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Surface volatilization modeling of (semi-)volatile hydrophobic organic compounds: the role of reference compounds

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Abstract

Volatilization of hazardous hydrophobic organic compounds is often observed in many water, wastewater and soil treatment (bio)processes. Several models have been developed to quantify and predict gas-liquid pollutant transfer, being the proportionality coefficient model (PCM) one of the most commonly used, particularly in wastewater treatment. The PCM is based on the use of oxygen as a reference compound, which has a low resistance to the transfer in the gas phase. However, this resistance might be important for (semi-)volatile organic compounds – or (semi-)VOCs, which may render the use of the PCM model inaccurate. This study proposes an experimental methodology and a modeling approach for the use of the two-reference compound model (2RCM) that considers both the liquid-side and the gas-side resistances, by using water and oxygen as references. Results showed that the 2RCM predicts more accurately the overall mass transfer coefficients than the PCM for a VOC and two semi-VOCs tested in this study. In addition, the 2RCM was found to be a more robust method to estimate mass transfer coefficient of any compound and its use can be extrapolated to all substances. Finally, the relevance and limitations of both models was established.

Keywords

Volatilization; Mass transfer modeling; Mass transfer kinetics; Henry’s law constant; HOCs; Reference compounds

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33 **Nomenclature**

34

| | |
|-----------------|---|
| A | Interfacial area for the mass transfer (m^2) |
| a | Interfacial area per unit of liquid volume ($m^2.m^{-3}$) |
| B | Constant in Eq. (22) |
| C_G | Concentration in the gas phase ($kg.m^{-3}$) |
| $C_{G,i}$ | Concentration at the gas-liquid interface ($kg.m^{-3}$) |
| C_G^* | Equilibrium concentration in the gas phase ($kg.m^{-3}$) |
| C_L | Concentration in the liquid phase ($kg.m^{-3}$) |
| $C_{L,i}$ | Concentration in the gas phase at the gas-liquid interface ($kg.m^{-3}$) |
| C_L^* | Equilibrium concentration in the liquid phase ($kg.m^{-3}$) |
| D | Reactor diameter (m) |
| D_G | Gas diffusivity ($m^2.s^{-1}$) |
| d_i | Impeller diameter (m) |
| D_L | Liquid diffusivity ($m^2.s^{-1}$) |
| DO | Dissolved oxygen ($mg.L^{-1}$) |
| H_C | Dimensionless Henry's law constant (-) |
| K_G | Overall mass transfer coefficient defined from the gas phase ($m.s^{-1}$) |
| k_G | Individual mass transfer coefficient in the gas film ($m.s^{-1}$) |
| $K_G a$ | Overall volumetric mass transfer coefficient defined from the gas phase (s^{-1}) |
| $k_G a$ | Individual volumetric mass transfer coefficient in the gas film (s^{-1}) |
| K_L | Overall mass transfer coefficient defined from the liquid phase ($m.s^{-1}$) |
| k_L | Individual mass transfer coefficient in the liquid film ($m.s^{-1}$) |
| $K_L a$ | Overall volumetric mass transfer coefficient defined from the liquid phase (s^{-1}) |
| $k_L a$ | Individual volumetric mass transfer coefficient in the liquid film (s^{-1}) |
| m | Gas diffusivity exponent (-) |
| N | Stirring speed (s^{-1}) |
| \dot{N} | Mass transfer rate ($kg.s^{-1}$) |
| N_P | Power number (-) |
| n | Liquid diffusivity exponent (-) |
| p | Exponent in Eq. (22) (-) |
| $\frac{P_N}{V}$ | Mechanical power input ($W.m^{-3}$) |
| Q_G | Airflow rate ($m^3.s^{-1}$) |
| r_c | Surface renewal rate (s^{-1}) |
| R_G | Gas-side resistance to transfer ($s.m^{-1}$) |
| R_L | Liquid-side resistance to transfer ($s.m^{-1}$) |
| R_T | Total resistance to transfer ($s.m^{-1}$) |
| S_d | Saturation degree (-) |
| S_p | Slope (s^{-1}) |
| t | time (s) |
| t_c | Contact time (s) |

| | |
|-------|---------------------------------|
| t_r | Bubble residence time (s) |
| V_G | Gas volume (m ³) |
| V_L | Liquid volume (m ³) |

Greek letters

| | |
|------------|---------------------------------|
| δ_G | Shear rate (s ⁻¹) |
| δ_L | Gas holdup (-) |
| Ψ | Proportionality coefficient (-) |
| ρ | Density (kg.m ⁻³) |

Subscripts

| | |
|-------|--|
| G | Relative to the gas phase |
| HOC | Relative to Hydrophobic Organic Compound |
| i | Relative to the interface |
| L | Relative to the liquid phase |
| O_2 | Relative to Oxygen |
| ref | Relative to a reference compound |
| W | Relative to Water |

Superscripts

| | |
|-------|------------------------------------|
| B | Relative to bubble volatilization |
| e | Estimated |
| in | Relative to the inlet |
| S | Relative to surface volatilization |
| out | Relative to the outlet |

Acronyms

| | |
|------|-----------------------------------|
| 2RCM | Two-reference compound model |
| HOC | Hydrophobic organic compound |
| NAP | Naphthalene |
| PAH | Polycyclic aromatic hydrocarbons |
| PCM | Proportionality coefficient model |
| PHE | Phenanthrene |
| TOL | Toluene |
| VOC | Volatile organic compound |

