Title: ASSESSING ODOR EMISSIONS FROM LIQUID AREA SOURCES

Article Type: Research Paper

Keywords: Specific Emission Rate; Olfactometry; Liquid Pools; Passive Area Sources; Volatilization Phenomena; Wind Tunnel.

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Abstract: Waste Water Treatment Plants are known to have significant emissions of several pollutants from the different treatment phases. Among such pollutants, volatile organic and inorganic compounds, often having low odour detection thresholds, cause odour nuisance to the population. One of the purposes of the present work is to determine which are the more suitable methodologies to assess the odour emissions from liquid passive area sources, by means of a thorough study of the models capable of describing the volatilization phenomena of the odoriferous compounds from such sources. Several different models were evaluated for the open field emission, selecting the most appropriate one. Moreover, the models describing volatilization under a forced convection regime inside a wind tunnel device have been investigated, in order to describe the situation inside this sampling device, typically used for sampling on liquid sources. By means of experimental tests involving pure liquid acetone and pure liquid butanone, it was verified that the model more suitable to describe precisely the volatilization inside the sampling hood is the model for the emission from a single flat plate in forced convection and laminar regime, with a fluid dynamic boundary layer fully developed and a developing mass transfer boundary layer. The proportionality coefficient for the model was re-evaluated in order to account for the specific characteristics of the adopted wind tunnel device. Due to the differences between the fluid dynamic conditions in the open field and inside the hood, it was deemed useful to devise a correlation that - according to the flush rate adopted inside the chamber - is capable of computing the wind velocity at a 10 m height that would cause the same emission flux that is estimated from the analysis of the sample collected with the wind tunnel. Finally, the field of application was clearly defined for the considered models during the project, discussing the two different kinds of compounds commonly found in emissive liquid pools or liquid spills, i.e. gas phase controlled and liquid phase controlled compounds.
Assessing Odour Emissions from Liquid Area Sources
Federico Lucernoni, Laura Capelli, Valentina Busini, Selena Sironi

Our work discusses a methodology for the determination of emission rates of pollutants like VOCs and odours from liquid area sources like waste water treatment plant tanks. The method entails sampling on the (simulated) liquid source with a Wind Tunnel device, calculating the Specific Emission Rate (SER) and finally rescaling the SER in order to be representative of the real conditions, outside the device, in the open field.

In the research, laboratory experiments were performed adopting a Wind Tunnel and a simulated liquid pool, investigating the emissions of two VOCs, acetone and butanone. We study a particular kind of sampling device, a Wind Tunnel, for field applications on liquid passive area sources, such as waste water treatment tanks. The present research is part of the ongoing effort in different parts of the world aimed to gaining a better understanding of how the hood devices work, what happens exactly inside them during sampling and how to use the obtained data in order to be able to obtain meaningful conclusions and insights concerning the problem of emissions assessment from area sources. Such problems are addressed and discussed also in other papers recently published on Atmospheric Environment (Parker et al., 2013).

The main results of the present study are highlighted, discussing how the proposed procedure for rescaling the emission rate to the open field scenario can be really useful, especially for atmospheric dispersion modelling purposes.

As novelty of this work and its contributions to the field of liquid surfaces emissions assessment and pollutants dispersion modelling, please consider our paper “Assessing Odour Emissions from Liquid Area Sources” for publication on Atmospheric Environment Journal.

We hope this paper will be of interest for the readers of the journal.

Best regards,

Federico Lucernoni and Laura Capelli
Highlights for the article “Assessing Odour Emissions from Liquid Area Sources”:

- Liquid area surfaces are significant sources of odours and VOCs emissions.
- Lawmakers concur that the emissions should be monitored.
- There are no widely accepted methodologies for emissions assessment.
- The paper tries to provide a method for evaluating liquid sources.
- The procedure entails also the recalculation of the emission in the field.
ASSESSING ODOUR EMISSIONS FROM LIQUID AREA SOURCES

