ABSTRACT

The aim of this work is the evaluation and the analysis of the different chemical-physical variables that affect the emission of volatile organic compounds (VOC) and odours from passive liquid area sources inside a wind tunnel, which is typically used for emission sampling. Three different compounds (acetone, butanol and ethanol), having different volatilization properties (e.g., boiling point, solubility), were studied in solution with water at different concentrations. The following physical parameters affecting the VOC volatilization in the Wind Tunnel system were evaluated: the velocity of the air flowing through the device, in a range from 0.01 to about 0.05 m/s, and the temperature of both the liquid source and the sweep air flow, in a range from 12°C to 42°C. The experimental results were compared with the existing volatilization models available in literature. In most cases the proposed theoretical model predicts well the experimentally measured concentration. Some discrepancies were observed for lower velocities and also by moving from the room temperature (20° C); and those were discussed by making some considerations about the volatilization phenomenon. Moreover, the study clearly shows that it is not the gas phase temperature that controls the emission, but the temperature of the liquid phase, due to the effect of the latter on the vapour pressure of the compound, which is the main driving force of the phenomenon.

1. INTRODUCTION

The establishment or enlargement of residential areas close to industrial sites has caused the growth of a new air quality issue, that is odour pollution (Yuwono and Lammers, 2004). It has been demonstrated that even at very low concentrations people can detect the presence of malodourous volatile organic compounds (VOC) (Laska and Hudson, 1991; Leonardos et al., 1969) , which may in some cases cause negative effects on their well-being (Hayes et al., 2017; Schiffman et al., 1995; Van Harreveld, 2001).

Therefore, in recent years, different European governments have issued new regulations related to odour emissions and olfactory discomfort. Big efforts have been made especially in the standardization of methods for the objective quantification of odour emissions. The European Norm 13725:2003, which standardizes the measurement of the so called “odour concentration” by dynamic olfactometry, also gives some indications about the sampling methods to be adopted for the different types of odour sources. For passive liquid area sources, such as wastewater treatment tanks, which represent in a lot of cases an important source of odour pollution and complaints, odour emission assessment is very difficult and – up to now - there is still no straight-forward nor established sampling procedure (Capelli et al., 2013). The methods that are most commonly applied for odour emission assessment on passive area sources are the so called “hood methods”, whereby a sort of enclosure is placed on the emission surface and air is blown through it to simulate the wind action over the monitored surface (Beghi et al., 2012; Bliss et al., 1995; Capelli et al., 2009; Gostelow et al., 2003; Hudson and Ayoko, 2008). Among “hood methods”, Wind Tunnels (WT) are widely used in many countries (Bliss et al., 1995; Ryden and Lockyer, 1985; Smith and Watts, 1994). In such systems, a sweep air flow parallel to the emitting surface is applied (Capelli et al., 2013, 2009; Frechen et al., 2004; Parker et al., 2010). With Wind Tunnels, the assessment of the odour emission rate (OER) involves three phases: on-site sampling (Capelli et al., 2009; Koziel et al., 2005), sample analysis (CEN, 2003) and data elaboration. Data elaboration is necessary in order to evaluate the Specific Odour Emission Rate (SOER), expressed in odour units emitted from the source per surface and time unit [$ou/m^2/s$], from the odour concentration that is the direct outcome of the olfactometric measurement. Moreover, for the purpose of emission assessment, the SOER must be referred to the neutral sweep air flow rate used during sampling (Capelli et al., 2009).

While researchers have analysed and modelled the volatilization of different VOC in the open field (Kawamura and Mackay, 1987; Sutton, 1934), these models cannot be applied as such to evaluate odour emissions. Environmental odours typically are complex mixtures with unknown composition, comprising hundreds of compounds having different physical and chemical properties, often in aqueous solution, and thus different volatilization behaviours. This is the reason why, for odour emission assessment purposes, experimental data shall be retrieved case by case for source characterization, giving that field sampling becomes a crucial issue. However, the literature about the volatilization inside the WT is very poor. Hudson and Ayoko, 2008 have highlighted that there are many different parameters having a strong influence on this phenomenon, such as WT geometry and dimensions, nature of VOC, temperature, and air velocity.

The aim of this work is to investigate the major factors affecting the volatilization of VOC from liquid area sources and analyse their effect in order to develop an effective model to describe volatilization inside the hood.

1.1. STATE-OF-THE-ART: WIND TUNNEL VOLATILIZATION MODELS

Different models exist in literature for describing liquid-gas mass transfer. A recent paper by (Prata A.A. et al., 2018) presents an extensive review of models for the mass transfer coefficients both on the gas and liquid phase. However, up to now, no general model has been proposed accounting for all the different situations that might take place inside the Wind Tunnel and affect the volatilization phenomenon. The models available in literature are sometimes scarcely reliable and affected by strong approximations. Below, two models are reported, which are the most representative for the case under investigation and were therefore considered for this study.

1.1.1. Model for single flat emissive surface (modified)

Lucernoni et al., 2017 developed the following model to describe volatilization of pure compounds inside the Wind Tunnel system. It is based on the Prandtl boundary layer theory (Incropera and DeWitt, 2002), according to the hypothesis that mass transfer under forced convection over a single flat emissive surface in laminar regime can properly approximate the conditions inside the Wind Tunnel.

The main contributors for the mass transfer is due to the gas motion just above the emitting surface, instead of the chemical diffusion. Therefore, in order to compute the coefficient for convective mass transfer, it is possible to use the correlation for the mass transfer from a single flat emitting surface:

$$K_{c,ave} = 0.664 \left(\frac{D_{i,air}^{4}}{L_{WT}{}^{3}\nu}\right)^{\frac{1}{6}} u_{WT}^{1/2} \qquad (1)$$

Where: $D_{i,air}$ is the compound molecular diffusivity in air in [m^2/s]; L_{WT} is the length of the WT central body in [m]; v is the air kinematic viscosity in [m^2/s]; u_{WT} is the air velocity inside the hood in [m/s].