36 **1. Introduction**

37 Over the last decades, the occurrence of hazardous hydrophobic organic compounds (HOCs)
38 as pollutants in the aquatic environments and soils has become a major environmental
39 concern. Among the pollutants concerned, many are volatile and semi-volatile and can thus be
40 transferred to the atmosphere due to mass transfer processes. Physicochemical and biological
41 processes are often used to remove these pollutants during wastewater treatment, water
42 purification treatments and soil remediation. In general, these processes need mixing to
43 improve the homogeneity and the reactor performance and/or the introduction of a gas phase
44 by a diffuser (aerobic biological treatment, ozonation, electro-Fenton, etc.) [1–5]. In systems
45 open to the atmosphere, the mechanical power input promotes the surface aeration of the
46 reactor, but it favors simultaneously the transfer of the most volatile molecules to the gas
47 phase. In the same way, bubble dispersion through the liquid phase favors the transfer of the
48 desired gas and at the same time the stripping of some volatile and semi-volatile compounds
49 [6]. However, despite the environmental and public health issues, the volatilization process
50 has been, in general, severely underestimated in wastewater treatment process [7] and even
51 not considered in many research papers [5].

52 The most susceptible compounds to transfer are usually called volatile organic compounds
53 (VOCs) and other compounds exhibiting the same behavior but in lesser extent (e.g.
54 polycyclic aromatic compounds or PAHs) are frequently referred as “semi-volatile
55 compounds”. In general, the Henry’s law constant determines the degree of volatilization of
56 any compound [8]. However, the limit between the “volatile” and the “semi-volatile”
57 categories is not clearly defined and there is no consensus in the literature regarding this issue.
58 Furthermore, it is difficult to generalize because the extent of the volatilization does not only
59 depend on the molecules properties but also on the local hydrodynamic conditions [9].

60 To predict the gas-liquid mass transfer rate of volatile and semi-volatile compounds, many
61 authors have used oxygen as a reference molecule [10–12]. They relate the mass transfer
62 coefficient of both the target compound and oxygen using a proportionality factor that only
63 depends on the ratio of the diffusion coefficients of the two molecules. This approach assumes
64 that the mass transfer is mainly controlled by the liquid-phase resistance, which tallies with
65 the low solubility property of oxygen. Nevertheless, this is only valid for very volatile
66 compounds. Conversely, for less volatile compounds for which the gas phase resistance
67 cannot be neglected more complex models should be used [13].

68 In this sense, two models have been proposed to predict the mass transfer coefficient of
69 (semi-)volatile molecules. The most complex is the two-reference compound model (2RCM).

70 To estimate the mass transfer coefficient of the molecule considered, the mass transfer
71 coefficient of two reference molecules need to be known; one whose transfer is controlled by
72 the gas phase and one whose transfer is controlled by the liquid phase [14]. The second
73 model, called the proportionality coefficient model (PCM), uses the sum of resistances of one
74 reference molecule (in general oxygen). Unlike the 2RCM, the PCM is based only on the
75 measurement of the liquid-phase resistance. The gas phase resistance is then estimated. Only
76 very few studies have been performed to validate these models and no comparison between
77 them have been done [10,11,14,15]. In addition, most models require values of Henry's law
78 constant (H_c) of the targeted compound. For many compounds, and particularly for HOCs,
79 the range of values can be very wide, comprising several orders of magnitudes in some cases
80 [16] which can lead to important errors in the estimation of the volatilization rates [17].
81 Therefore, there is a need to further investigate and to assess methodologies and models
82 allowing predicting mass transfer of volatile and semi-volatile molecules. In this context, the
83 objective of the present work was to study and model the gas-liquid surface mass transfer
84 process of HOCs using both the PCM and the 2RCM. Three HOCs with different H_c values
85 were selected as model molecules for the volatile and semi-volatile groups one VOC (toluene)
86 and two PAHs (naphthalene and phenanthrene). The Henry's law constants of these
87 compounds were experimentally estimated. Additionally, oxygen and water were used as the
88 reference compounds. Experimental and modeling results were used to elaborate a
89 comparative analysis of both the PCM and the 2RCM.

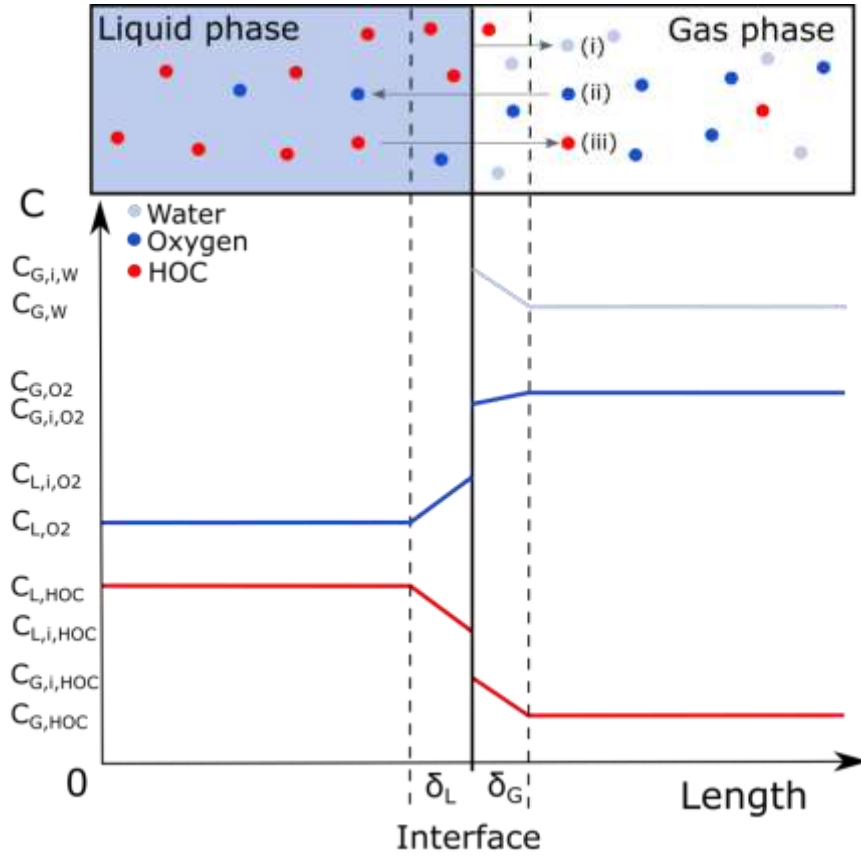
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91