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ABSTRACT

Waste Water Treatment Plants are known to have significant emissions of several pollutants from the different treatment phases. Among such pollutants, volatile organic and inorganic compounds, often having low odour detection thresholds, cause odour nuisance to the population. One of the purposes of the present work is to determine which are the more suitable methodologies to assess the odour emissions from liquid passive area sources, by means of a thorough study of the models capable of describing the volatilization phenomena of the odoriferous compounds from such sources. Several different models were evaluated for the open field emission, selecting the most appropriate one. Moreover, the models describing volatilization under a forced convection regime inside a wind tunnel device have been investigated, in order to describe the situation inside this sampling device, typically used for sampling on liquid sources. By means of experimental tests involving pure liquid acetone and pure liquid butanone, it was verified that the model more suitable to describe precisely the volatilization inside the sampling hood is the model for the emission from a single flat plate in forced convection and laminar regime, with a fluid
dynamic boundary layer fully developed and a developing mass transfer boundary layer. The proportionality coefficient for the model was re-evaluated in order to account for the specific characteristics of the adopted wind tunnel device. Due to the differences between the fluid dynamic conditions in the open field and inside the hood, it was deemed useful to devise a correlation that – according to the flush rate adopted inside the chamber – is capable of computing the wind velocity at a 10 m height that would cause the same emission flux that is estimated from the analysis of the sample collected with the wind tunnel.

Finally, the field of application was clearly defined for the considered models during the project, discussing the two different kinds of compounds commonly found in emissive liquid pools or liquid spills, i.e. gas phase controlled and liquid phase controlled compounds.

**Keywords:** Specific Emission Rate; Olfactometry; Liquid Pools; Passive Area Sources; Volatilization Phenomena; Wind Tunnel.

1. **INTRODUCTION**

Waste Water Treatment Plants (WWTP) are known to have significant emissions of several pollutants from the different treatment phases (Capelli et al., 2009a; Prata Jr. et al., 2016a; Santos et al., 2012). Among them, volatile organic and inorganic compounds, often having low odour detection thresholds, are typically a cause of odour nuisance to the near-living population (Capelli et al., 2009a; Parker et al., 2013; Prata Jr. et al., 2016a). Whereas point source, such as stacks (Bockreis and Steinberg, 2005; Capelli et al., 2013) are typically subject to periodical emission monitoring, this is not the case for area sources, such as WWTP tanks, which, however, often represent the main source of VOCs and odour emissions in this kind of plants (Capelli et al., 2008; 2009a). For this reason, area sources should be considered as well as point sources for odour emission characterization and impact assessment, as already provided by some regulations on the matter (D.g.r. n. IX/3018, 2012; VDI 3880, 2011). However, assessing odour emissions from area sources
such as wastewater treatment tanks, i.e. the so-called “passive” area sources, which means without outward flow, is typically a rather complicated task, since there is no straightforward nor established procedure (Capelli et al., 2013). First of all, already choosing the most appropriate technology for sampling is difficult among the different ones that have been proposed and are currently applied for this scope (Muezzinoglu, 2003; Blunden and Aneja, 2008; Beghi et al., 2012; Rumsey et al., 2012; Hentz et al., 2013; Hudson and Ayoko, 2008; Bliss et al., 1995; Kim and Park, 2008). In recent studies there is evidence that so-called “hood methods”, entailing an enclosure of some sort (e.g., wind tunnels), whereby emission rates are derived from the data regarding the concentration at the outlet of the sampling device combined with the dimensions of the device and the operating conditions, should be preferred for this purpose (Hudson and Ayoko, 2008; Capelli et al., 2013). There are different types of dynamic hoods, mainly distinguished between Flux Chambers (FC) (Klenbusch, 1986; Prata Jr. et al., 2016a) and Wind Tunnels (WT) (Smith and Watts, 1994; Jiang et al., 1995; Capelli et al., 2009b; Parker et al., 2010), the latter being considered for this study. With hood methods, the assessment of the odour emission rate (OER) involves 3 phases: on-site sampling (Capelli et al., 2009b; Koziel et al., 2005; Sironi et al., 2014a), sample analysis (CEN EN 13725, 2003) and data elaboration (Lucernoni et al., 2016; Ranzato et al., 2012). With the odour concentration it is possible to evaluate the Specific Odour Emission Rate (SOER), that is the odour units emitted from the source per surface and time unit [ou/m²/s] referred to the neutral sweep air flow rate used during sampling (Capelli et al., 2009b).

