Chemical characterization of odorous emissions: A comparative performance study of different sampling methods

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ABSTRACT

A comparison among different sampling methods (3 types of sorbent tubes and polymeric bags) commonly adopted in chemical analyses of odorous emissions was performed. To investigate the different performances, a lignocellulosic biomass storage plant was selected to obtain preliminary information about the chemical nature of odorous emissions. Samples of odorous emissions were collected at different biomass piles and analysed by dynamic olfactometry and TD-GC-MS. By comparing the two adopted sampling methods (tubes and bags), different performances are shown, depending on their specificity. By the comparison among the three types of sorbent tubes (*Multi-sorbent bed (Carbotrap, Carbopack X and Carboxen 569)*, *Tenax* and *Sulphur*), Sulphur and Multi-sorbent bed present similar performance, while Tenax TA tubes show a different trend in terms of type and numerosity of detected compounds. In addition, from the comparison between tubes and polymeric bags, the number and types of compounds detected in bags are more comparable to those observed in the Multi-sorbent bed and Sulphur tubes. However, a difference between the two methods appears, especially in the detection of low-molecular weight organic compounds. In this study, it is possible to highlight that, due to the complexity of odorous emissions, the selection of the sampling material may affect the obtained chemical results. The detection of different classes of compounds, is a crucial point, to obtaining the most complete characterization of mixtures and comparing the chemical profile with olfactometric results: care must be taken in the choice of sampling material and procedure.

1. Introduction

Analysis of volatile organic compounds (VOCs) present in industrial/waste odorous emissions has become an increasingly studied topic due to their possible impact on human health [1–8]. An increasing number of industrial/waste management activities are subject to odour emission monitoring. Therefore, at the regulatory level, often it is necessary not only to quantify the olfactory nuisance, using sensorial analysis (e.g. dynamic olfactometry), but also to chemically characterise these emissions, to evaluate, by knowing the chemicals present in odours and their concentrations, the molecules responsible for the odour harassment and their potential impact on citizens' and workers' health [9–13]. Indeed, odour can be correlated with odour-related symptoms, such as irritation, pain, headaches, eyes irritation and unusual tiredness [14,15], or health effects related to the odorous and hazardous compounds potentially contained in the odorous emissions [16]: so knowing the chemical composition is fundamental to investigate the potential health effects associated with odorous emissions. However, the characterization of VOCs in odorous emissions is particularly complex due to the variety of compounds potentially present, both in terms of quality (compounds with dissimilar characteristics, belonging to different family groups) and quantity (from ppt to volume percentage) [17–21]. In particular, compounds characterized by a non-negligible odour impact (i.e. low odour threshold, OT) can be present in the emissions in very low concentrations (*ppb* or *ppt* range) [22,23]. To obtain information about chemical composition of odorous emissions, chemical analysis, in particular using gas chromatography (GC) coupled with mass spectrometry (MS), can be conducted [24–26]. This technique allows the separation and the identification of compounds present in the odorous mixtures: knowing the compounds present in odorous gasses is useful to identify the best techniques to reduce them during the storage of the biomass. In addition, the identification of compounds can be useful to recognise

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compounds that could have a higher OT than their limit of exposure [27, 28]. However, due to the complexity of the odour matrix, different techniques and approaches to sample and chemically analyse odorous emissions exist [22,29–32]. Focusing on sampling and analysis of odorous emissions, even though passive sampling techniques such as SPME or IR instruments are also used [33–35], three methodologies are mainly adopted: sorbent tubes, stainless steel canisters and polymeric bags. These three methods differ in portability, applicability, sampling volumes and storage of samples. Focusing on storage time, canisters and tubes allow maintenance for longer times (up to 30 days), while bags can be stored for a shorter period, mainly due to the diffusion phenomena [36–39]. Although, canisters are voluminous, heavy and high operative costs are correlated with the cleaning procedures [40]. Sorbent tubes and sampling bags are cheaper, more practical and easier to use [17,41]. Discussing the analysis of odour emissions, the use of odourless sample containers, in particular polymeric bags, is prescribed by the standard regarding the quantification of odour concentration by dynamic olfactometry (EN 13725:2022) [42]. Therefore, this study aims to compare the performance of different sampling methods, commonly adopted in the analysis of odorous emissions, in particular polymeric bags and different sorbent tubes, by applying them to the monitoring of industrial odorous emissions.

