The Effect of Wood Species on Fine Particle and Gaseous Emissions from a Modern Wood Stove

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Abstract: Residential wood combustion (RWC) is a significant source of gaseous and particulate emissions causing adverse health and environmental effects. Several factors affect emissions, but the effects of the fuel wood species on emissions are currently not well understood. In this study, the Nordic wood species (named BirchA, BirchB, Spruce, SpruceDry, Pine and Alder) were combusted in a modern stove, and the emissions were studied. The lowest emissions were obtained from the combustion of BirchA and the highest from Spruce and Alder. The fine particle mass (PM$_{2.5}$) was mainly composed of elemental carbon (50–70% of PM$_{2.5}$), which is typical in modern appliances. The lowest PAH concentrations were measured from BirchA (total PAH 107 µg/m$^3$) and Pine (250 µg/m$^3$). In the ignition batch, the PAH concentration was about 4-fold (416 µg/m$^3$). The PAHs did not correlate with other organic compounds, and thus, volatile organic compounds (VOCs) or organic carbon (OC) concentrations cannot be used as an indicator of PAH emissions. Two birch species from different origins with a similar chemical composition but different density produced partially different emission profiles. This study indicates that emission differences may be due more to the physical properties of the wood and the combustion conditions than to the wood species themselves.

Keywords: residential wood combustion; wood species; emissions; fine particles; black carbon; polycyclic aromatic hydrocarbons

1. Introduction

The use of woody biomass such as firewood and wood pellets for residential heating and cooking is common all over the world. In Northern European countries, residential wood combustion (RWC) is mainly used for space heating and recreational activities such as sauna bathing. In Europe, about 65% of total energy used in households is used for heating [1]. More than 70 million solid fuel appliances are installed in European households, but most of them do not comply with current emission standards [1,2]. Due to poor combustion conditions, wood combustion is the major source of particulate emissions, for example, in Nordic countries. Despite these high emissions, the use of wood combustion for space heating in Europe is projected to increase (e.g., [3]).

RWC produces a significant amount of gaseous and particulate emissions such as fine particle mass (PM$_{2.5}$), black carbon (BC), particulate organic matter (POM), carbon monoxide (CO), volatile organic compounds (VOCs), nitrogen oxides (NOX) and polycyclic aromatic hydrocarbons (PAHs). In addition to primary particulate emissions, RWC emits gaseous precursors forming secondary organic and inorganic aerosols (SOAs and SIAs).
in the atmosphere [4–6]. The primary emissions are strongly dependent on combustion conditions, such as firebox temperature, oxygen availability and the mixing of combustion air and combustible gases, and depend also on the fuel properties.

Exposure to certain aerosol emissions from wood combustion has been associated with severe health effects. For instance, PAHs (e.g., benzo[a]pyrene) are carcinogenic and VOCs (e.g., phenols, cresols, acrolein and acetaldehyde) are ciliotoxic [7–10]. Transition metals such as zinc induce toxicological cell responses [11]. In 2019, 307,000 people died prematurely from illnesses attributed to chronic exposure to PM$_{2.5}$ in Europe [12]. Also, BC has adverse health effects, but it is primarily considered as a climate-warming element in particulate matter (PM). The net warming effect of PM depends on the concurrent emissions of cooling aerosols, such as organic carbon, and the mixing state of the different emission components [13]. In addition to composition, particle size and morphology affect the climate- and health-related properties of particulate emissions.

The emissions of RWC appliances have been widely studied, and an overall picture of the emissions has been obtained [10]. Conventional appliances produce very high particle concentrations, and the particles are dominated by organic compounds and soot [14]. Modern low-emission stoves have been studied less, but the proportion of organic matter is lower than in conventional appliance types [15,16]. The operational practices of appliances have a significant effect on the emissions in both modern and conventional appliances [17]. In addition, emission factors have a large variation due to the type of fuel (wood species, moisture content, physical sizes of the wood logs), burning rate and the characteristics of the combustion facility (dilution and sampling techniques), and thus the results are not entirely comparable [10,18]. Wood species usage varies globally, with hundreds of options available across different countries.

Many of the studies investigating the effects of wood species on emissions from wood stoves have been performed in North America [19–21], in South America [22,23], in Europe [24–28] and in Australia [29,30], and most of the studies have been conducted with old appliance types. In many emission studies, wood species are divided into two large groups: hardwood and softwood [19,20,25]. Softwood species generally have a higher lignin content (26–34%) and lower densities than hardwood species (23–30%) [31,32]. The age of the wood, geographic location, harvesting time and technique and contaminating materials (dust, dirt, soil) affect the chemical composition of wood logs [31].

Cereceda-Balic et al. [23] reviewed PM$_{2.5}$ emission factors from the literature and found that there is no general connection between emissions and whether the wood is hardwood or softwood, but differences in emissions between wood species can be explained by differences in their proportion of hemicellulose, lignin and cellulose when testing beech, eucalyptus, and pine [23]. It is also reported that softwoods, due to their lower densities, burn at higher rates than hardwoods, reducing the duration of their start-up phase and lowering overall PM emissions [10,26]. This is contrary to the fact that hardwoods contain more cellulose than softwoods [32] and non-aromatic cellulose chains are easily volatilized [33]. It has been shown that birch wood (hardwood) burns faster in a stove than pine or spruce woods (softwoods) [15,27,34]. Also, results from Amarall et al. [22] support this observation. It is proposed that birch burns faster, because of the presence of some essential oils that might act as fire accelerants [34]. In a theoretical study, it has been found that birch ignites about five times faster than spruce [35]. The differences in the burning rates of hardwoods and softwoods are also considered during the certification of RWC appliances. A new European testing standard [36] defines that, during the nominal and reduced heat output test, hardwood (beech, birch or hornbeam) shall be used as a test fuel, while softwood (fir) shall be used for the temperature safety test.

It is well-known that the physicochemical properties of bark and stem wood differ (e.g., [37]), also affecting emissions [38]. In most wood species, bark content is less than 10% of the overall wood [37], but bark thickness varies depending on wood species, age and growing conditions [39,40]. Typically, bark content has not been reported in most studies, although bark is a main source of ash and different extractives and has a significant effect
on the emissions of volatilized ash particles. Especially in good combustion conditions, ash content positively correlates with PM emissions, since it is one of the main fractions of PM [38,41]. The large amount of bark material in the wood logs is also connected to the high elemental carbon (EC) emissions from paper birch, which was also observed as visible black smoke during combustion [42]. Fine et al. [42] also noted that the high content of visually observed extractives on the surface of eastern white pine emitted high concentration of particulate matter, especially EC.

In conclusion, the overall picture of the effect of wood species on emissions remains unclear, although it has been studied considerably. Comparison of the emissions is also challenging due to differences in wood fuel chemical composition, physical properties (e.g., density, moisture content, log size, batch size) or combustion conditions (burning rate, air-to-fuel ratio) between experiments. This explains the contradictory results when differences in the emissions between wood species have been studied previously. The aim of this study is to investigate the factors affecting the emissions of different Nordic wood species on emissions in a modern stove. The wood species were combusted at the same combustion rate, to obtain comparable conditions for the comparison of emission formation, despite the large differences in wood densities. The fine particle and gaseous emissions were measured comprehensively with highly reliable instrumentation. Clear differences in emissions between wood species were found, but this study indicates that the differences may be due more to the physical properties of the wood batches and combustion conditions than to the wood species themselves.

