

Evaluation of the characteristics of vineyard pruning residues for energy applications: effect of different copper-based treatments

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Abstract

The role of biomass for increasing renewable energy sources mix is considered fundamental, despite some negative environmental impact of first-generation biofuels. The use of biomass obtained in a more sustainable way, as represented by agricultural wastes, should be favoured. The Mediterranean area and Italy in particular offer a large amount of vineyard pruning residues that can be converted into bioenergy. Since vineyards are exposed to treatments based on copper (Cu) and zinc, these metals last in wood residues during pruning and accumulate in the soil. In this study an evaluation of the concentrations of copper and other heavy metals in grapevine pruning wastes, when treated with common plant protection products, was carried out. The study was also extended to the soil, being potentially mixed to the biomass in the case of mechanical collection of pruning residues. The grapevine residues free of impurities that were collected during this study have typical values of copper in pruning wood, varying from 8.5 mg kg⁻¹ when treated with low Cu product, to 19.2 mg kg⁻¹ when treated with high Cu product. It was observed that contaminations during pruning with soil could increase the amount of copper in the residues. More in detail, every percentage point of soil that winds up on pruning residues involves an increase of 1 mg of Cu every kg of biomass. For this reason, we recommend the use of appropriate systems for the harvest of grapevine residues, particularly mechanical systems that avoid soil lifting. Moreover, we suggest the use of pruning residues preferably in large-scale power plants with appropriate emission filters instead of small-scale domestic boilers.

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Introduction

As indicated in the Renewable Energy Directive (RED) 2009/28/EC on the promotion of renewable energy sources, in the European Union the share of renewable energy in gross final energy consumption should move from 8.5% (in 2005) to 20% by 2020 (European Commission, 2009). Therefore, National Renewable Energy Action Plans (NREAPs) established in 2012 by the EU Member States (European Commission, 2014) expected the share of Renewable Energy Sources (RES) in the gross final energy consumption in the EU to overcome the 11.6% of 2010 and reach 20.7% in 2020. In particular, the total contribution of energy from biomass to the RES mix, representing almost 45% of RES mix, is expected to increase from about 3000 Petajoules (PJ) in 2010 to about 4600 PJ in 2020 (Szabò *et al.*, 2011).

In this context, the role of biomass for increasing RES mix appears to be fundamental even though some negative environmental impact of first-generation biofuels are under discussion: land use changes and damage to biodiversity, impact on food availability and real greenhouse gas emission reduction (Doornbosch and Steenblik, 2007; Gallagher, 2008; Searchinger *et al.*, 2008). From this point of view, the use of biomass obtained in a more sustainable way, as represented by agricultural residues, agro-industrial residues and wastes should be favoured. Due to their benefits many studies focused on the agricultural and agro-industrial residues potential for energy production in EU (Koukios, 1998; Diamantidis and Koukios, 2000; Nikolaou *et al.*, 2003; De Noord *et al.*, 2004; Siemons *et al.*, 2004; Ericsson and Nilsson, 2006; Bacenetti *et al.*, 2015), highlighting the great importance for their energetic utilisation. More in detail, considering the EU-27, the total bioenergy potential of agricultural crop residues (straw from cereals, stalks from maize, rapeseed and sunflower, vineyard and olive trees pruning) is estimated to consist in 1370 PJ EU-27 (Monforti *et al.*, 2013).

Among different kind of crop residues, the Mediterranean area and Italy in particular offer a large amount of vineyard pruning residues. In 2011, almost 3218.5 kha were cultivated with vineyards in Europe (EUROSTAT, 2014) and 725.1 kha in Italy (ISTAT, 2014). Referring to these data and considering appropriate production indexes evaluated by the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (Motola *et al.*, 2009) it is possible to estimate about 1400 kt dry matter of potential residues deriving from vine cultivation.