92 **2. Mass transfer modeling**

93 **2.1. The two-film theory**

94 According to the two-film theory, when a compound is transferred between two phases, it
95 passes through two thin films that are formed on each side of the interface between these
96 phases (Figure 1).



97

98

99

Figure 1. Two-film theory schema depicting three possible gas-liquid mass transfer processes: (i) evaporation, (ii) absorption and (iii) volatilization

100

101 The gradient of concentration in each layer decreases in the direction of the mass transfer and
 102 the relation between the concentrations at the interface is given by the Henry's law (Eq. (1)).
 103 Moreover, Henry's law defines also the equilibrium concentration of each phase through Eq.
 104 (2) and Eq. (3) [18–20].

$$C_{G,i} = H_c C_{L,i} \quad (1)$$

$$C_G^* = H_c C_L \quad (2)$$

$$C_L^* = \frac{C_G}{H_c} \quad (3)$$

105 Where $C_{G,i}$, C_G and C_G^* are respectively the gas interface concentration, the gas phase bulk
 106 concentration and the equilibrium concentration in the gas phase ($\text{kg}\cdot\text{m}^{-3}$); $C_{L,i}$, C_L and C_L^* are
 107 respectively the liquid interface concentration, liquid phase bulk concentration and the
 108 equilibrium concentration in the liquid phase ($\text{kg}\cdot\text{m}^{-3}$) and H_c is the dimensionless Henry's
 109 law constant (-).

110 Three possible cases are depicted in Figure 1: (i) the transfer of a liquid substance, such as
 111 water, to the gas phase at a temperature below its boiling point, known as evaporation; (ii) the
 112 transfer of a substance present in the gas phase, such as oxygen in air, into the liquid phase,
 113 called absorption; and (iii) the transfer of a substance dissolved in the liquid phase, in this
 114 case an HOCs, into the gas phase, usually called volatilization.

115 The mass transfer rate \dot{N} for any compound moving from the liquid phase to the gas phase is
 116 given by Eq. (4) (in the liquid film) and Eq. (5) (in the gas film) [19,20].

$$\dot{N} = k_L A (C_L - C_{L,i}) \quad (4)$$

$$\dot{N} = k_G A (C_{G,i} - C_G) \quad (5)$$

117 Where k_L and k_G are the individual mass transfer coefficients respectively in the liquid film
 118 and in the gas film ($\text{m}\cdot\text{s}^{-1}$) and A is the interfacial area (m^2).

119 If no accumulation in the layers is assumed, Eq. (4) and Eq. (5) can be equalized. Then,
 120 invoking Henry's law (Eq. (1-3)), the transfer rate by unit of volume of a compound from the
 121 liquid phase to the gas phase can be calculated using either Eq. (6) or Eq. (7), depending on
 122 the phase in which the relation is applied [18].

$$\frac{dC_L}{dt} = K_L a (C_L^* - C_L) \quad (6)$$

$$\frac{dC_L}{dt} = K_G a (C_G - C_G^*) \quad (7)$$

123 Where $K_L a$ and $K_G a$ are the overall volumetric mass transfer coefficient defined respectively
 124 for the liquid phase and the gas phase (s^{-1}).

125 The $K_L a$ in Eq. (6) is equal to the inverse of the sum of the reciprocals of the mass transfer
 126 coefficient of both the liquid layer and the gas layer (corresponding to a sum of resistances),
 127 as shown in Eq. (8). This coefficient is related to the one defined for the gas phase (in Eq. (7))
 128 by the Henry's law constant of the compound (Eq. (9)) [20].

$$K_L a = \frac{1}{\frac{1}{k_L a} + \frac{1}{H_C k_G a}} ; \frac{1}{R_T} = \frac{1}{R_L} + \frac{1}{R_G} \quad (8)$$

$$K_G a = H_C K_L a \quad (9)$$

129 Where R_T , R_L and R_G are respectively the total resistance to transfer, the liquid-side resistance
 130 to transfer and the gas-side resistance to transfer ($\text{s}\cdot\text{m}^{-1}$).

