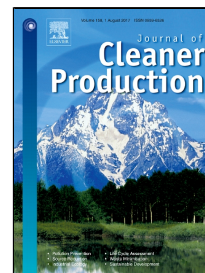


# Accepted Manuscript

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PII: S0959-6526(17)31143-5  
DOI: 10.1016/j.jclepro.2017.05.190  
Reference: JCLP 9730  
To appear in: *Journal of Cleaner Production*  
Received Date: 25 October 2016  
Revised Date: 11 April 2017  
Accepted Date: 28 May 2017

Please cite this article as: Pasquale Giungato, Pierluigi Barbieri, Sergio Cozzutto, Sabina Licen, Sustainable domestic burning of residual biomasses from the Friuli Venezia Giulia region, *Journal of Cleaner Production* (2017), doi: 10.1016/j.jclepro.2017.05.190

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Word counts: 8341

## Sustainable domestic burning of residual biomasses from the Friuli Venezia Giulia region

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**Keywords:** residual biomass, pellet, domestic burning, air quality, short supply chain.

### Abstract

The implementation of short supply chain of available biomass from forest and agriculture residues locally available aims to gain environmental benefits deriving from reduced transportation, avoided abiotic depletion of resources and reduced net emissions of green-house gases. The main objective of the present study was to analyze possible environmental impacts arising from domestic burning of residual biomasses, in terms air pollution. Three different types of woody residual biomasses (*Robinia pseudoacacia*, *Picea abies* and *Vitis vinifera*) were collected within the Friuli Venezia Giulia region in the form of wood chips, converted into pellets and used in controlled combustion

tests in a domestic stove. The efficiency of the combustion process and the amount of selected emitted pollutants (carbon monoxide, organic gaseous carbon, nitrogen oxides, benzene, polycyclic aromatic hydrocarbons and total suspended particulate matter) were evaluated. Moreover, the same analysis and combustion tests were carried out on three commercially available pellets (*Abies alba*, *Fagus sylvatica* and softwood mix) to achieve a better interpretation and contextualization of the results obtained. *Picea abies* developed significantly high concentrations of organic gaseous carbon, benzene and polycyclic aromatic hydrocarbons and rather high carbon monoxide emissions. *Vitis vinifera* was characterized by the highest total suspended particulate matter and carbon monoxide emissions. *Robinia pseudoacacia* was a very promising fuel showing both combustion and emission properties similar to the commercial pellets. Thus, with the outcomes of our work we highlighted that possible environmental drawbacks due to air pollution arising from residual biomass burning should be evaluated. Moreover, the scientific community of life cycle assessment scientists may benefit from having updated experimental measurements of air pollutants emitted by a domestic stove loaded with different locally available residual biomasses.

## 1. Introduction

The EU directive 2009/28/EC promoted the use of renewable energy, stimulating countries to introduce stable legislative frameworks to reach its mandatory targets (20% share of renewable energy in the Community's gross final consumption of energy within 2020, 20% reduction of GHGs emission, 20% improvement in energy efficiency) (European Parliament, 2009); recently the EU targets have been reviewed to the more ambitious ones (40-27-27) taking into account the progresses reached by the energy sector (European Council, 2014). This directive fostered the consumption of biomass for heating and electricity production in the EU which has constantly grown since 2005 and it is expected to further increase from 86.5 Mtoe in 2012 up to 110.4 Mtoe in

2020 to be used mainly for heating (90.4 Mtoe) and electricity production (20 Mtoe) (European Commission, 2014). Total gross inland consumption of fuels in EU28 in 2013 for energy purposes (excluding the production of materials) was about 1666 Mtoe, in which renewables accounted for 196.6 Mtoe, oil and gas 943 Mtoe, solid fossil fuels 286.6 Mtoe, nuclear 226.6 (Tobergte and Curtis, 2013). About 105.1 Mtoe of energy from renewables was represented by biomass consumed for heat production (78.4 Mtoe), electricity (13.5 Mtoe), biofuels for transportation (13.1 Mtoe). In the scenario proposed by the European Commission to achieve the goals of directive 2009/28/EC, it is recommended that the annual energy production from biomass should reach almost 139 Mtoe within 2020. On current trends of consumption, increasing use of biomass is not still sufficient to achieve the targets, and the growth in the use of this fuel should bridge almost 34 Mtoe. Imports accounted only for the 3.84% of the gross inland consumption of biomass and half of them are represented by solid wood fuels, so it can be stated that biomass is almost a full EU domestic fuel. In Italy, gross electricity final generation from bioenergy sources rocketed from 0.513 Mtoe (5.966 TWh) in 2008 to 1.47 Mtoe (17.090 TWh) in 2013 with an increase of 186%. According to the Italian National Energy Strategy the role of bioenergy in the electricity sector in 2020 will be increased up to 1.63 Mtoe (19 TWh) mainly by increasing the use of solid biomasses. In the heating and cooling sector, the goal is to increase in production up to 5.6 Mtoe with respect to a final renewable energy consumption of 11 Mtoe, in which the solid biomass contribution will be equal to over 90% of bioenergy. (Paiano and Lagioia, 2016). About the potential of the crop and forest residues, the Friuli Venezia Giulia region has an estimated availability of 31,868 t/y on dry basis of grapevine shoots and 65,130 t/y on dry basis of forest residues (Paiano and Lagioia, 2016). In a study aimed to identify and evaluate the energy demand and greenhouse gas emissions related to the production of round-woods, wood chips, shredded bundles and shredded stumps from a Sitka Spruce stand in Ireland, transport was the most energy and greenhouse gas emission intensive step in the life cycle supply chain of wood evidencing the importance of local production, but the use phase was excluded from this study (Murphy et al., 2014). An integrated site specific assessment of

forest wood short supply chain has been performed in the alpine area of “Intelvi” valley in Northern Italy. Traditional and mechanized operational modes in forestry activities were the scenarios compared considering the transport of wood material from felling to sawmills. The results pointed out that the fuel consumption was the main source of the environmental impacts. The choice of a short supply chain for wood supplying proved to be essential to mitigate the environmental impact, as well as the wise selection between traditional and mechanized operational modes according to site specific and context-related features. The approach however did not consider the production and use phase of wood chips or wood pellets in heating systems (Mirabella et al., 2014). When the system boundaries were extended, from wood extraction of residual forest biomasses to packed pellet production, ready to be delivered to final users, the results of the LCA (Life Cycle Assessment) studies pointed out the use of electricity during pellet production as the most important environmental burden (more than 90% of the total in most of the impact categories) with respect to forestry operations (from 1% to less than 10% depending on the impact category) (Laschi et al., 2016). In a first attempt to include also the use phase a LCA study was conducted on the use of woody residues from apple orchards for the production of bioenergy (including harvesting, chipping, transport to the energy plant and conversion into heat and power in a gasification unit) and the results confirmed better environmental profile of this scenario with respect to traditional fossil fuels as reference system (reduction of GHG emissions up to about 58 kt CO<sub>2eq</sub> per year and non-renewable energy consumption up to 16.5 kt oil-eq per year), but at expenses of higher toxicity impact potentials. The study evidenced that gasifying the biomass in cogeneration power plants instead of burning in lower efficient domestic stoves leads to a decrease in particulate matter formation and, moreover, disposal of post-combustion ashes was the process with the highest contribution to the toxicity impacts (Boschiero et al., 2016). However, the study did not consider biomass burning effluents as benzene and polycyclic aromatic hydrocarbons (benzo[a]pyrene among them) which are substances of very high concern for human health (IARC, 2015). Although the EU promoted an increased use of renewable energies, especially in the case of residuals of other