The energetic use in this case is particularly recommended because pruning residues are not an income source for farmers but in most situations, a cost. The disposal of vineyard residues usually consists in shredding and burying them or burning them. Nevertheless, both solutions have negative implications: the laying of residues underground has positive consequences in case of healthy vineyard but not for a vineyard

damaged by trunk disease pathogens because of increased inoculum. The burning of residues has environmental implications both for emissions in atmosphere and fire risk. The National decree 22/97 indicates that pruning residues become waste if disposed elsewhere, with a consequent cost of disposal (Italian Regulation, 1997). Instead, in the case of an energetic use, as stated in National decree 152/06, they can be considered biofuels (Italian Regulation, 2006). They are also indicated as biofuels in the technical standard ISO 17225-1:2014 (ISO, 2014). For this reason, vineyard-pruning residues can be used in the form of chips or pellets for the combustion in small, medium and large size boilers. Currently some vineyard pruning residues are employed in power plants (> 1 MWe) in addition to other biomasses. However, the common management of grapevine, mostly in organic agriculture, implies the use of plant protection products using copper (Cu) as active ingredient, together with other fungicides that can contain heavy metals (e.g., zinc, Zn) (Romanazzi *et al.*, 2014). Many studies have investigated about the movement of Cu²⁺ into the vine plant after usual treatments (Romeu-Moreno *et al.*, 1999; Lai *et al.*, 2010; Provenzano *et al.*, 2010; Juang *et al.*, 2012) and its solubility within the soil (Riboldi *et al.*, 2002; Komárek *et al.*, 2010; Ruyters *et al.*, 2013). Another study has dealt with the Cu content in wine production residues (Toscano *et al.*, 2013). The heavy metals contained in pesticides last partially on the surface of vines, and also on the pruning residues, causing the emission of pollutants in flue gas or ash during combustion in boilers (Oberberger *et al.*, 2006; Picchi *et al.*, 2013). This phenomenon arises particularly with small-scale domestic boilers, generally not equipped with flue gases abatement systems (Mc Donald, 2000).

In this context, the present study aims at evaluating the concentrations of copper and other heavy metals in grapevine pruning residues when treated with common plant protection products to better evaluate their suitability for an energetic application. The study was performed soon after the pruning collection and extended to the soil, being potentially mixed to the biomass in the case of mechanical collection of pruning residues.

Materials and methods

The grapevine pruning wood was collected in March 2014 from a 6-year-old vineyard. Usually in this period the residues are collected by means of appropriate machinery. Three different treatments were tested, compared with a conventional farming technique and an untreated control. Soil samples were also collected to investigate the metal concentrations due to the fall of the pesticide on the soil during the applications.

Pruning wood and soil samples have been collected on the same day and then delivered to the Biomass Lab of Marche Polytechnic University, where sample preparation and analytical analyses were performed.

Treatments in the vineyard

A randomised block design with 4 replicates was used, and the treatments were assigned to plots using a random number generator (Excel; Microsoft Corp., Redmond, WA, USA). Each plot consisted of seven vines along the row, and the treated rows were spaced each other by an untreated row. Three treatments were tested (Bordeaux mixture, copper hydroxide, laminarin combined with low copper rates) with a total of 11 weekly applications, since the beginning of May to the end of July 2013. The treatments were applied spraying a volume equivalent to 1000 L ha⁻¹ using a motorized backpack sprayer. Table 1 shows the active ingredients and the application rates employed.

Sampling

The sampling was carried out in March 2014. Pruning wood samples were taken manually from all the seven plants placed in a plot, forming the *plot sample*, which was approximately 1.5 kg and contained 30 to 40 lignified shoots of about 70 cm length. For each treatment, one sample per each plot was collected. Concerning soil samples, two samples of 1.5 kg each were collected from the first 2-3 cm below the plants of the plot. Further soil samples were harvested in a field cultivated with annual crops close to the vineyard.

Sample preparation

For pruning wood analyses, 30 lignified shoots were chosen randomly from each plot and combined together forming a sample, then divided in two sub-samples of 15 shoots each. Each shoot was cut in pieces of 100 mm length and submitted to the analytical procedure.

Concerning soil, for each treatment the plot samples were combined together, mixed and then divided into two parts using a riffle box (device recommended by UNI EN 14780:2011; UNI, 2011a). After the division, a part was discarded while the other one was split again using riffle box. The division was repeated until a sample of 50 g was produced. This procedure was used for each treatment. Each sample was then analysed for minor elements determination.

