

Fixed source monitoring system for marker emission during biomass combustion

Enrico Paris^a, Monica Carnevale^a, Ettore Guerriero^b, Adriano Palma^a, Beatrice Vincenti^a, Asma Khalid^c,
Elena Rantica^b, Andrea R. Proto^{d*}, Francesco Gallucci^{a,b}

^a*Council for Agricultural Research and Economics (CREA), Center of Engineering and Agro-Food Processing, Via della Pascolare 16, 00015 Monterotondo, Italy*

^b*National Research Council of Italy - Institute of Atmospheric Pollution Research (CNR-IIA), Monterotondo, Italy*

^c*Department of Environmental Sciences, Pir Mehr Ali Shah Arid Agriculture University, Shamsabad, Muree Road Rawalpindi - Pakistan*

^d*Department of AGRARIA, University of Reggio Calabria, Feo di Vito snc 89122, Reggio Calabria, Italy*

*Corresponding author: andrea.proto@unirc.it

Abstract

Emissions from biomass combustion depend on biomass characteristics, operating parameters and concern different types of compounds such as: CO₂, CO, SO₂, NO_x, inorganic and organic micro-pollutants, polycyclic aromatic hydrocarbons, polychlorinated byphenils, and particulate matter. The aim of this work is the development of a fixed source sampling method for total levoglucosan emission, commonly considered, along with its isomer mannosan and galactosan as an atmosphere tracers for Total Suspended Particles generated by biomass burning. The semi-volatile behavior of such compound was taken into account and its sampling occurred by depositing the main fraction on a filter and the volatile fraction sampled by impingers filled with specific solution. Subsequently, the emission factors of levoglucosan in Total Suspended Particles from burning of rice and wheat straw varying from 53.7 to 65.8 mg/kg_{fuel} were evaluated. The proposed method uses an isokinetic probe with quartz filter for particle fraction sampling and a system of impingers for the volatile fraction. The important result obtained from the experiment showed that a percentage between 30% and 50% of levoglucosan exceeds the filter and was sampled in the impingers. This result suggests the importance to collect both fractions

27 of levoglucosan emission in order to not neglect the volatile fraction which represents an important
28 component and must not be omitted.

29

30 **Keywords:** Burning, Levoglucosan, Total Suspended Particles, Cellulose, Sampling method.

31

32 **1. Introduction**

33 Biomass is expected to be a major source of sustainable energy in the future as the world transitions from
34 traditional carbon based fuels to carbon-neutral fuels [1,2] and its production is an important component
35 of farming systems leading to the generation of considerable amounts of crop residues worldwide
36 annually. Open combustion of biomass is the culprit for release of several atmospheric compounds such
37 as: CO₂, CO, SO₂, NO_x, inorganic and organic micro-pollutants, polycyclic aromatic hydrocarbons
38 (PAHs), polychlorinated byphenils (PCBs) and particulate matter (PM) [3–6]. Other sources of Total
39 Suspended Particles (TSP), crustal source that represents inputs of mineral particulate matter, traffic, and
40 industrial emissions, are represented by forest fires and residential wood smoke emissions [7]. In
41 addition, toxic and mutagenic [8–10] chemicals are present in wood smoke including polycyclic aromatic
42 hydrocarbons (PAHs) and aldehydes [11]. Cellulose is usually the most abundant component of
43 lignocellulosic biomass [12] and levoglucosan (C₆H₁₀O₅) is produced by the combustion and pyrolysis
44 of cellulose. Several studies have shown that levoglucosan is a dominant organic component emitted in
45 fine smoke particulate matter from biomass burning [13] so as to be considered as a relatively stable
46 reliable tracer of such emissions [14,15]. Many countries have adopted air quality standards and legal
47 actions for particulate matter (PM₁₀, and PM_{2.5}) monitoring in ambient air and started programs to
48 identify and quantify the contribution of TSP sources. Differently to other sugar-derivative compounds
49 that are generated during biomass burning (e.g. sugar alcohols, such as arabitol, mannitol and glycerol