productions, residential wood combustion issue gives rise to increasing concern as it has been identified as a major source of atmospheric pollution, in rural and urban areas (Calvo et al., 2015) and also in indoor environments (Dambruoso et al., 2013; de Gennaro et al., 2015, 2014). Although the use of biomass can be regarded as partly CO<sub>2</sub> neutral, its combustion is an important source of air pollutants as volatile organic compounds (VOCs), inhalable particulate matter with aerodynamic diameter smaller than 10 microns (PM<sub>10</sub>). Particulate matter may contain black carbon (BC), condensable organic compounds (COCs), secondary organic aerosols (SOAs), inorganic particles, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and furans (PCDDs/Fs) (Dambruoso et al., 2014; Nussbaumer, 2010). Indoor environments are of increasing concern especially in the case of public places as schools, transportations, in which people spend most of its time (de Gennaro et al., 2014). In 2010 the International Agency for Research on Cancer (IARC) has classified indoor emissions from household combustion of biofuels, in particular wood, as group 2A, probably carcinogenic to humans based both on the presence of PAHs and other carcinogenic compounds in wood smoke and on the evidence of mutagenicity of wood smoke in multiple studies that showed cytogenetic damage in exposed humans (IARC, 2010). Domestic wood combustion has proven to produce health damages not only on the respiratory system but also on cardiovascular one and premature mortality for both short-term (24 hours) and long-term (annual) exposures (WHO Regional Office for Europe, 2013). Among pollutants emitted from household combustion in traditional stoves, BC has an estimated 100 years global warming potential (GWP<sub>100</sub>), from 500 to 700 times the GWP<sub>100</sub> of CO<sub>2</sub>, (Bond, 2008). An unofficial estimate on BC made by IPCC gives GWP<sub>100</sub> of 460 and GWP<sub>20</sub> of 1600, pointing out its short term harmful potential (IPCC, 2007) although the estimates presented large uncertainties (IPCC, 2014). Heating with woodchips has an Environmental Impact Points (EIPs) per GJ of energy of 13,030 for NO<sub>x</sub>, 12,600 for PM<sub>10</sub>, 670 for CO<sub>2</sub> and 8200 for the sum of SO<sub>x</sub>, NH<sub>3</sub>, CH<sub>4</sub>, primary energy, residues and other pollutants, according to the ecological scarcity method (Klippel and Nussbaumer, 2007). The main objective of the present study has been to analyze the environmental

burdens arising from domestic burning of residual biomasses, in terms of outdoor air pollution and the resulting impact on indoor air, aiming to include these aspects in future LCA studies focused on short supply chain of biomasses for energetic purposes. It is mandatory to verify whether the environmental pollution is transferred from one phase to another and, in this case, the short chain provision of residual biomasses introduces a direct impact on air quality due to emission of unexpected pollutants. LCA methodology, which is one of the most recognized schemes to perform the environmental analysis, has been broadly applied for the evaluation of environmental benefits of short-supply chain of biomasses but a reduced number of references on the topic of emission of pollutants deriving from domestic biomass burning is available (International Organization for Standardization (ISO) 2006a, b). To the best of our knowledge, emissions of air pollutants during domestic biomass burning have not been evaluated and integrated under the LCA perspective to ensure the sustainability of fuels made from forestry and agricultural residues. Taking into account the possible emission potential of pollutants arising from domestic burning of locally available raw materials, we would like to provide to the research community the tools to ensure that shortening of supply chain did not affect air quality due to emission of toxic or carcinogenic air pollutants, and to evaluate the differences among available biomass residuals to prevent unsuitable choices. Moreover with the outcomes of this work we would like to stimulate the research community to challenge the comparison of different scenarios of their LCA studies, including also pollutant emissions to air deriving from woodchips or pellets made directly from locally available residual biomasses. For these reasons three types of woody biomasses, in the form of wood chips, were collected considering the availability as forestry and agricultural residuals in the region of Friuli Venezia Giulia in Northeastern Italy. To carry out this project it was decided to choose three representative types of biomasses following the suggestions of a report published in 2007, by AIEL for the Friuli Venezia Giulia region under the "Project for the construction of a Logistic-Commercial platforms for Biomass in the Friuli Venezia Giulia Region" which showed that biomass available from forestry and agricultural wastes were two types of hardwood in the Valleys of *Natisone*, and a

conifer in *Carnia* and *Gemonese*, which are currently used from different companies in wood chips productions. Furthermore, the most representative agricultural waste, was the grapevine shoots produced in the *Collio* and the *Carso* hill districts. Among the available biomasses, we selected wood chips of *Robinia Pseudoacacia*, *Picea Abies* and *Vitis vinifera*. According to the analysis of forestry area, in the region there is a potential biomass available for production of wood chips equal to 72,594 t/y with 30% of moisture. This figure should be limited by the accessibility of forest to woodcutter to 53,678 t/y (Francescato et al., 2007). Wood chips were converted into pellets, then their chemical-physical features (density, moisture, ash content, calorific value) were characterized and the biomasses were utilized in controlled combustion tests in a domestic stove. The efficiency of the combustion process, the quality of its duration in time, the types and the amount of selected emitted pollutants (CO, OGC, NO<sub>x</sub>, BTEX, PAHs and total suspended particulate matter) as well as the presence of markers of wood combustion (levoglucosan) were evaluated (Simoneit et al., 1999). Moreover the same analysis and combustion tests were carried out on three commercially available pellets to achieve a better interpretation and contextualization of the results obtained.

## 2. Materials and Methods

### 2.1 Sample preparation

Woodchips made from three different freely usable forest biomasses were used, the first one from *Robinia pseudoacacia* L. a hardwood of a pre-alpine area (Valleys of *Natisone*), the second one from *Picea abies* L. a conifer of an alpine area (*Carnia* and *Gemonese*) and the third one from an agricultural waste, grapevine (*Vitis vinifera*) shoots (from crops located on *Carso* hill district). The woodchips of *Robinia pseudoacacia* were provided by the cooperative-society *Natisone Energy Wood* (San Leonardo, Udine, Italy), the woodchips from *Picea abies* by *Vuerich* (Trasaghis, Udine,



Italy) and the *Vitis vinifera* woodchips by Milič Sagrado farmhouse (Sgonico, Trieste, Italy). The production of pellets from wood chips was carried out in the Serain (Papozze – Rovigo, Italy) pellet plant having a production capacity of 500 kg/h. In figure 1 are visible the differences in texture between the raw materials and the final woodchips. Three commercially available pellets made from fir wood (*Abies alba*), beech wood (*Fagus sylvatica*) and a softwood mix were used directly in the combustion tests.

*Figure 1 here*

Since the pelletization facility, on a regular basis, works on soybean and miscanthus wastes, to avoid contamination it was necessary to introduce about 200 kg of wood chips for each of the three samples to obtain about 15-20 kg of pellets free from impurities suitable for combustion tests. The pelletization process consisted of the following phases: drying, refining, conditioning, pressing, cooling and screening. The raw material was dried in indirect flame dryers to avoid toasting and to achieve the 10-14% optimum water content. During refining the size of the raw material was made as homogeneous as possible for all the three woodchips types obtaining a particle size of about 5 mm suitable to obtain pellets intended for a domestic use (6 mm diameter). In this way, the surface area of the wood particles was increased to favor the breaking of lignin, which is the natural ligand that fosters the pelletization process. Conditioning allowed optimizing and balancing the water content of the raw material to be mixed and, if necessary, water or steam was added if the moisture content (measured by a sensor) was lower than 10%. Conditioning process determined the softening of the lignin thus increasing the binding capacity of the wood particles and thereby improving the mechanical durability of the pellet produced. During the pressing step the mixture was pressed throughout controlled diameter holes (6 mm) obtaining cylindrical spindles that were cut in regular length, to obtain the final pellets. During pressing the friction causes an increase in temperature that can vary between 80°C and 130°C, so it is necessary to cool down the pellets to 25°C in the shortest

possible time. After cooling the sieving process removed the material that had not been fully pressed and did not adhere well to the single pellets. Chemical-physical characteristics as bulk density of pellet samples was determined following the UNI EN 15103: 2010, moisture content was determined following the UNI EN 14774-2: 2009, ash content was determined following the UNI EN 14775:2010 and calorific value was determined following the UNI EN 14918: 2010.

## 2.2 Controlled combustion tests

The stove used for controlled combustion tests was an Aida model Ecofire (Palazzetti Lelio Spa, Porcia, Pordenone, Italy) with a nominal heat output of 9 kW, average consumption of 2.2 kg pellet/h, connected with a flue gas dilution tunnel (A, figure 2) built to simulate atmospheric dilution of emissions from wood heaters according to the US-EPA method 5G (EPA, 2016).

*Figure 2 here*

The dilution tunnel ended with an isokinetic sampler Isostack Basic HV (Tecora, Corsico, Milan, Italy) for particulate sampling, placed in-line (D, figure 2) which allowed both the continuous monitoring of fluid tunnel parameters (including speed, temperature, dynamic pressure) and to maintain isokinetic sampling conditions with a pump (F, figure 2) as required by UNI EN 13284-1:2003. Continuous sampling of O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub>, Qs (combustion losses %),  $\lambda$  (excess air in the flue gas), ETA (yield of combustion %) (B, figure 2) was achieved by means of a Wöhler 600 probe (Wöhler Technik GmbH, Bad Wünnenberg, Germany) whereas Organic Gaseous Compounds (OGC) sampling was made (C, in figure 2) by means of a Flame Ionization Detector (FID) Ersatech SmartFID ER600 (Eco-Control srl, Vimodrone, Milan) that was calibrated against propane. Samples were burned for 1 h, with 4 replicates for each of the three in-house made pellets and 2 replicates for each of the commercial ones. Following the period of ignition, the average values were based on a 1 h of combustion in which the stove worked at its full capacity. As NO

concentration was found about two orders of magnitude greater than NO<sub>2</sub> concentration in all the samples, NO<sub>x</sub> concentration has been expressed as NO equivalent.