Analyses performed on samples

A total of 12 analytical samples of grape shoots were obtained and for each of them a full characterisation was performed determining moisture content, ash content, net calorific value, nitrogen content, chlorine and sulphur contents and also minor elements determination [lead (Pb), mercury (Hg), chromium (Cr), Cu, manganese (Mn), nickel (Ni), arsenic (As), cadmium (Cd), Zn].

For the moisture content determination, the samples were cut in 10 cm length pieces. For the other determinations, instead, the samples were stabilised in a forced ventilation oven [mod. M120-VF; MPM Instruments s.r.l., Bernareggio (MB), Italy] at 45±2°C temperature in air atmosphere, then milled with a blade mill (Retsch Mod. SM33-25Hz) and sieved through a 1 mm mesh.

Concerning soil, 6 samples were obtained in total and the minor elements determination was performed.

For each analysis, both with the shoots and with the soil samples, a duplicate determination was carried out. The values were submitted to variance analysis and the means were separated by Tukey's honest significant difference test, at P<0.05 (Statsoft, Tulsa, OK, USA).

Moisture content determination

According to UNI EN 14774-2:2010 (UNI, 2010a), the sample was dried at 105±2°C temperature in air atmosphere using forced ventilation oven (mod. M120-VF; MPM Instruments) until constant mass is achieved. Then the percentage moisture was calculated from the loss in mass of the sample.

Ash content determination

The ash content was determined using a thermo-gravimetric analyser (TGA Leco Mod. 701) according to UNI EN 14775:2010 (UNI, 2010b). The principle is that the sample is heated in air under controlled conditions of time, sample weight and equipment specifications until a temperature of 550±10°C using a muffle furnace. Then the ash content is determined by calculation from the mass of the remaining residue.

Nitrogen determination

According to UNI EN 15104:2011 (UNI, 2011b), a known mass of

sample is burnt in oxygen/carrier gas mixture, under such conditions that it is converted into ash and gaseous products of combustion. Oxides of nitrogen are reduced to nitrogen, and those products of combustion that would interfere with the subsequent gas-analysis procedures are removed. The carbon dioxide, water vapour and nitrogen mass fractions of the gas stream are then determined quantitatively. The combustion, the following separation by a gas chromatograph and the detection of the elements were carried out by an Elemental Analyzer (mod. 2400 Series II CHNS/O System, Perkin Elmer, Waltham, MA, USA).

Determination of net calorific value

An isoperibolic calorimeter (mod. C2000 basic; IKA, Staufen, Germany) was used to perform the sample combustion under specific conditions in a bomb calorimeter, according to UNI EN 14918:2010 (UNI, 2010c). The calorimeter was calibrated with benzoic acid standard (IKA Benzoic Acid C723). The net calorific value was determined by a formula indicated in the aforementioned technical standard starting from gross calorific value, water and hydrogen contents of the analytical sample.

Sulphur and chlorine determination

Sulphur and chlorine contents were measured by decomposition in calorimetric bomb with excess of oxygen and absorption of acid combustion gases in water (10^{-3} mm³), according to UNI EN 15289:2011 (UNI, 2011c). Detection of sulphate and chloride was performed by liquid ion chromatography (mod. 761 COMPACT IC; Metrohm, Herisau, Switzerland). The liquid ion chromatograph was calibrated using a series of standards prepared from a Multielement Standards Solution 1000 mg dm⁻³ (Fluka).

Minor element determination

The chemical analysis, carried out according to UNI EN 14918:2010 (UNI, 2010c), provides for the digestion of the biomass sample in a closed container, using a mixture of acids (HNO₃/H₂O₂/HF) and microwave oven (mod. Multiwave 3000; Anton Paar, Graz, Austria). The mineralisation product is then analysed by inductively coupled plasma optical emission spectrometry (ICP-OES mod. Optima 2100; PerkinElmer). The spectrometer was calibrated using a series of standards prepared from a Single-Element Standard 1000 mg dm⁻³ of Perkin Elmer. The elements detected were Pb, Hg, Cr, Cu, Mn, Ni, As, Cd, Zn.

Results and discussion

The amount of copper in the pruning residues ranges from 7.0 mg kg⁻¹ for the control to 19.2 mg kg⁻¹ for the Bordeaux mixture treatments (Table 2). Treatments with copper hydroxide, laminarin and the farm application did not provide results significantly different from the control test. On the contrary, they are all significantly different from the treatment with Bordeaux mixture.