131

132 For some compounds, the resistance in one of the phases can be considered negligible
 133 compared to the other phase. This is often the case for gases with low solubility (when the
 134 liquid phase is water), such as oxygen, that at standard conditions encounter very low
 135 resistance in the gas phase ($R_L \gg R_G$). Thus, $K_L a$ may be assimilated to the individual
 136 volumetric transfer coefficient of the liquid phase ($k_L a$) (Eq. (10)) and it is common to call
 137 these kind of processes “liquid-phase controlled mass transfer” [21].

$$K_L a \cong k_L a \quad (10)$$

138
 139 Conversely, for the substances with a higher affinity for the liquid phase, the mass transfer
 140 can be considered “gas-phase controlled”, meaning that the resistance in the liquid film can be
 141 considered negligible ($R_L \ll R_G$). In this case, $K_L a$ may be approximated to the individual
 142 volumetric transfer coefficient of the gas phase ($k_G a$) multiplied by the Henry’s law constant
 143 (Eq. (11)).

$$K_L a \cong H_C k_G a \quad (11)$$

144
 145
 146 **2.2. Mass transfer coefficient and diffusivity**

147 Most models indicate that the mass transfer coefficient in each layer is proportional to the
 148 diffusivity raised to some power, as mentioned by Munz and Roberts [13] (Eq. (12) and Eq.
 149 (13)).

$$k_L \propto (D_L)^n \quad (12)$$

$$k_G \propto (D_G)^m \quad (13)$$

150 Where D_L and D_G are the diffusivities respectively in the liquid and gas phase ($\text{m}^2 \cdot \text{s}^{-1}$) and n
 151 and m are respectively liquid and gas diffusivity exponents (-).

152 This means that, if the individual mass transfer coefficient in each layer of a reference
 153 compound and the exponent of the diffusivity term are known, it may be possible to estimate
 154 this parameter for any desired compound using Eq. (14) and Eq. (15).

$$\frac{k_L a}{k_L a_{ref}} = \left(\frac{D_L}{D_{L,ref}} \right)^n \quad (14)$$

$$\frac{k_G a}{k_G a_{ref}} = \left(\frac{D_G}{D_{G,ref}} \right)^m \quad (15)$$

155 Where $k_L a_{ref}$ and $k_G a_{ref}$ are respectively the $k_L a$ and $k_G a$ values of the reference
 156 compounds and $D_{L,ref}$ and $D_{G,ref}$ are respectively the D_L and D_G values of the reference
 157 compound.

158 Depending on the mass transfer theory used to relate the diffusivity and the mass transfer
 159 coefficient, as well as its underlying assumptions, m and n can take several values. Table 1
 160 shows the expression of the relation in Eq. (14) for the main mass transfer theories existing in
 161 the literature. Analogously, the same relations can be applied for the gas film (Eq. (15)).

162

163 *Table 1. Relation between the mass transfer coefficient and the diffusivity*

| Theory | Expression | Exponent n value | Reference |
|------------------------|----------------------------------|--------------------|-----------|
| Two-film theory | $k_L = \frac{D_L}{\delta_L}$ | 1 | [22] |
| Penetration theory | $k_L = 2 \sqrt{\frac{D_L}{t_c}}$ | 0.5 | [23] |
| Surface renewal theory | $k_L = \sqrt{D_L r_c}$ | 0.5 | [24] |

164 Where δ_L is the thickness of the liquid film (m), t_c is the contact time (s) and r_c is the surface renewal rate (s^{-1}).

165 In most studies, one of the theories and its corresponding value for m and/or n are chosen.
 166 However, some authors have estimated these values from experimental data by combining Eq.
 167 (8) and the ratio of diffusivities (Eq. (14) and/or Eq. (15)), which results in Eq. (16).

$$\frac{1}{K_L a} = \frac{1}{k_L a_{ref} \left(\frac{D_L}{D_{L,ref}} \right)^n} + \frac{1}{H_C k_G a_{ref} \left(\frac{D_G}{D_{G,ref}} \right)^m} \quad (16)$$

168 However, no consensus exists among the authors on the ranges, and even much less, on the
 169 specific values that these exponents might take [10,13,25,26].

170 Additionally, a number of empirical correlations exist that allow the calculation of the overall
 171 mass transfer coefficient for any substance in specific configurations [27,28]. However, it is
 172 important to observe the conditions in which the mentioned correlations are applicable.

173

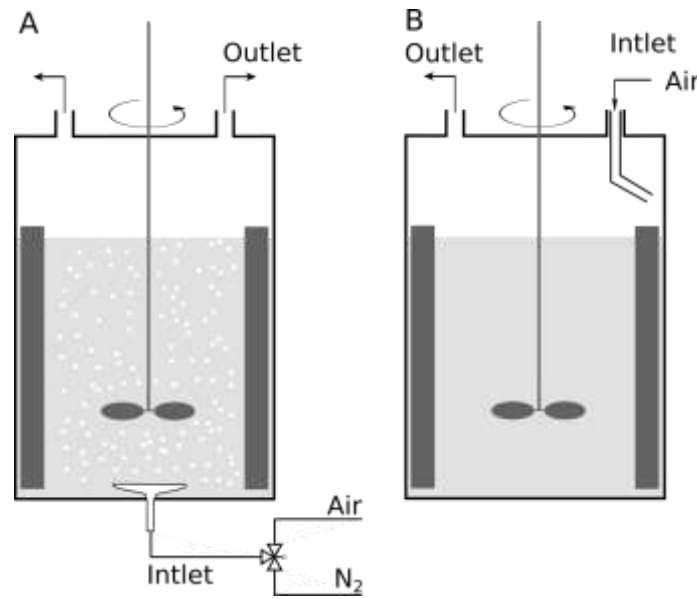
174 **3. Materials and methods**

175 **3.1. Experimental part**

176 **3.1.1. Reactor and operating conditions**

177 The experiments were carried out in a standard 4.2-l glass reactor (working volume) with a
 178 thermal jacket controlled at 20 °C and four baffles. The dimensions of the reactor are
 179 specified by Pino-Herrera et al. [29]. Two reactor set-up configurations were used (Figure 2):

