Non-carcinogenic occupational exposure risk related to foundry emissions: focus on the workers involved in olfactometric assessments

Elisa Polvara, Laura Maria Teresa Capelli & Selena Sironi

Published online: 05 May 2021.

Submit your article to this journal ↗

Article views: 360

View related articles ↗

View Crossmark data ↗

Taylor & Francis
Taylor & Francis Group

Non-carcinogenic occupational exposure risk related to foundry emissions: focus on the workers involved in olfactometric assessments

Elisa Polvara [ID], Laura Maria Teresa Capelli [ID], and Selena Sironi [ID]

Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milano, Italy

ABSTRACT

The scope of this work is the evaluation of the non-carcinogenic occupational risk related to foundry emissions, focusing on the category of workers involved in olfactometric assessments. Odor pollution from industrial activities such as foundries is a serious environmental concern. Sensorial techniques (e.g. dynamic olfactometry, EN13725:2003) currently represent the preferred method for odor emission characterization. During olfactometric analyses, human assessors are directly exposed to the odor at increasing concentrations, thus requiring the assessment of the associated exposure risk to guarantee workers' safety. This paper presents an investigation aiming to produce an inventory of compounds emitted from foundries together with their odor thresholds and toxicological limits (TLVs), with the final objective to propose a procedure for ensuring workers' safety during olfactometric analyses. Looking at the database resulting from this study, among the >100 compounds emitted by foundries, 8 have a maximum concentration above their TLV. Among those, ammonia, H_2S, phenol, toluene and trimethylamine, produce an odor stimulus before they reach a toxic concentration, thus not representing a risk for olfactometric workers. Benzene, formaldehyde and SO_2 are identified as the most critical compounds because they may reach toxic concentrations in foundry emissions, and they start being perceived by humans above their TLV. The proposed procedure entails a minimum dilution factor of 27'000 to be applied to odor samples analyzed by olfactometry, which however might result inapplicable in practical cases, thus pointing out the necessity to adopt chemical measurements to investigate specifically the concentration of the most critical compounds identified in this study.

Introduction

Odor pollution is a growing problem, as suggested by the increasing scientific interest about this topic.[1–5] In particular, odor emissions are one of the major environmental issues for several industrial categories,[6–14] and they often cause a multitude of complaints from the population to local authorities.[5,15,16] Among the industrial activities characterized by a relevant environmental and health impact, foundries represent one of the most critical categories, due to the correlated emissions of odor and potentially toxic compounds. Indeed, ferrous and non-ferrous foundries are considered major sources of hazardous air pollutants (HAPs) worldwide.[17] Indeed, among the 187 HAPs listed in the Clean Air Act Amendment (1990), some 40 compounds have been identified in the air emissions from foundries.[18] Besides that, foundries are often the cause of recurrent odor complaints among the near-living population.[19–21] The increasing number of complaints related to odors has led many countries to issue specific regulations regarding odor emissions and their impacts.[1,22–24] Among the different techniques that can be used to measure and characterize odors,[25–27] dynamic olfactometry is the reference method in Europe for quantifying odor emissions, and it is standardized at the European level by the EN 13725:2003. Dynamic olfactometry is a sensorial analysis, i.e., it uses the human nose as a sensor,[2] which provides information about the quantity of odor in terms of odor concentration, expressed in odor units per cubic meter (ou_E/m^3).[28] During an olfactometric analysis, the odor sample to be analyzed is diluted by means of an "olfactometer", which is a specific instrument that dilutes samples with reference air according to defined dilution ratios,[26] and presented to a panel of human assessors. Thus, during the analysis, the panel members (or panelists) are are directly exposed to the analyzed odor samples at increasing concentrations. However, odor samples may in some cases contain molecules potentially hazardous for human health, thus making that the examiners may be exposed to an unknown occupation exposure risk during the olfactometric analysis. For these reasons, in order to perform an olfactometric analysis of an odor sample in safety conditions, it is fundamental to evaluate the exposure risk for panelists involved and guarantee their

safety. Because the odor sample is presented to the examiners at increasing concentrations, the definition of a minimum dilution value not to be exceeded during the analysis can be a useful parameter to ensure the safety of the workers involved. The importance of surveillance and health protection of the panel involved in olfactometric analysis had already been emphasized in the EN 13725:2003,[28] and has been further reaffirmed in the recent revision of the standard.[29] In order to establish a minimum dilution factor to guarantee the panel safety, it is necessary to know the chemical nature of samples that are analyzed by dynamic olfactometry. The most common analytical technique applied to obtain qualitative and quantitative information about compounds in gaseous environmental matrices, such as odor, is Gas Chromatography coupled with Mass Spectrometry (GC-MS). This technique provides the complete identification and quantification of the chemical compounds – in particular the volatile organic compounds (VOCs)– in an odor sample.[4,30,31] VOCs are often associated with olfactory annoyances because very volatile chemicals are often characterized by a more or less intense and perceptible odor.[32–34] Information obtained by chemical analysis on the nature and concentration of compounds present in odor samples can be used for toxicological risk assessment of panelists involved in olfactometric analyses. However, the execution a detailed chemical assessment of odor samples previous to their presentation to the panel might result particularly complex, especially if there is no precise knowledge about the compounds to be identified.

One simplified approach proposed in the scientific literature [35] is to define a minimum safety dilution level to be adopted during olfactometric measurements; this minimum dilution factor can be evaluated based on literature data regarding the chemical concentrations of the potentially toxic copounds in the emissions. For this reason, in this work, we have explored the possibility to adopt a similar approach in the case of foundry emissions. Therefore, with the purpose to obtain preliminary chemical information about the composition of odor emissions from foundries, a deep literature research was conducted. Despite the relevance of this industrial sector related to its potential environmental and health impacts, only a limited number of studies can be found, which have been trying to identify and quantify the chemical compounds (in particular VOCs) emitted by foundries. It is even more difficult to find specific studies investigating the chemical composition of odor emissions from foundries. Indeed, one novel aspect of this work is that it represents a first attempt to produce an inventory of the VOCs that can be found in foundry emissions, based on a deep investigation of the existing scientific and technical literature. Based on the data avaailable in the literature, the toxicological evaluation was conducted establishing the non-carcinogenic risk for panelists' exposition. This is particularly relevant for the operators working in the field of olfactometry because, despite the fact that the EN 13725:2003 (and its recent revision) points out the necessity to address the issue of the panel safety, it does not define any specific procedure

to asses the occupational exposure risk for examiners involved in dynamic olfactometry. In the scientific literature, only two papers [35,36] have described a methodology to carry out this type of evaluation. Therefore, in this study, we applied the same model as proposed in the literature to assess the non-carcinogenic occupational risk for examiners involved during the olfactometric analysis of foundry odor samples.

In addition to the descriptions already given in the literature, this article proposes to also consider the odor threshold (OT) of pollutants for the evaluation of panelists occupational safety. Thus, another novel aspect of this paper is that it represents a first attempt to investigate the correlation between odor properties and potential health risks related to foundry emissions, by comparing the odor threshold concentrations (OTs) with the toxicological limits (TLVs) of the compounds that are found in this type of emissions. For this purpose, the research work was divided into two steps. After an initial investigation and description of the foundry process, the first step involved extensive bibliographic research considering scientific papers in which the gaseous emissions related to different foundry processes have been sampled and characterized by chemical analysis for the identification (speciation) and the quantification of the emitted pollutants. After the collection of information about the chemical species and their concentrations, the second step of the work involved a research of the relevant OT and the TLV-TWA values in specific databases, such as the database of the American Conference of Governmental Industrial Hygienists (ACGIH). Finally, in the last part of the paper, these values are discussed, by comparing the odor threshold values and TLVs of the chemical compounds emitted by foundries. From these elaborations, a minimum dilution value to be set during olfactometric analyses of odor samples from foundries was defined to guarantee panelists' safety.

Background: the foundry process and related emissions

The foundry process

The aim of the foundry process is the realization of metal products by a direct pouring of metals into molds, 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.[37] Globally, the total production in 2017 amounted to 318190 tons, with a slight rise over 2016.[38] The global production of the world foundry industry in different countries is shown in Figure 1.

As schematized in Figure 2, the foundry process is composed of the following major operations: [39,40]

1. *Melting of metal* (ferrous or non-ferrous metals);
2. *Metal treatment*;
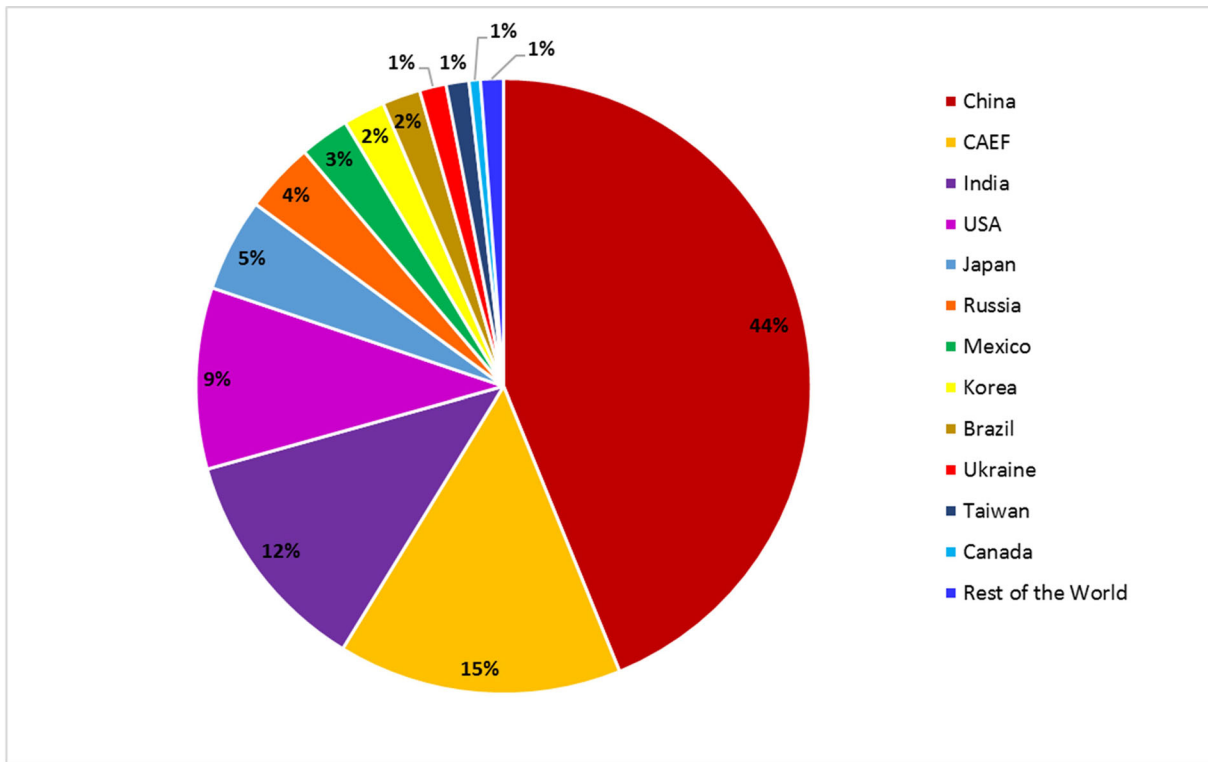3. *Mold making*-preparation of molds and cores;