The determination of copper was performed also in soil and results show the highest amount of copper in soil treated with Bordeaux mixture followed by copper hydroxide. The lowest value is given by the cultivated field near the grapevine, where grape was never cultivated, that is three times lower than the control, exposed in previous years to copper applications (Table 2).

The increase of copper in pruning wood and soils depends on the amount of copper distributed by the treatment of the year. Figure 1 shows how particularly marked is the increase of copper in soil with an increase of copper in treatments: the slope of trend line is 7.2 in soil

Table 1. Details of formulations, application rates and frequencies used in the present study.

Active ingredient (%)	Commercial product	Company	Application rate (g or mL/ha)	Number of applications	Copper absolute value (kg/ha)	Year trial
Bordeaux mixture (20)	Poltiglia Disperss	Cerexagri Italia S.r.l. (Italy)	5000	11	11.0	2013
Copper hydroxide (19.2)	Funguran	Certis Europe (Italy)	2800	11	5.8	2013
Laminarin + copper hydroxide/copper oxide (33)	Frontiere + Coptrel	BioAtlantis (Ireland); Kalosgate (Italy)	1000 + 500	11	1.8	2013
Farm application (variable percentages): dimetomorf, mandipropamid, metalaxyl ametocradin, metiram, copper hydroxide	Unstated	Several	Unstated	11	Unstated	2013
Control	Untreated	-	-	-	-	-

Table 2. Comparison between copper distributed and copper registered (mean values) in pruning wood and soil.

Thesis	Copper absolute value (kg/ha)	Copper concentration in the vine pruning (mg/kg)	Copper concentration in the soil (mg/kg)
Bordeaux mixture	11.0	19.2	113.4
Copper hydroxide	5.8	10.6	102.8
Laminarin + copper hydroxide/copper oxide	1.8	8.5	81.0
Farm application	4.3	10.9	86.3
Control	-	7.0	88.3

and 2.4 in treatments. For a complete characterisation of pruning wood and soil, the content of other heavy metals was determined (Tables 3 and 4). We noticed that also Zn shows a variable accumulation in pruning wood depending on treatments. In particular, the highest value is 15.5 mg kg⁻¹ given by Bordeaux mixture treatment and is significantly different from the control (5.4 mg kg⁻¹) and the farm application (7.3 mg kg⁻¹). On the contrary, no difference among treatments was found for Zn content in the soil.

As stated in the *Materials and Methods* section, the shoot samples were taken manually, so that no soil contamination occurred. However, the collection of grapevine residues is usually performed using appropriate machinery. In this case, a variable amount of soil could be harvested together with the pruning residues, especially wet soil, increasing the content of copper in pruning wood. In Table 5, a simulation of contamination with different percentages of soil (1-5%) is proposed taking into account the results of Cu determination carried out on soil and pruning for each thesis. The simulation concerns the increase of copper content, which reaches a maximum value of 23.9 mg kg⁻¹ when grapevine is treated with Bordeaux mixture and pruning wood is contaminated with 5% of soil. This indication can be useful to evaluate the possible Cu content of prunings collected in real operation in comparison with the Cu content of other biomasses currently employed for energy application.

Pruning samples were characterized also for an energetic application: Table 6 shows mean values of moisture content, ash content, net calorific value, nitrogen, chlorine and sulphur contents. Taking into account these results, the contamination of pruning wood with soil can affect obviously also these parameters, in particular increasing ash content and consequently decreasing the calorific value but to a limited extent.

Data about copper content in biomass for energy use are present in literature. The ISO 17225-1:2014, for instance, indicates for short rota-

tion coppice a typical value of 3±1 mg kg⁻¹, virgin bark materials up to 30 mg kg⁻¹ and logging residues ranging from 1 mg kg⁻¹ till 100 mg kg⁻¹ in coniferous wood and till 200 mg kg⁻¹ in broad-leaf wood (ISO, 2014). According to some authors (Riva *et al.*, 2009), industrial wood chips used in power plants can have high Cu values; the examples of power plants reported show a mean value of 7.0±11.0 mg kg⁻¹ and maximum value of 108.6 mg kg⁻¹ for the first power plant examined and a mean value of 10.3±18.2 mg kg⁻¹ and maximum value of 226.0 mg kg⁻¹ for the second power plant.