2. Materials and Methods
2.1. Combustion Facility

The experiments were conducted in the small-scale combustion simulator (SIMO) at the University of Eastern Finland (https://sites.uef.fi/fine/front-page/simo/, accessed on 15 July 2024). The experimental setup was exactly as in the study by Tissari et al. [27] except for the stove used, and in the instrumentation part, a nanoparticle surface area monitor (NSAM, Model 3550, TSI Inc., Shoreview, MN, USA) and electrical low pressure impactor (ELPI, Dekati Ltd., Kangasala, Finland) were used in a higher dilution ratio (see Section 2.4.1). The SIMO offers the testing of various small-scale wood combustion appliances and the measurement of their emissions. The setup allows the simultaneous monitoring and controlling of multiple parameters (e.g., ventilation, pressures, airflows, temperatures, combustion parameters and emission-sampling settings). The SIMO is composed of two marine containers. A measurement container is equipped with all the required measurement instruments, sampling systems and air ventilation systems. The stove is situated in another container. The flue gas flows through a steel chimney, with a flue gas fan for controlling and adjusting the draught required for the tests.

2.2. Combustion Appliance

The used combustion appliance in the experiment was a state-of-the-art new domestic elliptical-shaped modern wood stove. It was covered in soapstone to improve the heat accumulation properties of the stove and featured a nominal heat output of 6 kW and official thermal efficiency 81.9%. The dimensions of the stove were 1556 mm (height), 550 mm (width) and 438 mm (depth), while the weight of the stove was 289 kg. The appliance had a firebox which was 344 mm wide and 314 mm deep, and it had a door made of heat-resistant glass to prevent sparks from the burning wood and smoke from entering the room and to facilitate a pleasant heat radiation. The appliance comprised a baking oven on top of the stove and included a combustion air-staging system. The primary air came to the burning fuel through the ashpan and rift grate and could be regulated by an air regulator. The secondary air came to the area right above the burning fuel. Secondary airflow prevents the blackening of the front glass and takes part in the primary combustion process when the primary air intake is partially or completely sealed. This type of design supports the
better combustion of flue gases, increases the output of the heater and significantly reduces the amount of pollutants.

2.3. Operational Practices and Characteristics of Wood Species

The combustion of four wood species (Alder, Spruce, Pine and Birch) was performed (Table 1). The birch was collected from two separate origins, named BirchA and BirchB. Both the dry (SpruceDry, dried in the electric oven) and normal moisture contents of the spruce (Spruce) wood was used. Each combustion experiment included 6 batches, and the experiment was repeated twice for each wood species except SpruceDry (Table S1). The first (ignition) batch was always a normal moist birch (BirchA1). The ignition batch consisted of 3 logs of 500 ± 20 g, 3 logs of 333 ± 20 g and 5 logs of 100 g, and two fire starter bites of approximately 10 g per bite. The subsequent batches consisted of three wood logs.

Table 1. Physical characteristics of wood species.

<table>
<thead>
<tr>
<th></th>
<th>BirchA1</th>
<th>BirchA</th>
<th>BirchB</th>
<th>Alder</th>
<th>Pine</th>
<th>Spruce</th>
<th>SpruceDry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower heating value</td>
<td>MJ/kg</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>18.74</td>
<td>18.74</td>
<td>18.72</td>
<td>18.68</td>
<td>19.19</td>
<td>19.13</td>
<td>19.13</td>
</tr>
<tr>
<td>Calorific heating value</td>
<td>MJ/kg</td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>15.87</td>
<td>15.87</td>
<td>16.25</td>
<td>15.75</td>
<td>15.66</td>
<td>15.88</td>
<td>17.70</td>
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<tr>
<td>Moisture content</td>
<td>%</td>
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<td></td>
<td></td>
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<td></td>
<td>15.3</td>
<td>15.3</td>
<td>13.2</td>
<td>15.7</td>
<td>18.4</td>
<td>17.0</td>
<td>7.5</td>
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<tr>
<td>Density, dry</td>
<td>kg/m^3</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>621</td>
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<td>673</td>
<td>446</td>
<td>476</td>
<td>350</td>
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<tr>
<td>Log size</td>
<td>kg</td>
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<td></td>
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<tr>
<td></td>
<td>0.500</td>
<td>0.500</td>
<td>0.485</td>
<td>0.500</td>
<td>0.515</td>
<td>0.515</td>
<td>0.450</td>
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<tr>
<td>Batch size</td>
<td>kg</td>
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<td></td>
<td></td>
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<td></td>
<td>3.000</td>
<td>1.500</td>
<td>1.455</td>
<td>1.500</td>
<td>1.545</td>
<td>1.545</td>
<td>1.350</td>
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<tr>
<td>Batch volume</td>
<td>dm^3</td>
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<td></td>
<td>4.2</td>
<td>2.1</td>
<td>1.9</td>
<td>2.9</td>
<td>2.7</td>
<td>3.8</td>
<td>3.6</td>
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<td>Batch energy</td>
<td>MJ</td>
<td></td>
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<td></td>
<td>47.6</td>
<td>23.8</td>
<td>23.6</td>
<td>23.6</td>
<td>24.2</td>
<td>24.5</td>
<td>23.9</td>
</tr>
</tbody>
</table>

1 Defined by standard SFS-EN ISO 18125: Solid biofuels—determination of calorific value [43].

Due to the varied moisture contents of the fuels, the mass and size of the wood logs were adjusted to provide approximately the same amount of energy for combustion. Therefore, the calculation of log size was based on analyses of the caloric values of the wood species. The log sizes used for different wood species were, for BirchA and Alder, 500 g; for Pine and Spruce, 515 g; for BirchB, 485 g; and for SpruceDry, 450 g (Table 1). For discussion of the emission results, the density of the wood species was also defined by a method described in Supplementary Material, Chapter S1. The density of different wood species varied from 350 to 673 kg/m^3, which is within the normal variation between species [37], but in terms of combustion conditions and emission formation, the physical volume of the logs and batches varied. The obtained density differences mean that there were almost 2-fold differences in the volume of wood logs or batches between species.

To ensure a good comparability between wood species, the combustion conditions were adjusted to be as similar as possible. The first batch (BirchA1) differed from the other batches, and the goal was to stabilize the conditions in the firebox before adding the next batch. The ignition of the first batch was accomplished from the top. The draught was set to 6 Pa with a flue gas fan at ignition and, after 2 min, to 12 Pa for the entire experiments. The primary air to the combustion chamber was fully open for 3 min after the ignition and for 2 min at the beginning of each additional batch, and was set to open certain centimeters after that. In all tests, each additional batch was added when the CO_2 concentration in the flue gas dropped to 4.5%, and the same principle was also applied to end the combustion experiments.

There were differences in volatile substances between the wood species (Table S2). In BirchA and BirchB, the proportions were about 2–4% higher than in the other tree species. The ash content was the highest in Alder and Spruce: 0.7 and 0.6%, respectively. In the birch woods and Pine, the ash content was lower, between 0.3 and 0.4%, but all contents were at typical level for wood species [37]. The higher ash content of Alder was particularly evident in S, Ca, K and P concentrations. The content of Ca was also high in Spruce, as compared to birch woods and Pine. BirchA also had an elevated Ca content compared to BirchB and Pine. BirchB and Spruce had a higher K content than BirchA and Pine. In
both birch species, the zinc content (33–46 mg/kg) was clearly higher than in other wood species (6.6–17 mg/kg). Interestingly, the S content was the highest for Alder (230 mg/kg) as compared to other wood species (69–110 mg/kg).