Figure 1. Global production (expressed in percentage) for the foundry industry in the world. Adapted from.[37]
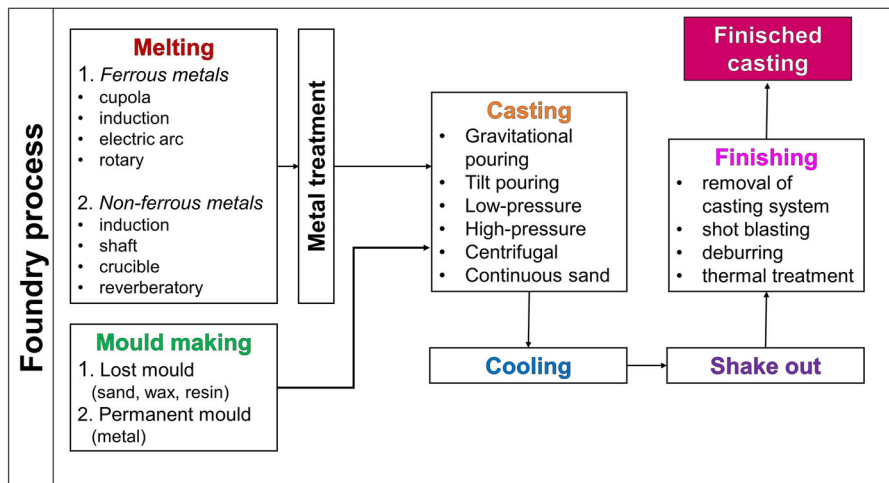
Figure 2. Schematization of the foundry process. Adapted from.[39]

4. *Casting*-pouring of the molten metal into the mold;
5. *Cooling* for casting solidification
6. *Shake out*-removing the casting from the mold;
7. *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 molding and core-making system, the casting system or finishing techniques applied.[39] Despite the complexity of the process, the different single operations can be resumed into two distinct main phases: the *melting* phase, in which a metal alloy is prepared, and a *molding* phase, in which the molds 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 molding types employed in the production.[39] Indeed, the mold realization differentiates significantly the phases of the production cycle. In general, two different molding systems exist and can be applied in foundry process: the permanent mold casting, that employs reusable molds, and lost mold casting, in which the mold material is constituted by sand. In both the typologies, molten metal is poured into a mold that remains until the material cools and solidifies into the desired part shape. The difference is related to the final part of process. Indeed, the lost mold casting uses a single use mold (generally sand), destroyed after each cycle. In this casting, the mold is realized with silicon sand mixed with ligands or additives useful

Figure 3. Principal sources of atmospheric emissions in the foundry process.[43]

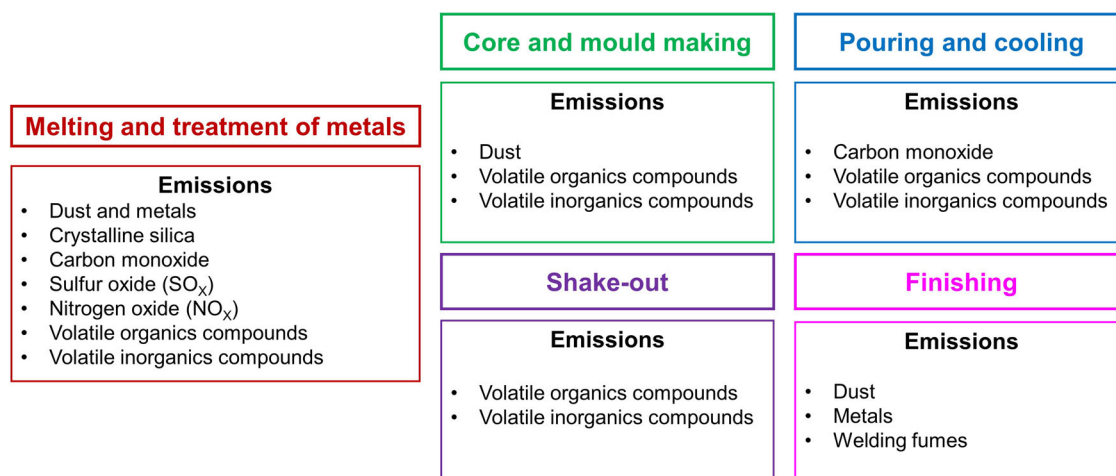to obtain the necessary molding proprieties. Instead, permanent mold casting uses a metal mold that can be reused for several thousands of cycles. While several combinations can be possible, in general, lost molds are mostly used into ferrous foundries and permanent molds are employed in non-ferrous foundries.[39]

Foundry odor emission sources

Like all industrial processes involving high temperatures and heat, the foundry process is characterized by emissions of VOCs that may have a negative impact both on the environment and human health.[41] Foundry is considered one of the most environmental polluting industries due to the consistent emissions of VOCs during each process step.[39,42] As shown in Figure 3, the foundry process gives rise to emissions of different nature, such as dust, metals, carbon monoxide, sulfur dioxide and NO_x in addition to organic and inorganic volatile compounds.[17,21,44,45]

The foundry productive phases involving the major emissions of VOCs are: [21,46,47]

- Core and mold making
- Melting and treatment of metals
- Pouring and cooling
- Shake-out

Emission of VOCs is frequently connected not only with toxicological risks, but also with odor problems.[44] 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 productions 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.[45]

Emissions from core and mold making
Core and mold making are characterized by high emissions of VOCs, correlated with unpleasant odors.[39] In addition,

these operations provoke the emission of silica and dust, which are particularly dangerous for human health.[48] In the core making process, sand is mixed with resins. During molding operation, an appropriate refractory material is shaped to form the cavity in which molten metal will be introduced. The material used for molding operations depends on the type of metal being cast and the final applications. The most common molding material is sand. Several type of resins exist with different chemical proprieties and physical characteristics.[49] Despite differences and technical improvements, the majority of the resins generates odors during the core making, core curing and metal casting processes.[50]

Emissions from melting and treatment of metals
The melting process is one of the most important source of pollutant emission.[51] 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.[45] 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.[39] 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.[43] The emission of gaseous pollutants is studied in particular for the melting and treatment of metals, with particular attention to cupola furnace emissions, connected with the coke combustion.[44] In this process, the VOCs emitted represent the primary odor source and they are directly related to the high sulfur content of coke.[52] In addition, the presence of different additives in the formulations used during the phase of metals treatment can be the origin of odor problems.

Emissions from pouring and cooling processes

The pouring and cooling processes are the main source of inorganic and organic compounds, which may represent a risk for human health, and are characterized by an unpleasant odor. Indeed, during these steps, the organic compounds used as binders, molding materials or coatings are decomposed thermally to produce toxic HAPs.[53–55] During thermal degradation, water vapor, CO, CO_2, NH_3, HCN, SO_2, H_2S, PH_3, phenol formaldehyde, BTEX (benzene, toluene ethylbenzene and xylene), isocyanates, polycyclic aromatic hydrocarbons (PAHs), dioxins and furans are produced.[50,56,57] The quantity and the composition of pollutants released are directly connected with the composition of products used during the mold preparation.[17,58,59] In particular, pyrolysis of carbonaceous additives and core binders during the casting process is the predominant source of the HAPs.[60] During these processes, approximately 330 different compounds can be emitted, part of which has a distinct odor.[54] Due to changes in the production process, casting quality, and environmental needs, the mold binders have changed over years. The introduction of new binders or additives in mold improved the proprieties of natural starch, such as solubility and viscosity.[61] In addition, 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, among which BTEX.[62] Despite these progresses, during molding, pouring and cooling processes the gases produced contain compounds, emitted in low concentrations and characterized by low odor thresholds, that may produce an unpleasant and oppressive odor.[54]

Materials and methods

Origin of the data

In order to obtain an exhaustive database of concentrations of VOCs emitted by foundry plants, an extensive bibliographic research was carried out, analyzing the scientific papers reporting the chemical identification and quantification of volatile compounds emitted by foundries. In particular, the research was focused on those VOCs having a non-negligible odor and/or toxic potential, because, as previously mentioned, the aim of this work is to investigate the correlation between odor properties and possible health effects of foundry odor emissions. For this reason, studies about particulate pollution or odorless gasses have not been considered in this paper. These constraints have limited the number of articles available that could be used to make a comparison and build a database. Therefore, no selection on the type of foundry (iron, steel, etc.) or time selections were adopted to build the dataset. Indeed, the literature search covered a timeframe of publication from 1986 to 2017: older papers could not be excluded from the analysis, because of the small number of papers that could be found about this specific topic. The papers considered in this study have investigated the emission of gaseous pollutants using mainly GC-MS analysis, in order to identify and quantify the chemical compounds present in the gaseous emissions from foundries. The main difference between the papers considered for this study concerns the sampling methods used. Indeed, the studies can be primarily divided into two different categories. The first one includes the articles that have studied the VOCs emissions directly in foundry plants, in the different production areas, in order to evaluate the emissions of all the production phases.[41,43,50,63–69] Other papers studied emissions in laboratory trials, by using samples of foundry materials and reproducing the foundry process in the lab. These papers usually focus mainly on molds emissions.[53,54,70,71]

VOCs concentrations

Once the articles of interest were selected, it was necessary to identify the emitting sources of VOCs and to standardize concentration units of the detected compounds in order to make the data from the different articles comparable. Indeed, VOC emissions can be expressed either in terms of concentration or of flowrate, and it is quite common that different papers use different units. Thus, it was first necessary to identify and classify the emission sources and convert all the data in the same unit. It was decided to convert the data on VOC emissions in terms of concentration in ppm, in order to enable the comparison between the emitted concentration and the OT and TLV values, respectively, which are also concentrations. Thus, the literature data expressed in terms of concentration or in terms of flowrate were all converted into ppm. Unfortunately, many papers do not provide the necessary information to calculate the emitted VOC concentration in ppm. These papers had to be excluded and the data could not be considered for this study. This has led to a further reduction of the useful literature data. The uniformed concentration data were finally grouped for each source and organized in form of a dataset, from which the maximum emitted concentration value could be extrapolated, which is the value that is most interesting for health and safety evaluations. Based on these re-organized data is was possible to carry out the comparison between the chemical concentrations of the VOCs and their OT and TLV values, respectively, in order to evaluate the correlation between odorous and toxicological impact of foundry emissions.

