

Characterization of diffuse odorous emissions from lignocellulosic biomass storage

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ARTICLE INFO

Handling Editor: Dr. Paul Williams

Keywords:

Odor potential
Emission
Lignocellulosic biomass
Wood heaps
Self-ignition

ABSTRACT

The use of lignocellulosic biomass for green energy production is increasing, but the wood storage may lead to ambient odor related issues. This study aims to assess the odor potential and to investigate the mechanisms that promote odorous emissions from wood chip heaps. To achieve this goal, four experimental campaigns were conducted in an Italian thermal power plant. During these campaigns, odor concentration and chemical-physical parameters, that should theoretically affect the odor potential of biomass heaps, were investigated. The first important outcome revealed a strong heterogeneity on the heaps surface, classified as *dry* or *smoking* according to the superficial humidity and smoke. Smoking areas proved to be much more emissive and at self-ignition risk than dry regions. Indeed, odor concentration on smoking regions reached values in the order of $10^5 \text{ ou}_E/\text{m}^3$, significantly higher than dry region ones ($10^2 \text{ ou}_E/\text{m}^3$). In addition, the highest values of odor concentration have been detected in the first days of storage, when fatty acids are oxidized and terpenes are released. Again, after 30 ÷ 80 days, i.e. about 20 days after the temperature peak caused by biological activity, odor concentration increases, suggesting a possible cause-effect mechanism between biological processes and odor release. Unexpectedly, odor emissions decreased during summer, reasonably due to the high ambient temperature which reduces the moisture content limiting biological activity. However, after about 100 days of storage, smoking regions extent and odor emissions can be considered negligible.

1. Introduction

Every year, a human being breathes in about 5 million litres of air through the nose. Inside the human nose there is a system based on chemoreceptors, particular cells aimed to respond to the presence of some chemical characteristics of odorous substances. Humans rely on this system for their sense of smell, and the wellness of this system affects people quality of life [1]. Industrial odor emissions have become a significant concern for the community, particularly in recent years, as they frequently lead to disputes raised by residents [2,3]. Despite that, unpleasant odorous emissions may not necessarily be related to toxicological risks, but they can have a negative impact on people life quality [4].

Odorous emissions are gaining relevance also at the normative level, where efforts are being made to standardize and update the current

technical standards [5,6].

Despite the abovementioned growing attention on odor impacts, literature is lacking, particularly for sources where estimating odor flux is complex (e.g., oil refinery tanks, landfill surfaces, heaps of solid material, wastewater treatment tanks) [7,8] in order to implement high-quality odor impact assessments, it becomes crucial to accurately characterize the emission sources [9–11].

Among these complex sources, woody biomass heaps are becoming increasingly widespread for green energy production, as demonstrated by some statistical data [12,13]. Actually, biomass is the main source of renewable primary energy in Europe [14]. European solid biomass sector overcame the 100 MTOE (Million Tonnes of Oil Equivalent) in 2017, with an increase of 64 % in the decade 2010 ÷ 2020 [15]. Biomass for bioenergy represents the main source of renewable primary energy in Europe, covering almost 60 % of renewable energy production. The

Abbreviations: Codor, Odor concentration; T_{surface} , Temperature measured on the Surface of a heap; T_{depth} , Temperature measured inside a heap; OT, Odor threshold; OER, Odor Emission Rate.

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<https://doi.org/10.1016/j.joei.2023.101440>

Received 30 May 2023; Received in revised form 23 October 2023; Accepted 24 October 2023

Available online 31 October 2023

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most extensively employed technique to exploit the energy potential of biomass is the thermal power plant, in particular co-generative plants [16]. These thermal plants generate almost half of their energy from solid biomass, including waste or woody biomass like vegetal carbon, wood pellets, and wood chips [17].

Over the past few decades, there has been a surge in the popularity of woody biomass power plants, driven by three primary factors. First of all, co-generative biomass thermal power plants represent an economically profitable expense. A 400 ton/year cogenerator's investment has a payback time limited to 2 ÷ 3 years, with a plant lifetime of more than 20 years [18]. Secondly, the amount of carbon dioxide released during combustion is equal to the amount absorbed by the tree over its lifetime, then burning biomass has no theoretical environmental impact due to CO₂ Global Warming Potential (GWP) [19–21]. A third factor promoting the spread of biomass plants is the ease with which particular types of process plants can be converted into biomass power plants. For instance, after the Common Market Organisation (CMO) reform in 2006, most of the Italian sugar production plants (15 of the 19 plants) ceased operations, and some of them were converted into biomass thermal plants, others are in conversion nowadays [22].

Despite woody biomass is currently widely used, there is still a relevant unexploited potential. One of the reasons is the general increase in biomass availability, e.g. in Europe, wooded area increases by about 0,06 % per year, mainly due to the abandonment of agricultural land portions [23].

The abovementioned data display the current and future relevance of biomass as a feedstock for thermal power plants. On the other hand, the significant environmental odor impact which can be associated with these plants, mainly due to biomass storage, is scarcely investigated.

Biomass in thermal power plants is typically stored in large amounts for long periods, not only to grant flexibility to the furnace but also to give enough time for biomass to dry, with consequent calorific value increase [24]. However, prolonged outdoor storage of woody biomass can result in biomass degradation and consequently in environmental emissions, constituted both of odorous and non-odorous compounds [25–28].

In literature, some studies on gaseous emissions from pellet wood piles discuss many different reactions which can occur inside lignocellulosic biomass [25].

In the first ten days of storage, chemical processes predominantly occur, especially auto-oxidation of fatty acids that produce aldehydes, ketones, and carboxylic acids [29]. Eventually, auto-ignition of woody biomass [30,31], a strongly undesirable reaction to safety concerns, calorific value loss and environmental impact [32], may occur.

Regarding biological processes, aerobic degradation takes place in two distinct stages. The first one is operated by mesophilic bacteria and rises temperature to 40 °C in a timespan of 2 ÷ 7 days. The second phase is the thermophilic one, during which temperature rises to over 70 °C in a time range from 10 days to 2 months [33,34]. At this temperature, any bacterial action is inhibited, therefore a temperature plateau is reached [35–37]. Anaerobic degradations occur mainly in the centre of the heap. They are responsible for methane production, which can be oxidized by methanotrophic bacteria before reaching the heap surface [38].

According to the literature, the most abundant VOCs molecules emitted from wood heaps storage are aldehydes, due to the oxidation reaction of unsaturated fatty acids, particularly hexanal is the main product of linoleic acid oxidation (it accounts for about 80 % of the aldehydes emitted) [25]. In addition to aldehydes, substantial emissions of monoterpenes are released from wood storage, especially pinene, carene, limonene, camphene, and terpinolene [39]. Furthermore, it is possible to detect emissions of carboxylic acids produced by hydrolysis of acetyl groups present in lignin and hemicellulose [39] as well as alcohols [40].

Despite the available literature studies, there is no clear knowledge about the intricate order and timing of chemical and biological processes

involved during the storage of woody biomass, especially in woodchip format (instead of the pellet) [25]. In addition, research on odorous emissions from wood chips storage is still unexplored.