The main problem is that emission rates, calculated as above-mentioned (Capelli et al., 2013), refer solely to the specific sampling conditions inside the hood, and therefore are not representative of the effective emissions from the source in the open field when subject to natural ventilation (Hudson and Ayoko, 2009; Leyris et al., 2005). In order to evaluate the SOER occurring in the open field at different wind conditions, it is necessary to scale the value obtained for the hood to the real situation, thereby adopting a suitable correlation. While sampling and analysis methodologies are fairly established (analysis more than sampling, as previously discussed), the elaboration of the datum is still an open issue. The studies of Sohn et al. (2005) and Sironi et al. (2014b) propose to use a correlation for the re-calculation of the SOER for the open
field based on the Prandtl’s boundary layer theory for laminar flow, assuming a proportionality of the SOER measured at the sampling conditions (i.e. sweep air velocity) and the SOER at the actual wind speed with the square root of the ratio between actual wind speed and sweep air velocity:

\[ \text{SER}_{\text{field}} = \text{SER}_{\text{WT}} \left( \frac{U_{10}}{U_{\text{WT}}} \right)^{0.5} \]  

(1)

The adoption of a dependence with the square root of the air velocity – typical of the laminar flow – does not account for the fact that in real situations the flow above a liquid area surface is typically turbulent (Sutton, 1934). Moreover, this approach clearly entails a big approximation of the real situation, since by relating the actual wind speed – conventionally measured at a height of 10 m above ground – with the sweep air speed inside the wind tunnel, on one hand it is assumed that the wind profile is constant with the height, which is typically not the case, the wind profile can be described by means of specific mathematical relationships (Bonan, 2005; Cook, 1997; Drew et al., 2013; Tieleman, 2008), and on the other hand it doesn’t consider the difference between open-field conditions and forced convection inside an enclosure (WT). For these reasons, this work aims to investigate a suitable model to relate the datum obtained from the WT to the real situation. For this purpose, a suitable model based on Prandtl’s boundary layer theory accounting for the volatilization inside the hood (Perry, 1997; Incropera et al., 2007) was experimentally verified and then related to a model describing the volatilization in the open field, thereby referring to the semi-empirical models existing for the estimation of emissions from liquid pools as a function of the wind speed. This relationship allowed to establish a new correlation for the recalculation of the SOER to the actual wind speed in the open field, thereby discussing reliability and field of application of this new proposed model.

2. MATERIALS AND METHODS

2.1. The Wind Tunnel device

The WT adopted 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. (2009b) and is depicted in Fig. 1 and 2. The central body has a 25x50 cm base section and is 8 cm high. The hood is open at the bottom and
is laid on top of the emissive surface. The body has two converging sections at the extremes, connected to
the inlet and outlet of the chamber that can be closed with specific fittings allowing to feed the neutral air
at the inlet and collect the sample at the outlet. The WT is made of PVC and is equipped with buoyant parts
that allow sampling on liquid sources.

Figure 1: The LabOlf Wind Tunnel

Figure 2: The Wind Tunnel scheme

2.2. Volatilization model for the open field

In the scientific literature there are several models that have been proposed in order to describe the
volatilization phenomena of chemical compounds from liquid pools in the open field. Such models, typically
developed in the field of industrial safety, for the most part rely on the theory developed by Sutton (1934).
Sutton for his research (1934) considered a pool of a pure liquid volatile compound, subject to the wind
action in the open field and he evaluated the dependence of the emission rate on the major factors that
can influence the phenomenon. The resulting correlation can be expressed as:

\[ SER = K U_h^{0.78} a^{0.89} x_0^{-0.11} \]  \hspace{1cm} (2)

Where: \( SER \) is the Specific Emission Rate; \( K \) is the proportionality constant; \( U_h \) is the wind speed at the
considered height; \( a \) is a constant depending on the physical characteristics of the atmosphere; \( x_0 \) is the
characteristic dimension of the pool in the leeward direction.
Relying on Sutton’s dissertation (1934), several later studies have been able to determine semi-empirically the constant terms \( K \) and \( \alpha \) (Kawamura and MacKay, 1987; Committee for the Prevention of Disasters, 1992). The values of these two parameters are usually what distinguish one model from the other. Among the variety of this kind of models, here the one adopted in the text “Methods for the calculation of physical effects” (Committee for the Prevention of Disasters, 1992) is considered because it has been validated by many authors and with different sets of data (Pasquill, 1943; Clancey 1974; Jeulink, 1983; MacKay and Matsugu, 1973). According to this model the emission in the open field can be expressed as:

\[
SER = 0.002 \ U_{10}^{0.78} X^{-0.11} \ M_i \ \frac{P_v(T_{pool})}{R T_{pool}} \tag{3}
\]