2.4. Emission Measurements and Analyses

2.4.1. Particle Sampling, Measurement and Analysis

The sampling of particle emissions was performed in a two-phase partial flow dilution system designed with the combination of porous tube diluter (PTD) and ejector diluter (ED) that has been validated in many previous scientific publications, e.g., in [16,27]. The sample flow from the flue gas stack was first led through a sampling probe with a 10 µm pre-cyclone. Then, the sample was directed towards the PTD via a heated (200 °C) sampling line. The first stage of dilution occurred in the PTD, in which particle losses and water vapor condensation were avoided. After that, the second stage of dilution was carried out in an ED which provided efficient mixing and a stable flow of sample to the rest of the sampling system. The dilution ratio (DR) was controlled with an online computer-based system, based on the concentrations of CO₂ in the flue gas (see Section 2.4.2), diluted sample and dilution air (Vaisala GMP343 probes, Vaisala Ltd., Vantaa, Finland). DR 90 was used for all wood species. Particle- and oil-free dilution air was generated by an air compressor consisting of cleaning and drying units. The flow of air to the two-stage dilution system was controlled by mass flow controllers (MFCs) in respective lines. The sample was further diluted by a factor of 7.7, with an additional ED placed upstream of the most sensitive instruments.

Several online instruments were used to measure the concentrations of various physical and chemical parameters of the particles. Particle number concentrations were measured using a condensation particle counter (CPC, model 3775, TSI Inc., Shoreview (MN), USA) with a flow rate of 1.5 lpm. Particle mass concentrations and number size distributions (3 nm to 10 µm) were measured by ELPI with 12 sintered impactor plates and a flow rate of 10 lpm. The equivalent black carbon (eBC) concentration was measured using an Aethalometer (AE33, Magee Scientific, Berkeley, CA, USA) with a flow rate of 2 lpm at an 880 nm wavelength. The absorption Ångström exponent (AAE), which describes the wavelength-dependence of optical absorption by light-absorbing particles, was calculated by using aethalometer data with two wavelengths (470/950 nm). The calculation of the AAE was performed as described in Helin et al. [44]. Instantaneous AAE values weighted with eBC mass concentrations were applied for the calculation of average AAEs. An NSAM instrument was used to measure the human lung-deposited surface area (LDSA) of the combustion particles.

For PM₂.₅ filter collection, the diluted sample was led through an impactor on the line which removed particles with a larger than 2.5 µm aerodynamic diameter. PM₂.₅ samples were collected on 47 mm Teflon (PTFE) and quartz fiber filters, with the use of a vacuum pump and mass flow controllers which created and controlled a constant sample flow on the sample collection line. The samples collected on the PTFE filters were used for the gravimetric and PAH analyses, while quartz filters were used for organic (OC) and elemental carbon (EC) analyses. The sample collection started 1 min after ignition, when a three-way valve and suction pumps were opened to make the sample flow towards the sample collectors. Similarly, sample collection was stopped by closing the three-way valve, after which, the sample flowed through a bypass line without interrupting the constant sample flow [27]. Samples were collected from each batch separately. The contents of the OC and EC were analyzed with a thermal–optical carbon analyzer (Sunset Laboratory Inc., Tigard, OR, USA) according to the NIOSH protocol.

PAH compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benzo[c]phenanthrene, benzo[a]anthracene, cyclopenta[c,d]pyrene, triphenylene, chrysene, 5-methylchrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[j]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene,
benzo[g,h,i]perylene, anthanthrene, dibenzo[a,l]pyrene, dibenzo[a,e]pyrene, coronene, dibenzo[a,i]pyrene and dibenzo[a,h]pyrene in PM$_{2.5}$ were analyzed from PTFE filter samples in the same way as described previously by Lamberg et al. [45]. The PM was extracted from the filters using dichloromethane and ultrasonic bath. Solid-phase extraction with an alumina column (Alumina B, EcoChrom, MP Biomedicals Germany GmbH, Eschwege, Germany) was used as a cleanup step prior to analysis. The analysis was carried out by a gas chromatograph–mass spectrometer (6890N GC, equipped with 5973 inert Mass Selective Detector, Agilent Technologies Ltd., Santa Clara, CA, USA) with an HP-17-MS column using the selected ion-monitoring (SIM) mode.

2.4.2. Gas Analysis

The concentrations of carbon dioxide (CO$_2$), carbon monoxide (CO) and nitrogen oxide (NO) were measured using two ULTRAMAT 23 infrared gas analyzers (Siemens AG, München, Germany) from a dried and cooled sample gas. The NO concentration was converted to NO$_x$ (expressed as NO$_2$ equivalent). Organic gaseous carbon was measured by a flame ionization detector (FID) (OGC, expressed as C$_3$H$_8$) from wet heated sample gas. Single volatile organic compounds (VOCs) were measured with a Fourier-transform infrared analyzer (FTIR, Gasmet Technologies Ltd., Vantaa, Finland). The sum of the 28 calibrated VOCs was used when comparing the portion of a single VOC to the total VOCs, but the 12 most common VOCs are presented in the Tables and Figures.

2.5. Data Analysis

The calculation of all the results was performed as described in Tissari et al. [27], and data was normalized to 1 atm, 20 °C and 13% oxygen content. The real-time data collection was started 1 min after the ignition and stopped at the end of the combustion of all batches when the CO$_2$ level was less than 4.5%. The collected data for 1 min before and 1 min after the batch additions were excluded from the real-time data, to avoid calculation errors that could be caused by temporary high changes in dilution when the firebox door was opened. For each burned fuel batch, both the real-time data and collected samples were averaged similarly as in the testing standards (e.g., in the European EN 16510:2022 [36]). The average value and standard deviation of all single batches were calculated for each tree species. Results from the batches where the ignition after the addition was not proper, causing very high emissions, were excluded from the data.

3. Results and Discussion

3.1. Combustion Conditions, Temperatures and Thermal Efficiency

The average burning rate was almost the same for all wood species, and varied between 2.00 kg/h (Spruce) and 2.29 kg/h (Alder) and was independent of the wood density (Tables 1 and 2). During the first batch, more primary combustion air was supplied, and the batch size was larger than in the other batches, causing the burning rate to also be higher.

Table 2. Combustion conditions, temperatures and efficiency (average ± sd). Values are averages of all single batches combusted.

<table>
<thead>
<tr>
<th>Unit</th>
<th>BirchA1</th>
<th>BirchA</th>
<th>BirchB</th>
<th>Alder</th>
<th>Pine</th>
<th>Spruce</th>
<th>SpruceDry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time $^1$</td>
<td>min</td>
<td>62.3 ± 5.8</td>
<td>40.5 ± 1.8</td>
<td>39.9 ± 5.9</td>
<td>39.6 ± 3.2</td>
<td>44.1 ± 3.0</td>
<td>45.7 ± 2.6</td>
</tr>
<tr>
<td>Burning rate $^1$</td>
<td>[kg/h]</td>
<td>2.92 ± 0.28</td>
<td>2.23 ± 0.10</td>
<td>2.24 ± 0.31</td>
<td>2.29 ± 0.17</td>
<td>2.12 ± 0.15</td>
<td>2.04 ± 0.12</td>
</tr>
<tr>
<td>Draught [Pa]</td>
<td></td>
<td>11.9 ± 0.4</td>
<td>12.1 ± 0.1</td>
<td>12.0 ± 0.1</td>
<td>12.1 ± 0.2</td>
<td>12.1 ± 0.3</td>
<td>11.9 ± 0.1</td>
</tr>
<tr>
<td>Temperature $^2$ [°C]</td>
<td>148 ± 14</td>
<td>234 ± 17</td>
<td>231 ± 21</td>
<td>239 ± 20</td>
<td>239 ± 13</td>
<td>244 ± 11</td>
<td>232 ± 20</td>
</tr>
<tr>
<td>Λ $^3$ [-]</td>
<td>2.95 ± 0.27</td>
<td>2.97 ± 0.11</td>
<td>2.77 ± 0.21</td>
<td>2.77 ± 0.18</td>
<td>2.99 ± 0.20</td>
<td>3.02 ± 0.18</td>
<td>2.70 ± 0.29</td>
</tr>
<tr>
<td>Efficiency [%]</td>
<td>85.0 ± 1.5</td>
<td>76.7 ± 1.0</td>
<td>78.3 ± 2.8</td>
<td>76.6 ± 1.5</td>
<td>76.0 ± 1.4</td>
<td>74.6 ± 1.2</td>
<td>78.1 ± 1.6</td>
</tr>
</tbody>
</table>