Given the growing interest in industrial odor emissions, the increasing spread of lignocellulosic biomass for energy production, and considering that odor release from woody biomass has only been partially explored in the literature, the primary objective of the study is to assess the odor potential of wood chip piles. Besides this, the study aims to investigate the timing and the main peculiarities of the processes occurring inside biomass heaps, resulting in a better understanding of the phenomenology responsible for odor impact.

To do this, it is necessary to identify:

1. The phenomena potentially responsible for odor emissions;
2. The timing with which these phenomena occur;
3. The measurable chemical-physical parameters that influence these phenomena.

To achieve this goal, different experimental campaigns were conducted in an Italian thermal power plant. During each campaign, other chemical and physical parameters (e.g. heap temperature, CO concentration), in addition to odor concentration, were measured.

2. Material and methods

Four experimental campaigns were conducted in an Italian thermal power plant, during which gas samples and field data were collected. These campaigns have been distributed in different periods throughout the year (October 2021, March 2022, June 2022, and November 2022), to assess whether and how emissions change with the seasons, specifically in response to changes in environmental temperature.

The site of inspection is the outdoor raw material storage of a biomass thermal power plant (*PowerCrop*) placed in central Italy. In this plant, lignocellulosic biomass is stored in piles of thousands of tons (from 2'000 to 12'000 tons) with length and height of respectively about 20 ÷ 30 m and 5 m, for a storage time from 3 to 7 months. This timespan enables biomass to achieve the conditions required for chemical and biological processes, as mentioned in Section 1. After at least 100 days of storage, the lignocellulosic biomass is fed to the furnace based on energy demand.

Stored heaps are made up of woody elements shaped as chips, characterized by a typical dimension of 1 ÷ 10 cm. Before being stocked, wood chips have been subject to only trituration (no pre-heating and compacting), and their origin can be from forest, end of waste, orchard, or poplar woods. Forest-type wood represents the large majority of the stored raw material: it accounts for about 50–60 % of the total biomass storage.

Heaps differ from each other in terms of wood origin, void fraction, storage time, chip dimension, and humidity content. Heterogeneity can also be noticed on the same heap, especially in terms of superficial humidity, as shown in Fig. 1. A depiction of the sampling system is reported in Fig. 2.

Because of this, it becomes necessary to collect field data on multiple points per heap to get representative results.

2.1. On-field measurements

The variables measured directly on the field are:

- Surface temperature: measured on the upper surface of the heaps with a thermal camera Bosch GTC 400C Professional.
- Depth temperature: measured with two Stainless Steel immersion sondes equipped with a thermometer, used in parallel to reduce the probability to measure outliers. The instruments are Temperature immersion sonde Volta TMS 150/280 and Thermometer Hanna



Fig. 1. Picture of a biomass heap taken in March 2022: it is possible to discern visually smoking regions from dry ones.



Fig. 2. Gas sampling system employed during experimental campaigns.

Instruments K + thermocouple sonde HI766TR4. They have a length of respectively 1.5 m and 2 m, and a precision of ± 1 °C and ± 1.5 °C.

- Flue-gas concentration (CO, CO₂, NO, SO₂): measured with an electrochemical and NDIR analyser (MRU Optima 7). The signal produced is converted and expressed in *ppm*.

2.2. Sample gas collection

To estimate odor and chemical concentration, it is necessary to collect gaseous samples on the field to be analyzed in laboratory. Although wood chip heaps are not totally devoid of flow, they can be considered passive sources because of their outward flow lower than 30 m³/h/m², as standardized in EN13725, 2022. For such kinds of sources, the technique suggested by the American standard [41] for gas sampling is the flux chamber. This system comprises a hood that isolates a section of the heap surface from the surrounding atmosphere. A controlled flow of neutral air (200 L/h) is introduced into the chamber through a Teflon tube connected to a cylinder. The gas emitted from the wood heap mixes with the neutral air blown inside the chamber, helped by a small fan placed inside the hood. A depression created by a vacuum pump (Gilian GilAir Plus) allows this diluted gaseous mixture to exit from the chamber

and to enter a 12 L Nalophan™ bag.

2.3. Sensorial analysis of gas samples: dynamic olfactometry

Dynamic olfactometry is the standardized method [3,42] to quantify odor concentration. It entails presenting some subsequent diluted portions of the gas sample to an appropriately selected panel. The olfactometer dilutes the sample with neutral air (de-odorized and de-humidified air) and provides it to the panels in a monotone decreasing way, starting from a dilution ratio such that none of the panel can perceive any odor and continuing until each panel detects an odor different from the neutral air. After numerous iterations and statistical elaboration of the detection threshold data, the final result of dynamic olfactometry is the odor concentration of the sample [ou_E/m^3]: it represents the dilution level necessary for making the odor perceivable to 50 % of the panel members. For the present research, samples have been analyzed by dynamic olfactometry the morning after the sampling, assuring that the EN-13725:2022 standard's 30-h maximum sample storage is respected. The olfactometric analysis has been carried out in the Olfactometric Laboratory of the Department of Chemistry, Materials, and Chemical Engineering 'Giulio Natta' of Politecnico di Milano. The

olfactometer is an Ecoma Mod. TO8, equipped with four testing stations. The panel is composed of four trained experts according to their sensibility and repeatability criteria to a referring specie (n-butanol), which has an odor threshold of 40 ppb. To be selected as a panel member, n-butanol odor should be perceived at a concentration in the range of 20–80 ppb.

2.4. Chemical analysis of gaseous samples: FID, GC-FID, and GC-MS

Gas samples collected on the field have been chemically analyzed with instrumental techniques that allow identification and quantification of the main chemical molecules contained in gaseous emissions from wood chip heaps.

Chemical analysis was conducted by means of:

- FID Ratfish RS 55-T (Flame Ionization Detector): used to quantify Total Organic Carbon (TOC) expressed in mg_C/Nm^3 , in accordance with EN12619, 2013 [47].
- Gas-Chromatographer Agilent mod.8890 - Mass Spectrometer Agilent 5877B MSD (GC – MS): used to identify molecules.
- Gas-Chromatographer Agilent mod.8890 - Flame Ionization Detector (GC – FID): used to quantify single Volatile Organic Compounds (VOC).

3. Results and discussion

3.1. Surface heterogeneity of lignocellulosic biomass

Due to the extreme heterogeneity visible on the pile in terms of humidity and smoke emitted by the different portions of the same pile (Fig. 1), and to thoroughly characterize the odor potential of lignocellulosic biomass, the heap surface was classified as ‘dry’ or ‘smoking’. Dry regions are characterized by a substantial absence of superficial moisture and emitted smoke, whereas smoking areas are localized, and humid and emit a visible amount of smoke. This classification has been found to be in line with experimental findings, wherein the smoking regions were notably more emissive compared to the dry ones, as will be discussed in the following. The distribution of smoking spots varies from one heap to another. Some piles exhibit smoking regions that extend over a significant portion of their surface area, while in other heaps, these smoking regions are either limited or entirely absent. This different behavior appears to be attributable to the age of the heap. In fact, heaps that have been stored for more than 100 ÷ 150 days exhibit smoking regions in minority proportions.