Where: \( SER \) is the Specific Emission Rate in \([\text{kg/m}^2/\text{s}]\); \( M_i \) is the molar mass of the evaporating compound in \([\text{kg/mol}]\); \( P_v(T_{pool}) \) is the vapour pressure of the liquid compound at the surface temperature in \([\text{Pa}]\); \( R \) is the universal gas constant equal to 8.314 \([\text{J/mol/K}]\); \( T_{pool} \) is the surface temperature of the pool in \([\text{K}]\); \( U_{10} \) is the wind velocity at 10 m in \([\text{m/h}]\); \( X \) is the characteristic dimension of the pool in the leeward direction in \([\text{m}]\); \( Sc \) is the mixed Schmidt’s number (i.e. air’s kinematic viscosity over compound’s diffusivity).

2.3. Volatilization models inside the Wind Tunnel

Since there are no available models in the literature for the particular situation of emissions inside a WT, among the various models (Perry, 1997; Incropera et al., 2007; Bejan and Kraus, 2003; Shah and London, 1978; Bliss et al., 1995), the one deemed more appropriate for the case at hand is the model for mass transfer under forced convection over a single flat emissive surface in laminar regime. In fact, for the air velocity range considered (Capelli et al., 2009b), the fluid dynamic regime is fully developed laminar. Thus, the thickness of the fluid dynamic boundary layer can be assumed equal to the 50% of the hood’s height (Bejan and Kraus, 2003) and the mass transfer boundary layer can be computed as:

\[
\delta_m = \delta_f \ Sc^{-\frac{1}{3}} \tag{4}
\]

Where: \( \delta_f \) is the fluid dynamic boundary layer thickness in \([\text{m}]\); \( \delta_m \) is the mass transfer boundary layer thickness in \([\text{m}]\); \( Sc \) is the mixed Schmidt’s number \( \left( \frac{\mu}{\nu} \right) \).
From this correlation, it is easy to see that for compounds with $Sc > 1$, as the case under evaluation, the mass transfer boundary layer develops inside the fluid dynamic one, with $\delta_m \leq \delta_f$ and therefore it is possible to assume that the top wall of the hood has a negligible effect on the volatilization and is non-influencing for the mass transfer phenomenon. Anyway, for the sake of comparison, the model for the situation of internal flows between emissive plates in laminar regime was considered as well (Perry, 1997; Incropera et al., 2007).

It is possible to write the mass balance between the inlet and outlet of the WT, obtaining:

$$Q \cdot C_{out} = Q \cdot C_{in} + K_{c,ave} \cdot (C_i - C_B) \cdot A \quad (5)$$

Where: $Q$ is the neutral air flow rate flushed in the WT in $[m^3/s]$; $C_{out}$ is the emitted compound concentration at the outlet in $[mol/m^3]$; $C_{in}$ is the emitted compound concentration at the inlet in $[mol/m^3]$, that is 0 if neutral air is used; $K_{c,ave}$ is the convective mass transfer coefficient, averaged over the exchange length, in $[mol/m^3]$; $A$ is the base area of the WT in $[m^2]$, $C_i$ is the gas-liquid interface concentration of the emitted compound in $[mol/m^3]$; $C_B$ is the emitted compound concentration in the bulk of the gas phase inside the hood in $[mol/m^3]$, which can be assumed equal to 50% of the outlet concentration, taking it as the average between inlet and outlet concentrations with a 0 inlet concentration (Bejan and Kraus, 2003). Thus:

$$C_{out} = \frac{K_{c,ave} \cdot C_i \cdot A}{(Q + \frac{K_{c,ave} \cdot A}{2})} \quad (6)$$

$$SER = \frac{C_{out} \cdot Q \cdot M_i}{A} \quad (7)$$

The values of $K_{c,ave}$ change from the “single surface” model to the “parallel surfaces” model, as here reported in Eq. (8) and Eq. (9) respectively (Perry, 1997; Incropera et al., 2007):

$$K_{c,ave} = 0.664 \left( \frac{D_i^3}{L_{WT} \cdot v} \right)^{1/6} U_{WT}^{1/2} \quad (8)$$

$$K_{c,ave} = 1.40 \left( \frac{D_i^2}{L_{WT} \cdot U_{WT}^{1/2}} \right)^{1/4} \quad (9)$$
Where: $D_i$ is the compound’s molecular diffusivity in air in $[m^2/s]$; $L_{WT}$ is the length of the WT central body in $[m]$; $\nu$ is the air’s kinematic viscosity in $[m^2/s]$; $h$ is the height of the WT in $[m]$; $U_{WT}$ is the air velocity inside the hood in $[m/s]$.