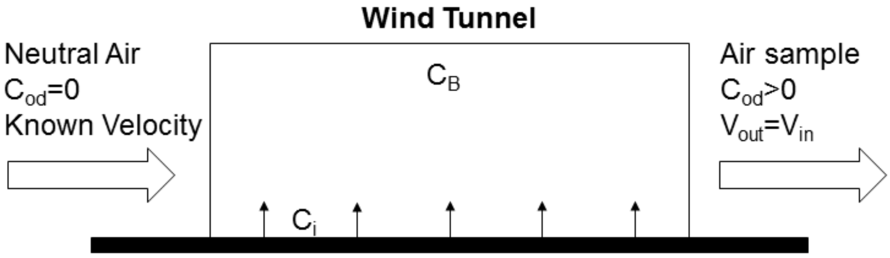

Figure 1. Simplified scheme for the wind tunnel system, according to the model of Lucernoni et al. (2017) [1 column fitting image]

The following step involves the mass balance on the system, between the inlet and the outlet of the WT:

$$Q \cdot C_{out} = Q \cdot C_{in} + K_{c,ave} \cdot (C_i - C_B)A \quad (2)$$

Where: Q is the neutral air flow rate blown in the WT in [m^3/s]; C_{out} is the compound concentration at the outlet in [mol/m^3]; C_{in} is the compound concentration at the inlet in [mol/m^3], that is null if neutral air is used; $K_{c,ave}$ is the convective mass transfer coefficient averaged over the exchange length, in [m/s]; A is the base area of the WT in [m^2].According to Lucernoni et al. (2017), it is the diffusion in the gas-film close to the interface (boundary layer) that affects the exchange rate. Thus, the gas-liquid interface concentration of the compound C_i in [mol/m^3] coincides with the concentration in the gas side of the gas-liquid interface, and is computed as follows:

$$C_i = \frac{P_{sat}(T_{liq})}{R * T_{liq}} \quad (3)$$

Where: $P_{sat}(T_{liq})$ is the vapour pressure of the compound, computed at the liquid temperature [Pa]; R is the universal gas constant equal to 8.314 [J/mol/K]; T_{liq} is the temperature of the liquid phase [K].

In this case, we didn't consider the classical single flat plate model, for which C_B, i.e. the compound concentration in the bulk of the gas phase inside the hood in [mol/m^3], is equal to the inlet concentration (in this case equal to zero since neutral air is used). A slight modification to this classical model was introduced in order to account for the particular geometry studied, thus making the same assumptions as in Lucernoni et al. (2017), who used the same kind of sampling hood. For this reason, according to Lucernoni et al. (2017), C_B, can be assumed equal to 50% of the outlet concentration, thus considering it as the average between inlet and outlet concentrations with a 0 inlet concentration:.

$$C_{out} = \frac{K_{c,ave} C_i \, A}{\left(Q + \frac{K_{c,ave} \, A}{2}\right)} \quad (4)$$

1.1.2.The two-film model

Parker et al. (2010) proposed a model for liquid mixtures, which was verified experimentally, and which takes into account two different factors that may affect the volatilization of compounds from liquid area sources: the air velocity and the Henry constant (strongly influenced by temperature). Several researchers have used the conventional two-film model for their studies on mass transport (Bianchi and Varney, 1997; Liss and Slater, 1974; Whitman, 1962).

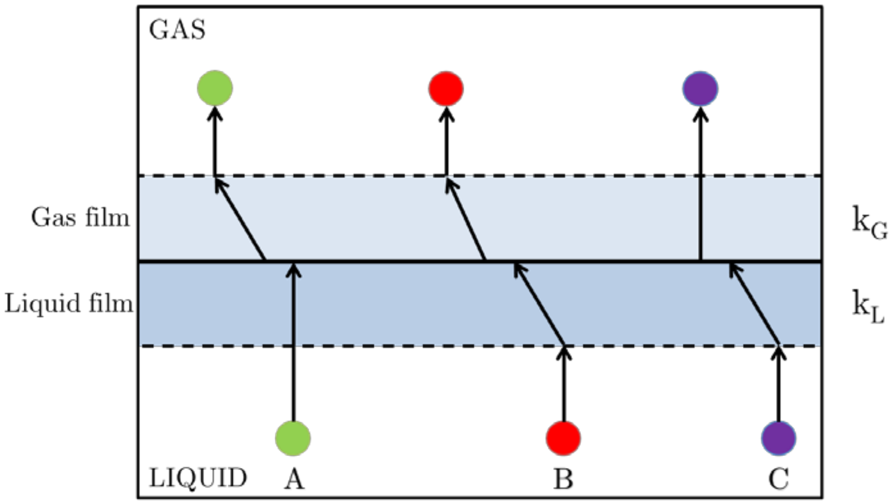

Figure 2. Conceptual scheme for the two-film model, representing the path of a gas-phase controlled molecule (A), an intermediate molecule (B) and a liquid-film controlled molecule (C). [1 column fitting image]

At the basis of this model there is the assumption that a VOC molecule moving from the liquid phase to the gas phase must pass through two different films: i.e. the liquid film and the gas film. Some molecules can experience a stronger resistance in one of the two films or even in both of them, as illustrated in Figure 2:

- Gas phase controlled molecules have a stronger resistance to the transport while passing through the gas film, and they follow the path of molecule A in the figure.
- Liquid phase controlled compounds face a major resistance in the liquid film and conceptually they follow the path of molecule C.
- The compounds that are neither gas phase controlled nor liquid phase controlled follow the path of molecule B.