### 2.3 BTEX analysis

BTEX were sampled at point E showed in figure 2 with Tenax® cartridges, by using a trapping flux of 400 mL/min generated by a Gilian (Sensidyne, LP, St. Petersburg, FL, U.S.A) pump. A volume of 10L of ambient “white” air was sampled before collecting 10L of the combustion sample. Tenax cartridges were desorbed on an Agilent 6890 gas chromatograph (Agilent, Santa Clara, CA, United States) connected to an Agilent 5973 mass spectrometer and equipped with a thermal desorber model Unity (Markes International GmbH, Frankfurt, Germany). The elution was made in a capillary column 122-1564 Agilent DB-VRX (60 m × 250μ, 1.40μ film thickness) using He as carrier gas and the following temperature program: from 35° C to 190° C at 12° C/min, holding for 2 minutes, raising up to 225° C at 6° C/min, holding for 1 minute. The mass spectrometer was used in TIC (Total Ion Current) mode and monitored the m/z ratios from 35.0 to 260.0 amu. HC BTEX mixture Mix, 2000 μL/mL in methanol, Lot. 4-7993, (Supelco, Bellefonte, Pennsylvania, USA) was used for quantification of each analyte by using the following m/z: Benzene (78), toluene (91), ethylbenzene (91), m,p - xylene (91), o-xylene (91).

### 2.4 Total suspended particulate analysis

Total suspended particulate was collected on two glass fiber filters (Whatman, Buckinghamshire, UK) with a diameter of 90 mm, by means of a sequential air sampler (Silent 10, FAI Instruments S.r.l., Roma, Italy). The filters were previously conditioned at 180°C for 12h in a muffle furnace and stored for 24h in a desiccator. The two filters were positioned in sequence as the total particulate matter accumulates on the first one, while the second one is used as a proof of the

quantitative accumulation on the first filter. The total sampled volume was measured by the isokinetic sampler with a relative uncertainty of 5%. The filters were weighed on an analytical balance Gibertini E42 (Gibertini Elettronica, Novate Milanese, Milan, Italy) having 0.1 mg sensitivity, before and after sampling to obtain particulate concentration over sampling volume. To perform the analysis of PAHs the filters were extracted with a Soxhlet apparatus using 200 mL of a 1:1 mixture of acetone/dichloromethane (Pestanal® Sigma - Aldrich), at constant temperature of 70° C for 12 h in a thermostatic bath. Before extracting the samples all the equipment was cleaned using the same mixture of solvents and maintaining the thermostatic bath at 70° C for 4h. For every test both the filters were introduced in a thimble of cellulose, added with 100 µL of a standard solution of 1.2 µg/ml deuterated-PAH L429 IS (Wellington Laboratories, Guelph, Canada) for the evaluation of the recoveries. At the end of the process, the extract was concentrated to 0.5 mL by using a rotating evaporator. Purification was performed with a packed column of silica gel (0.5 g) and eluting with 10 mL of dichloromethane. A second elution with 10 mL of methanol Pestanal® (Sigma-Aldrich, St. Louis, USA) has been used for levoglucosan extraction. The eluate in dichloromethane was concentrated under reduced pressure up to about 0.5 mL by a rotary evaporator and dried by a stream of dry N<sub>2</sub>. 100 µL of standard solution of deuterated-Pyrene (Sigma-Aldrich 490695-20 µg/mL) was added as internal standard together with 150 µL of cyclohexane (Sigma-Aldrich Pestanal®). The solution was transferred into an 2 mL ambered vial and analyzed in an Agilent 6890 gas chromatograph connected to a mass spectrometer Agilent 5973 Inert and equipped with a Gerstel MPS2 (Gerstel GmbH & Co., KG, Germany) autosampler. The column used for the analysis was an Agilent DB-5, 30m × 0.25 mm, 0.25µ film thickness. The analysis was carried out on 1µl of sample injected in pulsed splitless mode at 300° C. The Pulse pressure was 20 psi, pulse time 0.2 min and the purge flow 60 mL/min. The flow of the carrier (He) was maintained constant during the entire analysis to 1.2 mL/min. Temperature program was 55°C to 200°C at 25°C/min, from 200°C up to 320°C at 10°C/min and finally from 320°C to 325 at

25°C/min, holding for 10 min. The mass spectrometer monitored the  $m/z$  ratios from 35 to 450 amu. The analysis was conducted simultaneously both in TIC and in Single Ion Monitoring (SIM). To quantify the concentrations of PAHs six calibration solutions were prepared in dichloromethane by dilution of a certified standard mixture (PAH-EPA 610, Sigma-Aldrich) obtaining concentrations ranging from 1 ng/mL to 10 ng/mL. For the quantification the following  $m/z$  ratios were monitored in SIM mode: phenanthrene (Phe, 178), anthracene (Ant, 178), fluoranthene (Fth, 202), pyrene (Pyr, 202), benzo[a]anthracene (BaA, 228), chrysene (Chr, 228), benzo[b] fluoranthene (BbF, 252), benzo[k]fluoranthene (BkF, 252) (the last two summed and reported as BbkF), benzo[e]pyrene (BeP, 252), benzo[a]pyrene (BaP, 252), perylene (Per, 252), indeno [1,2,3-cd] pyrene (Ind, 276), dibenzo[a,h]anthracene (DahA, 278), and benzo[g,h,i]perylene (BghiP, 276). Recoveries of PAHs were calculated using the following deuterated PAHs: phenanthrene-d10 ( $m/z$  188, for Phe and Ant) fluoranthene-d10 ( $m/z$  212, for Fth and Pyr), benzo[a]anthracene-d12 ( $m/z$  240, for BaA and Chr), benzo [b] fluoranthene-d12 ( $m/z$  264, for BbF and BkF), benzo[a]pyrene-d12 ( $m/z$  264, for BeP, BaP and Per), indeno [1,2,3-cd] pyrene-d12 ( $m/z$  288, and for Ind and DahA), benzo [ghi] perylene-d12 ( $m/z$  288, for BghiP).

## 2.5 Levoglucosan analysis

The filters, previously extracted for the analysis of PAHs, were further extracted three times by sonication (Soltec Srl, Castelbarco, Milan, Italy) with 10 mL of a 3:1 mixture of ultrapure methanol (Sigma-Aldrich Pestanal®) and ultrapure water (MilliQ-Millipore), for 10 minutes. The extracts were combined, filtered on a Wathman filter paper (Whatman, Buckinghamshire, UK) and dried with a rotary evaporator. The extract was diluted with 0.5 mL of isopropanol and transferred to a 2 mL ambered vial together with methanolic eluate retrieved from the solid phase extraction column during PAHs analysis. The solution was dried with a  $N_2$  flow and was added with 100  $\mu$ L of a N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) + trimethylchlorosilane (TMCS) 1% (Sigma-

Aldrich, St. Louis, USA) silanizing solution and 10  $\mu\text{L}$  of pyridine (Sigma- Aldrich Pestanal®) to catalyze the reaction and 1880  $\mu\text{L}$  of cyclohexane (Sigma- Aldrich Pestanal®). The vials were closed and placed in an oven at 70° C for 150 min, then cooled to room temperature and immediately analyzed according to the same procedure described for PAHs. The analysis was conducted in total ion current (TIC) by monitoring  $m/z$  ratios from 35 to 450 amu. To quantify the concentration of levoglucosan five calibration standards were prepared with concentrations ranging from 2.5  $\mu\text{g}/\text{mL}$  to 12.5  $\mu\text{g}/\text{mL}$  in methanol. The levoglucosan was quantified by using its most abundant ion ( $m/z=60$  amu).

### 3. Results and discussion

Table 1 shows the main chemical-physical characteristics of the prepared pellets from the three woodchips used in this work, as well as of the commercial ones. Following the classification of UNI EN 14961 (2011) (UNI, 2011) the pellet from *Robinia pseudoacacia* was classified as suitable for non-industrial use (B class), the pellet from *Picea abies* was classified under the A2 class, this means it was of better quality essentially due to a lower ash content (less than 1.5%) whereas pellet from *Vitis vinifera*, having an ash content greater than 3.0%, was not classifiable under this norm. The values obtained regarding the commercial pellets were in accord with those reported on the packaging labels. The commercial pellet classification was A1, A2, A1 for *Abies alba*, *Fagus sylvatica* and softwood mix respectively. Table 2 shows flue gas combustion parameters recorded in the combustion chamber and in the chimney during the combustion tests.