It is clear that the Cu values of grapevine pruning wood under this study fall within the ranges of biomass for energy use found in literature, especially the biomass employed in large-scale boilers.

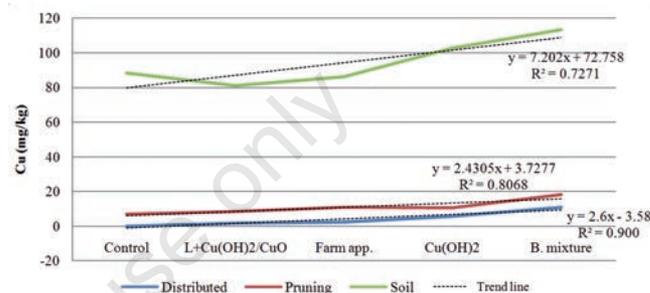


Figure 1. Correlation between copper distributed with treatments and copper found in pruning wood and soil, with related trend lines. L+Cu(OH)₂ CuO⁻¹ = Laminarin + copper hydroxide/copper oxide; Farm app. = Farm application; Cu(OH)₂ = Copper hydroxide; B. mixture = Bordeaux mixture.

Table 3. Amount of heavy metals in the pruning wood of the vine exposed to the different treatments.

Treatment	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Bordeaux mixture	<0.67 ^a	0.1±0.1 ^a	0.2±0.3 ^a	18.1±3.6 ^a	<0.01 ^a	34.3±20.9 ^a	1.0±0.7 ^a	<0.36 ^a	15.5±3.7 ^b
Copper hydroxide	<0.67 ^a	0.3±0.2 ^a	0.2±0.2 ^a	10.6±1.6 ^b	<0.01 ^a	47.9±10.4 ^a	1.8±1.4 ^a	<0.36 ^a	10.7±1.6 ^{ab}
Laminarin + copper hydroxide/copper oxide	<0.67 ^a	0.3±0.1 ^a	0.4±0.3 ^a	8.5±0.5 ^b	<0.01 ^a	36.5±2.9 ^a	1.8±0.8 ^a	<0.36 ^a	9.9±5.1 ^{ab}
Farm application	<0.67 ^a	0.3±0.1 ^a	0.2±0.1 ^a	10.9±2.5 ^b	<0.01 ^a	30.6±4.9 ^a	1.6±0.2 ^a	<0.36 ^a	7.3±1.6 ^a
Control	<0.67 ^a	0.3±0.1 ^a	0.2±0.1 ^a	7.0±0.6 ^b	<0.01 ^a	51.2±4.8 ^a	1.5±0.3 ^a	<0.36 ^a	5.4±3.6 ^a

As, arsenic; Cd, cadmium; Cr, chromium; Cu, copper; Hg, mercury; Mn, manganese; Ni, nickel; Pb, lead; Zn, zinc. ^{a,b}Values followed by different letters in the same column are significantly different according to Tukey's honest significant difference test (P<0.05).

Table 4. Amount of heavy metals in the soils of the different treatments.

Treatment	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Bordeaux mixture	9.7±0.2 ^a	0.2±0.1 ^a	87.2±3.1 ^a	113.4±5.8 ^a	<0.01 ^a	842.5±23.2 ^a	64.2±8.5 ^a	32.6±6.5 ^a	59.6±7.2 ^a
Copper hydroxide	10.1±0.3 ^a	0.1±0.1 ^a	95.3±2.8 ^a	102.8±4.4 ^a	<0.01 ^a	843.8±17.7 ^a	68.6±7.4 ^a	33.7±6.2 ^a	68.1±8.3 ^a
Laminarin + copper hydroxide/copper oxide	9.6±0.2 ^a	0.2±0.1 ^a	89.5±2.5 ^a	81.0±2.1 ^b	<0.01 ^a	827.9±13.6 ^a	65.0±8.4 ^a	29.2±5.6 ^a	59.5±6.8 ^a
Farm application	10.8±0.2 ^a	0.1±0.1 ^a	98.0±3.4 ^a	86.3±3.5 ^b	<0.01 ^a	799.1±14.6 ^{ab}	73.7±9.2 ^a	39.0±7.1 ^a	68.4±6.9 ^a
Cultivated field out of vineyard	6.3±0.1 ^a	0.1±0.1 ^a	74.0±3.2 ^b	28.1±0.8 ^c	<0.01 ^a	709.6±16.5 ^{ab}	51.0±8.0 ^a	24.1±6.2 ^a	47.9±6.1 ^a
Control	9.2±0.2 ^a	0.1±0.1 ^a	91.3±2.9 ^a	88.3±2.6 ^b	<0.01 ^a	799.8±21.4 ^b	67.2±7.4 ^a	32.6±7.0 ^a	64.7±7.0 ^a