The volatilization flux according to this model can be written as follows:

$$J = k_L\,(C_L - C_L^*) = k_G(C_G^* - C_G) \quad (5)$$

where J is the flux [kg/m^2/s], k_L is the liquid-film transfer coefficient [m/s], k_G is the gas-film transfer coefficient [m/s], C_L is the VOC concentration in the liquid phase [kg/m^3], C_G is the VOC concentration in the vapour phase [kg/m^3], C_L* is the VOC concentration in the liquid side of gas-liquid interface [kg/m^3], and C_G* is the VOC concentration in the gas side of gas-liquid interface [kg/m^3].

1.2. General models for volatilization inside Wind Tunnels

As previously mentioned, different models exist in literature for describing liquid-gas mass transfer (Prata A.A. et al., 2018) ; however, models accounting for the effect of the different variables evaluated in this study are limited in literature. Furthermore, there are fewer studies regarding the behaviour of aqueous solutions of volatile compounds compared to pure compounds.

However, several researchers have highlighted the importance of temperature and humidity in volatilization processes. Montes et al., 2010; Parker et al., 2010; Raimundo et al., 2014 analysed the evaporation of water inside a WT system by changing the operating conditions inside it (i.e. temperature, relative humidity and velocity of the sweep air flow); they elaborated their data to evaluate the evaporating flux from the tank and then compared it with different expressions available in literature. At the end, they also developed their own equation for the evaporating flux, which includes the different factors they had evaluated in their trial. Even if their study regarded a pure compound (water), it is very interesting, since they were able to develop a first equation accounting for all the parameters that were investigated also in our study, giving that it can be considered as an initial step for further developments in this field. In the present study, the influence of the humidity of the sweep air flow rate was not analysed: this because the aim here is to study the influence of the emission of organic compound in solution and not a pure water emission.

2. MATERIALS AND METHODS

2.1. Theoretical model

In this study we investigated the emission mechanism inside the wind tunnel. In this case, it was decided to evaluate the emission from an aqueous solution to have a situation much more similar to the real emitting situations, like in WWTPs.

Differently from the pure compound configuration, studied by (Lucernoni et al., 2017), in this case two different films affecting the transport phenomena shall be considered: the liquid film and the gas film, as illustrated for the case of molecule B in Figure 2.

Eq. 5 can still be assumed as valid, considering that the hypothesis of steady state mass transfer at the interface is still applicable. Since the measure of the concentration at the two side of the interface is not possible, equilibrium across the interface is assumed, giving that C_G^* and C_L^* lie on the equilibrium curve, and:

$$C_G^* = f(C_L^*) \quad (6)$$

To describe the rate of interface transport there are two different ways. The former is to use Equation 5 and 6 to calculate the interface concentration and then use the single phase mass transfer coefficients (k_G and k_L). The latter, and more used in literature (Bird, 2002; Thibodeaux and Mackay, 2010), is to introduce overall mass transfer coefficients by introducing equilibrium concentrations as:

$$J = K_L\left(C_L - C_L^{eq}\right) = K_G\left(C_G^{eq} - C_G\right) \quad (7)$$

Where C_L^{eq} is a liquid concentration in equilibrium with the bulk vapour concentration C_G (i.e., $C_L^{eq} = f(C_G)$), C_G^{eq} is a vapour concentration in equilibrium with the bulk liquid concentration C_L (i.e., $C_G^{eq} = f(C_L)$), while K_L and K_G are the overall mass transfer coefficients, which will be clarified later.

The main advantage of Equation 7 is that it is function of experimentally evaluable concentrations, i.e., C_G and C_L.

In the following part of the discussion it was decided to use the relation relevant to the liquid mass transfer:

$$J = K_L\,(C_L - f(C_G)) \quad (8)$$

The values for the mass transport coefficients for the two films are computed by means of equations recovered from literature. It is important to highlight that, for the liquid film the correlation is independent from the air velocity. This is only true in the case of static situations, in which the air flow does not induce movement on the liquid surface. For situations in which the fluid elements close to the surface are moving or in which the surface is not properly “quiescent”, because of the generation of waves due to the wind action, different models should be adopted (Prata et al., 2017).

On the other hand, for gas phase controlled compounds, there is a strong dependence from this factor, since the volatilization is mainly connected to forced convection.

For the gas film side, the considerations made by Lucernoni et al. (2017) are still valid. So, to evaluate the gas film coefficient, the following equation can be established, derived from Eq. (1):

$$k_G = 0.664\left(\frac{D_{i,air}^4}{{L_{WT}}^3\,\nu}\right)^{\frac{1}{6}} u_{WT}^{1/2} \quad (9)$$

Where k_G [m/s], is the gas film coefficient considered for the theoretical model of this work.

On the other side, for the liquid side exchange coefficient, for completely static liquid configurations, the Higbie penetration theory should be used (Cussler, 2009). In this case the transport coefficient for the liquid phase should be evaluated with the following equation:

$$k_L = \frac{2}{\sqrt{\pi}}\left(\frac{D_{i,H_2O}}{t_s}\right)^{\frac{1}{2}} \quad (10)$$

Where k_L [m/s] is the mass transfer coefficient for the liquid film, $D_{i,\ H2O}$ [m^2/s] is the diffusion coefficient of the compound in water, t_s is the sampling time [s].

By using the approach of Equation 7 and considering negligible the contribution of Poynting correction, by working at atmospheric pressure, the relation among C_G and C_L^{eq} can be evaluated through the Raoult's modified law (Carroll, 1991):

$$C_G = \frac{P_i°(T)\cdot\gamma_i}{RTC_L^{TOT}} C_L^{eq} \qquad (11)$$

Where $P_i°(T)$ [Pa] is the vapour pressure of the solute in the experimental conditions, R is the gas constant [J/mol K], T [K] the temperature, γ_i [-] the activity coefficient of the compound in solution, and C_L^{TOT} the liquid total molar concentration [mol/m^3].