3.2. Odor concentrations

In Fig. 3, odor concentrations (ou_E/m^3), measured on samples collected on dry (Fig. 3a) and smoking (Fig. 3b) regions, are reported as

a function of heaps storage time (days). It is worth noting that the smoking temporal trend (Fig. 3b) has a logarithmic scale on the y-axis.

The odor concentration on smoking regions is about one order of magnitude higher than that on dry regions, reaching values in the order of $10^5 \text{ ou}_E/\text{m}^3$. In addition, considering that most of dry odor concentration values are in the order of $10^2 \text{ ou}_E/\text{m}^3$, these areas seem not particularly significant as odor source. Furthermore, on smoking regions, odor emissions appear relevant in the first 100 days of storage and reach their maximum after 50 ÷ 80 days.

Since the odor concentration data on dry areas are 2 ÷ 3 orders of magnitude lower than smoking ones, it is reasonable to consider dry trends of no particular interest.

Further details regarding the odor concentration trend will be reported in Section 3.4.

Finally, no substantial differentiation of odor emissions according to wood type (forest, poplar, orchard, end of waste) was appreciated experimentally.

3.3. Influence of chemical and physical parameters on odor concentration

The goal of this experimental study is not only the evaluation of the odor potential of wood heaps, but also a more comprehensive understanding of the phenomenology occurring inside the heaps that leads to odor emissions. Therefore, the first step in data processing is to figure out whether some chemical and physical parameters, measured during the experimental campaigns or the subsequent chemical analysis, are correlated to odor concentration. Through this analysis, it becomes possible to make some hypotheses about the sequence of chemical and biological processes occurring within the biomass.

The estimation of the degree of correlation between two different parameters is done by computing the Pearson Correlation Index:

$$\rho_{x/y} = \text{Cov}_{x/y} / (\sigma_x \cdot \sigma_y) \quad (1)$$

$\rho_{x/y}$ is the Pearson Correlation Index between variables x and y, $\text{Cov}_{x/y}$ is the covariance of x with respect to y, $\sigma_{x,y}$ are the standard deviations.

$$\text{COV}_{x/y} = \frac{\sum_{i=1}^N (x_i - \bar{x}) \cdot (y_i - \bar{y})}{N} \quad (2)$$

x_i and y_i are the values of the variables ranging from $i = 1$ to $i = N$, \bar{x} and \bar{y} are the average values of x and y variables, N is the total number of x (or y) values.

Pearson Correlation Index can assume values between -1 and $+1$, with 1 indicating perfect direct correlation between the two variables, 0 indicating dissociation, and -1 perfect inverse correlation.

The correlation matrix (Table 1) shows that surface temperature, in-depth temperature, terpenes concentrations (limonene and terpinene), aldehydes and ketones concentrations (acetaldehyde and acetone), and

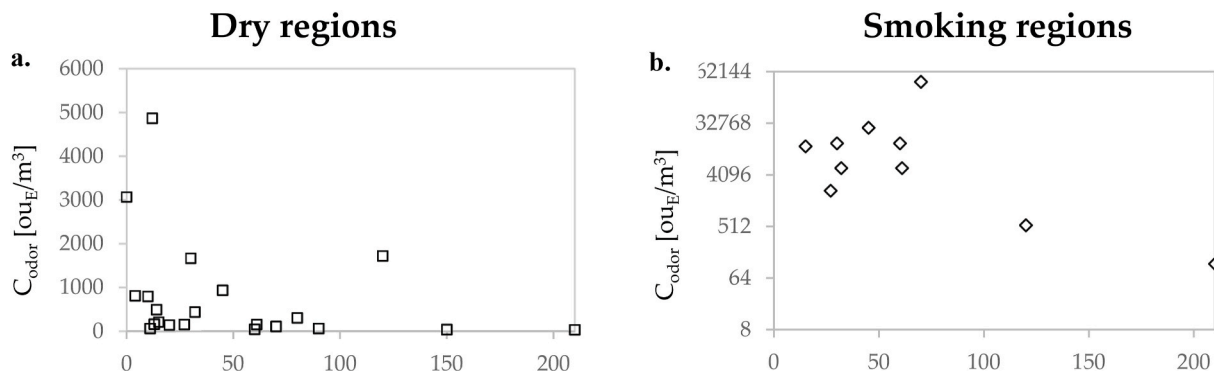


Fig. 3. Odor concentration (ou_E/m^3) trend over time corresponding to samples collected on dry regions (a) and smoking regions (b) during all the 4 experimental campaigns.

Table 1
Pearson Correlation Indexes computed among all the measured variables each other.

Correlation Index	C _{odor} [ou _E /m ³]	T _{surface} [°C]	T _{depth} [°C]	Acetaldehyde [mg/m ³]	Acetic acid [mg/m ³]	Acetone [mg/m ³]	CO [ppm]	Limonene [mg/m ³]	Terpinene [mg/m ³]	TOC [mg/Nm ³]	Heap age [days]	Initial heap mass [ton]
C _{odor} [ou _E /m ³]	1.00	0.50	0.46	0.90	0.12	0.89	0.98	0.51	0.57	0.13	0.04	0.21
T _{surface} [°C]	0.50	1.00	0.81	0.63	0.15	0.59	0.61	0.34	0.28	0.48	-0.15	0.00
T _{depth} [°C]	0.46	0.81	1.00	0.52	0.11	0.47	0.55	0.30	0.25	0.43	-0.29	0.04
Acetaldehyde [mg/m ³]	0.90	0.63	0.52	1.00	0.20	0.91	0.76	0.44	0.60	0.71	-0.10	-0.21
Acetic acid [mg/m ³]	0.12	0.15	0.11	0.20	1.00	0.08	0.00	-0.11	-0.08	-0.10	0.35	0.12
Acetone [mg/m ³]	0.89	0.59	0.47	0.91	0.08	1.00	0.72	0.52	0.47	0.68	-0.09	-0.21
CO [ppm]	0.98	0.61	0.55	0.76	0.00	0.72	1.00	0.34	0.32	0.16	0.03	0.19
Limonene [mg/m ³]	0.51	0.34	0.30	0.44	-0.11	0.52	0.34	1.00	0.51	0.80	-0.13	0.09
Terpinene [mg/m ³]	0.57	0.28	0.25	0.60	-0.08	0.47	0.32	0.51	1.00	0.84	-0.11	0.21
TOC [mg/Nm ³]	0.13	0.48	0.43	0.71	-0.10	0.68	0.16	0.80	0.84	1.00	-0.19	0.04
Heap age [days]	0.04	-0.15	-0.29	-0.21	0.12	-0.21	0.03	-0.13	-0.11	-0.19	1.00	0.34
Initial heap mass [ton]	0.21	0.00	0.04	-0.02	-0.19	-0.03	0.19	0.09	0.21	0.04	0.34	1.00

carbon monoxide concentration, have the best correlation with odor concentration. The corresponding correlation indexes are equal to 0.50 (T_{surface}), 0.46 (T_{depth}), 0.51 (limonene concentration), 0.57 (terpinene concentration), 0.90 (acetaldehyde concentration), 0.89 (acetone concentration), and 0.98 (CO concentration).

