

# Sustainability of using vineyard pruning residues as an energy source: combustion performances and environmental impact

Chiara Giorio<sup>1,\*</sup>, Sarah Pizzini<sup>2</sup>, Enrico Marchiori<sup>3</sup>, Rossano Piazza<sup>2,3</sup>, Stefano Grigolato<sup>4</sup>, Michela Zanetti<sup>4</sup>, Raffaele Cavalli<sup>4</sup>, Marco Simoncin<sup>5</sup>, Lidia Soldà<sup>1</sup>, Denis Badocco<sup>1</sup>, and Andrea Tapparo<sup>1</sup>

<sup>1</sup> Department of Chemical Sciences, University of Padova, Via Marzolo, 1 - 35131 Padova, Italy

<sup>2</sup> Institute for the Dynamics of Environmental Processes, National Research Council (CNR-IDPA), Via Torino, 155 - 30172 Venice Mestre (VE), Italy

<sup>3</sup> Department of Environmental Sciences, Informatics and Statistics, Ca'Foscari University of Venice, Via Torino, 155 - 30172 Venice Mestre (VE), Italy

<sup>4</sup> Department of Land, Environment, Agriculture and Forestry, University of Padova, Via dell'Università, 16 - 35020 Legnaro, Padova, Italy

<sup>5</sup> Uniconfort Srl, Via dell'Industria, 21 - 35018 San Martino di Lupari, Padova, Italy

\* Correspondence to: [chiara.giorio@unipd.it](mailto:chiara.giorio@unipd.it)

## Abstract

Open burning of agricultural waste is still a common practice as it is a rapid method for waste disposal, although natural biomass, including agriculture residues, can be exploited as a renewable energy source. We assessed the viability and sustainability of using vineyard pruning residues, as wood chips, for energy conversion. Wood chips, obtained from vineyards in the Prosecco DOCG region (Italy), were characterized in terms of chemical composition, calorific value, ash content and humidity. Combustion tests were performed in a medium-size biomass boiler (maximum power 500 kW) to assess the viability of the approach in terms of sustainable steady-state combustion. Primary emissions of both macro- and micro-pollutants were measured to assess the environmental impact. An analytical method was purposely developed for the determination of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in three matrices: fly ashes, condensate and gas. The results showed that vineyard pruning residues can be used for energy conversion in

31 medium- and large-scale biomass boilers. Primary emissions of measured pollutants were all below  
32 limit values set by current European legislation except for particulate matter, for which current  
33 available abatement technologies are required to contain emissions, thus making the use of vineyard  
34 pruning residues unsuitable for combustion in domestic appliances where such technologies are not  
35 installed. Bottom ashes produced during combustion were also characterized to assess whether they  
36 can be recycled in the vineyard as soil amendments/fertilizers. Copper content in combustion ashes  
37 exceeded limit values for ashes to be used as fertilizers in agricultural fields for some European  
38 countries but not for others, indicating that ashes may need to be disposed as waste.

39

#### 40 **Keywords**

41 Waste-derived fuel, Biomass, Vineyard residues, Wood boiler, Emissions, Persistent organic  
42 pollutants (POPs)

## 43 **1 Introduction**

44 The most recent scenarios depict a rise in world energy demand by 30% between today and 2040,  
45 which is equivalent of adding another China and India to today's global demand [1]. It is therefore  
46 imperative to shift towards renewable energy sources and increase energy efficiency in order to  
47 limit global temperature rise and meet the goals set by the Paris climate agreement [2].

48 Natural biomass, including agriculture residues, is a renewable energy source [3], although this  
49 definition does not consider the very different timescales when comparing carbon emissions during  
50 burning and resequstration during a plant's lifetime [4]. Currently, a significant part of the energy  
51 from agricultural by-products and wastes is lost: open burning is still a common practice as it is a  
52 rapid method for waste disposal [5–7] but with considerable detrimental impacts on air quality  
53 [8,9]. Besides the underestimated risk of fire, this practice not only causes uncontrolled release of  
54 greenhouse gasses without recovering any energy, but it can be also the cause of uncontrolled  
55 emissions of particulate matter (PM) and of persistent organic pollutants (POPs) in the  
56 environment, such as polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs),  
57 polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) [7,10,11]. These  
58 compounds are a cause of concern for human health and for the environment. Once emitted, these  
59 POPs tend to accumulate in fatty tissues and in the food chain. They are also very persistent and  
60 therefore subject to long-range atmospheric transport [12]. In fact, they have been detected even in  
61 the most pristine environments on Earth [13].

62 Modern air quality regulations aim at reducing both intentional and unintentional release of micro-  
63 pollutants in the environment. In this connection, open burning of agricultural residues has been  
64 strictly limited or prohibited by local authorities (for instance in Italy since 2010 with the  
65 Legislative Decree D.Lgs. 205/2010 [14]). Otherwise, the controlled burning of waste-derived  
66 biomasses for energy use can be a viable and safer alternative [15] to uncontrolled burning in the  
67 field. Anyway, the sustainability of this resource requires that other environmental aspects are  
68 correctly addressed, in particular those regarding the management (collection, transport and

69 processing) of the biomass to be used as fuel, the atmospheric emissions during controlled burning,  
70 and ash disposal.

71 In many countries, vineyard pruning residues (VPRs) represent a good example of agricultural  
72 waste that can become fuel. Recent studies have investigated the possibility to exploit this available  
73 biomass as an energy source, through the characterization of the biomass [16,17] and its use both as  
74 wood chips [18] and as pellets [19,20] in domestic appliances. However, due to the high ash content  
75 and humidity, maintaining an efficient steady-state combustion in domestic appliances has proven  
76 to be challenging [18,19] and the use of larger scale biomass boilers has been suggested as a better  
77 alternative [21].

78 In a densely inhabited area, the presence of large-scale thermal and power plants can be not well  
79 accepted by local residents. This highlights a contradictory opinion, on one side biomass thermal or  
80 power plants are considered fundamental to increase the share of renewable energy in the country,  
81 on the other side large size plants, especially when low quality biofuel is used, face opposition by  
82 local residents [22]. As a consequence, the type, location and operation of the facilities play a  
83 fundamental role on the social acceptance [23]. Besides this, the northern Italian Po valley  
84 represents a European hot-spot concerning aerosol pollution [24], where local authorities often limit  
85 the use of wood burning appliances in winter [25]. It follows the need to evaluate the environmental  
86 drawbacks of using biofuels derived from poor quality residual biomass, such as VPRs, in medium-  
87 size boiler.

88 In this study, for the first time, we investigate the possibility of exploiting VPRs, as wood chips, for  
89 energy conversion in a medium-size biomass boiler (maximum power 500 kW) taking into account  
90 also the related environmental drawbacks. The study aims at assessing the viability and the  
91 sustainability of the steady-state combustion of VPRs, as wood chips, in a medium-size biomass  
92 boiler. The overall environmental impact of the combustion process is here evaluated in terms of  
93 quality of the VPR wood chips as fuel, primary emissions of both macro- and micro-pollutants and  
94 ashes produced from the combustion process.

## 95 **2 Materials and methods**

### 96 **2.1 Characterization of the VPRs**

97 The VPR wood chips were collected in a specific geographical area in northern Italy, the Prosecco  
98 DOCG region, a hilly countryside area at the margin of the Po valley characterized by a significant  
99 high density of vineyards. In the Prosecco DOCG district (6650 ha) the estimated production of  
100 VPRs is of 25000 t/y. The sample used in this study was obtained by chipping VPRs using a  
101 purpose-build shredder machine, the Cobra Collina<sup>®</sup> of Peruzzo S.r.l. (Curtarolo, Padova, Italy).  
102 The main advantage in the use of purpose-build shredder machine lies in the versatility of the  
103 machine and in the logistics of storage and handling that is better suited to the vineries in the area  
104 even for limited storage spaces (the chipped VPRs occupy less space than the densified material  
105 balers).

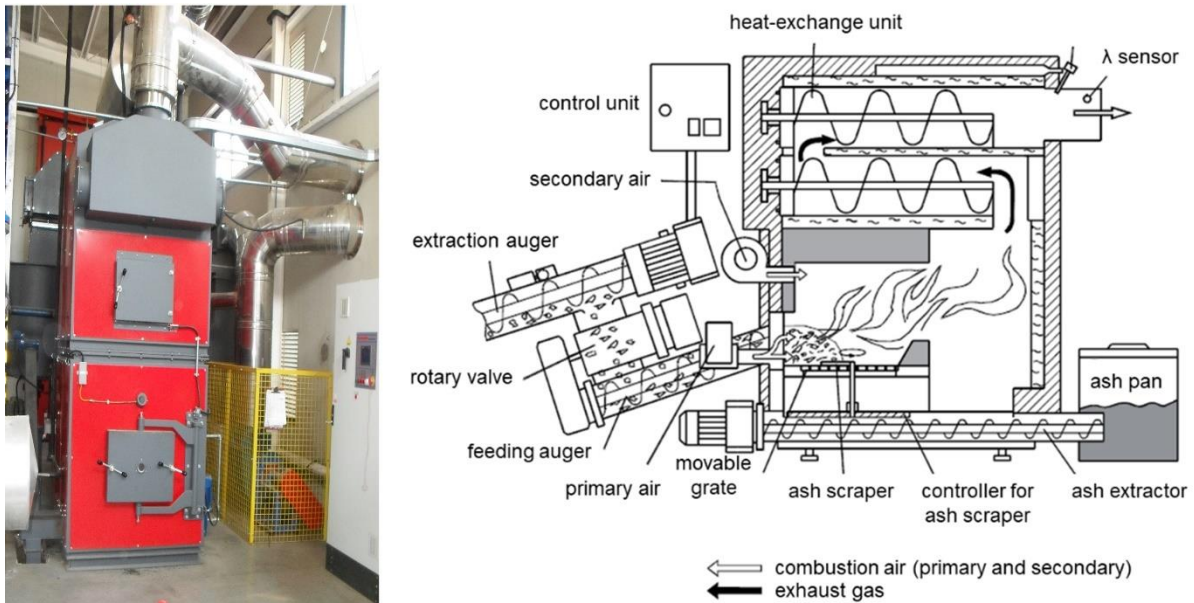
106 After harvesting, the wood chips were transported and stored in the proximity of the farm in  
107 covered piles for a period of 7 months. Covering the VPRs with an impermeable and breathable  
108 sheet has the advantage of accelerating the seasoning and preserving the quality of the material.  
109 Furthermore, with heaps with a contained height and a wide base, the preservation of the material is  
110 further encouraged. At the end of this period, the wood chips were transported in big-bags (volume  
111 of 1000 liters each) to the experimental biomass boiler site. Once stored at the experimental site,  
112 three samples of 50 liters of wood chips were collected and transported to the biofuel laboratory to  
113 be characterized in terms of physico-mechanical properties by the determination of moisture  
114 content, ash content, high heating value and particle size [19]. The three samples refer to the initial  
115 characterization done after 7-month seasoning in a covered pile, just before the first combustion  
116 test. While additional characterization tests over time were not done, it is expected that physical-  
117 mechanical characteristics of the fuel had not changed significantly afterwards. The values of the  
118 aforementioned parameters were assessed according with the recent in force ISO standards for solid  
119 biofuel quality assessment [26]. The moisture content of the sample was measured following the