$^1$ Combustion time of batch; $^2$ Flue gas temperature; $^3$ Air-to-fuel ratio.
The combustion times of the batches were very similar and varied between 40 and 46 min. Also, the average flue gas temperatures varied only slightly. However, the temperature rose from batch to batch similarly in all wood species (Figures S1 and S2). The average air-to-fuel ratios for all wood species were quite high, between 2.77 and 3.02 (Table 1). This is because in modern combustion appliances, most of the combustion air is supplied to the combustion chamber as secondary air, and typically, it may easily leave unreacted and thus increases the air-to-fuel ratio. A high air-to-fuel ratio also indicates that there has theoretically been enough air for combustion in all phases of combustion. However, there were rather large differences in the air-to-fuel ratios, from 2.4 to 3.4, between individual batches (standard deviation between 0.11 and 0.29, Table 2), indicating that the manually adjusted air supply was not exactly in the same position in each batch.

Since the temperatures and air-to-fuel ratios for the different wood species were almost the same, the differences in efficiencies were also small (Table 1). The thermal efficiency of modern combustion devices is mainly affected by the temperature of the flue gas and the air-to-fuel ratio, and chemical losses (through CO in the calculations) are usually low. Overall, it can be said that the parameters describing the combustion obtained were very similar across the different wood species, despite the different physical and chemical properties of the wood species.

3.2. Gaseous Emissions
3.2.1. Carbon Monoxide

Concentrations of gaseous compounds are presented in Table 3. The average concentration of CO was the smallest for BirchA and BirchB, 1270 and 1430 mg/m³ (Table 3), respectively, and were lower than the Ecodesign limit for stoves (Table S3 [46]). Also, the variation in concentrations was smallest in these wood species (Figure S3A). The highest average CO concentrations were measured from Spruce and Alder, 4280 and 2710 mg/m³, respectively, and were slightly lower with dry spruce logs than normal moisture content. The CO in the ignition batch slightly exceeded the average CO concentration with BirchA.

The consecutive batches had a mild decreasing trend of CO, except for Alder (Figure S3B). The CO properties of the wood species. Average concentrations (±variation in concentrations was smallest in these wood species (Figure S3A). The highest CO levels from 1600 to 10,700 mg/m³. Our results agree with several previous studies of the CO concentrations from wood stoves. The combustion times of the batches were very similar and varied between 40 and 46 min.

<table>
<thead>
<tr>
<th>Unit</th>
<th>BirchA1</th>
<th>BirchA</th>
<th>BirchB</th>
<th>Alder</th>
<th>Pine</th>
<th>Spruce</th>
<th>SpruceDry</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (%)</td>
<td>6.9 ± 0.7</td>
<td>6.9 ± 0.3</td>
<td>7.3 ± 0.6</td>
<td>7.3 ± 0.5</td>
<td>6.8 ± 0.5</td>
<td>6.7 ± 0.4</td>
<td>7.6 ± 0.8</td>
</tr>
<tr>
<td>H₂O, %, wet</td>
<td>7.8 ± 1.0</td>
<td>7.4 ± 0.3</td>
<td>8.0 ± 0.6</td>
<td>7.0 ± 0.4</td>
<td>6.2 ± 1.5</td>
<td>6.8 ± 0.5</td>
<td>6.8 ± 0.7</td>
</tr>
<tr>
<td>CO mg/m³</td>
<td>2190 ± 590</td>
<td>1270 ± 240</td>
<td>1430 ± 340</td>
<td>2710 ± 450</td>
<td>1880 ± 460</td>
<td>4280 ± 1080</td>
<td>2720 ± 580</td>
</tr>
<tr>
<td>NO₂ mg/m³</td>
<td>92.4 ± 12.6</td>
<td>132.8 ± 9.6</td>
<td>143.8 ± 13.5</td>
<td>188.8 ± 11.2</td>
<td>115.9 ± 8.7</td>
<td>149.5 ± 15.0</td>
<td>139.1 ± 14.9</td>
</tr>
<tr>
<td>NH₃ mg/m³</td>
<td>0.8 ± 0.2</td>
<td>2.3 ± 0.6</td>
<td>2.9 ± 0.9</td>
<td>7.1 ± 3.2</td>
<td>2.7 ± 0.5</td>
<td>6.5 ± 0.3</td>
<td>3.8 ± 1.8</td>
</tr>
<tr>
<td>NOX mg/m³</td>
<td>83.8 ± 42.0</td>
<td>21.8 ± 12.1</td>
<td>52.0 ± 34.5</td>
<td>98.9 ± 33.2</td>
<td>49.1 ± 22.1</td>
<td>142.4 ± 56.9</td>
<td>84.3 ± 46.3</td>
</tr>
<tr>
<td>Methane mg/m³</td>
<td>56.7 ± 25.1</td>
<td>28.2 ± 14.8</td>
<td>34.4 ± 12.5</td>
<td>56.1 ± 22.2</td>
<td>46.7 ± 18.4</td>
<td>69.6 ± 14.2</td>
<td>64.4 ± 23.8</td>
</tr>
<tr>
<td>Pentane mg/m³</td>
<td>32.8 ± 7.8</td>
<td>7.9 ± 4.4</td>
<td>11.0 ± 2.3</td>
<td>11.9 ± 3.5</td>
<td>14.7 ± 6.2</td>
<td>21.2 ± 5.4</td>
<td>14.7 ± 8.7</td>
</tr>
<tr>
<td>Acetylene mg/m³</td>
<td>14.2 ± 10.7</td>
<td>3.7 ± 2.1</td>
<td>11.5 ± 10.0</td>
<td>20.5 ± 10.6</td>
<td>7.9 ± 6.1</td>
<td>8.8 ± 0.1</td>
<td>15.9 ± 11.6</td>
</tr>
<tr>
<td>Ethylene mg/m³</td>
<td>22.5 ± 13.2</td>
<td>5.1 ± 3.2</td>
<td>14.6 ± 11.5</td>
<td>24.7 ± 9.3</td>
<td>16.7 ± 8.4</td>
<td>21.2 ± 3.9</td>
<td>22.1 ± 12.0</td>
</tr>
<tr>
<td>Propene mg/m³</td>
<td>29.4 ± 12.9</td>
<td>9.1 ± 4.1</td>
<td>16.3 ± 8.9</td>
<td>25.6 ± 7.4</td>
<td>18.1 ± 7.5</td>
<td>25.4 ± 4.6</td>
<td>25.8 ± 9.1</td>
</tr>
<tr>
<td>1,3-Butadiene mg/m³</td>
<td>13.4 ± 8.5</td>
<td>7.9 ± 1.6</td>
<td>8.4 ± 2.6</td>
<td>14.6 ± 6.7</td>
<td>15.8 ± 9.4</td>
<td>7.8 ± 0.3</td>
<td>6.3 ± 2.3</td>
</tr>
<tr>
<td>Benzene mg/m³</td>
<td>30.1 ± 13.5</td>
<td>11.8 ± 4.7</td>
<td>24.2 ± 15.7</td>
<td>36.8 ± 12.8</td>
<td>28.8 ± 10.4</td>
<td>30.3 ± 2.0</td>
<td>38.3 ± 22.0</td>
</tr>
<tr>
<td>Formic Acid mg/m³</td>
<td>4.7 ± 1.6</td>
<td>2.3 ± 1.1</td>
<td>2.2 ± 0.7</td>
<td>1.9 ± 1.1</td>
<td>2.4 ± 1.3</td>
<td>2.3 ± 1.0</td>
<td>2.4 ± 1.5</td>
</tr>
<tr>
<td>Acetic Acid mg/m³</td>
<td>75.4 ± 26.5</td>
<td>11.2 ± 5.8</td>
<td>13.9 ± 5.0</td>
<td>13.9 ± 10.0</td>
<td>10.7 ± 7.5</td>
<td>14.9 ± 6.2</td>
<td>15.4 ± 10.2</td>
</tr>
<tr>
<td>Formaldehyde mg/m³</td>
<td>298 ± 10.2</td>
<td>8.6 ± 2.6</td>
<td>10.9 ± 2.8</td>
<td>14.2 ± 4.6</td>
<td>15.4 ± 7.5</td>
<td>23.6 ± 6.7</td>
<td>18.0 ± 7.7</td>
</tr>
<tr>
<td>Acetaldehyde mg/m³</td>
<td>13.7 ± 7.3</td>
<td>2.9 ± 0.8</td>
<td>3.9 ± 1.2</td>
<td>4.3 ± 2.1</td>
<td>6.3 ± 3.5</td>
<td>8.9 ± 3.8</td>
<td>7.3 ± 4.0</td>
</tr>
<tr>
<td>Methanol mg/m³</td>
<td>15.7 ± 9.6</td>
<td>1.0 ± 0.5</td>
<td>1.6 ± 1.0</td>
<td>1.5 ± 0.3</td>
<td>2.0 ± 0.2</td>
<td>2.2 ± 1.8</td>
<td>1.9 ± 1.4</td>
</tr>
</tbody>
</table>
Generally, the CO concentration was high during the burnout phase (Figure 1). However, there was a clear difference in CO among wood species in the burnout phase, which can be partly explained by the amount of char produced by different wood species. Visually, birch woods produced the least and Spruce and Alder produced considerable amounts of char and CO. Kortelainen et al. [15] also observed that spruce produced more char residue and CO as compared to beech. In RWC, CO is a marker of incomplete combustion. It is generated especially in three cases: during the burning of the first batch when the firebox is cold, after the loading of additional batches of wood during the fast devolatilization of the fuel and the residual char-burning phase [14,15,17,27]. The reason for high CO emissions in the burnout phase is due to the low diffusion rate of oxygen into the fuel [15].

