yet been studied to a great extent, but has been flagged as a possibility (Garcia-Perez, 2008), especially in the presence of Cl (e.g. NaCl in food waste, or MgCl₂ from flocculation during sewage sludge cleaning), due to what is known about dioxin formation during combustion reactions (Stanmore, 2004). Dioxins have also been found at elevated levels in soils following forest fires (Kim et al., 2003). In addition, pyrolysis of materials with high concentrations of likely precursor compounds, such as bromo-phenol (Evans and Dellinger, 2003) and brominated flame retardants (Lai et al., 2007) has shown formation of brominated dioxins. Dioxins were detected at low levels in the WT biochar, at 1.5 ± 0.2 ng/kg TEQ (17 congeners). This was higher than concentrations found in biochars made from clean biomass (grass, shrubbery, leaves, wood etc.) – 0.005–0.22 ng/kg TEQ, but similar to concentrations in biochar from food waste containing elevated Cl-concentrations from salt (2.9–3.4%) – 0.008–1.20 ng/kg TEQ (Hale et al., 2012). Cl-content appears to be an important factor for chlorinated dioxin formation during combustion reactions, but only at concentrations above 1% according to Wikström et al. (1996). As the WT feedstock was not expected to contain elevated levels of Cl or Br, the potential for dioxin formation was considered low and dioxins were not measured in the emitted gases.

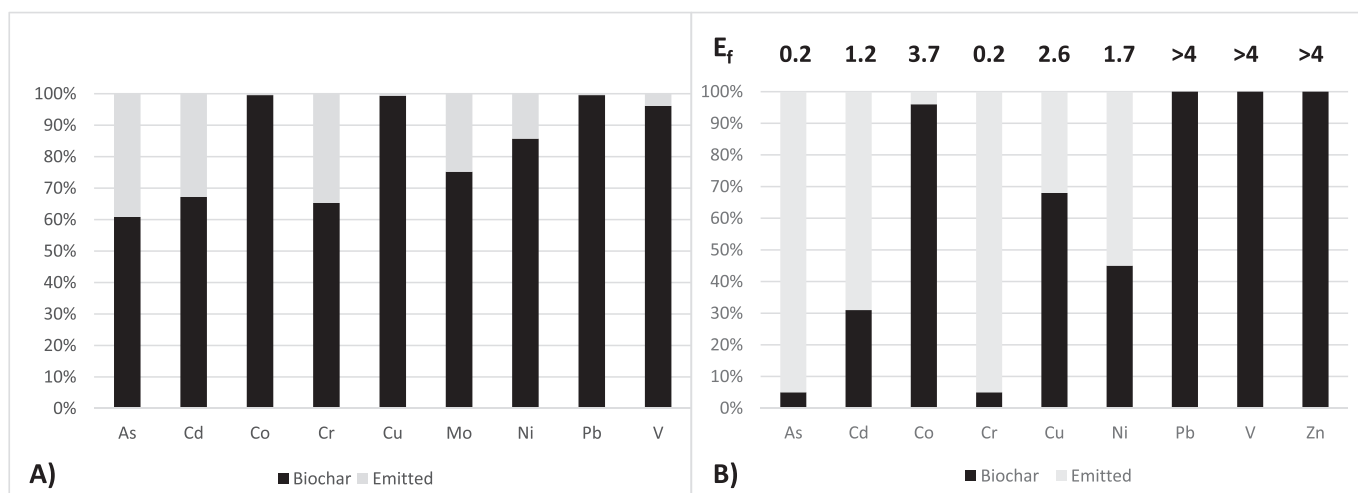


Fig. 4. Distribution of total metal content between produced biochar and emissions through pyrolysis exhaust, based on two methods: A) metals measured in biochar and emitted particles, and B) enrichment factors (E_f) between feedstock and biochar based on a mass balance calculation. E_f for which 4 is considered 100% enriched, shown.