Odor potential of VOCs emissions: odor threshold concentrations (OT)

Every chemical compound is characterized by a specific *odor threshold value* (OT). By definition, the OT is the lowest concentration of a certain odor compound that is perceivable by the human sense of smell.[72] The lower the OT value, the higher the compound odor potential.[73] The determination of the OT is a complex procedure. In the past, OT values of odorous compounds were determined in different ways, both experimental and theoretical. The experimental evaluation of the OT is strictly correlated with several factors, such as the presentation mode of the stimulus to the observer, the influence of extraneous odorants, the

type of observer used, the definition of the odor response and the chemical purity of the odorant.[74] As a result, for a single molecule, several different values of OT can be found in the literature and technical databases, or it is even more common to find a range of OT concentration values rather than a single value. Indeed, the research and selection of proper OT values has been a complex issue of this work. To obtain a complete and robust dataset to make comparisons and evaluations, the OT values were searched in different sources.[75–77] According to EN 13725:2003, the OT is equal to OT_{50}, defined as the concentration that is perceived by 50% of the population.[28] As previously explained for the chemical concentrations, also the OT values have been reported in ppm in order to enable the comparisons.

Toxicological potential of VOCs emissions: threshold limit values (TLV)

One of the most important problems connected with emissions of VOCs from foundries is their toxic potential. Indeed, most of the compounds produced in the different steps of the foundry process are characterized by a non-negligible impact on human health. To evaluate the toxicological impact of these compounds on workers involved in dynamic olfactometry, it is possible to use the so called threshold limit value (TLV) concentration of each compound, and compare it with the measured chemical concentration to which people are exposed. To conduct the evaluation of non-carcinogen effects for panelists during olfactometric analysis, a model proposed in the scientific literature has been adopted.[35] In theory, based on this model, the evaluation of non-carcinogenic health effects for sniffers should use as reference concentration the Threshold Limit Value - Short Term Exposure Limit (TLV-STEL) suggested by ACGIH (American Conference of Governmental Industrial Hygienists). If not available, the Threshold Limit Value – Time Weighted Average (TLV-TWA) or the Immediately Dangerous to Life or Health, IDLH values were used. This assumption was made considering that panels, during the working activities, are exposed to odor emission only for a few seconds, and the analysis sessions typically lasts 1 to maximum 2 hours. However, in order to conduct an even more precautionary assessment, in this study it was decided to use the TLV-TWA provided by the ACGIH as reference thresholds. By using these concentration thresholds, which refer to a period of continuous and long-term exposure (for a conventional 8-hour workday and a 40-hour workweek for the entire working lifetime) ,[78] it is reasonably certain that an approach of maximum protection for the workers involved is applied. According with this study,[35] it was assumed that the volatile compounds are inhaled for risk calculations. To evaluate the non-carcinogenic risk exposure, it is possible to evaluate the hazard quotient (HQ) for a single compound, which is calculated as follows (Equation 1):

$$HQ = \frac{C_{exp}}{C_{ref}} \qquad (1)$$

Where C_{exp} is the exposure concentration and C_{ref} is the reference dose, which represents an estimate of the pollutant concentration to which human can be exposed for all the lifetime period without any appreciable risk to develop deleterious health effects.[79–81] In order to ensure a precautionary approach, as exposure concentration (C_{exp}), it was decided to use the maximum concentration among all the values found in the considered scientific papers. Thus, as C_{ref} it was decided to consider the TLV-TWA and TLV-STEL values, respectively, depending on the data availability. For a complex matrix, such as atmospheric emissions from industrial activities, in which different compounds are present, in order to evaluate the non-carcinogenic risk exposure, it is necessary to calculate the hazard index (HI) according to the following expression (Equation 2):

$$HI = \sum_i HQ_i \qquad (2)$$

The risk in not considered acceptable either if HQ is ≥ 1 or HI ≥ 1.[82]

The HI value obtained can be used to set the minimum dilution value to be adopted during the olfactometric analysis of foundry samples.

Results

Identification and classification of foundry emission sources

The VOCs emitted from foundries come from different sources. Indeed, the entire production process originates emission of different chemical compounds, which are a potential cause of olfactory harassment. For this reason, the first step of this study involved the identification and the classification of the VOCs emission sources reported in the papers that were analyzed for the construction of the database. This step is crucial because it leads to the identification of those productive sections that are most significant in terms of emissions of chemical compounds. This first analysis led to the identification of 13 different emissions, each of them referred to a specific step of the foundry process (Table 1).

Comparison of maximum VOC concentrations, OT and TLV

Table 2 reports the list of all VOCs found in the literature search. For each compound, the table reports the maximum concentration value (C_{MAX}) among those found in the literature. This value is compared with the OT and the TLV (TLV-TWA and TLV-STEL) values of the compound and used to calculate the hazard quotient (HQ). The table also reports the reference from which the OT values for each compound were taken, whereas the TLV-TWA values are for all compounds fixed by the ACGIH.[83] Moreover, the HQ was calculated in order to estimate the risk exposure for non-carcinogenic effects for panelists involved in olfactometric analysis relevant to each compound. The TLV-TWA values were used as the reference dose (C_{ref}) for the HQ calculation. In the absence of the TLV-TWA value for one compound, its TLV-STEL was used for this purpose. All the

Table 1. Classification of VOCs sources from articles collected in our study.

VOC sources for foundry plants	
Source identified into the literature	General source for foundry process
Molding	Core and mold making
Electric arc furnace	Melting and metals treatment
Blast furnace	
Basic oxigen furnace	
Induction and cupola furnace	
Generic furnace	
Coke oven	
Hot forming	
Cold forming	
Pouring and cooling	Pouring and cooling
Sand thermal degradation	
Shake-out	Shake-out
Not specified	

concentration values are expressed in ppm. The compounds are reported in alphabetic order. For some compounds, the TLV and OT values could not be determined (N.D.). In Table 2 the compounds for which a HQ > 1 was evaluated are highlighted in red color, while compounds with OT values higher than TLV ones are highlighted in bold.

Discussion

From this comparison (Table 2), it is possible to observe that for most of the compounds considered, the HQ is <1, thus indicating that, in general, the risk for workers related to the exposure of VOCs, evaluated in terms of the maximum concentration found in the literature, is rather low for most of the pollutants detected. The compounds for which a HQ > 1 (highlighted in red in Table 2) was calculated, are: ammonia, benzene, formaldehyde, hydrogen sulfide, phenol, sulfur dioxide, toluene and trimethylamine. These compounds thus represent the pollutants that are more likely to produce a health effect, due to the fact that their observed concentration might be higher than their TLV. Based on this observation, for these compounds it was decided to carry out a deeper analysis in order to evaluate how the maximum concentration value among those found in literature, which is the one used for the calculation of the HQ as reported in Table 2, effectively is representative of the concentration distribution for each compound. In other words, if the maximum concentration considered for the calculation of the HQ is an outlier compared to the other values observed in the literature, then the effective risk related to this might be limited. In order to deepen the investigation of the exposure risks for panelists exposed to these odorous pollutants; it is important to account for the OT value and compare it with TLV values. From this comparison, it is possible to evaluate if a compound has an OT lower than the TLV, thus making that it can be perceived by the nose before it becomes dangerous for human health. This assessment is particularly pertinent to the case under consideration, as this type of worker is not subject to the habituation and adaptation effect found in the workplace. By looking at Table 2, it can be observed that the OT is lower than the TLV-TWA for the majority of the pollutants reported. This allows affirming that most of the compounds identified are detectable, during the olfactometric analysis,

by the nose before they prove to be dangerous for workers. Only four compounds (highlighted in bold in Table 2) present OT > TLV-TWA: benzene, chlorobenzene, formaldehyde and n-butane. These pollutants can have toxic effects before being perceived by the human nose and therefore they represent the most critical compounds for the safeguard of the olfactometric panel.