50 [16,17] or monosaccharides such as glucose and fructose [18]), levoglucosan is generated exclusively by
51 combustion and pyrolysis phenomena of biomass and does not come from the biogenic activity of plants.
52 Levoglucosan is a very suitable tracer and molecular marker emitted in large amounts and it does not
53 decay over 10 days in acidic conditions, similar to those of atmospheric liquid droplets. Recent studies
54 suggested that levoglucosan is semi-volatile, and therefore gas-phase oxidation leads to short lifetimes
55 of levoglucosan of approximately 1–2 days under room-temperature conditions [19]. However, the
56 lifetime is extremely variable and it is strongly influenced by many atmospheric factors such as
57 temperature, humidity and the presence of oxidizing atmospheric agents [20]. An interesting study of C.
58 Lai et al. [20], about degradation kinetics of levoglucosan subjected to oxidizing atmospheric agents (OH
59 radicals), shows that the levoglucosan lifetime is significantly increased when levoglucosan is mixed
60 with soot particles or other compounds such as NaCl and $(\text{NH}_4)_2\text{SO}_4$. In contrast to polycyclic aromatic
61 hydrocarbons, this monosaccharide derivative is formed from the cellulose and hemicellulose thermal
62 decomposition [21,22] at high temperatures ($>$ than 300°C) during combustion [23,24]. Being a product
63 of biomass combustion, however, it is impossible to distinguish the source that generates it: biomass
64 boilers, open burning phenomena, domestic fireplaces, forest fires, could all be potential emission
65 sources. Along with other tracers such as potassium oxalate and gaseous acetonitrile [25], levoglucosan
66 appears highly correlated with regional fires [3]. Levoglucosan is also used in other fields of chemistry
67 and engineering, such as pyrolysis and fire-retardants research [24,26], biofuel research [27,28], biology
68 [29,30], organic synthesis [31,32] and as a biomass burning tracer in sediment analysis [33]. Recent
69 studies investigated another source of levoglucosan emission, young coals such as peat, for which
70 sampling and analysis of levoglucosan are carried out only on the filter and the recovery of the semi-
71 volatile part is not foreseen [34,35]. Different analytical techniques have been developed and used for
72 the determination of levoglucosan: methods such as high-performance liquid chromatography with

73 pulsed amperometric detector (HPLC-PAD) and ionic chromatography with pulsed amperometric
74 detector (IC-PAD) are now widely used mainly due to the ease of preparation and analysis of the samples
75 [15,36–39]. Other authors through derivatization methods used gas chromatography/mass spectrometry
76 (GC/MS) methodology to determine the levels of levoglucosan in TSP in the air [13,40].

77 In this work two worldwide residual biomass are considered: rice and wheat straw. Rice is one of the
78 largest important cash crops and is predicted to rise by 58 to 567 million tonnes by 2030 [41]. , while
79 wheat straw has an annual global production of about 500 millions tonnes [42]. Given such huge
80 quantities produced, they are easily considered as potential fuels. Open burning of straw is a common
81 practice in rice straw management in Asia [43] and determines a high contribution to air pollution with
82 considerable amounts of atmospheric organic and inorganic macro and micro pollutants. These
83 phenomena have a significant impact on air quality [44]. Currently, although ambient air sampling
84 methods are well consolidated and include monitoring methods of both ambient air and fixed source
85 emissions, levoglucosan is the only compound for which monitoring is envisaged in ambient air and not
86 from a fixed source. However, the measuring method based on the recovering of the total extraction has
87 not yet been validated, and this represents a significant limitation that will affect the levoglucosan
88 measurements and analysis. Therefore, studies using levoglucosan as a marker may underestimate the
89 contribution of biomass burning to ambient aerosols. In literature, most of the studies concerning the
90 determination of levoglucosan in the atmosphere take into account only the solid fraction. On the other
91 hand, studies that also consider the volatile fraction do not propose a large-scale sampling method and
92 are limited to using a combustion chamber [45]. This study aims to validate the multi-phase method for
93 stack sampling of total levoglucosan emitted by biomass combustion by means of a sampling system
94 able to collect both solid and volatile fractions, and to evaluate the emission contribution to air pollution.