2.4. The experimental tests

In order to evaluate which volatilization model suits better the case under study and describes more accurately the emission phenomenon inside the WT, it was decided to perform a set of experimental runs with evaporating pure compounds. It was decided to adopt acetone first, as it is easily detectable by a GC-TCD and is volatile enough to be considered a gas-phase controlled compound for emissions (Fingas, 1998; 2013) and it is also a reasonably safe compound to use. Then, aiming to have further confirmation of the validity of the model for different substances, the experiments were performed also with another compound capable of providing a confirmation of the outcomes obtained with acetone. The chemical chosen for this second set of experiments is butanone, also a compound that can be easily detected via GC-TCD and reasonably safe.

For the tests, a small PE tank filled with the pure liquid compound, exactly fitting the WT central body, was placed under the hood simulating the liquid source. Then, the cylinder-fed neutral air was flushed through the inlet of the chamber, at different velocities, ranging from 0.0096 to 0.0527 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., 2009b; Koziel et al., 2005; Sironi et al., 2014a). The sample was then analysed by means of Dynamic Olfactometry (CEN, 2003) in order to determine its odour concentration.

3. RESULTS AND DISCUSSION

3.1. Experimental results and model validation

The samples analysis via GC-TCD allowed to obtain the outlet concentrations expressed as acetone or butanone ppm for each test. Since the concentration is a function of pool’s surface temperature, for each datum the value was expressed also as ppm fraction [ppmf], normalizing the values dividing by the
saturation concentration for the compound at the surface temperature of that specific run. This procedure allows to compare results obtained in different days with different temperatures and confront the experimental data with the forecasts of the two models considered (i.e. single and double plate). Fig. 3 and Fig. 4 report the values of concentration expressed as ppm fractions [ppmf], in function of the speed of the neutral flushing air inside the WT. The experimental data, for clarity’s sake, are reported in Table 1 and Table 2 for acetone and butanone respectively.

![Comparison models vs experimental data for acetone](image)

**Figure 3. Comparison model-experimental data for acetone**

**Table 1: Experimental data for acetone**

<table>
<thead>
<tr>
<th>$Q_{air}$ [l/h]</th>
<th>$v_{WT}$ [m/s]</th>
<th>$C_{exp}$ [ppmf]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1210</td>
<td>0.01826</td>
<td>0.06445</td>
</tr>
<tr>
<td>1790</td>
<td>0.02687</td>
<td>0.04396</td>
</tr>
<tr>
<td>2070</td>
<td>0.03117</td>
<td>0.04322</td>
</tr>
<tr>
<td>2360</td>
<td>0.03548</td>
<td>0.04672</td>
</tr>
<tr>
<td>2930</td>
<td>0.04409</td>
<td>0.03997</td>
</tr>
<tr>
<td>3500</td>
<td>0.0527</td>
<td>0.0366</td>
</tr>
</tbody>
</table>
It is possible to observe how the exponential dependency of concentration on air velocity obtained through the experiments is well described by the volatilization model for the single flat plate geometry. However, it is possible to see also an offset between experimental points and model prediction that seems to overestimate the concentration. Since mass transfer models have a semi-empirical nature and the peculiar case of the WT is somewhat different from the flat plate geometry, it was deemed reasonable to evaluate a new proportionality coefficient for the WT geometry that would fit better the situation at hand, substituting it to the value of 0.664 present in the original model. This would optimize the data-fitting of the model when applied to the specific case of the WT device. The values obtained are 0.33 for acetone and 0.30 for butanone. Therefore, an average value was considered of 0.315. Inserting this new coefficient into the equation for the definition of the convective mass transfer coefficient, a new expression is obtained:

$$K_{Cave} = 0.315 \left( \frac{D^4}{l_{WT}^3} \right)^{\frac{1}{2}} U_{WT}^{1/2}$$  \hspace{1cm} (10)
3.2. Correlation between wind speed in open field and air velocity inside the Wind Tunnel