Analysis of the concentrations of the most relevant pollutants

According to the comparison presented in the previous paragraph, which considers the maximum concentration values among those found in the literature, it turns out that ammonia, benzene, formaldehyde, hydrogen sulfide, phenol, sulfur dioxide, toluene and trimethylamine have HQ values > 1. In order to provide a deeper investigation about the effective potential toxicological effect of these compounds, it was decided to analyze more thoroughly the representativeness of the maximum concentration (C_{MAX}) with respect to the distribution of the concentration values found in the literature. Thus, for these pollutants, the distribution of concentrations were evaluated considering the abundance of data available and their statistical distribution. In order to provide an overview of the the distribution of data retrieved from the literature, Table 3 reports the number of concentration values retrieved in the literature, the mean concentration and their standard deviation. The distribution of the logarithms of the concentration values for the compounds listed in Table 3 is shown in Figure 4 in form of an histogram. This type of graph allows to make some considerations about the statistical distribution of observed data, which in this case seem to follow a log-normal-like distribution for most of the compounds considered. However, due to the relatively low number of data available, a deeper statistical analysis is hardly applicable. Nonetheless, by observing the average concentration values and the standard deviations reported in Table 3, and by looking at the graphical representation of the concentration distribution in Figure 4, it is possible to state that the maximum concentrations observed for all the compounds considered cannot be considered as outliers compared to the distribution of the rest of the concentration values. If considering for instance toluene (red columns in Fig. 4), it is possible to observe that, despite being the majority of data distributed between 10^{-1} and 10^1 ppm, the maximum concentration, which is in the range of 10^2 ppm, is not an isolated value. Indeed, there are 3 concentration values among those found in the literature in the same range. For benzene the situation is a little bit different, being the maximum concentration observed the only value in the range 10^4 ppm. However, there are other 3 values among those found in literature in the range 10^3 ppm, making that, also in this case, the maximum concentration value cannot be considered as an outlier compared to the rest of the distribution. Based on these considerations, it is possible to confirm the suitability to consider the maximum concentration value for safety evaluations, also because this means applying the most

Table 2. VOCs concentrations from foundry process.

Compound	CAS number	C_{MAX} [ppm]	Reference C_{MAX}	TLV (ACGIH) TWA [ppm]	STEL [ppm]	HQ	OT [ppm]	Reference OT
1,1,1-trichloroethane	71-55-6	0.04	[41]	350	450	1.14E-04	1.0	[76]
1,1,2-trichloroethane	79-00-5	0.01	[41]	10	N.D.	9.99E-04	N.D.	
1,2,3-trimethylbenzene	526-73-8	0.19	[41]	N.D.	N.D.	N.D.	N.D.	
1,2,4-trimethylbenzene	95-63-6	0.99	[41]	N.D.	N.D.	N.D.	0.1	[76]
1,2-Benzenedicarboxylic acid	88-99-3	0.00	[71]	N.D.	N.D.	N.D.	N.D.	
1,2-dichlorobenzene	95-50-1	0.01	[41]	25	50	2.80E-04	0.1	[76]
1,3,5-trimethyl-benzene	108-67-8	0.26	[41]	N.D.	N.D.	N.D.	0.2	[76]
1,4-dimethylbenzene	106-42-3	0.32	[50]	100	150	3.25E-03	0.058	[75]
1-butene	106-98-9	1.53	[41]	250	N.D.	6.13E-03	0.36	[75]
1-hexene	592-41-6	0.24	[41]	50	N.D.	4.84E-03	0.14	[75]
1-pentanamine	110-58-7	2.50	[50]	N.D.	N.D.	N.D.	N.D.	
1-pentene	109-67-1	0.17	[41]	N.D.	N.D.	N.D.	0.1	[75]
2,2,4-trimethylpentane	540-84-1	0.07	[41]	N.D.	N.D.	N.D.	0.67	[75]
2,2-dimethylbutane	75-83-2	0.16	[41]	500	1000	3.24E-04	20	[75]
2,3,4-trimethylpentane	565-75-3	0.06	[41]	N.D.	N.D.	N.D.	N.D.	
2,3-dimethylbutane	79-29-8	0.35	[41]	500	1000	7.06E-04	0.42	[75]
2,3-dimethylpentane	565-59-3	0.10	[41]	400	500	2.40E-04	38	[75]
2,4-dimethylpentane	108-08-7	0.02	[41]	400	500	5.75E-05	0.94	[75]
2,4-dimethylphenol	105-67-9	0.13	[50]	N.D.	N.D.	N.D.	0.0001	[76]
2-methylfuran	534-22-5	2.68E-05	[71]	N.D.	N.D.	N.D.	0.1	[76]
2-methylheptane	592-27-8	0.17	[41]	N.D.	N.D.	N.D.	0.11	[75]
2-methylhexane	591-76-4	0.35	[41]	400	500	8.72E-04	0.42	[75]
2-methylpentane	107-83-5	0.70	[41]	500	1000	1.40E-03	7	[75]
3-methylheptane	589-81-1	0.20	[41]	N.D.	N.D.	N.D.	1.5	[75]
3-methylhexane	589-34-4	0.43	[41]	400	500	1.08E-03	0.84	[75]
3-methylpentane	96-14-0	0.53	[41]	500	1000	1.06E-03	8.9	[75]
Acenaphthene	83-32-9	0.04	[67]	N.D.	N.D.	N.D.	N.D.	
Acenaphthylene	208-96-8	0.91	[67]	N.D.	N.D.	N.D.	N.D.	
Acrolein	107-02-8	0.08	[43]	N.D.	N.D.	N.D.	0.0036	[75]
Ammonia	7664-41-7	29.47	[43]	25	35	1.18	1.5	[77]
Anthracene	120-12-7	0.07	[67]	N.D.	N.D.	N.D.	N.D.	
Anthanthrene	191-26-4	5.57E-05	[68]	N.D.	N.D.	N.D.	N.D.	
Benz[a]anthracene	56-55-3	5.84E-04	[63]	N.D.	N.D.	N.D.	N.D.	
Benzene	**71-43-2**	**13520**	[66]	**0.5**	**2.5**	**27039.74**	**2.7**	[77]
Benzo[a]fluorene	238-84-6	2.49E-05	[68]	N.D.	N.D.	N.D.	N.D.	
Benzo[a]pyrene	50-32-8	0.01	[65]	N.D.	N.D.	N.D.	N.D.	
Benzo[b]chrysene	214-17-5	1.14E-03	[65]	N.D.	N.D.	N.D.	N.D.	
Benzo[b]fluoranthene	205-99-2	1.34E-03	[65]	N.D.	N.D.	N.D.	N.D.	
Benzo[b]fluorene	243-17-4	1.47E-05	[68]	N.D.	N.D.	N.D.	N.D.	
Benzo[b]naphtho[2,1-d]thiophene	239-35-0	6.26E-06	[68]	N.D.	N.D.	N.D.	N.D.	
Benzo[b + j + k]fluoranthene	N.D.	6.16E-05	[68]	N.D.	N.D.	N.D.	N.D.	
Benzo[e]pyrene	192-97-2	1.09E-03	[65]	N.D.	N.D.	N.D.	N.D.	
Benzo[ghi]fluoranthene	203-12-3	8.64E-06	[68]	N.D.	N.D.	N.D.	N.D.	
Benzo[ghi]perylene	191-24-2	1.53E-04	[63]	N.D.	N.D.	N.D.	N.D.	
Benzo[k]fluoranthene	207-08-9	3.63E-04	[65]	N.D.	N.D.	N.D.	N.D.	
Bromomethane	74-83-9	0.01	[41]	1	N.D.	1.20E-02	N.D.	
Carbon tetrachloride	56-23-5	2.70	[41]	5	10	0.54	4.6	[75]
Chlorobenzene	**108-90-7**	**0.72**	[41]	**10**	**N.D.**	**0.07**	**12.9**	[77]
Chloroform	67-66-3	0.06	[41]	10	N.D.	0.01	3.8	[75]
Chrysene	218-01-9	4.75E-04	[65]	N.D.	N.D.	N.D.	N.D.	
Cis-1,2-dichloroethylene	156-59-2	0.05	[41]	200	N.D.	2.60E-04	N.D.	
Cis-1,2-dichloropropene	563-54-2	4.90E-03	[41]	N.D.	N.D.	N.D.	N.D.	
Cis-2-butene	590-18-1	0.21	[41]	250	N.D.	8.32E-04	12.4	[76]
Cis-2-pentene	627-20-3	0.20	[41]	N.D.	N.D.	N.D.	N.D.	
Coronene	191-07-1	6.17E-04	[65]	N.D.	N.D.	N.D.	N.D.	
Cyclohexane	110-82-7	0.12	[41]	100	N.D.	1.16E-03	2.5	[75]
Cyclopenta[cd]pyrene	27208-37-3	8.93E-04	[65]	N.D.	N.D.	N.D.	N.D.	
Cyclopentane	287-92-3	0.28	[41]	600	N.D.	4.70E-04	1.3	[76]
Dibenz[a,h]anthracene	53-70-3	3.94E-04	[65]	N.D.	N.D.	N.D.	N.D.	
Dibenz[a,j]anthracene	224-41-9	2.02E-05	[68]	N.D.	N.D.	N.D.	N.D.	
Ethylbenzene	100-41-4	9.25	[66]	20	N.D.	0.46	0.17	[75]
Ethynylbenzene	536-74-3	7.18E-06	[71]	N.D.	N.D.	N.D.	N.D.	
Fluoranthene	206-44-0	0.01	[67]	N.D.	N.D.	N.D.	N.D.	
Fluorene	86-73-7	0.07	[67]	N.D.	N.D.	N.D.	N.D.	
Formaldehyde	**50-00-0**	**0.11**	[43]	**0.1**	**0.3**	**1.06**	**0.5**	[77]
Hexadecanoic acid	57-10-3	2.86E-06	[71]	N.D.	N.D.	N.D.	N.D.	
Hexamine	100-97-0	0.81	[50]	N.D.	N.D.	N.D.	N.D.	
Hydrogen cyanide	74-90-8	3.29	[43]	N.D.	N.D.	N.D.	0.00058	
Hydrogen sulfide	7783 − 06-4	1.13	[43]	1	5	1.13	0.00041	[77]
I-butane	75-28-5	4.21E-03	[54]	N.D.	1000	4.21E-06	0.421	[77]
Indeno[1,2,3-cd]pyrene	193-39-5	6.97E-05	[63]	N.D.	N.D.	N.D.	N.D.	
Isopentane	78-78-4	2.27	[41]	600	N.D.	3.78E-03	1.3	[75]

(continued)

Table 2. Continued.