![Figure 1. CO (black), OGC (red), CH₄ (green), NOₓ (grey) and NH₃ (blue) concentrations (mg/m³, normalized to 1 atm, 20 °C, 13% O₂) during combustion of BirchA.](image)

### 3.2.2. Nitrogen Oxides and Ammonium

The lowest NOₓ concentrations were determined in Pine experiments and the highest in Alder experiments (Table 3). All concentrations were below the Ecodesign limit (Table S3). Currently, the strictest limits in Europe are in the north provinces in Italy, where values are divided into 5-star classes (Table S3). All NOx values exceeded the 5-star limit, while all other wood species, except Alder, were below the 4-star limit. In RWC, NOₓ emissions are mainly dependent on fuel-N content [49,50]. Also, reducing the combustion conditions of the primary combustion zone affects the conversion of fuel-N to NOₓ [51]. In general, fuel-N is first converted to hydrogen cyanide (HCN) and NH₄ compounds during pyrolysis and becomes partially oxidized to NOₓ [52]. Also in this study, the N content of the fuel correlated well with the NOₓ concentration of the fuel (Figure S4). When comparing the results to the study of Tissari et al. [27], where the logs were drier and the combustion technology was traditional, the NOₓ emissions behaved in the same way between wood species (Figure 2). In this study, the concentrations were slightly higher than in the previous study, which may be due to the different stove type and higher air-to-fuel ratio in this study. Tissari et al. [27] also found that the bark in wood logs affects the result by increasing NOₓ emissions. Without bark, NOₓ concentrations were 13–30% lower than in logs with bark (Figure 2).
This study (as NO\textsubscript{X}, mg/m\textsuperscript{3})  

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Figure 2. Comparison of NO\textsubscript{X} concentrations (mg/m\textsuperscript{3}, normalized to 1 atm, 20 °C, 13% O\textsubscript{2}) obtained in this study and in literature [27] with Finnish wood species.

Typically, the NO\textsubscript{X} concentration increased batch by batch, excluding Alder and BirchB (Figure S5A). The concentration was clearly the lowest with BirchA in the first batch. At the beginning of each batch, the NO\textsubscript{X} concentration was the lowest, and during the glowing embers phase, it was the highest (Figure 1). On the contrary, Price Allison et al. [53], reported the highest NO\textsubscript{X} concentrations in the flaming phase and the lowest during the smoldering phase. In the combustion of different wood species, the N content of the fuel plays a significant role in the formation of NO\textsubscript{X} emissions, but the combustion conditions also affect the results.

The NH\textsubscript{3} concentration was clearly higher for Alder and Spruce (average 7.1 and 6.5 mg/m\textsuperscript{3}, respectively) than other wood species (2.3–3.8 mg/m\textsuperscript{3}). For Alder, NH\textsubscript{3} also increased clearly from batch to batch and was highest in batches 5 and 6, about 10 mg/m\textsuperscript{3} (Figure S5B). Gaseous NH\textsubscript{3} is an important compound, because it is the precursor for secondary aerosol formation in the atmosphere. However, experimental emission factors of NH\textsubscript{3} from RWC are limited in the literature. Li et al. [54] defined an emission factor of about 1 g/kg from the combustion of biomass in traditional heating and cooking stoves. In this study, NH\textsubscript{3} concentration values varied between 0.47 and 9.90 mg/m\textsuperscript{3}, which correspond to emission factors of 0.01–0.12 g/kg based on the calculation process presented in [14]. Thus, in this study, NH\textsubscript{3} emission factors were clearly lower as compared to traditional stoves, but due to the limited data available, more information on the NH\textsubscript{3} emission factors is needed.

3.2.3. Organic Gaseous Compounds and Single VOC Compounds

The OGC concentration was clearly the lowest in BirchA and the highest in Spruce (6.5-fold as compared to BirchA) and Alder (Table 3). Only Spruce exceeded the Ecodesign limit value, although Alder, Pine and Spruce exceeded it in individual samples (Table S3). For BirchA, the concentration was below the Italian 5-star category and for BirchB and Pine, below the 4-star category. The OGC concentrations were lower for all wood species as compared to previous studies [15,17,55]. However, the average OGC concentration varied significantly both between different fuels and among separate samples of the same fuel (Figure S6), indicating the high sensitivity of organic emissions to combustion conditions. Since the amount of energy produced was the same for different wood species, the physical sizes of the batches and logs varied. Spruce clearly had the lowest density (and largest batch volume), followed by Alder and Pine. Thus, in the combustion of Spruce and Alder, the distance between the wood logs and the secondary combustion air supply points was shorter than in other fuels, which can shorten the residence time and deteriorate the
mixing between gasification products and secondary air. This can be one reason for the high CO and OGC emissions measured from Spruce and Alder, and it underlines the very challenging and difficult nature of the realistic comparison of different wood species.