The scenario adopted to conduct this comparison was a lignocellulosic biomass storage plant. The energy valorisation of biomass has progressively increased in recent years, mainly due to the need to find alternative sources to fossil fuels [43,44]. However, during the storage of biomass, several reactions (both chemical and biological) occur, leading to the development of compounds, particularly VOCs, which have a non-negligible odour impact (e.g. aldehydes, terpenes, carboxylic acids) [45,46]. For these reasons, the monitoring of odorous emissions from these plants, both in terms of odour concentration and chemical composition, is fundamental to controlling the impact of these emissions on the surrounding area. However, the emission of VOCs from these plants is not fully explored in the literature. Therefore, this study aims to compare the performance of two sampling methods (polymeric sampling bags and different sorbent tubes) if applied to real odorous samples. In particular, the case study considered in this paper is a biomass storage plant, for which odorous emissions were sampled to perform a preliminary assessment of the chemical composition of this class of plant.

2. Materials and methods

2.1. Sampling procedure

A monitoring campaign was conducted in a lignocellulosic biomass storage plant. The plant is surrounded by agricultural land and it stores only untreated wood, in form of "wood chips" divided into different piles, according to their origin (Fig. 1).

To obtain preliminary information about the VOCs and odour emissions of these sources, the sampling was conducted only on two piles, composed of the same wood (forest mix) and characterized by different ageing of the wood (piles A and B), and on a pile of corn silage (pile C). Table 1 reports the characteristics of the piles sampled.

Both piles A and B were sampled at two different points: "dry zone" and "wet zone", according to the different humidity of wood materials. Contrarily, the surface of pile C (corn silage) appeared homogeneous and therefore it was not necessary to collect different samples. The samples were collected using a flux chamber (Fig. 2): the instrumentation was placed above the evaluated piles (Fig. 2). The air flux set during the sampling was 200 L/h. The gas emitted was collected inside Nalophan™ bags, using a vacuum pump, and subsequently analysed. This material respects the recommendation of European legislation on the determination of odour concentration [47]: Nalophan™ is odourless and characterized by a low permeability to VOCs [48].
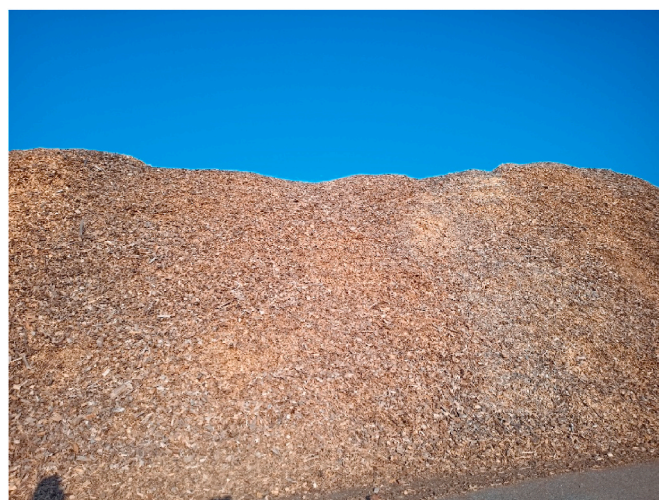

Fig. 1. Woodpile.

Table 1
Description of the piles sampled.

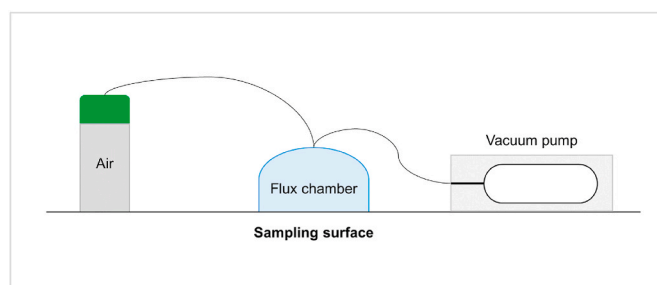| Pile	Materials	Pile ageing
A	Forest mix – wood chips	6 weeks (young pile)
B	Forest mix – wood chips	15 weeks (old pile)
C	Corn silage	–

Fig. 2. Diagram of the sampling method.

2.2. Analyses

The gaseous samples were analysed by dynamic olfactometry and chemical analysis, using Gas chromatography-mass spectrometry (GC-MS), to obtain the complete characterization of piles' emissions. In particular, for chemical analysis, two different sampling procedures were followed:

1. Bags sampled directly in field;
2. Sorbent tubes, into which the sampled emission in the bags was adsorbed. Three different sorbent tubes were adopted during the study to compare the suitability of the different adsorbing materials for VOCs sampling. Their characteristics will be discussed in the next section (GC-MS analysis – sorbent tubes).

Discussing the transferring of gaseous emissions from sampling bags to sorbent tubes was evaluated in a previous study [49]. According to previous results (good recovery values up to 2 days after sampling in bags), in this study the trespass from bags to sorbent tubes was performed in the laboratory the day after sampling (<24 h).