Of course, for diluted solutions it is not trivial to consider the Henry's Law as representative of the equilibrium situation, which is the approach more frequently found in literature. Eq. (12) reports the definition of Henry's constant (Smith et al., 2007):

$$H_i = \lim_{x_i \to 0} \frac{f_i}{x_i} \quad (12)$$

Where f_i [-] and x_i [-] are the fugacity and the mole fraction of the solute in water. By means of this equation, it is easy to understand that the Henry's law is valid when the fraction of the organic compound is close to zero, i.e. in the case of diluted solutions.

In these case, the following equation can be adopted, and considering the volatilization formula (Sander, 2015), Eq. (13) could be used:

$$C_G^{eq} = K_H^{cc} \cdot C_L^{eq} \qquad (13)$$

where K_H^{CC} is the dimensionless Henry's law constant, defined as:

$$K_H^{cc} = \frac{1}{H^{cp}\cdot RT} \quad (14)$$

Where H^{cp} [mol/m^{3}Pa] is the solubility Henry's constant, R is the gas constant, T [K] the temperature (for more detail about Henry's law and constants see Sander, 2015).

The Henry's law constant is fundamental for example in Parker's work (Parker et al., 2010), since it is the major discriminant for the classification of the different compounds: for K_H^{CC} values lower than 1x10^{-3} the main resistance to transport is located in the gas film (gas phase controlled); if K_H^{CC} is higher than 1x10^{-1} the compounds are liquid phase controlled; for intermediate values, both of the phases have a strong influence on the volatilization process (Hudson and Ayoko, 2008). In the same paper, Parker enlists a series of the main VOC with their values of the dimensionless Henry constant and divides them into the three different categories.

To compare the experimental results of our trials with the theoretical model, the mole fraction of 0.1 was stated as limit between the two equilibrium models: if the mole fraction of the compound in solution was smaller than 0.1, Henry's law (Eq. (13)) was used, even though the Raoult's modified law is always valid along the whole range of mole fractions. Otherwise, if mole fraction was greater than 0.1, Raoult's modified law was preferred (Eq. (11)). The numerical values of these parameters were obtained in different ways: Henry's constants were taken from the most recent results reported in Sander (2015); for the evaluation of the activity coefficients the free available online AIOMFAC model (Zuend et al., 2011) was used.

Despite the different thermodynamical model used to describe equilibrium, by rearranging with few calculus passages and considering the ideal gas law, it is possible to identify a unique equation to describe the equilibrium at the interface as:

$$C_G^{eq} = \Lambda_{eq} \cdot C_L^{eq} \quad (15)$$

Where Λ_{eq} [-] is the equilibrium constant deriving from Eq. (11) or Eq. (13) for each situation.

Through this correlation, it is possible to evaluate the overall mass flux and the relative coefficient:

$$J = K_L \left(C_L - \frac{C_G}{\Lambda_{eq}} \right) \quad (16)$$

$$K_L = \frac{k_L k_G \Lambda_{eq}}{k_G \Lambda_{eq} + k_L} \qquad (17)$$

Where J is the specific flux [kg/m^2/s], K_L [m/s] is the overall mass transfer coefficient, C_L and C_G [mol/m^3] are the concentrations of the VOC respectively in the bulk liquid and bulk vapour phase and Λ_{eq} [-] the equilibrium constant.

By knowing the volatilization flux contribution, and considering the wind tunnel configuration as reported in Figure 1, it is then possible to write the mass balance for the hood:

$$Q \cdot C_{out} = Q \cdot C_{in} + K_L \cdot \left(C_L - \frac{C_G}{\Lambda_{eq}}\right) A \qquad (18)$$

Where Q [m^3/s] is the neutral air flow rate blown in the WT, C_{out} and C_{in} [mol/m^3] are respectively the compound concentrations at the outlet and at the inlet of the hood, K_L [m/s] is the global mass transfer coefficient, which can be calculated by Eq. (17), C_L and C_G [mol/m^3] are the concentrations of the compound respectively in the bulk liquid and bulk gas phase, Λ_{eq} [-] the equilibrium constant, and A [m^2] is the base area of the WT.

As previously mentioned, for the evaluation of the concentration in the bulk phase the same assumptions as in Lucernoni et al. (2017) were made: due to the specific geometry of the wind tunnel considered, the bulk concentration was set equal to the average between inlet and outlet concentrations, with C_{in}=0. (C_G=C_{out}/2). By this assumption, the outlet concentration can be evaluated as:

$$C_{out} = \frac{K_L \cdot A \cdot C_L}{Q_{out} + \frac{K_L \cdot A}{2\Lambda_{eq}}} \qquad (19)$$

This theoretical model was used for comparison with all the experimental results obtained in the laboratory tests.

2.2. **Experimental setup**

The WT used for this work was designed and developed by the Olfactometric Laboratory at Politecnico di Milano. The structure of the hood is described in detail by Capelli et al. (2009), and is schematically illustrated in Figure 3. It is the same WT used by Lucernoni in his work (2017). The central body has a 25x50 cm base section and is 8 cm high. The hood has an open bottom to be placed over the emissive surface. It has two converging sections at the extremes, connected to the inlet and outlet. The WT is made of PVC and can be equipped with floating parts that allow sampling on liquid sources.