*Table 1 here*

*Table 2 here*

*Vitis vinifera* showed the lowest temperature in the flue gas both in the combustion chamber and chimney, whereas the highest values were found for *Abies alba* followed by *Picea abies*. CO concentrations of *Picea abies* and *Vitis vinifera* were almost two orders of magnitude higher than that of *Abies alba* and one order higher than the other pellet types. Moreover, CO averages in *Picea abies* and *Vitis vinifera* had rather high standard deviations indicating a no-constant combustion regime thus revealing an incomplete combustion process occurred (Perzon, 2010). The concentration of OGC in *Picea abies* was around two orders of magnitude greater than that of the other pellet types except for *Vitis vinifera* which showed an OGC concentration of only one order of magnitude lower than that of *Picea abies*. As a criterion of comparison in December 2012 an Italian law (Italian Minister of Economics, 2012) established that citizens can receive an economic support from State for the installation of domestic pellet stoves which prove to have CO emissions below  $250 \text{ mg/Nm}^3$  and OGC plus total particulate matter (in the form:  $\text{PM} + 0,42 \cdot \text{OGC}$ ) emissions below  $40 \text{ mg/Nm}^3$ , referred to 13% of  $\text{O}_2$ . Considering the results of the present study *Robinia pseudoacacia* and all the three commercial pellets emissions were in compliance with the law for both limits except for softwood mix which exceeded the limit for CO. Nitrogen oxide concentrations were higher in the flue gas of *Robinia pseudoacacia* samples followed by *Vitis vinifera* although all values were in the same order of magnitude, in agreement with results reported by Wöhler et al. (Wöhler et al., 2017). In table 3 are reported the BTEX concentrations in the flue gas of the three in-house pelletized biomasses evidencing how *Picea abies* showed higher concentrations of BTEX with respect to *Robinia pseudoacacia* and *Vitis vinifera*, in accord to OGC results. BTEX emissions of commercial pellets were negligible respect to those showed by in-house made pellets.

Table 3 here

Benzene concentration in particular followed the sequence: *Picea abies*, *Vitis vinifera*, *Robinia pseudoacacia*, with about one order of magnitude lower at every different wood type. Flue gas of *Vitis vinifera* presented higher values of total suspended particulate (about three times) with respect to *Picea abies* and *Robinia pseudoacacia*. During combustion of *Vitis vinifera* melting phenomena due to the great amount of ash formed in the combustion chamber were evident, thus the removal of ash between two tests has been necessary. The commercial pellets showed values three to five times lower than *Robinia pseudoacacia* (*Abies alba* 1.3 mg/Nm<sup>3</sup>, *Fagus sylvatica* 3.3 mg/Nm<sup>3</sup>, softwood mix 1.2 mg/Nm<sup>3</sup>). Concentrations of levoglucosan were of the same order of magnitude in the three in-house made pellets with slightly higher values for *Robinia pseudoacacia* (41.6 µg/Nm<sup>3</sup>) with respect to *Picea abies* (22.7 µg/Nm<sup>3</sup>) and *Vitis vinifera* (26.6 µg/Nm<sup>3</sup>). Levoglucosan (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>), derives from the pyrolysis of carbohydrates such as cellulose and it is commonly used as a marker of biomass burning (Simoneit et al., 1999) but its presence cannot be used exclusively as a tracer of quantitative estimation of residential wood combustion (Hedberg et al., 2006).

Aiming to obtain a pluralistic framework which considers both biomass combustion performances and possible environmental burden of emissions, we performed a Principal Component Analysis (PCA) on data collected during the combustion tests on in-house made pellets as well as commercial ones. PCA is a helpful tool which allows to reduce the number of variables revealing the internal structure of the dataset in a way which best explains the variance. The PCA results are reported by means of a bi-plot graph in figure 3. The first and second components explained 43.33% and 36.05% of the data variance respectively, which collectively accounted for nearly 80.0% of the total variance. Loadings of data collected in the combustion chamber and in the chimney were collinear revealing that there were no substantial differences.

Positive values of PC1 represented appropriate combustion conditions (oxygen excess) while negative values represented incomplete combustion processes (carbon monoxide excess). Positive values of PC2 represented high temperatures in the flue gas, which were characteristic of softwood pellets (*Picea abies*, *Abies alba*, softwood mix) according to the calorific values. Positive PC2



coupled with negative PC1 accounted for incomplete combustion processes which generated the emission of PAHs and OGC, which was a behavior showed mainly by *Picea abies*. In particular, data on PAH emissions (figure 4) showed that combustion of *Picea abies* generated an average concentration of total PAHs (16,452 ng/Nm<sup>3</sup>) 26 times higher than that of *Vitis vinifera* (640 ng/Nm<sup>3</sup>) and about 186 times compared to *Robinia pseudoacacia* (88 ng/Nm<sup>3</sup>).

Total PAHs of commercial pellets were 42 ng/Nm<sup>3</sup>, 47 ng/Nm<sup>3</sup> and 53 ng/Nm<sup>3</sup> for *Abies alba*, *Fagus sylvatica* and softwood mix respectively. Negative values of PC2 accounted for higher values of NOx emissions, showed mainly by *Vitis vinifera*, *Robinia pseudoacacia* and *Fagus sylvatica*. *Vitis vinifera* in particular showed both PC1 and PC2 negative values related to incomplete combustion, low flue gas temperatures and high particulate matter emissions. *Robinia pseudoacacia* in PCA bi-plot lied close to the commercial pellets area showing both combustion and emission properties more similar to them than the other in-house made pellets.

Noticeably, although *Robinia pseudoacacia* had an ash content considerably higher than that of commercial pellets, it seemed that the ash content did not hamper the efficiency of the combustion process.

*Figure 3 here*

Among individual PAHs, benzo[a]pyrene which is a IARC group I carcinogen, was more concentrated in the flue gas during combustion of pellets from *Picea abies* (820.7 ng/Nm<sup>3</sup>) followed by *Vitis vinifera* (41.3 ng/Nm<sup>3</sup>) and *Robinia pseudoacacia* (2.3 ng/Nm<sup>3</sup>). All commercial pellets showed BaP concentrations of about 0.7 ng/Nm<sup>3</sup>.

PAHs were produced by incomplete combustion, that was also responsible for the formation of benzene which is classified as group 1 by IARC (carcinogenic for humans), toluene and xylenes classified as group 3 by IARC (not classifiable as to its carcinogenicity to humans), ethylbenzene classified as group 2B (possibly carcinogenic to humans) with a trend that confirmed the biomass types sequence showed for PAHs.

Figure 4 here

In outdoor air pollution, particulate matter has been recently classified as group 1 by IARC, and due to confined ambient and consequently lower air exchange, indoor exposition could threaten even heavily human health (IARC, 2015). Considering this parameter, *Vitis vinifera* seems to be the worst biomass to be burned in a residential stove.

PAH diagnostic ratios have been extensively used for identification and apportionment of emission sources. With regards to identification, diagnostic ratios of several emission sources like rice straw burning (Huang et al., 2010) wheat residues burning (Hays et al., 2005) olive trees burning (Dambruoso et al., 2014) domestic fireplaces or wood stoves fed with wood (de Gennaro et al., 2015), traffic, coke and coal burning and steelmaking ((Di Gilio et al., 2017) have been reported in literature. In comparison with our results values of the diagnostic ratio BaP/BghiP in the flue gas of *Picea abies* were above the range detected for domestic fireplaces, urban dust and traffic, but below olive trees and wheat residues burning whereas *Robinia pseudoacacia* and *Vitis vinifera* during burning showed values in the range of domestic fireplaces (see table 4).

Table 4 here

Those results confirm the incomplete combustion hypothesis formulated in the case of *Picea abies* burning in which higher emissions of BaP were found. BaP/Ind diagnostic ratio confirmed that hypothesis as follow the same trend of the preceding diagnostic ratio, whereas other diagnostic ratios examined Ind/(Ind+BghiP) and Ind/BghiP were not indicative of a particular behavior of the analyzed biomasses with respect to other emission sources. It is noteworthy to consider that the diagnostic ratios calculated in this work were directly computed on the emission source and not on receptors located far apart, with all the uncertainties due to possible atmospheric reactions of PAHs that can modify randomly its values (Lohmann et al., 2000; Ravindra et al., 2008). Diagnostic ratios

for commercial pellets could not be evaluated because Ind and BghiP concentrations were below the detection limit.

