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Empowerment and Sustainability

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D2.6 Review on odour pollution and its relationship with chemical compounds and health issues

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Acronyms

- BTEX - Benzene, Toluene, Ethylbenzenes, Xylenes
- HQ - Hazard Quotient
- HI - Hazard Index
- OT - Odour Threshold
- PAH - Polycyclic Aromatic Hydrocarbons
- TLV- Threshold Limit Value
- VOC - Volatile Organic Compound

Summary

In the frame of the D-NOSES project, in order to reach the goal of increasing awareness towards the problem of odour pollution on a global level, it is extremely important to define the scientific framework of odorous emissions, by answering fundamental questions about its nature. In this context, one fundamental question is related to the chemical compounds in odour emissions, and their potential to cause health effects. This document provides an overview of the chemical compounds in the odour emissions from different plants, with the purpose of identifying the most “critical” compounds from the point of view of their potential toxicity, and provide a list of those compounds, which should effectively be investigated more carefully during monitoring activities. The study was focused on those odour-emitting activities, which also typically cause worries related to potential health effects, i.e. **foundries, landfills and refineries**. This work involved extensive bibliographic research of the studies that have chemically characterized emissions from the above-mentioned plants. For each of the activities analysed, the chemical compounds associated with their main odour emissions have been listed, together with their **Threshold Limit Values (TLVs)** and **Odour Thresholds (OTs)**. From these lists, the most “critical” compounds from the point of view of their potential toxicological effects on workers have been extracted based on their **Hazard Quotients (HQ)**, i.e. the ratio between the measured concentration and the TLV, with the aim of providing a limited list of the most relevant compounds for each activity, which would need to be most carefully analysed when performing monitoring and analysing of gaseous emissions of these type of industrial plants.

The document is structured in 4 chapters:

Chapter 1. INTRODUCTION: This section provides a general overview of the scopes of the document, its structure, the way the work was organized, and how the results should be interpreted. The structure of the work was inspired by a recent review regarding odour emissions from domestic wastewaters (Jiang et al., 2017). It is important to highlight that the considerations about potential toxicity have been focused on **occupational limits**. The reasons for this choice are related to the fact that risk assessment evaluations related to citizens’ exposure would require more specific evaluations, which cannot be generalized. On the other hand, the evaluations made for workers enable them to identify those compounds that are most “critical” in terms of toxicological potential, and thus represent the compounds that are most worthy of deeper investigations in the case of risk assessment studies.

Chapter 2. ODOUR EMISSIONS FROM FOUNDRIES: The second section of the document is dedicated to the compounds related to odour emissions from foundries. A brief description of foundries and their main odour emissions is provided. Then, a table is reported, listing the most relevant compounds identified in foundry emissions, together with their OTs and their TLVs. Finally, the most “critical” compounds from the point of view of their potential toxicity for workers have been extracted, with the aim of providing a limited list of the most relevant compounds, which would need to be most carefully monitored in foundry emissions.

Chapter 3. ODOUR EMISSIONS FROM LANDFILLS: The third section of the document is dedicated to the compounds related to odour emissions from landfills. A brief description of landfills and their main odour emissions is provided. Then, a table is reported, listing the most relevant compounds identified in landfill emissions and ambient air, as obtained from the study of the scientific literature. The table also reports, for each compound, the OT and the TLV. Finally, the most “critical” compounds from the point of view of their potential toxicity for workers have been extracted, with the aim of providing a limited list of the most relevant compounds, which would need to be most carefully monitored in landfills emissions.

Chapter 4. ODOUR EMISSIONS FROM REFINERIES: The fourth section of the document is dedicated to the compounds related to odour emissions from refineries. A brief description of refineries and their main odour emissions is provided. Then, a table is reported, listing the most relevant compounds identified in refinery emissions and ambient air, as obtained from the study of the scientific literature. The table also reports, for each compound, the OT and the TLV. Finally, the most “critical” compounds from the point of view of their potential toxicity for workers have been extracted, with the aim of providing a limited list of the most relevant compounds, which would need to be most carefully monitored in refinery emissions.

Chapter 5. MAIN OUTCOMES: The last section summarizes the main outcomes of this work.

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1. Introduction

This section provides a general overview of the scopes of the document, its structure, the way the work was organized, and how the results should be interpreted. The evaluations enabled to identify those compounds that are most “critical” in terms of toxicological potential, and thus represent the compounds that are most worthy of deeper investigations in the case of monitoring studies.

1.1 Background and scope of the work

In the frame of the D-NOSES project, in order to reach the goal of increasing awareness towards the problem of odour pollution on a global level, it is extremely important to define the scientific framework of odorous emissions, by answering fundamental questions about its nature.

In this context, one fundamental question is related to the chemical compounds that are present in the odour emissions from different types of activities, and their potential to cause effects on human health. Indeed, it is known that industrial odour emissions are composed of tens or hundreds of different chemical compounds, but – to the best of our knowledge – there are very few studies analysing in detail which type of compounds can be found in the emissions of specific activities.

The most significant study of this kind concerns wastewater treatment plants and was published in 2017 by Jiang et al. in *Critical Reviews in Environmental Science and Technology* “Odor emissions from domestic wastewater: A review” (DOI: 10.1080/10643389.2017.1386952).

This review paper has the aim to present a comprehensive data summary of chemical compounds related to sewers and wastewater treatment plants (WWTPs) and to propose a framework to identify priority odorants from wastewater emissions. The data summary includes concentrations of the compounds identified in sewers and WWTPs as identified from the scientific literature. For each compound identified, the Odour Thresholds (OTs) and the occupational exposure limits (Threshold Limit Values – TLVs) are also reported¹. The proposed prioritization framework is based on the classification of odorous compounds from wastewaters into different levels. The first level includes substances classified as carcinogenic. The second level includes those substances with the highest values of the ratio between the

¹ Odour threshold is defined as the minimum concentration at which an odorous compound can be perceived. Threshold limit values are the maximum concentration at which workers can be exposed during their working activity; these values typically depend on the duration of the exposure.

measured concentration and the TLV (which is defined as Hazard Quotient, as will be explained in the following sections): indeed, the paper states that any odour compound with a concentration above the TLV should be classified as priority level 2, considering the possible exposure hazard to humans. The level 3 odorous compounds can be prioritized using the approach proposed by Sivret et al. (2016), which is based mainly on the determination of the odour activity value, i.e. the ratio of the concentration of a specific odorant to its OT.

Based on this approach, it is clear that the compounds classified into the first two levels of priority are those compounds having the potential to produce toxicological effects on humans, whereas the third level refers to the potential of a compound to provoke an odour perception.

It should be also highlighted that the analysis proposed by Jiang et al. in their review regarding wastewater odours, since it is based on the consideration of TLVs, which are the limit values for occupational exposure, and since it reports the concentrations of chemical compounds measured at emissions (or in ambient air close to the emission sources), is an approach referred to the potential effects on workers, and not on citizens.

This choice might be related to the difficulties associated with the conduction of risk assessment studies evaluating the potential health effects of odour emissions on citizens. Indeed, we had published a paper in 2011 (Capelli et al., 2011) discussing a way to evaluate citizens' exposure to industrial odour emissions. However, such studies are extremely specific, since they need to account for the site-specific characteristics of the emissions and their atmospheric dispersion, as well as for the categories of potentially impacted receptors, and can thus hardly be universalized to a general approach.

Despite being related to workers' exposure, the approach proposed by Jiang et al. is extremely interesting, because:

- it is the first work presenting an extensive summary regarding the odour compounds present in wastewater emissions; this database is particularly valuable if considering that the retrieval of such huge amount of data regarding the concentrations of odorants, together with their OTs and TLVs, is not at all banal;
- it allows – based on a relatively “simple” evaluation of the compounds being either carcinogenic or having the highest values of Hazard Quotient (HQ) – to identify the most critical compounds in terms of toxicological potential for humans (specifically for workers), which thus represent the compounds that are most worthy of deeper investigations in the case of risk assessment studies. The obtainment of a limited list of compounds to be researched for risk assessment and monitoring studies is particularly valuable, because this allows to select and tune the most suitable analytical methods for their detection and quantification.

Because of the relevance of the work by Jiang et al., within this project, it was decided to follow a similar approach, and to focus on the analysis of the odour compounds emitted by other types of activities. Obviously, considering all possible types of odour-emitting activities would have been impossible. Therefore, we decided to limit our investigation, and for this purpose we selected three types of activities, which most often raise complaints about odours and

sometimes also worries about related potential health effects: i.e. foundries, landfills, and refineries.

Therefore, in analogy with the work done by Jiang et al. about sewers and WWTPs, the objectives of the present document are:

- the production of a comprehensive data summary of odour emissions from foundries, landfills, and refineries;
- the identification of the most critical compounds in terms of potential impact on workers' health in foundries, landfills, and refineries, which thus represent the priority compounds to be analysed in case of deeper investigations on exposure risk.

The next sections describe how the work was structured and organized.

1.2 Organization of the work

The first step of the work involved an extensive bibliographic research focusing on the scientific works dealing with the identification and quantification of the chemical compounds observed in odour emissions from the selected types of plants (i.e. foundries, landfills, and refineries).

As will be further described in the following sections, the retrieval of relevant scientific papers reporting data obtained from chemical analyses relevant to the odour emissions from the selected types of plants was in some cases very complex. The complexity of the research is associated on one hand with the limited number of scientific papers reporting quantitative data on this subject, but, most of all, it is associated with the inhomogeneity of the presented data, which in some cases is referred to emission, and in some other to ambient air.

This is one of the reasons why the evaluation of exposure risk has been considered out of the scope of this work, which instead has the aim to provide databases of the compounds related to the odour emissions from foundries, landfills and refineries, as reported in the scientific literature on the matter, and provide a list of “priority” compounds to be monitored and deepened for their potential impact, which were selected based on their carcinogenic potential and their relative Hazard Quotients (HQs). HQ is a simple and commonly used toxicological parameter, which is evaluated as the ratio between the single compound's exposure and its relative effects, and which may be used to express hazard referred to a single compound (Bleam, 2016; Solomon, 1999). In our elaboration, HQ values were calculated for each compound as the maximum concentration found in the scientific literature and the TLV. However, because of the above-mentioned inhomogeneity of the concentration data retrieved in the scientific literature, compounds' HQs were not reported as absolute values, but as relative contributions to the overall Hazard Index (HI), which is defined as the sum of the single HQ values, as follows:

$$HI = \sum_i HQ_i$$

In the case of foundries, the literature dealing with the chemical characterization of emissions is limited to a few units. For this reason, in this work, it was not possible to distinguish among single foundry emission sources, but “foundry emissions” were considered as a whole. It should be highlighted that, in the case of foundries, the literature data regarding chemical concentrations are not referred only to emissions, but in some cases ambient air samples were analysed, with the purpose of evaluating workers’ exposure during the working activities. Given the limited amount of data available, despite this inhomogeneity, in this work we decided not to exclude any of the values collected, in order to make the database more robust. It should be noted that, regarding workers’ exposure, foundry workers will typically not be exposed directly to emissions. However, the gaseous compounds that are released as conveyed emissions could be expected to be qualitatively similar to those that can be found as diffuse emissions in working environments, as a consequence of the not perfect suction from the foundry equipment (Manokhin et al., 2020). For this reason, it can be assumed that the type of compounds found in foundry emissions, and their concentration ratios, could be similar as those potentially inhaled by workers, although the exposure concentrations will be presumably lower than those at emissions.

The scientific literature regarding the chemical characterization of landfill emissions was the most abundant compared to the other two plant types considered here. Most research works differentiate their investigations based on the landfill emission source type. Indeed, in landfills, there are different sources of odours, which differ in terms of quality and quantity of chemical compounds emitted. For this reason, we decided to follow the same approach and consider each odour source separately for our evaluations. In the case of landfills, because of the typology of the odour emission sources (typically area sources, except for landfill gas), literature works often report concentrations data retrieved in ambient air – very close to the emission source – but not directly at the emission source (e.g., Termonia and Termonia, 1999). This type of data was considered in our study, because landfill ambient air is what landfill operators are most likely exposed to. On the other hand, chemical analyses carried out on pure landfill gas were also considered for the identification of the most critical compounds related to landfill emissions, because the possibility to have gas leaks in a landfill, which might lead to accidental inhalation by landfill workers, cannot be excluded. Because of these differences in the adopted sampling methods, in the chapter regarding landfill odour emission sources, it is specified whether the reported data were retrieved directly at emissions or in ambient air.

The second step of the work involved the “normalization” of the data retrieved in the scientific literature, in order to make data comparable. Indeed, the presentation of the results of the chemical analyses found in literature can vary very much from case to case. First, we decided to unify the units of measurements used for reporting compounds’ concentrations in the analysed papers, and to express all data in *ppm*. This didn’t imply only a conversion of measurement units but, in some cases, it was necessary to convert data regarding emitted flow rates (e.g., in g/s or in kg/y) into a concentration unit, thereby considering the specific sampling method adopted.

As a third step, for each compound, we extracted the highest concentration values among those found in literature. As previously mentioned, since the data presented in the scientific literature are very inhomogeneous, those maximum concentrations were not extracted for the

purpose of using them to directly evaluate risk exposure, but rather to identify those compounds having the highest relative HQ values, and thus compile a list of priority compounds that are most worthy of deeper investigations for specific risk assessment studies.

Finally, for each plant type considered, we produced “comparison tables”, where the list of chemical compounds as found in the scientific literature for the different emissions types are reported together with their Threshold Limit Values (TLVs) for occupational exposure and with their Odour Thresholds (OTs). The tables also report the number of times that the most critical compounds appear in the scientific literature considered, thereby providing an indication of the frequency with which it was identified in the analysed emissions. Moreover, the relative HQ of each compound has been reported as the ratio between the maximum concentration found in the literature and the TLV, divided by the total HI for the considered emission type.

$$HQ_{i,\%} = \frac{HQ_i}{HI} \cdot 100$$

The values of the relative HQ allow to identify the compounds that mostly contribute to the emission HI, and that thus represent the most critical compounds in terms of their potential health effects on workers. Finally, the last column of the table indicates whether the compound is considered carcinogenic and the category (1A, 1B or 2 group), according to the definition supplied in Part 3 of Annex VI to EU Regulation (EC) No 1272/2008.

Regarding the OT values, it is well known that the retrieval of representative values is a complex task. For this reason, we carried out an in-depth investigation in order to select the most appropriate OT value for each compound.

The main reference used for the determination of the OTs is Nagata and Takeuchi (2003).

For this work, we used the TLV values defined by the American Conference of Governmental Industrial Hygienists (ACGIH), revised and published annually in the TLV/BEI Documentation drafted by ACGIH (<https://www.acgih.org/science/tlv-bei-guidelines/>).

2. Odour emissions from foundries

This section of the document is dedicated to the compounds related to atmospheric emissions from foundries. A brief description of foundries and their main odour emissions is provided. Then, a table is reported, listing the most relevant compounds identified in foundry **emissions**, together with their OTs and their TLVs. Finally, the most “critical” compounds from the point of view of their potential toxicity for workers have been extracted, with the aim of providing a limited list of the most relevant compounds, which would need to be most carefully analysed when performing risk assessment evaluations related to foundry emissions. An extended version of the information here reported, specifically referring to the exposure of workers involved in olfactometry analysis, has been published in the *Journal of Environmental Science and Health, Part A*.

2.1. What is a foundry?

The aim of the foundry process is the realization of metal products by a direct pouring of metals into moulds, selecting the physical, metallurgical and dimensional characteristics of final products. The European foundry association (CAEF) reports that, in 2017, 12.3 million tons of non-ferrous metals and 4.5 million tons of iron and steel castings were produced (only) in Europe. Globally, the total production in 2017 amounted to 318190 tons, with a slight rise over 2016. The foundry process is composed of the following major operations (Polvara et al., 2021):

- Melting of metal (ferrous or non-ferrous metals);
- Metal treatment;
- Mould making-preparation of moulds and cores;
- Casting-pouring of the molten metal into the mould;
- Cooling for casting solidification

- Shake out-removing the casting from the mould;
- Finishing of the raw casting to obtain finished one.

In the foundry process, a variety of techniques, with specific technical, economic and environmental properties, advantages and disadvantages, can be employed depending on the type of furnace, the moulding and core-making system, the casting system or the finishing techniques applied. Despite the complexity of the process, the different single operations can be generically resumed into two distinct main phases: the *melting phase*, in which a metal alloy is prepared, and a *moulding phase*, in which the moulds are filled to obtain the final product. Typically, it is possible to classify foundry activities according to the metal alloys processed (ferrous or non-ferrous) or to the moulding types employed in the production. Indeed, the process for the mould realization differentiates significantly the phases of the production cycle. In general, two different moulding systems exist and can be applied in the foundry process: the permanent mould casting, that employs reusable moulds, and lost mould casting, in which the mould material is constituted by sand. In both the typologies, molten metal is poured into a mould that remains until the material cools and solidifies into the desired part shape. The difference is related to the final part of the process. Indeed, the lost mould casting uses a single use mould (generally sand), destroyed after each cycle. In this casting, the mould is realized with silicon sand mixed with ligands or additives useful to obtain the necessary moulding properties. Instead, permanent mould casting uses a metal mould that can be reused for several thousands of cycles. While several combinations can be possible, in general, lost moulds are mostly used in ferrous foundries and permanent moulds are employed in non-ferrous foundries (Polvara et al., 2021).

Referring to the foundry processes and emissions mentioned in the next paragraphs, the foundry areas in which workers may be exposed to Volatile Organic Compounds (VOCs) are the areas of core making, melting furnace, moulding, sand shakeout, grinding, sand recovery, as well as – to a minor extent – office areas (Liu et al., 2010). As will be further discussed in this document, in such areas, the VOCs that have most frequently been studied for the purpose of evaluating potential health effects on foundry workers are Polycyclic Aromatic Hydrocarbons (PAHs) and Benzenes, Toluenes, Ethylbenzenes and Xylenes (BTEX) (e.g., Holtzer et al., 2013; Liu et al., 2010).

2.2 Sources of odour emissions in foundries

Foundry is considered one of the most environmentally polluting industries due to the consistent emissions during each process step of gaseous pollutants, in particular Volatile Organic Compounds (VOCs). The foundry process gives rise to emissions of different nature, such as dust, metals, carbon monoxide, sulphur dioxide and NO_x in addition to organic and inorganic volatile compounds. The foundry productive phases involving the major emissions of VOCs are (Fatta et al., 2004; Fore et al., 2010):

- Core and mould making
- Melting and treatment of metals
- Pouring and cooling

- Shake-out

Emission of VOCs is frequently related to odours. Every single phase has a different environmental impact and the type and the quantity of compounds emitted vary greatly, depending on the characteristics of the production steps. Indeed, the productive parameters or apparatus (e.g., type of ligands, catalysts, metal alloys or melting furnace chosen) directly influence composition and quantity of the pollutants emitted.

Emissions from core and mould making

Core and mould making are characterized by high emissions of VOCs, correlated with unpleasant odours. In the core making process, sand is mixed with resins. During moulding operation, an appropriate refractory material is shaped to form the cavity in which molten metal will be introduced. The material used for moulding operations depends on the type of metal being cast and the final applications. The most common moulding material is sand. Out of moulding sands used in the foundry industry, sands with organic binders deserve a special attention (Holtzer et al., 2013). These binders are based on synthetic resins, which ensure obtaining the proper technological properties and sound castings. Several types of resins exist with different chemical properties and physical characteristics (Kmita et al., 2018). Despite differences and technical improvements, the majority of the resins generate odours during the core making, core curing and metal casting processes. Depending on the kind of the applied resin under the influence of temperature, different compounds such as furfuryl alcohol, formaldehyde, phenol, BTEX group (benzene, toluene, ethylbenzene, xylenes), and also polycyclic aromatic hydrocarbons (PAHs) can be formed and released into the working environment (Holtzer et al., 2013).

Emissions from melting and treatment of metals

The melting process is one of the most important sources of pollutant emission. Indeed, from furnaces, fugitive or non-fugitive emissions are produced. Fugitive emissions from furnaces occur during charging, back-charging, alloying, slag removal, oxygen lancing (in the case of steel melting furnaces) and tapping operations when the furnace lids and doors are open. Non-fugitive ones are produced inside the furnace, when doors and lids are closed. This type of emissions is collected directly by a control system. Indeed, VOCs emissions from melting and treatment of metals request an abatement system that collects the gaseous emissions and cleans them from pollutants. After these procedures, the air is released through a chimney. The type of metal processed and the furnace used influence considerably the chemical substances emitted during this process, in terms of nature and quantity. The emission of gaseous pollutants is studied mostly for the melting and treatment of metals. In this process, the VOCs emitted represent the primary odour source. In addition, the presence of different additives in the formulations used during the phase of metals treatment can be the origin of odour emissions.

Emissions from pouring and cooling processes

The pouring and cooling processes are the main sources of inorganic and organic compounds, causing unpleasant odour emissions. Indeed, during these steps, the organic compounds used as binders, moulding materials or coatings are decomposed thermally to produce VOC emissions (Faber et al., 2017; Tiedje et al., 2010; Wang et al., 2007). The quantity and the composition of pollutants released are directly connected with the composition of products used during the mould preparation. During these processes, approximately 330 different compounds can be emitted, part of which has a distinct odour (Faber et al., 2017). Due to changes in the production process, casting quality, and environmental needs, the mould binders have changed over the years. Because of the rising interest in environmental and human security, the use of these new products also produces a significant reduction of toxic organic compounds. Despite these progresses, during moulding, pouring and cooling processes the gases produced contain compounds, emitted in low concentrations and characterized by low odour thresholds, which may produce an unpleasant odour.

2.3 Analysis of foundry odour emissions

Considerations about the type of data found in the scientific literature

In order to obtain an exhaustive database of chemical compounds emitted by foundry plants, an extensive bibliographic research was carried out, analysing the scientific papers reporting the chemical identification and quantification of volatile compounds emitted by foundries.

This bibliographic research led to the identification of twelve scientific papers, published in a timespan between 1986 and 2017, which were further analysed for the construction of the database regarding the chemical compounds related to foundry odour emissions, and the evaluation of the priority compounds in terms of their potential health effects (Acharya et al., 2016; Bobrowski et al., 2016; Faber et al., 2017; Holtzer et al., 2013; Holtzer et al., 2016; Liu et al., 2010; Knecht et al., 1986; Staples and Zeiger, 2007; Tiedje et al., 2010; Tsai et al., 2008; Yang et al., 1998; Yang et al., 2002).

Since the number of scientific papers dealing with the chemical characterization of emissions is limited, in this work, it was not possible to distinguish among single foundry emission sources, but “foundry emissions” were considered as a whole. However, it should be highlighted that, in the case of foundries, the literature data regarding compounds’ concentrations are not referred solely to emissions (such as it is the case for instance in Tsai et al., 2008 or Yang et al., 2002) but, in many cases, ambient air samples were analysed (e.g., Liu et al., 2010; Staples and Zeiger, 2017), with the purpose of evaluating workers’ exposure to potentially toxic compounds. Given the limited amount of data available, despite this inhomogeneity, in this work we decided not to exclude any of the values, in order to make the database more robust. It should be noted that, regarding workers’ exposure, foundry workers will typically not be exposed directly to emissions. However, it is also true that the gaseous compounds that are released as conveyed emissions are expected to be qualitatively similar to those that can be

found as diffuse emissions in working environments, as a consequence of the not perfect suction from the foundry equipment (Manokhin, 2020). For this reason, it can be assumed that the type of compounds found in foundry emissions, and their concentration ratios, will be the same as potentially inhaled by workers, although the exposure concentrations will be presumably lower than those at emissions. Thus, as previously mentioned, considering that the scope of this work is not risk assessment, but rather the identification of the most critical compounds to be considered as most worthy of deeper investigation in case of specific risk assessment studies, the mixing of different values was deemed acceptable.

Data summary of the chemical compounds related to foundry odour emissions

The database regarding the chemical compounds related to foundry odour emissions (Table 1) was built by providing a list of the compounds identified at least once in the scientific papers that have investigated the chemical composition of foundry emissions (or ambient air), together with their OT and TLV.

As previously mentioned, the concentration values retrieved in the literature are not all homogeneous, because they are not all referred to the same sampling conditions: many of the concentrations reported in the literature refer to ambient air sampling (e.g., Liu et al., 2010; Staples and Zeiger, 2017), but some others refer to stack sampling (e.g., Tsai et al., 2008; Yang et al., 2002).

For this reason, in order to avoid mixing up two different things, we decided to avoid reporting the single concentration values in the table, but used those values – in particular the value of the maximum concentration found in the literature – in order to evaluate the relative HQ for each compound, expressed as the ratio between the HQ and the HI, as explained in section 1.2 of this document.

Finally, in the database (Table 1), the compounds classified as carcinogenic according to the definition supplied in Part 3 of Annex VI to EU Regulation (EC) No. 1272/2008 are identified as follows:

- Carcinogen if the compound is classified as carcinogens of category 1A or 1B.
- Suspected to have carcinogenic potential for human if the compound is classified as carcinogens of category 2.