120 method described in the EN ISO 18134-1 [27]. Three samples were placed in a ventilated oven at  
121  $105\pm 2^{\circ}\text{C}$  for up to 24 hours until constant weight was attained. The ash content was measured  
122 according to the EN ISO 18122 [28], using three samples of grounded chips of minimum 1 g each.  
123 The samples were weighed before and after their complete combustion that was carried out  
124 according to the temperature program stated in the EN ISO 18122 [28]. The reported ash contents  
125 are the average of the three repeats on a wet basis (as received). To measure the high heating value  
126 of the samples as received (HHV<sub>ar</sub>) an IKA<sup>®</sup> C-200 calorimeter was used (three repeats; IKA<sup>®</sup>-  
127 Werke GmbH & Co. KG). The high heating value on a dry basis and ash free (HHV<sub>daf</sub>) is  
128 calculated as indicated in the standard EN ISO 18125 [29]. To measure the particle size distribution,  
129 a volume of 8 liters of the wood chips have been sieved at moisture content below 20 w-% on a wet  
130 basis to prevent the fine particles from sticking together or losing moisture during the sieving  
131 process. Five circular sieves (metal plates) with round perforated holes from 3.15 to 63 mm, in  
132 accordance with ISO 3310-2 [30], have been used for particle size determination following the ISO  
133 17827-1 [31]. Since in the general requirement for solid biofuel EN ISO 17225-1:2014 [32] the  
134 VPRs are referred to as woody biomass and identified with origin number 1.1.7 “*Segregated wood*  
135 *from gardens, parks, roadside maintenance, vineyards, fruit orchards and driftwood from*  
136 *freshwater*”, the determination of particle size classes has been made in accordance with EN ISO  
137 17225-4:2014 [33], where the origin 1.1.7 is a subset of the 1.1 “*Forest, plantation and other virgin*  
138 *wood*”, and it refers to a B quality class.

## 139 **2.2 Combustion tests and measurements of gas and particulate emissions**

140 Three combustion tests and measurement campaigns were done on the 9<sup>th</sup> August 2012, 21<sup>st</sup>  
141 December 2012 and 24<sup>th</sup> April 2013 for a duration of about 10 hours each. The combustion tests of  
142 the VPRs were carried out in a medium-size experimental biomass boiler (Uniconfort S.r.l., San  
143 Martino di Lupari, Padova, Italy), with a maximum power of 500 kW (Figure 1). The boiler is  
144 equipped with an automatic feeding system which slowly brings the wood chips to the furnace by

145 means of a movable grate. After the furnace, exhaust gases are transported to the post-combustion  
146 chamber where they enter into contact with the heat-exchange unit. Combustion parameters (*e.g.*,  
147 furnace temperature, post-combustion chamber temperature, flue gas temperature, % O<sub>2</sub> in the flue  
148 gas) are monitored and self-adjusted in continuous to ensure maximum efficiency (O<sub>2</sub> 11%).  
149 Combustion ashes are removed continuously from the grate through an automatic extractor.



150

151

**Figure 1. Picture and schematic representation of the wood boiler.**

152

153 During the campaigns, continuous measurements of the concentrations of O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub>, SO<sub>2</sub>,  
154 C<sub>3</sub>H<sub>8</sub>, H<sub>2</sub>S in the exhaust, together with combustion efficiency, combustion air temperature, and  
155 exhaust air temperature, were done using a MRU<sup>®</sup> VARIOplus (MRU Instruments, Inc.) at about  
156 2 m down the flue from the heat-exchange unit (fume temperature 160-200°C).

157 Total suspended particles (TSP) were measured following the method EN 13284-1 [34], at a height  
158 of about 6 m (duct diameter 35 cm, fume temperature about 160-200°C). Isokinetic conditions (flue  
159 gas velocity of 3-5 m s<sup>-1</sup>) were maintained throughout the sampling (~5 minutes, 1-2 repetitions per  
160 experiment) by using nozzles with different internal diameters, monitoring the exhaust gas velocity  
161 in the duct and by manually adjusting the aspiration flow from the pump (ZB1 timer, Zambelli  
162 S.r.l., Milan, Italy). Filters used for TSP collection were made of quartz fiber (QFF, AQFA type,

163 Merck Millipore KGaA), and they were pre-treated at 400°C for 4 hours. Weighing of the filters  
164 was done, before and after sampling, after conditioning at a temperature of 20±1°C and relative  
165 humidity of 50±5% for at least 48 hours, as in previous studies [35]. The effect of weighing filters  
166 at 50% relative humidity rather than dry conditions is negligible in our experimental conditions  
167 because the hygroscopic growth factors at 50% relative humidity during hydration are small even  
168 for very hygroscopic particles like NaCl [36]. Flue gas velocity and volumetric flow were measured  
169 using the method UNI 10169 [37] in-between each sampling.

## 170 **2.3 Determination of PAHs, PCBs and PCDD/Fs**

### 171 *2.3.1 Sampling*

172 The sampling was carried out at a height of about 6 m (duct diameter 35 cm, fume temperature 160-  
173 200°C) in isokinetic regime using the “filter/condenser method” EN 1948-1 [38]. The sampler is  
174 composed of a glass probe inserted in a thermostated tube (120°C), a thermostated box (120°C)  
175 containing the filter holder fitted with a quartz fiber filter (QFF, AQFA type, Merck Millipore  
176 KGaA), a glass condenser maintained at 5°C using a chiller, a resin cartridge (~10 g of Amberlite®  
177 XAD®-2, Supelco® or XAD®-2 Ultra-Clean Resin, Restek Co.) at room temperature, and a constant  
178 flow pump. During sampling, gas velocity in the duct was continuously monitored using a Pitot  
179 tube. The isokinetic condition (flue gas velocity of 3-5 m s<sup>-1</sup>) was maintained by using nozzles with  
180 different internal diameters and by manually regulating the aspiration flow throughout the sampling  
181 (~3 hours, 1-2 repetitions per experiment). This system allows the collection of three different  
182 fractions: in the first step, the PM was collected on QFFs, then the vapors were condensed and  
183 collected in a glass bottle placed under the condenser, and finally the gaseous products were  
184 adsorbed in the resin cartridge. The filters used for PM collection were pre-treated at 400°C for 4  
185 hours and spiked with 4x100 µL of 4 <sup>13</sup>C-labelled PCB standards at 20 pg µL<sup>-1</sup> (PCB SYRINGE  
186 SPIKE, PCB-70/111/138/170, 1000 ng mL<sup>-1</sup>, CIL – Cambridge Isotope Laboratories, Inc., diluted  
187 2:100 in iso-octane, >99.3%, ROMIL-SpS™) before sampling.



188 2.3.2 *Extraction*

189 Three different extraction procedures for the three different matrices (fly ash on the QFFs,  
190 condensate, gas adsorbed on the resins) were used, following the indications of the method EN  
191 1948-2 [39]. Nevertheless, in order to enhance repeatability and reduce contamination risks,  
192 automated instruments were used for analytes extraction, while toluene was replaced with low-  
193 boiling and less toxic extraction solvents in order to shorten the concentration step and avoid the  
194 loss of the most volatile analytes (*e.g.*, PAHs; see Figure S1 in the Supplementary Material). All  
195 solvents used were Super Purity Solvents (SpS™, Romil Ltd.). All the tools and glassware were  
196 washed with an aqueous 2% (v/v) Contrad® 2000 solution, dried with acetone and rinsed three  
197 times with dichloromethane and three times with *n*-hexane.

198 For greater clarity, the steps of the proposed analytical method are summarized in the flow chart in  
199 Figure S2.

200 Prior to extraction, blanks and samples were spiked with a known amount of isotope-labelled  
201 solution (3 <sup>13</sup>C-labelled PAHs at 1 ng μL<sup>-1</sup>, 21 <sup>13</sup>C-labelled PCBs at 40 pg μL<sup>-1</sup> and 15 <sup>13</sup>C-labelled  
202 PCDD/Fs at 10-20 pg μL<sup>-1</sup>; CIL Inc.) as internal standards.

203 Concerning QFF samples, PAHs, PCBs and PCDD/Fs were extracted by means of a Pressurized  
204 Liquid Extractor (PLE™ system, FMS, Fluid Management System Inc.) equipped with stainless  
205 steel extraction cells, using *n*-hexane/dichloromethane (1:1, v/v). QFFs were broken in small pieces  
206 and mixed with anhydrous sodium sulfate, diatomaceous earth and Ottawa sand (Sigma-Aldrich  
207 Co., Applied Separation Inc.). The operative conditions were previously optimized for enhanced  
208 extraction efficiency and to minimize the amount of solvent required [40,41]. The extractions were  
209 performed at 100°C and 100 bar, with 3 static cycles of 7 min each. An acid pre-treatment, before  
210 extraction, is often done for analysis of organic compounds in fly ashes [42]. The attack with acid is  
211 carried out to disrupt the mineral conglomerates that are formed in the combustion process. These  
212 conglomerates (solid sphere, cenosphere, solid unshaped carbon particles) are formed at high  
213 temperature (1400°C) and are composed of Fe (Fe<sub>2</sub>O<sub>3</sub>), Al (Al<sub>2</sub>O<sub>3</sub>), Si (SiO<sub>2</sub>), along with Ca, K, and

214 Mg [43–45]. The temperature reached in biomass boilers are much lower (in this work 500-700°C),  
215 for these reasons the acid pretreatment was not performed in this study.