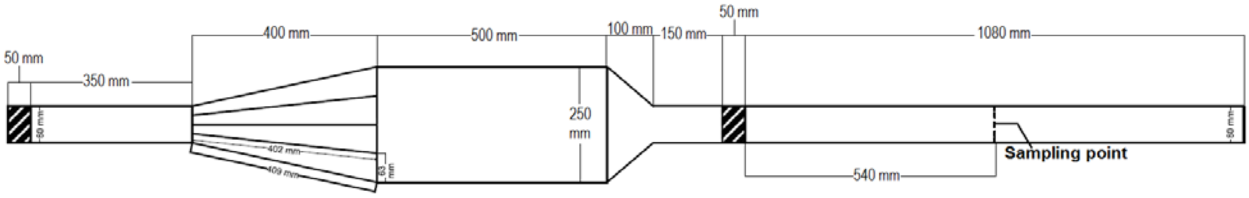

Figure 3. Wind tunnel scheme. [1 column fitting image]

In order to better understand the volatilization phenomenon in the WT, it was decided to perform a set of experiments with different compounds, in diluted solution with water (e.g. acetone, ethanol and n-butanol).

The compounds were chosen due to their high volatility and possibility to be detected by a GC-FID. Details about the analytic method are reported in the Supplementary Material (SM1).

For the tests, a small polyethylene tank exactly fitting the WT central body, filled with the liquid, with a depth of 5 cm, was placed under the hood. Three sets of different experiments were performed, whereby for each set of experiments a different parameter was evaluated (velocity, and temperature). The neutral air was flushed through the chamber at different velocities, ranging from 0.01 to 0.05 m/s. In order to have a uniform and reliable collection of the gaseous sample at the outlet, a PET tube, equipped with a sampling port, was connected to the outlet of the WT. The sample was collected by means of a Nalophan® bag and a sampling vacuum pump (Capelli et al., 2009). The analysis of the sample was performed by means of a GC-FID, in order to determine the outlet concentration.

In the case of tests sets at different temperatures, the solution and the air flow were cooled down or warmed up according to the temperature required for each test. To modify the temperature of the air, the inlet air tube was put in a temperature-controlled bath before entering in the wind tunnel. For the liquid phase, the solutions were warmed/cooled before the start, and then keep constant for the duration of the trials. The temperatures tested ranged from 12°C to 42°C.

3. RESULTS AND DISCUSSION

3.1. Influence of velocity on volatilization at room temperature

In this section, the results obtained in the experiments with dry air (RH<3.8%) are shown. For all the experiments, the theoretical curve of concentration at the wind tunnel outlet was drawn as a function of the air velocity inside the wind tunnel, by representing both the model proposed here (dashed line), compared with the obtained experimental evaluation.

All the samplings were repeated, in order to evaluate the repeatability of the obtained data: the black dots on the graphs report each experimental result. The ordinate reports the outlet concentrations obtained for different sweep air velocity values, which in turn are reported on the abscissa. The different coloured lines represent the theoretical model trends considering the two approaches used to describe the interface equilibrium: the yellow one corresponds to the model based on the Raoult's modified law, whereas the red one is relevant to the model based on the Henry's law, as discussed in paragraph 2.1. The Henry's law trends are reported only when the molar fraction of the compound is below 0.1.

This paragraph addresses the results of experiments in which the room temperature was maintained at around 20°C. The top of Figure 4 reports the results for the ethanol solutions, at a concentration of 50 mL/L_{H2O} and 500 mL/L_{H2O}, in the middle the results for the n-butanol solutions, respectively at 5 mL/L_{H2O} and 50 mL/L_{H2O} and in the bottom part the acetone solution trends, with three different concentration of liquid solution, i.e. 50 mL/L_{H2O}, 250 mL/L_{H2O} and 500 $mL/L_{H2O.}$

The different concentrations used for n-butanol compared to the other compounds were chosen in order to work below the solubility limit of the compound.