In Table 1, compounds not belonging to the categories established by the EU Regulation have been left blank. The compounds not available in the EU Regulation are reported in the table as *not available*.

| Compound | CAS number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | HQ _i ,% | Carcinogenic |
|------------------------|------------|---------------|----------------|----------|--------------------|---------------|
| 1,1,1-trichloroethane | 71-55-6 | 350 | 450 | | 4.21E-07 | |
| 1,1,2-trichloroethane | 79-00-5 | 10 | N.D. | | 3.69E-06 | Carc. 2 |
| 1,2,3-trimethylbenzene | 526-73-8 | N.D. | N.D. | | N.D. | Not available |

| | | | | | | |
|--------------------------------|-----------|------|------|--------|----------|---------------|
| 1,2,4-trimethylbenzene | 95-63-6 | 25 | N.D. | 0.1 | 1.46E-04 | |
| 1,2-Benzenedicarboxylic acid | 88-99-3 | N.D. | N.D. | | N.D. | Not available |
| 1,2-dichlorobenzene | 95-50-1 | 25 | 50 | | 1.03E-06 | |
| 1,3,5-trimethyl-benzene | 108-67-8 | 25 | N.D. | 0.2 | 3.86E-05 | |
| 1,4-dimethylbenzene (p-xilene) | 106-42-3 | 100 | 150 | 0.058 | 1.20E-05 | |
| 1-butene | 106-98-9 | 250 | N.D. | 0.36 | 2.26E-05 | |
| 1-hexene | 592-41-6 | 50 | N.D. | 0.14 | 1.78E-05 | Not available |
| 1-pentanamine | 110-58-7 | N.D. | N.D. | | N.D. | Not available |
| 1-pentene | 109-67-1 | N.D. | N.D. | 0.1 | N.D. | Not available |
| 2,2,4-trimethylpentane | 540-84-1 | 300 | N.D. | | 8.85E-07 | |
| 2,2-dimethylbutane | 75-83-2 | 500 | 1000 | 20 | 1.19E-06 | |
| 2,3,4-trimethylpentane | 565-75-3 | N.D. | N.D. | | N.D. | |
| 2,3-dimethylbutane | 79-29-8 | 500 | 1000 | 0.42 | 2.60E-06 | |
| 2,3-dimethylpentane | 565-59-3 | 400 | 500 | 4.5 | 8.85E-07 | |
| 2,4-dimethylpentane | 108-08-7 | 400 | 500 | 0.94 | 2.12E-07 | |
| 2,4-dimethylphenol | 105-67-9 | 1 | N.D. | | 4.76E-04 | |
| 2-Hydroxybenzaldehyde | 90-02-8 | N.D. | N.D. | | N.D. | Not available |
| 2-Methylfuran | 534-22-5 | N.D. | N.D. | | N.D. | Not available |
| 2-methylheptane | 592-27-8 | 300 | N.D. | 0.11 | 2.11E-06 | |
| 2-methylhexane | 591-76-4 | 400 | 500 | 0.42 | 3.22E-06 | |
| 2-methylpentane | 107-83-5 | 500 | 1000 | 7 | 5.16E-06 | |
| 3-methylheptane | 589-81-1 | 300 | N.D. | 1.5 | 2.43E-06 | |
| 3-methylhexane | 589-34-4 | 400 | 500 | 0.84 | 3.97E-06 | |
| 3-methylpentane | 96-14-0 | 500 | 1000 | 8.9 | 3.91E-06 | |
| Acenaphthene | 83-32-9 | 10 | 15 | | 1.51E-05 | |
| Acenaphthylene | 208-96-8 | 10 | 15 | | 3.36E-04 | |
| Acrolein | 107-02-8 | 0.1 | | 0.0036 | 2.90E-03 | |
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 4.35E-03 | |
| Anthracene | 120-12-7 | 10 | 15 | | 2.51E-05 | Not available |
| Anthanthrene | 191-26-4 | 50 | N.D. | | 4.11E-09 | Not available |
| Benz[a]anthracene | 56-55-3 | N.D. | N.D. | | N.D. | Carc. 1B |

| | | | | | | |
|---------------------------------|------------|------|------|------|----------|---------------|
| Benzaldehyde | 100-52-7 | N.D. | N.D. | | N.D. | |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.7 | 9.98E+01 | Carc. 1A |
| Benzo[a]fluorene | 238-84-6 | N.D. | N.D. | | N.D. | Not available |
| Benzo[a]pyrene | 50-32-8 | 10 | 15 | | 4.10E-06 | Carc. 1B |
| Benzo[b]chrysene | 214-17-5 | 10 | 15 | | 4.22E-07 | Not available |
| Benzo[b]fluoranthene | 205-99-2 | 10 | 15 | | 4.94E-07 | Carc. 1B |
| Benzo[b]fluorene | 243-17-4 | N.D. | N.D. | | N.D. | Not available |
| Benzo[b]naphtho[2,1-d]thiophene | 239-35-0 | N.D. | N.D. | | N.D. | Not available |
| Benzo[b+j+k]fluoranthene | N.D. | 10 | 15 | | 2.27E-08 | Not available |
| Benzo[e]pyrene | 192-97-2 | 10 | 15 | | 4.01E-07 | Carc. 1B |
| Benzo[ghi]fluoranthene | 203-12-3 | 10 | 15 | | 3.19E-09 | Not available |
| Benzo[ghi]perylene | 191-24-2 | N.D. | N.D. | | N.D. | Not available |
| Benzo[k]fluoranthene | 207-08-9 | 10 | 15 | | 1.34E-07 | Carc. 1B |
| Bromomethane | 74-83-9 | 1 | N.D. | | 4.43E-05 | |
| Carbon tetrachloride | 56-23-5 | 5 | 10 | 4.6 | 1.99E-03 | Carc. 2 |
| Chlorobenzene | 108-90-7 | 10 | N.D. | | 2.64E-04 | |
| Chloroform | 67-66-3 | 10 | N.D. | 3.8 | 2.21E-05 | Carc. 2 |
| Chrysene | 218-01-9 | N.D. | N.D. | | N.D. | Carc. 1B |
| cis-1,2-Dichloroethylene | 156-59-2 | 200 | N.D. | | 9.59E-07 | |
| cis-1,2-Dichloropropene | 563-54-2 | N.D. | N.D. | | N.D. | Not available |
| cis-2-Butene | 590-18-1 | 250 | N.D. | | 3.07E-06 | |
| cis-2-Pentene | 627-20-3 | N.D. | N.D. | | N.D. | Not available |
| Coronene | 191-07-1 | N.D. | N.D. | | N.D. | Not available |
| Cyclohexane | 110-82-7 | 100 | N.D. | 2.5 | 4.28E-06 | |
| Cyclopenta[cd]pyrene | 27208-37-3 | N.D. | N.D. | | N.D. | Not available |
| Cyclopentane | 287-92-3 | 600 | N.D. | | 1.73E-06 | |
| Dibenz[a,h]anthracene | 53-70-3 | 10 | 15 | | 1.45E-07 | Carc. 1B |
| Dibenz[a,j]anthracene | 224-41-9 | 10 | 15 | | 7.45E-09 | Not available |
| Ethylbenzene | 100-41-4 | 20 | N.D. | 0.17 | 1.71E-03 | |
| Ethynylbenzene | 536-74-3 | N.D. | N.D. | | N.D. | Not available |
| Fluoranthene | 206-44-0 | 10 | 15 | | 3.58E-06 | Not available |

| | | | | | | |
|------------------------|------------|------|------|---------|----------|---------------|
| Fluorene | 86-73-7 | 10 | 15 | | 2.69E-05 | Not available |
| Formaldehyde | 50-00-0 | 0.1 | 0.3 | 0.5 | 3.91E-03 | Carc. 1B |
| Hexadecanoic acid | 57-10-3 | N.D. | N.D. | | N.D. | Not available |
| Hexamine | 100-97-0 | N.D. | N.D. | | N.D. | |
| Hexanal | 66-25-1 | N.D. | N.D. | 0.00028 | N.D. | Not available |
| Hydrogen cyanide | 74-90-8 | N.D. | N.D. | | N.D. | |
| Hydrogen sulfide | 7783 -06-4 | 1 | 5 | 0.00041 | 4.18E-03 | |
| i-Butane | 75-28-5 | 1000 | N.D. | | 1.55E-08 | |
| Indeno[1,2,3-cd]pyrene | 193-39-5 | 10 | 15 | | 2.57E-08 | Not available |
| Isopentane | 78-78-4 | 600 | 750 | 1.3 | 1.40E-05 | |
| Isoprene | 78-79-5 | N.D. | N.D. | 0.048 | N.D. | Carc. 1B |
| Isopropylbenzene | 98-82-8 | 50 | N.D. | 0.0084 | 6.25E-05 | |
| m/p Cresol | N.D. | 5 | N.D. | | 4.42E-05 | |
| m-Diethylbenzene | 141-93-5 | N.D. | N.D. | 0.07 | N.D. | Not available |
| Methane | 74-82-8 | 1000 | N.D. | | 2.65E-05 | |
| Methyl benzoate | 93-58-3 | N.D. | N.D. | | N.D. | Not available |
| Methylcyclohexane | 108-87-2 | 400 | N.D. | 0.15 | 1.47E-06 | Not available |
| Methylcyclopentane | 96-37-7 | 500 | 1000 | 1.7 | 1.01E-06 | Not available |
| m-Ethyltoluene | 620-14-4 | N.D. | N.D. | 0.018 | N.D. | Not available |
| m-Xilene | 108-38-3 | 100 | N.D. | 0.041 | 2.69E-05 | |
| Naphthalene | 91-20-3 | 5 | N.D. | | 2.54E-03 | Carc. 2 |
| n-Butane | 106-97-8 | 1000 | N.D. | 1200 | 3.23E-06 | |
| n-Decane | 124-18-5 | N.D. | N.D. | 0.62 | N.D. | Not available |
| n-Heptane | 142-82-5 | 400 | 500 | 0.67 | 3.73E-06 | |
| n-Hexane | 110-54-3 | 50 | N.D. | 1.5 | 2.59E-05 | |
| n-Nonane | 111-84-2 | 200 | N.D. | 2.2 | 2.47E-06 | Not available |
| n-Octane | 111-65-9 | 300 | N.D. | 1.7 | 3.53E-06 | |
| n-Pentane | 109-66-0 | 600 | N.D. | 1.4 | 6.26E-06 | |
| n-Propylbenzene | 103-65-1 | N.D. | N.D. | 0.0038 | N.D. | |
| o-Cresol | 95-48-7 | 5 | N.D. | 0.00028 | 5.33E-05 | |
| o-Ethyltoluene | 611-14-3 | N.D. | N.D. | 0.074 | N.D. | Not available |

| | | | | | | |
|---------------------|-----------|------|------|---------|----------|---------------|
| o-Xylene | 95-47-6 | 100 | 150 | 0.38 | 7.53E-05 | |
| p-Diethylbenzene | 105-05-5 | N.D. | N.D. | 0.00039 | N.D. | Not available |
| Perylene | 198-55-0 | 10 | 15 | | 8.28E-07 | Not available |
| p-Ethyltoluene | 622-96-8 | N.D. | N.D. | 0.0083 | N.D. | Not available |
| Phenanthrene | 85-01-8 | N.D. | N.D. | | N.D. | Not available |
| Phenol | 108-95-2 | 5 | N.D. | 0.0056 | 3.76E-03 | |
| phenylethanol | 98-85-1 | N.D. | N.D. | | N.D. | Not available |
| Propanol | 71-23-8 | N.D. | N.D. | 0.09 | N.D. | |
| Pyrene | 129-00-0 | N.D. | N.D. | | N.D. | Not available |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 3.63E-04 | |
| Sulphur dioxide | 7446-09-5 | N.D. | 0.25 | 0.87 | 5.65E-02 | |
| Tetrachloroethylene | 127-18-4 | 25 | 100 | 0.77 | 5.44E-05 | Carc. 2 |
| Thiophene | 110-02-1 | N.D. | N.D. | 0.00056 | N.D. | Not available |
| Toluene | 108-88-3 | 20 | N.D. | 0.33 | 8.27E-02 | |
| trans-2-Butene | 624-64-6 | 250 | N.D. | | 3.07E-06 | |
| trans-2-Pentene | 646-04-8 | N.D. | N.D. | | N.D. | Not available |
| Trichloroethylene | 79-01-6 | 10 | 25 | 3.9 | 1.57E-04 | Carc. 1B |
| Triethylamine | 121-44-8 | 1 | 3 | 0.0054 | 5.97E-02 | |

Table 1. Analysis of chemical compounds related to foundry emissions

Evaluation of priority compounds related to foundry emissions

According to the approach proposed by Jiang et al. (2017), the first group of priority compounds are those classified as carcinogens. Based on the classification proposed by the EU Regulation (EC) No. 1272/2008, the carcinogenic compounds (categories 1A and 1B) identified in foundry emissions are the following:

- Benz[a]anthracene (1B)
- Benzene (1A)
- Benzo[a]pyrene (1B)
- Benzo[b]fluoranthene (1B)
- Benzo[e]pyrene (1B)
- Benzo[k]fluoranthene (1B)
- Chrysene (1B)
- Dibenz[a,h]anthracene (1B)
- Formaldehyde (1B)
- Isoprene (1B)
- Trichloroethylene (1B)

Always according to the above-mentioned EU Regulation, the suspected carcinogenic compounds (category 2) in foundry emissions are:

- 1,1,2-trichloroethane
- Carbon tetrachloride
- Chloroform
- Naphthalene
- Tetrachloroethylene

In order to evaluate potential risks related to those chemicals in foundries it is possible to refer to the scientific literature, where different papers dealing with the carcinogenic risk assessment related specifically to PAHs and BTEXs in foundry emissions (e.g., Liu et al., 2010; Omland et al., 1994) can be found.

Considering the most critical compounds of foundry emissions in terms of their potential to cause non-carcinogenic health effects, it is possible to refer to their relative HQ. As can be seen from Table 1, Benzene is by far the compound that most contributes to the overall HI of foundry emissions (Benzene alone accounts for about 99.8% of the overall HI), evaluated based on the concentration data that we retrieved in the scientific literature.

In order to highlight the other compounds that have a non-negligible contribution on the HI of foundry emissions, we considered the next 15 compounds after Benzene having the highest values of relative HQ ($HQ_{i,\%}$), which are, in decreasing order of relative HQ:

- Toluene
- Triethylamine
- Sulphur dioxide
- Ammonia
- Hydrogen sulfide
- Formaldehyde
- Phenol
- Acrolein
- Naphthalene
- Carbon tetrachloride
- Ethylbenzene
- 2,4-dimethylphenol
- Styrene
- Acenaphthylene
- Chlorobenzene

Those 16 compounds together contribute by 99.9999% to the overall HI of foundry emissions. If not considering Benzene, then the above-listed 15 compounds, which include i) inorganic compounds such as Ammonia, Hydrogen Sulphide and Sulphur Dioxide, ii) Trimethylamine, iii) aldehydes (i.e. Formaldehyde and Acrolein), and iv) other aromatic and phenolic compounds (e.g., Toluene, Phenol, Ethylbenzene, etc.), contribute by 99.5% of the overall HI of foundry emissions (Table 2, Figure 1).

Table 2 also includes a column reporting the number of concentration values found in the scientific literature for each of the reported compounds. This number represents the frequency with which the compound has been identified in the analysed samples.

| Compound | CAS number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | No. of values | HQ _i % (without benzene) |
|----------------------|------------|---------------|----------------|----------|---------------|-------------------------------------|
| Toluene | 108-88-3 | 20 | N.D. | 0.33 | 31 | 36.46 |
| Triethylamine | 121-44-8 | 1 | 3 | 0.0054 | 4 | 26.35 |
| Sulphur dioxide | 7 446-09-5 | N.D. | 0.25 | 0.87 | 11 | 24.94 |
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 11 | 1.92 |
| Hydrogen sulfide | 7783 -06-4 | 1 | 5 | 0.00041 | 11 | 1.84 |
| Formaldehyde | 50-00-0 | 0.1 | 0.3 | 0.5 | 11 | 1.72 |
| Phenol | 108-95-2 | 5 | N.D. | 0.0056 | 15 | 1.66 |
| Acrolein | 107-02-8 | 0.1 | | 0.0036 | 11 | 1.28 |
| Naphthalene | 91-20-3 | 5 | N.D. | | 38 | 1.12 |
| Carbon tetrachloride | 56-23-5 | 5 | 10 | 4.6 | 4 | 0.88 |
| Ethylbenzene | 100-41-4 | 20 | N.D. | 0.17 | 16 | 0.75 |
| 2,4-dimethylphenol | 105-67-9 | 1 | N.D. | | 4 | 0.21 |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 13 | 0.16 |
| Acenaphthylene | 208-96-8 | 10 | 15 | | 23 | 0.15 |
| Chlorobenzene | 108-90-7 | 10 | N.D. | | 10 | 0.12 |

Table 2. Identification of the most critical compounds in terms of potential non-carcinogenic health effects related to foundry emissions

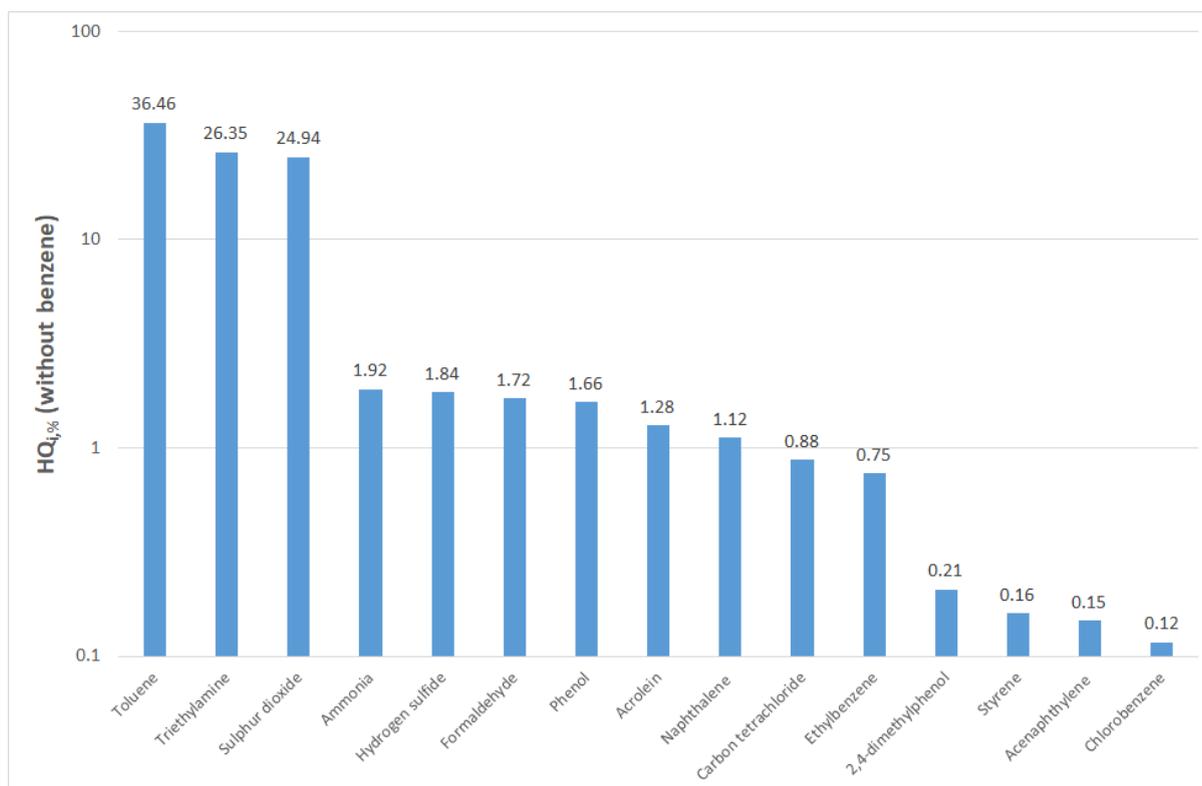


Figure 1. Graphical identification of the most critical compounds in terms of potential non-carcinogenic health effects related to foundry emissions

In order to correctly interpret those results, it should be noted that for the HQ calculation of Sulphur Dioxide, we used the value of the TLV-STEL instead of the value of the TLV-TWA, because it is not defined by ACGIH.

In general, all compounds having a low OT have the potential to cause an odour perception. However, it should be highlighted that the perception of an odour is not directly correlated with a potential health risk. As can be seen from Figure 2, there is no direct correlation between TLVs and OTs of the chemical compounds found in foundry emissions.

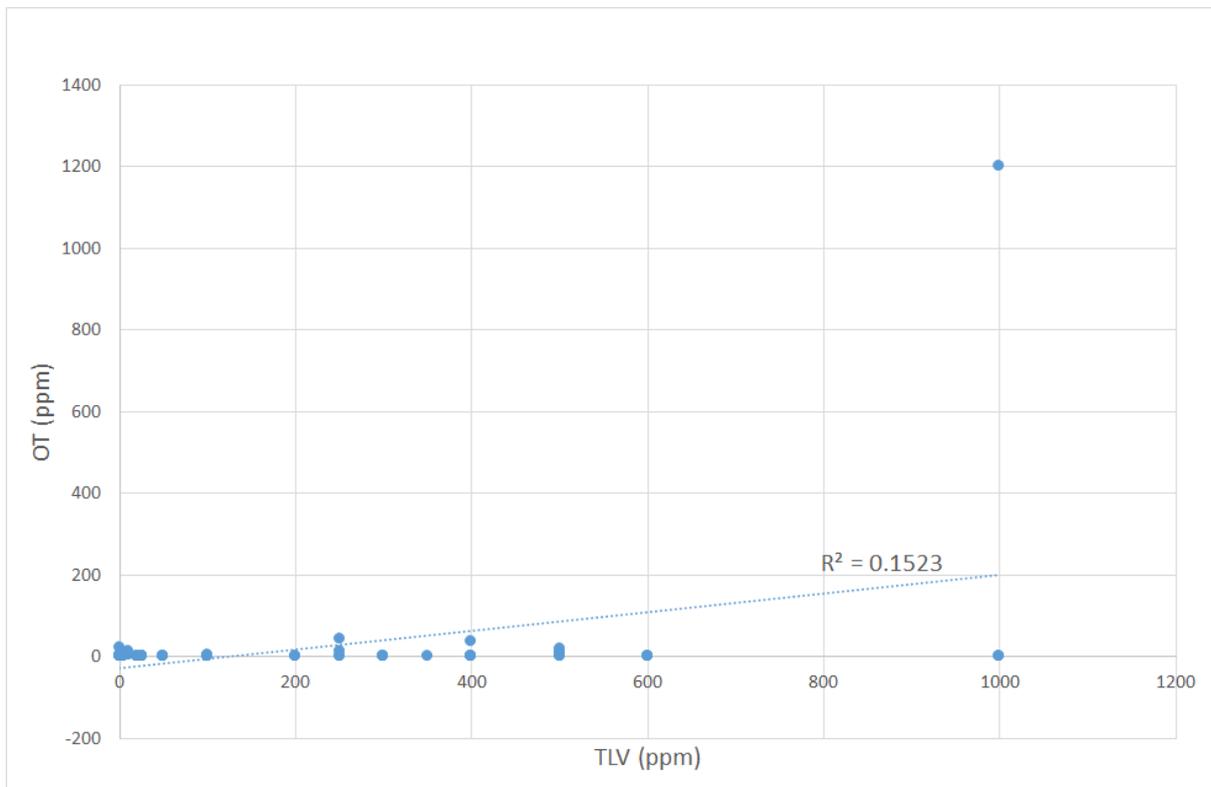


Figure 2. Correlation between TLVs and OTs (both in ppm) of the compounds related to foundry emissions

3. Odour emissions from landfills

This section of the document is dedicated to the compounds related to atmospheric emissions from landfills. A brief description of landfills and their main odour emissions is provided. Then, a table is reported, listing the most relevant compounds identified in landfill **emissions** and **ambient air**, as obtained from the study of the scientific literature. The table also reports, for each compound, the OT and the TLV. Finally, the most “critical” compounds from the point of view of their potential toxicity for workers have been extracted to provide a limited list of the most relevant compounds, which would need to be most carefully analysed during monitoring and control activities.

3.1. What is a landfill?

A landfill is a site for the controlled disposal of waste, whose surface can vary from a few tens to hundreds of hectares. Landfills are still one of the most common systems for waste disposal worldwide (Vaverková, 2019).

The filling of a landfill is carried out by sectors. Once a portion (or lot) of a landfill is filled, it is necessary to cover the waste with a layer of soil or clay, having a thickness of 1-2 m. Besides this final cover, wastes shall be covered daily with a layer of soil of a few centimetres thickness in order to prevent the emissions of odours and other pollutants into the atmosphere.

After landfilling, inside the waste mass, anaerobic conditions are quickly established, with consequent depletion of free oxygen and oxygenated species. Landfills act as anoxic basins in which a consistent gas (mainly methane) production takes place through a microbiological pathway, at temperature and pressure conditions that are slightly above ambient conditions. Waste fermentation in anaerobic conditions thus causes the generation of a significant amount of gas, which is commonly called “landfill gas”.

In general, the landfill gas extracted from landfill wastes consists of 50-60% methane (in volume). For this reason, in most cases, landfill gas is sucked from the landfill body by means of dedicated gas extraction wells or horizontal extractors, which have the function of reducing

emissions to the atmosphere and recover energy from the methane combustion (Bogner et al., 1995).

3.2 Sources of odour emissions in landfills

Landfills are a significant source of odour emissions, as proven by the significant amount of scientific papers dealing with this issue (e.g., Capelli et al., 2008; Capelli and Sironi, 2018; Sarkar et al., 2003; Sonibare et al., 2019; Wu et al., 2017). The following paragraphs briefly summarize the main sources of odour emissions in landfills, and their potential relationships to the exposure of landfill workers.

Emissions related to fresh waste disposal

The odour emissions related to waste disposal in landfills are caused by the decomposition processes that occur in the fresh waste mass deposited onto the landfill surface. Such emissions are particularly relevant during the day, before the daily cover with soil or clay.

Landfill workers are typically exposed to fresh waste odours and related VOCs released into the landfill ambient air, especially in the waste tipping areas during the operations of refuse unloading and compacting (Kiviranta et al., 1999).

The type of odours and VOCs emitted from wastes depend on several factors, including age and type of the wastes. Odours emitted from fresh waste are usually characterized by the presence of esters and alcohols. On the contrary, emissions related to older wastes, in which the putrefaction processes are more advanced, are dominated by the presence of sulphur compounds and mercaptans having much lower odour thresholds.

Regarding the type of waste, different waste components produce different odorous compounds (Fang et al., 2012; Pierucci et al., 2005). Alcohol, volatile fatty acids (VFAs), as well as aldehydes and ketones are the products of carbohydrate degradation. Ammonia is the product of fat and protein degradation. H₂S is the result of protein degradation (e.g. rotten eggs). Rotten vegetables produce mercaptan and Carbon Disulfide. Rotten fish, spicy food, some livestock and poultry waste produce Ethylamine, Trimethylamine and indole amines. Sweets and seafood produce Formic Acid, Acetic Acid and other acidic gases (Romain et al., 2008, Scaglia et al., 2011).

Emissions related to leachate collection and storage

Leachate is the result of the removal of soluble compounds by the intermittent and non-uniform infiltration of water through the waste mass. Soluble compounds can be present in the fresh waste, or they can be formed during the chemical and biological processes occurring during decomposition of the complex organic molecules. Percolating water comes mainly from precipitation (meteoric water), which causes the infiltration of water through the landfill cover or, in minor part, to the initial waste moisture content. Also the waste

decomposition caused by the microbiological activity can contribute to the formation of leachate.

The quantity of leachate formed is site-specific; it is a function of the availability of water and the meteorological conditions, but it also depends on the waste properties, the landfill surface, and the quality of the soil.

The composition and odour properties of leachate depend mainly on the landfill fermentation stage. Existing data show high leachate concentrations of all components in the early acid phase due to strong decomposition and leaching. In the long methanogenic phase, a more stable leachate, with lower concentrations and a low BOD/COD-ratio, is observed. Generally, very low concentrations of heavy metals are observed. In contrast, the concentration of ammonia does not decrease, and often constitutes a major long-term pollutant in leachate (Kjeldsen et al., 2002).