As described below (section GC-MS analysis – polymeric bags and GC-MS analysis – sorbent tubes), both types of samples were subsequently analysed by GC-MS analysis to identify the specific compounds

present in the air samples collected.

2.3. Dynamic olfactometry

Dynamic olfactometry allows quantifying odour concentration (C$_{od}$) of gaseous emissions. Odour concentration is expressed in terms of European odour units per cubic metre (ou$_E$/m^3) and, according to the standard, it is defined as the number of times the air sample is diluted with neutral air before the odour of the sample is no longer perceivable [42]. The determination of odour concentrations is conducted, at increasing concentrations, by a panel of selected examiners. The dilutions are performed by an olfactometer. In this specific, the olfactometric analyses were conducted using an olfactometer (TO8, Ecoma GmbH) based on the "yes/no" method. The panel involved were selected through tests of olfactory sensitivity, according to the criteria prescribed by the standard [42].

2.4. GC-MS analysis – polymeric bags

The emissions collected in the Nalophan™ bags were analysed by using a gas-chromatographer coupled with a mass spectrometer (GC-MS), equipped with a thermal desorber (TD). The study was performed using a capillary gas chromatograph (Agilent 8890 GC)/mass spectrometry (Agilent 5977B MSD). The air was collected directly from the bag, using a calibrated pump (Markes, Air Server-xr) and directly sent to thermal desorption (Markes, Unity-xr). After the sampling of the gas from the bag, the gas was sent to a cryofocusing trap maintained at −27 °C. After this step, the cold trap was rapidly heated from −27 °C to 300 °C. After this step, the compounds were transferred by hot transfer line (200 °C) onto the capillary column (DB-Sulphur SCD, 60 m × 0.320 mm × 4.20 μm, provided by Agilent J&W, Folsom, CA, USA). The column oven temperature started at 40 °C for 1 min, increased to 230 °C at a rate of 6 °C min^{-1} and then maintained at 230 °C for 5 min. Mass spectral data were acquired over a mass range of 45–350 u. Helium was used as the carrier gas with a flow rate of 5 mL min^{-1}. The identification of the VOCs was carried out by comparing the spectra with the NIST20 database (NIST/EPA/NIH Mass Spectral Library, Version 2.4 Mar 25, 2020).

2.5. GC-MS analysis – sorbent tubes

The analysis of sorbent tubes was conducted using three different tubes types:

1. Multi-sorbent bed (Carbotrap 20/40, 70 mg; Carbopack X 40/60, 100 mg and Carboxen 569 20/45, 90 mg), obtained from Supelco (Bellefonte, PA, USA), achieved as described in Ref. [31] and called as *Multi-sorbent bed* in the text;
2. Tenax TA, obtained from Supelco (60/80, 200 mg, obtained from Supelco (Bellefonte, PA, USA)) and defined as *Tenax* in the text;
3. Tubes specific for sulphur and odorous compounds (Markes International Ltd., UK) defined as *Sulphur* in the text

Tubes were analysed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry (MS), using a Markes UNITY–ULTRA-xr and an Agilent 8890 GC coupled

with an Agilent 5977 MSD. The methodology is described in other papers [31,50]. Briefly, thermal desorption of the sampling tubes was conducted at 300 °C with a flow rate of 53 mL min^{-1} for 10 min (primary desorption), during which time the eluted compounds were swept from the tube to a cryofocusing trap maintained at −30 °C, applying a flow split of 11 mL min^{-1}. After the first desorption, the cold trap was rapidly heated from −30 °C to 300 °C (secondary desorption) and then maintained at this temperature for 10 min. During the secondary desorption, the compounds were submitted to a flow split of 11 mL min^{-1} and were injected onto the capillary column (DB-624, 60 m × 0.30 mm × 1.8 μm, provided by J&W, Folsom, CA, USA) via a transfer line heated at 200 °C. The column oven temperature program was the same as described in section GC-MS analysis – polymeric bags. Helium carrier gas flow in the analytical column was 1.8 mL min^{-1}. Mass spectral data were acquired over a mass range of 30–300 u. The identification of the VOCs was carried out by comparing the spectra with the NIST20 database (NIST/EPA/NIH Mass Spectral Library, Version 2.4 Mar 25, 2020).

3. Results

The results obtained for the five samples collected are shown below, divided by the techniques adopted. The result will be discussed in the Discussion.

3.1. Odour concentration

In Table 2, the odour concentration and the relative uncertainty interval (evaluated according to Ref. [42]) of all the samples collected are reported.