Contrary to what might be expected [25], TOC and heap mass at the beginning of biomass storage (ton) resulted independent from odor concentration (Table 1).

Regarding heap mass, the apparent lack of correlation with the other variables is likely because all the other monitored factors (e.g., terpenes, temperature), including odor concentration, were measured at the same storage time (i.e. when sample is collected). Conversely, the heap mass, which is measured at the beginning of storage, remains unaffected by the chemical and biological processes taking place within the pile during the storage period.

Regarding the absence of correlation between odor concentration and TOC, an explanation would be linked to the presence of methane: this molecule may be generated by wood piles, and despite it is odorless, it can be well detected by FID and considered in TOC quantification.

The variables most correlated with odor concentration have been analyzed in detail by plotting their trend as a function of storage time. Through their temporal trends (Figs. 4 and 6), it is possible to reach a better understanding of the phenomenology responsible for odor emissions, making some hypotheses about chemical and biological processes responsible for odorous emissions.

It is worth noting that the smoking trend of CO concentration (Fig. 4f) has a logarithmic scale on the y-axis, while all the others have a linear scale on the y-axis.

3.3.1. T_{surface} and T_{depth}

Concerning surface temperature, the difference between dry and smoking regions is significant. In Fig. 5 it is possible to recognize hot regions (smoking areas) and colder ones (dry areas) on the same heap surface.

Smoking regions have a surface temperature about 15 ÷ 30 °C higher than the temperature on dry regions of the same age. This difference is less noticeable during colder seasons and when considering in-depth temperature measurements, indicating that heterogeneity is a predominantly superficial and localized phenomenon. Surface temperatures reach their maximum after 30 ÷ 70 days of storage, when the temperature on the smoking areas may exceed 70 °C. This timing is in line with the time needed by bacteria to achieve their most enhanced activity in

the thermophilic phase, as reported in the scientific literature [25]. When the temperature exceeds 70 °C, the risk of spontaneous combustion increases, thus it is worth paying attention to smoking areas as areas where spontaneous combustion phenomena are more likely to occur [35].

Another aspect to take into account is the seasonality. During the third campaign (June), higher ambient temperature probably had an effect on the surface temperature, especially in dry areas where the surface temperature is naturally lower. As a result, temperatures measured on dry areas during the third campaign (◆) are clearly above the average. On the contrary, the intrinsically high surface temperature of smoking spots makes these regions less affected by the ambient temperature. Seasonality effect appears to have an influence also on odor concentration, as will be discussed in Section 3.4.

3.3.2. CO concentration

As suggested by the Pearson correlation index between CO and odor concentrations (0.98), the carbon monoxide trends (Fig. 4e and f) are consistent with odor concentration ones. Indeed, according to Ref. [25], CO is produced primarily by fatty acid oxidation, which releases also odorous species (e.g. acetaldehyde and butanone). The main difference between C_{odor} and CO trends can be observed on dry regions in the very first days of storage when terpenes emission occurs. As a result, due to the low odor threshold of these molecules, elevated odor concentrations can be detected at the beginning of the storage, as will be discussed in the following.

Moreover, the maximum production of CO occurs chronologically in response to elevated temperatures. The cause-and-effect relationship between temperature and CO is evidenced by the approximately 20-day delay in the CO emissions trend (Fig. 4f) compared to the temperature trend (Fig. 4b).

As for odor concentration, also CO concentrations are one order of magnitude higher on smoking regions (10² ppm) than in dry ones (10¹ ppm).

3.3.3. Terpenes concentrations

Wood resins contain terpenes, which are biomolecules whose most volatile fraction (light terpenes) has been largely detected in gaseous emissions from wood chips heaps [43,44].

Chemical analysis on gaseous samples revealed that the most emitted terpenes are limonene, terpinene, α-pinene, and β-pinene. Limonene and terpinene were chosen as “reference” molecules for the analysis of the