As, arsenic; Cd, cadmium; Cr, chromium; Cu, copper; Hg, mercury; Mn, manganese; Ni, nickel; Pb, lead; Zn, zinc. ^{a-c}Values followed by different letters in the same column are significantly different according to Tukey's honest significant difference test (P<0.05).

Table 5. Copper variation during the simulation of different percentages of soil contamination on pruning residues.

Thesis	Copper in pruning wood (mg/kg)	Copper in soil (mg/kg)	Copper in pruning at different % soil contamination (mg/kg)				
			1%	2%	3%	4%	5%
Bordeaux mixture	19.2	113.4	20.1	21.1	22.0	23.0	23.9
Copper hydroxide	10.6	102.8	11.5	12.4	13.4	14.3	15.2
Laminarin + copper hydroxide/copper oxide	8.5	81.0	9.2	10.0	10.7	11.4	12.1
Farm application	10.9	86.3	11.7	12.4	13.2	13.9	14.7
Control	7.0	88.3	7.8	8.6	9.4	10.3	11.1

Table 6. Energetic characterisation of pruning wood.

Thesis	Moisture (% a.r.)	Ash (% d.m.)	NCV (MJ/kg d.m.)	N (% d.m.)	Cl (% d.m.)	S (% d.m.)
Bordeaux mixture	40.6	3.3	17.669	0.6	0.03	0.04
Copper hydroxide	41.8	3.3	17.607	0.7	0.02	0.03
Laminarin + copper hydroxide/copper oxide	41.1	3.2	17.565	0.6	0.01	0.02
Farm application	40.3	3.1	17.668	0.6	0.01	0.03
Control	42.7	3.3	17.779	0.5	0.02	0.04
Overall average	41.4	3.3	17.658	0.6	0.02	0.03

NCV, net calorific value; N, nitrogen; Cl, chlorine; S, sulphur; a.r., as received; d.m., dry matter.

Conclusions

In the present study an evaluation of vineyard pruning wood characteristics for energy use was performed. Since vineyards are exposed to treatments based on Cu and Zn, those metals last in wood residues during the pruning and accumulate in the soil.

The grapevine residues free of impurities that we collected during this study have typical values of copper in pruning wood varying from 8.5 mg kg⁻¹ when treated with low Cu product until 19.2 mg kg⁻¹ when treated with high Cu product. Zinc varies from 9.9 mg kg⁻¹ (low Cu product) until 15.5 mg kg⁻¹ (high Cu product). No significant variation was stated for the other minor elements. Concerning energetic parameters, the typical values are the overall averages shown in Table 6, since the treatments did not entail variations.

We observed that contaminations of pruning residues with soil could increase the amount of copper. More in detail, every percentage point of soil that winds up on pruning wood involves an increase of 1 mg of Cu every kg of biomass. For this reason, we recommend to use appropriate systems for the harvest of grapevine residues, particularly mechanical systems that avoid soil lifting. On the market are yet available specific machineries for the correct collection of vineyard pruning residues for energy application. Some of these harvesters produce bales while others produce short sticks limiting soil contamination and preserving biomass quality.

In any case, the Cu values detected in pruning wood are in line with those found in literature. In particular, the European Standard about general requirements of solid biofuels establishes that typical Cu values of different biomasses for energy use can vary and be higher than the values found in this study. Moreover, it was pointed out that industrial chips used in power plants could have up to 226 mg kg⁻¹ Cu value. For this reason, we suggest to use pruning residues preferably in large-scale power plants with appropriate emission filters instead of small-scale domestic boilers.

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