The leachate produced in the first fermentation stage is called “young” leachate, and it is typically a black liquid with a strong odour, with high levels of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) (Bhalla et al., 2012). With time and with the progression of the fermentation reactions, the leachate COD and BOD decrease (Vaverková, 2019), together with its odour. Different factors affect the odorous nature of leachate, such as the waste compositions and the adopted operational procedures for waste disposal.

Landfill leachate management is focused on minimising contamination and preventing leachate from polluting groundwater. Therefore, leachate is typically removed from the base of the site through a suitable leachate collection and management system (Hadžikadić and Avdaković, 2017). Leachate collection can occur in vertical tanks (Figure 3, left) equipped with vents either directly connected to the atmosphere or conveyed to treatment units, or in open-air tanks where the liquid surface is directly exposed to the atmosphere (Figure 3, right). After collection, leachate is usually removed from the landfill by means of trucks and sent to suitable wastewater treatment units. In other cases leachate can be treated onsite.



Figure 3. Examples of landfill leachate collection tanks

Landfill workers can be exposed to the volatile components of leachate that are emitted into the landfill ambient air from the leachate collection tanks (especially in the case of open-air tanks as depicted in Figure 3, right), or from the vents placed over the trucks for the leachate removal during the operations of truck loading (Figure 4). The frequency of the truck loading operations vary strongly depending on different factors, including the landfill dimensions and age, the type of landfilled wastes and their potential to form leachate, and the meteorological conditions of the site and the type of landfill cover, which are related to the quantity of rainwater entering the landfill body.



Figure 4. Vent on a truck for landfill leachate transportation

Emissions related to landfill gas

Even though inside the landfilled waste mass, initially, a short phase of aerobic decomposition occurs, the subsequent anaerobic phase is dominant over the life of the landfill, and it is most important from the point of view of the gas formation.

The anaerobic decomposition can be described by different stages during which the organic matter is decomposed in Methane (CH_4) and Carbon Dioxide (CO_2). These stages are highly interdependent, and they include hydrolysis, acidogenesis, acetogenesis, and methanogenesis.

In general, the decomposition of the organic matter proceeds sequentially from the more complex molecules to the simpler ones. It begins with the hydrolysis of complex molecules into simpler polymers, like proteins, hydrocarbons and lipids, which are further hydrolysed to form biomonomers such as amino acids, sugars and fat acids with high molecular weight. Amino acids and sugars are converted into intermediate by-products (e.g., Propionic Acid, Butyric Acid, or other volatile acids) or fermented directly to Acetic Acid. The fat acids with high molecular weight are oxidized to intermediate by-products and Hydrogen. The generation of Methane and Carbon Dioxide occurs mainly through the dissociation of Acetic Acid. Methane is produced also from the reduction of Carbon Dioxide with Hydrogen. In a landfill, these reactions are often limited by the presence or absence of Oxygen.

Landfill gas (LFG) quality strongly depends on the age of the landfill. In the condition of stable methanogenesis, which is the most important stage for the landfill characterization, Methane and Carbon Dioxide are by far the main LFG components, constituting over 90% of the generated LFG volume. Indeed, landfill gas is a mixture of several, mainly non-odorous gases (i.e. CH_4 , CO_2 , N_2 , O_2 , H_2 are non-odorous). However, LFG also contains small amounts of Hydrogen Sulphide, and trace amounts of other organic compounds (collectively referred to as

non-methane organic compounds (NMOC)) in varying proportions. The total volume of NMOCs is about 1% of the total LFG volume (Durmusoglu et al., 2010).

At least 100 components have been identified as trace compounds in LFG, including hydrocarbons, esters, terpenes and organic sulphur compounds, such as mercaptans and sulphides (Young and Parker, 1983). In general, the main worries related to workers' exposure to LFG emissions are related to its content in BTEX (e.g., Durmusoglu et al., 2010; Lakhouit et al., 2020).

LFG emissions are usually minimized by installing vertical or horizontal wells that collect the gas from the landfill body and pull it to a cogeneration system, a flare, or a treatment unit. Nonetheless, gas collection and extraction systems at landfills are not 100% efficient, making that LFG diffuse cannot be completely avoided (Capaccioni et al., 2011).

As a consequence, landfill workers are typically exposed to LFG diffuse emissions that occur through the landfill surface. However, it should be highlighted that the LFG VOCs concentration is significantly reduced while crossing the landfill surface (Lucernoni et al., 2016), and that the concentrations inhaled by workers will be further reduced by dilution with air. Moreover, it should be noted that the extent of diffuse emissions is usually related to the type of landfill cover: LFG emissions from temporarily capped landfills are usually 1 to 2 orders of magnitude higher than LFG emissions from landfills with a permanent cover (Environmental Agency, 2010). For this reason, emissions from landfill surfaces with permanent cover were not considered in this study, since their emissions are considered to be negligible compared to the other landfill sources.

Nonetheless, in case of gas leaks or malfunctioning, or during particular maintenance operations on LFG extraction wells, landfill workers might still be exposed to much higher concentrations of LFG, sometimes very close to the concentrations of pure LFG.

For these reasons, when considering LFG emissions, it is important to distinguish at least two different sources: pure LFG and LFG emitted through the landfill surface.

3.3. Analysis of landfill odour emissions

Considerations about the type of data found in the scientific literature

In order to obtain an exhaustive database of chemical compounds emitted by landfills, an extensive bibliographic research was carried out, analysing the scientific papers reporting the chemical identification and quantification of volatile compounds emitted by landfills. The research was focused, but not limited to, the emissions from Municipal Solid Waste (MSW) landfills.

The scientific literature is relatively rich in studies regarding the identification of compounds emitted by landfills. For this reason, based on the classification of landfill odour emissions discussed in the previous paragraph, for our analysis we decided to consider only those papers that enabled to differentiate the analysis source by source, according to the following classification:

- Emissions of pure landfill gas;
- Emissions related to the collection and storage of landfill leachate;
- Emissions related to the disposal of fresh waste;
- Diffuse emissions from temporarily covered landfill surfaces.

This constraint led to discard some interesting papers on the subject (e.g., Wu et al., 2017), because the compounds' identification considered landfill emissions as a whole, and did not consider the different sources separately.

Nonetheless, 21 papers were considered for our analysis, published in a timespan ranging from 1997 to 2019 (Allen et al., 1997; Carriero et al., 2018; Cheng et al., 2019; Davoli et al., 2003; Dincer et al., 2006; Duan et al., 2014; Durmusoglu et al., 2010; Fang et al., 2012; Gallego et al., 2012; Gallego et al., 2014; González et al., 2013; Kim et al., 2005; Kim et al., 2006; Parker et al., 2002; Rodríguez-Navas et al., 2012; Sadowska-Rociek et al., 2009; Scaglia et al., 2011; Scheutz et al., 2008; Schweigkofler and Niessner, 1999; Termonia and Termonia, 1999; Ying et al., 2012).

As previously mentioned, emissions from landfill surfaces with permanent cover were not considered in this study, since their emissions are considered to be negligible compared to the other landfill sources.

It should be highlighted that, depending on the paper and on the type of source considered, the literature data regarding the chemical compounds' concentrations related to landfill emissions, have been obtained using different sampling techniques.

In the case of the identification of chemical compounds in pure landfill gas, samples are collected directly at the extraction wells, or at the inlet of the LFG combustion facilities.

Regarding the emissions associated with landfill leachate, these were characterized by collecting ambient air samples in the vicinity of the leachate collection tanks (e.g., Sadowska-Rociek et al., 2009, Ying et al., 2012). Such samples cannot be considered quantitatively directly representative of the emission source; nonetheless, they can be used for the purpose of this study, which is related to the potential exposure of landfill workers.

In the case of the characterization of the emissions from the covered landfill surface (with temporary capping), and from the fresh waste (i.e. uncovered landfill surface), two main types of sampling methods can be identified. In some papers (e.g., Duan et al., 2014; Termonia and Termonia, 1999; Ying et al., 2012) samples were collected in ambient air over the landfill surface. In other cases (e.g., Dincer et al., 2006; Gallego et al., 2014; Gonzalez et al., 2013; Scheutz et al., 2008), samples were collected by means of a sampling hood called flux chamber. Flux chambers are commonly used to determine emission fluxes from landfill surfaces by introducing a known flux of neutral air inside a sampling hood, and then collecting a sample at the hood outlet (Capelli et al., 2013).

Despite being more representative of the emitted flux, the concentrations measured at flux chamber outlets are not necessarily higher compared to concentrations measured in ambient air, since the introduction of a neutral air flow inside the hood produces a dilution of the emitted compounds.

Indeed, in order to evaluate which type of concentration data to be considered for this study, we tried to compare the maximum concentration values of the chemical compounds obtained by means of hood sampling vs. ambient air sampling. As an example, Figure 5 illustrates the comparison carried out for fresh waste emissions. As can be seen from Figure 5, for the 23 compounds considered, it is not possible to highlight any trend proving one sampling method produces more conservative concentration values than the other one.

Based on this evidence, and considering that the scope of this work is not risk assessment, but rather the identification of the most critical compounds to be considered as most worthy of deeper investigation in case of more specific exposure evaluations, we decided to consider both type of concentration data for our study, and thus to evaluate the HQ based on the maximum concentration value obtained independently from the sampling method adopted.

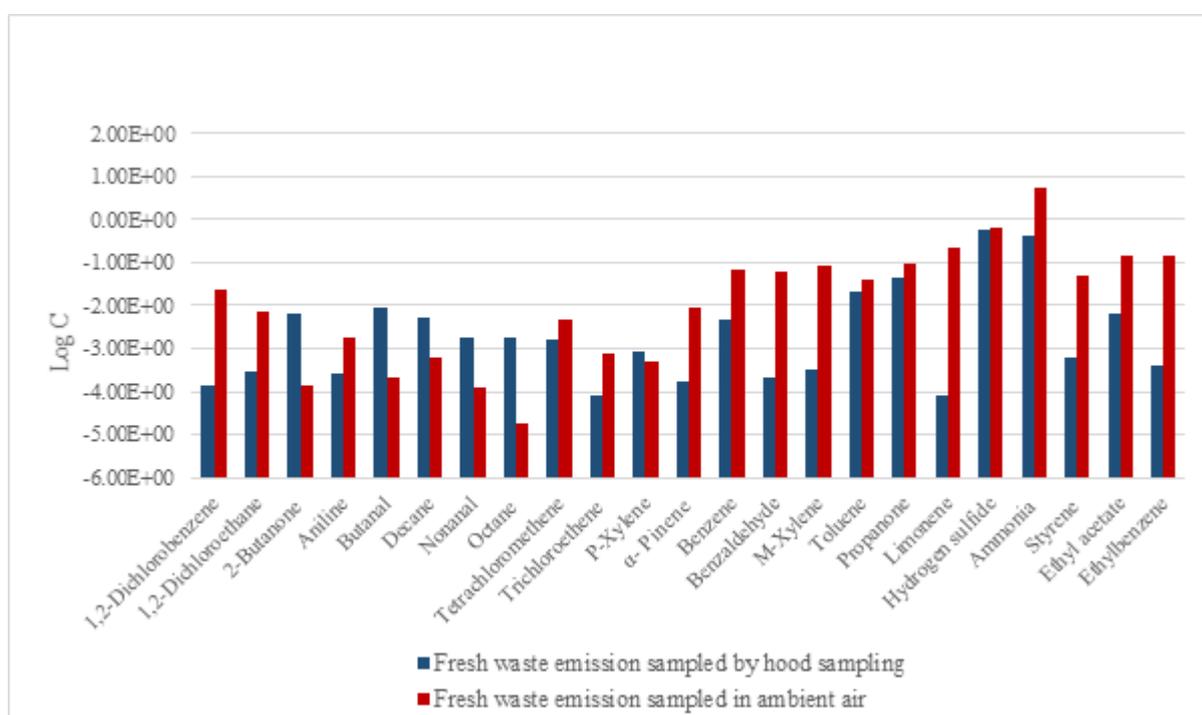


Figure 5. Comparison of maximum concentrations related to fresh waste emissions obtained by means of flux chamber (blue) vs. ambient air sampling (red)

Data summary of the chemical compounds related to pure landfill gas

The database regarding the chemical compounds related to pure landfill gas (Table 3) was built by providing a list of the compounds identified at least once in the scientific papers that have investigated the chemical composition of pure landfill gas, together with their OT and TLV.

As previously mentioned, the concentration values retrieved in the literature refer to pure LFG samples collected in correspondence of the LFG collection and extraction system.

As for foundries, we used the value of the maximum concentration found in the literature in order to evaluate the relative HQ for each compound, expressed as the ratio between the HQ and the HI, as explained in section 1.2 of this document.

Finally, in the database (Table 3), the compounds classified as carcinogenic according to the definition supplied in Part 3 of Annex VI to EU Regulation (EC) No. 1272/2008 are identified as follows:

- Carcinogen if the compound is classified as carcinogens of category 1A or 1B.
- Suspected to have carcinogenic potential for humans if the compound is classified as carcinogens of category 2.

In Table 3, compounds not belonging to the categories established by the EU Regulation have been left blank. The compounds not available in the EU Regulation are reported in the table as *not available*.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | HQ _i ,% | Carcinogenic |
|--|------------|---------------|----------------|----------|--------------------|---------------|
| 1,1,2-Trichloro-1,2,2-trifluoroethane | 76-13-1 | 1000 | 1250 | | 1.50E-05 | Not available |
| 1,1,2-Trichloroethane | 79-00-5 | 10 | | | 6.30E-03 | |
| 1,1,3,3-Tetramethylcyclopentane | 50876-33-0 | | | | | Not available |
| 1,1,3-Trimethylcyclohexane | 3073-66-3 | | | | | Not available |
| 1,1-Dichloroethane | 75-34-3 | 100 | | | 2.08E-02 | |
| 1,1-Dimethylcyclopropane | 1630-94-0 | | | | | Not available |
| 1,2,3-Trimethylbenzene | 526-73-8 | 25 | | | 3.82E-07 | Not available |
| 1,2,4-Trimethylbenzene | 95-63-6 | 25 | | 0.12 | 1.83E-07 | |
| 1,2,4-Trimethylcyclohexane | 2234-75-5 | | | | | Not available |
| 1,2,4-Trimethylcyclopentane | 4850-28-6 | | | | | Not available |
| 1,2-Dichloro-1,1,2-trifluoroethane | 354-23-4 | | | | | Not available |
| 1,2-Dichlorobenzene | 95-50-1 | 25 | 50 | | 7.52E-04 | |
| 1,2-Dichloroethane | 107-06-2 | 10 | | | 4.81E-05 | Carc. 1B |
| 1,2-Dichloroethene | 540-59-0 | 200 | | | 4.37E-03 | |
| 1,2-Dichloropropane | 78-87-5 | 10 | | | 2.48E-05 | Carc. 1B |
| 1,2-Dimethyl-3-(1-methylethyl), cyclopentane | 489-20-3 | | | | | Not available |
| 1,2-Dimethylcyclohexane | 583-57-3 | | | | | Not available |
| 1,2-Dimethylcyclopentane | 2452-99-5 | | | | | Not available |
| 1,2-Dimethylcyclopropane | 2511-95-7 | | | | | Not available |

| | | | | | | |
|--|------------|------|------|-------|----------|---------------|
| 1,3,5-Trimethyl benzene | 108-67-8 | 25 | | 0.17 | 8.23E-03 | |
| 1,3,5-Trimethylcyclohexane | 1839-63-0 | | | | | Not available |
| 1,3-Dichlorobenzene | 541-73-1 | | | | | |
| 1,3-Diethylbenzene | 141-93-5 | | | 0.07 | | Not available |
| 1,3-Dimethylcyclohexane | 591-21-9 | | | | | Not available |
| 1,3-Dimethylcyclopentane | 2453-00-1 | | | | | Not available |
| 1,3-Pentadiene | 504-60-9 | | | | | Not available |
| 1,4-Dimethylcyclohexane | 589-90-2 | | | | | |
| 1-Butene | 106-98-9 | 250 | | 0.36 | 4.22E-05 | |
| 1-Chloro-1,1-difluoroethane | 75-68-3 | | | | | Not available |
| 1-Chloro-1-fluoroethane | 1615-75-4 | | | | | Not available |
| 1-Ethyl-2-methylbenzene | 611-14-3 | | | 0.074 | | Not available |
| 1-Ethyl-2-methylcyclohexane | 3728-54-9 | | | | | Not available |
| 1-Ethyl-2-methylcyclopentane | 930-90-5 | | | | | Not available |
| 1-Ethyl-3-methylcyclohexane | 3728-55-0 | | | | | Not available |
| 1-Ethyl-3-methylcyclopentane | 3726-47-4 | | | | | Not available |
| 1-Ethyl-4-methylcyclohexane | 3728-56-1 | | | | | Not available |
| 1-Heptene | 592-76-7 | 400 | 500 | 0.37 | 3.40E-05 | Not available |
| 1-Hexene | 592-41-6 | 50 | | 0.14 | 2.16E-04 | Not available |
| 1-Methyl-2-propylbenzene | 1074-17-5 | | | | | Not available |
| 1-Methyl-2-propylcyclopentane | 932-44-5 | | | | | Not available |
| 1-Methyl-3-propyl benzene | 1074-43-7 | | | | | Not available |
| 1-Methyl-4-(1-methylethyl)-cyclohexane | 99-82-1 | | | | | Not available |
| 1-Pentene | 109-67-1 | 1000 | | 0.1 | 8.65E-06 | Not available |
| 1-Propanol | 71-23-8 | 100 | | 0.094 | 4.26E-04 | |
| 1-Propene | 115-07-1 | 500 | | 13 | 2.44E-07 | |
| 2,2-Dimethylheptane | 1071-26-7 | 200 | | | 5.10E-06 | Not available |
| 2,2-Dimethylpentane | 590-35-2 | 400 | 500 | 38 | 8.15E-07 | |
| 2,3,4-trimethylpentane | 565-75-3 | 300 | | | 3.09E-05 | |
| 2,3,6-Trimethyloctane | 62016-33-5 | | | | | Not available |
| 2,3-Dimethylbutane | 79-29-8 | 500 | 1000 | 0.42 | 3.57E-07 | |

| | | | | | | |
|--|------------|-----|-----|-------|----------|---------------|
| 2,3-Dimethylheptane | 3074-71-3 | 200 | | | 2.12E-04 | Not available |
| 2,3-Dimethylhexane | 584-94-1 | 300 | | | 2.54E-05 | |
| 2,3-Dimethyloctane | 7146-60-3 | | | | | Not available |
| 2,4,4-trimethylpentane | 540-84-1 | 300 | | 0.67 | 2.58E-05 | |
| 2,4,6-trimethylheptane | 2613-61-8 | | | | | Not available |
| 2,4-Dimethylheptane | 2213-23-2 | 200 | | | 6.05E-02 | Not available |
| 2,4-Dimethylhexane | 589-43-5 | 300 | | | 3.32E-05 | |
| 2,4-Dimethylpentane | 108-08-7 | 400 | 500 | 0.94 | 3.15E-07 | |
| 2,5-Dimethylfuran | 625-86-5 | | | | | Not available |
| 2,5-Dimethylhexane | 592-13-2 | 300 | | | 5.71E-06 | |
| 2,6,10-Trimethyldodecane | 3891-98-3 | | | | | Not available |
| 2,6-Dimethylbenzaldehyde | 1123-56-4 | | | | | Not available |
| 2,6-Dimethylheptane | 1072-05-5 | 200 | | | 1.78E-04 | Not available |
| 2,6-Dimethylnonane | 17302-28-2 | | | | | Not available |
| 2,6-Dimethyloctane | 2051-30-1 | | | | | Not available |
| 2-Butanol | 78-92-2 | 100 | | 0.22 | 2.06E-03 | |
| 2-Butanone | 78-93-3 | 200 | 300 | 0.44 | 1.60E-03 | |
| 2-Butene | 107-01-7 | 250 | | | 2.56E-05 | |
| 2-Ethyl furan | 3208-16-0 | | | | | Not available |
| 2-Ethyl-1,3-dimethylbenzene | 2870-04-4 | | | | | Not available |
| 2-Ethylcycloheptanone | 3183-41-3 | | | | | Not available |
| 2-Hexanone | 591-78-6 | 5 | 10 | 0.024 | 2.25E-03 | |
| 2-Hexene | 4050-45-7 | | | | | Not available |
| 2-Methyl-1,3-butadiene | 78-79-5 | | | 0.048 | | Carc. 1A |
| 2-Methyl-1,3-dioxolane | 497-26-7 | | | | | Not available |
| 2-Methyl-1-butene | 563-46-2 | | | | | Not available |
| 2-Methyl-1-pentene | 763-29-1 | | | | | Not available |
| 2-Methyl-1-propene | 115-11-7 | 250 | | 10 | 9.30E-05 | |
| 2-Methyl-5-(1-methylethyl)-cyclohexanone | 59471-80-6 | | | | | Not available |
| 2-Methylbutane | 78-78-4 | 600 | | 1.3 | 2.22E-04 | |
| 2-Methyldecane | 6975-98-0 | | | | | Not available |

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|------------------------|-------------|-----|------|--------|----------|---------------|
| 2-Methylheptane | 592-27-8 | 300 | | 0.11 | 7.83E-05 | |
| 2-Methylhexane | 591-76-4 | 400 | 500 | 0.42 | 3.46E-05 | |
| 2-Methylnonane | 871-83-0 | | | | | Not available |
| 2-Methylpentane | 107-83-5 | 500 | 1000 | 7 | 7.37E-06 | |
| 2-Methylpropyl-benzene | 538-93-2 | | | | | Not available |
| 2-Pentene | 109-68-2 | | | | | Not available |
| 2-propanol | 67-63-0 | 200 | 400 | 26 | 4.24E-04 | |
| 2-Propylthiophene | 1551-27-5 | | | | | Not available |
| 3,5-Dimethyloctane | 15869-93-9 | | | | | Not available |
| 3-Ethylhexane | 619-99-8 | 300 | | | 7.77E-06 | |
| 3-Ethylpentane | 617-78-7 | 400 | 500 | 0.37 | 2.10E-05 | |
| 3-Methyldecane | 13151-34-3 | | | | | Not available |
| 3-Methylheptane | 589-81-1 | 300 | | 1.5 | 9.36E-05 | |
| 3-Methylhexane | 589-34-4 | 400 | 500 | 0.84 | 3.84E-05 | |
| 3-Methylnonane | 5911-04-6 | | | | | Not available |
| 3-Methyloctane | 2216-33-3 | 200 | | | 5.06E-04 | Not available |
| 3-Methylpentane | 96-14-0 | 500 | 1000 | 8.9 | 5.39E-05 | |
| 3-Pentanone | 96-22-0 | 200 | 300 | 0 | 3.84E-06 | |
| 4,5-Dipropyloctane | 20905-05-09 | | | | | Not available |
| 4,7-Dimethylundecane | 17301-32-5 | | | | | Not available |
| 4-Methyl-2-pentanone | 108-10-1 | 20 | 75 | 0.17 | 2.31E-03 | |
| 4-Methylcyclohexanone | 589-92-4 | | | | | Not available |
| 4-Methyldecane | 2847-72-5 | | | | | Not available |
| 4-Methylnonane | 17301-94-9 | | | | | Not available |
| 4-Methyloctane | 2216-34-4 | 200 | | | 1.13E-05 | Not available |
| 5-Methyldecane | 13151-35-4 | | | | | Not available |
| 6-Pentadecen-1-ol | 64437-42-9 | | | | | Not available |
| 7-Methyl-3,4-octadiene | 37050-05-8 | | | | | Not available |
| Acetaldehyde | 75-07-0 | | 25 | 0.0015 | 5.35E-05 | Carc. 1B |
| Acetic acid | 64-19-7 | 10 | 15 | 0.006 | 1.36E-03 | |
| Acrolein | 107-02-8 | | 0.1 | 0.0036 | 8.36E-03 | |