3.2. GC-MS analysis – bags and sorbent tubes: qualitative information

Table 3 reports the compounds detected by GC-MS analysis in the investigated samples, divided according to the different sampling types (Nalophan™ bags and sorbent tubes (Multi-sorbent bed, Tenax and Sulphur)). Table 3 also shows the value of odour threshold (OT) from Refs. [51,52] and the occupational exposure limit defined by European Community for long-term exposure (8 h), available in GESTIS database - International limit values for chemical agents [53]. The EU OEL values were selected due to their legal value at international level, as described in Refs. [16,54].

In Fig. 3, the total number of compounds observed for the different sampling points according to the sampling method used is shown.

4. Discussion

From the results illustrated in Results, it is possible to observe a general distinction between the different investigated sampling and analysis strategies. About the wood chips piles, it can be observed that the wet zones appear to have a higher emissive potential than the dry ones, both in terms of odour and the presence of VOCs. In addition, from the comparison between the two wood piles (A, young pile and B, old pile) it appears that the ageing of the wood materials can influence the emission potential: the old pile (B) presents higher values of odour concentration and VOCs than the young one (A), for both wet and dry areas. These differences may be due to the development of different

Table 2
Odour concentration of samples analysed.

Sampling area/location	Odour concentration [ou$_E$/m^3]	Uncertainty interval 95% [ou$_E$/m^3]
A – *dry zone, young pile*	91	40 ÷ 170
A - *wet zone, young pile*	1100	500 ÷ 2100
B - *dry zone, old pile*	300	130 ÷ 560
B - *wet zone, old pile*	350,000	150,000 ÷ 640,000
C	140,000	61,000 ÷ 250,000

Table 3
Compounds identified (highlighted with ●) from GC-MS analysis of emissions (tubes and bag). The results are divided by sampling point and sampling method considered: bag, or tube: M. = Multi-sorbent bed tubes, T. = Tenax tubes, S. = Sulphur tubes. Compounds are listed in elution order, using retention time (RT) observed for each sample type.

Compound	OT [mg/m^3]	EU OEL – 8 h [mg/m^3]	RT Tubes	RT Bag	A-dry M	A-dry T	A-dry S	A-dry Bag	A-wet M	A-wet T	A-wet S	A-wet Bag	B-dry M	B-dry T	B-dry S	B-dry Bag	B-wet M	B-wet T	B-wet S	B-wet Bag	C M	C T	C S	C Bag
2-Butene	4.8 [a]	N.D.		4.2																●				
Methyl Alcohol	43.2 [b]	260	4.7		●	●	●		●	●	●		●	●	●		●	●	●	●	●	●	●	
Methyl formate	319 [b]	125	4.9	4.5												●	●	●	●	●				
Trichloromonofluoromethane			5.5														●							
Propanal	0.002 [b]			5.7				●												●				●
Ethanol	1.0 [b]		5.7		●	●	●		●	●	●		●	●	●		●	●	●	●	●	●	●	
Furan	27.6 [b]		5.9	6.1									●	●										
3-Butyn-2-amine, 2-methyl-		N.D.		6.2													●							
1,3-Propanediol		N.D.	6.2																		●	●		
Acetone	99.8 [b]	1210	6.3	5.6												●	●	●	●	●				
Isopropyl Alcohol	63.9 [b]	N.D.	6.4			●				●											●	●		
Dimethyl sulfide	0.008 [b]	N.D.	6.4																		●	●		
Acetic acid, methyl ester	5.2 [b]	N.D.	6.8	6.7													●	●	●	●	●	●	●	●
Cyclopentane		N.D.	7.1														●							
4-Aminoheptane		N.D.		7.5													●							●
Butanal	0.002 [b]	N.D.	7.6														●							
1-Propanol	0.2 [b]	N.D.	8.1																		●	●	●	
2,3-Butanedione	0.0002 [b]	0.07		8.2																●				
Ethene, ethoxy-		N.D.	8.8															●						
2-Butanone	1.3 [b]	600	8.9														●	●						
Ethyl Acetate	3.1 [b]	734	9	9																	●	●	●	●
Methyl propionate	0.4		9.4	9.4																	●	●	●	●
Butanal, 2-ethyl-				10												●								
Butanal, 3-methyl-	0.0004 [b]	N.D.	10.5	10.5													●	●	●	●			●	●
Butanal, 2-methyl-				10.9													●							●
Acetic acid	0.02 [b]	25	11		●	●	●		●	●	●		●	●	●		●	●	●		●	●	●	
Benzene	8.6 [b]	3.25		11.3						●														
Propanoic acid, ethyl ester	0.03 [b]		11.9																		●	●	●	
n-Propyl acetate	1.0 [b]	N.D.	12	12.5																	●	●	●	●
p-Xylene	0.3 [b]	221	14.9							●			●											
Toluene	1.2 [b]	192	15							●					●									
Propanoic acid, propyl ester	0.3 [b]	N.D.	15	15.1																	●	●	●	●
Hexanal	0.001 [b]	N.D.		15.5													●							
Pyrimidine, 4-methyl-		N.D.	16						●															
Pyrazine, methyl-	2 [a]		16.1						●				●				●							
Cyclopentene, 1-ethenyl-3-methylene-		N.D.	16.3								●			●										
2,4-Hexadien-1-ol	0.8 [a]		16.6														●							
Furfural	2.8 [a]	N.D.	17.2						●				●				●	●	●		●			
1-Butanol, 3-methyl-, acetate	1.95 [a]	270		18.1																				●
Ethylbenzene	0.7 [b]	442		18.3									●											
o-Xylene	1.7 [b]	221		18.5									●											
α-Pinene	0.1 [b]	N.D.	18.8							●							●							
Camphene	26 [a]		19.5	21.7						●				●			●	●	●					
1-Pentanol, 2-methyl-, acetate				20.1																	●		●	
Octanal	0.0001 [b]		20.1																				●	
β-Phellandrene			20.2						●															
β-Pinene	0.2 [b]	N.D.	20.3						●				●				●							
Acetic acid, hexyl ester	0.01 [b]	N.D.		21.1																				●
ᴅ-Limonene	0.2 [b]	N.D.	21.1	23.8	●	●	●		●	●	●		●	●	●		●	●	●	●	●	●	●	
Cyclohexene, 4-ethenyl-1,4-dimethyl-			21.2			●			●		●										●			