Compound	CAS number	C_{MAX} [ppm]	Reference C_{MAX}	TLV (ACGIH) TWA [ppm]	STEL [ppm]	HQ	OT [ppm]	Reference OT
Isoprene	78-79-5	0.16	[41]	N.D.	N.D.	N.D.	0.048	[75]
Isopropylbenzene	98-82-8	0.85	[41]	50	N.D.	0.02	0.0084	[75]
M/p cresol	N.D.	0.06	[50]	5	N.D.	0.01	N.D.	
M-diethylbenzene	141-93-5	0.14	[41]	N.D.	N.D.	N.D.	0.07	[75]
Methane	74-82-8	7.18	[54]	1000	N.D.	7.18E-03	1.5	[76]
Methyl benzoate	93-58-3	0.01	[50]	N.D.	N.D.	N.D.	0.0003	[76]
Methylcyclohexane	108-87-2	0.16	[41]	400	N.D.	3.97E-04	0.15	[75]
Methylcyclopentane	96-37-7	0.14	[41]	N.D.	N.D.	N.D.	1.7	[75]
M-ethyltoluene	620-14-4	0.32	[41]	N.D.	N.D.	N.D.	0.018	[75]
M-xilene	108-38-3	0.73	[43]	100	150	0.01	0.041	[75]
Naphthalene	91-20-3	3.44	[67]	5	N.D.	0.69	0.1	[76]
N-butane	**106-97-8**	**0.88**	[41]	**N.D.**	**1000**	**8.75E-04**	**1200**	[77]
N-decane	124-18-5	0.03	[41]	N.D.	N.D.	N.D.	0.62	[75]
N-heptane	142-82-5	0.40	[41]	400	500	1.01E-03	0.67	[75]
N-hexane	110-54-3	0.35	[41]	50	N.D.	7.02E-03	1.5	[75]
N-nonane	111-84-2	0.13	[41]	200	N.D.	6.70E-04	2.2	[75]
N-octane	111-65-9	0.29	[41]	300	N.D.	9.56E-04	1.7	[75]
N-pentane	109-66-0	1.02	[41]	600	N.D.	1.70E-03	1.4	[75]
N-propylbenzene	103-65-1	0.11	[41]	N.D.	N.D.	N.D.	0.0038	[75]
O-cresol	95-48-7	0.07	[50]	5	N.D.	0.01	0.00028	[75]
O-ethyltoluene	611-14-3	0.19	[41]	N.D.	N.D.	N.D.	0.074	[75]
O-Xylene	95-47-6	2.04	[41]	100	150	0.02	0.38	[75]
P-diethylbenzene	105-05-5	0.16	[41]	N.D.	N.D.	N.D.	0.00039	[75]
Perylene	198-55-0	0.00	[65]	N.D.	N.D.	N.D.	N.D.	
P-ethyltoluene	622-96-8	0.43	[41]	N.D.	N.D.	N.D.	0.0083	[75]
Phenanthrene	85-01-8	0.06	[67]	N.D.	N.D.	N.D.	0.0075	
Phenol	108-95-2	5.10	[50]	5	N.D.	1.02	0.0056	[77]
Phenylethanol	98-85-1	0.01	[50]	N.D.	N.D.	N.D.	0.06	[76]
Pyrene	129-00-0	0.01	[67]	N.D.	N.D.	N.D.	N.D.	
Styrene	100-42-5	1.97	[41]	20	40	0.10	0.035	[75]
Sulfur dioxide	7446-09-5	3.83	[43]	0	0.25	15.32	0.87	[77]
Tetrachloroethylene	127-18-4	0.37	[41]	25	100	0.01	0.77	[75]
Thiophene	110-02-1	1.45E-05	[71]	N.D.	N.D.	N.D.	0.00056	[75]
Toluene	108-88-3	448.04	[67]	20	N.D.	22.40	0.33	[77]
Trans-2-butene	624-64-6	0.21	[41]	250	N.D.	8.32E-04	0.9	[76]
Trans-2-pentene	646-04-8	0.18	[41]	N.D.	N.D.	N.D.	N.D.	
Trichloroethylene	79-01-6	0.43	[41]	10	25	0.04	3.9	[75]
Triethylamine	121-44-8	16.19	[50]	1	3	16.19	0.53	[77]

Table 3. Analysis of the concentration data for the most critical compounds.

Compound	C_{MAX} [ppm]	C_{mean} [ppm]	DV STD	Numerosity of data (n)
Ammonia	29.47	4.43	9.87	11
Benzene	13519.87	1027.37	2930.75	28
Formaldehyde	0.11	0.03	0.03	11
Hydrogen sulfide	1.13	0.30	0.39	11
Phenol	5.10	0.55	1.34	15
Sulfur dioxide	3.83	0.53	1.17	11
Toluene	448.04	32.63	98.58	31
Triethylamine	16.19	5.60	7.35	4

precautionary approach to the evaluation of the risk for examiners exposed to VOCs emissions from foundries during olfactometric analysis.

Evaluation of the potential hazard related to odor emissions from foundries

This paragraph has the aim to summarize and to comment the results of our investigation and propose a sort of decision tree that can be adopted in order to evaluate the potential risk of exposure to hazardous odorous compounds of examiners involved in olfactometric analysis of odor samples from foundries. In order to evaluate the exposure risk for the category of workers, the first parameter that shall be considered is the HQ. As described previously and discussed

in the scientific literature,[35,36] the HQ is the parameter used to assess non-carcinogenic risk for the olfactometric worker. In our study, the assessment is based on the maximum measured concentration to obtain a more cautious assessment. From the data reported in Table 2, only eight pollutants have a Cmax > TLV-TWA, thus having HQ > 1. Since dealing with pollutants, in order to evaluate the exposure risk, it is important to consider not only the TLV, but also the OT of the compounds. Indeed, the odor molecules having an OT lower than the TLV, have the potential to be perceived by panelists before producing any adverse effect on human health. By comparison of the OT and TLV-TWA values relevant to the pollutants analyzed here, it is possible to observe that most of these compounds present OT values lower than their TLV-TWA. However, there are some compounds for which this condition is not fulfilled, and their TLV is lower than their odor threshold, meaning that they have the potential to be toxic before being perceived by the human nose. A schematization of the logical process for the evaluation of the potential hazard for workers related with the compounds that are emitted from foundries is reported in Figure 5. As shown in Figure 5, for most VOCs examined by means of our literature study, even the maximum concentration among those found is lower than TLV-TWA concentration. If this condition is fulfilled, then these pollutants
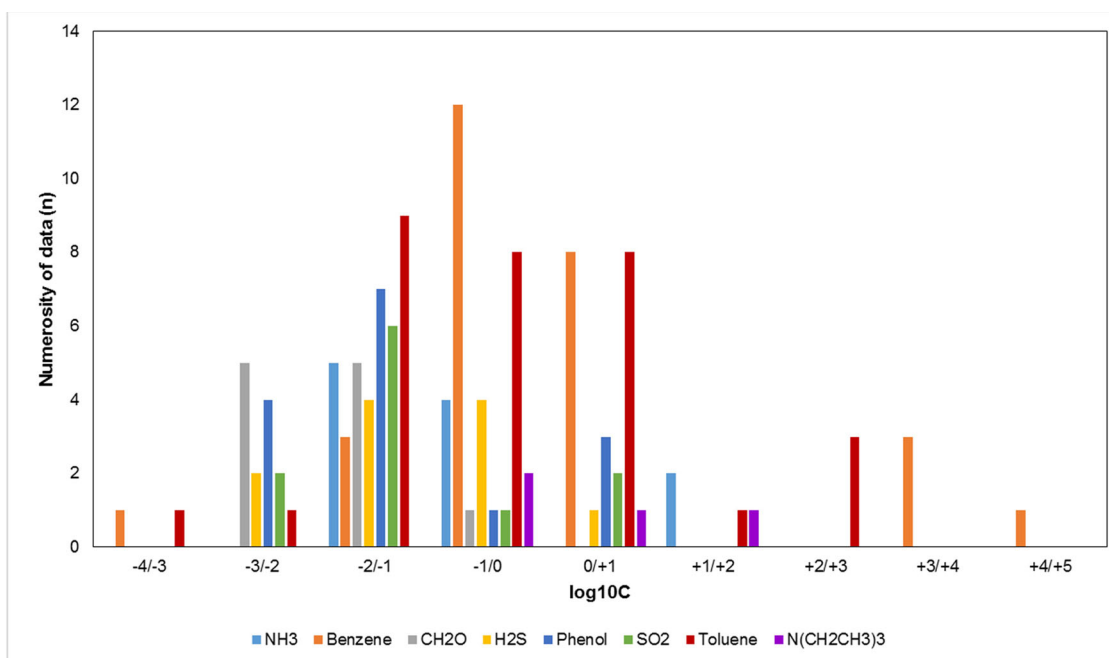
Figure 4. Histogram of the logarithms of the concentration values of the critical pollutants.
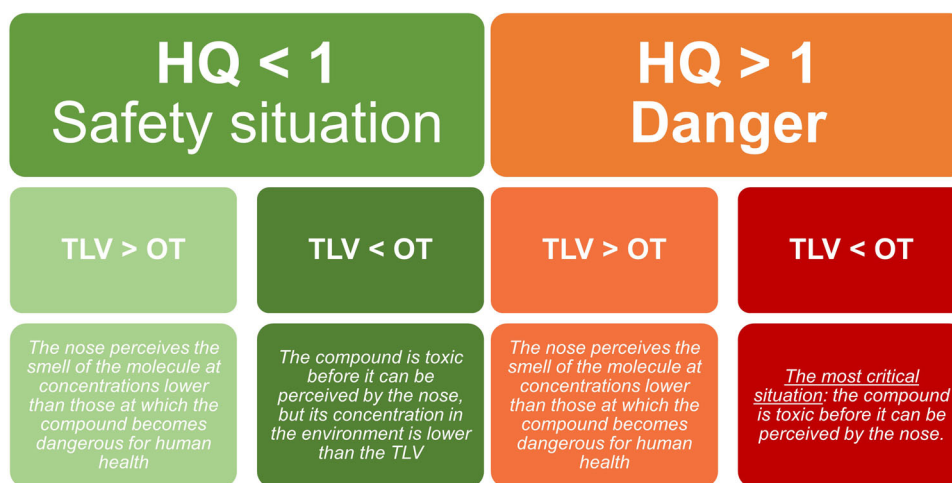

Figure 5. Schematization of the decision tree to evaluate the potential health hazards associated with odorous emissions from foundries.