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|-------------------------------|------------|------|-----|---------|----------|---------------|
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 1.37E-03 | |
| Aniline | 62-53-3 | 2 | | | 4.77E-05 | Carc. 2 |
| Benzaldehyde | 100-52-7 | | | | | |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.7 | 1.42E-01 | Carc. 1A |
| Benzyl chloride | 100-44-7 | 1 | | | 9.55E-05 | Carc. 1B |
| Butanoic acid | 107-92-6 | | | 0.00019 | | |
| Butanol | 71-36-3 | 20 | | 0.038 | 4.72E-03 | |
| Butyl acetate | 123-86-4 | 150 | 200 | 0.016 | 1.04E-06 | |
| Camphene | 79-92-5 | | | | | Not available |
| Carbon disulphide | 75-15-0 | 1 | | 0.21 | 1.02E-01 | |
| Chlorodifluoromethane | 75-45-6 | 1000 | | | 3.02E-03 | Not available |
| Chloroethane | 75-00-3 | 100 | | | 5.79E-04 | Carc. 2 |
| Chloroethene | 75-01-4 | 1 | | | 6.49E-01 | Carc. 1A |
| Chlorofluoromethane | 593-70-4 | | | | | Not available |
| Cinnamaldehyde | 14371-10-9 | | | | | Not available |
| Cis-1,3-Dimethylcyclohexane | 638-04-0 | | | | | Not available |
| Cyclobutane | 287-23-0 | 1000 | | | 4.05E-06 | Not available |
| Cycloheptane | 287-92-3 | | | | | |
| Cyclohexane | 110-82-7 | 100 | | 2.5 | 1.72E-03 | |
| Cyclopentene | 142-29-0 | | | | | Not available |
| Decahydro-2-methylnaphthalene | 2958-76-1 | | | | | Not available |
| Decahydronaphthalene | 91-17-8 | | | | | Not available |
| Decamethylcyclopentasiloxane | 541-02-6 | 10 | | | 1.37E-04 | Not available |
| Decamethyltetrasiloxane | 141-62-8 | | | | | Not available |
| Delta-3-Carene | 13466-78-9 | 20 | | | 3.49E-03 | Not available |
| Dichlorodifluoromethane | 75-71-8 | 1000 | | | 8.92E-04 | Not available |
| Dichloromethane | 75-09-2 | 50 | | 160 | 9.34E-03 | Carc. 2 |
| Diethyl benzene | 25340-17-4 | | | | | Not available |
| Diethyl ether | 60-29-7 | 400 | 500 | | 3.63E-05 | |
| Diethyl phthalate | 84-66-2 | 0.55 | | | 2.43E-06 | Not available |
| Dimethoxymethane | 109-87-5 | 1000 | | | 2.48E-09 | Not available |

| | | | | | | |
|----------------------------|------------|------|------|--------------|----------|---------------|
| Dimethyl disulphide | 624-92-0 | 0.5 | | 0.0022 | 1.06E-02 | Not available |
| Dimethyl ether | 115-10-6 | | | | | |
| Dimethyl pentene | 762-62-9 | | | | | Not available |
| Dimethyl sulphide | 75-18-3 | 10 | | 0.003 | 4.32E-02 | Not available |
| Dimethyl trisulfide | 3658-80-8 | | | | | Not available |
| Dodecane | 112-40-3 | | | 0.11 | | Not available |
| Ethanol | 64-17-5 | | 1000 | 0.53 | 1.31E-05 | |
| Ethyl acetate | 141-78-6 | 400 | | 0.87 | 7.37E-06 | |
| Ethyl cyclohexane | 1678-91-7 | | | | | Not available |
| Ethyl cyclopentane | 1640-89-7 | | | | | Not available |
| Ethyl cyclopropane | 1191-96-4 | | | | | Not available |
| Ethyl disulphide | 110-81-6 | | | 0.002 | | Not available |
| Ethyl toluene | 622-96-8 | | | 0.0083 | | Not available |
| Ethylbenzene | 100-41-4 | 20 | | 0.17 | 1.30E-02 | |
| Eucalyptol | 470-82-6 | | | | | Not available |
| Formaldehyde | 50-00-0 | | 0.3 | 0.5 | 3.11E-03 | Carc. 1B |
| Furan | 110-00-9 | | | 9.9 | | Carc. 1B |
| Furfuryl alcohol | 98-00-0 | 10 | 15 | | 4.34E-06 | Carc. 2 |
| Hexachlorobutadiene | 87-68-3 | 0.02 | | | 9.55E-04 | Not available |
| Hexadecane | 544-76-3 | | | | | Not available |
| Hexaldehyde | 66-25-1 | | | 0.00028 | | Not available |
| Hexamethylcyclotrisiloxane | 541-05-9 | 0.3 | | | 2.86E-03 | Not available |
| Hexamethyldisiloxane | 107-46-0 | | | | | Not available |
| Hydrogen sulphide | 7783-06-04 | 1 | 5 | | 9.82E+01 | Not available |
| Isobutane | 75-28-5 | 1000 | | | 2.85E-05 | |
| Isopropyl benzene | 98-82-8 | 50 | | 0.0084 | 1.57E-04 | |
| Isovaleraldehyde | 590-86-3 | | | 0.0001 | | Not available |
| Isovaleric acid | 503-74-2 | | | 0.00007 8 | | Not available |
| d-Limonene | 5989-27-5 | | | | | |
| Longifolene | 475-20-7 | | | | | Not available |
| Methanethiol | 74-93-1 | 0.5 | | 0.00007 | 2.71E-01 | |

| | | | | | | |
|------------------------------|------------|------|------|---------|----------|---------------|
| Methanol | 67-56-1 | 200 | 250 | 33 | 4.12E-06 | |
| Methyl butyrate | 623-42-7 | | | 0.0071 | | Not available |
| Methyl cycloheptane | 4126-78-7 | | | | | Not available |
| Methyl cyclopentane | 96-37-7 | 500 | 1000 | 1.7 | 1.93E-05 | Not available |
| Methyl Furan | 534-22-5 | | | | | Not available |
| Methyl styrene | 98-83-9 | 10 | | 0 | 3.95E-04 | |
| Methylamine | 74-89-5 | 5 | 15 | 0.035 | 2.92E-04 | |
| Methylcyclobutane | 598-61-8 | | | | | Not available |
| Methylcyclohexane | 108-87-2 | 400 | | 0.15 | 1.11E-04 | |
| Methylcyclopropene | 3100-04-07 | | | | | Not available |
| Methyl-ethyl cyclohexane | 696-29-7 | | | | | Not available |
| Methyl-propyl cyclohexane | 4258-93-9 | | | | | Not available |
| m-xylene | 108-38-3 | 100 | 150 | 0.041 | 9.74E-04 | |
| Naphthalene | 91-20-3 | 10 | 15 | | 1.49E-05 | Carc. 2 |
| n-Butane | 106-97-8 | 1000 | | 1200 | 1.47E-04 | |
| n-Butyraldehyde | 123-72-8 | | | 0.00067 | | |
| n-Decane | 124-18-5 | | | 0.62 | | Not available |
| n-Heptane | 142-82-5 | 400 | 500 | 0.67 | 2.48E-04 | |
| n-Hexane | 110-54-3 | 50 | | 1.5 | 3.04E-03 | |
| n-Nonane | 111-84-2 | 200 | | 2.2 | 1.73E-03 | Not available |
| n-Octane | 111-65-9 | 300 | | 1.7 | 3.72E-04 | |
| n-Pentane | 109-66-0 | 600 | 750 | 1.4 | 3.57E-04 | |
| Octamethylcyclotetrasiloxane | 556-67-2 | 10 | 15 | | 4.43E-03 | |
| Octamethyltrisiloxane | 107-51-7 | | | | | Not available |
| o-Xylene | 95-47-6 | 100 | 150 | 0.38 | 1.88E-02 | |
| p-Cymene | 99-87-6 | | | | | Not available |
| Pentanol | 71-41-0 | | | 0.1 | | |
| Phellandrene | 99-83-2 | | | | | Not available |
| Propanal | 123-38-6 | 20 | | 0.001 | 6.66E-07 | |
| Propane | 74-98-6 | 1000 | | 1500 | 4.03E-07 | |
| Propanone | 67-64-1 | 200 | 500 | 42 | 2.35E-06 | |

| | | | | | | |
|--------------------------------|------------|-----|------|--------------|----------|---------------|
| Propionic acid | 79-09-4 | 10 | | 0.0057 | 1.08E-04 | |
| Propyl acetate | 109-60-4 | 200 | 250 | 0.24 | 4.56E-07 | |
| Propyl benzene | 103-65-1 | | | 0.0038 | | |
| Propyl cyclohexane | 1678-92-8 | | | | | Not available |
| Propyl thiophene | 1518-75-8 | | | | | Not available |
| p-Tolualdehyde | 104-87-0 | | | | | Not available |
| p-Xylene | 106-42-3 | 100 | 150 | 0.058 | 1.75E-02 | |
| Sabinyl acetate | 3536-54-7 | | | | | Not available |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 2.18E-02 | |
| Tert-Butylbenzene | 98-06-6 | | | | | Not available |
| Tetrachloroethene | 127-18-4 | 25 | 100 | 0.77 | 2.81E-02 | Carc. 2 |
| Tetrachloromethane | 56-23-5 | 5 | 10 | 4.6 | 1.28E-02 | Carc. 2 |
| Tetrahydrofuran | 109-99-9 | 50 | 100 | | 3.65E-04 | Carc. 2 |
| Thiophene | 110-02-1 | | | 0.00056 | | Not available |
| Toluene | 108-88-3 | 20 | | 0.33 | 2.43E-01 | |
| trans-1,3-Dimethylcyclohexane | 2207-03-6 | | | | | Not available |
| trans-1,3-Dimethylcyclopentane | 1759-58-6 | | | | | Not available |
| Trichloroethene | 79-01-6 | 10 | 25 | 3.9 | 5.40E-02 | Carc. 1B |
| Trichlorofluoromethane | 75-69-4 | | 1000 | | 2.52E-04 | Not available |
| Trimethyl hexane | 921-47-1 | | | | | Not available |
| Trimethylamine | 75-50-3 | 5 | 15 | 0.00003 2 | 9.09E-05 | |
| Trimethylbenzene | 25551-13-7 | 25 | | | 2.90E-02 | Not available |
| Trimethylsilanol | 1066-40-6 | | | | | Not available |
| Undecane | 1120-21-4 | | | | | Not available |
| Undecene | 821-95-4 | | | | | Not available |
| Valeric acid | 109-52-4 | | | 0.00003 7 | | |
| Xylene (mix) | 1330-20-7 | 100 | 150 | | 1.02E-03 | |
| α- Pinene | 80-56-8 | 20 | | 0.018 | 1.51E-02 | Not available |
| α-Thujone | 546-80-5 | | | | | Not available |
| β- Pinene | 127-91-3 | 20 | | 0.033 | 1.99E-03 | Not available |

| | | | | | | |
|---------------------|----------|--|--|--|--|---------------|
| β -Thujone | 471-15-8 | | | | | Not available |
| γ -Terpinene | 99-85-4 | | | | | Not available |

Table 3. Analysis of chemical compounds related to pure landfill gas

Evaluation of priority compounds related to pure landfill gas

According to the approach proposed by Jiang et al. (2017), the first group of priority compounds are those classified as carcinogens. Based on the classification proposed by the EU Regulation (EC) No. 1272/2008, the carcinogenic compounds (categories 1A and 1B) identified in pure landfill gas are the following:

- 1,2-Dichloroethane (1B)
- 1,2-Dichloropropane (1B)
- 2-Methyl-1,3-butadiene (1A)
- Acetaldehyde (1B)
- Benzene (1A)
- Benzyl Chloride (1B)
- Chloroethene (1A)
- Formaldehyde (1B)
- Furan (1B)
- Trichloroethene (1B)

Always according to the above-mentioned EU Regulation, the suspected carcinogenic compounds (category 2) in pure landfill gas are:

- Aniline
- Chloroethane
- Dichloromethane
- Furfuryl Alcohol
- Naphthalene
- Tetrachloroethene
- Tetrachloromethane
- Tetrahydrofuran

Considering the most critical compounds in pure landfill gas in terms of their potential to cause non-carcinogenic health effects, it is possible to refer to their relative HQ. As can be seen from Table 3, Hydrogen Sulphide is by far the compound that most contributes to the overall HI of pure landfill gas (Hydrogen Sulphide alone accounts for over 98% of the overall HI), evaluated based on the concentration data that we retrieved in the scientific literature.

In order to highlight the other compounds that have a non-negligible contribution on the HI of pure landfill gas emissions, we considered the next 20 compounds after Hydrogen Sulphide having the highest values of relative HQ ($HQ_{i,\%}$), which are, in decreasing order of relative HQ:

- Chloroethene
- Methanethiol
- Toluene
- Benzene
- Carbon Disulphide
- 2,4-Dimethylheptane
- Trichloroethene
- Dimethyl Sulfide
- 1,2,4-Trimethylbenzene
- Tetrachloroethene
- Styrene
- 1,1-Dichloroethane
- o-Xylene
- p-Xylene
- α - Pinene
- Ethylbenzene
- Tetrachloromethane
- Dimethyl Disulfide
- Dichloromethane
- Acrolein

Those 21 compounds together contribute by 99.994% to the overall HI of pure landfill gas. If not considering Hydrogen Sulphide, then the above-listed 20 compounds, which include i) halogenated hydrocarbons, ii) aromatic compounds, iii) organic sulphur compounds (sulphides and mercaptans), and iv) Acrolein, contribute by over 96% of the overall HI of pure landfill gas emissions (Table 4, Figure 6).

Table 4 also includes a column reporting the number of concentration values found in the scientific literature for each of the reported compounds. This number represents the frequency with which the compound has been identified in the analysed samples.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | No. of values | HQ _{4%} (without H ₂ S) |
|---------------------|------------|---------------|----------------|----------|---------------|---|
| Chloroethene | 75-01-4 | 1 | | | 18 | 3.53E+01 |
| Methanethiol | 74-93-1 | 0.5 | | 0.00007 | 32 | 1.47E+01 |
| Toluene | 108-88-3 | 20 | | 0.33 | 77 | 1.32E+01 |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.70 | 76 | 7.71E+00 |
| Carbon disulphide | 75-15-0 | 1 | | 0.21 | 39 | 5.55E+00 |
| 2,4-Dimethylheptane | 2213-23-2 | 200 | | | 4 | 3.29E+00 |
| Trichloroethene | 79-01-6 | 10 | 25 | 3.9 | 21 | 2.93E+00 |

| | | | | | | |
|---------------------|------------|-----|-----|--------|----|-----------------|
| Dimethyl sulphide | 75-18-3 | 10 | | 0.003 | 41 | 2.34E+00 |
| Trimethylbenzene | 25551-13-7 | 25 | | | 2 | 1.58E+00 |
| Tetrachloroethene | 127-18-4 | 25 | 100 | 0.77 | 24 | 1.52E+00 |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 26 | 1.18E+00 |
| 1,1-Dichloroethane | 75-34-3 | 100 | | | 18 | 1.13E+00 |
| o-Xylene | 95-47-6 | 100 | 150 | 0.38 | 54 | 1.02E+00 |
| p-Xylene | 106-42-3 | 100 | 150 | 0.058 | 54 | 9.52E-01 |
| α - Pinene | 80-56-8 | 20 | | 0.018 | 19 | 8.22E-01 |
| Ethylbenzene | 100-41-4 | 20 | | 0.17 | 64 | 7.08E-01 |
| Tetrachloromethane | 56-23-5 | 5 | 10 | 4.60 | 9 | 6.93E-01 |
| Dimethyl disulphide | 624-92-0 | 0.5 | | 0.0022 | 37 | 5.75E-01 |
| Dichloromethane | 75-09-2 | 50 | | 160 | 23 | 5.07E-01 |
| Acrolein | 107-02-8 | | 0.1 | 0.0036 | 1 | 4.54E-01 |

Table 4. Identification of the most critical compounds in terms of potential non-carcinogenic health effects related to pure landfill gas

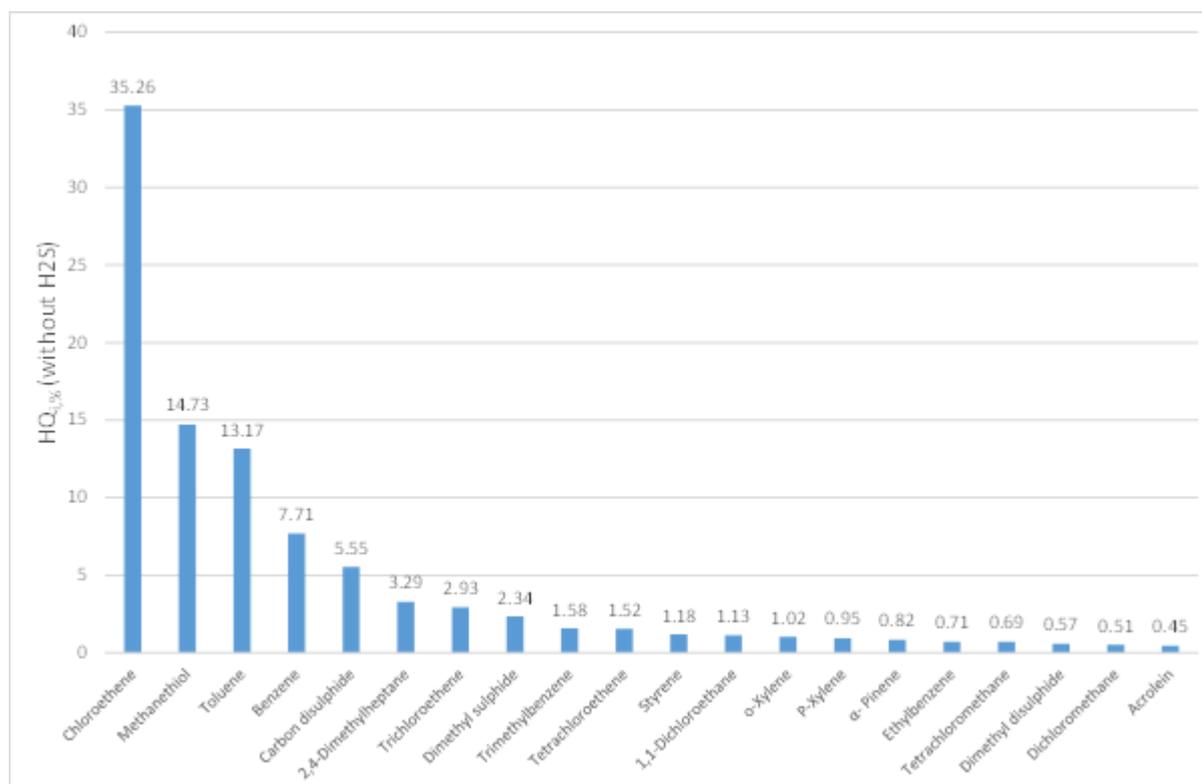


Figure 6. Graphical identification of the most critical compounds in terms of potential non-carcinogenic health effects related to pure landfill gas

In general, all compounds having a low OT have the potential to cause an odour perception. However, it should be highlighted that the perception of an odour is not directly correlated with a potential health risk. As can be seen from Figure 7, there is no direct correlation between TLVs and OTs of the chemical compounds found in pure landfill gas.

- Carcinogen if the compound is classified as carcinogens of category 1A or 1B.
- Suspected to have carcinogenic potential for humans if the compound is classified as carcinogens of category 2.

In Table 5, compounds not belonging to the categories established by the EU Regulation have been left blank. The compounds not available in the EU Regulation are reported in the table as *not available*.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | HQ _{4%} | Carcinogenic |
|-------------------------------|------------|---------------|----------------|----------|------------------|---------------|
| 1 Octene | 111-66-0 | | | 0.001 | | Not available |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 1 | | | 8.15E-04 | |
| 1,1,2-Trichloroethane | 79-00-5 | 10 | | | 3.07E-04 | Carc. 2 |
| 1,2,3,5-Tetramethylbenzene | 527-53-7 | | | | | Not available |
| 1,2,3-Trichloropropane | 96-18-4 | 10 | | | 4.62E-05 | Carc. 1B |
| 1,2,3-Trimethylbenzene | 526-73-8 | 25 | | | 2.03E-03 | Not available |
| 1,2,4-Tribromobenzene | 615-54-3 | | | | | Not available |
| 1,2,4-Trichlorobenzene | 120-82-1 | | 5 | | 7.53E-05 | |
| 1,2,4-Trimethylbenzene | 95-63-6 | 25 | | 0.12 | 5.10E-01 | |
| 1,2-Dichlorobenzene | 95-50-1 | 25 | 50 | | 9.27E-06 | |
| 1,2-Dichloroethane | 107-06-2 | 10 | | | 4.92E-04 | Carc. 1B |
| 1,2-Dichloropropane | 78-87-5 | 10 | | | 8.85E-03 | Carc. 1B |
| 1,3 Dichlorobenzene | 541-73-1 | | | | | |
| 1,3,5-Trimethyl benzene | 108-67-8 | 25 | | 0.17 | 5.30E-04 | |
| 1,4-Dichlorobenzene | 106-46-7 | 10 | | | 9.27E-05 | Carc. 2 |
| 1-Ethyl-2-methylbenzene | 611-14-3 | | | 0.074 | | Not available |
| 1-Ethyl-2-methylcyclopropane | 19781-69-2 | | | | | Not available |
| 1-Ethyl-3-methyl benzene | 620-14-4 | | | 0.018 | | Not available |
| 1-Methyl-2-pentyl cyclohexane | 54411-01-7 | | | | | Not available |
| 1-Methyl-3-propyl benzene | 1074-43-7 | | | | | Not available |
| 1-Nitrobutane | 627-05-4 | | | | | Not available |
| 2,4,6-Trichloroaniline | 634-93-5 | | | | | Not available |
| 2,4-Dimethylhexane | 589-43-5 | 300 | | | 6.97E-06 | |
| 2,6,10-Trimethyldodecane | 3891-98-3 | | | | | Not available |

| | | | | | | |
|--|------------|------|-----|---------|----------|---------------|
| 2-Butoxyethanol | 111-76-2 | 20 | | 0.043 | 3.48E-04 | |
| 2-Methyl-1,3-dioxolane | 497-26-7 | | | | | Not available |
| 3,4-Dihydropyran | 110-87-2 | | | | | Not available |
| 3,5-Dimethylbenzaldehyde | 5779-95-3 | | | | | Not available |
| 3-Pentanone | 96-22-0 | 200 | 300 | | 1.15E-03 | |
| 4,7-Dimethylundecane | 17301-32-5 | | | | | Not available |
| 4-Methyl-2-pentanone | 108-10-1 | 20 | 75 | 0.17 | 1.87E-04 | |
| 5-Methyl-2-(1-methylethyl)-cyclohexanone | 10458-14-7 | | | | | Not available |
| 5-Methyl-3-(1-methylethyl)-cyclohexanone | 89-80-5 | | | | | Not available |
| 6-Pentadecen-1-ol | 64437-42-9 | | | | | Not available |
| 7-Methyl-3,4-octadiene | 37050-05-8 | | | | | Not available |
| Acenaphthylene | 208-96-8 | | | | | Not available |
| Acetaldehyde | 75-07-0 | | 25 | 0.0015 | 3.79E-02 | Carc. 1B |
| Acetic acid | 64-19-7 | 10 | 15 | 0.006 | 7.87E+00 | |
| Acrolein | 107-02-8 | | 0.1 | 0.0036 | 4.39E+00 | |
| Acrylonitrile | 107-13-1 | 2 | | 8.8 | 6.10E-03 | Carc. 1B |
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 1.61E+01 | |
| Aniline | 62-53-3 | 2 | | | 3.41E-01 | Carc. 2 |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.7 | 7.87E+00 | Carc. 1A |
| Bromoform | 75-25-2 | 0.5 | | | 2.97E-03 | |
| Butane | 106-97-8 | 1000 | | 1200 | 6.97E-06 | |
| Butanoic acid | 107-92-6 | | | 0.00019 | | |
| Butyl acetate | 123-86-4 | 150 | 200 | 0.016 | 1.37E-05 | |
| Butyl formate | 592-84-7 | | | 0.087 | | |
| Camphene | 79-92-5 | | | | | Not available |
| Camphor | 76-22-2 | 2 | 3 | | 1.16E-01 | Not available |
| Caproic acid | 142-62-1 | | | 0.0006 | | |
| Carbon disulphide | 75-15-0 | 1 | | 0.21 | 2.23E-01 | |
| Chlorobenzene | 108-90-7 | 10 | | | 6.66E-04 | |
| Cinnamaldehyde | 14371-10-9 | | | | | Not available |
| Cis-1,4-Dichloro-2-butene | 1476-11-5 | | | | | Not available |

| | | | | | | |
|---------------------------------------|------------|------|------|-----------|----------|---------------|
| Cyclohexanone | 108-94-1 | 20 | 50 | | 6.97E-05 | |
| Cyclopropane, 1-butyl-2-pentyl-, cis- | 74663-88-0 | | | | | Not available |
| Decamethylcyclopentasiloxane | 541-02-6 | 10 | | | 4.43E+00 | Not available |
| Decamethyltetrasiloxane | 141-62-8 | | | | | Not available |
| Decanal | 112-31-2 | | | 0.0004 | | Not available |
| Decane | 124-18-5 | | | 0.62 | | Not available |
| Dichloroethylene | 540-59-0 | 200 | | | 3.86E-03 | |
| Dichloromethane | 75-09-2 | 50 | | 160 | 9.76E-05 | Carc. 2 |
| Diethyl phthalate | 84-66-2 | 0.55 | | | 1.27E-03 | Not available |
| Dimethyl disulphide | 624-92-0 | 0.5 | | 0.0022 | 1.07E+01 | Not available |
| Dimethyl sulphide | 75-18-3 | 10 | | 0.003 | 4.36E-02 | Not available |
| Dimethyl trisulfide | 3658-80-8 | | | | | Not available |
| Dimethylamine | 124-40-3 | 5 | 15 | 0.033 | 4.54E-01 | |
| Dodecane | 112-40-3 | | | 0.11 | | Not available |
| Ethanol | 64-17-5 | | 1000 | 0.53 | 1.28E-02 | |
| Ethyl mercaptan | 75-08-1 | 0.5 | | 0.0000087 | 1.21E-02 | |
| Ethylbenzene | 100-41-4 | 20 | | 0.17 | 5.05E+00 | |
| Eucalyptol | 470-82-6 | | | | | Not available |
| Formaldehyde | 50-00-0 | | 0.3 | 0.5 | 2.53E+00 | Carc. 1B |
| Formic acid | 64-18-6 | 5 | 10 | | 1.80E-02 | |
| Heptanal | 111-71-7 | | | 0.00018 | | Not available |
| Heptane | 142-82-5 | 400 | 500 | 0.67 | 2.00E-04 | |
| Heptanoic acid | 111-14-8 | | | | | |
| Hexadecane | 544-76-3 | | | | | Not available |
| Hexamethylcyclotrisiloxane | 541-05-9 | 0.3 | | | 4.64E+00 | Not available |
| Hexamethyldisiloxane | 107-46-0 | | | | | Not available |
| Hexane | 110-54-3 | 50 | | 1.5 | 2.37E-05 | |
| Hydrogen sulphide | 7783-06-4 | 1 | 5 | 0.00041 | 2.44E+01 | |
| Isobutyric acid | 79-31-2 | | | 0.0015 | | |
| Isopropyl benzene | 98-82-8 | 50 | | 0.0084 | 5.84E-04 | |
| Isopropyl toluene | 99-87-6 | | | | | Not available |

| | | | | | | |
|------------------------------|-----------|-----|-----|----------|----------|---------------|
| Isovaleric acid | 503-74-2 | | | 0.000078 | | Not available |
| Limonene | 5989-27-5 | | | | | |
| Methanethiol | 74-93-1 | 0.5 | | 0.00007 | 1.74E-01 | |
| Methanol | 67-56-1 | 200 | 250 | 33 | 8.64E-03 | |
| Methyl propionate | 554-12-1 | | | 0.098 | | |
| Methylamine | 74-89-5 | 5 | 15 | 0.035 | 7.66E-02 | |
| Methylcyclohexane | 108-87-2 | 400 | | 0.15 | 5.21E-04 | |
| Naphthalene | 91-20-3 | 10 | 15 | | 2.66E-05 | Carc. 2 |
| n-Butanone | 78-93-3 | 200 | 300 | 0.44 | 1.64E-03 | |
| n-Butyraldehyde | 123-72-8 | | | 0.00067 | | |
| Nonanal | 124-19-6 | | | 0.00034 | | |
| Nonane | 111-84-2 | 200 | | 2.2 | 8.64E-02 | Not available |
| Octamethylcyclotetrasiloxane | 556-67-2 | 10 | 15 | | 4.01E+00 | |
| Octamethyltrisiloxane | 107-51-7 | | | | | Not available |
| Octane | 111-65-9 | 300 | | 1.7 | 6.96E-02 | |
| o-Xylene | 95-47-6 | 100 | 150 | 0.38 | 1.28E-01 | |
| Pentanol | 71-41-0 | | | 0.1 | | |
| Phthalic anhydride | 85-44-9 | 1 | | | 4.18E-03 | |
| Propanal | 123-38-6 | 20 | | 0.001 | 6.75E-04 | |
| Propanone | 67-64-1 | 200 | 500 | 42 | 6.13E-03 | |
| Propionic acid | 79-09-4 | 10 | | 0.0057 | 1.54E-01 | |
| Propyl benzene | 103-65-1 | | | 0.0038 | | |
| Pyridine | 110-86-1 | 1 | | 0.063 | 3.45E-03 | |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 2.29E-01 | |
| Tetrachloroethene | 127-18-4 | 25 | 100 | 0.77 | 3.42E-03 | Carc. 2 |
| Toluene | 108-88-3 | 20 | | 0.33 | 2.40E+00 | |
| Trans-1,4-Dichloro-2-butene | 110-57-6 | | | | | Not available |
| Trichloroethene | 79-01-6 | 10 | 25 | 3.9 | 4.52E-03 | Carc. 1B |
| Trimethylamine | 75-50-3 | 5 | 15 | 0.000032 | 5.30E-02 | |
| Trimethylsilanol | 1066-40-6 | | | | | Not available |
| Undecane | 1120-21-4 | | | | | Not available |

| | | | | | | |
|-----------------------|----------|----|----|----------|----------|---------------|
| Valeric acid | 109-52-4 | | | 0.000037 | | |
| Vinyl acetate | 108-05-4 | 10 | 15 | | 4.36E-04 | Carc. 2. |
| α - Pinene | 80-56-8 | 20 | | 0.018 | 2.75E+00 | Not available |
| α -Terpinene | 99-85-4 | | | | | Not available |
| α -Terpinolene | 586-62-9 | | | | | Not available |
| β - Pinene | 127-91-3 | 20 | | 0.033 | 2.63E-02 | Not available |

Table 5. Analysis of chemical compounds related to landfill leachate emissions

Evaluation of priority compounds related to landfill leachate emissions

According to the approach proposed by Jiang et al. (2017), the first group of priority compounds are those classified as carcinogens. Based on the classification proposed by the EU Regulation (EC) No. 1272/2008, the carcinogenic compounds (categories 1A and 1B) identified in ambient air samples collected in the vicinity of landfill leachate collection and storage tanks are the following:

- 1,2,3-Trichloropropane (1B)
- 1,2-Dichloroethane (1B)
- 1,2-Dichloropropane (1B)
- Acetaldehyde (1B)
- Acrylonitrile (1B)
- Benzene (1A)
- Formaldehyde (1B)
- Trichloroethene (1B)

Always according to the above-mentioned EU Regulation, the suspected carcinogenic compounds (category 2) in landfill leachate emissions are:

- 1,1,2-Trichloroethane
- 1,4-Dichlorobenzene
- Aniline
- Dichloromethane
- Naphthalene
- Tetrachloroethene
- Vinyl acetate

Considering the most critical compounds related to landfill leachate emissions in terms of their potential to cause non-carcinogenic health effects, it is possible to refer to their relative HQ ($HQ_{i,\%}$). In this case, there isn't one unique compound accounting for almost the overall HI. Hydrogen Sulphide is the compound having the highest relative HQ (accounting for 24.4% of the overall HI), followed by Ammonia and Dimethyl Disulphide (accounting for 16.1% and 10.7% of the overall HI, respectively).