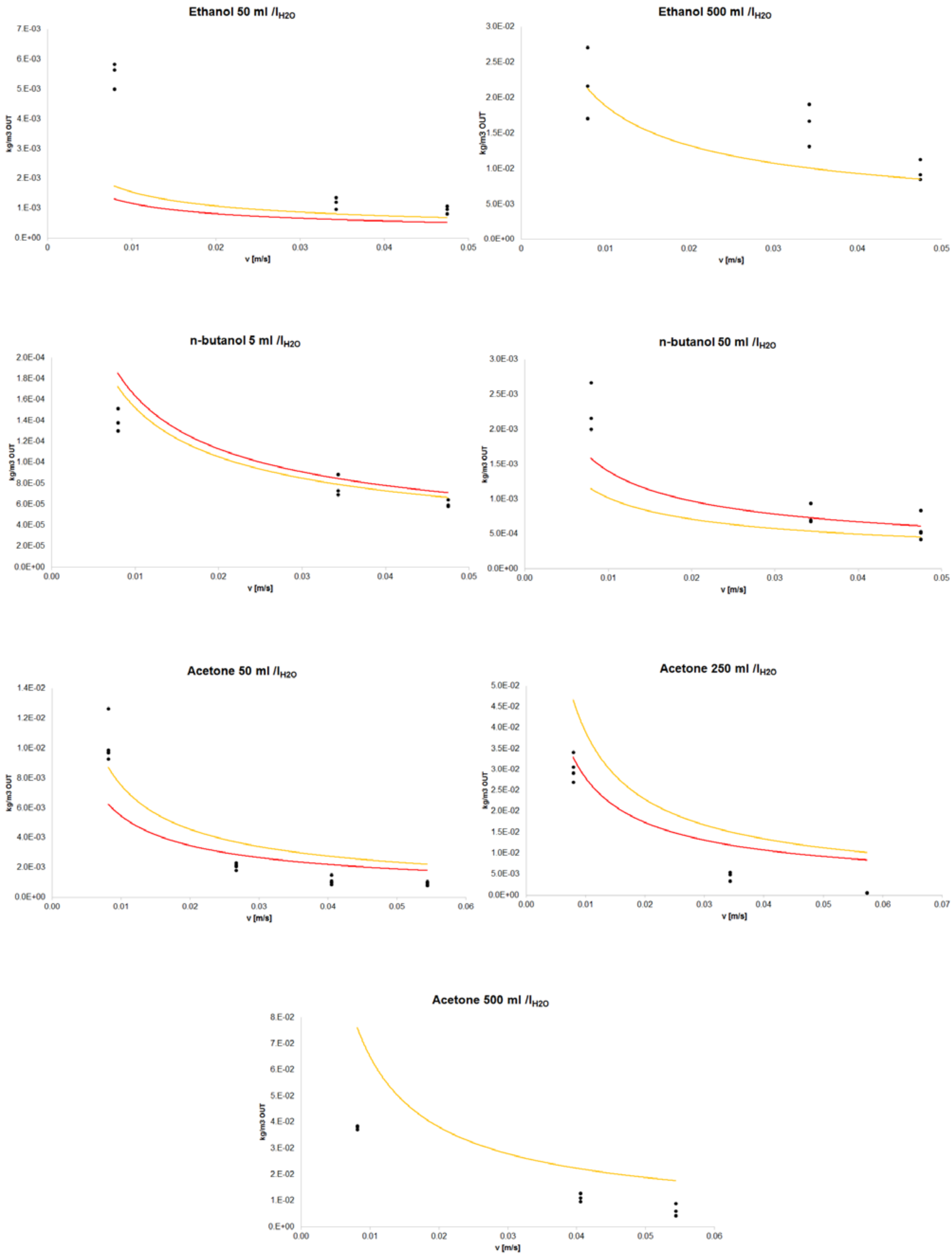
Ethanol 50 ml /l$_{H2O}$
Ethanol 500 ml /l$_{H2O}$
n-butanol 5 ml /l$_{H2O}$
n-butanol 50 ml /l$_{H2O}$
Acetone 50 ml /l$_{H2O}$
Acetone 250 ml /l$_{H2O}$
Acetone 500 ml /l$_{H2O}$
kg/m3 OUT
v [m/s]

Figure 4. Outlet concentration in the case of an aqueous solution of different compounds at room temperature. The yellow line represents the results of the theoretical model based on Raoult's modified law, the red one the model based on Henry's law evaluated only for the diluted solutions. The dots represents every measured concentration.. [2 column fitting image]

In Parker's work, two of the used compounds were classified as "gas phase controlled" (ethanol and n-buthanol), while acetone is reported as partially gas phase controlled, meaning that the emission is a function of the velocity of the gas phase. The first studies reporting this dependence in wind tunnels are those of Jiang et al. (1995), who operated their wind tunnel at high sweep air velocities causing turbulent conditions inside the hood. An improvement to this was proposed by Frechen et al. (2004), who first argued the necessity to operate wind tunnels at low speeds (laminar conditions), in order to prevent from excessive dilution of the sampled flow.

The trends obtained here – using laminar conditions as in Frechen et al. (2004) - show this dependence, thus being in agreement with the above mentioned studies.

However, it was impossible to find a unique correlation among concentration and velocity like in previous studies on pure liquids (Lucernoni et al., 2017). This could be explained by the fact that the present work was carried out using aqueous solutions instead of pure compounds. This entails diffusive limitations also on the liquid side (and not only in the gas side as it is the case for pure compounds): the air flow over the liquid surface causes the evaporation of the volatile compound at the interface, thus reducing the driving force for emission. For this reason, not only the transfer coefficient in the gas phase can be accounted for the explanation of the phenomenon, but also the transfer coefficient in the liquid phase shall be considered, thus giving that the model becomes more complex as it was the case considered by Lucernoni et al. (2017).

Further comparison with other more recent literature works is hardly done because, as previously mentioned, studies dealing specifically with this problem, i.e. the dependence of the emission of aqueous solutions of organic compounds inside wind tunnels from sweep air flow and temperature, are limited.

Generally speaking, it is possible to observe a good correlation between experimental data and theoretical model (a better representation for the comparison of the agreement between experimental data and model is given in Figure SM2). The more important differences can be found in the lowest velocities where the forced flow condition is less defined, while for the other sweep air conditions the accordance is quite good.

3.2. **Influence of velocity on volatilization at different temperatures**

In order to investigate the influence of different physical parameters on volatilization, similar tests were conducted by changing the temperature of the whole system. To do this, both of the two contacted fluids were modified, either by heating them or by cooling them. The temperature of the system was varied between 12 and 42 °C.

Figure 5 reports the experimental results of this test set. As in the previous case, all samplings were repeated to increase the reliability of the data. The black dots indicate the experimental results, while the coloured lines represent the trends of the theoretical models considered in Par. 2.1. In this case the trials were conducted only for acetone at two different concentrations (50 mL/L_{H2O} and 500 mL/L_{H2O}) and n-butanol (50 mL/L_{H2O}). The temperature of the experimental system is reported over each graph.