The six most common VOCs were methane (22–29%), benzene (12–16%), propene (9–11%), ethylene (5–11%), formaldehyde (6–10%) and acetic acid (6–11%). VOCs appeared especially during the first batch, but high momentary peaks were also observed after the new batch addition on the glowing char bed (see e.g., OGC in Figure 1). Some VOCs such as methane and propene were also present during the glowing ember phase (Figures 1 and 3). Acetic acid and methanol were concentrated in the first batch (Figure S6E,F), and they were averagely 7- and 15-fold as compared to the next batches, respectively, with BirchA. Thus, there was a high variation in VOC concentrations during the combustion process. Acetylene, ethylene, 1,3-butadiene and benzene had no clear trend between batches, except for the combustion of Alder (Figure S7). Acetylene is a key component and benzene is an intermediate product in soot formation through the HACA (Hydrogen Abstraction–Carbon Addition) mechanism [56]. In addition, formaldehyde, acetaldehyde and formic acid had a clear decreasing trend from batch to batch (Figure 3; Figure S6B–D). This agrees with the observation of Reda et al. [34] that most of the carbonyls were emitted during the first two batches, regardless of the type of wood used. Formic acid was formed primarily in the first batch, and peaks existed in every batch only during the ignition of the fuel just after the additions (Figure 3).

![Figure 3. Specific VOC concentrations (mg/m³, normalized to 1 atm, 20 °C, 13% O₂) during combustion of BirchA.](image)
There were only small differences in the VOC profiles between different wood species. Ethylene was lower in BirchA than in other wood species (Table 3). 1,3-butadiene was higher in Pine and BirchA than in other wood species, although overall VOC concentrations were lower with Pine and BirchA. The proportion of acetic acid was higher in both investigated birch wood species compared to other wood species. Birch wood species produced a lower concentration of benzene as compared to other wood species.

Generally, increased VOC concentrations due to the use of moist wood have also been found in many studies [19,21,27]. In this study, the use of dry spruce slightly reduced average OGC emissions compared to spruce with a normal moisture content, but for example, acetylene and benzene were lower with normal moist than with dry wood (Table 3). These compounds are connected to the soot formation mechanisms, as discussed earlier, and are seen in the EC emission factors between dry and moist fuels (see Section 3.3.1).

3.3. Fine Particles

3.3.1. Average Values of Particle Parameters

All measured particle parameters were the lowest with BirchA as compared to other wood species, except for AAE values. The average PM$_{2.5}$ for all wood species was low and ranged from 22.4 with BirchA to 48.8 mg/m$^3$ with BirchB and 49.6 mg/m$^3$ with Alder (Figure 4, Table 4). Higher PM$_{2.5}$ concentrations for BirchB and Alder were in line also with the larger geometric mean diameter (GMD) of the particles of these fuels measured by ELPI. Average concentrations were below the Ecodesign limit for BirchA and Pine, and were slightly higher for BirchB, Alder and Spruce, but in all tested fuels, at least some single samples were below the Ecodesign limits (Table S3). However, it is important to note that particulate matter limit values are obtained using the hot filter method, whereas we used a dilution method. The PM measurement method affects the measured PM concentration [55], and thus, the measured PM values are not fully comparable with limit values.

![Figure 4](image_url)  
Figure 4. Chemical fractionation of PM$_{2.5}$ (Other = PM$_{2.5}$-EC-OC). Concentrations are normalized to 1 atm, 20 °C, 13% O$_2$ and dry conditions.
Table 4. Particle-sampling parameters and average values of measured particle properties (±sd). Concentrations are normalized to 1 atm, 20 °C, 13% O2 and dry conditions. Values are averages of all single batches combusted. ND = not detected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit</th>
<th>BirchA</th>
<th>BirchA</th>
<th>BirchB</th>
<th>Alder</th>
<th>Pine</th>
<th>Spruce</th>
<th>SpruceDry</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR</td>
<td>°C</td>
<td>21.7 ± 1.7</td>
<td>26.4 ± 4.5</td>
<td>28.5 ± 3.9</td>
<td>25.6 ± 3.9</td>
<td>27.0 ± 2.5</td>
<td>29.9 ± 2.0</td>
<td>25.4 ± 2.6</td>
</tr>
<tr>
<td>PM2.5</td>
<td>mg/m³</td>
<td>32.0 ± 6.1</td>
<td>22.4 ± 4.7</td>
<td>24.8 ± 16.5</td>
<td>49.6 ± 16.4</td>
<td>32.2 ± 10.5</td>
<td>43.2 ± 10.6</td>
<td>74.6 ± 36.1</td>
</tr>
<tr>
<td>OC</td>
<td>mg/m³</td>
<td>5.5 ± 1.0</td>
<td>3.3 ± 1.8</td>
<td>10.3 ± 6.0</td>
<td>12.1 ± 5.2</td>
<td>6.7 ± 3.7</td>
<td>11.1 ± 3.2</td>
<td>9.6 ± 7.4</td>
</tr>
<tr>
<td>EC</td>
<td>mg/m³</td>
<td>21.4 ± 6.0</td>
<td>14.3 ± 3.9</td>
<td>34.6 ± 11.0</td>
<td>28.5 ± 9.3</td>
<td>22.0 ± 8.7</td>
<td>21.3 ± 8.6</td>
<td>46.4 ± 29.4</td>
</tr>
<tr>
<td>PM1ELPI</td>
<td>mg/m³</td>
<td>36.4 ± 8.1</td>
<td>25.4 ± 7.4</td>
<td>42.2 ± 14.0</td>
<td>45.3 ± 10.3</td>
<td>35.6 ± 15.3</td>
<td>30.7 ± 19.0</td>
<td>ND</td>
</tr>
<tr>
<td>GMDELPI</td>
<td>µm</td>
<td>0.050 ± 0.023</td>
<td>0.072 ± 0.005</td>
<td>0.100 ± 0.010</td>
<td>0.098 ± 0.012</td>
<td>0.077 ± 0.010</td>
<td>0.067 ± 0.015</td>
<td>ND</td>
</tr>
<tr>
<td>eBC</td>
<td>mg/m³</td>
<td>26.0 ± 4.0</td>
<td>13.1 ± 4.6</td>
<td>28.6 ± 9.3</td>
<td>18.6 ± 4.5</td>
<td>19.7 ± 7.7</td>
<td>14.6 ± 7.6</td>
<td>34.7 ± 23.6</td>
</tr>
<tr>
<td>AAE</td>
<td>-</td>
<td>1.27 ± 0.02</td>
<td>1.25 ± 0.07</td>
<td>1.18 ± 0.12</td>
<td>1.30 ± 0.11</td>
<td>1.26 ± 0.04</td>
<td>1.47 ± 0.16</td>
<td>1.19 ± 0.10</td>
</tr>
<tr>
<td>PNELPI</td>
<td>1 × 10⁷/#/cm³</td>
<td>7.7 ± 5.3</td>
<td>1.8 ± 0.4</td>
<td>2.1 ± 0.4</td>
<td>2.5 ± 0.3</td>
<td>2.3 ± 0.4</td>
<td>2.9 ± 0.4</td>
<td>ND</td>
</tr>
<tr>
<td>PNCTC</td>
<td>1 × 10⁷/#/cm³</td>
<td>16.6 ± 14.9</td>
<td>1.2 ± 0.2</td>
<td>1.5 ± 0.5</td>
<td>1.7 ± 0.2</td>
<td>1.2 ± 0.2</td>
<td>2.2 ± 0.5</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>LDSA</td>
<td>1 × 10⁴/µm²/cm³</td>
<td>1.8 ± 0.5</td>
<td>0.7 ± 0.2</td>
<td>1.1 ± 0.3</td>
<td>1.2 ± 0.2</td>
<td>0.9 ± 0.2</td>
<td>1.0 ± 0.1</td>
<td>1.2 ± 0.5</td>
</tr>
</tbody>
</table>