180 A) for Henry's law constant determination of HOCs, the gas phase was injected from the
 181 bottom of the reactor through a porous glass sparger connected to a three-port L-shaped valve,
 182 providing the choice between an air flow and a nitrogen flow as needed (Figure 2A); and B)
 183 for surface oxygen, water and HOCs mass transfer, the gas phase was introduced to the
 184 reactor using a plastic tube passing through holes in the lid, directing the air flow to the wall
 185 of the reactor. In this way, when the gas phase enters the reactor, preferential pathways for a
 186 direct exit and perturbations on the liquid surface were avoided (Figure 2B).
 187



188
 189

Figure 2. Experimental set-up: (A) Bubble mass transfer and (B) Surface mass transfer

190 Mechanical agitation was supplied by a motor with digital controlled stirring speed coupled
 191 with a single marine propeller ($d_i = D/3$, where D is the reactor diameter). The reactor was
 192 operated varying the corresponding operational parameters per test in the ranges given in
 193 Table 2. The power input was calculated using the power number (Eq. (17)). The power
 194 number N_p is constant and equal to 0.35 for a marine propeller at turbulent conditions
 195 ($Re > 10^4$), which is the case for all conditions tested in this study [30].

$$\frac{P_N}{V} = \frac{N_p \rho N^3 d_i^5}{V_L} \quad (17)$$

196 Where P_N/V is the mechanical power input ($\text{W}\cdot\text{m}^{-3}$), N_p is the power number (-), ρ is the
 197 water density ($\text{kg}\cdot\text{m}^{-3}$), N is the stirring speed (s^{-1}), d_i is the impeller diameter (m) and V_L is
 198 the liquid volume (m^3).

199
 200

201
202
203
204

Table 2. Operational parameters used in this study.

| Reactor configuration | | Operational parameter | Units | Range |
|-----------------------|---|-----------------------|-----------------------------------|---------------|
| A | B | | | |
| | × | $Q_G (\times 10^4)^a$ | $\text{nm}^3 \cdot \text{s}^{-1}$ | 2.9 |
| × | | $Q_G (\times 10^4)^b$ | $\text{nm}^3 \cdot \text{s}^{-1}$ | 0.375 – 2.18 |
| × | × | P_N/V | $\text{W} \cdot \text{m}^{-3}$ | 17.65 – 94.52 |
| × | × | T | $^{\circ}\text{C}$ | 20 |

205
206

^a surface airflow, ^b bubble airflow

207
208

3.1.2. HOC solutions and monitoring

3.1.2.1. HOC solutions

209 The HOCs used in this research work (toluene, naphthalene and phenanthrene) were obtained
210 from Sigma-Aldrich chemicals ($\geq 98\%$ purity). Solvents (methanol and acetonitrile, HPLC
211 grade) and phosphoric acid were obtained from VWR chemicals. Diffusivity of the
212 compounds used in this study in air and water are shown in Table S1.

213 A solution of the three HOCs in water was prepared. For phenanthrene and naphthalene, a
214 concentrated solution in methanol was previously prepared and 2 ml of this solution were
215 added to 5 l of tap water, containing 3 ml of toluene. The amount of methanol in solution (<
216 0.04%) was low enough not to modify the mass transfer and the surface tension of the liquid
217 in the system [31]. The solution was magnetically stirred until no droplets of toluene were
218 observed and then filtered to remove any possible PAH crystals remaining in suspension
219 before it was added to the reactor (4.2 L).

220
221

3.1.2.2. HOC concentration monitoring during mass transfer experiments

222 For each HOC mass transfer experiments, samples of the liquid phase were taken before and
223 after starting either the bubble or the surface airflow at appropriate times and analyzed for
224 HOC concentrations. Samples were measured using an HPLC (Hitachi *LaChrom Elite*® *L-*
225 *2400*) coupled with UV/VIS detector (set to 254 nm) and a fluorescence detector (Excitation
226 wavelength set to 250 nm and Emission wavelength set to 350 nm). The separation was
227 performed using a RP C-18 end capped column (Purospher®, Merck) (5 mm, 25 cm \times 4.6
228 mm) placed in an oven at 40 $^{\circ}\text{C}$. The mobile phase was a mixture of water (at pH adjusted

229 to 2.5 using phosphoric acid) and acetonitrile (25:75 v/v) with a flow rate of 0.8 ml.min⁻¹ in
230 isocratic mode. The injection volume was 20 µl.

231
232

233 **3.1.3. HOC Henry's law constant determination in bubbly reactor**

234 The theoretical development for the determination of Henry's law constant is developed in
235 Appendix A. For the Henry's law constant determination of the selected HOCs, the reactor
236 set-up configuration shown in Figure 2A was used. An HOC solution was prepared as
237 explained in section 3.1.2 and introduced in the reactor (4.2 l) and, after introducing the
238 bubbly flow, the depletion of the HOC concentrations in the liquid phase was measured over
239 time. Experiments were performed adjusting the operating parameters within the ranges given
240 in Table 2.