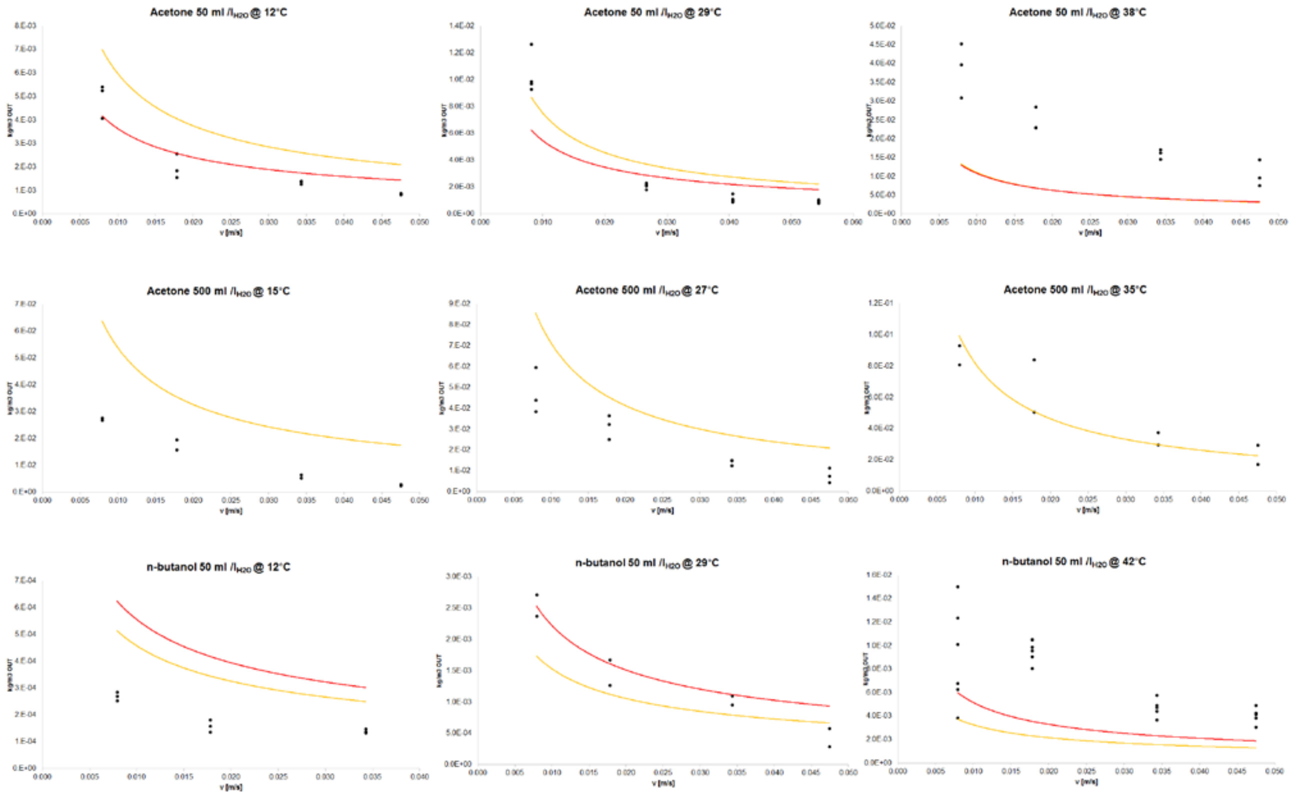

Figure 5. Outlet concentration in the case of an aqueous solution of different compounds. In this case the system once has been cooled and twice as been warmed. The yellow line represents the results of the theoretical model based Raoult's modified law, the red one the model based on Henry's law, and the dots are the measured concentrations .[2 column fitting image]

Also in these experiments, conducted at different temperatures, the laboratory results are in agreement with the trends of the considered theoretical model (also in this case, a better representation for the comparison of the agreement between experimental data and model is given is Figure SM3). A little deviation from the theoretical results is observed at the temperatures that are more distant from 20 °C. In particular, the theoretical model overestimates the experimental results at low temperatures, while it underestimates the trends at high temperature. This behaviour is observed both for acetone and butanol solutions. This might also be partially connected to an increased experimental error when operating at temperatures that are far from the room temperature and thus more difficult to be maintained with precision. Further investigations are needed to confirm this assumption.

3.3. **Comparison of the effect of temperature and sweep air velocity**

To compare the influence of the sweep air flow rate and the effect of the temperature on the emission, all the trials referred to the same solution have been plotted in the same graph. Figure 6 reports the experimental results for the solutions of acetone at 50 ml /l_{H2O}, acetone at 500 ml /l_{H2O} and n-butanol 50 at ml/L_{H2O}, respectively, at the different temperatures investigated.

Due to the evidence of the strong dependence of the emission on the temperature of the system, a further investigation was carried out in order to verify the temperature of which side of the interface (i.e. liquid or gas) has a stronger influence on the release.

In order to obtain this information, experiments were conducted using different temperatures for the liquid and for the sweep air flow. For the diluted acetone (50 ml/L_{H2O}) two different tests were conducted: one with a liquid temperature of 12°C and an inlet air temperature of 27°C, and a second one with a liquid temperature of 43°C and an inlet air temperature of 12°C. For the solution of n-butanolat 50 ml/L_{H2O}, a liquid temperature of 12°C and an inlet air temperature of 28°C were tested, and then a liquid temperature of 38°C and an inlet air temperature of 12°C. All these experimental results are reported in Figure 6.

