EXPERIMENTAL STUDY ABOUT THE INFLUENCE OF WIND VELOCITY AND TEMPERATURE ON THE EMISSION RATE OF VOCs FROM LIQUID SURFACE

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Abstract
The characterization of passive liquid area sources for the study of Volatile Organic Compounds (VOCs) emission is a matter of great concern. The volatilization of these compounds is a complex phenomenon, being potentially affected by different chemical and physical parameters. In view of this, the present study aims to investigate the influence of wind velocity and temperature on the emission of VOCs from liquid surfaces. For the purpose of this study, the behaviour of acetone and butanol in solution with water are examined by varying some parameters inside a wind tunnel system. In particular, the wind velocity flowing through the device is varied in a range from 0.02 m/s to about 0.06 m/s and the temperature of the liquid source in a range from 20 °C to 35 °C. The obtained results show as the emission rate of these two compounds appears not to be significantly affect by the wind velocity. In view of this, the approach commonly suggested to take into account a dependence of the odour emission rate on the square root of the wind velocity appears to excessively overestimate the emission rate. On the contrary, the liquid temperature highly influences the emission phenomenon leading to an increase of one order of magnitude of the emission rate. This effect is more pronounced for butanol, consistently with the trend of several chemical-physical parameters governing the volatilization process as a function of temperature.

1. Introduction
Volatile organic compounds (VOCs) emitted from wastewater treatment plants (WWTPs) are well known to have adverse impacts on human health and environment (Melcer, 1994; Yang et al., 2012; Yang et al., 2014) whereas odour nuisance associated with the emission of these species is becoming a matter of public concern in the last decades (Beghi et al., 2012; Jiang et al., 2017; Sazakli and Leotsinidis, 2020).

However, despite odour emissions from WWTPs is continuously receiving attention in view of improving life quality and people wellness, it still remains a challenging issue. As pointed out by the new provisional version of EN13725 (CEN, 2018), the European Standard for olfactometry, the quantification of a proper emission rate is quite tricky, since the release of VOCs from this type of sources and their dispersion into the atmosphere represents a complex phenomenon being potentially affected by different chemical and physical parameters (Blunden and Aneja, 2007; Invernizzi et al., 2020).

In view of this, the present paper aims to investigate the influence of wind velocity and temperature on the emission of VOCs from liquid surfaces. The choice of these variables is justified by the fact that they potentially represent two parameters of great concern. Indeed, the convective mechanism promoted by the wind represents the driving force of the emission (Upstill-Goddard et al., 1989; Watson et al., 1991; Bianchi and Varney, 1996) whereas the temperature affects several parameters governing the volatilization phenomenon (Cetin et al., 2003; Ding et al., 2015; Rajabi et al., 2020).
Currently, there are some studies concerning the influence of wind velocity on the evaporation from liquid surfaces (e.g. Mihelcic et al., 1993; Fingas, 1998; Parker et al., 2010; Invernizzi et al., 2019). Overall, they propose the existence of two different mechanisms governing the mass transfer between liquid and gas phases. In some cases, VOC diffuses rapidly inside the liquid phase reaching the interface in short time. Here, the mass transfer mechanism is controlled by the VOC stripping due to the forced convection promoted by the wind velocity. These compounds are identified as gas phase controlled. On the contrary, the emission of molecules which encounter the major resistance inside the liquid phase should not be affected by the air velocity (compounds referred to as liquid phase controlled). Then, there are some species with an intermediate behaviour, identified as gas-liquid phase controlled.

Several studies (e.g. Bliss et al., 1995; Capelli et al., 2009) available in literature and the guidelines currently available in Italy in the field of odour regulation generally suggest taking into account a dependence of the odour emission rate on the square root of the wind velocity. However, in the Italian Lombardy Region, the proposed regulatory approach points out that other methods to account for the influence of wind velocity may be adopted if justified by scientific evidence. Also, in the technical standardization of some regions (e.g. Legge Regionale Puglia n.32, 2018) the dependence from the air velocity is not mentioned at all. In view of the complexity of the topic, the recent revision of the standard pr-EN 13725:2018 only mentions the dependence on the square root of the air velocity in an informative annex, without deepening this issue. Thus, a universally accepted methodology has not been defined yet.