95

96 2. Materials and Methods

97 2.1 Biomass Characterization

98 The test on levoglucosan emission and its sampling method were carried out using residual biomass
99 widely spread globally: rice and wheat straws. The latter, *Triticum aestivum* quality, was produced at
100 CREA-IT in Monterotondo (Italy), basmati rice straw (*Oryza sativa*) was imported from Pakistan. The
101 biomass has been shredded and open-air dried, thus facilitating the combustion process. The rice straw
102 samples were chopped to 4 mm before being sent to the boiler as feed. The same biomasses were milled
103 with a ball mill, homogenized, and subsequently characterized to determine their chemical and physical
104 characteristics (Table 1). The moisture content was measured by means of the Memmert UFP800 drying
105 oven according to EN ISO 18134-1:2015. In particular, the biomass sample was dried at $105 \pm 2^\circ\text{C}$ and
106 the moisture content was calculated taking into account the weight loss of the sample due to the drying
107 process that lasted 24 hours, until constant weight. For the characterization tests of heating value,
108 elemental composition and ash content, the dried sample was grinded first with the Retsch SM 100
109 cutting mill for a preliminary size reduction and thereafter through the Retsch ZM 200 rotor mill. The
110 higher heating value (HHV) was determined by means of the Anton Paar 6400 isoperibol calorimeter
111 according to ISO 18125:2018. The sample was prepared in a pellet form of about 1 g through a pellet
112 press and then it was inserted into the bomb. Following the initiation of the reaction through a cotton
113 thread connected to the electrodes, the sample undergoes the combustion process in an oxidizing
114 atmosphere at high pressure. The lower calorific value (LHV) was calculated from the higher calorific
115 value, considering the hydrogen content. The elemental composition in terms of carbon (C), hydrogen
116 (H), nitrogen (N), sulphur (S), was determined by means of the Costech ECS 4010 CHNS-O elemental
117 analyser (EN ISO 16948:2015). The oxygen content (O) was measured by difference on a dry basis. The
118 ash content was measured by means of the Lenton EF11/8B muffle furnace (EN ISO 18122:2016). About

119 1 g of sample was prepared on a porcelain dish and inserted in the furnace. The temperature of the furnace
120 was set with two different heating rates related to two steps: the first up to 250°C and the second from
121 250°C to 550°C.

122

123 *2.2 Emission sampling and measurements*

124 For combustion was used the boiler GSA-80 (D'Alessandro Termomeccanica Series GSA 80kW_{th}) in
125 which the fuel was conveyed it towards the fall hole in the upper auger. A star valve has the dual function
126 of dosing the fuel towards the auger, feeding the burner, and breaking the continuity of the fuel between
127 the two augers, preventing the return of any flames that could rise up from the hopper of the fuel. The
128 rotation speed of the lower auger determines the correct feeding of the brazier and is therefore a
129 determining factor for the correct operation of the plant. The fuel burned with the introduction of primary
130 and secondary combustion air. For the flue gas sampling, a multigas portable analyzer was used for
131 measurements of NO_x, SO_x, CO, CO₂, and O₂. The multigas portable analyzer was Horiba Model PG-
132 250 specifically designed for compliance with 40 CFR 60. Total gaseous hydrocarbon concentrations
133 (THC) were determined using a Ratfisch Model RS 53-T heated flame ionization detector (FID). The
134 THC concentration was continuously monitored from the exhaust gas by means of a heated probe and a
135 filter holder. A heat-traced line (180°C) transported the sample gas from the filter holder outlet to the
136 analyzer inlet. For TSP and metals, the sampling system (Fig. 1) was equipped with a heated titanium
137 sampling probe at 120±5°C, a filter holder, quartz microfiber filters (47mm) without binders, with
138 particle retention 99,9995% (0,3 µm) MK-360 Munktell, a cooling device and a pumping system able to
139 ensure isokinetic conditions, necessary to avoid errors due to the sampling of TSP as requested by the
140 European method (EN 13284-1:2017), and EPA (2018). Furthermore, three impingers have been used
141 (A, B, and C), inserted into the cooling device (6 ± 2°C), and each filled with a 100 ml aqueous solution