216 The condensate was extracted through a liquid-liquid extraction. The samples (about 70-100 mL)  
217 were put in a separating funnel with 10 mL of dichloromethane. The funnel was shaken for 15  
218 minutes and the organic phase was collected in a glass bottle. The extraction was repeated three  
219 times in total. The three aliquots of organic phase were then combined and anhydriified with sodium  
220 sulfate ( $\geq 99.0\%$ , anhydrous, ACS reagent, Sigma-Aldrich®). The procedural blank was prepared as  
221 follow. A fourth aliquot of organic phase was used for extraction from the same sample and  
222 disposed. Successively, the sample was spiked again with  $^{13}\text{C}$ -labelled internal standards and the  
223 extraction procedure was repeated another three times. The three aliquots of organic phase,  
224 constituting the procedural blank, were then combined and anhydriified.

225 The volatile compounds adsorbed onto the XAD<sup>®</sup>-2 resin were extracted using Accelerated Solvent  
226 Extraction (ASE<sup>™</sup> 200, Thermo Scientific, Dionex, Inc.). The resin samples were extracted using  
227 *n*-hexane/acetone (1:1, v/v) at a temperature of 100°C and a pressure of 120 bar using the procedure  
228 optimized by Yang *et al.* [46]. The extraction procedure, 5 minutes static extraction after a 5 min  
229 equilibration time, was repeated three times. After extraction, the cell was rinsed with the extraction  
230 solvent and flushed with N<sub>2</sub>. The total extraction volume was about 70 mL. The same extraction  
231 procedure was also done on blank resin samples.

### 232 2.3.3 Clean-up

233 The clean-up procedure is the same for all extracts of the three matrices. The extracts were reduced  
234 to a volume of 500  $\mu\text{L}$  under a gentle 5.0 (99.999%) nitrogen flow at 23°C (Turbovap<sup>®</sup> II, Caliper  
235 Life Science Inc.), recovered with 5 mL of *n*-hexane, and reduced again to 500  $\mu\text{L}$  in the same  
236 conditions. Purification was performed by directly injecting the sample into a disposable neutral  
237 silica column in an automated system (Power-Prep<sup>™</sup>, FMS Inc.) and by eluting it with 30 mL of *n*-  
238 hexane and 30 mL of *n*-hexane/dichloromethane (1:1, v/v). The eluates were collected as one single

239 fraction. Purified samples were reduced to 100  $\mu\text{L}$  under a gentle nitrogen flow at 23°C and spiked  
240 with a known amount of the recovery standard solution (1  $^{13}\text{C}$ -labelled PAHs at 1 ng  $\mu\text{L}^{-1}$ , 2  $^{13}\text{C}$ -  
241 labelled PCBs at 40 pg  $\mu\text{L}^{-1}$  and 2  $^{13}\text{C}$ -labelled PCDD/Fs at 20 pg  $\mu\text{L}^{-1}$ ; CIL Inc.) according to the  
242 method fully described in Pizzini *et al.* [41,47].

#### 243 2.3.4 Instrumental analysis

244 According to the method EN 1948-3 [48], analyses were performed by High-Resolution Gas  
245 Chromatography coupled both with Low and High-Resolution Mass Spectrometry (HRGC/LRMS  
246 and HRGC/HRMS respectively), while quantification was performed using internal standards and  
247 the isotopic dilution technique, using perfluorotributylamine (PFTBA; Sigma-Aldrich Co.) as the  
248 reference compound. 16 priority PAHs, 127 out of 209 possible PCB congeners and 17 2,3,7,8-  
249 substituted PCDD/Fs were investigated. All the results were corrected using the instrumental  
250 response factor and for the procedural blanks.

251 Instrumental determination of PAHs and PCBs was carried out using a HRGC/LRMS (Agilent  
252 7890A Series GC System, coupled with an Agilent 5975 inert Mass Selective Detector, Agilent  
253 Technologies Inc.) operating in electron impact mode (EI, 70 eV). Acquisition was performed in  
254 selected ion monitoring (SIM) mode.

255 PCDDs and PCDFs were determined using a HRGC (Hewlett Packard - Agilent 6890 Series GC  
256 System, Agilent Technologies Inc.) coupled with a HRMS (Thermo Finnigan MAT 95XP, Thermo  
257 Fisher Scientific Inc.) operating in electron impact mode (EI, 45 eV, with  $R \geq 10\,000$ ). Acquisition  
258 was performed using multiple ion detection (MID). Experiments were carried out monitoring the  
259 two most intense peaks of the EI spectra for each analyte.

260 Both instruments were equipped with a 60 m HP5-MS column (0.25 mm I.D., 0.25  $\mu\text{m}$  film  
261 thickness, Agilent Technologies Inc.).

262 Operating conditions, reference and target ion masses are presented in detail in Tables S1-S6.

263 2.3.5 *Data quality for the analysis of organic contaminants*

264 Analytical bias and precision were estimated by analyzing different Standard Reference Materials  
265 (SRMs) as similar as possible to the matrices under investigation. The instrumental detection limits  
266 (IDLs) were evaluated as three times the standard deviation of the blank signal and ranged between  
267 0.2 and 15 pg for PAHs, 0.2 and 6 pg for PCBs and 0.1 and 0.3 pg for PCDD/Fs (as injected  
268 amounts). Since preliminary tests on real samples showed that concentrations of PCDD/Fs were  
269 always below IDL, the analytical method for these classes of compounds was not validated further  
270 and following discussion refers to PAHs and PCBs only.

271 Initial tests on the QFFs were done on *Fly Ash Reference Material* EDF-5369 (CIL Inc.), which  
272 derives from the filter of a municipal waste incinerator in northern Italy. Nevertheless, this kind of  
273 matrix contains high levels of cenospheres, requiring an acid pretreatment that breaks up these  
274 conglomerates before the analysis. In order to be more consistent with the analytical protocol used  
275 in this work, it was therefore decided to use SRM 1649B (*Urban Dust*) from NIST (National  
276 Institute of Standard and Technology) to check the analytical quality of the method. Indeed, this  
277 SRM has a micro- and macroscopic structure more similar to the real samples, even if it does not  
278 come from direct combustion sources.

279 About 0.05 g of SRM were deposited on a QFF and analyzed for PAHs and PCBs as previously  
280 described. Precision, measured as relative standard deviation (RSD) of three replicated analyses of  
281 the same SRM, ranged from 0.2 to 12% for PCBs, with an average value of 2%. As for PAHs,  
282 precision for single compounds ranged from 1 to 17% for high molecular weight (4-6 rings)  
283 compounds, while for low molecular weight (2-3 rings) PAHs, RSD were 33% (with a total average  
284 value of 12%). This high variability can be explained by their greater volatility and, hence,  
285 sensitivity to the two steps of volume reduction that are required by the pre-analytical procedure.  
286 The accuracy tests led to good results, with a relative error ( $E_R$ ) in the range of 1-23% for PCBs,  
287 while more than 60% of the certified analytes were accurate within  $2\sigma$  for PAHs.

288 Concerning condensate, since there is no available SRM for this matrix, it was necessary to spike  
289 tap water, previously extracted according to the method described, with a known amount of the  
290 surrogate standard solution of each class of analytes. About 100 mL of spiked water were analyzed  
291 for PAHs and PCBs. Three repetitions were executed. The precision, expressed as repeatability,  
292 ranges between 4 and 10% for PCBs, with an average value of 6%. As for the PAHs, RSD ranges  
293 between 2 and 21%, with an average value of 9%. The results for most of the PCB target  
294 compounds were in good agreement with the certified/reference values, with the  $E_R$  in the range of  
295 1-19%, while for PAHs  $E_R$  ranges from 1 to 44%, with the exception of Benzo[ghi]perylene,  
296 systematically underestimated.

297 Concerning resin samples, in absence of a SRM to verify accuracy and precision of the analytical  
298 procedure, a blank XAD<sup>®</sup> resin was spiked with a known amount of the surrogate standard solution  
299 of each class of analytes and analyzed as described. Nevertheless, these kinds of resins contain high  
300 background levels of PCBs causing an interference in the analysis. Therefore, the method was not  
301 validated for this type of matrix and the concentration values obtained from its analyses are to be  
302 considered as indicative values.

#### 303 **2.4 Analysis of combustion ashes**

304 Combustion ashes were collected at the end of each test and analyzed according to the procedure  
305 already described elsewhere [19,49]. Briefly, 0.3 g of ashes were treated with 3 g of nitric acid  
306 (69%, PROLABO S.r.l., Milan, Italy) in a CEM Discover SP-D (CEM Corp., Matthews, NC, USA)  
307 microwave digester, with a temperature ramp from 20°C to 200°C at 30 bar in 4 min, and  
308 maintained at the final conditions for 2 min. After digestion, solutions were diluted in a 50 mL  
309 volumetric flask with ultrapure water, produced by a Millipore Plus System (Milan, Italy, resistivity  
310 18.2 M $\Omega$  cm<sup>-1</sup>), and analyzed by ICP-MS (Agilent 7700x; Agilent Technologies, Santa Clara, CA,  
311 USA).

## 312 **3 Results and discussion**

### 313 **3.1 VPR wood chips quality**

314 Physico-mechanical characteristics of the VPR wood chips are reported in Table 1. The moisture  
315 content (MC), the calorific values (HHV<sub>daf</sub> and HHV<sub>ar</sub>) and the granulometric classifications  
316 satisfy the requirement described in the EN ISO 17225-4:2014 [33] for type B wood chip samples  
317 but also for A1 and A2 classes. In fact the MC of the three wood chip samples, obtained thanks to  
318 the covering of the pile of VPRs with a breathable paper for 7 months, is  $\leq 15\%$  (see “*Table 2 —*  
319 *Specification of graded wood chips*” of the EN ISO [33]), the calorific value of the wood chips is  
320 not set by the standard (as minimum value to be stated), while the particle size distribution P31S  
321 with 3.8% of fine fraction content is one of the classes included in the “*Table 1 — Particle size of*  
322 *graded wood chips*” of the EN ISO standard [33]. Even if all of the above classification parameters  
323 corresponded to the requirements for a class A graded wood chips, VPRs cannot be qualified as  
324 type A due to their origin (not included in the list of those allowed for a type A samples) and their  
325 ash content that is  $> 3\%$  (Table 1), the limit set in the EN ISO standard [33] for type B wood chips.  
326 Due to their ash content, VPRs cannot be burned in domestic appliances. In any case, previous  
327 studies showed that maintaining an efficient steady-state combustion in domestic appliances is  
328 challenging with VPRs both as wood chips and pellets [18,19]. Indeed, as demonstrated in a  
329 previous study on the combustion of VPR pellets in a domestic stove, the high amount of ashes  
330 produced during combustion can compromise the combustion itself because burning VPRs requires  
331 a larger amount of injected air which in turn means a colder combustion chamber and higher  
332 pollutant emissions [19].