3.3.3. Metal enrichment

For the pyrolysis of WT, the distribution between biochar and particles in the exhaust varied for the different metals (Fig. 4A); As, Cd and Cr were emitted through exhaust to the largest degree, as only 60.8, 68.8 and 65.3% respectively, remained in the biochar. For Co, Cu and Pb a small release was seen with 99.6, 99.4 and 99.6% respectively, remaining in the biochar. Zn was detected at high concentrations in the biochar (2100 ± 2800 mg/kg), but as Zn emissions during pyrolysis could not be quantified, the Zn mass balance is unknown. There was however, no significant difference (t -test, $p = 0.24$) between the ratio of Zn and Pb in feedstock (13 ± 25) and biochar (17 ± 25), and it was therefore likely that Zn, like Pb, was retained in the biochar rather than being released. Furthermore, enrichment factors (E_f) for the WT biochar (Fig. 4B) reflect the trend seen for the biochar/exhaust distribution, as Co, Cu, Pb and Zn with E_f of 3.7, 2.6, >4 and >4 respectively are heavily enriched metals, while As, Cd, Cr and Ni with E_f of 0.21, 1.2, 0.20 and 1.7 respectively are the least enriched metals. Here it is assumed that with a yield of 26%, an E_f of 4 equals 100% enriched in the biochar. The low E_f of As and Cr (0.2), indicate that a significant fraction of these two metals is also released through the vapour phase.

Literature on volatilization of metals during pyrolysis suggests that this process is controlled by reductive conditions, pyrolysis temperature, metal speciation and feedstock type (Devi and Saroha, 2014; Dong et al., 2015; Helsen and Van den Bulck, 2000; Kistler et al., 1987). Cd has been found to be volatilized to an increasing degree with temperature during the pyrolysis of paper mill effluent (PME), as the biochar E_f drops from about 1 at 300 °C down to 0.5 at 700 °C (Devi and Saroha, 2014). Kistler et al. (1987) however, found that a temperature of >600 °C is needed for Cd to start being volatilized in sewage sludge, owing to a high content of carbonates in the sludge that combine with Cd and require a higher temperature to volatilize compared to pure Cd-compounds. As was found to be volatilized during the pyrolysis of chromium-copper-arsenate (CCA)-treated wood at temperatures >350 °C, due to a reduction of As(V) to As(III), which forms the volatile As_4O_6 (Helsen and Van den Bulck, 2000). Zn has been reported as non-volatile in paper mill effluent, as E_f increased from 1.04 at 200 °C up to 1.72 at 700 °C (Devi and Saroha, 2014) and sewage sludge, as Zn was completely retained up to 750 °C (Kistler et al., 1987). Cu and Pb have been identified as non-volatile in several investigated matrices (Devi and Saroha, 2014; Dong et al., 2015; Kistler et al., 1987), in accordance with the present study. Dong et al. (2015) however, suggests through thermodynamical equilibrium calculations that the trends for both Pb

and Zn could start reversing at pyrolysis temperatures >750 °C, above which these two metals would start to be volatilized to a large extent (>90% for both Pb and Zn at 800 °C). Meanwhile, the presence of other elements, such as Cl and S, will affect the volatilization degree, as Cl stimulates the formation of volatile Cl-species, reducing E_f , whereas S results in the formation of solid sulphide species, increasing E_f (Dong et al., 2015).

3.3.4. Biochar quality

The concentrations of several detected compounds exceeded threshold values for basic and premium quality biochar according to the European Biochar Certificate (EBC, 2012). Unlike the reference sample of clean wood, the WT biochar failed to meet these requirements, due to high concentrations of Cu (50 ± 130 mg/kg), Pb (120 ± 70 mg/kg), Zn (2100 ± 2800 mg/kg) and PAHs (14 ± 5 mg/kg). Cu, Pb and PAH concentrations were within the same order of size as the benchmark EBC-values (Table 3), but Zn exceeded basic quality biochar by >5 times the threshold. Full details from the screening of contaminants in the biochar can be found in the SI (Table S5). According to EBC (2012) these results show that biochar made from WT should not be used for agricultural soil improvement. The use of WT biochar should rather be focused on less sensitive applications, such as immobilizing soil contaminants (Ahmad et al., 2014; Rajapaksha et al., 2016), sorbents for wastewater treatment plants (Wu and Wu, 2019) or inclusion in construction materials (Gupta and Kua, 2019).