The other compounds that have a non-negligible contribution on the HI of landfill leachate emissions are, in decreasing order of relative HQ:

- Acetic Acid
- Benzene
- Ethylbenzene
- Hexamethylcyclotrisiloxane
- Decamethylcyclopentasiloxane
- Acrolein
- Octamethylcyclotetrasiloxane
- α - Pinene
- Formaldehyde
- Toluene
- 1,2,4-Trimethylbenzene
- Dimethylamine
- Aniline
- Styrene
- Carbon Disulphide
- Methanethiol
- Propionic acid
- o-Xylene
- Camphor

Those 22 compounds, which include i) organic acids, ii) aromatic compounds, iii) siloxanes, iv) aldehydes, and v) organic sulphur compounds, together contribute by 99.5% to the overall HI of landfill leachate emissions (Table 6, Figure 8)

Table 6 also includes a column reporting the number of concentration values found in the scientific literature for each of the reported compounds. This number represents the frequency with which the compound has been identified in the analysed samples.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | No. of values | HQ _{4%} |
|------------------------------|------------|---------------|----------------|----------|---------------|------------------|
| Hydrogen sulphide | 7783-06-4 | 1 | 5 | 0.00041 | 3 | 2.44E+01 |
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 3 | 1.61E+01 |
| Dimethyl disulphide | 624-92-0 | 0.5 | | 0.0022 | 4 | 1.07E+01 |
| Acetic acid | 64-19-7 | 10 | 15 | 0.006 | 5 | 7.87E+00 |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.7 | 12 | 7.87E+00 |
| Ethylbenzene | 100-41-4 | 20 | | 0.17 | 12 | 5.05E+00 |
| Hexamethylcyclotrisiloxane | 541-05-9 | 0.3 | | | 4 | 4.64E+00 |
| Decamethylcyclopentasiloxane | 541-02-6 | 10 | | | 4 | 4.43E+00 |

| | | | | | | |
|------------------------------|----------|-----|-----|---------|----|----------|
| Acrolein | 107-02-8 | | 0.1 | 0.0036 | 4 | 4.39E+00 |
| Octamethylcyclotetrasiloxane | 556-67-2 | 10 | 15 | | 4 | 4.01E+00 |
| α - Pinene | 80-56-8 | 20 | | 0.018 | 7 | 2.75E+00 |
| Formaldehyde | 50-00-0 | | 0.3 | 0.5 | 2 | 2.53E+00 |
| Toluene | 108-88-3 | 20 | | 0.33 | 15 | 2.40E+00 |
| 1,2,4-Trimethylbenzene | 95-63-6 | 25 | | 0.12 | 1 | 5.10E-01 |
| Dimethylamine | 124-40-3 | 5 | 15 | 0.033 | 2 | 4.54E-01 |
| Aniline | 62-53-3 | 2 | | | 2 | 3.41E-01 |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 2 | 2.29E-01 |
| Carbon disulphide | 75-15-0 | 1 | | 0.21 | 4 | 2.23E-01 |
| Methanethiol | 74-93-1 | 0.5 | | 0.00007 | 4 | 1.74E-01 |
| Propionic acid | 79-09-4 | 10 | | 0.0057 | 4 | 1.54E-01 |
| o-Xylene | 95-47-6 | 100 | 150 | 0.38 | 5 | 1.28E-01 |
| Camphor | 76-22-2 | 2 | 3 | | 1 | 1.16E-01 |

Table 6. Identification of the most critical compounds in terms of potential non-carcinogenic health effects related to landfill leachate emissions

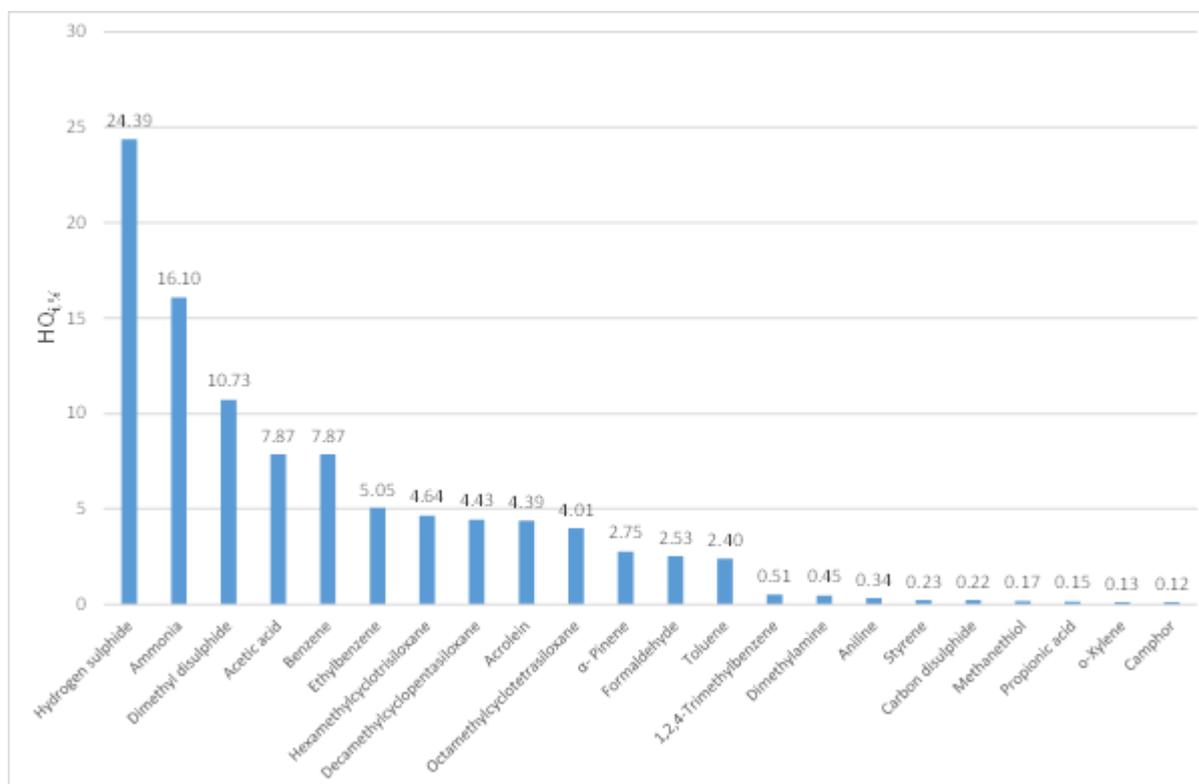


Figure 8. Graphical identification of the most critical compounds in terms of potential non-carcinogenic health effects related to landfill leachate emissions

In general, all compounds having a low OT have the potential to cause an odour perception. However, it should be highlighted that the perception of an odour is not directly correlated with a potential health risk. In general, there is no direct correlation between TLVs and OTs of chemical compounds.

Regarding the chemical compounds found in ambient air samples collected in the vicinity of landfill leachate collection and storage tanks, a weak correlation can be observed from the graph depicted in Figure 9. This apparent weak correlation is attributable only to the presence of one compound having a very high OT, i.e. Butane, whose OT is considered equal to 1200 ppm. By eliminating this point from the graph (Figure 10), it becomes immediately evident that such correlation does not exist.

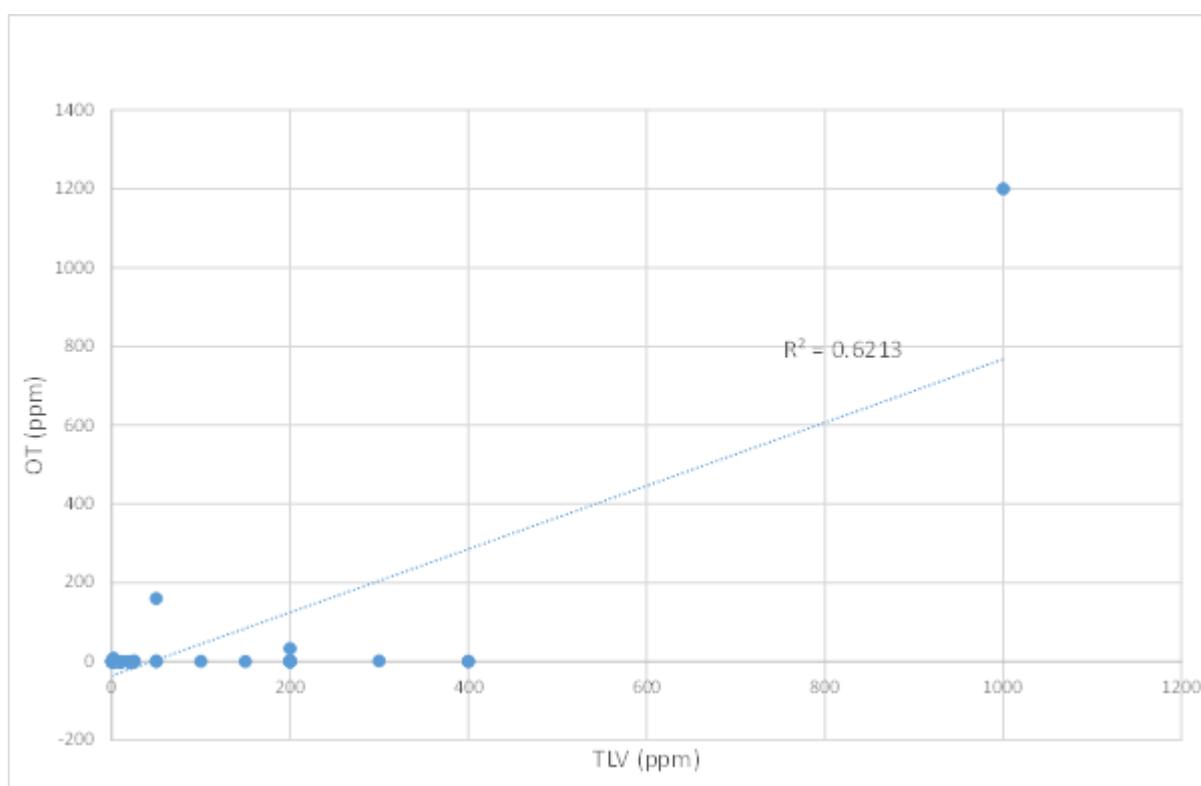


Figure 9. Correlation between TLVs and OTs (both in ppm) of the compounds related to landfill leachate emissions

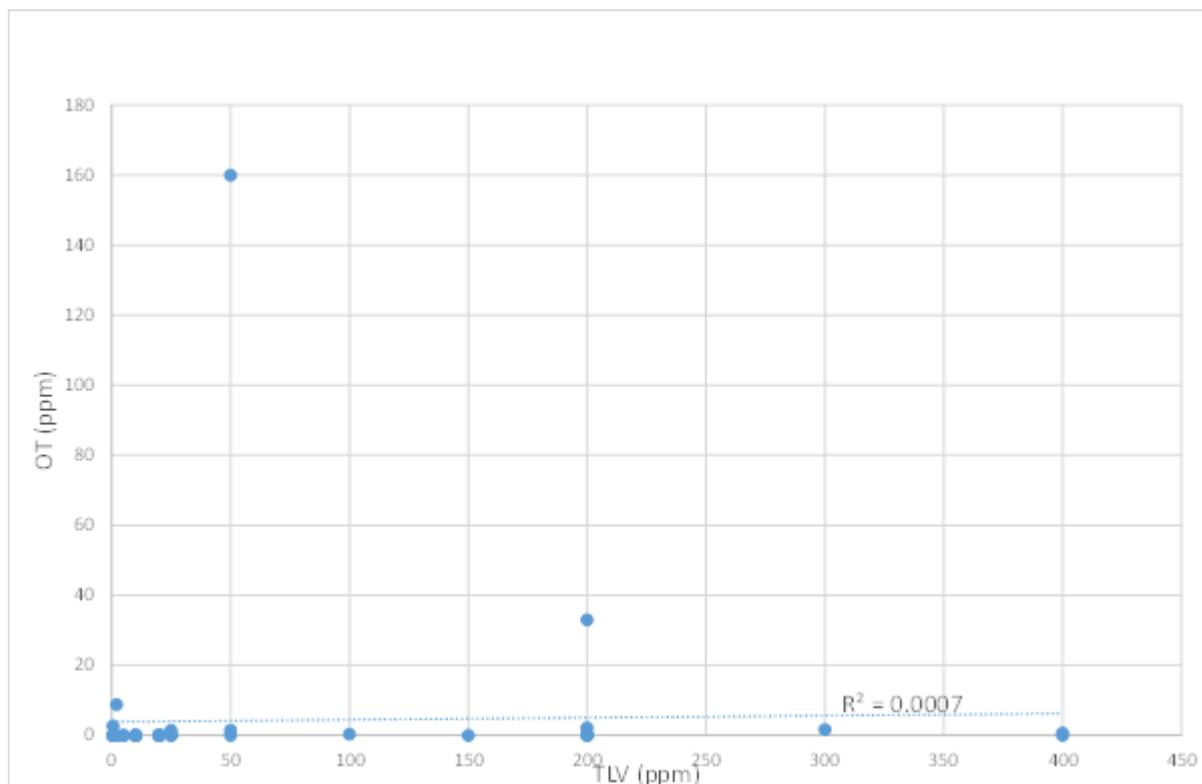


Figure 10. Correlation between TLVs and OTs (both in ppm) of the compounds related to landfill leachate emissions without considering Butane

Data summary of the chemical compounds related to the disposal of fresh waste

The database regarding the chemical compounds related to the disposal of fresh waste in landfills (Table 7) was built by providing a list of the compounds identified at least once in the scientific papers that have investigated the atmospheric emissions in the landfill areas where fresh waste is unloaded and compacted, together with their OT and TLV.

As previously mentioned, the concentration values retrieved in the literature relevant to fresh waste emissions refer to samples collected in two different ways. Most compounds (>100) were identified in ambient air samples collected on the portion of landfill where fresh waste is disposed (e.g., Termonia and Termonia, 1999; Ying et al., 2012). A smaller amount of compounds (ca. 30) were identified in samples collected by means of a flux chamber placed directly on the fresh waste (e.g., Gonzalez et al., 2013).

As discussed previously (Figure 5), since it is not possible to theoretically justify nor to identify from the experimental results a trend proving that one sampling method provides more precautionary (i.e. higher) concentration values than the other, for our evaluations, aiming to the identification of the most critical compounds related to fresh waste disposal, we decided to unify the list of compounds obtained with the two methods. The relative HQ values were then calculated (see section 1.2 of this document) based on the maximum concentration value retrieved in the literature, independently from the sampling method adopted.

It should be highlighted that, for those compounds for which the TLV-TWA was not available, the value of the TLV-STEL was used for the calculation of the HQ.

Finally, in the database (Table 7), the compounds classified as carcinogenic according to the definition supplied in Part 3 of Annex VI to EU Regulation (EC) No. 1272/2008 are identified as follows:

- Carcinogen if the compound is classified as carcinogens of category 1A or 1B.
- Suspected to have carcinogenic potential for humans if the compound is classified as carcinogens of category 2.

In Table 7, compounds not belonging to the categories established by the EU Regulation have been left blank. The compounds not available in the EU Regulation are reported in the table as *not available*.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | HQ ₄ % | Carcinogenic |
|--|-------------|---------------|----------------|----------|-------------------|---------------|
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 1 | | | 8.14E-03 | |
| 1,1,2-Trichloroethane | 79-00-5 | 10 | | | 5.54E-03 | Carc. 2 |
| 1,1,3-Trimethylcyclohexane | 3073-66-3 | | | | | Not available |
| 1,2,3,5-Tetramethylbenzene | 527-53-7 | | | | | Not available |
| 1,2,3-Trichloropropane | 96-18-4 | 10 | | | 4.03E-05 | Carc. 1B |
| 1,2,3-Trimethylbenzene | 526-73-8 | 25 | | | 8.74E-04 | Not available |
| 1,2,4-Tribromobenzene | 615-54-3 | | | | | Not available |
| 1,2,4-Trichlorobenzene | 120-82-1 | 5 | | | 1.21E-02 | |
| 1,2,4-Trimethylbenzene | 95-63-6 | 25 | | 0.12 | 6.50E-02 | |
| 1,2-Dibromoethane | 106-93-4 | | | | | Carc. 1B |
| 1,2-Dichlorobenzene | 95-50-1 | 25 | 50 | | 5.42E-02 | |
| 1,2-Dichloroethane | 107-06-2 | 10 | | | 4.35E-02 | Carc. 1B |
| 1,2-Dichloropropane | 78-87-5 | 10 | | | 1.83E-02 | Carc. 1B |
| 1,3,5-Trimethyl benzene | 108-67-8 | 25 | | 0.17 | 4.40E-01 | |
| 1,3-Dichlorobenzene | 541-73-1 | | | | | |
| 1,4-Dichlorobenzene | 106-46-7 | 10 | | | 1.43E-01 | Carc. 2 |
| 1-Ethyl-2-methylbenzene | 611-14-3 | | | 0.074 | | Not available |
| 1-Ethyl-2-methylcyclopropane | 19781-69-2 | | | | | Not available |
| 1-Methyl-2-pentyl cyclohexane | 215231-33-7 | | | | | Not available |
| 1-Methyl-4-(1-methylethyl)-cyclohexane | 99-82-1 | | | | | Not available |

| | | | | | | |
|--------------------------|------------|-----|-----|---------|----------|---------------|
| 1-Nitrobutane | 627-05-4 | | | | | Not available |
| 2,3-Dimethylnonane | 2884-06-2 | | | | | Not available |
| 2,4,6-Trichloroaniline | 634-93-5 | | | | | Not available |
| 2,4-Dimethylhexane | 589-43-5 | | | | | |
| 2,6,10-Trimethyldodecane | 3891-98-3 | | | | | Not available |
| 2-Hexanone | 591-78-6 | 5 | 10 | 0.024 | 6.80E-03 | |
| 2-Methyl-1,3-dioxolane | 497-26-7 | | | | | Not available |
| 3-Pentanone | 96-22-0 | 200 | 300 | | 1.64E-02 | |
| 4,7-Dimethylundecane | 17301-32-5 | | | | | Not available |
| 4-Methyl-2-pentanone | 108-10-1 | 20 | 75 | 0.17 | 1.63E-04 | |
| 6-Pentadecen-1-ol | 64437-42-9 | | | | | Not available |
| 7-Methyl-3,4-octadiene | 37050-05-8 | | | | | Not available |
| Acenaphthylene | 208-96-8 | | | | | Not available |
| Acetaldehyde | 75-07-0 | 25 | | 0.0015 | 6.92E-02 | Carc. 1B |
| Acetic acid | 64-19-7 | 10 | 15 | 0.006 | 1.27E+01 | |
| Acrolein | 107-02-8 | 0.1 | | 0.0036 | 5.89E+00 | |
| Acrylonitrile | 107-13-1 | 2 | | 8.8 | 1.09E-02 | Carc. 1B |
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 1.38E+01 | |
| Aniline | 62-53-3 | 2 | | | 5.77E-02 | |
| Anisole | 100-66-3 | 5 | 10 | | 3.05E-03 | Not available |
| Benzaldehyde | 100-52-7 | | | | | |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.7 | 8.38E+00 | Carc. 1A |
| Bromoform | 75-25-2 | 0.5 | | | 5.17E-03 | |
| Butanal | 123-72-8 | | | 0.00067 | | |
| Butanoic acid | 107-92-6 | | | 0.00019 | | |
| Butanol | 71-36-3 | 20 | | 0.038 | 1.63E-02 | |
| Butyl acetate | 123-86-4 | 150 | 200 | 0.016 | 3.64E-02 | |
| Butyl formate | 592-84-7 | | | 0.087 | | |
| Camphene | 79-92-5 | | | | | Not available |
| Camphor | 76-22-2 | 2 | 3 | | 2.73E-03 | Not available |
| Caproic acid | 142-62-1 | | | 0.0006 | | Not available |

| | | | | | | |
|---------------------------|-----------|------|-----|-----------|----------|---------------|
| Carbon disulphide | 75-15-0 | 1 | | 0.21 | 2.20E+00 | |
| Chloroacetaldehyde | 170-20-0 | 1 | | | 7.95E-04 | Not available |
| Chlorobenzene | 108-90-7 | 10 | | | 5.95E-02 | |
| Cis-1,4-Dichloro-2-butene | 1476-11-5 | | | | | Not available |
| Crotonaldehyde | 4170-30-3 | | 0.3 | 0.023 | 2.34E-01 | |
| Cyclohexanone | 108-94-1 | 20 | 50 | | 3.51E-03 | |
| Decanal | 112-31-2 | | | 0.0004 | | Not available |
| Decane | 124-18-5 | | | 0.62 | | Not available |
| Dichlorodifluoromethane | 75-71-8 | 1000 | | | 1.25E-03 | Not available |
| Dichloroethylene | 540-59-0 | 200 | | | 4.99E-03 | |
| Diethyl phthalate | 84-66-2 | 0.55 | | | 2.21E-02 | Not available |
| Diethyl sulphide | 352-93-2 | 10 | | 0.000033 | 2.75E-01 | Not available |
| Dimethyl disulphide | 624-92-0 | 0.5 | | 0.0022 | 4.76E+00 | Not available |
| Dimethyl sulphide | 75-18-3 | 10 | | 0.003 | 2.43E-01 | Not available |
| Dimethyl trisulfide | 3658-80-8 | | | | | Not available |
| Dimethylamine | 124-40-3 | 5 | 15 | 0.033 | 3.40E-01 | |
| Ethanol | 64-17-5 | 1000 | | 0.53 | 1.06E-02 | |
| Ethyl acetate | 141-78-6 | 400 | | 0.87 | 2.20E-02 | |
| Ethyl disulphide | 110-81-6 | | | 0.002 | | Not available |
| Ethyl mercaptan | 75-08-1 | 0.5 | | 0.0000087 | 2.30E-02 | |
| Ethyl propionate | 105-37-3 | | | 0.007 | | |
| Ethylbenzene | 100-41-4 | 100 | 125 | 0.17 | 8.68E-02 | |
| Eucalyptol | 470-82-6 | | | | | Not available |
| Formaldehyde | 50-00-0 | 0.3 | | 0.5 | 3.78E+00 | Carc. 1B |
| Formic acid | 64-18-6 | 5 | 10 | | 1.79E-02 | |
| Furfural | 98-01-1 | 2 | | | 1.48E-02 | Carc. 2 |
| Heptanal | 111-71-7 | | | 0.00018 | | |
| Heptane | 142-82-5 | 400 | 500 | 0.67 | 2.22E-06 | |
| Heptanoic acid | 111-14-8 | | | | | |
| Hexachlorobutadiene | 87-68-3 | 0.02 | | | 2.73E+00 | Not available |
| Hydrogen sulphide | 7783-06-4 | 1 | 5 | 0.00041 | 3.78E+01 | |

| | | | | | | |
|--------------------|-----------|-----|-----|----------|----------|---------------|
| Isobutyric acid | 79-31-2 | | | 0.0015 | | |
| Isopropyl benzene | 98-82-8 | 50 | | 0.0084 | 5.19E-04 | |
| Isovaleraldehyde | 590-86-3 | | | 0.0001 | | Not available |
| Isovaleric acid | 503-74-2 | | | 0.000078 | | Not available |
| Limonene | 5989-27-5 | | | | | |
| Methanethiol | 74-93-1 | 0.5 | | 0.00007 | 4.80E+00 | |
| Methanol | 67-56-1 | 200 | 250 | 33 | 5.54E-03 | |
| Methyl cyclohexane | 108-87-2 | 400 | | 0.15 | 1.40E-04 | |
| Methyl pentane | 107-83-5 | | | 7 | | |
| Methyl propionate | 554-12-1 | | | 0.098 | | |
| Methylamine | 74-89-5 | 5 | 15 | 0.035 | 3.61E-02 | |
| Methylene chloride | 75-09-2 | 50 | | 160 | 3.30E-02 | Carc. 2 |
| m-Xylene | 108-38-3 | 100 | 150 | 0.041 | 5.22E-02 | |
| Naphthalene | 91-20-3 | 10 | 15 | | 4.61E-02 | Carc. 2 |
| n-Butanone | 78-93-3 | 200 | 300 | 0.44 | 5.50E-03 | |
| n-Hexane | 110-54-3 | 50 | | 1.5 | 4.99E-02 | |
| n-Hexanol | 111-27-3 | | | 0.006 | | |
| Nonanal | 124-19-6 | | | 0.00034 | | Not available |
| n-Undecane | 1120-21-4 | | | 0.87 | | Not available |
| Octane | 111-65-9 | 300 | | 1.7 | | |
| o-Xylene | 95-47-6 | 100 | 150 | 0.38 | 1.32E-02 | |
| p-Cymene | 99-87-6 | | | | | Not available |
| Pentanol | 71-41-0 | | | 0.1 | | |
| p-Ethyl toluene | 622-96-8 | | | 0.0083 | | Not available |
| Phenol | 108-95-2 | 5 | | 0.0056 | | |
| Propanal | 123-38-6 | 20 | | 0.001 | 4.82E-02 | |
| Propanone | 67-64-1 | 500 | 750 | 42 | 1.12E-02 | |
| Propionic acid | 79-09-4 | 10 | | 0.0057 | 9.35E-02 | |
| p-Xylene | 106-42-3 | 100 | 150 | 0.058 | | |
| Pyridine | 110-86-1 | 1 | | 0.063 | 2.90E-03 | |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 1.53E-01 | |

| | | | | | | |
|-----------------------------|-----------|------|-----|----------|--------------|---------------|
| Tetrachloroethylene | 127-18-4 | 25 | 100 | 0.77 | 2.75E-0 2 | Carc. 2 |
| Tetrachloromethane | 56-23-5 | 5 | 10 | 4.6 | | Carc. 2 |
| Tetrahydrofuran | 109-99-9 | 50 | 100 | | 2.60E-0 2 | Carc. 2 |
| Toluene | 108-88-3 | 20 | | 0.33 | 1.16E-0 1 | |
| Trans-1,4-Dichloro-2-butene | 110-57-6 | | | | | Not available |
| Trichloroethene | 79-01-6 | 10 | 25 | 3.9 | 4.85E-0 3 | Carc. 1B |
| Trichlorofluoromethane | 75-69-4 | 1000 | | | 4.26E-0 2 | Not available |
| Trichloromethane | 67-66-3 | 10 | | 3.8 | | Carc. 2 |
| Trimethylamine | 75-50-3 | 5 | 15 | 0.000032 | 3.36E-0 2 | |
| Valeric acid | 109-52-4 | | | 0.000037 | | |
| Vinyl acetate | 108-05-4 | 10 | 15 | | 3.08E-0 4 | Carc. 2 |
| α - Pinene | 80-56-8 | 20 | | 0.018 | 2.78E-0 2 | Not available |
| α -Terpinene | 99-86-5 | | | | | Not available |
| α -Terpinolene | 1124-27-2 | | | | | Not available |
| β -Phellandrene | 555-10-2 | | | | | Not available |
| γ -terpinene | 99-85-4 | | | | | Not available |