333

334 **Table 1. Average values (and standard deviations) of the physico-mechanical characteristics of chips from**  
 335 **vineyard pruning residues (VPRs) according to in force standards (MC: Moisture Content; HHVdaf: High**  
 336 **Heating Value on a dry basis and ash free; HHV<sub>ar</sub>: High Heating Value as received; A: Ash content; P: particle**  
 337 **size distribution; F: fine fraction). The three samples were collected from a covered pile after 7-month seasoning,**  
 338 **before the first combustion test.**

Wood chips Sample #	MC (%)	HHVdaf (MJ kg <sup>-1</sup> )	HHV <sub>ar</sub> (MJ kg <sup>-1</sup> )	A (%)	P class
1	11.7 (0.04)	18.07 (0.04)	17.57 (0.04)	3.10 (0.09)	P31S (F: 3.8%)
2	11.5 (0.03)	18.04 (0.04)	17.59 (0.03)	3.07 (0.15)	
3	11.6 (0.07)	18.01 (0.01)	17.58 (0.01)	3.08 (0.03)	

339  
 340 Furthermore, the concentrations of metals measured in the ashes (Table 2) produced during the  
 341 combustion tests showed a very high amount of Cu, 274±72 mg kg<sup>-1</sup>, above the limit value of 10  
 342 mg kg<sup>-1</sup> for combustion in domestic appliances [33]. In addition to Cu, other elements such as As,  
 343 Cr, Ni, Zn far exceed the limits imposed by the legislation for use in household appliances [33].  
 344 Nevertheless, large scale combustion facilities are equipped with abatement technologies for fly  
 345 ashes, like cyclones [50] or bag house filters [51], and so, for this reason, the high metal content  
 346 would not necessarily constitute a problem for atmospheric emissions. Concerning the possibility of  
 347 re-using bottom ashes as soil amendments, in Italy there are not guidelines for the application of  
 348 biomass ashes on agricultural fields. For this reason, trace element content has been compared with  
 349 limits set in other European countries [52–54], such as Austria, Germany, Denmark, Sweden, and  
 350 Finland (Table 2). For all elements, concentrations in VPR ashes were below all limits set by the  
 351 aforementioned countries with the exception of Cu for which the amount exceeded limit values of  
 352 some countries, namely Germany and Austria, but not others. Therefore, combustion ashes may  
 353 need to be disposed as waste rather than be re-utilized in the agricultural fields as fertilizer.

354  
 355 **Table 2. Measured concentrations (and standard deviations) of metals in the ashes collected from the wood**  
 356 **boilers at the end of each experiment and range of limit values set in different European countries by current**  
 357 **legislation (where available) for re-use of ashes as fertilizers in agricultural fields.**

Measured concentrations	Range of limit values
-------------------------	-----------------------

	(standard deviations) (mg kg <sup>-1</sup> )	in EU countries <sup>a</sup> (mg kg <sup>-1</sup> )
Fe	15.1 (4.7) ·10 <sup>3</sup>	
Al	8.3 (2.6) ·10 <sup>3</sup>	
Mn	1000 (22)	
Cu	274 (72)	70-600
Zn	130 (70)	1000-7000
Cr	34.7 (8.7)	100-300
Ni	24.4 (5.7)	30-100
V	22.0 (8.2)	70-100
Pb	5.9 (1.1)	100-300
Co	4.9 (1.7)	
As	4.7 (1.9)	20-40
Mo	2.60 (0.87)	
Sn	1.22 (0.60)	
Cd	0.060 (0.068)	1.5-8
W	0.08 (0.10)	

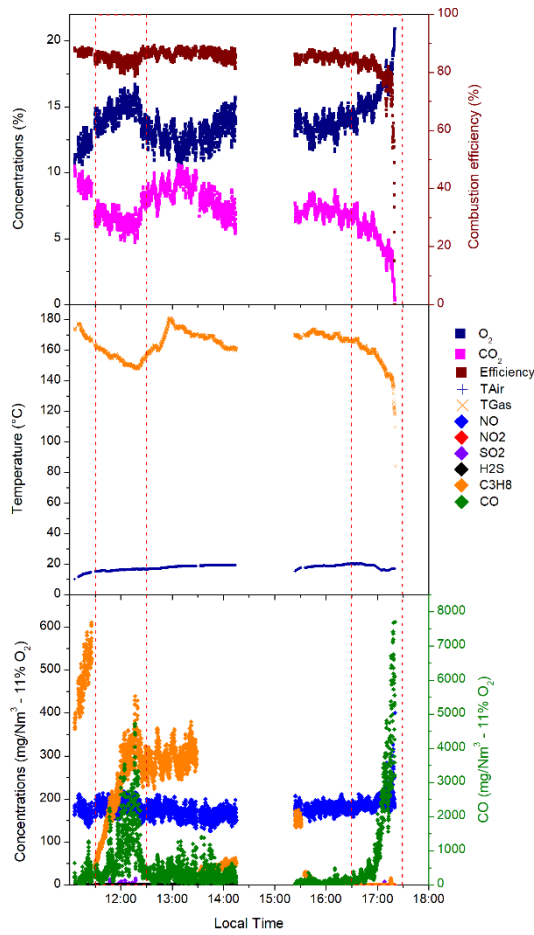
<sup>a</sup> Range of limit values in Germany, Austria, Denmark, Sweden and Finland for ashes to be re-used in agricultural soils.

### 358 3.2 Combustion tests and characterization of the emissions

359 While VPRs cannot be burned in domestic appliances, combustion tests performed in this study  
360 showed that VPRs can be used as an energy source in medium-size wood boilers (experimental  
361 boiler used had a maximum power 500 kW). In normal operating conditions, with automatic  
362 control/adjustment of combustion parameters, the combustion was stable throughout the entire  
363 duration of the experiments (up to 10 h). Typical conditions were characterized by a combustion  
364 chamber temperature of 500-750°C, exhaust gas temperature (after the heat-exchange unit) of 180-  
365 240°C, O<sub>2</sub> and CO<sub>2</sub> concentrations in the exhaust gas of 12-13% and 8-9%, respectively, providing  
366 a combustion efficiency of 86-89% with 12-20 kg h<sup>-1</sup> of fuel consumption (Figure 2).

367





368

369 **Figure 2. Evolution of the concentrations of macro-pollutants, air and fume temperatures during the combustion**  
 370 **test performed on the 21<sup>st</sup> December 2012 as an example of typical boiler running conditions. Dashed red squares**  
 371 **indicates a period of low-energy demand triggering a stand-by phase of the boiler and the shut-down period.**

372

373 Concerning macro-pollutants, their concentrations in the exhaust air were well below limit values of  
 374 current legislation (Italian Legislative Decree, D.Lgs. 152/2006 [55] and EU standards for  
 375 machineries [56]) for most of them, especially NO<sub>x</sub> due to relatively low temperatures in the  
 376 combustion chamber, and SO<sub>2</sub> due to low S content in the fuel (Table 3). CO concentrations were  
 377 well below the limit values for most of the duration of the tests (steady-state phase). CO  
 378 concentrations increased significantly only in non-optimal combustion conditions encountered  
 379 during start-up, shut-down and low energy demand phases (*e.g.*, the central heating system of the  
 380 factory was switched-off, therefore not dissipating the energy produced and triggering a stand-by  
 381 phase of the biomass boiler; Figure 2). Conversely, TSP concentrations were always above limit  
 382 values (Table 3). It is worthwhile to notice that the experimental boiler used was not equipped with

383 emission abatement devices, which are indeed mandatory to use in commercial wood boilers of  
 384 similar sizes. Therefore, the problem of particle emissions would be dramatic only for small  
 385 size/domestic boilers in which such devices are not deployed. In any case, such small size/domestic  
 386 appliances are not fit for purpose, as evidenced also in previous studies, because of difficulties in  
 387 maintaining stable combustion conditions due to excessive production of fly ashes with the fuel  
 388 under study in both wood chip and pellet forms [18,19].

389 Compared with other types of woody biomasses, emissions of macro-pollutants were higher than  
 390 emissions from combustion of beech as log woods in biomass boilers for CO (780±410 vs. 15  
 391 mg MJ<sup>-1</sup> for VPRs and beech, respectively), NO<sub>x</sub> (650±200 vs. 157 mg MJ<sup>-1</sup> for VPRs and beech,  
 392 respectively) and TSP (1200±800 vs. 18 mg MJ<sup>-1</sup> for VPRs and beech, respectively) but lower for  
 393 SO<sub>2</sub> (2.6±4.5 vs. 10 mg MJ<sup>-1</sup> for VPRs and beech, respectively) [57]. Emissions of macro-pollutants  
 394 were significantly higher than emissions from combustion of spruce in the form of wood chips (CO  
 395 75 mg MJ<sup>-1</sup>, NO<sub>x</sub> 127 mg MJ<sup>-1</sup>, TSP 32 mg MJ<sup>-1</sup>) and pellets (CO 17 mg MJ<sup>-1</sup>, NO<sub>x</sub> 81 mg MJ<sup>-1</sup>,  
 396 TSP 14 mg MJ<sup>-1</sup>) except for SO<sub>2</sub> (2.6±4.5 vs. 8 mg MJ<sup>-1</sup> for VPRs as wood chips and spruce as  
 397 pellets, respectively) [57].