Once the volatilization model has been defined, it was possible to proceed to the derivation of the formula for the estimation of the wind speed in the open field, at 10 m, that would cause the same emission rate from the source as the one obtained with the WT device $U_{10}^\ast$. This is the velocity that will be used for the recalculation of the SER, at the actual value of the wind speed recorded at 10 m by a meteorological station, starting from the WT data. The equations for the assessment of the SER in the two cases are equalled, adopting Eq. (3) for the open field and Eq. (5)-(7) for the WT, yielding:

$$0.002 U_{10}^{0.78} X^{-0.11} M_i C_i = \frac{0.315 \left( \frac{U_{WT}^i}{L} \right)^{0.5} \frac{1}{2} \frac{1}{2} \frac{1}{2} Q M_i}{Q + 0.315 \left( \frac{U_{WT}^i}{L} \right)^{0.5} \frac{1}{2} \frac{1}{2} \frac{1}{2} A} \quad (11)$$

It is possible then to get the value of the velocity at 10 m ($U_{10}^\ast$), as a function of the velocity in the WT ($U_{WT}^i$), as here shown:

$$U_{10}^\ast = \sqrt[0.78]{157.5 - \frac{L^{-0.39} \frac{1}{6} U_{WT}^i T}{r D_i^{-0.67} + 0.5} \frac{1}{2} \frac{1}{2} \frac{1}{2} L^{0.5} \frac{1}{6} \frac{1}{6} U_{WT}^i T^{-0.5}} \quad (12)$$

From the application of such correlation, the emission rate value can be then scaled according to the actual wind velocities of interest, as depicted in Eq. (13):

$$SER_{field} = SER_{WT} \left( \frac{U_{10}}{U_{10}^\ast} \right)^{0.78} \quad (13)$$

This correlation relies on the exponential dependency between the emission rate and the wind velocity for turbulent conditions. In order to investigate the differences between the proposed model and the SER scaling procedure commonly adopted (Sohn et al., 2005; Sironi et al., 2014b), it was deliberately chosen a concentration of 1000 ppm at the outlet of the WT, with an air speed inside the chamber of 0.035 m/s. The chosen parameters values are summarized in Table 3:

<table>
<thead>
<tr>
<th>$v_{WT}$ [m/s]</th>
<th>$c_{out}$ [ppm]</th>
<th>$SER_{WT}$ [mol/m2/s]</th>
<th>$U_{10}$ range [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.035</td>
<td>1000</td>
<td>0.000233</td>
<td>0-5</td>
</tr>
</tbody>
</table>

Table 3: Parameters values chosen for the comparison
By applying the model and comparing the forecast with the new model and the one obtained with the “regular” procedure, it was possible to obtain the plots depicted in Fig. 5.

![Figure 5: SER recalculation method for acetone (blue line) vs SER recalculation method for butanone (purple line) vs traditional SER recalculation method (red line) as a function of the wind speed (Fig. 5a). Zoom for the 0-0.2 wind speed U,10 range (Fig. 5b).]

It is possible to see that the two new models behave quite differently with respect to the old one, forecasting SER values that become more distant as the wind speed at 10 m increases. The new models indicate much higher emissions for strong winds with respect to the “regular” method. This difference can be explained as mostly due to the different exponent used for the SER recalculation in the two methodologies. In fact, the “regular” method considers the air speed inside the WT equal to the wind speed in the open field at the same height and relies on the scaling formula reported in Eq. (1). Looking at Fig. 5b, it is possible to see how for low wind speeds the new models actually forecast lower emissions with respect to the traditional method. This is due to the fact that for such speed range, the velocities are too low for the new exponent (0.78) effect to be predominant and it is possible to observe how the wind speed recalculation formula (Eq. 12) leads to forecasting lower emissions.

As discussed above, the most suitable exponent to use in the SER recalculation formula is 0.78, as it is an expression for scaling the emission rate in the open field, in the lower atmosphere, that is typically turbulent.

4. GENERALIZATION TO ODOUR EMISSIONS
In order to be able to generalize the models previously presented to the field of olfactometry, it is necessary to clearly define their field of application.

According to the studies carried out by Fingas (1998; 2013), the volatilization phenomena concerning compounds like paraffins with a chain longer than 10 carbon atoms, are not gas phase controlled (GPC) and therefore the velocity of the wind swiping the source’s surface has no influence on the SER.