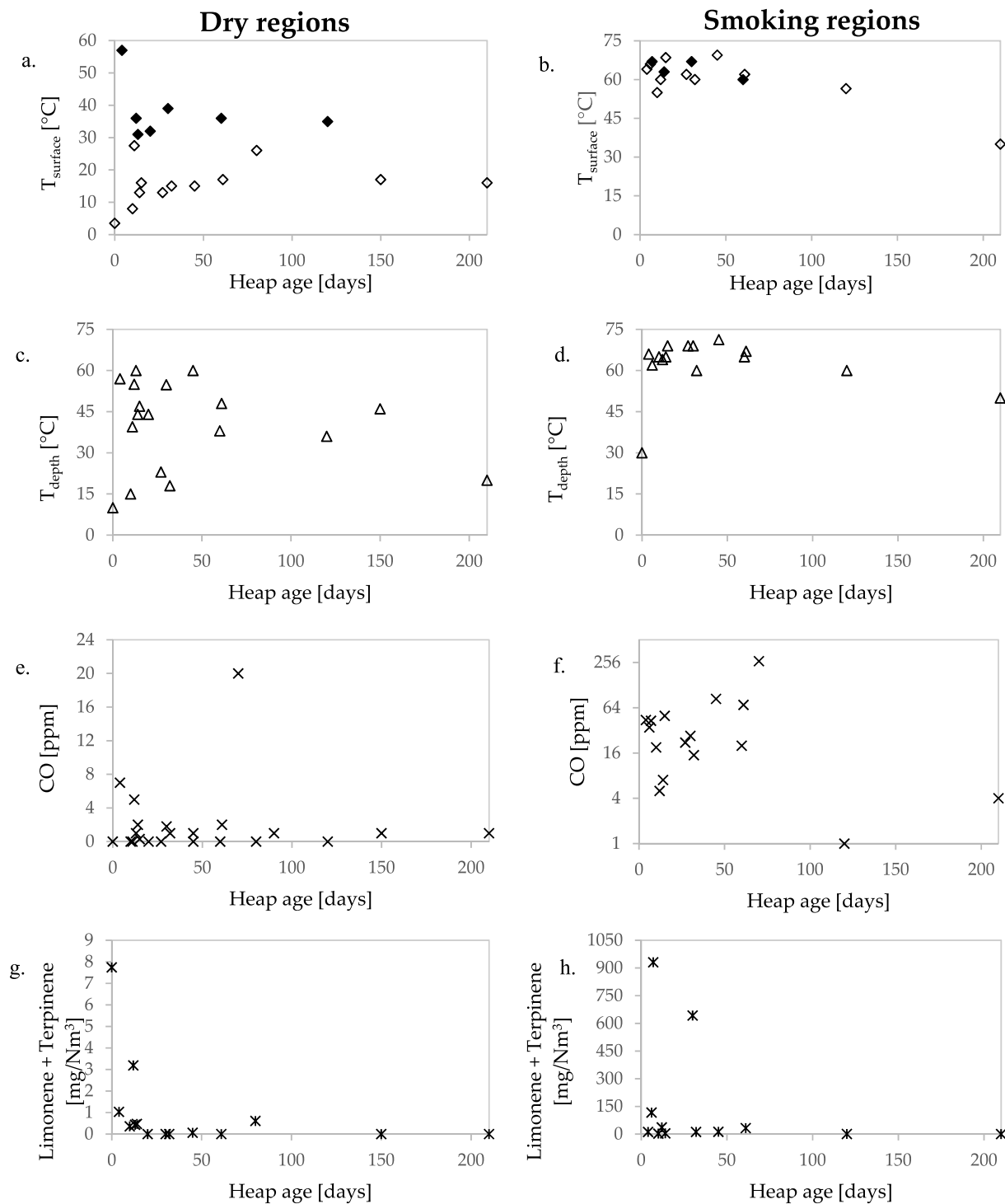


Fig. 4. Temporal trends for samples collected on dry regions (a, c, e, g) and smoking regions (b, d, f, h) of surface temperature (a, b) (\diamond), temperature in depth (c, d) (Δ), CO concentration (e, f) (\times), and Limonene + Terpinene concentrations (g, h) (*). In figures (a, b), (\blacklozenge) indicates samples collected during the campaign of June 2022, whereas (\diamond) indicates samples of the other 3 campaigns.

terpene's concentration trend over time because of their nearly constant relative ratio (limonene about 20 % of terpinene) as well as the fact that they are the most abundant terpenes in most samples.

As indicated by the existing literature, it has been experimentally verified that coniferous wood (referred to as forest wood in this study) emits significantly larger quantities of terpenes compared to broadleaf wood, regardless of the heap age [40]. Since terpene concentrations in broadleaves are negligible independently from heap age, plots in Fig. 4g and h take into account terpenes concentrations collected only on

coniferous wood heaps.

In addition, Fig. 4g and h demonstrate the greater order of magnitude of terpenes concentration emitted by smoking areas compared to dry regions, confirming the higher emissive potential of smoking areas, also in terms of terpenes.

One notable characteristic of the temporal trends in terpene concentrations is their nearly monotonous decrease over time, in contrast to all the other variables examined thus far, which exhibit a maximum over time. The reason is the different release mechanism of terpenes, which is

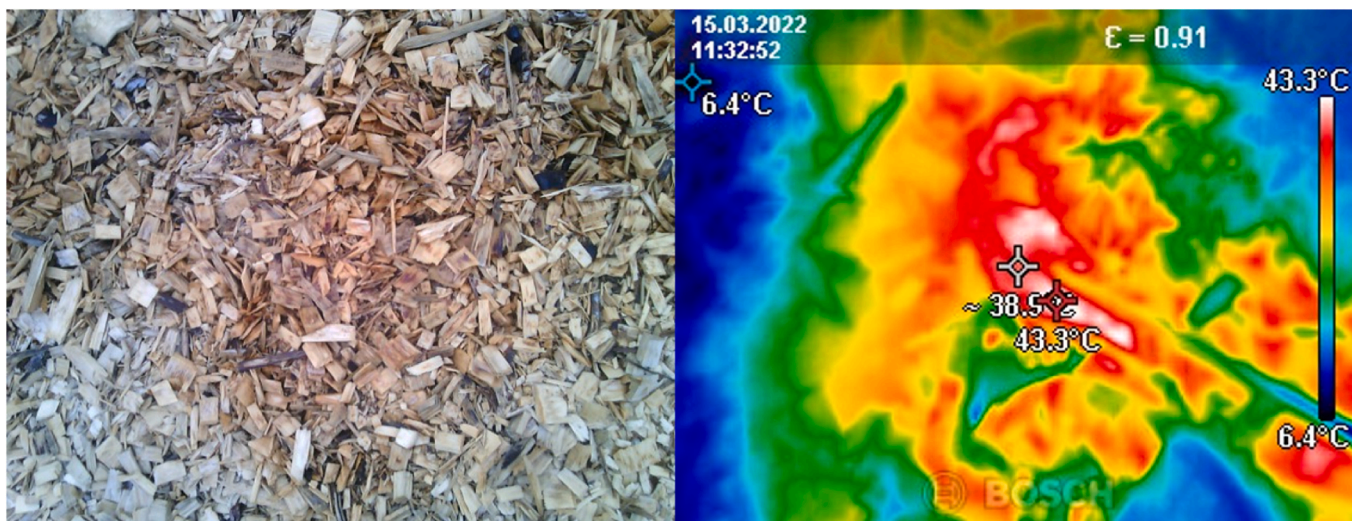


Fig. 5. On the left a picture of a portion of heap 2 collected during the second campaign (march 2022), on the right the same picture taken with thermal camera.