## 5. Conclusions

Transition to equitable, sustainable, post fossil-carbon societies by means of biomass usage as food, feed, fiber, energy and chemical feedstock to manufacture products, should be implemented in a holistically integrated way, to be sure to reach the target of mitigating the environmental impacts. In the target to reduce the environmental impacts with the implementation of short supply chain of available biomass from forest and agriculture residues locally available, the burdens due to air pollutant emissions must be taken into account to ensure that the holistic approach do not lead to a global worst scenario with respect to the use of fossils. In the present study three different types of residual woody biomasses (from forestry and agricultural practices: *Robinia pseudoacacia*, *Picea abies* and *Vitis vinifera*) available in the Friuli Venezia Giulia region (North-East of Italy) in the form of wood chips, were converted into pellets, characterized and used in controlled combustion tests in a domestic stove, under continuous monitoring of flue gas and combustion parameters. Moreover three commercially available pellets made from fir wood (*Abies alba*), beech wood (*Fagus sylvatica*) and a softwood mix were characterized and used in the combustion tests as well, allowing to compare the pellet performances. During burning in a domestic stove, pellets from *Picea abies* developed in the flue gas significantly higher concentrations of OGC, BTEX (including benzene) and PAHs (including benzo[a]pyrene) and rather high CO emissions with respect to the other examined pellets. This result poses an important issue about the sustainability of domestic burning of biomasses from *Picea abies* in terms of emission of pollutants and air quality. Pellets from *Vitis vinifera* were characterized by the highest total suspended particulate matter and CO emissions and rather low temperature in the combustion chamber because combustion was visibly

hampered by the great amount of ash formed. Thus it is possible that a more regular combustion process and a following decrease of pollutant emissions could be obtained by use of a stove provided with an automatic ash removing equipment. *Robinia pseudoacacia* showed both combustion and emission properties more similar to commercial pellets than the other in-house made pellets. Noticeably, although it had an ash content considerably higher than that of commercial pellets, it seemed that the ash content did not hamper the efficiency of the combustion process. However *Robinia pseudoacacia* produced the highest emissions of NO<sub>x</sub>, although of the same order of magnitude of the commercial pellets. The outcomes obtained in this work, in which the residual biomasses analyzed behave differently and some revealed an obvious non-applicability in realizing short-chain supply of energy feedstocks for domestic heating, contribute to foster the awareness regarding the need to evaluate the possible environmental impacts by pollutant emissions to air together with the environmental benefits due to reduced transportation, avoided abiotic depletion of resources and reduced net provision of green-house gases, to obtain an overall picture with respect to fossils. Policies fostering sustainable domestic burning of residual woody biomasses (from forestry and agricultural practices) in the Friuli Venezia Giulia region, need an integrated approach in order to take into account the necessity to develop a regional short supply chain of raw material for domestic burning without affecting the indoor and outdoor air quality. Transferring the environmental impacts from a compartment to another is one of the major targets of integrated policies as pointed out by the holistic and integrated approaches like life cycle assessment. This work represents a paradigmatic case in which the efforts of the stakeholder's policies directed towards the development of residual forestry and agricultural biomasses short chain provision for burning in residential stoves, aiming to reach the targets of the EU directive 2009/28/EC, conflict with the air quality issues. Although the use of biomasses can be considered almost carbon neutral and shortening of the supply chain may have beneficial effects on fuel and resources consumption, domestic wood combustion has proven to produce health damages not only on the respiratory system but also on the cardiovascular one. Moreover there exist marked differences among

biomasses and the related pellets obtained. This case study pointed out the necessity to use an integrated approach in studying the environmental effects of domestic burning of residual biomasses provided by short regional supply chains, as it should be taken into account not only the emissions of pollutants due to stove burning but also the different pollutant emissivity depending on the biomass used. Air quality issues in residential biomass burning pose an important question about the balance between the benefits and drawbacks of policies aimed to foster the transition to sustainable bio-economies, that uses less impacting biomasses for combustion in residential burners and stoves. Not all the forestry and agricultural residuals can be suitable for the scope and accurate selection of raw materials, in light of the evidence obtained, should be made. Such integrated policies over time could lead to an economic benefit in the short regional agro-energy supply chain. The scientific community of LCA scientists may benefit from having updated experimental measurements of air pollutants emitted by a domestic stove, useful in refining LCA studies on different locally available residual biomasses from agricultural and forestry practices. Moreover the data obtained by use of residual biomasses are compared to those obtained by use of commercially available biomasses at the same experimental conditions. We have highlighted that, despite the local availability and a subsequent advantage in the shortening of the supply chain, environmental benefits, in some cases, may be surpassed by the environmental concerns due to air pollution.

**Acknowledgments:**

S. Licen grant was funded by the European Social Fund, Operative Program of Friuli Venezia Giulia Region 2007/2013 the S.H.A.R.M. - Supporting Human Assets in Research and Mobility (D.PReg. n.87, 29/04/2010, CUP J93C11000050009). The authors acknowledge Dr. Valter Francescato, Technical Director of the Italian Agro-forestry Energies Association (AIEL, Legnaro, Padua) for his invaluable suggestions about the choice of raw materials to be used in this research project. The authors acknowledge the cooperative-society Natisone Energy Wood (San Leonardo, Udine, Italy), Vuerich (Trasaghis, Udine, Italy) and Milič Sagrado farmhouse (Sgonico, Trieste,

Italy) for the helpfulness in providing the raw biomass, as well as Serain (Papozze – Rovigo, Italy) for the helpfulness in the raw biomass conversion into pellets. The authors acknowledge Palazzetti Lelio Spa (Porcia, Pordenone, Italy) as well for providing the pellet stove for the combustion tests. This work is the result of the authors' commitment, starting from the idea and ending with its accomplishment. The authors contribute equally in study conception, acquisition of samples, data analysis and statistics, drafting of manuscript.

### **Notation List**

BC = black carbon

BSTFA = N,O-bis(trimethylsilyl)trifluoroacetamide

BTEX = Benzene, toluene, ethylbenzene and xilenes

COC = condensable organic compound

EIP = Environmental Impact Point

ETA = yield of combustion

FID = Flame Ionization Detector

GHG = Green-House Gas

GWP100 = 100 years global warming potential

GWP20 = 20 years global warming potential

IARC = International Agency for Research on Cancer

IPCC = Intergovernmental Panel on Climate Change

LCA = Life Cycle Assessment

Mtoe = Millions tons of oil equivalent

NO<sub>x</sub> = Nitrogen oxides

OGC = Organic Gaseous Carbon

oil-eq = oil equivalent

PAH = polycyclic aromatic hydrocarbon

PCA = principal component analysis

PCDD = polychlorinated dibenzo-p-dioxin

PCDF = polychlorinated dibenzo furan

PM10 = inhalable particulate matter with aerodynamic diameter smaller than 10 microns

Qs = combustion losses

SOA = secondary organic aerosol

SO<sub>x</sub> = Sulphur oxides

TIC = total ion current

TMCS = trimethylchlorosilane

US-EPA = United States – Environmental Protection Agency

VOC = Volatile Organic Compounds

WHO = World Health Organization

$\lambda$  = excess air in the flue gas

Ant = anthracene

BaA = benzo[a]anthracene

BaP = benzo[a]pyrene

BbF = benzo[b] fluoranthene

BbkF= sum of benzo[b] fluoranthene and benzo[k]fluoranthene

BeP = benzo[e]pyrene

BghiP = benzo[g,h,i]perylene

BkF = benzo[k]fluoranthene

Chr = chrysene

DahA = dibenzo[a,h]anthracene

Fth = fluoranthene

Ind = indeno [1,2,3-cd] pyrene

Per = perylene

Phe = phenanthrene

Pyr = pyrene

### List of captions

**Figure 1.** Differences in texture between the raw materials (woodchips) and the final pellets; a=hardwood of *Robinia pseudoacacia* (pre-alpine area - Valleys of *Natisone*), b=softwood of *Picea abies* (alpine area - *Carnia* and *Gemonese*), c=grapevine (*Vitis vinifera*) shoots produced on *Carso* hill district.

**Figure 2.** Experimental setup for combustion tests. A = flue gas dilution tunnel, B= O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub>, Qs, λ, ETA sampler, C=OGC sampler, D=isokinetic sampler equipped with filters for the total suspended particulate sampling, E=BTEX sampler, F=isokinetic pump.

**Figure 3.** PCA of selected parameters under investigation, the circles represent the pellet types, the points the replicate tests. Legend of score boxes: a=*Robinia pseudoacacia*, b=*Picea abies*, c=*Vitis vinifera*, (d) *Abies alba*, (e) *Fagus sylvatica* and (f) softwood mix. The in-house made pellets are represented by black dots, the commercial pellets by star symbols. Legend of loadings: PM=total suspended particulate, OGC = Organic Gaseous Carbon, T = temperature, PAHs = Polycyclic Aromatic Hydrocarbons, BaP = benzo[a]pyrene; for all the parameters: (c) indicates a measure in the combustion chamber, (h) indicates a measure in the chimney (see also table 2).