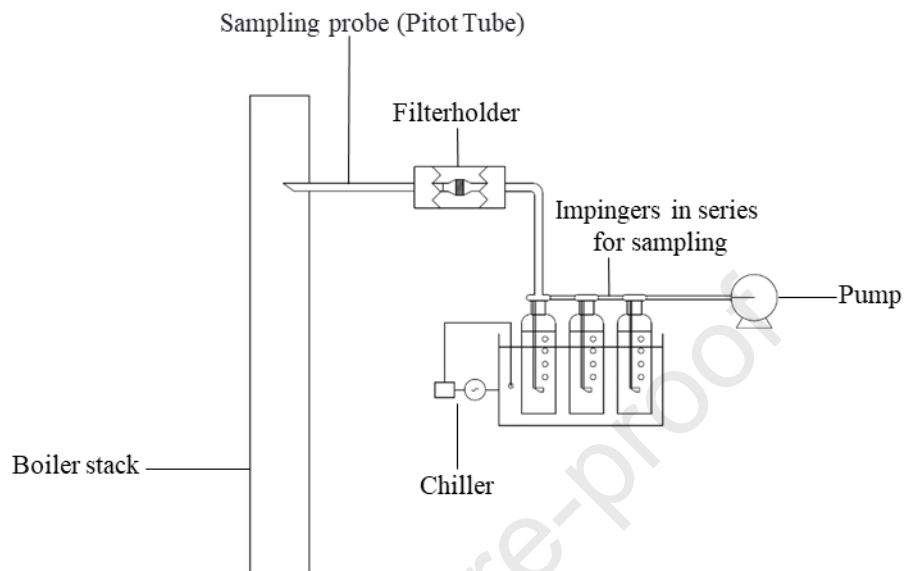
142 containing $\text{HNO}_3/\text{H}_2\text{O}_2$ as absorbing solution according to the method (EN 14385:2004). Each of the
143 sampling methods was stabilized for about 30 minutes as a test run for emissions. After the mineralization
144 of the samples, with a microwave Milestone START D, the metal content was determined by means of
145 the ICP-MS 7700 Agilent according to EN ISO 17294-2 (2016). According to EN 13284-1 (2017) each
146 sampling lasted an average of 30 min and was performed with an automatic isokinetic sampler (ST5,
147 Dadolab). Both samplings and the analysis for the biomass characterization were carried out in triplicate.

148

149 *2.3 Experimental setup, method proposed for sampling levoglucosan*

150 An innovative method has been investigated for sampling levoglucosan emitted by the consequent
151 thermal degradation of carbohydrates. For this purpose, the sampling technique allows to capture both
152 phases in which the levoglucosan is partitioned: the particle fraction is deposited on the quartz filter, the
153 volatile fraction is trapped into the impingers, similarly to the isokinetic system, previously described for
154 metal sampling, replacing the oxidizing solutions used for metals. The collection system, used to assess
155 the validity of the sampling is based on three impingers, the first two are used for the effective sampling,
156 while the third one, placed in series, is defined as the backup impinger. The latter is analyzed to check
157 that concentration of the sampled analyte is lower than 5% respect to the concentration obtained from
158 the analysis of the first two impingers. If this is true, the sampling is considered valid. This sampling
159 technique with the use of the structural apparatus of impingers (Fig. 1), is already widely consolidated
160 and applied for the sampling of metals content in emission, and in this study represent an innovative
161 application that complete the collection of the total content of levoglucosan, able to collect in addition,
162 the volatile fraction at no additional costs and using H_2O Milli-Q as an adsorbent solution. The
163 levoglucosan volatile fraction is determined by impingers solution and the levoglucosan particle fraction
164 deposited on the filter is determined by the extractive solution obtained from the extraction process in

165 which the filter is placed in an ultrasonic bath with H₂O Milli-Q. The solutions had an acid character due
166 to the acidity of the combustion fumes. This acidity interfered with the subsequent analysis in ionic
167 chromatography. With the addition of ammonia, the pH was brought to neutrality.



168

169 **Fig. 1.** Sampling system scheme of TSP, metals and the volatile levoglucosan fraction in the impingers.

170

171 2.4 Analytical methods

172 Although many studies have established different methods for detecting levoglucosan in environmental
173 samples, most of them relate to dry samples, especially aerosols [13,53]. As mentioned before, analysis
174 of levoglucosan is typically performed by gas chromatographic (GC) separation with mass spectrometric
175 (MS) detection [53–56]. However, this compound is particularly challenging to analyze by GC/MS due
176 to its polar nature, requiring labour-intensive and expensive sample preparation. Typical preparation of
177 a filter-collected aerosol sample for GC/MS analysis of anhydrosugars involves serial extraction with
178 one or more organic solvents, evaporation of the majority of the solvent and generally chemical
179 derivatization [57]. To overcome these problems and to facilitate research on atmospheric aerosols,