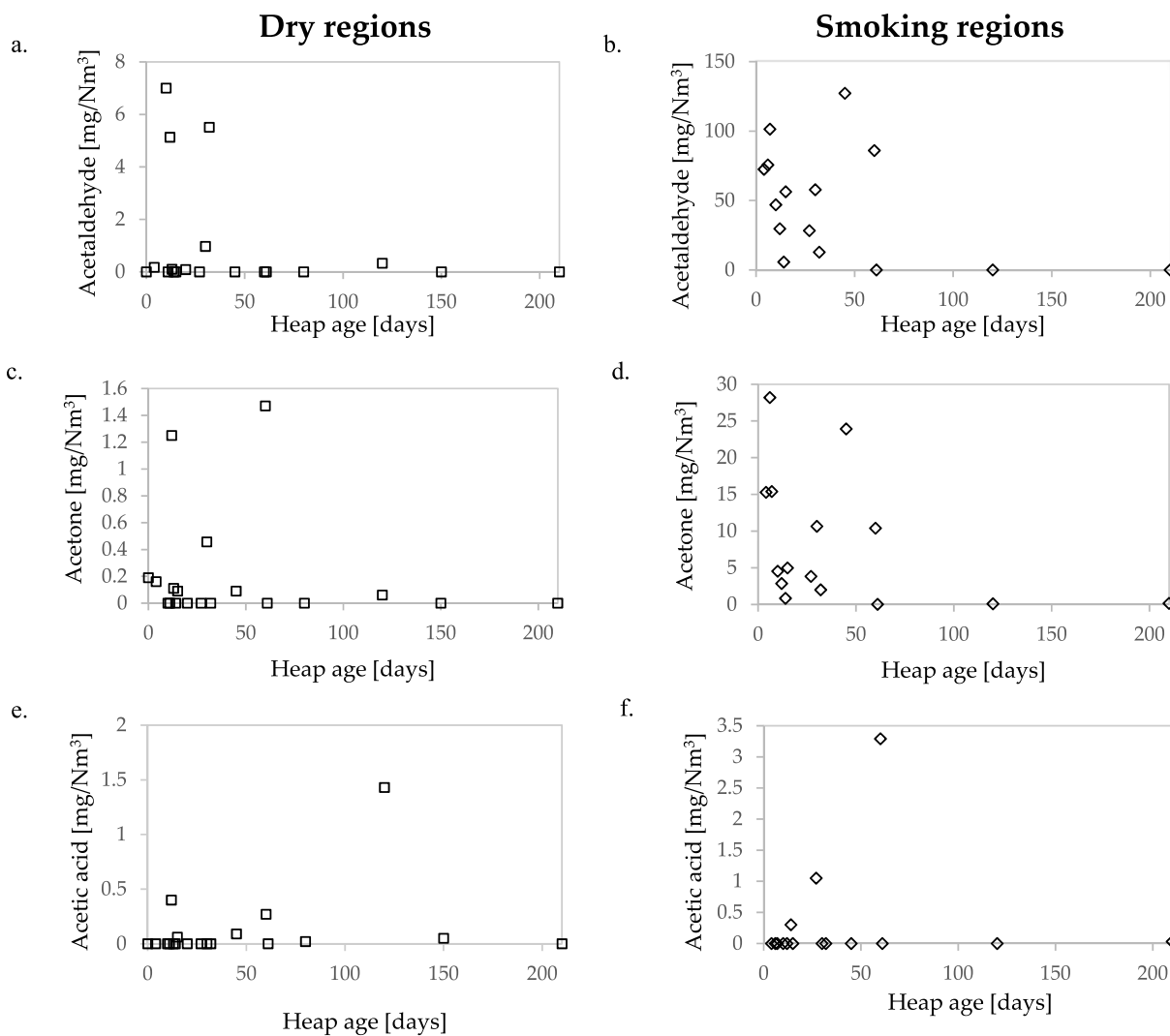


Fig. 6. Temporal trends of light oxygenates concentration (mg/Nm^3) detected on samples collected on dry regions (a, c, e) and smoking regions (b, d, f). Figures (a) and (b) refer to acetaldehyde, figures (c) and (d) refer to acetone, figures (e) and (f) refer to acetic acid.

a simple physical release in the atmosphere, different from all the other species which are chemically or biologically produced inside the biomass heaps. After roughly 40 ÷ 50 days, terpenes emissions can be considered negligible.

3.3.4. Light oxygenates concentrations

The other group of chemical molecules, besides the terpenes, which, according to their odor thresholds (OT) and Pearson Correlation Indexes, is expected to be the main contributor to the odor impact, are the light oxygenates. It is therefore noteworthy to study their evolution over time.

In this study aldehydes, ketones, and carboxylic acids are the main classes of light oxygenates detected in the emissions of lignocellulosic biomass heaps, in accordance with the literature [25,40,45].

As in the case of terpenes, a few reference molecules that are indicative of all light oxygenates emissions have been chosen, according to their frequency of detection by GC-MS. In detail, the selected reference molecules are acetaldehyde (OT = 0.0027 mg/m³) for aldehydes, acetone (OT = 99.8 mg/m³) for ketones, and acetic acid (OT = 0.015 mg/m³) for carboxylic acids [46]. Fig. 6 shows the temporal trends of concentration of these molecules, detected in gas samples collected both on dry regions and smoking regions.

Smoking regions consistently demonstrate significantly higher emissions compared to dry areas, even in the case of light oxygenates.

Regarding the concentration trends, aldehydes and ketones (Fig. 6a, b, 6c, 6d) show high concentration values in the first days of storage, when it is reasonable to expect fatty acids oxidation and therefore light oxygenates production [25]. An increase in concentration is also observed after 30 ÷ 80 days of storage, probably due to the increase in temperature, which kinetically promotes oxidation reactions and the transport to the surface.

Acetic acid (Fig. 6e and f) shows a slightly different trend, which does not have high values in the first days of storage, but only a concentration peak after 60 ÷ 120 days. The reason is most likely due to a different reaction that produces carboxylic acids, which is not the fatty acids oxidation, but the hydrolysis of acetyl groups (de-acetylation) present in b and hemicellulose [39].

The temporal trends of acetaldehyde and acetone suggest that aldehydes and ketones probably have the same formation processes. Furthermore, their Pearson Correlation Index, approximately 0.90, indicates that they can be considered as a substantial contributor to odor emissions. In contrast, acetic acid displays a distinct temporal evolution and a low Pearson Correlation Index (0.12), probably due to its different production process (de-acetylation).

3.4. Additional considerations on odor concentration

After the analysis of the temporal trends of heap temperatures, CO and terpenes concentrations, it is possible to make some additional considerations about the odor concentration trend over time.

Odor concentration exhibits high values in the first few days of storage due to the release in the atmosphere of light terpenes (e.g., terpinene and limonene) and due to the consumption of fatty acids immediately available to oxidation, as demonstrated by the decreasing trend of aldehydes and ketones (Fig. 6a and d). Odor concentration rises again after 50 ÷ 80 days of storage, as a result of rising temperature (a cause-effect mechanism), which kinetically promotes chemical reactions such as deacetylation, as demonstrated by the peak in acetic acid concentration after 50 ÷ 100 days.

However, after a storage period of about 100 ÷ 150 days, biomass odorless emission can be considered negligible on both dry and smoking areas.

Given the significant difference in odor concentration between smoking and dry regions (about 3 orders of magnitude), it is reasonable to consider dry regions almost a negligible emission source, both of odor and chemical species.

Since CO is well correlated with odor concentration,

Given the strong correlation between CO and odor concentration, it can be effectively used as an auxiliary parameter for monitoring odor emissions from wood heaps. This approach can significantly reduce the technical and economic challenges associated with odor monitoring. The effect of seasonality (fast drying of the biomass due to high ambient temperature) appears to be reflected also in a reduction of the smoking areas during hot seasons. The decrease of the humidity content of the heap looks to limit the bacteria activity, resulting in lower odor concentrations during summer season.

4. Final considerations and conclusions

The objective of this experimental work is to quantify the odor potential of lignocellulosic biomass storage, as well as to deepen the knowledge about the possible phenomenology responsible for odor emissions. It is reasonable to conclude that the obtained results corroborate most of the hypotheses made at the beginning of the experimental work, appearing consistent with the available scientific literature.

The initial finding of the study highlights the notable heterogeneity observed on the surface of the wood heap, which is characterized by distinct dry and smoking regions. These regions differ from each other in terms of surface humidity and the presence of visible smoke.

Gaseous emissions seem to be strictly related to surface heterogeneity: odor concentrations detected on smoking regions are significantly higher (10⁵ ou_E/m³) than concentration values estimated on dry areas (10² ou_E/m³). Therefore, from an emissive perspective, smoking areas can be regarded as more significant and worthy of attention than dry zones. In addition, heterogeneity appears to be an almost superficial phenomenon, indeed T_{depth} is more homogeneous between dry and smoking regions than T_{surface}.