**Figure 4.** Distribution of PAH concentrations in the particulate matter from flue gas of the three biomass samples examined during controlled combustion of pellets made from *Robinia pseudoacacia*, *Picea abies* and *Vitis vinifera*. Legend: Phe = phenanthrene, Ant = anthracene, Fth = fluoranthene, Pyr = pyrene, BaA = benzo[a]anthracene, Chr = chrysene, BbkF = sum of benzo[b]fluoranthene and benzo[k]fluoranthene, BeP = benzo[e]pyrene, BaP = benzo[a]pyrene, Per



= perylene, Ind = indeno [1,2,3-cd] pyrene, DahA = dibenzo[a,h]anthracene, BghiP = benzo[g,h,i]perylene.

**Table 1.** Main characteristic, averaged on two replicates (in parentheses the standard deviations), of the pellets prepared from woodchips of *Robinia pseudoacacia* (a), *Picea abies* (b), *Vitis vinifera* (c) and of the three commercial pellets (d) *Abies alba*, (e) *Fagus sylvatica* and (f) softwood mix.

**Table 2.** Parameter averages detected in the combustion chamber and chimney (on four replicates for the in-house made pellets and two for the commercial ones, in parentheses the standard deviations) for each of the three pellets obtained from woodchips as well as the three commercial ones. Legend: (a)=*Robinia pseudoacacia*, (b)=*Picea abies*, (c)=*Vitis vinifera*, (d) *Abies alba*, (e) *Fagus sylvatica* and (f) softwood mix.

**Table 3.** Averages of BTEX (two replicates), total suspended particulate (PM – four replicates), levoglucosan in the PM collected for each of the three pelletize biomass samples (in parentheses the standard deviations). Legend: (a)=*Robinia pseudoacacia*, (b)=*Picea abies*, (c)=*Vitis vinifera*.

**Table 4.** Diagnostic ratios in the present (a, b and c samples) and other studies. Legend: (a)=*Robinia pseudoacacia*, (b)=*Picea abies*, (c)=*Vitis vinifera*.

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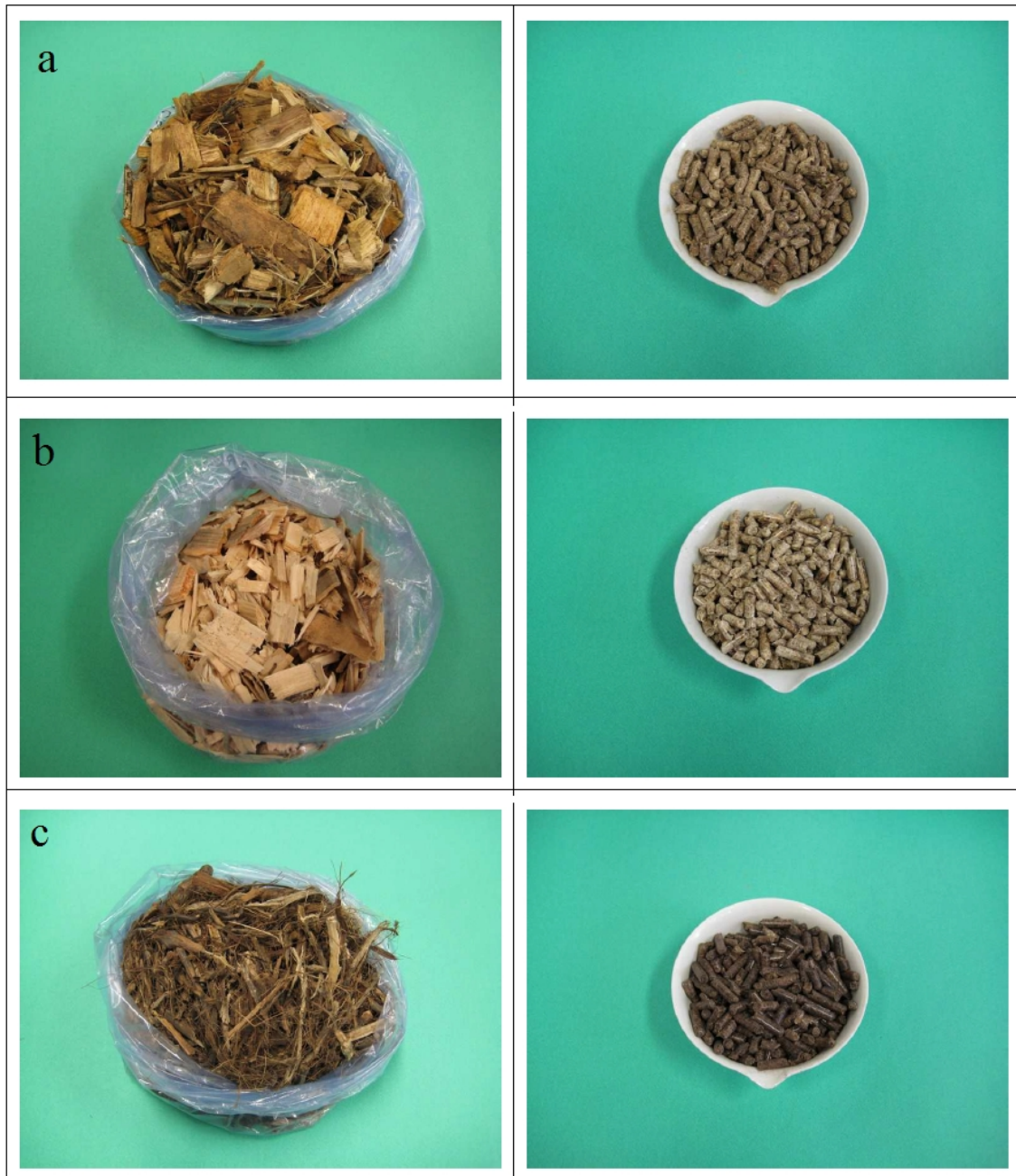
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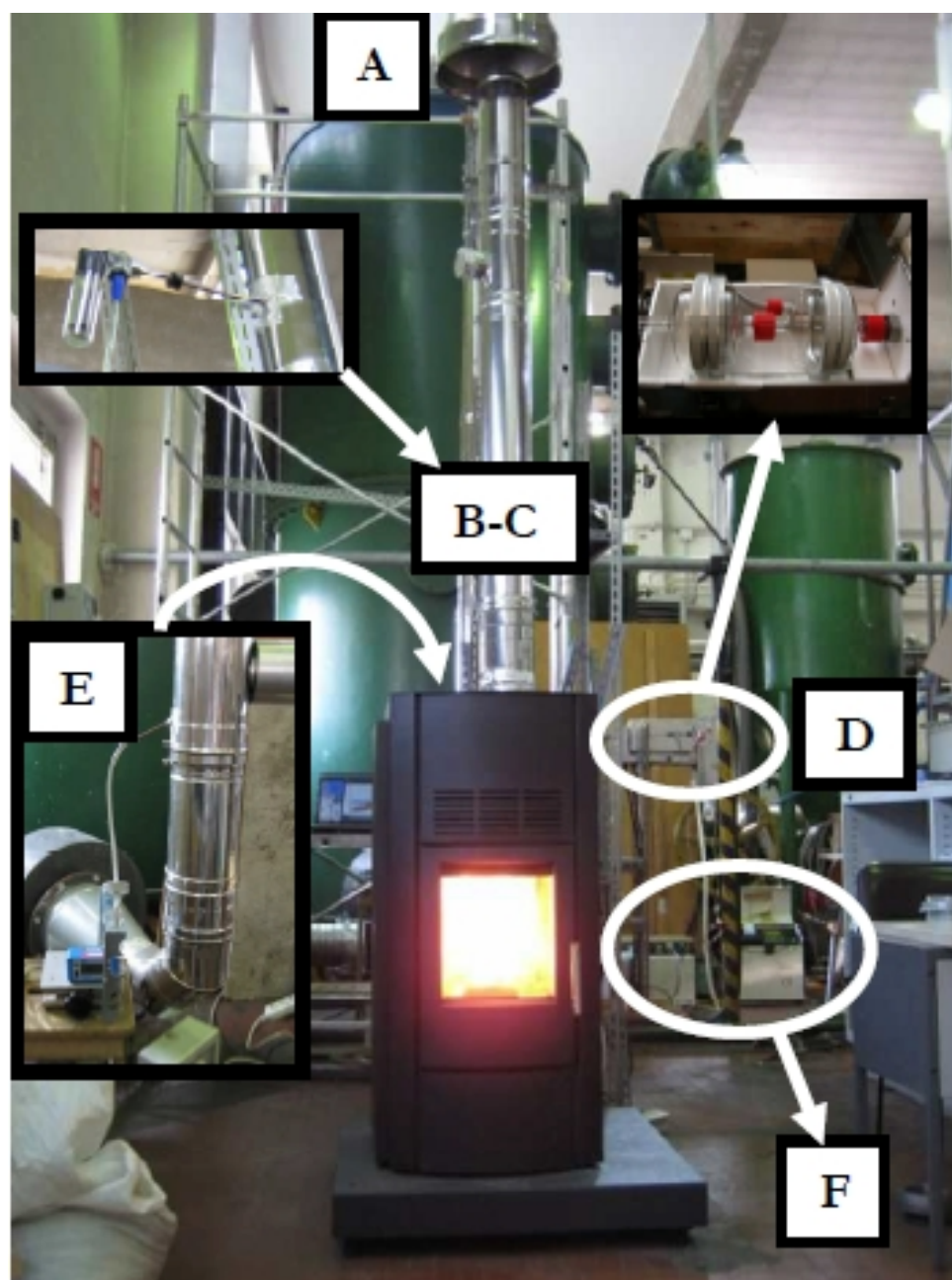
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Figure 1