180 methods based on the extraction of aqueous phase of the samples have been developed. Specifically, the
181 sample is analyzed as it is separated by liquid chromatography and, subsequently, the levoglucosan is
182 detected by various detectors. In the literature, there are several articles in which levoglucosan has a
183 volatile behaviour, while currently in ambient air sampling it is deposited on the filters and evaluated by
184 HPLC [58]. This study deduce that the nature is twofold, it is a semi-volatile compound. For this reason,
185 in this manuscript, a sampling method of the filter and in addition to the impingers, in order to evaluate
186 what goes beyond the filter, is proposed. Analytical determination was performed by high-performance
187 anion-exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD). It has
188 been used as an IC mode. DX-500 (Dionex Corporation, USA) consisting of a DC ICS-3000
189 Chromatography Oven, a GP40 Gradient Pump, and a Dionex ED50 Electrochemical Detector utilizing
190 disposable gold electrodes. Separation of the individual anhydrosugars was achieved using a Dionex
191 CarboPac PA10 Analytical Column with an 18 mM aqueous sodium hydroxide (NaOH) eluent at a flow
192 rate of 0.5 ml/min [59]. The calibration line was obtained by making 5 solutions at different
193 concentrations (0.5 - 1 - 2 - 5 - 10 ppm) made up of a mix of characteristic sugars.

194

195 **3. Results and Discussion**

196 *3.1 Chemical and physical characterization of biomass samples*

197 Two different types of biomass were characterized and the results provided, as from previous studies
198 [6,60], confirmed to be interesting for the study of the parameters that influence the quality of combustion
199 and emissions. The characterization results carried out on a dry basis are shown in Table 1.

200

201

202

203 **Table 1.** Characterization of biomass

	Biomass Characterization	
	Rice straw	Wheat straw
Moisture (%)	9.7	10.5
Ash (%)	16.9	7.6
HHV(MJ/kg)	14.7	17.0
LHV (MJ/kg)	13.5	15.7
C (%)	37.3	43.2
H (%)	5.8	6.1
N (%)	0.6	0.6
S (%)	0.1	1.7
O* (%)	39.1	40.8

204 * calculated by difference.

205

206 The comparison shows similar values in terms of moisture content: this parameter is closely linked not
 207 only to the properties of the matrix, but also to the storage conditions. A parameter in which the studied
 208 biomass differ considerably is predominantly the ash content. Rice has a significantly higher ash content,
 209 which results in a greater number of unburnt compounds, lower calorific value and worse combustion
 210 conditions. The apparently high value of ash content is even lower than that usually determined for rice
 211 straws, in fact, from the comparison of the data present in the Phyllis database (EC, 2013) an average of
 212 18.53% of ash content for this biomass is obtained from the comparison of 13 articles.

213

214 *3.2 Combustion and gas flow conditions*

215

216 The combustion tests carried out simulated an open burning process, i.e no use of any emission abatement
 217 system has been made. Table 2 shows the operative parameters recorded by the isokinetic probe system
 218 at the stack.. Table 3 shows the generated macro-pollutants detected by the multiparameter detector
 219 HORIBA PG250 and with FID Ratfisch Model RS 53-T. It has been observed that the combustion even
 220 operating with a high content of oxygen, produced high concentrations of carbon monoxide. This fact
 221 tells us that the combustion of straw is a bad combustion due to the high concentrations of ash content
 222 that do not allow combustion in a homogeneous phase. This scenario indicates that the boiler conditions
 223 are extremely uncontrolled and have very bad mixing in the furnace. The process is similar to an open
 224 burning phenomenon.

225

226 **Table 2.** Operative parameters

Parameters	Rice Straw	Wheat Straw
Moist standard (T_{norm} P_{norm}) (Nm^3/h)	142.1	134.3
Dry standard (T_{norm} P_{norm}) (Nm^3/h)	130.6	123.6
Velocity (m/s)	1.1	1.0
Stack temperature ($^{\circ}\text{C}$)	126.5	98.1
Stack Pressure (kPa)	102.5	101.6
Probe temperature ($^{\circ}\text{C}$)	103.0	110.7
Filter temperature ($^{\circ}\text{C}$)	103.8	118.5
Outlet temperature ($^{\circ}\text{C}$)	63.3	65.4
Ambient Pressure (kPa)	102.5	101.7

227

228

229

230 **Table 3.** Content of gas in emissions

Gas in emission	Rice straw	Wheat straw
CO (ppm)	3177.9	2843.5
CO ₂ (%)	3.0	2.1
NO _x (ppm)	67.7	56.2
O ₂ (%)	17.5	18.9
SO ₂ (ppm)	25.6	26.0
THC (mgC/m ³)	312.9	498.6

231

232 *3.3 Metal content*

233 As regards the metal content in the emissions (Table 4), high alkaline and alkaline-earth metal contents
 234 are observed. Biomasses are usually rich of these metals which are found in large quantities in the water
 235 which allows the growth of plants and in the soil, but considering metals following the combustion of
 236 biomass, we will not investigate their derivation [61–64]. Rice straw has significantly higher
 237 concentrations of metals, this is partly due to the higher ash content. A higher ash content implies higher
 238 content of inorganic fractions (including metals). For these reasons, rice straw has proven to be
 239 particularly rich in terms of heavy metals when compared with wheat straw.