The abovementioned pr-EN 13725:2018 cites the liquid temperature as a possible factor of influence on the emission rate of passive area sources. Indeed, several chemical-physical variables governing the volatilization process (e.g. vapour pressure, Henry constant) are significantly affected by this parameter. Therefore, as previous studies suggest (Capelli et al., 2009; Ding et al., 2015), it is interesting to investigate the variation of the emission rate due to a change of the liquid temperature.

A recent experimental study (Tagliaferri et al., 2021), conducted on acetone in solution with water, points out a possible influence of the emission rate on the square root of wind velocity at high concentrations (i.e. at least 50 mL/L). However, the most interesting outcome is the negligible effect when considering more diluted conditions, which is typically the case of real emission phenomena from wastewater tanks. However, this study only focuses on the behaviour of acetone, a gas-liquid phase controlled species.

Building on the achievements of the abovementioned study, the present paper aims to investigate if the low influence of the wind velocity at low concentrations may be extended to gas phase controlled compounds (e.g. butanol) whose emission rate, according to the literature, is expected to be affected by air velocity. Therefore, the behaviour of butanol and acetone, in solution with water at 5 mL/L, when changing the air velocity inside a wind tunnel system is discussed. The choice of testing the concentration of 5 mL/L is justified by the fact that, in the case of real WWTPs, the concentrations generally do not exceed this value.

In addition, the influence of the liquid temperature on the emission phenomenon is tested to identify which of the investigated variables may lead to greater variations in the emission rate.

2. Materials and methods

As mentioned in the previous paragraph, acetone and butanol are tested in solution with water at a concentration of 5 mL/L. In particular, three different air flow rates are investigated (i.e. 1500 sL/h, 2500 sL/h, 4000 sL/h), representative of different wind velocities inside the wind tunnel ranging from 0.02 m/s to 0.06 m/s.
Furthermore, for each flow rate, two temperatures are tested in order to evaluate the influence of this parameter on the emission phenomenon. First, the experimental trials are carried out at 20°C, representative of an average temperature during mild months. Then, the tests are replicated at 35°C in order to simulate the emission during the warmer months, thus the worst-case condition.

The wind tunnel (Errore. L’origine riferimento non è stata trovata.) device adopted for this experimental study has a central body with a base area of 0.125 m² and it was developed by the olfactometric laboratory of Politecnico di Milano, fully described by Capelli et al. (2009). This hood has an open bottom to be placed over the emissive surface, realized by introducing the tested compounds in solution with water inside a polyethylene container with a capacity of 4 L. A known amount of neutral air flow rate is flushed through the wind tunnel device. This way, it is possible to simulate the real emission conditions of liquid area sources promoted by natural ventilation. In order to collect a gaseous sample of the investigated compound at the outlet section, a PET tube is used to connect the outlet of the wind tunnel with a Nalophan® bag (3L of capacity) and a vacuum pump enables the air blown thorough the hood to fill the sampling bag. For each sample, the outlet concentration is measured by means of a portable photoionization detector (PID), ION Tiger LT, since it ensures a reliable response quickly.

It is worth underlining that for each test (i.e. different compounds, different temperatures and flow rates) three gaseous samples are collected in order to reduce the random error on measured values as much as possible.

The experimental setup described above is slightly modified when testing the emission at high temperature (i.e. 35°C). In this case, it is necessary to introduce a proper system to heat the liquid surface and to keep the temperature constant over the entire test. For this purpose, a steel container placed over a hot plate is used.

3. Results and discussion

In this section, the results obtained testing acetone and butanol in water at different flow rates are presented reporting the trend (Figure 1) of the emission rates as a function of wind velocity at 20°C and at 35°C. In addition, the trend line (power line) is drawn highlighting the corresponding equation.

Looking at the plots, it seems that, for both temperatures, the wind velocity does not significantly affect the emission rate of acetone and butanol. To clarify this, it is interesting to look at the trend line, observing the power exponent to which the independent variable (i.e. air velocity) is elevated. These coefficients, reported in Table 1, are an indication of how much the wind velocity affects the emission rate.