The highest odor concentrations on dry regions were detected in the first days of storage (Fig. 3), when the wood is still rich in light terpenes, that are progressively released into the atmosphere. Terpenes are also emitted by smoking areas, but their influence on odor concentrations is less pronounced because of the high odor concentration values (160'000 ou_E/m³) detected a few days later on these areas due to light oxygenates emissions, which reduce the relative importance of the other peaks.

In addition to terpenes concentration and heap temperature, which, as previously discussed, influence the odor concentration trend, CO concentration exhibits a temporal evolution similar to odor concentration (Pearson Correlation Index 0.98). This is a result of the mechanisms that promote CO production leading to the emission of odor compounds too. Thanks to this strict correlation with odor concentration, CO appears to be an auxiliary expeditious parameter for monitoring odorous emissions.

Another relevant finding is that, unexpectedly, during summer season, emissions appear less relevant, regardless of the age of the heap. This phenomenon can be attributed to the high ambient temperatures, which facilitate rapid drying of the biomass, consequently reducing biological activity.

Although this study represents an important step forward in the assessment of odor potential of wood heaps, several future developments are possible to deeply characterize lignocellulosic biomass piles as complex odor sources.

First, it would be interesting to evaluate the effect of different meteorological conditions on odor emissions from wood heaps, for instance focusing on the wind convection phenomenon, or physical variables related to the lignocellulosic biomass, such as moisture content. The main future challenge may be the measurement of the extent of smoking areas, which is not trivial considering the surface heterogeneity of wood piles. Consequently, it would be possible to estimate the Odor Emission Rate (OER) of the wood piles, which represents the fundamental parameter to be implemented in atmospheric dispersion models to assess odor impact on citizens.

Funding

This research project is the result of a collaboration between the Olfactometric Laboratory of Politecnico di Milano and the company PowerCrop SpA.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We would like to thank all PowerCrop SpA staff for their kindness and valuable cooperation.