A possible way to reduce the amount of certain metals and PAHs in the biochar could be to optimize the pyrolysis for metal and PAH volatilization/release, e.g. at temperatures >800 °C, where thermodynamic equilibria suggest that Pb and Zn could be volatilized under reducing conditions (Dong et al., 2015). A high-performance scrubber/particle filter would then be needed to avoid an increase in emissions. This has however, yet to be tested for the WT feedstock. Also, increasing the pyrolysis temperature will require more energy and result in a lower biochar yield (Lehmann and Joseph, 2015). Thus, there will be a potential trade-off between energy consumption and biochar yield, and the possible reduction of metals.

The high standard deviations of the triplicate analysis done for both feedstock and biochars show that some of the samples have high metal contents compared to others. This is likely due to heterogeneity of metal fragments left in the feedstock after sorting and chipping. A gravimetric fractionation test (see SI, section 2 for more details) showed that it is likely that there are pieces of metal scraps containing Zn in the chipped WT samples, but that these are so small that they are not immediately

visible. Removing these metal pieces from the WT chips before pyrolysis would therefore be challenging. Efforts should hence be focused on whether the current processes for removal of metal from the feedstock before chipping can be improved.

PAHs in the WT-biochar were dominated by naphthalene and phenanthrene, which will evaporate at 218 and 336 °C respectively (Mackay et al., 2006). Thus, PAH contents in biochar could possibly be reduced by allowing more time for a gradual cooling, in combination with a separation of the pyrolysis gasses and the biochar.

3.3.5. Contaminant leaching

The leachable amount of Zn from the WT biochar was 0.9 ± 0.6 mg/kg (Table S7), despite the high total concentration of Zn (2100 ± 2800 mg/kg). Thus, only 0.04% of the solid phase Zn was leached at L/S 10. Similar observations were made for Cu (50 ± 130 mg/kg) and Pb (120 ± 70 mg/kg) where the leachable contents were 0.021 ± 0.005 mg/kg (fraction 0.04%) and 0.0023 ± 0.0005 mg/kg (fraction 0.002%) respectively. The low leachability is a result of the eluate pH being the alkaline range (8.6 ± 0.1), as Cu, Pb and Zn all have low solubilities at this pH (Sauvé et al., 2000; Stumm and Morgan, 1995). A similar observation was made by Kistler et al. (1987) who found that the pH of sludge biochar favours a low metal solubility and thus a low risk for leaching. However, the leachable fraction of these metals could change upon application of WT biochar in a matrix with a higher or lower pH. The actual mobility and bioavailability of metals in WT biochar should therefore be investigated under the specific conditions of a certain application. The leachability and bioavailability of PAHs and PCDD/Fs were not investigated as Hale et al. (2012) previously found that the bioavailable concentrations of these compounds were negligible in terms of environmental risk in a wide range of biochars.

3.4. Future work

This study has shown that pyrolysis is a promising waste handling alternative for waste timber – as emissions were relatively low (see Section 3.2) and biochar yield ($26 \pm 4\%$) and quality (Table 3) such that further use is warranted. However, emissions need to be documented for other pyrolysis units, e.g. a unit with an external energy supply, and a unit with a particle scrubber. Furthermore, the effect of changing pyrolysis process conditions, such as a higher temperature or a more gradual cooling, on the resulting content of heavy metals and PAHs in the biochar should be investigated, as a better biochar quality will give more possibilities for reuse. With regard to biochars with a high content of heavy metals, like the WT biochar produced in this study, too little is known about the mobility and bioavailability of these metals under in situ soil conditions.

Pyrolysis of other types of contaminated organic waste have been studied, among some are paper mill effluent (Devi and Saroha, 2014), sewage sludge (Barry et al., 2019; Kistler et al., 1987) and municipal solid waste (Dong et al., 2015). There are however, other contaminated waste fractions that could be potential feedstocks for biochar production – e.g. food waste, waste from fisheries and abattoirs, and reject and digestate from biogas production. There is also a need to explore the fate of organic contaminants and macro-/microplastics in these feedstocks following the pyrolysis process.