241

242 **3.1.4. Surface mass transfer in gas and liquid films**

243 **3.1.4.1. Oxygen mass transfer coefficient**

244 The oxygen transfer coefficients were obtained using the configuration shown in Figure 2B
245 and were measured using the dynamic method (gassing out), described by García-Ochoa and
246 Gomez [21]. The curve of oxygen absorption was recorded using an inoLab® Oxi 7310 DO
247 sensor connected to a Cellox 325 probe (WTW). From the oxygen absorption curves, the
248 surface oxygen mass transfer coefficients ($k_L a_{O_2}^S$) in Eq. (18) were estimated, taking into
249 account the response time of the electrode. The influence of power input on this parameter
250 was measured within the range shown in Table 2.

$$\frac{dC_{L,O_2}}{dt} = k_L a_{O_2}^S (C_{L,O_2}^* - C_{L,O_2}) \quad (18)$$

251 Where subscript O_2 refers to oxygen, superscript S refers to surface.

252

253 **3.1.4.2. Water mass transfer coefficient**

254 The water transfer coefficients were obtained using the configuration shown in Figure 2B. An
255 airflow was continuously introduced to the upper part of the experimental system and steady
256 state conditions in the gas phase was reached. Then, the gas phase relative humidity and
257 temperature was measured using a KIMO® AMI 310 multifunction meter at the inlet and the
258 outlet of the reactor. The airflow was introduced in the gas phase from the top of the reactor,
259 avoiding disturbances in the liquid surface and the saturation of the gas phase. The surface

260 water transfer coefficient was subsequently obtained by performing a mass balance for the
261 humidity in the gas phase (Eq. (19)), knowing the psychrometric conditions of the air at the
262 inlet and the outlet of the reactor.

$$C_{G,W}^{in}Q_G + k_G a_W^S (C_{G,W}^* - C_{G,W}) = C_{G,W}^{out}Q_G \quad (19)$$

263 Where $C_{G,W}$ is the vapor concentration in air, the superscripts *in* and *out* refer respectively to
264 the inlet and outlet airflow, the subscript *W* refers to water and $C_{G,W}^*$ is the saturated vapor
265 concentration calculated at the air temperature using the equilibrium vapor pressure
266 correlation developed by Lowe [32]. Since $C_{G,W}$ varies throughout the reactor headspace, the
267 logarithmic mean vapor concentration between the inlet and outlet airflow was used in order
268 to estimate the driving force for water evaporation along the water surface.

269

270 Several airflow rates (Q_G) were tested for all agitation conditions to check that this parameter
271 did not affect the transfer coefficient and that the saturated vapor concentration was not
272 reached in the outlet airflow. An average airflow rate on the surface of $2.9 \times 10^{-4} \text{ m}^3 \cdot \text{s}^{-1}$ was
273 fixed. The influence of power input on this parameter was measured within the range shown
274 in Table 2.

275

276 **3.1.4.3. Surface HOCs mass transfer coefficient**

277 The overall HOC surface mass transfer coefficients were obtained using the reactor set-up
278 configuration in Figure 2B. An HOC solution was prepared as explained in section 3.1.2 and
279 introduced in the reactor. An airflow was introduced from the top of the reactor through the
280 lid avoiding disturbances in the liquid surface to remove any accumulation of HOCs in the gas
281 phase. In this case, HOC gas phase concentration was considered negligible, since the gas
282 phase was continuously renewed (concentration in the inlet gas $C_G = 0$). This hypothesis was
283 further confirmed by demonstrating the nominal gas phase HOC concentration (maximal
284 HOC mass flux divided by Q_G) was negligible in comparison with the $C_{G,HOC}^*$.

285 A batch volatilization experiment where the HOC concentration was measured as a function
286 of time led to a first order equation from which the HOC surface mass transfer coefficient was
287 easily calculated (Eq. (6)). The influence of power input on this parameter was measured
288 within the range shown in Table 2.

289

290 **3.2. HOC mass transfer modeling**

291 In this study, two models to predict the individual and the overall gas-liquid mass transfer
 292 coefficients of the HOCs were tested and compared: the 2RCM and the PCM.

293

294 3.2.1. Two-reference-compound model (2RCM)

295 In liquid-controlled mass transfer processes, oxygen is often used as reference compound
 296 because its gas-side resistance can be considered negligible and Eq. (10) can be applied.
 297 Conversely, in aqueous solutions, water presents a virtually non-existent transfer resistance in
 298 the liquid phase, which allows the use of Eq. (11). Then, by introducing oxygen and water as
 299 reference compounds in Eq. (16), the HOC mass transfer coefficient could be estimated using
 300 Eq. (20).

$$\frac{1}{K_L a_{HOC}^S} = \frac{1}{k_L a_{O_2}^S \left(\frac{D_{L,HOC}}{D_{L,O_2}} \right)^n} + \frac{1}{H_C k_G a_W^S \left(\frac{D_{G,HOC}}{D_{G,W}} \right)^m} \quad (20)$$

301 The exponents of each diffusivity ratio (m and n) were chosen according to the hydrodynamic
 302 conditions expected at each side of the interface as explained in section 3.2.3. The HOC mass
 303 transfer coefficients estimated using the experimental oxygen and water mass transfer
 304 coefficients and the Henry's law constant for each HOC were compared to those obtained
 305 experimentally and the deviations were calculated for each compound tested.