Table 7. Analysis of chemical compounds related to fresh waste disposal

Evaluation of priority compounds related to the emissions associated with fresh waste disposal in landfills

According to the approach proposed by Jiang et al. (2017), the first group of priority compounds are those classified as carcinogens. Based on the classification proposed by the EU Regulation (EC) No. 1272/2008, the carcinogenic compounds (categories 1A and 1B) identified in the emissions associated with the disposal of fresh waste in landfills are the following:

- 1,2,3-Trichloropropane (1B)
- 1,2-Dibromoethane (1B)
- 1,2-Dichloroethane (1B)
- 1,2-Dichloropropane (1B)
- Acetaldehyde (1B)
- Acrylonitrile (1B)
- Benzene (1A)
- Formaldehyde (1B)
- Trichloroethene (1B)

Always according to the above-mentioned EU Regulation, the suspected carcinogenic compounds (category 2) related to fresh waste disposal are:

- 1,1,2-Trichloroethane
- 1,4-Dichlorobenzene
- Furfural
- Methylene chloride
- Naphthalene
- Tetrachloroethylene
- Tetrachloromethane
- Tetrahydrofuran
- Trichloromethane
- Vinyl Acetate

Considering the most critical compounds related to the disposal of fresh waste in landfills in terms of their potential to cause non-carcinogenic health effects, it is possible to refer to their relative HQ ($HQ_{i,\%}$). In this case, there isn't one unique compound accounting for almost the overall HI. Hydrogen Sulphide is the compound having the highest relative HQ (accounting for 37.8% of the overall HI), followed by Ammonia and Acetic Acid (accounting for 13.8% and 12.7% of the overall HI, respectively).

The other compounds that have a non-negligible contribution on the HI related to the emissions associated with fresh waste are, in decreasing order of relative HQ:

- Benzene
- Acrolein
- Methanethiol
- Dimethyl Disulphide
- Formaldehyde
- Hexachlorobutadiene
- Carbon Disulphide
- 1,3,5-Trimethylbenzene
- Dimethylamine
- Diethyl Sulphide
- Dimethyl Sulphide
- Crotonaldehyde
- Styrene
- 1,4-Dichlorobenzene
- Toluene
- Propionic acid
- Ethylbenzene
- Acetaldehyde
- 1,2,4-Trimethylbenzene

Those 22 compounds, which include i) aromatic compounds, ii) aldehydes, iii) sulphur compounds (sulphides and mercaptans), iv) halogenated organic compounds, and v) amines, together contribute by over 99% to the overall HI of related to the emissions associated with fresh waste (Table 8, Figure 11).

Table 8 also includes a column reporting the number of concentration values found in the scientific literature for each of the reported compounds. This number represents the frequency with which the compound has been identified in the analysed samples.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | No. of values | HQ _i % |
|-------------------------|------------|---------------|----------------|----------|---------------|-------------------|
| Hydrogen sulphide | 7783-06-4 | 1 | 5 | 0.00041 | 22 | 3.78E+01 |
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 6 | 1.38E+01 |
| Acetic acid | 64-19-7 | 10 | 15 | 0.006 | 5 | 1.27E+01 |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.7 | 34 | 8.38E+00 |
| Acrolein | 107-02-8 | 0.1 | | 0.0036 | 4 | 5.89E+00 |
| Methanethiol | 74-93-1 | 0.5 | | 0.00007 | 15 | 4.80E+00 |
| Dimethyl disulphide | 624-92-0 | 0.5 | | 0.0022 | 27 | 4.76E+00 |
| Formaldehyde | 50-00-0 | 0.3 | | 0.5 | 2 | 3.78E+00 |
| Hexachlorobutadiene | 87-68-3 | 0.02 | | | 2 | 2.73E+00 |
| Carbon disulphide | 75-15-0 | 1 | | 0.21 | 26 | 2.20E+00 |
| 1,3,5-Trimethyl benzene | 108-67-8 | 25 | | 0.17 | 3 | 4.40E-01 |
| Dimethylamine | 124-40-3 | 5 | 15 | 0.033 | 2 | 3.40E-01 |
| Diethyl sulphide | 352-93-2 | 10 | | 0.000033 | 11 | 2.75E-01 |
| Dimethyl sulphide | 75-18-3 | 10 | | 0.003 | 21 | 2.43E-01 |
| Crotonaldehyde | 4170-30-3 | | 0.3 | 0.023 | 1 | 2.34E-01 |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 18 | 1.53E-01 |
| 1,4-Dichlorobenzene | 106-46-7 | 10 | | | 24 | 1.43E-01 |
| Toluene | 108-88-3 | 20 | | 0.33 | 34 | 1.16E-01 |
| Propionic acid | 79-09-4 | 10 | | 0.0057 | 4 | 9.35E-02 |
| Ethylbenzene | 100-41-4 | 100 | 125 | 0.17 | 33 | 8.68E-02 |
| Acetaldehyde | 75-07-0 | 25 | | 0.0015 | 2 | 6.92E-02 |
| 1,2,4-Trimethylbenzene | 95-63-6 | 25 | | 0.12 | 3 | 6.50E-02 |

Table 8. Identification of the most critical compounds in terms of potential non-carcinogenic health effects related to fresh waste disposal in landfills

In general, all compounds having a low OT have the potential to cause an odour perception. However, it should be highlighted that the perception of an odour is not directly correlated with a potential health risk. As can be seen from Figure 12, there is no direct correlation between TLVs and OTs of the chemical compounds found in the emissions related to the disposal of fresh waste in landfills.

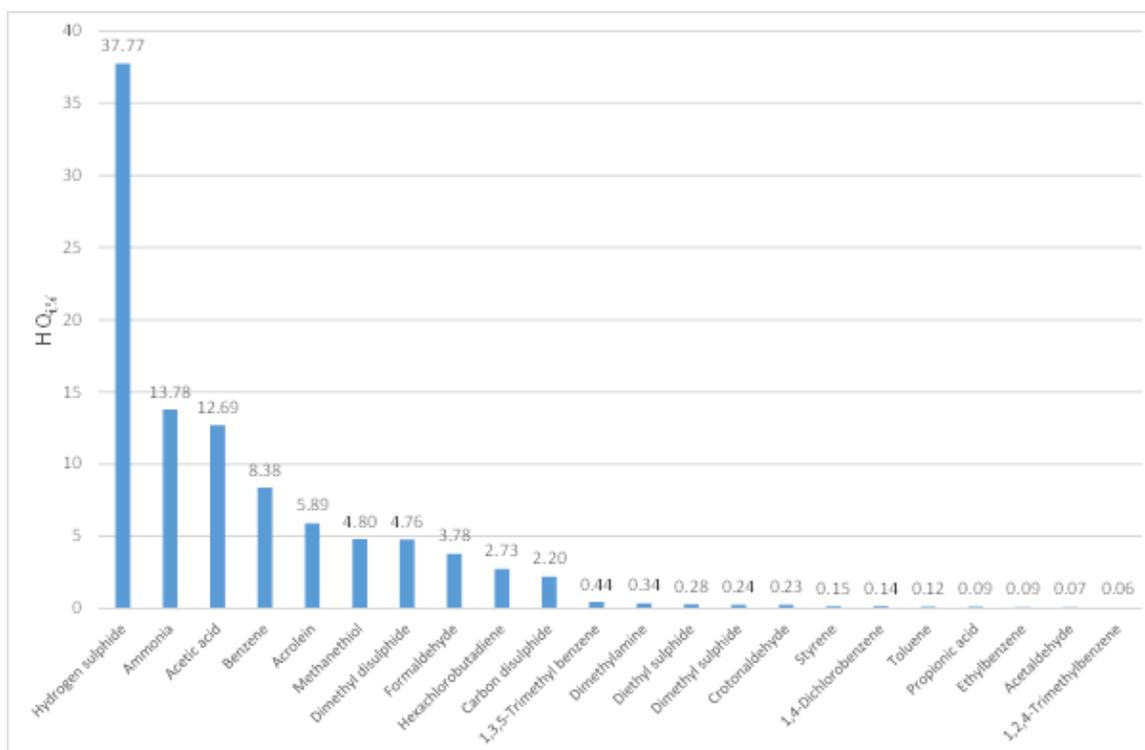


Figure 11. Graphical identification of the most critical compounds in terms of potential non-carcinogenic health effects related to the disposal of fresh waste in landfills

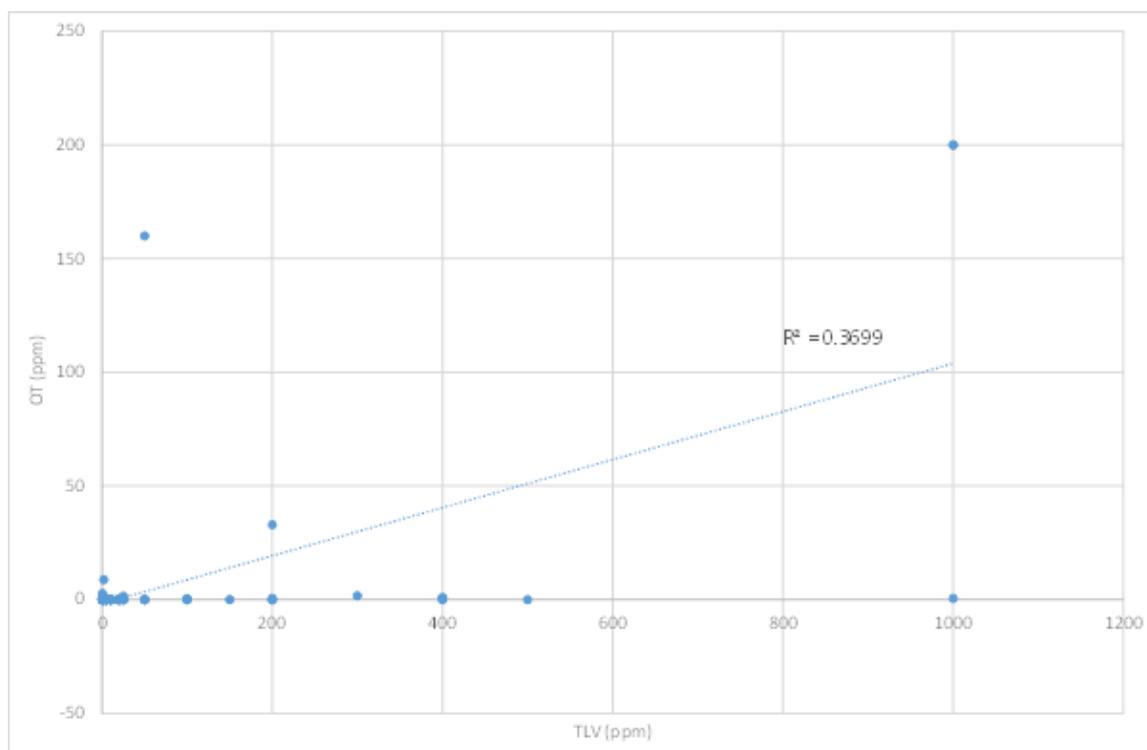


Figure 12. Correlation between TLVs and OTs (both in ppm) of the compounds related to fresh waste disposal in landfills

Data summary of the chemical compounds related to the diffuse emissions from temporarily covered landfill surfaces

The database regarding the chemical compounds related to the diffuse emissions from temporarily covered landfill surfaces (Table 9) was built by providing a list of the compounds identified at least once in the scientific papers that have investigated such types of emissions, together with their OT and TLV.

As previously mentioned, the concentration values retrieved in the literature relevant to emissions from landfill surfaces refer to samples collected in two different ways. Most compounds (ca. 90) were identified in samples collected by means of a flux chamber placed directly on the landfill surface (e.g., Dincer et al., 2006; Gonzalez et al., 2013), whereas another ca. 50 compounds were identified in ambient air samples collected over the landfill surface (Davoli et al., 2003).

Also in this case, given the impossibility to identify a method providing more precautionary (i.e. higher) concentration values, for our evaluations, aiming to the identification of the most critical compounds in the diffuse emissions from landfill surfaces, we decided to unify the list of compounds obtained with the two methods. The relative HQ values were then calculated (see section 1.2 of this document) based on the maximum concentration value retrieved in the literature, independently from the sampling method adopted.

It should be highlighted that, for those compounds for which the TLV-TWA was not available, the value of the TLV-STEL was used for the calculation of the HQ.

Finally, in the database (Table 9), the compounds classified as carcinogenic according to the definition supplied in Part 3 of Annex VI to EU Regulation (EC) No. 1272/2008 are identified as follows:

- Carcinogen if the compound is classified as carcinogens of category 1A or 1B.
- Suspected to have carcinogenic potential for humans if the compound is classified as carcinogens of category 2.

In Table 9, compounds not belonging to the categories established by the EU Regulation have been left blank. The compounds not available in the EU Regulation are reported in the table as *not available*.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | HQ _i % | Carcinogenic |
|--|------------|---------------|----------------|----------|-------------------|---------------|
| 1,1,1,2-Tetrachloroethane | 79-34-5 | 1 | | | 1.11E-03 | |
| 1,1,2-Trichloroethane | 79-00-5 | 10 | | | 2.25E-04 | Carc. 2 |
| 1,1,3,3-Tetramethylcyclopentane | 50876-33-0 | | | | | Not available |
| 1,1-Dichloro-1-fluoroethane | 1717-00-6 | 500 | | | 1.28E-06 | |
| 1,1-Dichloroethane | 75-34-3 | 100 | | | 7.56E-06 | |
| 1,2,3-Trimethylbenzene | 526-73-8 | 25 | | | 2.51E-03 | Not available |
| 1,2,4-Trimethylbenzene | 95-63-6 | 25 | | | 9.79E-04 | |
| 1,2-cis-Dichloroethylene | 156-59-2 | 200 | | | 5.36E-05 | |
| 1,2-Dichlorobenzene | 95-50-1 | 25 | 50 | 0.12 | 3.57E-04 | |
| 1,2-Dichloroethane | 107-06-2 | 10 | | | 4.61E-03 | Carc. 1B |
| 1,3,5-Trimethyl benzene | 108-67-8 | 25 | | | 1.16E-03 | |
| 1,3-Dichlorobenzene | 541-73-1 | | | | | |
| 1-Ethyl-2-methylbenzene | 611-14-3 | | | | | Not available |
| 1-Ethyl-2-methylcyclopropane | 19781-69-2 | | | 0.17 | | Not available |
| 1-Methyl-2-pentyl cyclohexane | 54411-01-7 | | | | | Not available |
| 1-Methyl-2-propylbenzene | 1074-17-5 | | | | | Not available |
| 1-Methyl-4-(1-methylethyl)-cyclohexane | 99-82-1 | | | 0.074 | | Not available |
| 2,3,6-Trimethyloctane | 62016-33-5 | | | | | Not available |
| 2,3-Dimethylnonane | 2884-06-2 | | | | | Not available |
| 2,4-Dimethylheptane | 2213-23-2 | | | | | Not available |

| | | | | | | |
|--|-------------|------|-----|---------|----------|---------------|
| 2,4-Dimethylhexane | 589-43-5 | 300 | | | 1.43E-04 | |
| 2-Butanone | 78-93-3 | 200 | 300 | | 1.21E-02 | |
| 2-Butoxyethanol | 111-76-2 | 20 | | | 3.06E-04 | |
| 2-Hexanone | 591-78-6 | 5 | 10 | | 1.09E-02 | |
| 2-Methyl-1,3-dioxolane | 497-26-7 | | | | | Not available |
| 2-Methyl-5-(1-methylethyl)-cyclohexanone | 59471-80-6 | | | 0.024 | | Not available |
| 4,5-Dipropyloctane | 20905-05-09 | | | | | Not available |
| 4,7-Dimethylundecane | 17301-32-5 | | | | | Not available |
| 4-Methyl-1-(methyl ethyl)-bicyclo-(3,10)-hex-3-ene | 28634-89-1 | | | | | Not available |
| 4-Methyl-2-pentanone | 108-10-1 | 20 | 75 | 0.17 | 7.85E-04 | |
| 4-Methylcyclohexanone | 589-92-4 | | | | | Not available |
| 5-Methyl-3-(1-methylethyl)-cyclohexanone | 89-80-5 | | | | | Not available |
| 6-Pentadecen-1-ol | 64437-42-9 | | | | | Not available |
| 7-Methyl-3,4-octadiene | 37050-05-8 | | | 0.0015 | | Not available |
| Acetic acid | 64-19-7 | 10 | 15 | 0.006 | 3.32E-02 | |
| Acrolein | 107-02-8 | | 0.1 | 0.0036 | 1.78E+00 | |
| Acrylonitrile | 107-13-1 | 2 | | 8.8 | 7.05E-03 | Carc. 1B |
| Ammonia | 7664-41-7 | 25 | 35 | 1.5 | 2.63E+00 | |
| Anisole | 100-66-3 | 5 | 10 | | 4.42E-03 | Not available |
| Benzaldehyde | 100-52-7 | | | | | |
| Benzene | 71-43-2 | 0.5 | 2.5 | | 1.15E+00 | Carc. 1A |
| Butanal | 123-72-8 | | | 2.7 | | |
| Butane | 106-97-8 | 1000 | | | 3.98E-05 | |
| Butanol | 71-36-3 | 20 | | 0.00067 | 1.50E-01 | |
| Butyl acetate | 123-86-4 | 150 | 200 | 0.00019 | 1.62E-03 | |
| Butyl formate | 592-84-7 | | | 0.038 | | |
| Butyric acid | 107-92-6 | | | 0.016 | | |
| Camphene | 79-92-5 | | | 0.087 | | Not available |
| Caproic acid | 142-62-1 | | | | | Not available |
| Carbon disulphide | 75-15-0 | 1 | | | 2.48E-01 | |
| Chlorobenzene | 108-90-7 | 10 | | 0.0006 | 3.99E-04 | |

| | | | | | | |
|-------------------------|------------|------|-----|---------------|----------|---------------|
| Cinnamaldehyde | 14371-10-9 | | | 0.21 | | Not available |
| Cis-1,3-Dichloropropene | 10061-01-5 | 1 | | | 2.36E-03 | |
| Crotonaldehyde | 4170-30-3 | | 0.3 | | 4.62E+00 | |
| Cyclohexanone | 108-94-1 | 20 | 50 | | 1.74E-02 | |
| Decanal | 112-31-2 | | | 0.023 | | Not available |
| Decane | 124-18-5 | | | | | Not available |
| Diethyl phthalate | 84-66-2 | 0.55 | | 0.0004 | 1.94E-02 | Not available |
| Ethyl acetate | 141-78-6 | 400 | | 0.62 | 1.53E-05 | |
| Ethylbenzene | 100-41-4 | 20 | | | 8.71E-03 | |
| Eucalyptol | 470-82-6 | | | | | Not available |
| Formic acid | 64-18-6 | 5 | 10 | | 7.10E-01 | |
| Furfural | 98-01-1 | 2 | | 0.00003 3 | 3.46E-02 | Carc. 2 |
| Heptanal | 111-71-7 | | | 0.0022 | | Not available |
| Heptanoic acid | 111-14-8 | | | 0.003 | | |
| Hexaldehyde | 66-25-1 | | | | | Not available |
| Hydrogen sulphide | 7783-06-4 | 1 | 5 | 0.033 | 8.78E+01 | |
| Iodomethane | 74-88-4 | 2 | | 0.53 | 3.95E-04 | Carc. 2 |
| Isobutyric acid | 79-31-2 | | | 0.87 | | |
| Isocaproic acid | 646-07-1 | | | 0.002 | | Not available |
| Isovaleric acid | 503-74-2 | | | 0.00000 87 | | Not available |
| Limonene | 5989-27-5 | | | 0.007 | | |
| Methyl propionate | 554-12-1 | | | 0.17 | | |
| Methylene chloride | 75-09-2 | 50 | | | 7.01E-03 | Carc. 2 |
| m-Xylene | 108-38-3 | 100 | 150 | 0.5 | 3.58E-03 | |
| n-Hexanol | 111-27-3 | | | | | |
| Nonanal | 124-19-6 | | | | | Not available |
| n-Pentanol | 71-41-0 | | | 0.00018 | | |
| Octanal | 124-13-0 | | | 0.67 | | Not available |
| Octane | 111-65-9 | 300 | | | 9.84E-04 | Not available |
| p-Cymene | 99-87-6 | | | | | Not available |

| | | | | | | |
|-----------------------------|----------|-----|-----|----------|----------|---------------|
| Pentadecane | 629-62-9 | | | 0.00041 | | Not available |
| Pentanal | 110-62-3 | 50 | | 0.0015 | 1.67E-03 | Not available |
| Phenol | 108-95-2 | 5 | | 0.0084 | 7.44E-02 | |
| Phthalic anhydride | 85-44-9 | 1 | | 0.0001 | 2.45E-02 | |
| Propanal | 123-38-6 | 20 | | 0.000078 | 1.24E-01 | |
| Propanone | 67-64-1 | 200 | 500 | | 4.09E-02 | |
| Propionic acid | 79-09-4 | 10 | | 0.00007 | 1.78E-02 | |
| Propyl benzene | 103-65-1 | | | 33 | | |
| p-xylene | 106-42-3 | 100 | 150 | 0.15 | 3.92E-03 | |
| Styrene | 100-42-5 | 20 | 40 | 7 | 2.59E-02 | |
| Tetrachloroethene | 127-18-4 | 25 | 100 | 0.098 | 8.26E-03 | Carc. 2 |
| Tetrachloromethane | 56-23-5 | 5 | 10 | 0.035 | 3.60E-02 | Carc. 2 |
| Tetrahydrofuran | 109-99-9 | 50 | 100 | 160 | 4.09E-03 | Carc. 2 |
| Toluene | 108-88-3 | 20 | | 0.041 | 1.19E-01 | |
| Trans-1,3. Dichloropropene | 542-75-6 | 1 | | | 3.03E-03 | |
| Trans-1,4-Dichloro-2-butene | 110-57-6 | | | 0.44 | | Not available |
| Trichloroethene | 79-01-6 | 10 | 25 | 1.5 | 1.79E-01 | Carc. 1B |
| Trichloromethane | 67-66-3 | 10 | | 0.006 | 2.08E-02 | Carc. 2 |
| Undecene | 821-95-4 | | | 0.00034 | | Not available |
| Valeric acid | 109-52-4 | | | 0.87 | | |
| Vinyl acetate | 108-05-4 | 10 | 15 | 1.7 | 9.95E-03 | Carc. 2 |
| α- Pinene | 80-56-8 | 20 | | 0.38 | 3.90E-03 | Not available |

Table 9. Analysis of chemical compounds related to the diffuse emissions from temporarily capped landfill surfaces

Evaluation of priority compounds related to the diffuse emissions from temporarily covered landfill surfaces

According to the approach proposed by Jiang et al. (2017), the first group of priority compounds are those classified as carcinogens. Based on the classification proposed by the EU Regulation (EC) No. 1272/2008, the carcinogenic compounds (categories 1A and 1B) identified in the diffuse emissions from temporarily covered landfill surfaces are the following:

- 1,2-Dichloroethane (1B)

- Acrylonitrile (1B)
- Benzene (1A)
- Trichloroethene (1B)

Always according to the above-mentioned EU Regulation, the suspected carcinogenic compounds (category 2) related to the diffuse emissions from temporarily covered landfill surfaces are:

- 1,1,2-Trichloroethane
- Furfural
- Iodomethane
- Methylene chloride
- Tetrachloroethene
- Tetrachloromethane
- Tetrahydrofuran
- Trichloromethane
- Vinyl acetate

Considering the most critical compounds related to the diffuse emissions from temporarily covered landfill surfaces in terms of their potential to cause non-carcinogenic health effects, it is possible to refer to their relative HQ ($HQ_{i,\%}$). In this case, Hydrogen Sulphide is by far the compound that most contributes to the overall HI related to the diffuse emissions from temporarily covered landfill surfaces (hydrogen sulphide alone accounts for over 87% of the overall HI).