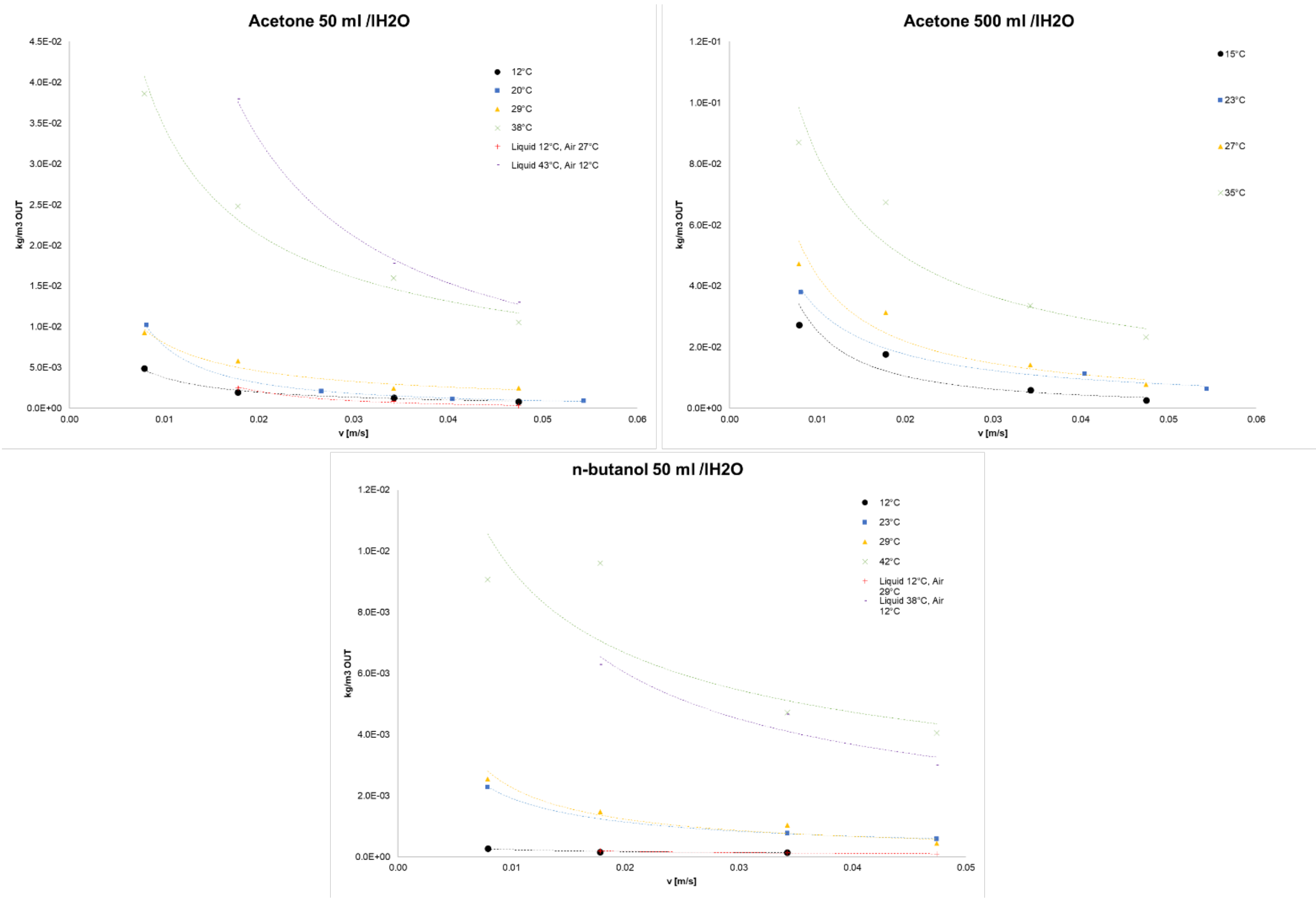

Figure 6. Experimental outlet concentrations for the solutions of acetone at 50 and 500 ml per litre and n-butanol at 50 ml per litre of water, at different temperatures and sweep air velocities. [2 column fitting image]

Based on these results, the very strong dependence of the emitted concentration on the temperature is evident: the higher the system temperature, the higher the quantity emitted. The emission is less dependent from the sweep air flow rate at lower temperatures, while this dependence becomes stronger at high temperatures.

This observation is presumably connected to the trend of the vapour pressure, which grows exponentially with temperature. Therefore, even a small increase of the temperature results in a significant increase in the vapour pressure, giving that the quantity of “available” organic compound on the gas-side of the interface, which can be stripped away by the sweep air flow, is significantly increased.

From the results, it is also clear that the temperature of the liquid phase controls the emission and not the gas phase temperature. This is also linked to the vapour pressure of the compound, which is the main driving force of the phenomenon: the vapour pressure depends on the liquid temperature, and the sweep air flow, due to its small heat capacity, cannot produce a significant change in the liquid film temperature. For these reasons, at the interface, where chemical and thermic equilibrium was assumed, the liquid side appears to control the temperature.

4. CONCLUSIONS

This work evaluates the effect of different variables on the emission of volatile organic compounds from liquid area sources. The experiments were conducted using a wind tunnel as sampling hood. A theoretical model to predict the outlet concentration of the air flow passing over the solution surface is also presented.

Different organic compounds were used and mixed at different concentrations. In most cases the proposed theoretical model predicts well the experimentally measured concentration. However, some discrepancies were observed for lower velocities, where the forced flow condition is less defined. Also by moving from room temperature (20° C), the theoretical model tends to overestimate the experimental results at low temperatures, while it underestimates the trends at high temperatures.

The effect of the temperature, both of the liquid solution and of the air, was investigated. The temperature of the liquid significantly affects the interface evaporation and consequently the outlet concentrations, while the air temperature plays a negligible role. The dependence of the outlet concentration values on temperature is proven to be the same as for the interface concentration, thus proving the great importance of the latter on the overall phenomenon.

Based on these findings, it is clear that during wind tunnel sampling the liquid temperature of the area source should be taken into consideration, besides the chamber design and the sweep air flow rate. This fact should be taken into account also in the legislations and norms about odour sampling. Neglecting the liquid temperature variations could lead to big mistakes in the experimental assessment of VOC or odour emissions from WWTPs.

Further studies are certainly needed to better understand the effect of humidity on the atmospheric emission of different compounds from liquid solutions. In order to give an exhaustive overview, it would also be interesting to investigate the behaviour to volatilization of substances having different properties (e.g., very low solubility in water) from the ones here considered.

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