**Figure 1.** Differences in texture between the raw materials (woodchips) and the final pellets; a=hardwood of *Robinia pseudoacacia* (pre-alpine area - Valleys of *Natisone*), b=softwood of *Picea abies* (alpine area - *Carnia* and *Gemonese*), c=grapevine (*Vitis vinifera*) shoots produced on *Carso* hill district.

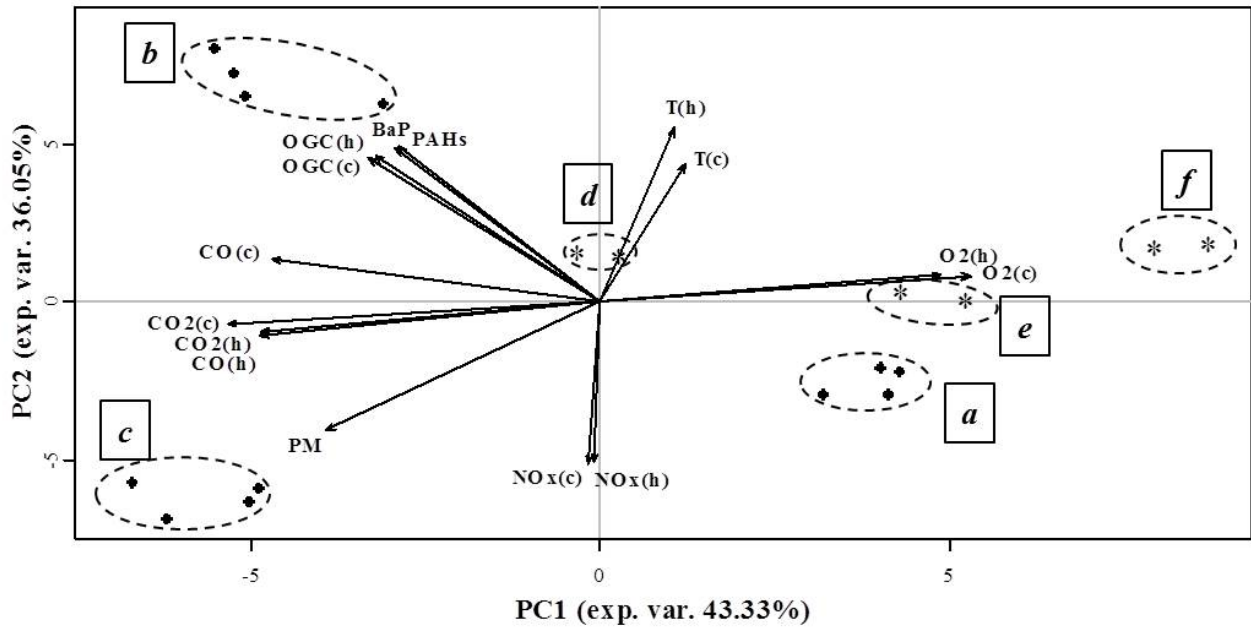
Figure 2



**Figure 2.** Experimental setup for combustion tests. A = flue gas dilution tunnel, B= O<sub>2</sub>, CO<sub>2</sub>, CO, NO<sub>x</sub>, Q<sub>s</sub>,  $\lambda$ , ETA sampler, C=OGC sampler, D=isokinetic sampler equipped with filters for the total suspended particulate sampling, E=BTEX sampler, F=isokinetic pump.

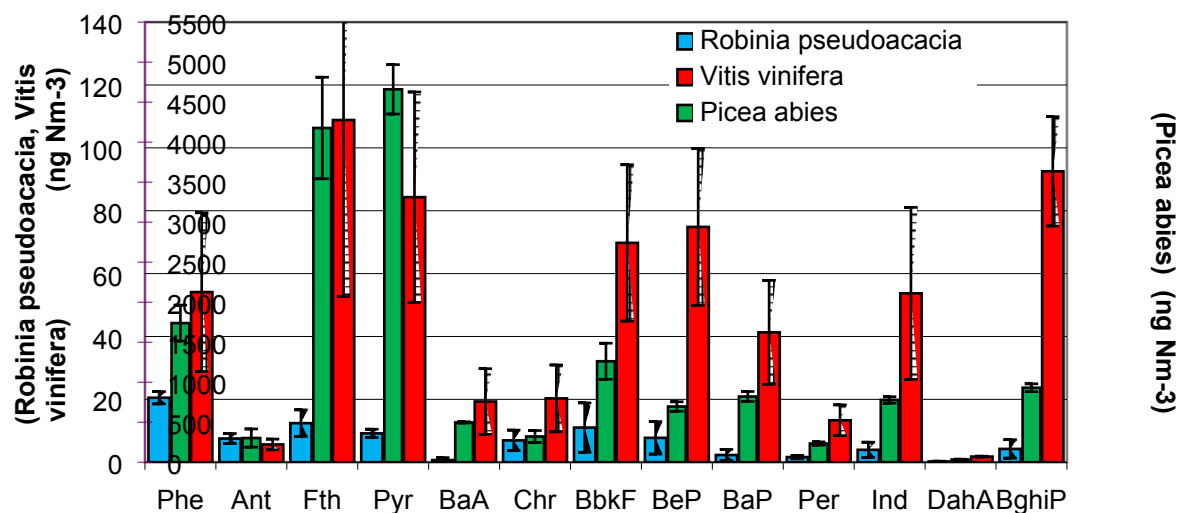


Figure 3



**Figure 3.** PCA of selected parameters under investigation, the circles represent the pellet types, the points the replicate tests. Legend of score boxes: a=*Robinia pseudoacacia*, b=*Picea abies*, c=*Vitis vinifera*, (d) *Abies alba*, (e) *Fagus sylvatica* and (f) softwood mix. The in-house made pellets are represented by black dots, the commercial pellets by star symbols. Legend of loadings: PM=total suspended particulate, OGC = Organic Gaseous Carbon, T = temperature, PAHs = Polycyclic Aromatic Hydrocarbons, BaP = benzo[a]pyrene; for all the parameters: (c) indicates a measure in the combustion chamber, (h) indicates a measure in the chimney (see also table 2).

Figure 4



**Figure 4.** Distribution of PAH concentrations in the particulate matter from flue gas of the three biomass samples examined during controlled combustion of pellets made from *Robinia pseudoacacia*, *Picea abies* and *Vitis vinifera*. Legend: Phe = phenanthrene, Ant = anthracene, Fth = fluoranthene, Pyr = pyrene, BaA = benzo[a]anthracene, Chr = chrysene, BbkF = sum of benzo[b]fluoranthene and benzo[k]fluoranthene, BeP = benzo[e]pyrene, BaP = benzo[a]pyrene, Per = perylene, Ind = indeno [1,2,3-cd] pyrene, DahA = dibenzo[a,h]anthracene, BghiP = benzo[g,h,i]perylene.