Table 3 (*continued*)

Compound	OT [mg/m³]	EU OEL – 8 h [mg/m³]	RT Tubes	RT Bag	A-dry M	A-dry T	A-dry S	A-dry Bag	A-wet M	A-wet T	A-wet S	A-wet Bag	B-dry M	B-dry T	B-dry S	B-dry Bag	B-wet M	B-wet T	B-wet S	B-wet Bag	C M	C T	C S	C Bag
p-Mentha-1,8-dien-7-ol			21.3														●				●			
3-Carene	9.3 [a]	N.D.	21.3	21.1	●		●		●		●	●	●	●	●		●	●	●		●			
2-Carene			21.4			●							●											
Cyclohexene, 1-methyl-5-(1-methylethenyl)-			21.7		●	●	●						●	●									●	
o-Cymene		N.D.	21.9		●		●		●	●	●		●		●		●	●	●		●			
γ-Terpinene	55 [a]		22.5			●					●				●				●					
Decane	3.6 [b]	N.D.		22.6								●												
1,3,8-*p*-Menthatriene				23.4													●							
Cyclohexene, 1-methyl-4-(1-methylethylidene)-			23.4						●				●				●					●		
1-Octanol	0.01 [b]	N.D.	23.6																				●	
1-Phenyl-1-butene			23.8														●							
p-(1-Propenyl)-toluene			23.9		●	●	●						●	●										
Linalyl acetate	0.04 [a]		24.3								●													
Fenchol	0.1 [a]		25.4														●	●						
Cyclohexene, 3-methyl-6-(1-methylethylidene)			25.5										●						●					
Fenchone	2.3 [a]		25.5														●							
Camphor	2.8 [a]	N.D.	26.6											●	●		●	●	●					
Terpinen-4-ol	0.6 [a]		26.8						●				●					●			●			
endo-Borneol	0.05 [a]		27															●						
α-Terpineol	0.9 [a]		27.3		●				●				●					●			●			
Ethanone, 1-(2-methylphenyl)-			27.6				●																	
Longifolene			32.4														●	●						

OT Reference: [a] L.J. van Gemert, 2011. "Flavour Thresholds: Compilations of Flavour Threshold Values in Air, Water and Other Media" [52]; [b] Y. Nagata, 2003. "Measurement of Odour Threshold by Triangle Odor Bag Method" [51]