306

307 3.2.2. Proportionality coefficient model (PCM)

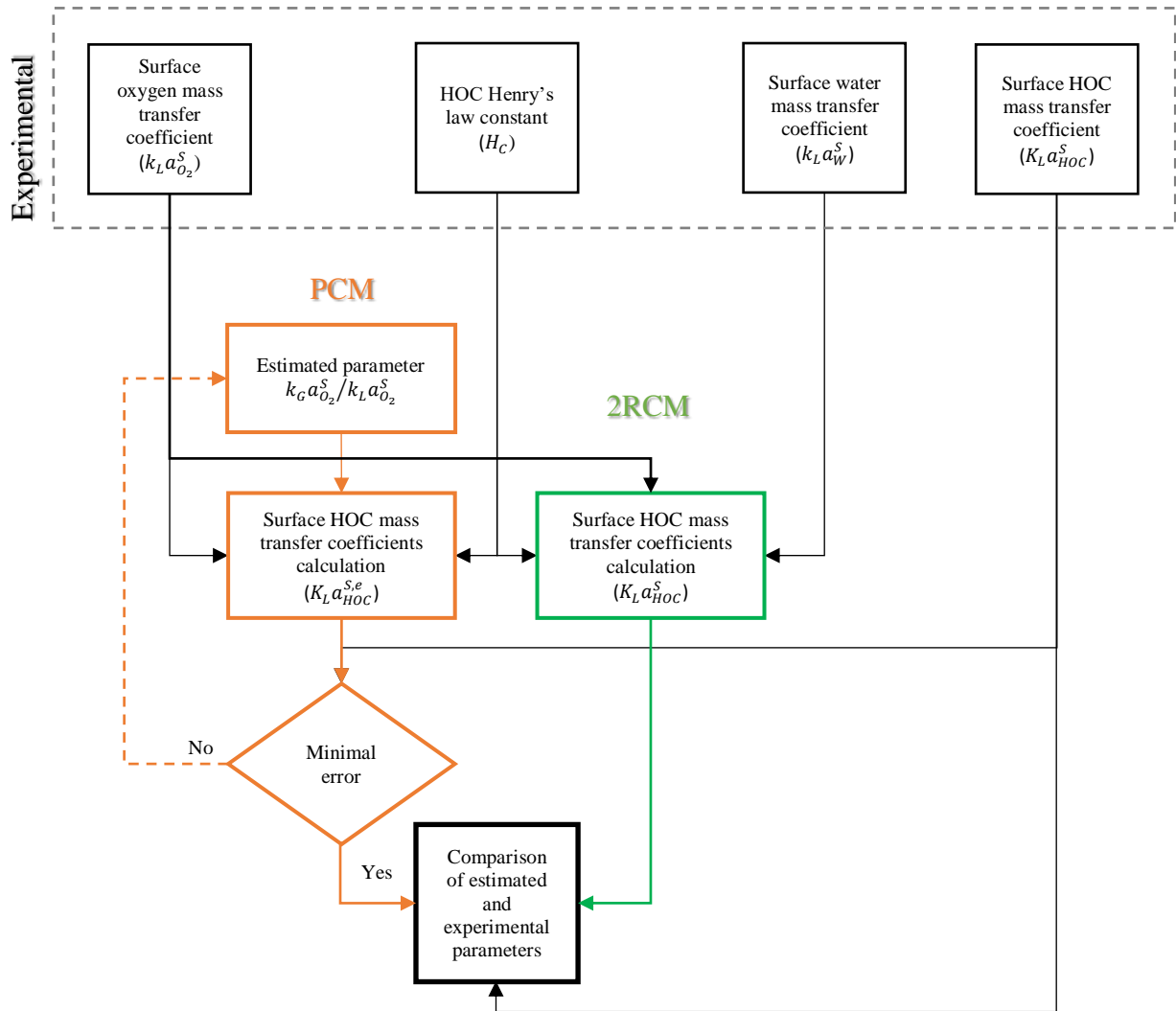
308 Hsieh et al. [11] transformed Eq. (16) by using only oxygen as the reference compound and
 309 defining the proportionality coefficient (Ψ) as shown in Eq. (21). This relation was also tested
 310 by fixing both exponents n and m as described in section 3.2.3. However, in this case, the
 311 ratio of individual oxygen mass transfer coefficients ($k_G a_{O_2}^S / k_L a_{O_2}^S$) was not known. Thus,
 312 this parameter was estimated using the experimental Ψ obtained for each HOC tested in this
 313 study at different power input conditions.

$$\Psi = \frac{K_L a_{HOC}^S}{K_L a_{O_2}^S} = \frac{1}{\frac{1}{\left(\frac{D_{L,HOC}}{D_{L,O_2}} \right)^n} + \frac{1}{H_C (k_G a_{O_2}^S / k_L a_{O_2}^S) \left(\frac{D_{G,HOC}}{D_{G,O_2}} \right)^m}} \quad (21)$$

314

315 Figure 3 shows a scheme of the parameter estimation followed in this study. First, from the
 316 experimental data and an assumed $k_G a_{O_2}^S / k_L a_{O_2}^S$, the HOC overall mass transfer coefficients
 317 for each power input tested were calculated. Then, the sum of the squared errors between the

318 calculated coefficients and the experimental ones was minimized by modifying the initial
 319 assumed parameters. Once the minimal error was reached, the estimated and calculated
 320 parameters for each model were analyzed and compared. Both models were tested and
 321 compared based on their accuracy and their robustness to predict HOC overall mass transfer
 322 coefficients.



323

324

325 *Figure 3. Modeling approach using the proportionality coefficient model (PCM) and the two-reference-*
 326 *compound model (2RCM)*

327

328 3.2.3. Selection of the diffusivity exponents (n and m)

329 In order to predict HOC mass transfer coefficients using Eq. (20) and Eq. (21), it is necessary
 330 to estimate or to fix the values for the exponents m and n . Several approaches for this
 331 estimation have been used in the literature, but, in general, they imply some assumptions that
 332 are difficult to test experimentally. For example, Hsieh et al. [11], Soltanali and Shams
 333 Hagani [26] and Munz and Roberts [13], assumed that both exponents are equal, due to the

334 uncertainty in their calculation and the lack of information regarding the parameters
335 influencing them. Additionally, the latter authors have found that the diffusivity exponents are
336 virtually independent of the mixing intensity. Moreover, some authors, such as
337 Chrysikopoulos et al. [33], Smith et al. [14] and Libra [34], have considered that the
338 diffusivity exponents depend on the type of compound. Since there is no consensus among the
339 authors, the values for these exponents were fixed according to the hydrodynamic conditions
340 at each side of the interface in this study. For the liquid side, the exponent n was fixed to 0.5,
341 which correspond to Higbie's penetration theory that is typically applied for turbulent regimes
342 [23]. In the case of the gas side, the mixing regime was not completely defined. Thus, the
343 exponent m was fixed to a value of 1, corresponding to the two-film theory [24].