The fine particles from wood combustion are formed primarily from incomplete combustion (EC and OC) and vaporized alkali metal compounds (i.e., fine ash) [14]. In this study, we found that PM2.5 was mainly composed of EC (50–70% of PM2.5), and EC concentrations were clearly lower than in previous studies. In addition, OC concentrations were low, but were the highest for Alder, Spruce and BirchB: 12.1, 11.1 and 10.3 mg/m³ respectively. EC and eBC provided almost similar results (Figure S8), excluding Alder, where the EC was clearly higher (28.5 mg/m³) than eBC (18.6 mg/m³) (Table 4). Fine et al. [57] reported that from 40% to almost 100% of fine particle mass was organic material in the case of a conventional fireplace. In the nominal burn rate of a wood stove, Nyström et al. [15] measured a higher OC fraction than EC, while a higher EC fraction was measured in air-starved conditions with a high burn rate. In previous studies, OC/EC ratio values for softwoods have been close to 1 and, for hardwoods, from 1 to 5 [24,25]. In this study we found that the OC/EC for birches (hardwoods) was between 0.23–0.30 and for other species (softwoods), 0.30–0.52. Thus, the results from experiments in this study differ from many previous studies in terms of particle composition.

Regarding differences between wood species, the results are also contrary to our previous results with a similar sampling system with both modern and traditional combustion appliances [15,17]. In the study of Kortelainen et al. [15], spruce produced the lowest EC (23 mg/m³) while birch wood produced the highest EC concentration (100 mg/m³) in a modern stove. Similarly, in our other study [17], the EC from birch, alder and pine was quite similar in level, about between 130 and 190 mg/m³, whereas spruce emitted lower concentrations, about 90 mg/m³, with traditional combustion appliances. At least one reason is that in the previous studies, we used an exactly similar mass of wood batches, whereas in this study, we produced similar amount of energy with a similar burning rate by adjusting the air settings to be similar for each fuel. In both cases, the volume of fuels in the firebox has been varied, because of the differences in wood densities. Based on previous results, a higher combustion rate between wood species leads to higher EC emissions, not the wood species itself. Thus, it seems that the EC emissions are more connected to the combustion conditions in the firebox than wood species.

A higher OC concentration for Spruce and Alder was in line with higher AAE values than in other wood species. AAE describes the light absorption fraction of OC in the visible and near-UV wavelengths, playing a role in the radiative forcing of RWC aerosols. Generally, AAE values varied only a little, between 1.18 to 1.47 for all wood species. Values were at a similar level to those previously found from wood combustion [16,43,58], but notably lower than the assumption of AAE = 2 for biomass combustion [59]. AAEs up to 1.4 have been found even for pure BC particles [60,61]. Thus, there seemed to be only a mild variation in the light absorption properties of different wood species.
Differences in number concentrations (PN) between wood species were low, and average concentrations varied between 1.2 and $2.2 \times 10^7$ #/cm$^3$ by CPC and 1.8 and $2.9 \times 10^7$ #/cm$^3$ by ELPI and were of a very typical level as compared to the literature [15–17,27,30]. Wardoyo et al. [30] observed that hardwoods produced higher particle number concentrations than softwoods in the fast-burning condition, but in this study, this kind of division was not found. LDSA values varied only a little, between 7 and $12 \times 10^3$ μm$^2$/cm$^3$.

A PN increase in temporary incomplete combustion conditions, e.g., in the firing phase of the stoves [14,15], can be seen also in this study (Figure 5). Released ash particles also play an important role in the formation of the PN [14], although inorganics account for about 10% of the PM in RWC [15]. The vaporization of alkali metals is mainly dependent on the chemical composition of the wood and the reactions of inorganic species, but the combustion (grate) temperature also has an important influence on vaporization. Greater amounts of ash particles are released at higher temperatures [14,26,38]. It is also found that incomplete combustion produced a lower PN but larger particle sizes than in more complete combustion [62]. Thus, in this study, lower PNs from BirchA, BirchB and Pine than other fuels might be due to a slightly lower temperature in birch woods (Table 2) and the low concentration of ash and zinc in Pine wood (Table S1).

![Figure 5. PN (red by CPC, blue by ELPI) and LDSA (black) concentrations normalized to 1 atm, 20 °C, 13% O$_2$ and dry conditions during combustion of BirchA.](image)

In the previous studies [18,19,21,27], the noticeable effects of moisture contents on the quantity and type of particulate and gaseous emissions from small-scale domestic combustion have been observed. In the study of Shen et al. [18], which investigated the combustion of poplar wood with varied moisture contents in a brick cooking stove, all emissions except EC were increased. In this study, PM$_{2.5}$ concentrations measured from SpruceDry combustion experiments were 1.7 times higher than Spruce. This was mainly due to the higher proportion of EC in particle emissions, since the OC was lower with dry wood. Acetylene and benzene concentrations were also higher with dry than moist spruce experiments, indicating that high concentrations of acetylene and benzene promote the formation of soot through the HACA mechanism [56]. The AAE was 1.19 for SpruceDry (moisture content 7%) and 1.47 for Spruce (moisture content 17%), and the result is in line with Basnet et al. [58]. They found that when the fuel moisture content increased from 11% to 28% in a traditional stove, the AAE changed from 1.26 to 1.61.
3.3.2. Behavior of Particle Concentration between Different Batches

There was no systematic behavior of particle parameters from batch to batch. Only the GMD seemed to slightly increase during consecutive batches, especially for BirchB and Alder (Figures S9 and S10). However, the particle concentrations were the highest in the first batch in BirchA. The PM$_{2.5}$, OC and EC were 1.4–1.7-fold more in the first batch than sequent batches with BirchA (Table 4). The highest difference between the first and sequent batches can be seen in particle number values that are several times higher in the first batch than sequent batches (Figure S10). These differences can be explained with a lower combustion temperature and poorer combustion conditions during the first batch producing a higher content of both OC and EC.

3.3.3. Real-Time Particle Concentrations

Particle emissions are generally very sensitive to combustion conditions in the firebox that can be seen in the real-time curves of the concentrations (Figures 5 and 6). Short peaks were typically observed during the addition of new fuel batches, sometimes during the main combustion phase [15], but also at the end of the batches, especially regarding eBC, PM$_{1,ELPI}$ and LDSA values. The first short peak at the beginning of the batch originated from the short pyrolysis of the wood before the flames have fully ignited, producing very small organic particles [15]. This can be seen also in the peaks of particle numbers and AAE curves (Figures 5 and 6). Similar behavior was also recorded in the paper by Basnet et al. [58]. Later peaks are mainly BC, as seen in Figure 6. BC is formed in flame by surface growth via the conversion of large PAHs into recipient soot particles, PAHs being important precursors of BC [63]. Thus, the eBC primarily existed during the flaming phase and was significantly reduced during the glowing embers phase. In many cases, the eBC increased remarkably to the end of the batch, and high peaks of BC can be found just before the flames go out.

3.3.4. PAH Concentrations

The PAH concentrations in different wood species are shown in Table S4. The highest total PAH concentrations were measured from Alder and SpruceDry, since BirchA emitted the lowest concentrations of PAHs (Table S4, Figure S11). In the ignition batch in BirchA1, the emissions were about 4-fold (416 µg/m$^3$) as compared to BirchA (107 µg/m$^3$). Pine, BirchB and Spruce also had relatively low concentrations, 250, 285 and 309 µg/m$^3$, re-
spectively, as compared to the literature [25,29,64,65]. Achten et al. [64] observed higher concentrations of PAHs from hardwood species (birch, beech and wood briquettes) compared to softwood species, and Ihantola et al. [28] measured two to threefold higher concentrations of PAHs and Oxy-PAHs from pine compared to spruce combustion. The literature results are contradictory with this study. Pine emitted a lower concentration than Spruce, and there was not a clear connection of soft or hardwood to PAHs, since BirchB was between Spruce and Pine.