EU OEL – 8h: EU Community Occupational Exposure Limits for long-term exposure available in GESTIS database [41]. N.D. = not defined by EU; empty cell = compound not present in the GESTIS database
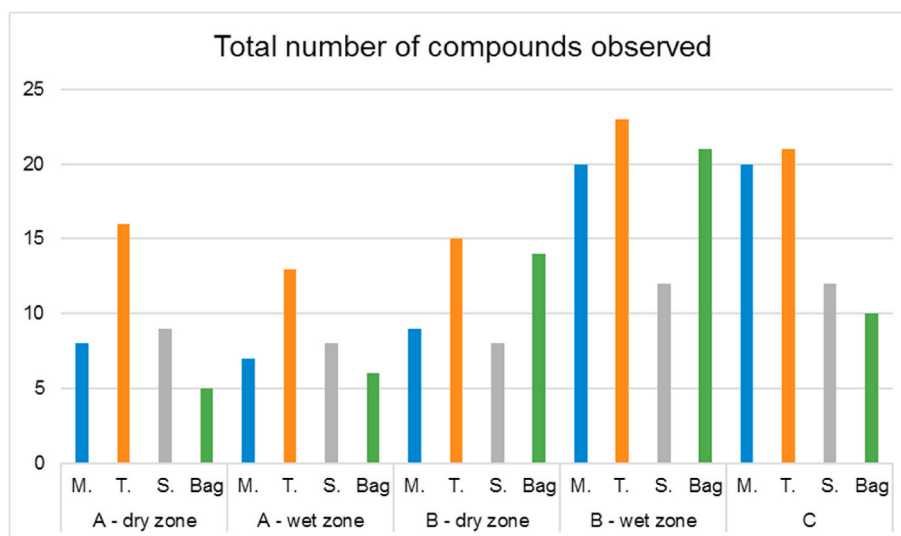
Fig. 3. Total number of compounds observed in the samples, divided by sources and sampling method adopted.

reactions (both chemical and biological) that provoke an increase in the temperature and gaseous emissions within the pile during wood storage [55].

Discussing the samples collected on two different types of material (forestall wood and corn silage), it is possible to evidence a difference between the stocked materials, in terms of odour concentration and chemical composition. By observing the different compositions of the two emissions (Table 3), the sample collected at wood pile B – wet area present aldehydes and fatty acid esters, which were not detected in the sample of corn silage heap (pile C). These compounds, characterized by a low odour threshold (e.g. Propanal, OT = 0.002 mg/m^3; Hexanal, OT = 0.001 mg/m^3) [51], may have a non-negligible odour contribution and this could explain the differences observed between the two samples.

Focusing on the qualitative analysis obtained using GC-MS, the general trends observed for olfactometric analysis are confirmed. Indeed, the samples collected in the wet zones of wood piles (A and B) are generally characterized by a higher number of volatile compounds. In particular, terpenes are predominantly observed in the wet zone emissions [56,57]. Discussing the differences related to the pile ageing in wet conditions (higher emissivity), the sample collected from the old pile (B) - wet zone is characterized by the presence not only of terpenes but also of aldehydes and fatty acid esters [46,57]. The presence of these compounds, characterized by a low OT, is in accordance with what has been observed for odour concentration (Cod A < Cod B). Focusing on health effect, from Table 3 it is possible to underline that a limited number of species are described by an occupational exposure limit for long exposure (EU OEL- 8 h): therefore, for the majority of compounds detected, a toxicological limit for the inhalation is not defined by European level. For the compounds characterized by a OEL value, the majority present an OT lower than the EU-OEL value: by this comparison, it is possible to evidence that, according to previous studies [27,28], these compounds can be detected by human nose before became dangerous for human health. The only exceptions are the methyl formate and benzene, characterized by an OT higher than the EU-OEL 8 h: for these compounds, therefore, particular attention should be applied during quantification because they precisely cannot be perceived by the nose before they reach their threshold of toxicity.

Discussing the differences between the two sampling types analysed (bags and sorbent tubes), it is possible to notice that the general trend is observable using both methods. However, a difference between the two methods appears, especially in the determination of particular classes of compounds. By observing the results reported in Table 3, the most significant variance between the two methods is the detection of low-molecular weight organic compounds, such as methanol and ethanol, detected only by analyses with sorbent tubes. This may be mainly due to the need to set a different mass spectrometer mass-to-charge (m/z) ratio for the two types of samples. The tube, through the double desorption, allows a reduction in the volume of the matrix (e.g. air) introduced during the analysis and therefore a lower m/z range can be set, which is useful for detecting very small molecules. In addition, due to their concentration capacity, it is possible to inject a greater sample volume using sorbent tubes [49]. On the contrary, when using bags, the matrix interference is more predominant and therefore a slightly higher m/z range is required. Therefore, if more precise information is to be obtained on high-volatile, low-molecular weight compounds, the correct handling of this parameter is essential to choosing the right instrumentation. However, from the conducted analysis, in general, the use of bags allows the same sample to be analysed by both chemical and olfactometric analyses, for which the use of these containers is required [47]. Furthermore, bags require little handling (bags are disposable and do not require special storage temperatures) and are easier to construct and cheaper than tubes. However, even if bags are easier to handle, sorbent tube samples may be stored for much more time (storage up to one month at 4 °C) without interferences or loss of compounds.

Despite this difference, it is interesting to note that some compounds, in particular aldehydes and esters of carboxylic acids (e.g Propanal, Hexanal and Acetic acid, methyl ester), were only observed in bag samples. The detection of these compounds, characterized by a low OT, is important for comparing the olfactometric measure.