398

399 **Table 3. Average concentrations (and standard deviations) of macro-pollutants in the flue gas, compared with**  
 400 **the limit values enforced in Italy, and emission factors (flue gas volumetric flow 700-1040 Nm<sup>3</sup> h<sup>-1</sup>) measured**  
 401 **during the three measurement campaigns. LDL=Lower than Detection Limit.**

	Concentrations in the flue gas (standard deviations)		Emission factors (standard deviations)			Limit values <sup>a</sup>
	mg Nm <sup>-3</sup>	mg Nm <sup>-3</sup> O <sub>2</sub> 11%	g h <sup>-1</sup>	g kg <sup>-1</sup>	g MJ <sup>-1</sup>	mg Nm <sup>-3</sup> O <sub>2</sub> 11%
CO <sup>b</sup>	200 (100)	270 (150)	200 (100)	12.3 (6.5)	0.78 (0.41)	350
NO	143 (16)	184.3 (1.5)	169 (51)	10.3 (3.1)	0.65 (0.20)	
NO <sub>2</sub>	LDL <sup>c</sup>	LDL	LDL	LDL	LDL	
NO <sub>x</sub> <sup>d</sup>	220 (24)	283.0 (3.0)	259 (78)	15.8 (4.8)	1.00 (0.30)	500
SO <sub>2</sub>	0.7 (1.2)	0.7 (1.2)	0.7 (1.2)	0.041 (0.071)	0.0026 (0.0045)	200
H <sub>2</sub> S	LDL <sup>e</sup>	LDL	LDL	LDL	LDL	
C <sub>3</sub> H <sub>8</sub>	71 (53)	95 (76)	76 (51)	4.6 (3.1)	0.29 (0.20)	
TSP <sup>f</sup>	330 (160)	450 (270)	310 (220)	19 (13)	1.2 (0.8)	100

<sup>a</sup> Italian Legislative Decree D.Lgs. 152/2006 for boilers of > 150 kW and ≤ 3 MW, more restrictive than the EU

---

standards for boilers of  $\leq 500$  kW: CO  $1200 \text{ mg Nm}^{-3}$ , TSP  $150 \text{ mg Nm}^{-3}$  [56]; <sup>b</sup> Average of 2<sup>nd</sup> and 3<sup>rd</sup> experiments; <sup>c</sup> LDL (NO<sub>2</sub>) = 5 ppm; <sup>d</sup> Calculated based on the molecular mass of NO<sub>2</sub>; <sup>e</sup> LDL(H<sub>2</sub>S) = 5 ppm; <sup>f</sup> Average of 1<sup>st</sup> and 2<sup>nd</sup> experiments.

402

### 403 **3.3 Emissions of micro-pollutants**

404 In the perspective of a sustainable management of vineyard practices, the environmental impact of  
405 using VPRs as energy source needs to be evaluated. After estimating the performances of the  
406 proposed analytical method, determination of PAHs, PCBs and PCDD/Fs was carried out on  
407 samples coming from the three different combustion tests at the wood boiler (approximate sampling  
408 volume of 1.5-3 Nm<sup>3</sup>). For each sample, three different matrices were collected: fly ash deposited  
409 on QFFs, condensed and flue gas adsorbed on XAD<sup>®</sup> resins. The distribution pattern of the different  
410 analytes was also investigated. Finally, quality standards and limits set by the Italian regulations  
411 were used to verify if and when emissions exceeded limit values for emissions in the atmosphere  
412 (Italian Legislative Decree, D.Lgs. 152/06 [55]), and the much more restrictive limit values for  
413 emissions from waste incinerators (Italian Legislative Decree, D.Lgs. 46/2014 [58]).

414 The combustion tests have highlighted some critical issues that may arise when using VPRs for  
415 energy conversion, especially concerning the difficulties in selecting and cleaning the material used  
416 as fuel. Indeed, mixed together with the VPR wood chips, plastic residues were found deriving from  
417 vineyard practices such as transport bags and shelters (plastic pipes for the protection of the base of  
418 the vine). In the specific case of the study, it has been estimated that the plastic residues were below  
419 0.5%. This fact may result in a supply of chlorine at high enough quantity to allow the occasional  
420 formation of PCDD/Fs during combustion.

421 Measured PAH and PCB concentrations for each sampled matrix are reported in Table 4 as  
422 averages and in Table S7 as single values for each experiment at the wood boiler. The most  
423 abundant contaminants in the analyzed samples were, as expected, PAHs followed by PCBs.  
424 Conversely, PCDD/Fs were always below detection limits.

425

426 **Table 4. Persistent Organic Pollutants (POPs) analyzed in three different combustion tests. Concentration levels**  
 427 **as averages (and standard deviations) of the three experiments for polycyclic aromatic hydrocarbons (PAHs; as**  
 428 **single compounds and total, ng Nm<sup>-3</sup>) and polychlorinated biphenyls (PCBs; as chlorination classes and total, pg**  
 429 **Nm<sup>-3</sup>) for each matrix analyzed. LDL = Lower than Detection Limit, n.a. = not analyzed.**

POPs		Concentrations in the flue gas (standard deviations)				Concentrations in the flue gas at O <sub>2</sub> 11% (standard deviations)			
		<i>F</i> <sup>a</sup>	<i>C</i> <sup>b</sup>	<i>R</i> <sup>c</sup>	<i>Total</i>	<i>F</i>	<i>C</i>	<i>R</i>	<i>Total</i>
<b>PAHs</b> (ng Nm <sup>-3</sup> ) <sup>3</sup>	Naphthalene	10.63 (0.84)	101 (65)	2010 (500)	2120 (520)	13.8 (1.7)	128 (80)	2630 (800)	2770 (810)
	Acenaphthylene	2.1 (1.8)	86 (88)	1060 (830)	1150 (920)	2.8 (2.3)	110 (120)	1400 (1100)	1500 (1200)
	Acenaphthene	0.35 (0.24)	2.0 (1.7)	4.7 (1.8)	7.1 (3.7)	0.44 (0.25)	2.4 (2.0)	6.0 (1.6)	8.8 (3.7)
	Fluorene	0.44 (0.20)	8.7 (8.3)	17.0 (5.5)	26 (14)	0.56 (0.22)	11 (11)	21.7 (6.3)	33 (17)
	Phenanthrene	17 (13)	440 (240)	780 (540)	1230 (730)	22 (17)	550 (290)	1020 (720)	1590 (960)
	Anthracene	1.74 (0.91)	24 (11)	45 (27)	71 (28)	2.2 (1.2)	30 (12)	59 (37)	91 (38)
	Fluoranthene	80 (110)	720 (600)	390 (590)	1200 (1300)	110 (150)	940 (790)	510 (770)	1600 (1700)
	Pyrene	130 (170)	1000 (1000)	530 (850)	1600 (2000)	170 (220)	1300 (1300)	700 (1100)	2200 (2600)
	Benz[a]anthracene	13.5 (8.1)	30.2 (4.1)	0.65 (0.73)	44 (12)	18 (11)	39.4 (8.9)	0.85 (0.95)	58 (20)
	Chrysene	34 (27)	85 (18)	2.0 (2.0)	121 (43)	46 (36)	110 (23)	2.6 (2.7)	158 (60)
	Benzo[b]fluoranthene	19 (18)	25 (17)	0.70 (0.64)	44 (35)	25 (23)	32 (22)	0.89 (0.84)	58 (46)
	Benzo[k]fluoranthene	4.8 (4.2)	11.4 (3.6)	0.113 (0.071)	16.3 (5.9)	6.3 (5.5)	15.0 (6.2)	0.145 (0.092)	21.5 (8.9)
	Benzo[a]pyrene	9.6 (5.3)	10.4 (5.8)	2.21 (0.56)	22 (11)	12.7 (7.2)	13.7 (7.8)	2.83 (0.48)	29 (15)
	Benzo[ghi]perylene	10.5 (6.6)	8.3 (6.5)	0.038 (0.066)	19 (11)	13.3 (8.4)	11.0 (8.7)	0.044 (0.076)	24 (14)
	Indeno[1,2,3-cd]pyrene	65 (72)	20 (16)	0.10 (0.17)	86 (88)	85 (95)	27 (22)	0.11 (0.20)	112 (115)
	Dibenz[a,h]anthracene	LDL	LDL	LDL	LDL	LDL	LDL	LDL	LDL
Total (Σ <sub>16</sub> PAHs)	400 (430)	2600 (2000)	4800 (3300)	<b>7800</b> <b>(5700)</b>	530 (570)	3300 (2600)	6300 (4400)	<b>10200</b> <b>(7500)</b>	
<b>PCBs</b> (pg Nm <sup>-3</sup> ) <sup>3</sup>	Cl-1	70 (120)	2200 (2800)	n.a.	2300 (2800)	90 (150)	2600 (3200)	n.a.	2700 (3100)
	Cl-2	300	3400	n.a.	3600	400	4100	n.a.	4500

		(470)	(3800)		(3700)	(620)	(4400)		(4300)
	Cl-3	210 (320)	2600 (2100)	n.a.	2800 (2300)	250 (370)	3200 (2500)	n.a.	3400 (2700)
	Cl-4	110 (140)	2800 (2900)	n.a.	3000 (3000)	150 (190)	3600 (3700)	n.a.	3800 (3900)
	Cl-5	53 (88)	4300 (3900)	n.a.	4300 (4000)	70 (120)	5400 (5100)	n.a.	5500 (5200)
	Cl-6	46 (79)	13000 (13000)	n.a.	13000 (13000)	60 (100)	17000 (17000)	n.a.	17000 (17000)
	Cl-7	90 (150)	9800 (8400)	n.a.	9800 (8500)	110 (190)	12000 (11000)	n.a.	12000 (11000)
	Cl-8	LDL	910 (640)	n.a.	910 (640)	LDL	1140 (800)	n.a.	1140 (800)
	Cl-9	0.53 (0.91)	LDL	n.a.	0.53 (0.91)	0.6 (1.1)	LDL	n.a.	0.6 (1.1)
	Cl-10	LDL	18 (17)	n.a.	18 (17)	LDL	22 (20)	n.a.	22 (20)
	Total ( $\Sigma_{127}$ PCBs)	880 (900)	39000 (32000)	n.a.	<b>40000</b> <b>(32000)</b>	1100 (1200)	49000 (40000)	n.a.	<b>50000</b> <b>(42000)</b>

430 <sup>a</sup> Fly ash deposited on quartz fiber filters; <sup>b</sup> Condensate; <sup>c</sup> Flue gas adsorbed on XAD<sup>®</sup> resins.