The other compounds that have a non-negligible contribution on the HI relevant to the diffuse emissions from temporarily covered landfill surfaces are, in decreasing order of relative HQ:

- Hydrogen Sulphide
- Crotonaldehyde
- Ammonia
- Acrolein
- Benzene
- Formic acid
- Carbon disulphide
- Trichloroethene
- Butanol
- Propanal
- Toluene
- Phenol
- Propanone
- Tetrachloromethane
- Furfural
- Acetic Acid
- Styrene
- Phthalic anhydride

Those 18 compounds, which include i) aldehydes and other short-chain oxygenated organic compounds (alcohols, ketones and acids), ii) ammonia, iii) aromatic compounds, iv) halogenated organic compounds, and v) Carbon Disulphide, together contribute by over 99.8% to the overall HI relevant to the diffuse emissions from temporarily covered landfill surfaces (Table 10, Figure 13).

Table 10 also reports a number representing the sum of concentration values found in the scientific literature for each of the reported compounds. This number represents the frequency with which the compound has been identified in the analysed literature.

| Compound | CAS Number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | No. of values | HQ _i % |
|--------------------|------------|---------------|----------------|----------|---------------|-------------------|
| Hydrogen sulphide | 7783-06-4 | 1 | 5 | 4.10E-04 | 1 | 8.78E+01 |
| Crotonaldehyde | 4170-30-3 | | 0.3 | 2.30E-02 | 5 | 4.62E+00 |
| Ammonia | 7664-41-7 | 25 | 35 | 1.50E+00 | 1 | 2.63E+00 |
| Acrolein | 107-02-8 | | 0.1 | 3.60E-03 | 4 | 1.78E+00 |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.70E+00 | 5 | 1.15E+00 |
| Formic acid | 64-18-6 | 5 | 10 | 5.21E-04 | 3 | 7.10E-01 |
| Carbon disulphide | 75-15-0 | 1 | | 2.10E-01 | 5 | 2.48E-01 |
| Trichloroethene | 79-01-6 | 10 | 25 | 3.9 | 4 | 1.79E-01 |
| Butanol | 71-36-3 | 20 | | 3.80E-02 | 1 | 1.50E-01 |
| Propanal | 123-38-6 | 20 | | 2.02E-06 | 4 | 1.24E-01 |
| Toluene | 108-88-3 | 20 | | 0.33 | 6 | 1.19E-01 |
| Phenol | 108-95-2 | 5 | | 0.0056 | 1 | 7.44E-02 |
| Propanone | 67-64-1 | 200 | 500 | 8.42E-04 | 5 | 4.09E-02 |
| Tetrachloromethane | 56-23-5 | 5 | 10 | 4.61E-03 | 1 | 3.60E-02 |
| Furfural | 98-01-1 | 2 | | 7.13E-04 | 1 | 3.46E-02 |
| Acetic acid | 64-19-7 | 10 | 15 | 6.00E-03 | 3 | 3.32E-02 |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 4 | 2.59E-02 |
| Phthalic anhydride | 85-44-9 | 1 | | 5.28E-05 | 1 | 2.45E-02 |

Table 10. Identification of the most critical compounds in terms of potential non-carcinogenic health effects related to the diffuse emissions from temporarily covered landfill surfaces

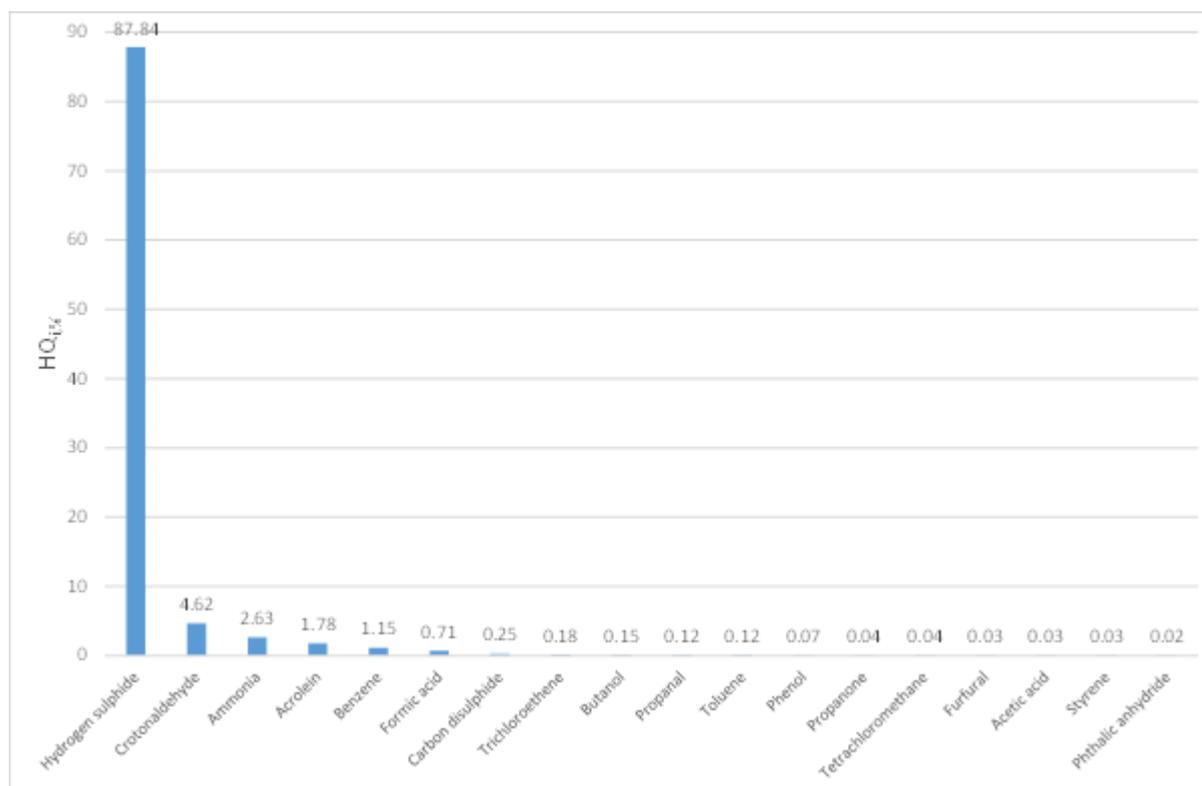


Figure 13. Graphical identification of the most critical compounds in terms of potential non-carcinogenic health effects related to the diffuse emissions from temporarily covered landfill surfaces

In general, all compounds having a low OT have the potential to cause an odour perception. However, it should be highlighted that the perception of an odour is not directly correlated with a potential health risk. In general, there is no direct correlation between TLVs and OTs of chemical compounds.

Regarding the chemical compounds found in ambient air samples collected in the vicinity of temporarily covered landfill surfaces, a weak correlation can be observed from the graph depicted in Figure 14. This apparent weak correlation is attributable only to the presence of one compound having a very high OT, i.e. Butane, whose OT is considered equal to 1200 ppm. By eliminating this point from the graph (Figure 15), it becomes immediately evident that such correlation does not exist.

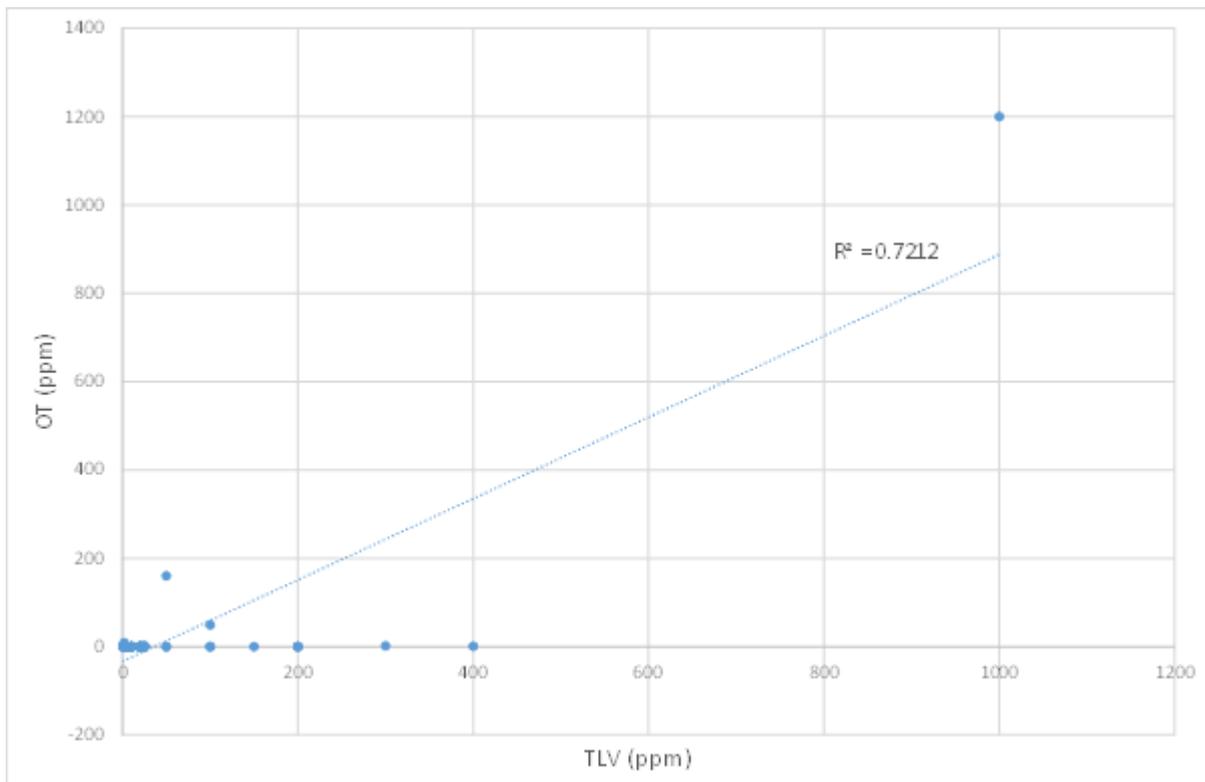


Figure 14. Correlation between TLVs and OTs (both in ppm) of the compounds related to the diffuse emissions from temporarily covered landfill surfaces

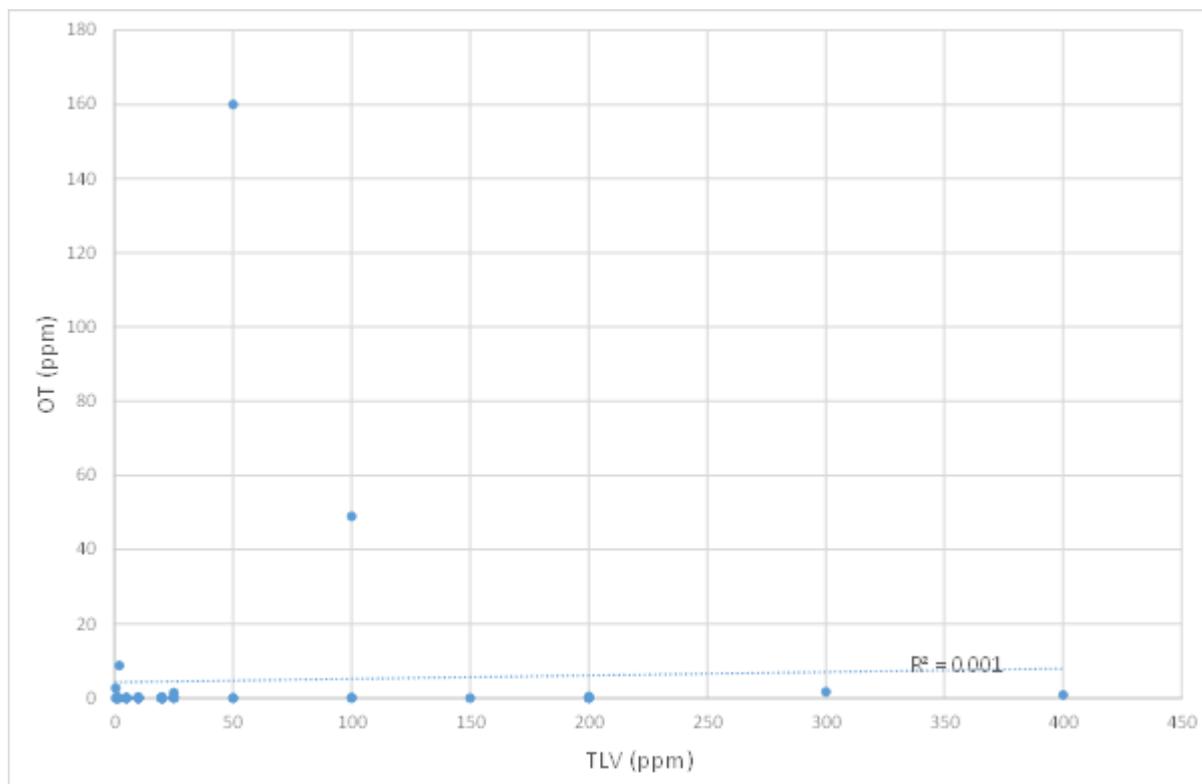


Figure 15. Correlation between TLVs and OTs (both in ppm) of the compounds related to the diffuse emissions from temporarily covered landfill surfaces without considering Butane

4. Odour emissions from refineries

This section is dedicated to the compounds related to atmospheric emissions from refineries. A brief description of refineries and their main odour emissions is provided. Then, a table is reported, listing the most relevant compounds identified in refinery **emissions** and **ambient air**, as obtained from the study of the scientific literature. The table also reports, for each compound, the OT and the TLV. Finally, the most “critical” compounds from the point of view of their potential toxicity for workers have been extracted, with the aim of providing a limited list of the most relevant compounds, which would need to be most carefully analysed when performing risk assessment evaluations related to refinery emissions. The information regarding refinery operations and their odour emissions are taken from the Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas issued in 2015.

4.1. What is a refinery?

Petroleum products (i.e. crude oil and natural gas) are mixtures of many different hydrocarbons and small amounts of impurities, with a composition that can vary significantly depending on the source.

The purpose of a refinery is to convert those natural raw materials into useful saleable products, such as:

- fuels for cars, trucks, aeroplanes, ships and other forms of transport;
- combustion fuels for the generation of heat and power for industry and commercial and domestic use;
- raw materials for the petrochemical and chemical industries;
- speciality products such as lubricating oils, paraffins/waxes and bitumen;
- energy as a by-product in the form of heat (steam) and power (electricity).

The production of a large number of fuels is by far the most important function of refineries and will generally determine the overall configuration and operation. Nevertheless, some refineries also produce valuable non-fuel products, such as feedstocks for the chemical and petrochemical industries. Examples are mixed naphtha feed for a steam cracker, recovered propylene, butylene for polymer applications and aromatics manufacture. Other specialty products from a refinery include bitumen, lubricating oils, waxes and high-grade coke for industrial use.

The refining of crude oil into usable petroleum products can be separated into two phases and a number of supporting operations. The first phase is the desalting of crude oil and the subsequent distillation into its various components or 'fractions'. Further distillation of the lighter components and naphtha is carried out to recover Methane and Ethane for use as refinery fuel, LPG (Propane and Butane), gasoline-blending components and petrochemical feedstocks. This light product separation is done in every refinery.

The second phase is made up of three different types of 'downstream' processes: i.e. breaking, combining, and reshaping fractions. These processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. The goal of these processes is to convert some of the distillation fractions into marketable petroleum products through a combination of downstream processes.

These processes define the various refinery types. The amounts of the various products obtained are determined almost entirely by the crude composition. If the product mix no longer matches the market requirements, conversion units can be added to restore the balance.

Market demand has for many years obliged refineries to convert heavier fractions to lighter fractions with a higher commercial value. These refineries separate the atmospheric residue into vacuum gas oil and vacuum residue fractions by distillation under high suction, and then feed one or both of these cuts to the appropriate conversion units. Thus, by the inclusion of conversion units, the product slate can be altered to suit market requirements, irrespective of the crude type. The number and the possible combinations of conversion units are large.

The simplest conversion unit is the thermal cracker, by which the residue is subjected to such high temperatures that the large hydrocarbon molecules in the residue convert into smaller ones. Thermal crackers can handle virtually any feed, but produce relatively small quantities of light products. An improved type of thermal cracker is the coker, in which all of the residues is converted into distillates and a coke product. In order to increase the degree of conversion and to improve product quality, a number of different catalytic cracking processes have evolved, of which fluid catalytic cracking and hydrocracking are the most prominent. Recently, residue gasification processes have been introduced within refineries, which enable refineries to eliminate heavy residues completely and to convert them into clean syngas for captive use and to produce hydrogen, steam and electricity via combined cycle techniques.

Supporting operations are those not directly involved in the production of hydrocarbon fuels but that serve a supporting role. They may include energy generation, wastewater treatment,

sulphur recovery, additive production, waste gas treatment, blowdown systems, handling and blending of products and the storage of products. As will be discussed in the following paragraph, such supporting operations are particularly relevant in terms of VOCs and odour emissions.

Worldwide there are in total approximately 650 refineries. Refineries are complex plants, which can have different configurations and include different process units. In general, there are about 25 typical refinery processes used in the refinery industry. The simplest type is the so-called hydro skimming refinery, which comprises a minimum of 5 processing units (Figure 16), and merely desulphurises and catalytically reforms selected cuts from the distillation unit.

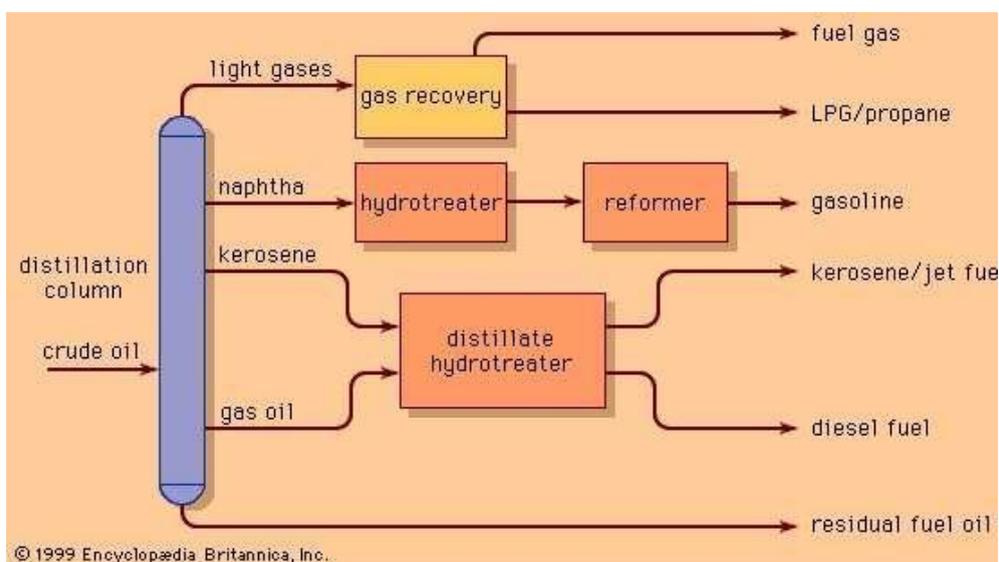


Figure 16. General scheme of a hydroskimming refinery (source: Encyclopædia Britannica)

Some large and complex refineries can comprise up to 15 different processing units or more (Figure 17).

The combination and sequence of processes are usually very specific to the characteristics of the raw materials and the products to be produced. In addition, differences in owner strategy, market situation, location and age of the refinery, historic development, available infrastructure and environmental regulation are among other reasons for the wide variety in refinery concepts, designs and modes of operation.

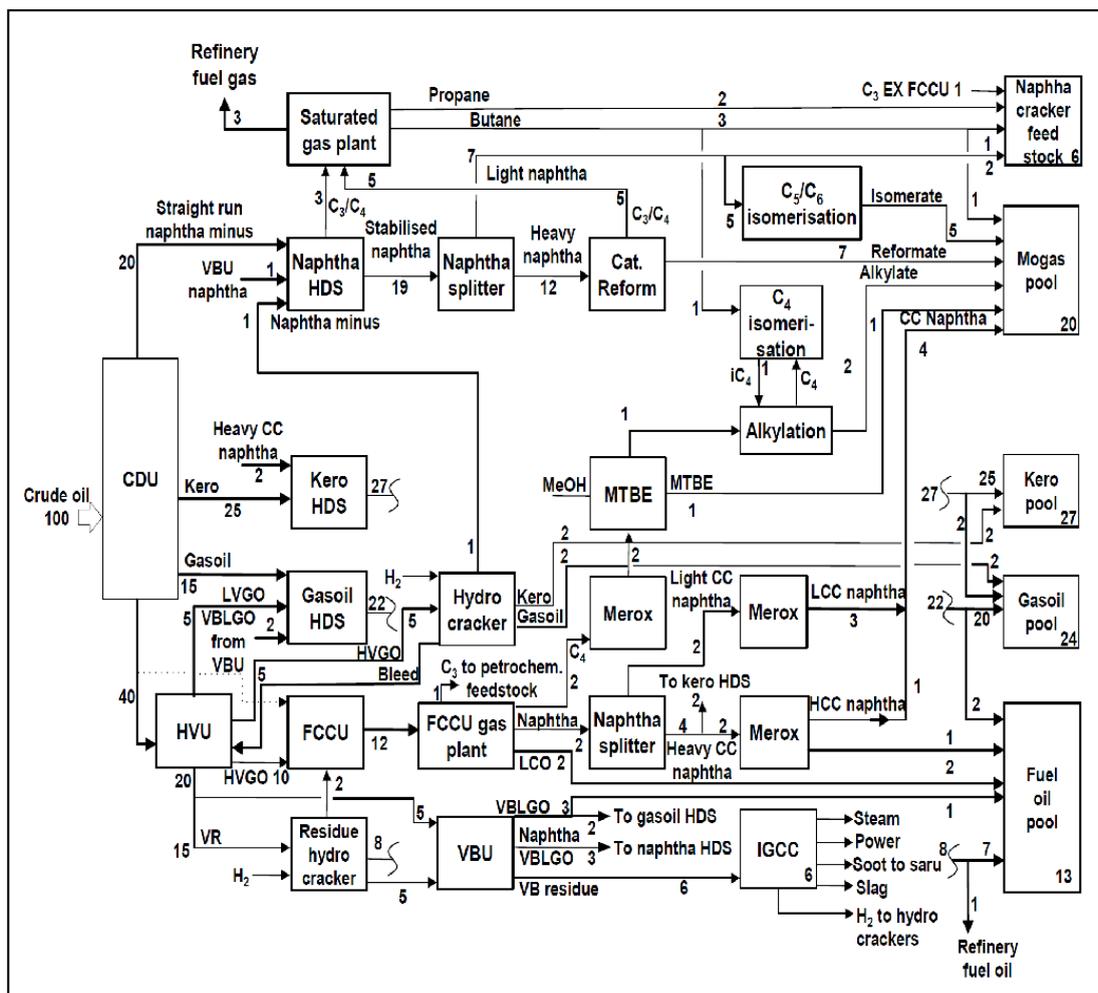


Figure 17. Example of complex refinery with hydroconversion and IGCC (source: Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas)

4.2 Sources of odour emissions in refineries

General overview of refinery odour and VOC emissions

Refineries are industrial sites that manage huge amounts of raw materials and products, and they are also intensive consumers of energy and water used to carry out the processes. In their storage and refining processes, refineries generate emissions to the atmosphere, to water and to the soil. Environmental management has become a major factor for refineries. The refining industry is a mature industry, and pollution abatement programmes have been carried out in most refineries for a long time to different extents. As a result, the emissions generated by refineries have declined per tonne of crude processed and are continuing to decline.

Regarding odours, odour emissions from refineries are mainly related to their emissions of VOCs. As reported in the Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas (European IPPC Bureau, 2015), most of the European

refineries emit from 50 to 1000 g of VOCs per tonnes of total feed processed. A recent study by Roveda et al. (2020), published within the framework of the D-NOSES project, confirms this range by estimating an emission factor of 188 ± 166 g of VOCs per tonne of crude oil processed.

Among those VOCs, Benzene is usually considered the most relevant compound in risk assessment studies related to refinery workers (e.g., Edokpolo et al., 2015; Schnatter, 2000).

The source of VOC emissions is the evaporation and leakage of hydrocarbon fractions potentially associated with all refining activities, e.g. fugitive emissions from pressurised equipment in process units, storage and distribution losses, and wastewater treatment evaporation.

Hydrocarbons are also emitted during non-optimal combustion conditions from process furnaces and boilers, and from regenerators of catalytic processes (e.g., Fluid Catalytic Cracking), but these represent a smaller contribution (European IPPC Bureau, 2015). Moreover, it should be considered that VOCs and odours emitted by refinery stacks, because of the high flow rates and the stacks' height, will have a minor impact on the refinery workers compared to diffuse emissions that are released closer to the soil, and without plume rise effects, which directly affect the quality of the refinery ambient air.

Therefore, the main sources of VOCs and odours in refineries, to which refinery workers' are typically most exposed, can be summarized as follows (European IPPC Bureau, 2015):

- Storage and handling facilities
- Wastewater treatment plants
- Fugitive emissions (valves, flanges, etc.)
- Flare systems

Emissions from storage and handling facilities

In general, over half of a refinery is occupied by storage tanks (Invernizzi et al., 2018). These systems serve to store various types of product: primarily mineral oil, the raw material to be treated, but also the various types of the semi-finished product resulting from the different refinery process units for hydrocarbon separation or conversion. Tanks are also used to store finished products which, in turn, are blended (mixed) for subsequent dispatch for sale.

Typically, two types of storage tanks are used in refineries: fixed roof tanks and floating roof tanks (Invernizzi et al., 2018; Invernizzi and Sironi, 2021).

Fixed roof tanks are used for the storage of heavier products such as diesel, bitumen and fuel oils. The upper part of their construction (the roof) is immobile in relation to the lower part (the shell).

Their contents are normally characterised by low volatility and a true vapour pressure (TVP) of less than 14 kPa. The vapour emissions typical of these tanks which are capable of generating an olfactory nuisance are:

- Filling losses: when the tank is filled, the saturated vapour in equilibrium with the stored liquid phase inside the tank, is released into the atmosphere.
- Breathing losses: the tank is fitted with air release valves in order to compensate for the pressure and temperature differences generated from day to night.