Genotoxic PAHs describes concentrations of the most harmful PAH compounds of total PAHs (Table S4, [66]). The portion of genotoxic PAHs was high with Spruce and Alder (>90% of total PAHs), and clearly the lowest from BirchA1 and BirchA (ca. 71% of total PAHs) (Table S4). The most general PAH compounds were pyrene, chrysene, benzo[g,h,i]perylene and benzo[a]anthracene. The PAH profiles were quite similar with BirchA1 and BirchB, except for anthracene, which was clearly higher for BirchA1 than BirchB (Figure 7). The BirchA1 (ignition batch) and BirchB profiles concentrated more to heavy PAHs than BirchA. When comparing Pine and Spruce, the PAH profile concentrated more to heavy PAHs in the Spruce experiments than in the Pine experiments (Figure 7).

Figure 7. Comparison of PAH profiles of selected wood species. Concentrations are normalized to 1 atm, 20 °C, 13% O₂ and dry conditions.
PAH concentrations varied systematically, but differently, from batch to batch with BirchA and Alder (Figure S13), since other wood species had no clear trend between batches. With BirchA, PAH concentrations were the highest in the first batch and had a steady or mild decreasing trend from batch to batch, except for that chrysene and benzo[a]anthracene increased slightly from the second to fifth batch (Figure S13). Interestingly, the PAH concentrations measured with Alder increased clearly from batch to batch. The only exception was that concentrations of anthracene decreased between the third and sixth batches (Figure S13). PAHs from the combustion of Alder also had quite good positive correlations with other emission parameters such as PM$_{2.5}$, EC, benzene and acetylene, whereas these correlations were not found with other wood species. A very interesting observation was also that the AAE value decreased when the PAHs increased with Alder. As a conclusion, PAH emissions from different wood species are mainly due to the impact of combustion conditions, which possibly explain the differences in emission factors also found in other studies [25,26,29,64,65].

4. Summary and Conclusions

In this study, the effect of different Nordic wood species on particulate and gaseous emissions was studied in a low-emissions modern stove. Despite large differences in wood densities (350–673 kg/m$^3$), the wood species were combusted at nearly the same combustion conditions. The average burning rate varied only a little (2.00–2.29 kg/h) and was independent on the wood density. The combustion times of the batches varied between 40 and 46 min and the average air-to-fuel ratios between 2.77 and 3.02.

Generally, the lowest gaseous emissions were obtained from the combustion of BirchA. Spruce and Alder produced the highest CO and OGC concentrations, and Alder the highest NOx concentrations, compared to other wood species. The N content of the fuel was found to be the main parameter affecting NOx formation. The ignition batch of BirchA clearly produced more acetic acid, formaldehyde, acetaldehyde and methanol compared to the following batches, but there were only small differences in the VOC profiles between different wood species. 1,3-butadiene was higher in Pine and BirchA than in other wood species, although overall VOC concentrations were lower with Pine and BirchA. The proportion of acetic acid was higher in both of the investigated birch wood species compared to other wood species. Clear explanations of the differences in VOC emissions between wood species were not found.

PM$_{2.5}$ was mainly composed of EC (50–70% of PM$_{2.5}$), since OC concentrations were low, as typically in modern appliances. Previously, bark has been found to be a main source of ash, different extractives and elements, and it has a significant effect on the emissions of volatilized ash particles. In this study, the proportion of fine ash in the PM$_{2.5}$ was small. The EC in the particle emission was particularly large for BirchA1, BirchA and SpruceDry, where the OC/EC ratio was between 0.23 and 0.26. The light absorption fraction of the OC described in the AAE value varied only a little, between 1.18 to 1.47 for all wood species. The values are notably lower than the assumption for biomass combustion and support the observation that the particle organic fraction in modern combustion stoves is low. Thus, the light absorption potential of these types of particles is lower than previously estimated. Particulate PAH emissions were relatively low compared to the literature, but the differences between wood species diverged slightly from other emissions. Clearly, the lowest PAH concentrations were still measured from BirchA (total PAH 107 µg/m$^3$), and in the ignition batch, the emissions were about 4-fold (416 µg/m$^3$). Pine, BirchB and Spruce also had relatively low concentrations: 250, 285 and 309 µg/m$^3$, respectively. Although Spruce had high CO and VOC concentrations, the OC was slightly higher and the AAE value was clearly higher than other wood species, the PAH concentrations were still low. This indicates that PAHS are not directly related to other organic fractions in the emissions, and thus, other organic emissions cannot be used as an indicator of PAH emissions.

Regarding the two separate origins of the birch fuels (BirchA and BirchB), the CO and NOx concentrations were at quite a similar level in both fuels, but the OGC, PM$_{2.5}$, OC and
EC were 2–3-fold and the particle number (CPC) and LDSA 1.2–1.5-fold from BirchB as compared to from BirchA. BirchB was slightly dryer and the density was higher than in BirchA, but the chemical compositions were similar, and thus, differences may be due to the physical differences in the wood batches between these fuels (slightly different log and batch size). The amount and composition of extractives and ash of the wood fuels, and bark content, cause differences in emissions between wood species. However, this study indicates that the differences may be due more to the physical properties of the wood and the combustion conditions than to the wood species themselves. When comparing wood species, a selection between the produced energy and log/batch size of the fuels must be chosen. If the same amount of energy is selected, the physical volume of fuels is different. If a similar physical size of logs/batches is chosen, the produced energy is different. In both cases, general combustion conditions, such as primary and secondary air supply for the combustion, need to be similar for a valid comparison. The results of this study underline the very challenging and difficult nature of a realistic comparison of different wood species in real-life appliances. Although the concentration values were generally below the limit values, differences between wood species and between single samples were so high that it should be considered in the official testing of the appliances. Especially, the use of too dry or too moist fuels and the wrong setting of the manually adjusted air supplies cause high emissions and a large variation in emissions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos15070839/s1, Table S1: A schematic of the test procedure and wood species used in the tests; Table S2: Characteristics of fuel properties; Table S3: The limit values of PM, CO, NOx and OGC compared to EU Ecodesign, German Blue Angel and Italian star limits; Table S4: Average PAH concentrations measured from the combustion of different wood species; Figure S1: Description of combustion process. Flue gas temperature, efficiency, and CO₂ and H₂O concentrations from BirchA experiment; Figure S2: Evolution of flue gas temperature from batch to batch from combustion of different wood species; Figure S3: Average CO concentrations from each investigated batch and evolution of CO concentrations from batch to batch; Figure S4: Correlation between fuel-N content and NOx concentration in this study and in Tissari et al. [27]; Figure S5: Evolution of NOx and NH₃ concentrations from batch to batch; Figure S6: Evolution of VOC concentrations from batch to batch; Figure S7: Evolution of VOC concentrations from batch to batch; Figure S8: Correlation between eBC and EC with samples from all wood species; Figure S9: Trends of particulate parameters from batch to batch; Figure S10: Trends of particulate parameters (GMD (ELPI), number (ELPI and CPC) and LDSA from batch to batch; Figure S11: Average PAH concentrations from each investigated batch and evolution of PAH concentrations from batch to batch; Figure S12: Evolution of concentrations of selected PAH compounds from batch to batch with BirchA and Alder; Figure S13: A figure of the wood stove used in the experiments.

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