do not provoke long-term non-carcinogenic effects. However, there are 8 compounds for which this condition is not fulfilled, and thus have a HQ value above 1. Fort these compounds, it is useful to further compare the TLV value with the OT, in order to verify if the compound can be perceived by the human nose before reaching a toxic concentration. If the OT is lower than the TLV for one compound, then it means that its odor is perceivable by the human nose before becoming dangerous for the panelists' health. Based on this consideration, Table 4 reports the TLV and OT values for the compounds with HQ > 1, in order to evaluate their dangerousness. From this comparison, it is possible to observe that the most critical compounds among those investigated are benzene, formaldehyde and sulfur dioxide. Not only their maximum concentration observed in foundry emissions is higher than the TLV-TWA concentration, but they are not perceived through the human sense of smell even at toxic concentrations, thus making them

particularly worthy of attention. As these compounds represent a real health risk, it is necessary to establish a minimum dilution value not to be exceeded when analyzing foundry samples in order to ensure the safety of exposed examiners. To establish this value, the HQ values obtained for the different compounds reported in the literature were summed. This shows that the minimum dilution level not to be exceeded when analyzing a generic foundry odor sample is 27'000. Hovever, typical odor concentrations measured for foundry emissions reported in the literature range between 200 and 6'000 ou_E/m^3.[19,43,84,85] This means that, in practice, the a-priori application of a minimum dilution factor of 27'000 would make the olfactometric analysis of foundry emissions impossible. Because of the practical inapplicability of this simple, but apparently too precautionary approach, previous to olfactometric analysis, it is essential to evaluate the potential hazardousness of the samples to be analyzed to the panel involved, on a case-by-case basis. In the case of
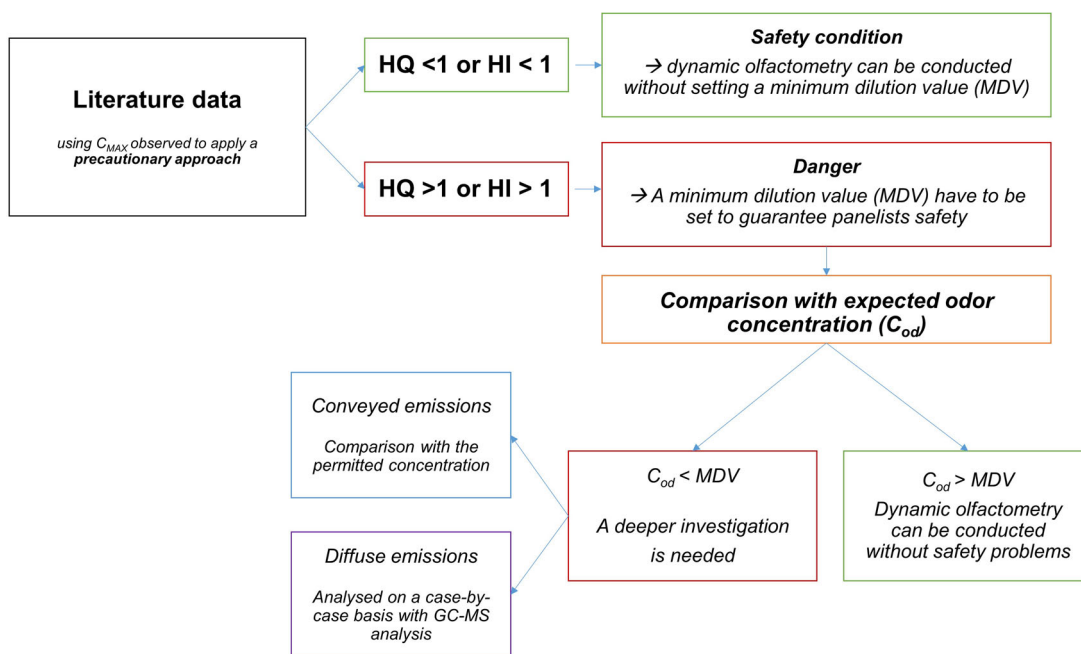
Figure 6. Schematization of the decision tree to evaluate the minimum dilution value to be applied during olfactometric analysis to guarantee panelists safety.

Table 4. Comparison between OT and TWA values for the most critical compounds.

Compound	TLV (ACGIH)		OT [ppm] Min	Reference OT
	TWA [ppm]	STEL [ppm]		
Ammonia	25	35	1.5	[75]
Benzene	**0.5**	**2.5**	**2.7**	[75]
Formaldehyde	**0.1**	**0.3**	**0.5**	[75]
Hydrogen sulfide	1	5	0.00041	[75]
Phenol	5	N.D.	0.0056	[75]
Sulfur dioxide	**N.D.**	**0.25**	**0.87**	[75]
Toluene	20	N.D.	0.33	[75]
Triethylamine	1	3	0.53	[76]

conveyed emissions, often an emission limit value for total VOCs is established by the authorities. In such cases, a preliminary evaluation can be based referring to those authorized limits in order to estimate the maximum concentration of pollutants potentially present in the odor sample. The limit values reported in the authorization, in particular for benzene which has been found to be the most critical compound, can be compared with the occupational exposure limits by following the toxicological assessment reported. If using the maximum authorized concentration, the HQ value is lower than 1, it can be assumed that, in the absence of malfunctions, the safety of the panel is guaranteed. However, in the case of odor evaluations, samples are often collected where no concentration limits for VOCs are applied (or applicable), as for instance at the inlet of abatement system or in diffuse emissions.

In such cases, for which there is no authorized limit, the sample must be analyzed on a case-by-case basis, by applying chemical analysis, in particular gas chromatography coupled with mass spectrometry (GC-MS). Indeed, analyzing odorous samples with GC-MS, it is possible to obtain information on the chemical composition, in terms of quantification and indentification of the pollutants present. From these data, a precise toxicological assessment can be

conducted to evaluate the minimum dilution value to be adopted to protect the health of the panelists involved in the olfactometric analysis. The added value of the investigation proposed in this paper is that, by identifying the compounds that are most worthy of attention in foundry emissions, it limits the amount of compounds resulting from a chromatogram for which a precise quantification is needed.

To summarize the whole process, a decision tree for assessing the minimum dilution value to be applied during olfactometric analysis to protect the health of the panel is shown in Figure 6.

Conclusion

Foundries represent an important industrial source of odorous pollutants and, frequently, their odorous emissions generate complaints correlated with the potential toxicological implications of these emissions. For this reason, it is important to investigate the chemical composition of foundry gaseous emissions, in terms of identification and quantification of pollutants. The aim of this paper was the investigation of the scientific literature involving the chemical characterization of gaseous emissions from foundries, in order to evaluate the potential toxicological non-carcinogenic risk for workers involved in olfactomeric analysis, who are directly exposed to these pollutants during the analysis. addition, this paper wants to suggest a critical process to correlate the toxicological parameters (TLV and HQ index) with the OT values, in order to establish the dangerousness of odorous gaseous emissions from industrial plants. These considerations are particularly useful considering the particular type of exposure panelists are subjected to during their work. In this case, in fact, no adaptation or olfactory fatigue is observed, as commonly occurs in working areas. In this case, however, repeated inhalation of the same odor can cause olfactory fatigue,[86] which results in a

reduction in the ability to detect the odor and the ability to perceive the odor can no longer be used as a warming signal.[87] Thus, a critical literature review and an extensive elaboration of data and comparison between TLV and OT values was conducted, with the aim to define and evaluate the panelists' exposure risk to toxic odorous compounds. Based on our evaluations, it is possible to state that the great majority of VOCs emitted by foundries have reported maximum concentrations lower than their TLV-TWA values, thus making that their HQ is lower than 1. This is not the case for 8 pollutants (ammonia, benzene, formaldehyde, hydrogen sulfide, phenol, sulfur dioxide, toluene and trimethylamine) for which their HQ is higher than 1, thus meaning that the maximum concentration reported in the literature has the potential to produce a toxicological effect. A further investigation on these compounds was performed in order to verify if the compound can be perceived by the human nose before reaching a toxic concentration. This investigation showed that ammonia, hydrogen sulfide, phenol, toluene and trimethylamine, despite potentially reaching toxic concentrations in foundry emissions, produce a characteristic smell that is perceived before the compound becomes dangerous, thus protecting the exposed person. On the other hand, the most critical compounds among those investigated are benzene, formaldehyde and sulfur dioxide: not only their HQ is >1, but they are not perceived by the human sense of smell at toxic concentrations, thus making them particularly worthy of attention. Benzene, in particular, is the most critical compound due to the high concentrations observed in the literature. Therefore, from this elaboration, to guarantee panelists' safety during the olfactometric analyses, the minimum dilution value to be set is 27'000. However, the value obtained is not applicable when compared to the average odor concentrations measured for foundrie emissions. For this reason, chemical analysis by GC-MS has to be carried out on odor samples before they are analyzed by means of dynamic olfactometry, in order to assess the minimum dilution value to be adopted to guarantee the safety of the panelists involved.

Declaration of interests

The authors declare no conflict of interest.

Funding

ORCID

Elisa Polvara http://orcid.org/0000-0002-6252-2854
Laura Maria Teresa Capelli http://orcid.org/0000-0003-0002-3619
Selena Sironi http://orcid.org/0000-0002-9680-6847

References

[1] Nicell, J. A. Assessment and Regulation of Odour Impacts. Atmos. Environ. 2009, 43, 196–206. DOI: 10.1016/j.atmosenv. 2008.09.033.

[2] Sironi, S.; Capelli, L.; Céntola, P.; Del Rosso, R.; Il Grande, M. Odour Emission Factors for Assessment and Prediction of Italian MSW Landfills Odour Impact. Atmos. Environ. 2005, 39, 5387–5394. DOI: 10.1016/j.atmosenv.2005.05.023.

[3] Ying, D.; Chuanyu, C.; Bin, H.; Yueen, X.; Xuejuan, Z.; Yingxu, C.; Weixiang, W. Characterization and Control of Odorous Gases at a Landfill Site: A Case Study in Hangzhou, China. Waste Manage. 2012, 32, 317–326. DOI: 10.1016/j.wasman. 2011.07.016.