240

241 **Table 4.** Metals concentration in emission and related emissions factor

Metals in emission	Rice straw		Wheat straw	
	($\mu\text{g}/\text{Nm}^3$)	(mg/kg fuel)	($\mu\text{g}/\text{Nm}^3$)	(mg/kg fuel)
Li	1499.6	11389.1	3.8	30.0
Na	1452.2	11029.1	1524.7	12045.3
Mg	541.2	4110.3	48.0	379.2

Al	77.7	590.1	35.0	276.5
K	51723.3	392825.2	724.4	5722.8
Ca	405.8	3081.9	63.8	504.0
Cr	3.8	28.9	5.5	43.5
Mn	27.2	206.6	1.7	13.4
Fe	98.8	750.4	84.7	669.1
Ni	9.1	69.1	4.4	34.8
Cu	34.7	263.5	10.6	83.7
Zn	105.2	799.0	39.5	312.1
Sr	14.6	110.9	2.0	15.8
Ag	0.1	0.8	0.5	4.0
Cd	0.7	5.3	0.6	4.7
Ba	3.4	25.8	< LOQ	< LOQ
Tl	0.1	0.8	0.4	3.2
Pb	14.1	107.1	4.0	31.6
Bi	6.7	58.9	5.4	42.7

242

243 *3.4 Levoglucosan determination*

244 The total levoglucosan emitted by combustion of rice and wheat straw is shown in Table 5 (the reported
245 data refer to a reference oxygen content of 6%). Among the results it is interesting to observe how the
246 content of levoglucosan is lower than 5% in the third impinger (C) rather than the sum of concentration
247 of the first two (A + B) for both biomass samples. This demonstrates how the proposed method was
248 quantitative in sampling the volatile fraction of levoglucosan present in emission at the stack. It is thus

249 clear the importance to evaluate the total content of levoglucosan in impingers combined with the filters
 250 in order to appreciate the relevance of the proposed method. Indeed, the results on the volatile
 251 levoglucosan content trapped in the impingers show that such fraction is not a negligible amount.

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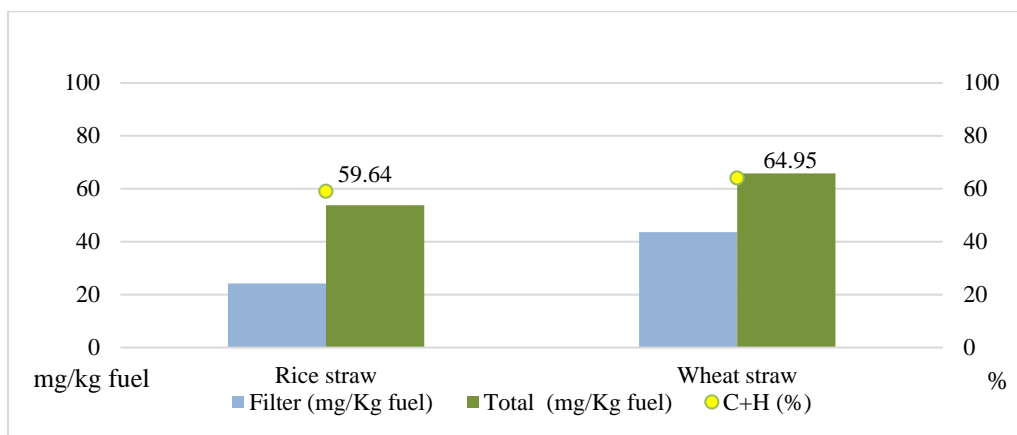
253 **Table 5.** Total levoglucosan emitted and related emissions factor