**Table 1.** Main characteristic, averaged on two replicates (in parentheses the standard deviations), of the pellets prepared from woodchips of *Robinia pseudoacacia* (a), *Picea abies* (b), *Vitis vinifera* (c) and of the three commercial pellets (d) *Abies alba*, (e) *Fagus sylvatica* and (f) softwood mix.

| Sample                            | (a)         | (b)         | (c)         | (d)          | (e)          | (f)          |
|-----------------------------------|-------------|-------------|-------------|--------------|--------------|--------------|
| Moisture (% w/w)                  | 7.6 (0.1)   | 6.5 (0.1)   | 7.3 (0.1)   | 7.0 (0.1)    | 6.5 (0.1)    | 7.9 (0.1)    |
| Ash (%)                           | 2.36 (0.04) | 1.34 (0.01) | 3.38 (0.07) | 0.19 (0.03)  | 1.09 (0.18)  | 0.33 (0.08)  |
| Calorific value (MJ/kg)           | 17.7 (0.2)  | 18.3 (1.2)  | 17.6 (0.8)  | 18.06 (0.04) | 17.34 (0.30) | 17.88 (0.46) |
| Bulk density (kg/m <sup>3</sup> ) | 628.6 (1.3) | 653.8 (1.3) | 674.0 (1.4) | 678.4 (1.7)  | 671.9 (1.5)  | 656.8 (2.2)  |

**Table 2.** Parameter averages detected in the combustion chamber and chimney (on four replicates for the in-house made pellets and two for the commercial ones, in parentheses the standard deviations) for each of the three pellets obtained from woodchips as well as the three commercial ones. Legend: (a)=*Robinia pseudoacacia*, (b)=*Picea abies*, (c)=*Vitis vinifera*, (d) *Abies alba*, (e) *Fagus sylvatica* and (f) softwood mix.

| Sample                                   | (a)          | (b)           | (c)          | (d)         | (e)          | (f)          |
|--|--------------|---------------|--------------|-------------|--------------|--------------|
| Qs (%)                                   | 13.7 (0.2)   | 13.4 (0.1)    | 10.6 (0.3)   | 11.8 (0.0)  | 13.8 (0.3)   | 15.8 (0.4)   |
| Ta (°C)                                  | 18.0 (0.8)   | 19.8 (0)      | 18.2 (0.8)   | 21.1 (0.2)  | 21 (0.4)     | 20.6 (0.2)   |
| ETA (%)                                  | 86.3 (0.2)   | 86.6 (0.1)    | 89.4 (0.3)   | 88.2 (0.0)  | 86.2 (0.3)   | 84.3 (0.4)   |
| $\lambda$                                | 2.4 (0.1)    | 2.2 (0.1)     | 2.0 (0)      | 1.9 (0.0)   | 2.4 (0.1)    | 2.9 (0.1)    |
| <b>Combustion chamber</b>                |              |               |              |             |              |              |
| T off-gases (°C)                         | 541.9 (10.7) | 580.9 (12.5)  | 484.6 (7.4)  | 642.7 (1.0) | 587.5 (16.1) | 539.9 (7.3)  |
| O <sub>2</sub> (%)                       | 11.8 (0.3)   | 10.4 (0.2)    | 9.7 (0.2)    | 10.1 (0.2)  | 12.2 (0.4)   | 13.7 (0.2)   |
| CO <sub>2</sub> (%)                      | 8.6 (0.2)    | 10.0 (0.2)    | 10.6 (0.2)   | 10.3 (0.3)  | 8.4 (0.4)    | 7 (0.2)      |
| CO (mg/Nm <sup>3</sup> )*                | 382 (155)    | 4418 (1577)   | 3643 (827)   | 85.7 (11.5) | 509 (109.7)  | 816.5(120.4) |
| NO <sub>x</sub> (mg/Nm <sup>3</sup> ) *§ | 312.1 (19.9) | 117.8 (5.8)   | 281.9 (9.7)  | 83.8 (1.3)  | 192.8 (0.8)  | 110.5 (5.0)  |
| OGC(mg/Nm <sup>3</sup> ) *‡              | 4.3 (1.1)    | 247.6 (49.9)  | 32.2 (3.5)   | 3 (0.4)     | 6.2 (0.6)    | 10.8 (2.8)   |
| <b>Chimney</b>                           |              |               |              |             |              |              |
| T off-gases (°C)                         | 171.3 (3.4)  | 181.4 (1.7)   | 157.2 (4.8)  | 179.3 (2.1) | 174.3 (1.7)  | 171.1 (1.6)  |
| O <sub>2</sub> (%)                       | 12.2 (0.2)   | 11.1 (0.1)    | 10.4 (0.2)   | 10.1 (0.1)  | 12.2 (0.3)   | 13.5 (0.3)   |
| CO <sub>2</sub> (%)                      | 8.3 (0.2)    | 9.3 (0.1)     | 10.0 (0.2)   | 10.3 (0.1)  | 8.3 (0.3)    | 7.1 (0.2)    |
| CO (mg/Nm <sup>3</sup> ) *               | 270 (73.5)   | 1919 (106.7)  | 2765 (683.6) | 66.3 (5.9)  | 274 (52.5)   | 368.2 (68.5) |
| NO <sub>x</sub> (mg/Nm <sup>3</sup> ) *§ | 315.0 (19.2) | 115.8 (4.9)   | 290.3 (14.6) | 84.5 (1.9)  | 193.4 (1.5)  | 107 .0(1.9)  |
| OGC(mg/Nm <sup>3</sup> ) *‡              | 4.45 (0.5)   | 470.3 (111.6) | 59.4 (10.2)  | 3.8 (1.2)   | 6.5 (4)      | 6.0 (0.9)    |

Qs (combustion losses); Ta (ambient temperature); ETA (yield of combustion);  $\lambda$  (excess air in the flue gas).

\* the values are normalized to 13% oxygen; § the values are expressed as NO equivalent; ‡ the values are expressed as propane equivalent

**Table 3**

**Table 3.** Averages of BTEX (two replicates), total suspended particulate (PM – four replicates), levoglucosan in the PM collected for each of the three pelletize biomass samples (in parentheses the standard deviations). Legend: (a)=*Robinia pseudoacacia*, (b)=*Picea abies*, (c)=*Vitis vinifera*.

| Substance                                  | Sample (a)  | (b)        | (c)        |
|--|-------------|------------|------------|
| Benzene ( $\mu\text{g}/\text{m}^3$ )       | 2.14 (0.03) | 626 (61)   | 58 (35)    |
| Toluene ( $\mu\text{g}/\text{m}^3$ )       | nd          | 96 (9)     | 1.4 (0.2)  |
| Ethylbenzene ( $\mu\text{g}/\text{m}^3$ )  | nd          | 8.9 (0.5)  | nd         |
| m,p-xylene ( $\mu\text{g}/\text{m}^3$ )    | nd          | 14.3 (0.3) | nd         |
| o-xylene ( $\mu\text{g}/\text{m}^3$ )      | nd          | 5.2 (0.3)  | nd         |
| PM ( $\text{mg}/\text{Nm}^3$ )             | 8.7 (1.0)   | 9.6 (0.4)  | 32.8 (2.1) |
| Levoglucosan ( $\mu\text{g}/\text{Nm}^3$ ) | 41.6 (15.4) | 22.7 (7.9) | 26.6 (8.6) |

nd = value below limit of detection

**Table 4.** Diagnostic ratios in the present (a, b and c samples) and other studies. Legend: (a)=*Robinia pseudoacacia*, (b)=*Picea abies*, (c)=*Vitis vinifera*.

| Sample                                  | Diagnostic Ratio | BaP/BghiP | Ind/(Ind+BghiP) | BaP/Ind | Ind/BghiP |
|---|------------------|-----------|-----------------|---------|-----------|
| (a)                                     |                  | 0.54      | 0.48            | 0.58    | 0.93      |
| (b)                                     |                  | 0.88      | 0.46            | 1.05    | 0.84      |
| (c)                                     |                  | 0.46      | 0.37            | 0.77    | 0.58      |
| Urban dust <sup>a</sup>                 |                  | 0.63      | 0.43            | 0.83    | 0.75      |
| Olive trees <sup>b</sup>                |                  | 1.55      | 0.53            | 1.38    | 1.12      |
| Wheat residues <sup>c</sup>             |                  | 1.43      | 0.55            | 1.22    | 1.28      |
| Domestic fireplaces (wood) <sup>d</sup> |                  | 0.50      | 0.30            | 1.10    | 0.50      |
| Traffic <sup>e</sup>                    |                  | 0.5-0.6   | 0.17            |         |           |
| Coke <sup>e</sup>                       |                  | ≥1.25     | 0.33            |         |           |
| Coal burning <sup>e</sup>               |                  | 0.9-6.6   | 0.56            |         |           |
| Steelmaking <sup>e</sup>                |                  | 0.27-1.55 | 0.29-0.56       |         |           |

<sup>a</sup> NIST SRM 1649b - Urban Dust

<sup>b</sup> D'ambrosio et al. 2014

<sup>c</sup> Hays et al. 2005

<sup>d</sup> de Gennaro et al. 2015

<sup>e</sup> Di Gilio et al. 2017