Finally, focusing on the comparison of different sorbent tubes, the *Multi-sorbent bed* and *Sulphur* types present a similar performance, in terms of detected compounds, while *Tenax* tubes show different performances. In particular, from the results reported in Table 3 and Fig. 3, it is possible to highlight that Tenax tubes are characterized by a higher number of compounds if compared with other sampling methods. In addition, a comparison of the frequency of detection of compounds, expressed as the number of times a compound was detected within the five samples analysed by the different methods used, was conducted. From this comparison, it appears that Tenax tubes could retain a higher number of compounds, not detected with other sampling materials, as visible in Fig. 4.

Focusing on the detected compounds, it is possible to evidence a difference in performances among the sorbent tubes according to the chemical properties of the detected compounds. In particular, the volatility of compounds can influence the sorption performance of tubes.
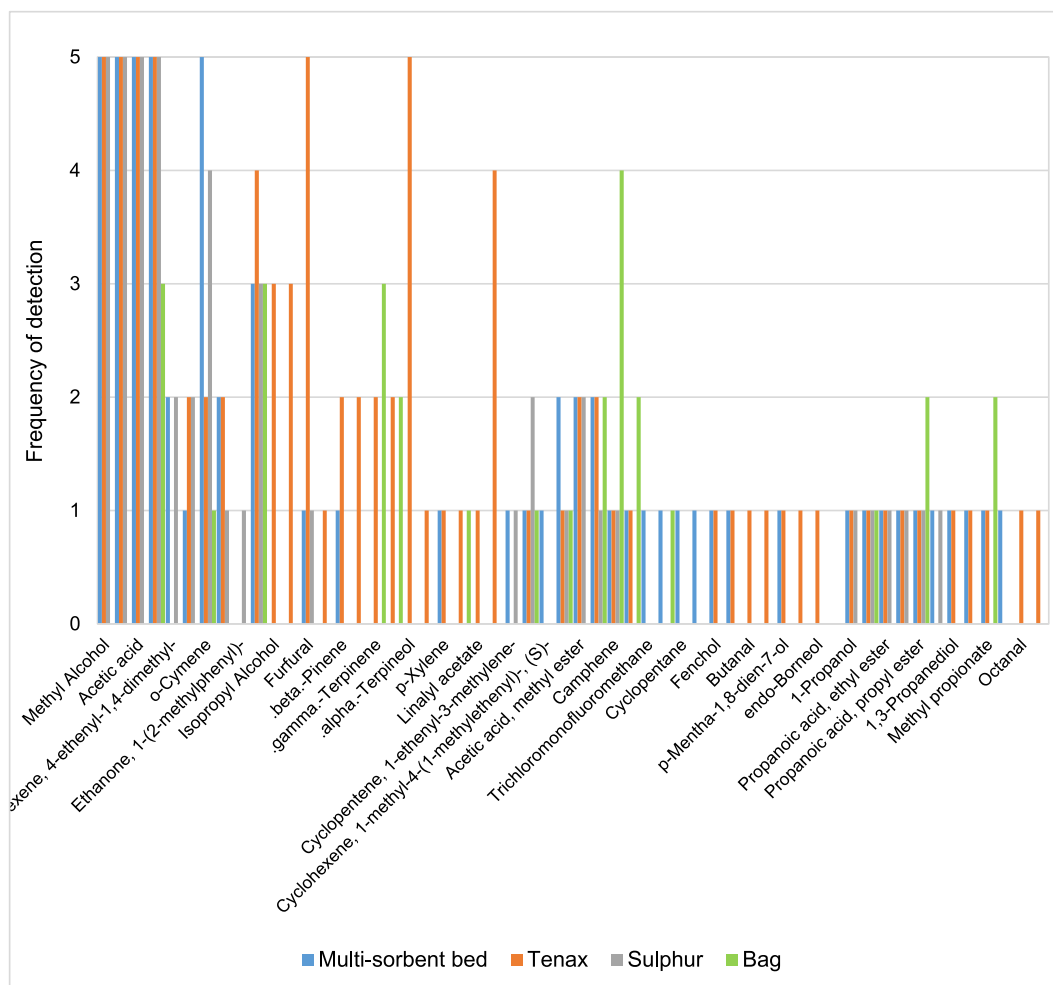
Fig. 4. Frequency of detection of VOCs in the different sample types (tubes and bag).
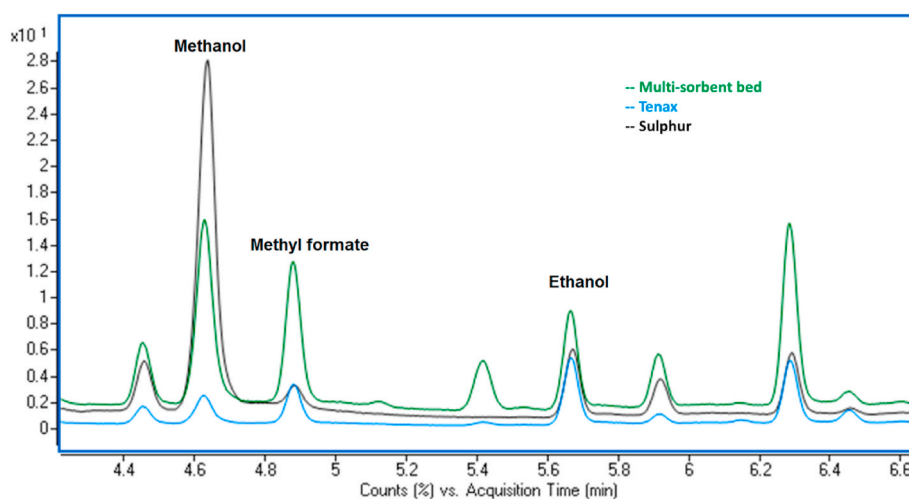