	Levoglucosan concentrations			
	Rice straw mg/Nm ³	Wheat Straw mg/Nm ³	Rice straw mg/kg fuel	Wheat Straw mg/kg fuel
Quartz Filter	13.3	39.3	24.2	43.6
A+B Impingers	16.3	17.9	29.0	20.3
C Impinger	0.3	1.6	0.46	1.82
Total	29.8	58.8	53.7	65.8

254

255

256 As previously stated, it has been established through literature data and Phyllis database that for rice
 257 straw and wheat, it has a cellulose + hemicellulose content about of 59% and 64% respectively, so the
 258 gap is only 5%. If we consider only the particle fractions deposited on the filters, for rice straw and wheat
 259 straw, the levoglucosan produced is respectively 24.2 mg/kg fuel and 43.6 mg/kg fuel, i.e., the first is
 260 about half of the second and this data is not in agreement with a cellulose + hemicellulose difference of
 261 just 5% between the two matrices. However, taking into consideration the total levoglucosan (filter +
 262 impingers) we have for rice straw and wheat respectively 53.7 mg/kg fuel and 65.8 mg/kg fuel. These
 263 values shown in Fig. 2 are in accordance with the literature data and justify the quality of the proposed
 264 method of sampling and analysis.



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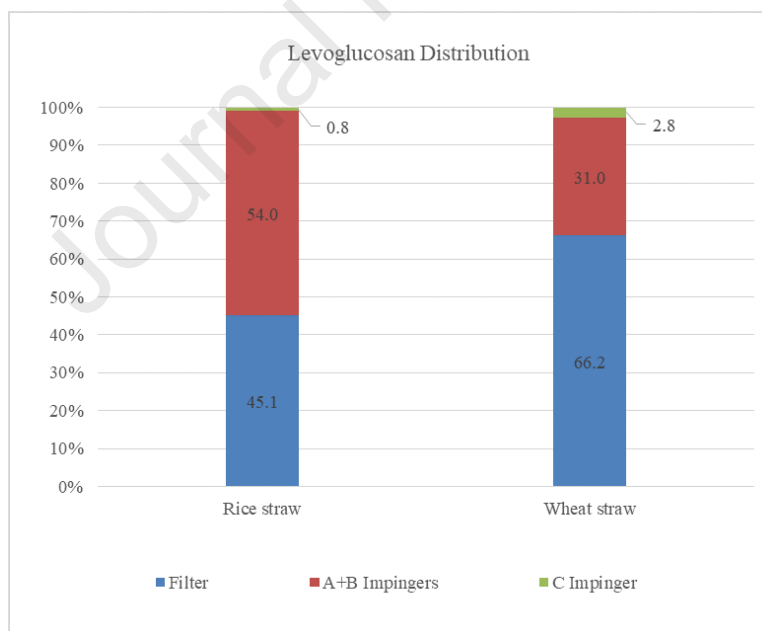
266 **Fig. 2.** Relationship between levoglucosan on the filter and total depending on the content of cellulose +
 267 hemicellulose in rice and wheat straw

268

269 In Figure 3, it has been observed that the content of levoglucosan represents 0.8% in C impinger, 54%
 270 in A+B impingers from rice straw combustion, and 2.8% in C impinger and 31% in A+B impingers from
 271 wheat straw combustion. . These results demonstrated the efficiency of the method because the content
 272 of levoglucosan collected in impingers represents a percentage comparable, and not negligible, to the
 273 content of levoglucosan on filter. For this reason, it is essential to collect the total levoglucosan, not only
 274 on the filter but also in impingers, avoiding data underestimation. The method presented allows to
 275 quantify the entire amount of levoglucosan emitted to the chimney from the combustion of woody
 276 biomass. By measuring it directly at the source it is therefore possible to know precisely and without
 277 underestimating the real levoglucosan concentration emitted, and a more realistic estimation of the
 278 combustion processes contribution to air quality. Although the aim of the work was to provide a method
 279 for the complete sampling of levoglucosan in emission, as far as the volatile part of levoglucosan is
 280 concerned, it can be asked what its fate may be once emitted. In fact, even the current environmental
 281 sampling methods do not consider the volatile component of levoglucosan. It can be hypothesized that
 282 after the emission, part of the levoglucosan may simply be lost due to volatility or other artifacts such