[4] Dincer, F.; Odabasi, M.; Muezzinoglu, A. Chemical Characterization of Odorous Gases at a Landfill Site by Gas Chromatography-Mass Spectrometry. J. Chromatogr. A 2006, 1122, 222–229. DOI: 10.1016/j.chroma.2006.04.075.

[5] Capelli, L.; Sironi, S.; Del Rosso, R.; Guillot, J. M. Measuring Odours in the Environment vs. Dispersion Modelling: A Review. Atmos. Environ. 2013, 79, 731–743. DOI: 10.1016/j. atmosenv.2013.07.029.

[6] Capelli, L.; Sironi, S.; Del Rosso, R.; Céntola, P.; Il Grande, M. A Comparative and Critical Evaluation of Odour Assessment Methods on a Landfill Site. Atmos. Environ. 2008, 42, 7050–7058. DOI: 10.1016/j.atmosenv.2008.06.009.

[7] Harrison, E. Z.; Oakes, S. R. Investigation of Alleged Health Incidents Associated with Land Application of Sewage Sludges. New Solut. 2002, 12, 387–408. DOI: 10.2190/0FJ0-T6HJ-08EM-HWW8.

[8] Shusterman, D. Critical Review: The Health Significance of Environmental Odor Pollution. Arch. Environ. Health. 1992, 47, 76–87. DOI: 10.1080/00039896.1992.9935948.

[9] Adams, G.; Witherspoon, J. Identifying and Controlling Odor in the Municipal Wastewater Environment Phase 1: Literature Search and Review. Water Intell., 2015, 3, 9781780404103. DOI: 10.2166/9781780404103.

[10] Rappert, S.; Müller, R. Odor Compounds in Waste Gas Emissions from Agricultural Operations and Food Industries. Waste Manage. 2005, 25, 887–907. DOI: 10.1016/j.wasman. 2005.07.008.

[11] Brambilla, M.; Navarotto, P. Sensorial Analysis of Pig Barns Odour Emissions. Chem. Eng. Trans. 2010, 23, 243–248.

[12] Gostelow, P.; Parsons, S. A.; Stuetz, R. M. Odour Measurements for Sewage Treatment Works. Water Res. 2001, 35, 579–597. DOI: 10.1016/S0043-1354(00)00313-4.

[13] Van Harreveld, A. P. From Odorant Formation to Odour Nuisance: New Definitions for Discussing a Complex Process. Water Sci. Technol. 2001, 44, 9–15. DOI: 10.2166/wst.2001. 0498.

[14] Dinçer, F.; Dinçer, F. K.; Sarı, D.; Ceylan, Ö.; Ercan, Ö. Dispersion Modeling and Air Quality Measurements to Evaluate the Odor Impact of a Wastewater Treatment Plant in İzmir. Atmos. Pollut. Res. 2020, 11, 2119–2125. DOI: 10.1016/j. apr.2020.05.018.

[15] Hayes, J. E.; Stevenson, R. J.; Stuetz, R. M. The Impact of Malodour on Communities: A Review of Assessment Techniques. Sci. Total Environ. 2014, 500–501, 395–407. DOI: 10.1016/j.scitotenv.2014.09.003.

[16] Henshaw, P.; Nicell, J.; Sikdar, A. Sikdar, A. Parameters for the Assessment of Odour Impacts on Communities. Atmos. Environ. 2006, 40, 1016–1029. DOI: 10.1016/j.atmosenv.2005.11. 014.

[17] Pare, A.; Kumar Modi, Y.; Vardhan Rai, H. Environmental Impact Comparison of Binder Systems for Sand Moulding Process Using Cradle-to-Grave Approach. In IOP Conference Series: Materials Science and Engineering, 2018; Vol. 377.

[18] Goudzwaard, J.; Kurtti, C.; Cannon, J. H. A. F. S.; Voigt, R.; Furness, J. E. F. J. C.; Sipple, D. Foundry Emissions Effects with an Advanced Oxidation Blackwater System. Trans. Am. Foundry Soc. 2003, 111, 1191–1211.

[19] Sluis, N. I.; Vossen, F. J. H. Odour Assessment at an Iron Foundry in The Netherlands. In Proceedings of the 3rd International Water Association Conference on Odours and VOCs, Barcelona, Spain, 2008.

[20] Tapola, M. M.; Sara Hihnala, M. *Odour and Hazardous Emission Abatement of Foundries*; **2014**.

[21] Fatta, D.; Marneri, M.; Papadopoulos, A.; Savvides, C.; Mentzis, A.; Nikolaides, L.; Loizidou, M. Industrial Pollution and Control Measures for a Foundry in Cyprus. *J. Clean. Prod.* **2004**, *12*, 29–36. DOI: 10.1016/S0959-6526(02)00180-4.

[22] Brancher, M.; Schauberger, G.; Franco, D.; Melo Lisboa, D. H. Odour Impact Criteria in South American Regulations. *Chem. Eng. Trans.* **2016**, *54*, 169–174.

[23] Diaz, C. I. C.; Capelli, L.; Arias, R.; Salas Seoane, R. A. N. *Analysis of Existing Regulation in Odour Pollution, Odour Impact Criteria 1*. D-NOSES, H2020-SwafS-23-2017-789315, **2019**.

[24] Lisboa, H.; de, M.; Sivret, E.; Stuetz, R. M. Odour Regulations-Experiences from Australia. *Chem. Eng. Trans.* **2014**, *40*, 181–186.

[25] McGinley, M. A.; St, P.; McGinley, C. M.; Chateau Laurier, F. Developing a Credible Odor Monitoring Program. In *Presentation at the 2004 ASAE/CSAE Annual International Meeting Sponsored by ASAE/CSAE*, **2004**.

[26] Bax, C.; Sironi, S.; Capelli, L. How Can Odors Be Measured? An Overview of Methods and Their Applications. *Atmosphere (Basel)* **2020**, *11*, 92. DOI: 10.3390/atmos11010092.

[27] Héroux, M.; Pagé, T.; Gélinas, C.; Guy, C. Evaluating Odour Impacts from a Landfilling and Composting Site: Involving Citizens in the Monitoring. *Water Sci. Technol.* **2004**, *50*, 131–137. DOI: 10.2166/wst.2004.0242.

[28] EN 13725:2003. *Ambient Air - Determination of Odour Concentration by Dynamic Olfactometry*; CEN, Ed.; **2003**.

[29] PrEN 13725:**2019**.

[30] Davoli, E.; Gangai, M. L.; Morselli, L.; Tonelli, D. Characterisation of Odorants Emissions from Landfills by SPME and GC/MS. *Chemosphere* **2003**, *51*, 357–368. DOI: 10.1016/S0045-6535(02)00845-7.

[31] Nie, E.; Zheng, G.; Ma, C. Characterization of Odorous Pollution and Health Risk Assessment of Volatile Organic Compound Emissions in Swine Facilities. *Atmos. Environ.* **2020**, 223.

[32] Roveda, L.; Polvara, E.; Invernizzi, M.; Capelli, L.; Sironi, S. Definition of an Emission Factor for VOC Emitted from Italian and European Refineries. *Atmosphere (Basel)* **2020**, *11*, 564. DOI: 10.3390/atmos11060564.

[33] Invernizzi, M.; Ilare, J.; Capelli, L.; Sironi, S. Proposal of a Method for Evaluating Odour Emissions from Refinery Storage Tanks. *Chem. Eng. Trans.* **2018**, *68*, 49–54.

[34] American Industrial Hygiene Association. *Odor Thresholds for Chemicals with Established Occupational Health Standards*, Amer Industrial Hygiene Assn, **1989**.

[35] Davoli, E.; Zuccato, E.; Bianchi, G.; Palmiotto, M.; Il Grande, M.; Bonati, S.; Rossi, A. N. Dynamic Olfactometry and Potential Sample Toxicity. Guidelines for a Safe Occupational Health Approach. *Chem. Eng. Trans.* **2012**, *30*, 7-12.

[36] Davoli, E.; Zuccato, E.; Bianchi, G.; Il Grande, M.; Bonati, S.; Rossi, A. N.; Porporato, C.; Pereno, M.; Soldati, S. Dynamic Olfactometry and Sample Toxicity. A Case Study for a MSW Incinerator Odour Assessment Project. *Chem. Eng. Trans.* **2016**, *54*, 13–18.

[37] CAEF. *The European Foundry Association 2018 - Annual Statistics and National Reports*, **2018**.

[38] World Foundry Organization (WFO). *Global Foundry Report 2018 Actual Situation of the Worldwide Casting Industry World Foundry Organization*, **2018**.

[39] European Commision. *Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Smitheries and Foundries Industry*, **2005**.

[40] Evironmental Proctection Agency. *Profile of the Metal Casting Industry*, **1997**.

[41] Tsai, J. H.; Lin, K. H.; Chen, C. Y.; Lai, N.; Ma, S. Y.; Chiang, H. L. Volatile Organic Compound Constituents from an Integrated Iron and Steel Facility. *J. Hazard. Mater.* **2008**, *157*, 569–578. DOI: 10.1016/j.jhazmat.2008.01.022.

[42] Emissions Measurement Team Casting Emission Reduction Program. *Foundry Process Emission Factors: Baseline Emissions from Automotive Foundries in Mexico Emissions Measurement Team Casting Emission Reduction Program*, **1999**.

[43] Sironi, S.; Corelli, G. *La Riduzione Delle Emissioni a Bassa Soglia Olfattiva Originate Dai Processi Di Fonderia Molestie Olfattive*, **2018**.

[44] Weber, H. J. Air Pollution Problems of the Foundry Industry. *J. Air Pollut. Control Assoc.* **1961**, *11*, 157–172. DOI: 10.1080/00022470.1961.10467985.

[45] Fore, S.; Mbohwa, C. T. Cleaner Production for Environmental Conscious Manufacturing in the Foundry Industry. *J. Eng. Des. Tech.* **2010**, *8*, 314–333. DOI: 10.1108/17260531011086180.

[46] Energetics Incorporated. *Energy and Environmental Profile of the U.S. Metalcasting Industry Energetics*, Incorporated, **1999**.

[47] World Bank Group. *Pollution Prevention and Abatement Handbook - Foundries*, World Bank, **1998**.