Fig. 5. Comparison of the chromatograms obtained using different sorbent tubes.

Discussing the chromatograms obtained for the samples collected in the wet zone of wood pile B (Fig. 5 - zoom at low retention time), it can be noticed that the Tenax material has not the best performance for the analysis of very volatile compounds (e.g. methanol and ethanol) [17, 18]: the areas of the corresponding peaks are less intense (blue line) if comparing with the different investigated tubes' materials, and therefore more difficult to detect. This difference could be explained by the particular properties of Tenax TA adopted as sorbent material, not appropriate for the collection of very volatile compounds (boiling point lower than 100 °C) [18]. This property renders Tenax TA material not so efficient for the sorption and detection of very volatile organic compounds.

From the different reported results, it can however be observed that for the analysis of complex matrices, such as odours, which are characterized by a great variability (in terms of quality and quantity) of the present molecules, the choice of sample collection method can strongly influence the result, both in terms of different handling and in terms of the observed molecules in samples. This observation allows to state that untargeted analysis of odour samples is a balance between the capabilities of currently available analytical techniques and the need to characterise the sample to be analysed as completely as possible.

5. Conclusion

From the obtained results by this preliminary comparison of the two analysed sample types (polymeric bags and sorbent tubes), it is possible to observed that they have different performances, depending on their specificity. By the evaluation between the three types of sorbent tubes (*Multi-sorbent bed*, *Tenax* and *Sulphur*), Tenax tubes show a different trend in terms of the compounds detected: in particular, this material appears not so suitable for the detection of very volatile organic compounds (VVOCs), such as methanol and ethanol, due to its specific properties. Focusing instead on Sulphur and Multi-sorbent bed, they present more similar performances. In addition, from the comparison between tubes and polymeric bags, the number and types of compounds detected in bags are more comparable to those observed in the Multi-sorbent bed and Sulphur tubes. However, a difference between the two methods (tubes and polymeric bags) appears, especially in the detection of low-molecular weight organic compounds. By this study, although preliminary and limited to samples collected at only one industrial category (biomass storage plants), it is possible to highlight that the odour matrix is characterized by significant complexity, in terms of quality and quantity of compounds and, for each laboratory, it is fundamental to understand the advantages/disadvantages of the available sampling methods to select the most useful for the complete chemical characterization of emissions. Indeed, due to this complexity, the selection of the sampling material may affect the obtained chemical results. The detection of different classes of compounds is a crucial point to obtain the most complete characterization of mixtures and compare the chemical profile with olfactometric results. Therefore, untargeted analysis is required and selecting materials specific to compounds' classes may be ineffective from the perspective of being able to identify every single compound in the mixture. For these reasons, to analyse odorous samples, in terms of odour concentration and chemical composition, it is necessary to strike a balance between the matrix complexity and the need to obtain the widest possible information. A future development of this study will be the investigation of comparative performances of these sampling methods in industrial contexts different from biomass storage plants (e.g. refineries, wastewater treatment plants, food industry, paper mills).

Credit author statement

Elisa Polvara: Data curation, Investigation, Writing - original draft, Visualization; **Eva Gallego:** Resources, Writing - Review & Editing, Formal analysis, Supervision; **Marzio Invernizzi:** Visualization, Writing - Review & Editing, Formal analysis; **José Francisco Perales:** Writing - Review & Editing, Visualization; **Selena Sironi**: Resources, Writing - Review & Editing, Conceptualization, Supervision.

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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.

Data availability

The data that has been used is confidential.

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