431

### 432 3.3.1 PAHs

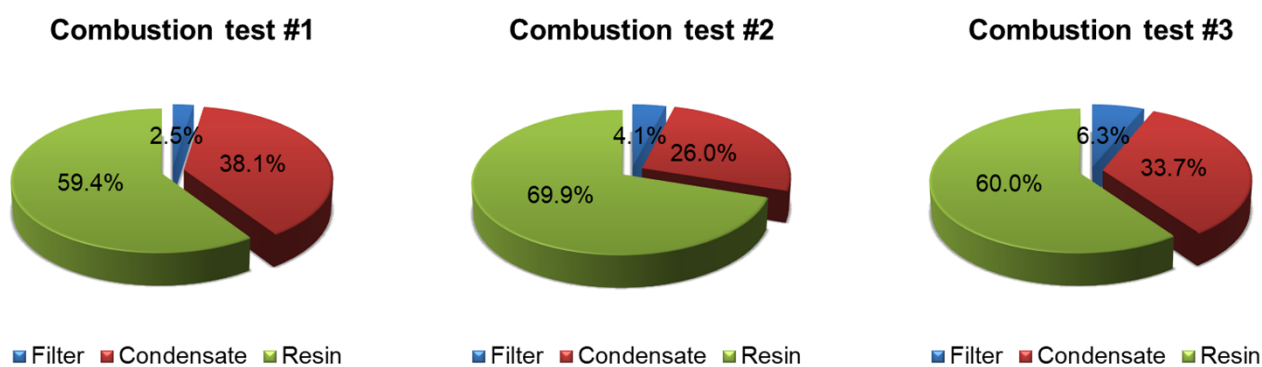
433 The detected concentrations of PAHs ranged widely, from 4.13 to 14.3  $\mu\text{g Nm}^{-3}$  as sum of all PAHs  
434 (with an average value of 7.81  $\mu\text{g Nm}^{-3}$ ). Nevertheless, the first two sampling campaigns showed a  
435 moderate variability, with a RSD of 13%. All the samples show a distinct pattern of PAH  
436 compounds in their distribution, generally enriched in Pyrene, Phenanthrene, Fluoranthene and  
437 Acenaphthylene. The predominant compound is Naphthalene, with values ranging from 1.62 to 2.66  
438  $\mu\text{g Nm}^{-3}$  (with an average value of 2.12  $\mu\text{g Nm}^{-3}$ ), except for the third sampling campaign where  
439 other heavier compounds dominated (*i.e.* Pyrene and Fluoranthene). Dibenz[a,h]anthracene was not  
440 detected in any of the samples, whereas Benzo[ghi]perylene and Indeno[1,2,3-cd]pyrene were  
441 detected only in the resin sample of the first sampling campaign.

442 As regards the estimation of carcinogenic potency and of degree of toxicity of these compounds, the  
443 analyzed samples present a pattern enriched of PAHs with a low value of Toxicity Equivalence  
444 Factor (TEF) [59]. Conversely, Benzo[a]pyrene and Dibenz[a,h]anthracene, that are generally  
445 considered the most toxic and carcinogenic among the 16 U.S. Environmental Protection Agency

446 priority PAHs [60], showed levels of concentration respectively two order of magnitude lower  
447 (from 12.9 to 33.7 ng Nm<sup>-3</sup>) or always below the IDL.

448 The distribution pattern of compounds in the three matrices was rather similar and unvaried, as  
449 shown in Figure 3. The highest levels of PAHs were detected in resin samples (with an average  
450 value of 4.84 µg Nm<sup>-3</sup>) and were mainly ascribable to Naphthalene and Acenaphthylene, which  
451 jointly accounted on average for 70% of the total; slightly lower PAH concentrations were found in  
452 condensate (with an average value of 2.57 µg Nm<sup>-3</sup>), while the values for fly ash samples were  
453 comprised between 0.104 and 0.901 µg Nm<sup>-3</sup> as sum of all PAHs.

454



455  
456

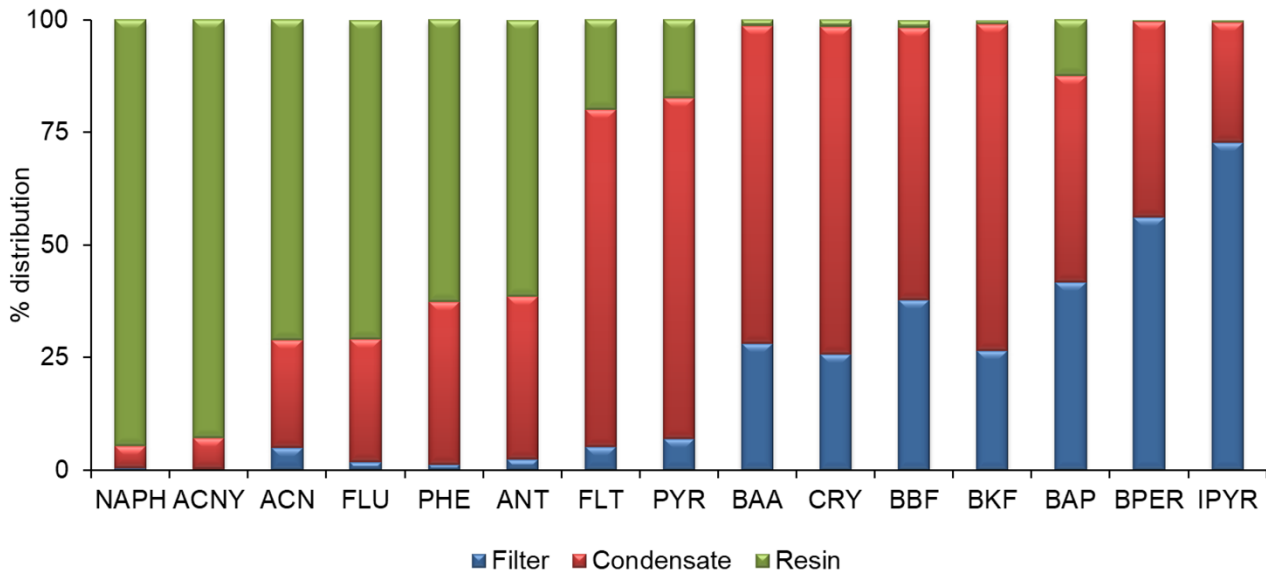
**Figure 3. Percentage distribution pattern of PAH compounds in the three matrices in analysis.**

457

458 When each single compound is considered, the distribution pattern remains relatively constant and  
459 showed a different matrix subdivision as the molecular weight of the analytes changes (Figure 4).

460 The lightest compounds (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene and  
461 Anthracene) are more volatile and, hence, they were adsorbed on the resin. Conversely, fly ash  
462 deposited on QFFs were generally enriched in high molecular weight compounds (4 to 6 aromatic  
463 rings). This is consistent with the physical-chemical properties of PAHs, in particular with the  
464 decrease in vapor pressure with increasing molecular weight.

465



466

467

468

469

470

471

472

473

474

475

476

477

478

479

480

481

482

483

484

485

**Figure 4. Average percentage distribution of concentration levels of single PAH compound analyzed in the three different matrices for each sampling campaign. NAPH: Naphthalene; ACNY: Acenaphthylene; ACN: Acenaphthene; FLU: Fluorene; PHE: Phenanthrene; ANT: Anthracene; FLT: Fluoranthene; PYR: Pyrene; BAA: Benz[a]anthracene; CRY: Chrysene; BBF: Benzo[b]fluoranthene; BKF: Benzo[k]fluoranthene; BAP: Benzo[a]pyrene; BPER: Benzo[ghi]perylene; IPYR: Indeno[1,2,3-cd]pyrene.**

The detected concentrations are significantly lower than the threshold values indicated by the legislation for large combustion plants ( $0.1 \text{ mg Nm}^{-3}$  for single compound,  $150 \text{ mg Nm}^{-3}$  for Naphthalene, Italian Legislative Decree, D.Lgs. 152/06 [55]), and for the more restrictive ones related to waste incinerators ( $10 \text{ } \mu\text{g Nm}^{-3}$  as the sum of 11 compounds, Italian Legislative Decree, D.Lgs. 46/2014 [58]).

### 3.3.2 PCBs

Samples were analyzed for 127 of the 209 possible congeners of PCBs (namely for those related to the Aroclor commercial mixtures and the non-Aroclor PCB-11). Not all of them were found in all the samples analyzed: for instance, Octa- and Deca-chlorinated compounds were not detectable in any of the filter samples, while Nona-chlorinated compounds were always below the detection limits in condensates, as reported in Table 4. As previously explained, due to high background values of PCBs found in the commercial XAD<sup>®</sup> resin, it was not possible to determine the concentration of this class of analytes in the resin samples.

486 As reported for PAHs, the levels of concentration of PCBs ranged widely, from 4.91 to 68.8 ng Nm<sup>-3</sup>  
487 <sup>3</sup> (average value of 40.1 ng Nm<sup>-3</sup>) with the second sampling campaign one order of magnitude lower  
488 than the others. The congeners composition is enriched in compounds with a high degree of  
489 chlorination: Hexa- and Hepta- represent, on average, 56% of the total distribution.

490 Also in this case, the distribution pattern of congeners in the two matrices under analysis is rather  
491 constant. PCBs are preferentially distributed on the condensate (which represents 97.3-98.6% of the  
492 PCB contamination), rather than on the filters where many homologue groups were below the  
493 detection limits.

494 The obtained results are considerably lower than the threshold limit values for PCB emissions from  
495 both large combustion plants (0.5 mg Nm<sup>-3</sup>, Italian Legislative Decree, D.Lgs. 152/06) and waste  
496 incinerators (Italian Legislative Decree, D.Lgs. 46/2014).

### 497 3.3.3 PCDD/Fs

498 As anticipated, concentrations of PCDD/Fs were all below detection limits, therefore no particular  
499 concern was evidenced. This fact could be ascribed to the low percentage of chlorine present in  
500 VPR wood chips (about 8%). A further explanation may derive from insufficient sampling volumes  
501 for the determination of compounds usually present at very low concentrations like PCDD/Fs.  
502 Nevertheless, we have still done an evaluation of the potential overrun of the limits imposed by the  
503 different legislations (10 µg Nm<sup>-3</sup> for Italian Legislative Decree, D.Lgs. 152/06 and 0.1 ng Nm<sup>-3</sup> for  
504 Italian Legislative Decree, D.Lgs. 46/2014) comparing them with our highest instrumental detection  
505 limit value (30 pg Nm<sup>-3</sup>) and using International Toxicity Equivalence Factors (I-TEFs) defined by  
506 Van den Berg *et al.* [61]. Even our highest instrumental detection limit values are significantly  
507 lower than the limits imposed by the Italian legislation, indicating that the use of VPRs as biofuel  
508 does not present risks of POPs contamination.



## 509 **4 Conclusions**

510 In this study, we assessed the viability and sustainability of using VPRs, as wood chips, for energy  
511 conversion. Wood chips from VPRs were characterized as fuel in terms of chemical composition,  
512 calorific value, ash content and humidity. Results showed that VPRs comply with type B standards,  
513 however due to high ash content they are not suitable for burning in domestic appliances.

514 Combustion tests were performed in a medium-size biomass boiler (maximum power 500 kW) to  
515 assess the viability of the approach in terms of sustainable steady-state combustion. We found that  
516 VPRs can be used successfully in medium-size boilers and the combustion was stable for all the  
517 duration of the experiments (~10 h) with a combustion efficiency of 86-89%.