[48] Rao, M. N.; Rao, H. V. N. *Air Pollution*; McGraw-Hill Education: New York; **1989**.

[49] Kmita, A.; Fischer, C.; Hodor, K.; Holtzer, M.; Roczniak, A. Thermal Decomposition of Foundry Resins: A Determination of Organic Products by Thermogravimetry–Gas Chromatography–Mass Spectrometry (TG–GC–MS). *Arab. J. Chem.* **2018**, *11*, 380–387. DOI: 10.1016/j.arabjc.2016.11.003.

[50] Staples, E.; Zeiger, K. *On-Site Measurement of VOCs and Odors from Metal Casting Operations Using an Ultra-Fast Gas Chromatograph*, **2006**.

[51] Tossavainen, A. Metal Fumes in Foundries. *Scand. J. Work. Environ. Health* **1976**, *2*, 42–49. DOI: 10.5271/sjweh.2833.

[52] Zakaria, A. Evaluation of Occupational Hazards in Foundries. *J. Egypt Public Health Assoc.* **2005**, *80*, 434-462.

[53] Tiedje, N.; Crepaz, R.; Eggert, T.; Bey, N. Emission of Organic Compounds from Mould and Core Binders Used for Casting Iron, Aluminium and Bronze in Sand Moulds. *J. Environ. Sci. Health Part A* **2010**, *45*, 1866–1876. DOI: 10.1080/10934529.2010.520595.

[54] Faber, J.; Perszewska, K. Identification Odor Compounds Emitted during the Heating of Molding Sands. *Arch. Foundry Eng.* **2017**, *17*, 178–182. DOI: 10.1515/afe-2017-0071.

[55] Wang, Y.; Cannon, F. S.; Salama, M.; Goudzwaard, J.; Furness, J. C. Characterization of Hydrocarbon Emissions from Green Sand Foundry Core Binders by Analytical Pyrolysis. *Environ. Sci. Technol.* **2007**, *41*, 7922–7927. DOI: 10.1021/es071657o.

[56] Siewiorek, A.; Nowak, R.; Chojecki, A.; Mocek, J. Gas Evolution Rate from Heated Moulding Sands Bonded with Organic Binders. *Arch. Foundry Eng.* **2011**, 11, 87–92.

[57] Loch, J.; Grabowska, B.; Kaczmarska, K. BTEX Emissions from BioCo2 from Bonded Moulding Sands. *Metall. Foundry Eng.* **2013**, *39*, 25–31.

[58] IPCC. *Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry*, **2001**, Vol. 1.

[59] Bates, C. E.; Scott, W. D. Decomposition of Resin Binders and the Relationship between Gases Formed and the Casting Surface Quality - 2. Gray Iron. *Trans. Am. Foundrymen's Soc.* **1977**, *84*, 2019.

[60] Wang, Y.; Huang, H.; Cannon, F. S.; Voigt, R. C.; Komarneni, S.; Furness, J. C. Evaluation of Volatile Hydrocarbon Emission Characteristics of Carbonaceous Additives in Green Sand Foundries. *Environ. Sci. Technol.* **2007**, *41*, 2957–2963. DOI: 10.1021/es0628295.

[61] Zhou, X.; Yang, J.; Qu, G. Study on Synthesis and Properties of Modified Starch Binder for Foundry. *J. Mater. Process. Technol.* **2007**, *183*, 407–411. DOI: 10.1016/j.jmatprotec.2006.11.001.

[62] Kaczmarska, K.; Bobrowski, A.; Żymankowska-Kumon, S.; Grabowska, B. Studies on the Gases Emission under High Temperature Condition from Moulding Sands Bonded by Modified Starch CMS-Na. *Arch. Foundry Eng.* **2017**, *17*, 79–82. DOI: 10.1515/afe-2017-0014.

[63] Yang, H. H.; Lai, S. O.; Hsieh, L.; Te; Hsueh, H. J.; Chi, T. W. Profiles of PAH Emission from Steel and Iron Industries. *Chemosphere* **2002**, *48*, 1061–1074. DOI: 10.1016/s0045-6535(02)00175-3.

[64] Liu, H. H.; Yang, H. H.; Chou, C.; Da; Lin, M. H.; Chen, H. L. Risk Assessment of Gaseous/Particulate Phase PAH Exposure in Foundry Industry. *J. Hazard. Mater.* **2010**, *181*, 105–111. DOI: 10.1016/j.jhazmat.2010.04.097.

[65] Yang, H. H.; Lee, W. J.; Chen, S. J.; Lai, S. O. PAH Emission from Various Industrial Stacks. *J. Hazard. Mater.* **1998**, *60*, 159–174. DOI: 10.1016/S0304-3894(98)00089-2.

[66] Holtzer, M.; Dańko, R.; Kmita, A. Influence of a Reclaimed Sand Addition to Moulding Sand with Furan Resin on Its Impact on the Environment. *Water Air Soil Pollut.* **2016**, *227*, 16. DOI: 10.1007/s11270-015-2707-9.

[67] Holtzer, M.; Dańko, R.; Kmita, A.; Bobrowski, A.; Żymankowska-Kumon, S. Assessment of Harmfulness of Phenolic Resins Hardened by CO 2 in an Aspect of Emission of Substances from BTEX and PAH Groups. *Arch. Foundry Eng.* **2013**, *13*, 39–43.

[68] Knecht, U.; Elliehausen, H. J.; Woitowitz, H. J. Gaseous and Adsorbed PAH in an Iron Foundry. *Br. J. Ind. Med.* **1986**, *43*, 834–838. DOI: 10.1136/oem.43.12.834.

[69] Abedghars, M. T.; Hadji, A.; Bouhouch, S. Monotoring of Air Quality in an Iron Foundry (Case of NOx, SO2, Benzene and Dust). *J. Mater. Environ. Sci.* **2011**, *2*, 501–506.

[70] Bobrowski, A.; Żymankowska-Kumon, S.; Drożyński, D.; Grabowska, B.; Kaczmarska, K. TG/DTG/DTA, FTIR and GC/MS Studies of Oil Sand for Artistic and Precision Foundry with the Emission of Gases Assessment. *Arch. Foundry Eng.* **2017**, *17*, 25–30. DOI: 10.1515/afe-2017-0125.

[71] Acharya, S. G.; Vadher, J. A.; Kanjariya, P. V. Identification and Quantification of Gases Releasing from Furan No Bake Binder. *Arch. Foundry Eng.* **2016**, *16*, 5–10. DOI: 10.1515/afe-2016-0039.

[72] Epa, U. S. *Reference Guide to Odor Thresholds for Hazardous Air Pollutants Listed in the Clean Air Act Amendments of 1990*; U.S. Environmental Protection Agency: Washington, DC, **1992**, 100.

[73] Abraham, M. H.; Sá Nchez-Moreno, R.; Cometto-Muñ Iz, J. E.; Cain, W. S. An Algorithm for 353 Odor Detection Thresholds in Humans. *Chem. Senses.* **2012**, *37*, 207–218. DOI: 10.1093/chemse/bjr094.

[74] Leonardos, G.; Kendall, D.; Barnard, N. Odor Threshold Determinations of 53 Odorant Chemicals. *J. Air Pollut. Control Assoc.* **1969**, *19*, 91–95. DOI: 10.1080/00022470.1969.10466465.

[75] Nagata, Y. Measurement of Odor Threshold by Triangle Odor Bag Method. *Odor Meas. Rev* **2003**, 118–127.

[76] van Gemert, L. J. *Flavour Thresholds: Compilations of Flavour Threshold Values in Air, Water and Other Media*; Oliemans Punter & Partners BV: Zeist, The Netherlands, **2011**.

[77] Murnane, S. S.; Lehocky, A. H.; Owens, P. D. *Odor Thresholds for Chemicals with Established Occupational Health Standards*, American Industrial Hygiene Association, Virginia, **2016**.

[78] ACGIH®. *ACGIH® Threshold Limit Values (TLVs®) and Biological Exposure Indices (BEIs®)*, **2020**.

[79] Palmiotto, M.; Fattore, E.; Paiano, V.; Celeste, G.; Colombo, A.; Davoli, E. Influence of a Municipal Solid Waste Landfill in the Surrounding Environment: Toxicological Risk and Odor Nuisance Effects. *Environ. Int.* **2014**, *68*, 16–24. DOI: 10.1016/j.envint.2014.03.004.

[80] USA EPA. *Reference Dose (RfD): Description and Use in Health Risk Assessments*, **1988**, Vol. 8.

[81] Barnes, D. G.; Dourson, M.; Dourson, M.; Preuss, P.; Barnes, D. G.; Bellin, J.; Derosa, C.; Engler, R.; Erdreich, L.; Farber, T. Reference Dose (RfD): Description and Use in Health Risk Assessments. *Regul. Toxicol. Pharmacol.* **1988**, *8*, 471–486. DOI: 10.1016/0273-2300(88)90047-5.

[82] Chaiklieng, Suggaravetsiri, Autrup, Risk Assessment on Benzene Exposure among Gasoline Station Workers. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2545. DOI: 10.3390/ijerph16142545.

[83] ACGIH. *ACGIH - Association Advancing Occupational and Environmental Health.* https://www.acgih.org/.

[84] Szklarczyk, M.; Zwoździak, J.; Sówka, I. Industrial Sources of Odour Emissions. In *Contemporary Problems of Odours*; WNT: Warsaw, **2010**; pp 54–84.

[85] Sówka, I.; Miller, U.; Karski, L. Analysis of Legal and Technical Solutions in Terms of Odours in Poland. *Environ. Prot. Eng* **2019**, *45*, 127–138.

[86] Greenberg, M. I.; Curtis, J. A.; Vearrier, D. The Perception of Odor is Not a Surrogate Marker for Chemical Exposure: A Review of Factors Influencing Human Odor Perception. *Clin. Toxicol.* **2013**, *51*, 70–76. DOI: 10.3109/15563650.2013.767908.

[87] Paustenbach, D. J.; Gaffney, S. H. The Role of Odor and Irritation, as Well as Risk Perception, in the Setting of Occupational Exposure Limits. *Int. Arch. Occup. Environ. Health.* **2006**, *79*, 339–342. DOI: 10.1007/s00420-005-0021-3.