Floating roof tanks must be constructed in such a way that the upper part (the roof) lays on the liquid surface and therefore moves jointly with the liquid, i.e. vertically in relation to the lower part (the shell).

Typically, the liquid contained in this type of tank is a light hydrocarbon with a vapour pressure above 14 kPa but below 86 kPa under normal storage conditions. The roof floats on the stored liquid (e.g. mineral oil or gasoline) in such a way as to prevent the formation of air-fuel mixtures, which could fall within the explosive limits of the mixture itself.

Typical losses from floating roof tanks are:

- Standing losses: losses from the rim seals and roof equipment, which are mainly influenced by the stock vapour pressure.
- Handling losses: during emptying of the tank, a liquid film is left 'clinging' to the walls, and its evaporation causes emissions into the atmosphere.

As stated by the BAT Reference Document for the Refining of Mineral Oil and Gas (European IPPC Bureau, 2015), a floating roof tank can provide a 95% reduction in total losses compared to a fixed roof tank and therefore a consequent saving in terms of product stocks.

Currently, the United States Environmental Protection Agency (EPA), whose objective is to protect human health and the environment, recommends the use of the TANKS 4.09d software to assess the VOC mass emissions from the different tank types (Invernizzi and Sironi, 2021).

Emissions related to crude oil and product storage typically represent 20 – 40 % of the refinery emissions (European IPPC Bureau, 2015).

Emissions from wastewater treatment plants

Large volumes of wastewater are released by the petroleum refining industry. Wastewater treatment plants are advanced environmental protection systems for the control of surface water pollution. However, as this treatment is not complete the resulting discharges still contain pollutants that can contaminate the receiving environment. Moreover, during treatment, a portion of the pollutants evaporate, leading to aerial emissions that may be significant depending on the type of treatment applied. The contributors to the influence of the treatment process are the desalters, storage tank drainage systems, slop system and other processes that have direct water-product contacts.

The air emissions from wastewater treatment plants stem from evaporation (hydrocarbons, benzene, H₂S, NH₃, mercaptans) from the numerous tanks, ponds and sewerage system drains that expose their surfaces to the air. The sewage system and the wastewater treatment in a

refinery may be sources of odour nuisance, particularly from open drains and from oil separators. VOCs are also emitted during air stripping in flotation units and in the biotreater.

Indeed, refinery wastewater treatment areas have been identified as major risk areas for refinery workers (Zhang et al., 2018)

According to the German technical guideline VDI 2400:2000 “Emission control - Mineral oil refineries”, the HC emissions from the waste water systems can be determined by calculation from the exposed surface area of the oil-contaminated untreated water tank (API separator) and an empirical oil evaporation factor of:

- 20 g/m² per hour for open oil separator;
- 2 g/m² per hour for covered oil separator;
- 2 g/m² per hour for flotation;
- 0.2 g/m² per hour for biological treatments

Depending on VOC-reducing techniques applied, WWTPs usually generate 5 - 30 % of the total site emissions (European IPPC Bureau, 2015).

Fugitive emissions

Fugitive VOC emissions from process equipment, such as (single) seals from pumps, compressors, valves and flanges, and leaks in pipelines and equipment may contribute 20 - 50 % to the total VOC emissions (European IPPC Bureau, 2015).

Valves are considered to account for approximately 50 - 60 % of fugitive emissions. A major portion of fugitive emissions comes from only a small fraction of the sources (e.g. less than 1 % of valves in gas/vapour service can account for over 70 % of the fugitive emissions of a refinery).

The VOCs that are typically emitted as fugitive emissions are: Alkanes (Paraffins), Alkenes (Olefins), Aromatics, Cyclic Hydrocarbons, and Methane. Also, H₂S is a typical constituent of fugitive emissions, especially from those equipment involved in the products desulphurisation and sulphur recovery units.

Emissions from flares

Flaring is both a source of air emissions and has the potential to burn valuable products. Therefore, for environmental and energy efficiency reasons, its use must be limited and the amount of flared gas reduced as much as possible. It is generally restricted to unplanned shutdowns or emergency cases.

Flares emit at least CO, CO₂, SO₂ and NO_x. Under specific conditions, flaring leads to soot formation and VOC emissions. Small amounts of complex hydrocarbons (e.g. PAH), may also be released. Indeed, there is a link between soot formation and small emissions of PAH compared to other sources. Emissions of dioxins from flaring are considered non-existent, mainly due to

the absence of necessary formation conditions. Conditions for emissions of PCB were regarded as highly unlikely (European IPPC Bureau, 2015).

The composition depends on a number of factors, including the composition of flare gas, flaring rate, flare system, wind and combustion efficiency at the flare tip. Flares are a very important point source of refinery emissions. Some plants still use older, less efficient waste gas flares. Because these flares usually burn at temperatures lower than necessary for complete combustion (minimum 850 °C), larger emissions of hydrocarbons and particulate matter, as well as H₂S, can occur.

4.3. Analysis of refinery odour emissions

Considerations about the type of data found in the scientific literature

In order to obtain an exhaustive database of chemical compounds emitted by refineries, an extensive bibliographic research was carried out, analysing the scientific papers reporting the chemical identification and quantification of volatile compounds emitted by foundries.

Unfortunately, the scientific literature is not very rich in papers dealing with the identification and quantification of chemical compounds related to refinery emissions, to which refinery workers could be exposed to. Our bibliographic research led to the identification of just 6 scientific papers, published in a time span between 2004 and 2020, which were further analysed for the construction of the database regarding the chemical compounds related to refinery odour emissions, and the evaluation of the priority compounds in terms of their potential health effects (Lin et al., 2004; Ou-Yang et al., 2020; Pandya et al., 2006; Tong et al., 2019; Wei et al., 2014; Zhang et al., 2018).

It should be highlighted that all of the papers found in the scientific literature refer to analyses carried out in refinery ambient air, with the purpose of evaluating refinery workers' exposure to potentially toxic compounds. Indeed, refinery workers will normally not be exposed directly to emissions. It is however possible that, in case of particular maintenance operations, malfunctioning or gas leaks, workers might be exposed to higher concentrations than those of ambient air, sometimes very close to the concentrations at refinery emissions. On the other hand, it should be also highlighted that, during maintenance operations, refinery workers are typically equipped with specific IPDs (*Individual Protection Devices*) like gas masks, which have the function of reducing their exposure to potentially toxic agents.

Finally, it should be noted that, despite the possibility for such exceptional cases, this document does not have the ambition to cover all possible situations for workers' exposure, but rather to provide an extensive review of the data published to the best of our knowledge in the scientific literature up to now.

For this reason, and because the number of scientific papers dealing with the chemical characterization of emissions is limited to few units, in this work, it was not possible to distinguish among single refinery emission sources, but "refinery emissions" were considered as a whole.

Thus, we decided to build our database based on the literature data referred to refinery ambient air, as reported in Table 11.

Data summary of the chemical compounds related to refinery emissions

The database regarding the chemical compounds related to refinery odour emissions (Table 11) was built by providing a list of the compounds identified at least once in the scientific papers that have investigated the chemical composition of refinery ambient air, together with their OT and TLV.

As previously mentioned, the concentration values retrieved in the literature refer to ambient air sampling. Also in this case, we decided to avoid reporting the single concentration values in the table, but used those values – in particular the value of the maximum concentration found in the literature – in order to evaluate the relative HQ for each compound, expressed as the ratio between the HQ and the HI, as explained in section 1.2 of this document.

Finally, in the database (Table 11), the compounds classified as carcinogenic according to the definition supplied in Part 3 of Annex VI to EU Regulation (EC) No. 1272/2008 are identified as follows:

- Carcinogen if the compound is classified as carcinogens of category 1A or 1B.
- Suspected to have carcinogenic potential for human if the compound is classified as carcinogens of category 2.

Compounds not belonging to the categories established by the EU Regulation have been left blank. The compounds not available in the EU Regulation are reported in the table as *not available*.

| Compound | CAS number | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | HQ _i ,% | Carcinogenic |
|------------------------|------------|---------------|----------------|----------|--------------------|---------------|
| 1,2,3-Trimethylbenzene | 526-73-8 | 25 | | | 5.27E+00 | Not available |
| 1,2,4-Trimethylbenzene | 95-63-6 | 25 | | 0.12 | 6.03E+00 | |
| 1,3,5-Trimethylbenzene | 108-67-8 | | | 0.17 | | |
| 1-Butene | 106-98-9 | 250 | | 0.36 | 1.41E-02 | |
| 1-Hexene | 592-41-6 | 50 | | 0.14 | 4.31E-03 | Not available |
| 1-Pentene | 109-67-1 | | | 0.1 | | Not available |
| 2,2,4-Trimethylpentane | 540-84-1 | 300 | | 0.67 | 4.29E-04 | |
| 2,2-Dimethylbutane | 75-83-2 | 500 | 1000 | 20 | 1.30E+00 | |
| 2,3,4-Trimethylpentane | 565-75-3 | 300 | | | 7.11E-03 | |
| 2,3-Dimethylbutane | 79-29-8 | 500 | 1000 | 0.42 | 1.36E+00 | |
| 2,3-Dimethylpentane | 565-59-3 | 400 | 500 | 4.5 | 5.38E-04 | |

| | | | | | | |
|---------------------|-----------|------|------|--------|----------|---------------|
| 2,4-Dimethylpentane | 108-08-7 | 400 | 500 | 0.94 | 2.68E-04 | |
| 2-Methylheptane | 107-83-5 | 500 | 1000 | 0.11 | 2.18E-01 | |
| 2-Methylhexane | 591-76-4 | 400 | 500 | 0.42 | 2.30E-01 | |
| 2-Methylpentane | 107-83-5 | 500 | 1000 | 7 | 5.08E-01 | |
| 3-Methylheptane | 96-14-0 | 500 | 1000 | 1.5 | 8.82E-02 | |
| 3-Methylhexane | 589-34-4 | 400 | 500 | 0.84 | 7.52E-02 | |
| 3-Methylpentane | 96-14-0 | 500 | 1000 | 8.9 | 5.49E-01 | |
| Acetylene | 74-86-2 | | | | | |
| Benzene | 71-43-2 | 0.5 | 2.5 | 2.7 | 7.52E+01 | Carc. 1A |
| cis-2-Butene | 590-18-1 | 250 | | | 6.02E-03 | |
| cis-2-Pentene | 627-20-3 | | | | | Not available |
| Cyclohexane | 110-82-7 | 100 | | 2.5 | 2.26E-02 | |
| Cyclopentane | 287-92-3 | 600 | | | 4.87E-02 | |
| Ethane | 74-84-0 | 1000 | | | 1.38E-02 | |
| Ethene | 74-85-1 | 200 | | | 1.03E-01 | |
| Ethylbenzene | 100-41-4 | 20 | | 0.17 | 1.67E+00 | |
| Isobutane | 75-28-5 | | 1000 | | 1.03E-02 | |
| Isopentane | 78-78-4 | 600 | | 1.3 | 1.45E-02 | |
| Isoprene | 78-79-5 | | | 0.048 | | Carc. 1B |
| Isopropylbenzene | 98-82-8 | 50 | | 0.0084 | 2.43E-03 | |
| m+p-Xylene | 1330-20-7 | 100 | 150 | | 8.55E-02 | |
| m-Diethylbenzene | 141-93-5 | | | 0.07 | | Not available |
| Methylcyclohexane | 108-87-2 | 400 | | 0.15 | 4.93E-02 | |
| Methylcyclopentane | 96-37-7 | | | 1.7 | | Not available |
| m-Ethyltoluene | 620-14-4 | | | 0.018 | | Not available |
| Naphtalene | 91-20-3 | 10 | 15 | | 4.41E-02 | Carc. 2 |
| n-Butane | 106-97-8 | | 1000 | 1200 | 5.36E-02 | |
| n-Decane | 124-18-5 | | | 0.62 | | Not available |
| n-Dodecane | 112-40-3 | | | 0.11 | | Not available |
| n-Heptane | 142-82-5 | 400 | 500 | 0.67 | 8.25E-03 | |
| n-Hexane | 110-54-3 | 50 | | 1.5 | 5.18E-01 | |

| | | | | | | |
|------------------|-----------|------|-----|---------|----------|---------------|
| n-Nonane | 111-84-2 | 200 | | 2.2 | 5.62E-01 | Not available |
| n-Octane | 111-65-9 | 300 | | 1.7 | 3.35E-03 | |
| n-Pentane | 109-66-0 | 600 | | 1.4 | 1.88E-02 | |
| n-Propane | 74-98-6 | 1000 | | 1500 | 2.80E-02 | |
| n-Propylbenzene | 103-65-1 | | | 0.0038 | | |
| n-Undecane | 1120-21-4 | | | 0.87 | | Not available |
| o-Ethyltoluene | 611-14-3 | | | 0.074 | | Not available |
| o-Xylene | 95-47-6 | 100 | 150 | 0.38 | 1.07E-02 | |
| p-Diethylbenzene | 105-05-5 | | | 0.00039 | | Not available |
| p-Ethyltoluene | 622-96-8 | | | 0.0083 | | Not available |
| Propene | 115-07-1 | 500 | | 13 | 1.00E-01 | |
| Styrene | 100-42-5 | 20 | 40 | 0.035 | 1.20E-03 | |
| t-2-Butene | 624-64-6 | 250 | | | 6.45E-03 | |
| t-2-Pentene | 646-04-8 | | | | | Not available |
| Toluene | 108-88-3 | 20 | | 0.33 | 5.46E+00 | |
| Xylene (mix) | 1330-20-7 | 100 | 150 | | 2.45E-01 | |

Table 11. Analysis of chemical compounds related to refinery ambient air samples

Evaluation of priority compounds related to refinery emissions

According to the approach proposed by Jiang et al. (2017), the first group of priority compounds are those classified as carcinogens. Based on the classification proposed by the EU Regulation (EC) No. 1272/2008, the carcinogenic compounds (categories 1A and 1B) identified in foundry emissions are the following:

- Benzene (1A)
- Isoprene (1B)

Always according to the above-mentioned EU Regulation, the suspected carcinogenic compounds (category 2) in foundry emissions are:

- Naphthalene

Considering the most critical compounds related to refinery emissions in terms of their potential to cause non-carcinogenic health effects, it is possible to refer to their relative HQ ($HQ_{i,\%}$). In this case, Benzene is by far the compound that most contributes to the overall HI related to refinery emissions, accounting for over 75% of the overall HI.

The other compounds that have a non-negligible contribution on the HI relevant to the diffuse emissions from temporarily covered landfill surfaces are, in decreasing order of relative HQ:

- 1,2,4-Trimethylbenzene
- Toluene
- 1,2,3-Trimethylbenzene
- Ethylbenzene
- 2,3-Dimethylbutane
- 2,2-dimethylbutane
- n-Nonane
- 3-Methylpentane
- n-Hexane
- 2-Methylpentane
- Xylene (mix)
- 2-Methylhexane
- 2-Methylheptane
- Ethene
- Propene
- 3-Methylheptane
- m+p-Xylene

Those 18 compounds, which include i) aromatic compounds (BTEX and Trimethylbenzenes) ii) linear and ramified paraffins, and iii) short-chain olefins, together contribute by over 99.5% to the overall HI relevant to the refinery emissions (Table 12, Figure 18).

Table 12 also reports a number representing the number of concentration values found in the scientific literature for each of the reported compounds. This number represents the frequency with which the compound has been identified in the analysed samples.

In general, all compounds having a low OT have the potential to cause an odour perception. However, it should be highlighted that the perception of an odour is not directly correlated with a potential health risk. As can be seen from Figure 19, there is no direct correlation between TLVs and OTs of the chemical compounds found in the emissions related to refinery emissions.

| Compound | CAS number | Cmax [ppm] | TLV-TWA [ppm] | TLV-STEL [ppm] | OT [ppm] | No. of Values | HQ _i ,% |
|------------------------|------------|------------|---------------|----------------|----------|---------------|--------------------|
| Benzene | 71-43-2 | 6.73E-01 | 0.5 | 2.5 | 2.7 | 88 | 7.52E+01 |
| 1,2,4-Trimethylbenzene | 95-63-6 | 2.70E+00 | 25 | | 0.12 | 39 | 6.03E+00 |
| Toluene | 108-88-3 | 1.95E+00 | 20 | | 0.33 | 100 | 5.46E+00 |
| 1,2,3-Trimethylbenzene | 526-73-8 | 2.36E+00 | 25 | | | 13 | 5.27E+00 |
| Ethylbenzene | 100-41-4 | 5.99E-01 | 20 | | 0.17 | 77 | 1.67E+00 |
| 2,3-Dimethylbutane | 79-29-8 | 1.22E+01 | 500 | 1000 | 0.42 | 31 | 1.36E+00 |

| | | | | | | | |
|--------------------|-----------|----------|-----|------|------|----|----------|
| 2,2-dimethylbutane | 75-83-2 | 1.16E+01 | 500 | 1000 | 20 | 14 | 1.30E+00 |
| n-Nonane | 111-84-2 | 2.01E+00 | 200 | | 2.2 | 22 | 5.62E-01 |
| 3-Methylpentane | 96-14-0 | 4.91E+00 | 500 | 1000 | 8.9 | 23 | 5.49E-01 |
| n-Hexane | 110-54-3 | 4.63E-01 | 50 | | 1.5 | 24 | 5.18E-01 |
| 2-Methylpentane | 107-83-5 | 4.54E+00 | 500 | 1000 | 7 | 31 | 5.08E-01 |
| Xylene | 1330-20-7 | 4.38E-01 | 100 | 150 | | 5 | 2.45E-01 |
| 2-Methylhexane | 591-76-4 | 1.65E+00 | 400 | 500 | 0.42 | 23 | 2.30E-01 |
| 2-Methylheptane | 107-83-5 | 1.95E+00 | 500 | 1000 | 0.11 | 20 | 2.18E-01 |
| Ethene | 74-85-1 | 3.69E-01 | 200 | | | 49 | 1.03E-01 |
| Propene | 115-07-1 | 8.94E-01 | 500 | | 13 | 53 | 1.00E-01 |
| m+p-Xylene | 1330-20-7 | 1.53E-01 | 100 | 150 | | 80 | 8.55E-02 |

Table 12. Identification of the most critical compounds in terms of potential non-carcinogenic health effects related to refinery ambient air samples

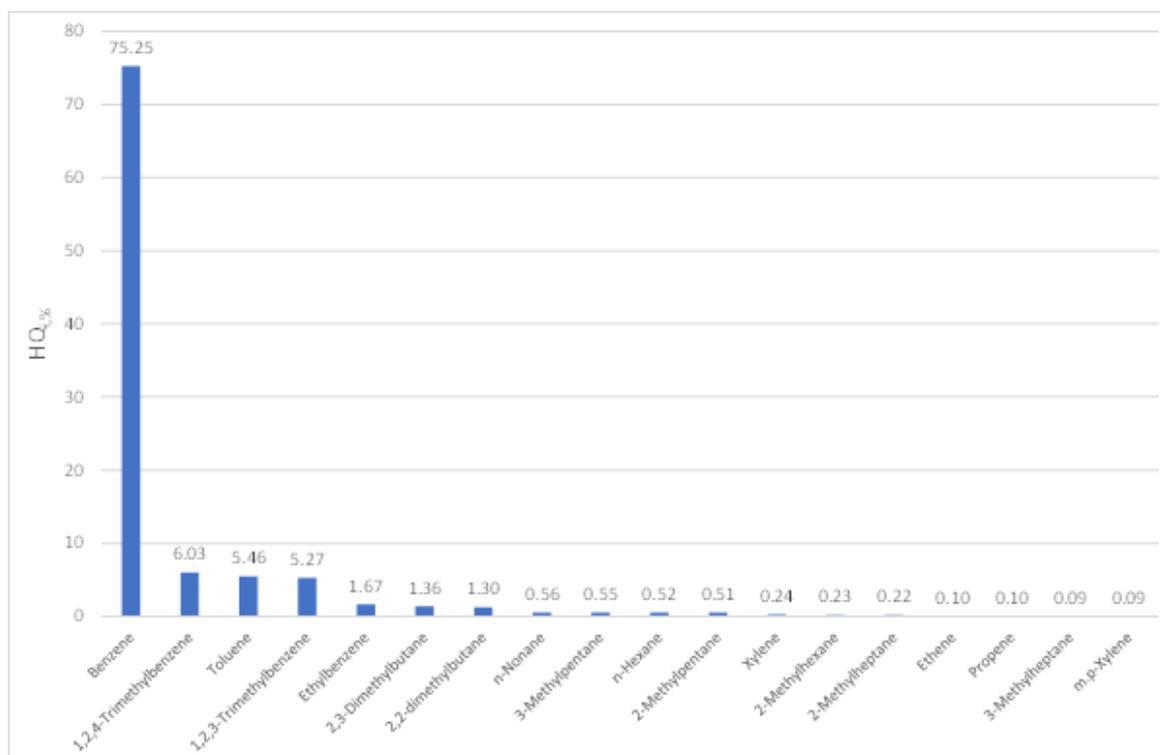


Figure 18. Graphical identification of the most critical compounds in terms of potential non-carcinogenic health effects related to refinery emissions

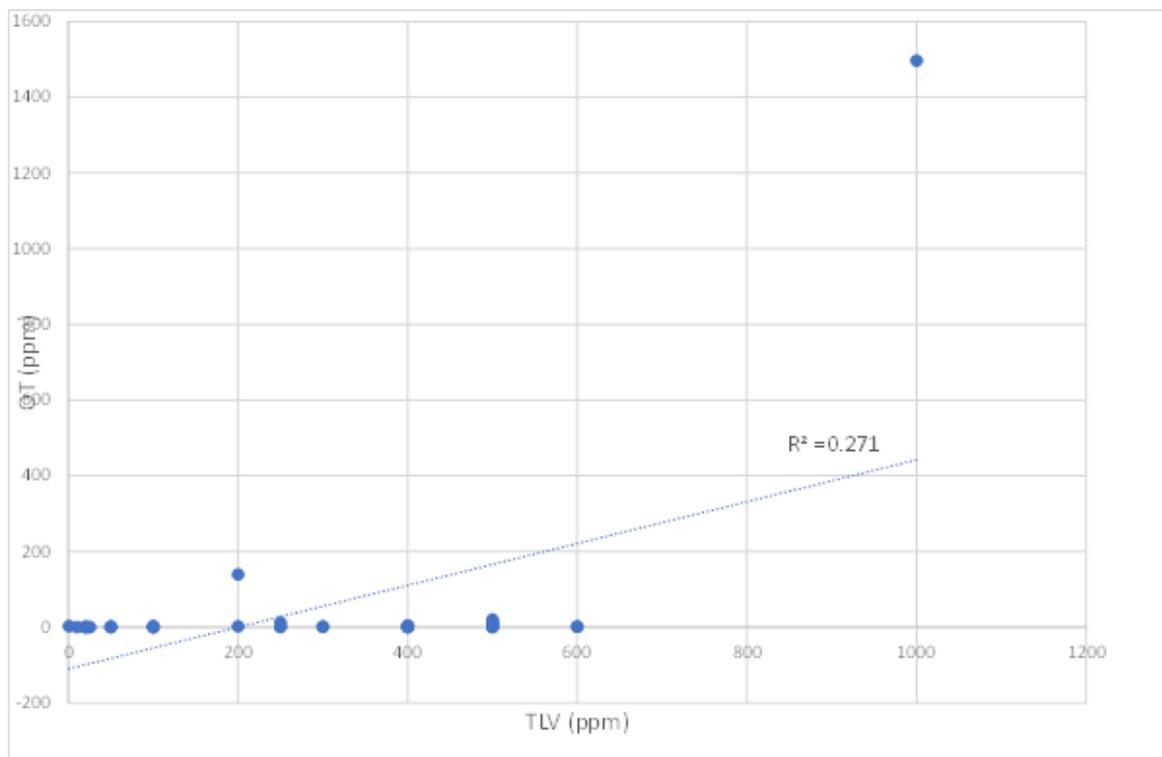


Figure 19. Correlation between TLVs and OTs (both in ppm) of the compounds related to refinery emissions

5. Main outcomes

This section summarizes the main outcomes of this work.

In order to summarize the main outcomes of this work, it is important to resume its objectives, as well as its limitations.

The present work doesn't have the pretence to carry out a detailed toxicological evaluation relevant to the analysed types of plants.

As a matter of fact, it is not possible to extract from this document information useful for a risk assessment related to citizens' exposure to odour emissions. Indeed, such types of studies require very specific evaluations regarding the emission sources and their dispersion into the atmosphere, as well as the sensitive groups of receptors and their localization with respect to the emission sources.

Nonetheless, this work provides useful information regarding the odour emissions from foundries, landfills and refineries and related health effects on human health, discussing workers exposure.

Indeed, based on an extensive bibliographical research, we produced a comprehensive data summary of the chemical compounds identified in the emissions from foundries, landfills, and refineries, together with their Odour Thresholds (OTs) and the occupational exposure limits (Threshold Limit Values – TLVs). Considering the difficulty to retrieve exhaustive collections of such data, those summaries can be considered particularly valuable to make general considerations based on the chemical composition of such emissions. As an example, based on these databases, it is possible to identify the compounds that are mostly responsible for the emitted odours. This knowledge can be further used to design specific monitoring or abatement strategies.

It should be highlighted that the concentration values found in the scientific literature do not always come from emission measurements, but sometimes they are referred to ambient air samples. However, since the objective of this work is not to directly evaluate risk exposure, but rather to identify those compounds having the highest relative HQ values, and thus compile a list of priority compounds that are most worthy of deeper investigations for specific risk assessment studies, the fact of mixing such inhomogeneous concentration data was deemed acceptable.

Indeed, this work contributes to the identification of the most critical compounds in terms of potential impact on workers' health in foundries, landfills, and refineries, which thus represent the priority compounds to be analysed in case of deeper investigations on exposure risk.

In order to identify such priority compounds, we followed the prioritization approach proposed by Jiang et al. (2017) for wastewater treatment plants. According to this approach

the first level of priority compounds includes the substances classified as carcinogenic (or potentially carcinogenic) according to the EU Regulation (EC) No. 1272/2008.

The second level of priority compounds includes those substances with the highest relative Hazard Quotient, which was calculated as the ratio between the maximum concentration found in the literature for each compound and its TLV, divided by the total HI for the considered emission type.

The fact of knowing which are the most critical compounds that are most worthy of deeper investigations for specific risk assessment studies is very useful, because this allows to specifically select and tune the most suitable analytical methods for their detection and quantification.

Finally, by proving the absence of a correlation between OT and TLV values for the different compounds identified in the analysed emission types, it was possible to state that the perception of an odour is not directly correlated with a potential health risk.

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