518 Primary emissions of both macro- and micro-pollutants were measured to assess the environmental  
519 impact. Primary emissions of macro-pollutants, such as CO<sub>2</sub>, CO, NO<sub>x</sub>, and SO<sub>2</sub>, were below limit  
520 values of current European legislation except for PM emissions that were above the limits in all  
521 combustion tests. It is worth noting that medium- and large-size biomass boilers need to be  
522 equipped with abatement technologies for particle emissions, not used in this series of experiments,  
523 therefore this potential environmental drawback would only be relevant for small-size domestic  
524 appliances that cannot anyhow be used with this type of fuel. Concerning micro-pollutants, both  
525 PAH and PCB concentrations in the particulate, condensate and volatile fractions collected from the  
526 flue were well below limit values set for large scale biomass boilers and also for incinerators, for  
527 which limits are much more restrictive. PCDD/Fs were always below detection limits of our method  
528 and therefore combustion of VPRs does not pose risks for production of POPs.

529 Bottom ashes produced during combustion were also characterized to assess whether they can be  
530 recycled in the vineyard as soil amendments/fertilizers. Heavy metal content was compared with  
531 limit values set in other European countries as Italy does not have limit values for ashes distributed  
532 in the field. All trace metals were below limit values except for copper, whose concentration  
533 exceeded limit values for some countries but not for others, therefore bottom ashes may need to be  
534 disposed as waste rather than used as soil amendments in agricultural fields.

535 The present study was based on a relatively homogeneous VPR sample with processing and storage  
536 conditions that respect the local good practices. The use of wetter wood chips, wood chips with a  
537 high percentage of fine particles or wood chips treated with chlorinated pesticides could influence  
538 negatively the quality of emissions, especially in small- and medium-sized installations such as the  
539 one used for this series of tests.

540 The analytical method developed for the determination of micro-pollutants, *i.e.* PAHs, PCBs and  
541 PCDD/Fs, is fit-for-purpose to assess risks posed by emissions of compounds that are harmful for  
542 public health. Further improvements of the analytical method may be done by testing the use of  
543 polyurethane foam rather than XAD<sup>®</sup> resins for sampling the volatile components – because  
544 background levels of PCBs in the XAD<sup>®</sup> resins were very high –, and by increasing sampling  
545 volume to obtain a more accurate evaluation of PCDD/F concentrations.

546 While our study demonstrated the viability and sustainability of using VPRs for energy conversion,  
547 more studies are needed to assess both the potential for aerosol formation in the atmosphere from  
548 oxidation of emitted volatile organic compounds and whether additional abatement strategies would  
549 be required.

550

## 551 **Acknowledgements**

552 This work was supported by the “PRO.S.E.C.CO” project (Italian acronym for Sustainable  
553 Production of Energy from Combustion and of Compost – Rural Development Program (PSR)  
554 2007-2013, Measure 124 – Veneto Region DGR 745 March 15, 2010). Combustion tests were  
555 performed using the laboratory facilities of Uniconfort S.r.l.; authors are grateful to the R&D team  
556 for their technical support during the experiments at the biomass boiler.

557

558 **Declaration of competing interests**

559 MS is an employee of Uniconfort S.r.l., producer of biomass boilers who fully collaborated in the  
560 present study. The producer did not provide funding for the research activity; had no role in the  
561 design of the study; in the collection, analyses or interpretation of data; in the writing of the  
562 manuscript, or in the decision to publish the results.

563

564 **References**

565 [1] International Energy Agency (IEA). World Energy Outlook 2017: A world in transformation.  
566 2017. <http://www.iea.org/weo2017/> (accessed June 27, 2018).

567 [2] Rogelj J, den Elzen M, Höhne N, Fransen T, Fekete H, Winkler H, et al. Paris Agreement  
568 climate proposals need a boost to keep warming well below 2 °C. *Nature* 2016;534:631–9.  
569 doi:10.1038/nature18307.

570 [3] Vassilev S V, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical  
571 composition of biomass. *Fuel* 2010;89:913–33. doi:10.1016/j.fuel.2009.10.022.

572 [4] Cornwall W. Is wood a green source of energy? Scientists are divided. *Science* (80- ) 2017.  
573 doi:10.1126/science.aal0574.

574 [5] Yevich R, Logan JA. An assessment of biofuel use and burning of agricultural waste in the  
575 developing world. *Global Biogeochem Cycles* 2003;17:n/a-n/a. doi:10.1029/2002GB001952.

576 [6] Singh J, Singhal N, Singhal S, Sharma M, Agarwal S, Arora S. Environmental Implications  
577 of Rice and Wheat Stubble Burning in North-Western States of India. *Adv. Heal. Environ.*  
578 *Saf.*, Springer, Singapore; 2018, p. 47–55. doi:10.1007/978-981-10-7122-5\_6.

579 [7] Kim Oanh NT, Permadi DA, Hopke PK, Smith KR, Dong NP, Dang AN. Annual emissions  
580 of air toxics emitted from crop residue open burning in Southeast Asia over the period of

- 581 2010–2015. *Atmos Environ* 2018;187:163–73. doi:10.1016/J.ATMOSENV.2018.05.061.
- 582 [8] Lemieux PM, Lutes CC, Santoianni DA. Emissions of organic air toxics from open burning:  
583 a comprehensive review. *Prog Energy Combust Sci* 2004;30:1–32.  
584 doi:10.1016/j.pecs.2003.08.001.
- 585 [9] Estrellan CR, Iino F. Toxic emissions from open burning. *Chemosphere* 2010;80:193–207.  
586 doi:10.1016/j.chemosphere.2010.03.057.
- 587 [10] Lohmann R, Breivik K, Dachs J, Muir D. Global fate of POPs: Current and future research  
588 directions. *Environ Pollut* 2007;150:150–65. doi:10.1016/j.envpol.2007.06.051.
- 589 [11] Li X, Wang S, Duan L, Hao J, Li C, Chen Y, et al. Particulate and Trace Gas Emissions from  
590 Open Burning of Wheat Straw and Corn Stover in China. *Environ Sci Technol*  
591 2007;41:6052–8. doi:10.1021/es0705137.
- 592 [12] Lerche D, Van de Plassche E, Schwegler A, Balk F. Selecting chemical substances for the  
593 UN-ECE POP Protocol. *Chemosphere* 2002;47:617–30. doi:10.1016/S0045-6535(02)00028-  
594 0.
- 595 [13] Giorio C, Kehrwald N, Barbante C, Kalberer M, King ACF, Thomas ER, et al. Prospects for  
596 reconstructing paleoenvironmental conditions from organic compounds in polar snow and  
597 ice. *Quat Sci Rev* 2018;183:1–22. doi:10.1016/j.quascirev.2018.01.007.
- 598 [14] Italian Legislative Decree, D.Lgs. 205/2010, Implementation of the EU Directive  
599 2008/98/EU n.d. <http://www.camera.it/parlam/leggi/deleghe/10205dl.htm> (accessed July 11,  
600 2018).
- 601 [15] Kothari R, Tyagi VV, Pathak A. Waste-to-energy: A way from renewable energy sources to  
602 sustainable development. *Renew Sustain Energy Rev* 2010;14:3164–70.

- 603 doi:10.1016/J.RSER.2010.05.005.
- 604 [16] Toscano G, Riva G, Duca D, Pedretti EF, Corinaldesi F, Rossini G. Analysis of the  
605 characteristics of the residues of the wine production chain finalized to their industrial and  
606 energy recovery. *Biomass and Bioenergy* 2013;55:260–7.  
607 doi:10.1016/j.biombioe.2013.02.015.
- 608 [17] Duca D, Toscano G, Pizzi A, Rossini G, Fabrizi S, Lucesoli G, et al. Evaluation of the  
609 characteristics of vineyard pruning residues for energy applications: effect of different  
610 copper-based treatments. *J Agric Eng* 2016;47:22. doi:10.4081/jae.2016.497.
- 611 [18] Picchi G, Silvestri S, Cristoforetti A. Vineyard residues as a fuel for domestic boilers in  
612 Trento Province (Italy): Comparison to wood chips and means of polluting emissions control.  
613 *Fuel* 2013;113:43–9. doi:10.1016/j.fuel.2013.05.058.
- 614 [19] Zanetti M, Brandelet B, Marini D, Sgarbossa A, Giorio C, Badocco D, et al. Vineyard  
615 pruning residues pellets for use in domestic appliances: a quality assessment according to the  
616 EN ISO 17225. *J Agric Eng* 2017;48:99–108. doi:10.4081/jae.2017.612.
- 617 [20] Giungato P, Barbieri P, Cozzutto S, Licen S. Sustainable domestic burning of residual  
618 biomasses from the Friuli Venezia Giulia region. *J Clean Prod* 2018;172:3841–50.  
619 doi:10.1016/j.jclepro.2017.05.190.
- 620 [21] Spinelli R, Nati C, Pari L, Mescalchin E, Magagnotti N. Production and quality of biomass  
621 fuels from mechanized collection and processing of vineyard pruning residues. *Appl Energy*  
622 2012;89:374–9. doi:10.1016/j.apenergy.2011.07.049.
- 623 [22] Ribeiro F, Ferreira P, Araújo M, Braga AC. Public opinion on renewable energy technologies  
624 in Portugal. *Energy* 2014;69:39–50. doi:10.1016/j.energy.2013.10.074.

- 625 [23] Botelho A, Pinto LMC, Lourenço-Gomes L, Valente M, Sousa S. Social sustainability of  
626 renewable energy sources in electricity production: An application of the contingent  
627 valuation method. *Sustain Cities Soc* 2016;26:429–37. doi:10.1016/j.scs.2016.05.011.
- 628 [24] Bigi A, Ghermandi G. Trends and variability of atmospheric PM<sub>2.5</sub> and PM<sub>10-  
629 2.5</sub> concentration in the Po Valley, Italy. *Atmos Chem Phys* 2016;16:15777–88.  
630 doi:10.5194/acp-16-15777-2016.
- 631 [25] Castellani V, Piazzalunga A, Sala S. Research findings and decision making: The case of  
632 renewable energy. *Environ Sci Eur* 2013;25:1–11. doi:10.1186/2190-4715-25-22.
- 633 [26] Zanetti M, Costa C, Greco R, Grigolato S, Aalmo GO, Cavalli R. How wood fuels' quality  
634 relates to the standards: A class-modelling approach. *Energies* 2017;10:1–14.  
635 doi:10.3390/en10101455.
- 636 [27] EN ISO 18134-1:2015. Solid biofuels. Determination of moisture content. Oven dry method  
637 Part 1: Total moisture — Reference method. Geneva: ISO; 2015.
- 638 [28] EN ISO 18122:2015. Solid biofuels. Determination of ash content. Geneva: ISO; 2015.
- 639 [29] EN ISO 18125:2018. Solid biofuels -- Determination of calorific value. Geneva: ISO; 2018.
- 640 [30] EN ISO 3310-2: 2013. Test sieves. Technical requirements and testing. Part 2: Test sieves of  
641 perforated metal plate. Geneva: ISO; 2013.
- 642 [31] EN ISO 17827-1:2016. Solid biofuels. Determination of particle size distribution for  
643 uncompressed fuels. Part 1: Oscillating screen method using sieves with apertures of 3,15  
644 mm and above. Geneva: ISO; 2016.
- 645 [32] EN ISO 17225-1:2014. Solid biofuel. Fuel specifications and classes. Part 1: General  
646 requirements. Norm ISO 17225-1:2014. Geneva: ISO; 2014.