Figure 1. Emission rate of acetone and butanol in aqueous solution at 20°C (left) and 35°C (right) as a function of air velocity
Table 1: Power coefficients of the equations associated to the trend lines obtained for the different investigated concentrations

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Species</th>
<th>Power coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Acetone</td>
<td>-0.15</td>
</tr>
<tr>
<td>20</td>
<td>Butanol</td>
<td>0.12</td>
</tr>
<tr>
<td>35</td>
<td>Acetone</td>
<td>0.06</td>
</tr>
<tr>
<td>35</td>
<td>Butanol</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 1 reports the exponent obtained using a power-law regression of the experimental data: at the investigated concentration (i.e. 5 mL/L) the influence of wind velocity on emission rate appears not or slightly significant. It is worth noting that this outcome appears to be consistent not only with the experimental results obtained for acetone but also for the gas phase controlled species (i.e. butanol) which, according to the literature, is expected to be affected by the air flow. In view of this, the approach commonly suggested to take into account a dependence of odour emission rate on the square root of the wind velocity (i.e. coefficient of 0.5) appears too conservative, with the risk of excessively overestimate the emission rate.

As mentioned in the Introduction, the emission rate of the species has been also evaluated when changing the temperature of the liquid. As an example, Table 2 reports the emission rates of acetone and butanol obtained at 20°C and 35°C keeping constant the air flow rate at 2500 sL/h (the same experimental tests carried out at 1500 sL/h and 4000 sL/h lead to very similar results). The last column of Table 2 shows the ratio between the emission rate of the investigated species at 20°C and 35°C.

Table 2: Emission Rates of acetone and butanol obtained at 20°C and 35°C (2500 sL/h)

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Species</th>
<th>Emission Rate (ER) [mg/s]</th>
<th>ER (35°C)/ER(20°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Acetone</td>
<td>0.32</td>
<td>4.4</td>
</tr>
<tr>
<td>20</td>
<td>Butanol</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Acetone</td>
<td>1.41</td>
<td>9.8</td>
</tr>
<tr>
<td>35</td>
<td>Butanol</td>
<td>0.45</td>
<td></td>
</tr>
</tbody>
</table>

Differently from the wind velocity, the experimental tests conducted at different temperatures show a significant influence of the temperature: when passing from 20°C to 35°C, the emission rate almost increases of one order of magnitude.

Finally, it is interesting to observe the different behaviour of butanol and acetone as a result of temperature variation. Indeed, the influence of the investigated variable on the emission rate of butanol appears more significant as compared to acetone, leading to a factor of variation inside the tested range of about 10 (instead of 4.4). This outcome seems consistent with the theoretical trend of several chemical-physical parameters, which govern the volatilization process, as a function of temperature. For butanol, the variation of vapour pressure and Henry constant with temperature (inside the investigated range of 20°C – 35°C) is more pronounced than acetone. Therefore, a grater variation of the emission rate is expected.

4. Conclusions
Many odour regulations all over the world are defined based on the application of dispersion modelling. However, to obtain reliable results from the modelling study, a fundamental input datum is represented by the emission rate whose estimation, in some situations, represents a challenging task.

This experimental study arises from this intent. It evaluates the influence of wind velocity and temperature on the emission rate from passive liquid area sources. More in detail, butanol and acetone in solution are tested in solution with water inside a wind tunnel system with the aim to find out whether the air flow (tested in the range 1500-400 sL/h) and the water temperature (20 °C – 35°C) influences the emission phenomenon.

From the results of this study, it turns out that, while the wind velocity seems to slightly influence the emission rate, the effect of the temperature is much more pronounced. Thus, the recommended approach to implement an odour emission rate dependent on the square root of wind velocity seems too excessively overestimate the emission rate. In addition, while the behaviour of acetone and butanol appears quite similar when changing the wind velocity, the influence of the temperature appears more significant for butanol as compared to acetone, consistently with the trend of several chemical-physical parameters (e.g. vapour pressure) as a function of temperature.

This work represents a preliminary step to deepen the knowledge about the emission of VOCs in solution with water. Anyway, further studies are certainly needed to better understand the effect of other parameters, such as humidity, on the atmospheric emission from liquid solutions. Finally, a future challenge should be focused on the development of a theoretical model able to predict an emission rate consistent with open-field experimental evidence.