Finally, pyrolysis as a waste handling method for contaminated organic waste should be compared to current waste handling processes in a life cycle analysis (LCA), as to estimate whether pyrolysis is a better alternative while taking into account the trade-offs of energy input/output, emissions and possibilities for further use.

4. Conclusion

The measured emissions from the pyrolysis of WT in a Pyreg 500 unit were low compared to the few other reported emissions in literature (e.g. Cornelissen et al., 2016). Modern pyrolysis units, like the

Pyreg 500, have the benefit of a combustion chamber for pyrolysis gasses that efficiently reduce the emissions of CO, CH₄ and other PICs to almost an order of magnitude lower than simpler pyrolysis technologies like the Flame Curtain Kiln (see Fig. S3). It is expected that these emissions can be lowered further by increasing the AFR of the combustion chamber from 1.01 to e.g. 1.04, but one should take care to not increase it above 1.10 to avoid production of more NO_x (Sehn and Gerber, 2007).

The emission of lighter 2- and 3-ringed PAHs, especially naphthalene and phenanthrene, was mostly through the gas phase (Table 2). Heavier, 4-, 5- and 6-ring PAHs however, are mainly released through particle emissions (Table 2). PAH emissions can thus be reduced significantly (about 45% assuming 100% efficiency of particle removal) by adding a particle filter/scrubber to the unit. The quantified metal emissions, that were dominated by As (2.35 g/t), Cr (1.9 g/t) and Pb (0.52 g/t), were all associated with particles, and can therefore also be reduced/eliminated by removing particles from the pyrolysis unit's exhaust.

The enrichment of metals, such as Cu (50 ± 130 mg/kg; $E_f = 2.6$), Pb (120 ± 70 mg/kg; $E_f > 4$) and particularly Zn (2100 ± 2800 mg/kg; $E_f > 4$), in the WT biochar, along with the produced PAHs (14 ± 5 mg/kg), makes the present WT-biochar unsuited for agricultural soil improvement according to the EBC. There is a possibility however, of reducing the biochar concentration of Pb and Zn by both using a higher pyrolysis temperature (>800 °C), as this could increase the volatilization of these two metals, and by a better sorting of the feedstock material. Bioavailable concentrations of PAHs are expected to be negligible, as documented in the literature (Hale et al., 2012). Nevertheless, technical adaptations to the pyrolysis process could potentially lower the PAH concentration in the WT biochar if the aim is to comply with threshold such as EBC basic quality (\sum PAH-16 < 12 mg/kg). Metals did not leach to water to any significant degree ($<0.1\%$ of total content) under the natural pH (8.4) of the biochars in this study nor in studies by Kistler et al. (1987) or Devi and Saroha (2014). Considering these observations, it is recommended that leachable/bioavailable concentrations should be included in the quality standards such as the EBC, as total concentrations in the solid phase alone are poor predictors of actual environmental risk (Reichenberg and Mayer, 2006).

This study has shown that pyrolysis is a promising waste handling alternative for waste timber. However, emissions need to be documented for other pyrolysis units, e.g. a unit with an external energy supply, along with the effect of better filtering technology on particle emissions. In addition, future work should be focused on testing pyrolysis as a waste handling alternative for other organic waste fractions, such as food waste and reject and digestate from biogas production, preferably in a life cycle perspective.

CRediT authorship contribution statement

Erlend Sørmo: Investigation, Formal analysis, Writing - original draft, Writing - review & editing. **Ludovica Silvani:** Methodology, Investigation, Writing - review & editing. **Gorm Thune:** Conceptualization, Funding acquisition, Resources, Writing - review & editing. **Helmut Gerber:** Resources, Methodology, Writing - review & editing. **Hans Peter Schmidt:** Methodology, Writing - review & editing. **Andreas Botnen Smebye:** Conceptualization, Writing - review & editing. **Gerard Cornelissen:** Funding acquisition, Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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