The research by Parker et al. (2010), investigating the volatilization of the compounds usually found in the wastewaters of industrial activities or animal feeding operations, has highlighted that – if the liquid source is a diluted aqueous solution – the solubility value for the considered compounds in water plays a crucial role in determining what phenomenon is controlling the overall volatilization process. In order to compare the different chemical species, the non-dimensional Henry’s constant \( H_{cc} \) was referred to. The non-dimensional Henry’s coefficient \( H_{cc} \) can be determined from the Henry Law coefficient \( H_{cp} \), according to Eq. 14:

\[
H_{cc} = \frac{1}{H_{cp} \cdot R \cdot T}
\]

Where: \( H_{cc} \) is the non-dimensional Henry coefficient; \( H_{cp} \) is the dimensional Henry coefficient in \([\text{mol/m}^3/\text{Pa}]\); \( R \) is the universal gas constant in \([\text{J/mol/K}]\); \( T \) is the room temperature in [K].

It was found out that only for the compounds with a very low dimensionless Henry’s constant \( H_{cc} < 0.001 \), the velocity of the gas sweeping the surface of the liquid surface is the controlling phenomenon in the volatilization process and such compounds are defined Gas Phase Controlled (GPC). On the contrary, for compounds characterized by a high non-dimensional Henry’s constant \( H_{cc} \gg 0.001 \), typically characterized by a low solubility in water, the effect of the wind velocity becomes negligible, compared to the phenomena occurring in the liquid phase bulk. For intermediate values of the dimensionless Henry’s constant, both phenomena in the liquid phase and in the gas phase play an important role and should be accounted for properly. In order to better understand the range of \( H_{cc} \) values for the distinction between GPC, LPC and “intermediate” compounds, it is possible to refer to the dissertation proposed by Parker et al. (2010). Relying on the work of Parker et al. (2010), in fact, it is possible to infer that compounds with
\( H_{cc} < 0.0006 \) can be classified as GPC, compounds with \( H_{cc} > 0.0562 \) can be classified as LPC and compounds with \( 0.0006 < H_{cc} < 0.0562 \) can be classified as “intermediate”.

In Table 4, the values for the diffusivities in air are listed along with the non-dimensional Henry coefficients for several odorous compounds usually found in WWTP tanks, both GPC and LPC, indicating as well for each compound whether it is Gas Phase Controlled (GPC) or Liquid Phase Controlled (LPC). In order to compile Table 4, the dimensional Henry coefficients were taken from R. Sander (2015). Table 4, for clarity’s sake, was compiled grouping the LPC compounds in the upper rows and GPC compounds in the lower rows.

**Table 4: Values for the diffusivities and non-dimensional Henry’s coefficients for the considered odorous compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diffusivity in air @ 20 °C [m²/s]</th>
<th>( H_{cc} @ 25 °C [-] )</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl-mercaptan</td>
<td>1.21398E-05</td>
<td>0.106162606</td>
<td>LPC</td>
</tr>
<tr>
<td>Ethyl-mercaptan</td>
<td>1.01292E-05</td>
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<td>0.733487094</td>
<td>LPC</td>
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<td>Valeric Acid</td>
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In order to evaluate the variability of the correlation between wind speed in the open field and air velocity inside the WT, in function of the change in the compound’s diffusivity in air, the same calculations described in par. 3.2 were performed to assess the SER for a set of odoriferous compounds typically found in liquid passive area sources. The compounds considered are characterized by low values of the non-dimensional Henry’s constant (\(< 10^{-3}\) ), thus fall within the field of application of the models (i.e. GPC compounds).
It can be seen how Fig. 6 focuses only on the so-called Gas Phase Controlled compounds characterized by values of the non-dimensional Henry coefficient $H_{cc}$ lower than 0.001 (GPC in Table 4). In particular, the compounds considered in Fig. 6 are: acetone, butanone, acetic acid, ethanol, butyric acid, propionic acid, valeric acid, n-butanol and phenol. The resulting SER values showed a maximum variability of 12% (Fig. 6) if GPC compounds only are considered. Such value of variability can be considered acceptable, given that, the experimental uncertainty in olfactometry can be as much as 50% (CEN EN 13725, 2003); thus, it is possible to take an averaged value of diffusivity for the application of the model to odour, this value being $9.65 \times 10^{-6}$ m$^2$/s.