283 as oxidation by ozone or OH radicals [65,66] and therefore not visible in ambient air monitoring.
284 Recently some studies have indicated that levoglucosan is not stable in the atmosphere and its partially
285 degradation can occur in the solid [19,20,67], aqueous [68,69] and gas [70–72] phases. However, part of
286 the levoglucosan formed remains in the atmosphere, for example by aggregating to the carbonaceous PM
287 produced by biomass combustion. Probably, in this case the oxidizing action of the atmospheric agents
288 are mitigated by the reducing nature of the carbonaceous particulates. In [20] is shown as levoglucosan
289 degradation is reduced from 65% to 10% when the levoglucosan is combined with soot and other PM
290 compounds. Therefore, it is often detected on the filters of atmospheric monitoring units [17,59], where
291 it is recognized as a unique marker of PM produced by biomass combustion.
292 For these reasons, a reliable method capable of fully sampling the levoglucosan from emissions is the
293 first step in understanding how the controlled combustion of biomass can affect air quality.

294



295

296 **Fig. 3.** Levoglucosan distribution in filters and impingers of rice and wheat straw

297

298 The gravimetric analysis of the filters collected in triplicate for each biomass under examination led to
299 the determination of the TSP emitted by the combustion process. The results are, respectively, 93.30
300 mg/Nm³ for wheat straw and 176.01 mg/Nm³ for rice straw. This difference is probably linked (Tab. 1)
301 to the greater percentage of ash of rice biomass which determine a greater amount of unburnt material
302 and a worse quality of the combustion conditions. A number of factors may influence the emission rates
303 and the amount variability of levoglucosan produced during biomass burning that depends on the biomass
304 type, type of appliance and burning conditions. The intensity, aeration, duration, and temperature of the
305 fire were essential in controlling the production and emission rate of levoglucosan during biomass
306 burning. Consequently, all these factors contributed to the flux and preservation of levoglucosan [37].
307 Several works in the literature [59,73] show the relationship between levoglucosan/TSP in order to
308 identify the contribution of biomass combustion to air pollution in urban, suburban and rural areas.
309 However, these works do not take into account the semi-volatile fraction of levoglucosan that is lost
310 during the sampling carried out by the atmospheric monitoring stations.

311

312 **4. Conclusions**

313 Levoglucosan is a major organic component emitted from biomass burning. Its sampling, detection and
314 quantification from fixed sources represents a challenge in many aspects. It is generally accompanied by
315 other monosaccharide derivatives and biomarker compounds, and can be used as a specific indicator for
316 the presence of emissions from biomass burning in TSP. The experimentation highlighted the importance
317 of considering and determining both the solid and the volatile fraction of levoglucosan. An emerging
318 method for sampling levoglucosan from a fixed sources has been evaluated, based on the coupling of an
319 isokinetic probe for particulate sampling coupled to a series of three refrigerated impingers. It has been
320 demonstrated how this method allows to collect quantitatively both the particle and the volatile fraction

321 of levoglucosan and can be considered accurate because having carried the sampling at the stack of the
322 plant, so as to exclude the probability of sampling levoglucosan from other sources. This sampling
323 procedure has been successfully applied to different biomasses and represents an advantage for sampling
324 other potential markers of biomass burning. The proposed activity is an innovative methodological
325 approach aimed at quantitatively sampling the main TSP marker generated by biomass combustion,
326 directly at a fixed source. Moreover, the work suggests that current atmospheric sampling units, which
327 are based only on the capture of particle fraction on the filter, neglect the volatile fraction of levoglucosan
328 and underestimate the real data. In future studies, the intention is to compare results coming from biomass
329 burning emission through this sampling method, with data obtained in ambient air monitoring to allow a
330 clear comparison between the two phases and also to consider the extent of the reactions that occur in
331 the atmosphere responsible for the degradation of levoglucosan.

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340

341 **CRediT authorship contribution statement**

342 **Enrico Paris:** Conceptualization; Methodology, Investigation; Writing - original draft. **Monica Carnevale:**
343 Methodology, Writing - original draft. **Ettore Guerriero:** Conceptualization, Methodology, Investigation.
344 **Adriano Palma:** Methodology, Investigation; Writing - original draft. **Beatrice Vincenti:** Investigation,
345 Validation. **Asma Khalid:** Investigation, Methodology. **Elena Rantica:** Methodology, Investigation; **Andrea R.**

346 **Proto:** Conceptualization, Investigation. Writing - original draft & editing. **Francesco Gallucci:** Funding
347 acquisition, Writing - original draft & editing, Conceptualization, Supervision, Project administration.

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