- 647 [33] EN ISO 17225-4:2014. Fuel specifications and classes. Part 4: Graded wood chips. Geneva:  
648 ISO; 2014.
- 649 [34] European Committee for Standardization. Stationary source emissions - Determination of  
650 low range mass concentration of dust - Manual gravimetric method. EN 13284-1: 2001.
- 651 [35] Giorio C, Tapparo A, Scapellato ML, Carrieri M, Apostoli P, Bartolucci GB. Field  
652 comparison of a personal cascade impactor sampler, an optical particle counter and CEN-EU  
653 standard methods for PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>1</sub> measurement in urban environment. *J Aerosol*  
654 *Sci* 2013;65:111–20. doi:10.1016/j.jaerosci.2013.07.013.
- 655 [36] Laskina O, Morris HS, Grandquist JR, Qin Z, Stone EA, Tivanski A V, et al. Size Matters in  
656 the Water Uptake and Hygroscopic Growth of Atmospherically Relevant Multicomponent  
657 Aerosol Particles. *J Phys Chem A* 2015;119:4489–97. doi:10.1021/jp510268p.
- 658 [37] Ente Nazionale Italiano di Unificazione. Emission measurement - Determination of velocity  
659 and flow rate in conveyed gas flow by Pitot tube. UNI 10169: 2001.
- 660 [38] European Committee for Standardization. Stationary source emissions - Determination of the  
661 mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 1: Sampling of  
662 PCDDs/PCDFs. EN 1948-1: 2006.
- 663 [39] European Committee for Standardization. Stationary source emissions - Determination of the  
664 mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 2: Extraction and clean-up  
665 of PCDDs/PCDFs. EN 1948-2: 2006.
- 666 [40] Piazza R, Gambaro A, Argiriadis E, Vecchiato M, Zambon S, Cescon P, et al. Development  
667 of a method for simultaneous analysis of PCDDs, PCDFs, PCBs, PBDEs, PCNs and PAHs in  
668 Antarctic air. *Anal Bioanal Chem* 2013;405:917–32. doi:10.1007/s00216-012-6464-y.

- 669 [41] Pizzini S, Piazza R, Cozzi G, Barbante C. Simultaneous determination of halogenated  
670 contaminants and polycyclic aromatic hydrocarbons: a multi-analyte method applied to filter-  
671 feeding edible organisms. *Anal Bioanal Chem* 2016;408:7991–9. doi:10.1007/s00216-016-  
672 9897-x.
- 673 [42] Balampanis DE, Coulon F, Simms N, Longhurst P, Pollard SJT, Fenech C, et al. An  
674 assessment of different extraction and quantification methods of penta- and hexa-  
675 chlorobenzene from SRF fly-ash. *Anal Chem Res* 2017;12:28–33.  
676 doi:10.1016/j.ancr.2017.01.003.
- 677 [43] Kutchko BG, Kim AG. Fly ash characterization by SEM-EDS. *Fuel* 2006;85:2537–44.  
678 doi:10.1016/j.fuel.2006.05.016.
- 679 [44] Ranjbar N, Kuenzel C. Cenospheres: A review. *Fuel* 2017;207:1–12.  
680 doi:10.1016/j.fuel.2017.06.059.
- 681 [45] Fenelonov VB, Mel'gunov MS, Parmon VN. The properties of cenospheres and the  
682 mechanism of their formation during high-temperature coal combustion at thermal power  
683 plans. *KONA Powder Part J* 2010;28:189–208. doi:10.14356/kona.2010017.
- 684 [46] Yang JS, Lee SK, Park YH, Lee DW. Analytical method for dioxin and organo-chlorinated  
685 compounds: (II) Comparison of extraction methods of dioxins from XAD-2 adsorbent. *Bull*  
686 *Korean Chem Soc* 1999;20:689–95.
- 687 [47] Pizzini S, Marchiori E, Piazza R, Cozzi G, Barbante C. Determination by HRGC/HRMS of  
688 PBDE levels in edible Mediterranean bivalves collected from north-western Adriatic coasts.  
689 *Microchem J* 2015;121:184–91. doi:10.1016/j.microc.2015.03.010.
- 690 [48] European Committee for Standardization. Stationary source emissions - Determination of the  
691 mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 3: Identification and



- 692 quantification of PCDDs/PCDFs. EN 1948-3: 2006.
- 693 [49] Badocco D, Lavagnini I, Mondin A, Tapparo A, Pastore P. Limit of detection in the presence  
694 of instrumental and non-instrumental errors: Study of the possible sources of error and  
695 application to the analysis of 41 elements at trace levels by ICP-MS technique. *Spectrochim*  
696 *Acta - Part B At Spectrosc* 2015;107:178–84. doi:10.1016/j.sab.2015.03.009.
- 697 [50] Salcedo RLR, Chibante VG, Fonseca AM, Cândido G. Fine particle capture in biomass  
698 boilers with recirculating gas cyclones: Theory and practice. *Powder Technol* 2007;172:89–  
699 98. doi:10.1016/j.powtec.2006.10.027.
- 700 [51] Khan AA, de Jong W, Jansens PJ, Spliethoff H. Biomass combustion in fluidized bed  
701 boilers: Potential problems and remedies. *Fuel Process Technol* 2009;90:21–50.  
702 doi:10.1016/j.fuproc.2008.07.012.
- 703 [52] Nogales R, Delgado G, Quirantes M, Romero M, Romero E, Molina-Alcaide E.  
704 Characterization of Olive Waste Ashes as Fertilizers. In: Insam H, Knapp B, editors. *Recycl.*  
705 *Biomass Ashes*, Springer, Berlin, Heidelberg; 2011, p. 57–68.
- 706 [53] Haglund N. Guideline for Classification of Ash from Solid Biofuels and Peat Utilised for  
707 Recycling and Fertilizing in Forestry and Agriculture. NT technical 613. Nordic Innovation  
708 Centre, Oslo, Norway. 2008:34. [http://www.nordtest.info/images/documents/nt-technical-](http://www.nordtest.info/images/documents/nt-technical-reports/NT_TR_613_Guideline_for_classification_classification_of_ash_from_solid_biofuels_and_peat_utilised_for_recycling_and_fertilizing_in_forestry_and_agriculture_Nordtest_Technical_Report.pdf)  
709 [reports/NT TR 613\\_Guideline for classification classification of ash from solid biofuels and](http://www.nordtest.info/images/documents/nt-technical-reports/NT_TR_613_Guideline_for_classification_classification_of_ash_from_solid_biofuels_and_peat_utilised_for_recycling_and_fertilizing_in_forestry_and_agriculture_Nordtest_Technical_Report.pdf)  
710 [peat utilised for recycling and fertilizing in forestry and agriculture\\_Nordtest Technical](http://www.nordtest.info/images/documents/nt-technical-reports/NT_TR_613_Guideline_for_classification_classification_of_ash_from_solid_biofuels_and_peat_utilised_for_recycling_and_fertilizing_in_forestry_and_agriculture_Nordtest_Technical_Report.pdf)  
711 [Report.pdf](http://www.nordtest.info/images/documents/nt-technical-reports/NT_TR_613_Guideline_for_classification_classification_of_ash_from_solid_biofuels_and_peat_utilised_for_recycling_and_fertilizing_in_forestry_and_agriculture_Nordtest_Technical_Report.pdf) (accessed July 16, 2018).
- 712 [54] Obernberger I, Supancic K. Possibilities of ash utilisation from biomass combustion plants.  
713 *Proceedings of the 17th European Biomass Conference & Exhibition, Hamburg: ETA-*  
714 *Renewable Energies (Ed.); 2009, p. 12.*

- 715 [55] Italian Legislative Decree, D.Lgs. 152/ 2006.  
716 <http://www.camera.it/parlam/leggi/deleghe/06152dl.htm> (accessed July 9, 2018).
- 717 [56] European Committee for Standardization. Heating boilers Part 5 : Heating boilers for solid  
718 fuels , manually and automatically stoked , Terminology , requirements , testing and  
719 marking. EN 303-5: 2012.
- 720 [57] Orasche J, Seidel T, Hartmann H, Schnelle-Kreis J, Chow JC, Ruppert H, et al. Comparison  
721 of emissions from wood combustion. part 1: Emission factors and characteristics from  
722 different small-scale residential heating appliances considering particulate matter and  
723 polycyclic aromatic hydrocarbon (PAH)-related toxicological potential o. *Energy and Fuels*  
724 2012;26:6695–704. doi:10.1021/ef301295k.
- 725 [58] Italian Legislative Decree, D.Lgs. 46/2014, Implementation of the EU Directive 2010/75/EU  
726 n.d. <http://www.governo.it/sites/governo.it/files/74990-9771.pdf> (accessed July 9, 2018).
- 727 [59] Nisbet ICT, LaGoy PK. Toxic equivalency factors (TEFs) for polycyclic aromatic  
728 hydrocarbons (PAHs). *Regul Toxicol Pharmacol* 1992;16:290–300. doi:10.1016/0273-  
729 2300(92)90009-X.
- 730 [60] Samburova V, Zielinska B, Khlystov A. Do 16 Polycyclic Aromatic Hydrocarbons Represent  
731 PAH Air Toxicity? *Toxics* 2017;5:17. doi:10.3390/toxics5030017.
- 732 [61] Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, et al. The  
733 2005 World Health Organization reevaluation of human and mammalian toxic equivalency  
734 factors for dioxins and dioxin-like compounds. *Toxicol Sci* 2006;93:223–41.  
735 doi:10.1093/toxsci/kfl055.
- 736