5. CONCLUSIONS AND FUTURE PERSPECTIVES

The need of a method to define the Specific Odour Emission Rate (SOER), after odour sampling with a WT and recalculate the SOER at the different wind speeds in the open field, implies knowing the models most suitable for describing the volatilization phenomena inside the WT and in the open field. This is why in the present work it was necessary in the beginning to analyse thoroughly the different models describing such processes. For the open field scenario, it was chosen as reference the model proposed in the textbook “Methods for the calculation of physical effects” (Committee for the prevention of disasters, 1992).

Conversely, for describing the phenomenon inside the hood, as there are no models specific for the particular configuration of the Wind Tunnel, two models have been considered. The two models are the
ones describing the situations closer to the WT configuration. Eventually, the model for mass transfer under forced convection from a single flat emitting surface in fully developed laminar motion regime and developing mass transfer boundary layer, was preferred as the most appropriate to describe the real situation. The decision was reached as a consequence of theoretical considerations. In order to verify the applicability of the chosen model to the WT case, experimental tests were carried out with pure liquid acetone and butanone. The outcomes confirmed that the mass transfer model for a single flat plate forecasts a dependency of the emission on the sweep velocity equal to the dependency obtained experimentally. However, the experimental concentration values are clearly lower than the model prevision. Therefore, it was proposed to modify the model equation, varying the proportionality coefficient, defining a value specific for the peculiar case of the WT.

Additional studies are necessary and should be carried out testing different compounds, GPC as well as LPC, in order to improve the estimation of the suitable generalized experimental coefficient reported in Eq. (19), also investigating the effects of the inlet zone on the phenomenon.

Furthermore, a correlation was defined that from the flush air speed in the WT, allows to assess the wind velocity in open field at 10 m that would cause the same emission as the one calculated with the data obtained in the WT. The correlation has the great advantage to account for the differences existing between volatilization in the open field and volatilization in the WT. The formula returns a wind velocity value that can then be used to recalculate the obtained SOER/SER to the wind velocities of interest: e.g., in the case of an odour impact assessment with atmospheric dispersion modelling, these are the wind velocities of the whole time domain of the simulation. Throughout the present work, it was taken great care in the definition of the field of application of the presented models and correlations. Relying of previous studies (Fingas, 1998; 2013), it is possible to say that the volatilization of low-volatility compounds, is not influenced by the velocity of the wind sweeping the liquid surface. Moreover, the researches by Hudson and Ayoko (2008) and Parker et al. (2010), led to concluding that for diluted solutions, only for the case of compounds with dimensionless Henry’s constant < \(10^{-3}\) the volatilization process is controlled exclusively by the wind velocity on the surface. As a consequence of these findings, a possible future development of this project would be to incorporate the models here described into a more
general model framework, capable of describing the volatilization of compounds that are not only controlled by forced convection. In addition, it would be necessary to extend the validation of the proposed models, performing other experiments with compounds different from acetone and butanone, both pure and in aqueous solution. Furthermore, it would be useful to define a methodology to better compare the experimental data with the forecasts of the model. This may entail carrying out chemical analysis as well as olfactometric analysis. The latter has the additional criticality of performing the olfactometric analysis directly in the field in ambient air, a difficult task. Finally, it would be interesting to investigate the adoption of the friction velocity instead of simply the wind velocity in the model, considering the effects that waves on the liquid surface may have on the friction velocity and the emission rate itself, effects that some recent researches seem to indicate are actually not negligible (Prata Jr. et al., 2016b).
References


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Figures Captions

Figure 1. The PoliMi LabOlf Wind Tunnel.

Figure 2. The Wind Tunnel scheme.

Figure 3. Comparison model-experimental data for acetone.

Figure 4. Comparison model-experimental data for butanone.

Figure 5: SER recalculation method for acetone (blue line) vs SER recalculation method for butanone (purple line) vs traditional SER recalculation method (red line) as a function of the wind speed (Fig. 5a). Zoom for the 0-0.2 wind speed U,10 range (Fig. 5b).

Figure 6. SER recalculation for several odorous compounds.
Tables Captions

Table 1. Experimental data for acetone.

Table 2. Experimental data for butanone.

Table 3. Parameters values chosen for the comparison among the considered models.

Table 4. Values for the diffusivities and non-dimensional Henry’s coefficients for the considered odorous compounds.