References

- [1] M.D. Kirk-smith, D.A. Booth, Chemoreception in human behaviour: experimental analysis of the social effects of fragrances, *Chem. Senses* 12 (1987) 159–166, <https://doi.org/10.1093/chemse/12.1.159>.
- [2] R. Hu, G. Liu, H. Zhang, H. Xue, X. Wang, P.K.S. Lam, Odor pollution due to industrial emission of volatile organic compounds: a case study in Hefei, China, *J. Clean. Prod.* (2020), <https://doi.org/10.1016/j.jclepro.2019.119075>.
- [3] Y. Wang, L. Shao, X. Kang, H. Zhang, F. Lü, P. He, A critical review on odor measurement and prediction, *J. Environ. Manag.* 336 (2023), 117651, <https://doi.org/10.1016/J.JENVMAN.2023.117651>.
- [4] S.S. Schiffman, C.M. Williams, Science of odor as a potential health issue, *J. Environ. Qual.* 34 (2005) 129–138.
- [5] M. Brancher, K.D. Griffiths, D. Franco, H. de Melo Lisboa, A review of odour impact criteria in selected countries around the world, *Chemosphere* 168 (2017) 1531–1570, <https://doi.org/10.1016/j.chemosphere.2016.11.160>.
- [6] C. Varela-Bruce, C. Antileo, Assessment of odour emissions by the use of a dispersion model in the context of the proposed new law in Chile, *J. Environ. Manag.* 295 (2021), 113208, <https://doi.org/10.1016/J.JENVMAN.2021.113208>.
- [7] M. Invernizzi, S. Sironi, Odour emission rate estimation methods for hydrocarbon storage tanks, *Chem. Eng. Trans.* 85 (2021) 67–72, <https://doi.org/10.3303/CET2185012>.
- [8] F. Tagliaferri, M. Invernizzi, S. Sironi, Experimental evaluation on liquid area sources: influence of wind velocity and temperature on the wind tunnel sampling of VOCs emissions from wastewater treatment plants, *Chemosphere* 312 (2023), 137337, <https://doi.org/10.1016/j.chemosphere.2022.137337>.
- [9] L. Capelli, S. Sironi, R. Del Rosso, P. Céntola, M. Il Grande, A comparative and critical evaluation of odour assessment methods on a landfill site, *Atmos. Environ.* 42 (2008) 7050–7058, <https://doi.org/10.1016/J.ATMOSENV.2008.06.009>.
- [10] F. Tagliaferri, M. Invernizzi, S. Sironi, L. Capelli, Influence of model parameters when simulating landfill odour emission, *Chem. Eng. Trans.* 85 (2021) 169–174, <https://doi.org/10.3303/CET2185029>.
- [11] F. Tagliaferri, M. Invernizzi, S. Sironi, L. Capelli, Influence of modelling choices on the results of landfill odour dispersion, *Detritus* 12 (2020) 92–99, <https://doi.org/10.31025/2611-4135/2020.13998>.
- [12] E. Huth, S. Paltrinieri, J. Thiele, Bioenergy and its effects on landscape aesthetics – a survey contrasting conventional and wild crop biomass production, *Biomass Bioenergy* 122 (2019) 313–321, <https://doi.org/10.1016/J.BIOMBIOE.2019.01.043>.
- [13] A.K. Vuppalladadiyam, S.S. Varsha Vuppalladadiyam, V.S. Sikarwar, E. Ahmad, K. K. Pant, M. S. A. Pandey, S. Bhattacharya, A. Sarmah, S.-Y. Leu, A critical review on biomass pyrolysis: reaction mechanisms, process modeling and potential challenges, *J. Energy Inst.* 108 (2023), 101236, <https://doi.org/10.1016/j.joei.2023.101236>.
- [14] J.R.C. European Commission, *Brief on Biomass for Energy in the European Union*, 2019.
- [15] *EurObserv'Er, Biofuels Barometer 2018*, 2018.
- [16] Scarlet Nicolae, Dallemand Jean-Francois, Nigel Taylor, Banja Manjola, Sanchez Lopez Javier, Avraamides Marios, *Brief on Biomass for Energy in the European Union | EU Science Hub, EC Publ.*, 2019, 1–8.
- [17] R.S. Gse, *Energia da fonti rinnovabili in Italia - Rapporto Statistico, GSE*, 2021.
- [18] Evonat, *Esempio cogenerazione cippato 50 kw: costi e benefici Dettaglio dei costi, Eng. Procure. Constr.* (2016) 1–11.
- [19] M. Costa, D. Piazzullo, D. Di Battista, A. De Vita, Sustainability assessment of the whole biomass-to-energy chain of a combined heat and power plant based on biomass gasification: biomass supply chain management and life cycle assessment, *J. Environ. Manag.* 317 (2022), 115434, <https://doi.org/10.1016/J.JENVMAN.2022.115434>.
- [20] A. Kumar, Anushree, J. Kumar, T. Bhaskar, Utilization of lignin: a sustainable and eco-friendly approach, *J. Energy Inst.* 93 (2020) 235–271, <https://doi.org/10.1016/j.joei.2019.03.005>.
- [21] P. Yadav, D. Athanassiadis, D.M.M. Yacout, M. Tysklind, V.K.K. Upadhyayula, Environmental impact and environmental cost assessment of methanol production from wood biomass, *Environ. Pollut.* 265 (2020), 114990, <https://doi.org/10.1016/j.envpol.2020.114990>.
- [22] R. Pedersini, *Representativeness of the European Social Partner Organisations: Sea Fisheries* 1–62, 2012.
- [23] M. Palmero-Iniesta, J. Pino, L. Pesquer, J.M. Espelta, Recent forest area increase in Europe: expanding and regenerating forests differ in their regional patterns, drivers and productivity trends, *Eur. J. For. Res.* 140 (2021) 793–805, <https://doi.org/10.1007/s10342-021-01366-z>.
- [24] X. He, A.K. Lau, S. Sokhansanj, Effect of moisture on gas emissions from stored woody biomass, *Energies* 13 (2019), <https://doi.org/10.3390/en13010128>.
- [25] E. Alakoski, M. Jämsén, D. Agar, E. Tampio, M. Withersaari, From wood pellets to wood chips, risks of degradation and emissions from the storage of woody biomass - a short review, *Renew. Sustain. Energy Rev.* 54 (2016) 376–383, <https://doi.org/10.1016/j.rser.2015.10.021>.
- [26] L. Eriksson, L. Gustavsson, Comparative analysis of wood chips and bundles - costs, carbon dioxide emissions, dry-matter losses and allergic reactions, *Biomass Bioenergy* 34 (2010) 82–90, <https://doi.org/10.1016/j.biombioe.2009.10.002>.
- [27] E. Polvara, E. Gallego, M. Invernizzi, J.F. Perales, S. Sironi, Chemical characterization of odorous emissions: a comparative performance study of different sampling methods, *Talanta* 253 (2023), <https://doi.org/10.1016/j.talanta.2022.124110>.
- [28] F. Tagliaferri, F. Panzeri, M. Invernizzi, S. Sironi, Challenges in characterization of odour emissions from wood chip storage, *Chem. Eng. Trans.* 95 (2022) 115–120, <https://doi.org/10.3303/CET2295020>.
- [29] M.Z.M. Salem, M. Böhm, Understanding of formaldehyde emissions from solid wood: an overview, *Bioresources* 8 (2013) 4775–4790, <https://doi.org/10.15376/biores.8.3.4775-4790>.
- [30] F. Ferrero, C. Lohrer, B.M. Schmidt, M. Noll, M. Malow, A mathematical model to predict the heating-up of large-scale wood piles, *J. Loss Prev. Process. Ind.* 22 (2009) 439–448, <https://doi.org/10.1016/j.jlp.2009.02.009>.
- [31] J.Y. Yeo, B.L.F. Chin, J.K. Tan, Y.S. Loh, Comparative studies on the pyrolysis of cellulose, hemicellulose, and lignin based on combined kinetics, *J. Energy Inst.* 92 (2019) 27–37, <https://doi.org/10.1016/j.joei.2017.12.003>.
- [32] C. Whittaker, N. Yates, I. Shield, *STREAMLINING THE SUPPLY CHAIN : GREENHOUSE GAS EMISSIONS AND DRY MATTER LOSSES Rothamsted Research : Role in Supergen*, 2014.
- [33] G. Holighaus, N.F. Versuchsanstalt, P. Thakeew, Wood production, wood technology, and biotechnological impacts, *Wood Prod. Wood Technol. Biotechnol. Impacts* (2017), <https://doi.org/10.17875/gup2007-262>.
- [34] S.G. Sommer, H.B. Møller, Emission of greenhouse gases during composting of deep litter from pig production - effect of straw content, *J. Agric. Sci.* 134 (2000) 327–335, <https://doi.org/10.1017/S0021859699007625>.
- [35] E. Anerud, G. Larsson, L. Eliasson, Storage of wood chips: effect of chip size on storage properties, *Croat. J. For. Eng.* 41 (2020) 277–286, <https://doi.org/10.5552/crojfe.2020.663>.
- [36] A.H. Bedane, M.T. Afzal, S. Sokhansanj, Simulation of temperature and moisture changes during storage of woody biomass owing to weather variability, *Biomass Bioenergy* 35 (2011) 3147–3151, <https://doi.org/10.1016/j.biombioe.2011.04.008>.
- [37] S.M. Tiquia, N.F.Y. Tam, I.J. Hodgkiss, Composting of spent pig litter at different seasonal temperatures in subtropical climate, *Environ. Pollut.* 98 (1997) 97–104, [https://doi.org/10.1016/S0269-7491\(97\)00116-4](https://doi.org/10.1016/S0269-7491(97)00116-4).
- [38] X. Kuang, T.J. Shankar, X.T. Bi, S. Sokhansanj, C. Jim Lim, S. Melin, Characterization and kinetics study of off-gas emissions from stored wood pellets, *Ann. Oper. Hyg.* 52 (2008) 675–683, <https://doi.org/10.1093/annhyg/men053>.
- [39] F. Bulian, *Le emissioni di sostanze organiche volatili dal legno e dai suoi derivati* 1–4, 2021.
- [40] M. Czajka, B. Fabisiak, E. Fabisiak, Emission of volatile organic compounds from heartwood and sapwood of selected coniferous species, *Forests* 11, <https://doi.org/10.3390/f11010092>.
- [41] US EPA, *Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber, User's Guide*, 1986, <https://doi.org/10.1080/10473289.1992.10467102>.
- [42] *En, EN13725:2022 - Stationary Source Emissions - Determination of Odour Concentration by Dynamic Olfactometry and Odour Emission Rate*, 2022.
- [43] F. Bulian, C. Fragassa, VOC Emissions from Wood Products and Furniture : a Survey about Legislation , Standards and Measures Referred to Different Materials VOC Emissions from Wood Products and Furniture : a Survey about Legislation , Standards and Measures Referred to Different, 2016, <https://doi.org/10.5937/fmet1604358B>.
- [44] A.M. Strömvall, G. Petersson, Monoterpenes emitted to air from industrial barking of Scandinavian conifers, *Environ. Pollut.* 79 (1993) 215–218, [https://doi.org/10.1016/0269-7491\(93\)90092-3](https://doi.org/10.1016/0269-7491(93)90092-3).
- [45] P. Bengtsson, M. Sanati, Evaluation of hydrocarbon emissions from heart- and sapwood of Scots pine using a laboratory-scale wood drier, *Holzforchung* 58 (2004) 660–665, <https://doi.org/10.1515/HF.2004.120>.
- [46] Y. Nagata, *Measurement of odor threshold by triangle odor bag method, Odor Meas. Rev.* 118–127 (2003).
- [47] *En, Stationary Source Emissions - Determination of the Mass Concentration of Total Gaseous Organic Carbon - Continuous Flame Ionisation Detector Method*, 2013, p. EN12619, <https://doi.org/10.31030/1907768>.