344

345 **4. Results and discussion**

346 **4.1. HOC Henry's law constant**

347 To calculate the Henry's law constant by the method described in section 3.1.3, the compound
348 saturation concentration when the bubbles leave the liquid phase in the reactor need to be
349 reached. Given that it was not possible to measure the gas phase concentration for the
350 experiments performed in this study, indirect methods to ensure the bubble saturation were
351 used. A linear relation was observed between the slope for bubble volatilization experiments
352 tested (Sp^B) and the airflow rate at different mechanical power inputs (Figure S1). Likewise,
353 there is no significant effect of the mechanical power input on this parameter. These
354 corroborations allow to draw the conclusions that, for the three molecules tested in this
355 research work, saturation was reached [17] and that the bubble residence time was negligible
356 in comparison to the variation of C_L in time (Eq. (A.2)).

357 The results for the H_C calculation are reported in Table 3. The calculated values for the
358 Henry's law constant are within the range of those found in the literature, which further
359 confirms the hypothesis of the bubble saturation. Additionally, it is interesting to observe that
360 the Henry's law constants for HOCs presented in Table 3 show a wide range of values. This
361 might be due to the different experimental set-ups and conditions in which they have been
362 measured. Therefore, as H_C is a key parameter, it should be obtained experimentally whenever
363 possible.

364

365 *Table 3. Estimated Henry's law constants and comparison with literature values.*

| Compound | H_C estimated (-) | Range of experimental H_C reference values* |
|----------|---------------------|---|
|----------|---------------------|---|

| | | |
|--------------|-----------------------|---|
| Toluene | 1.78×10^{-1} | $1.46 \times 10^{-1} - 5.26 \times 10^{-1}$ |
| Naphthalene | 1.44×10^{-2} | $6.84 \times 10^{-3} - 3.16 \times 10^{-2}$ |
| Phenanthrene | 1.04×10^{-3} | $9.77 \times 10^{-4} - 2.56 \times 10^{-3}$ |

*According to the H_C compilation made by Sander [16]

4.2. Surface mass transfer

4.2.1. Oxygen and water

Figure 4 shows the results of the test performed to measure the influence of P_N/V on the surface mass transfer coefficients of oxygen ($k_L a_{O_2}^S$) and water ($k_G a_W^S$). These coefficients are positively correlated to P_N/V . In addition the trends in both cases follow a power-type curve fit, which is in accordance with the literature for many compounds [11,13,21]. However, for oxygen transfer, the power coefficient is five times higher than the one for water transfer.

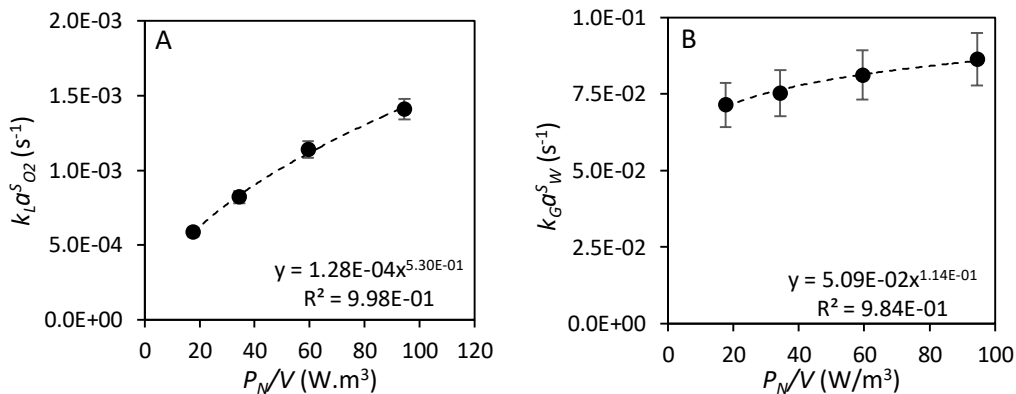


Figure 4. Influence of the power input on the surface mass transfer coefficient for (A) Oxygen and (B) Water.

The P_N/V increases can lead to two effects at the surface: (i) since the agitation is being directly applied to the liquid phase, it induces a faster surface renewal (or a decreased film thickness) at the liquid side of the surface; (ii) higher agitation produces an increase of the gas-liquid interfacial area due to surface deformation. This effect was visible to the naked eye in the reactor. Since oxygen is transferred from the gas phase to the liquid phase, both phenomena affect its transfer. However, the continuous liquid phase is constituted by water, which means that the water transfer occurs at gas side of the gas-liquid interface. Hence, the first effect does not have any consequence and only the gas-liquid interfacial area

388 modification is influencing this water transfer. These phenomena can explain the significant
 389 difference in the influence of the power input in the transfer of these two substances.
 390 Additionally, the exponent of the power relation for the oxygen transfer is in agreement with
 391 the results found by Hsieh et al. [11] for similar operating systems.

392

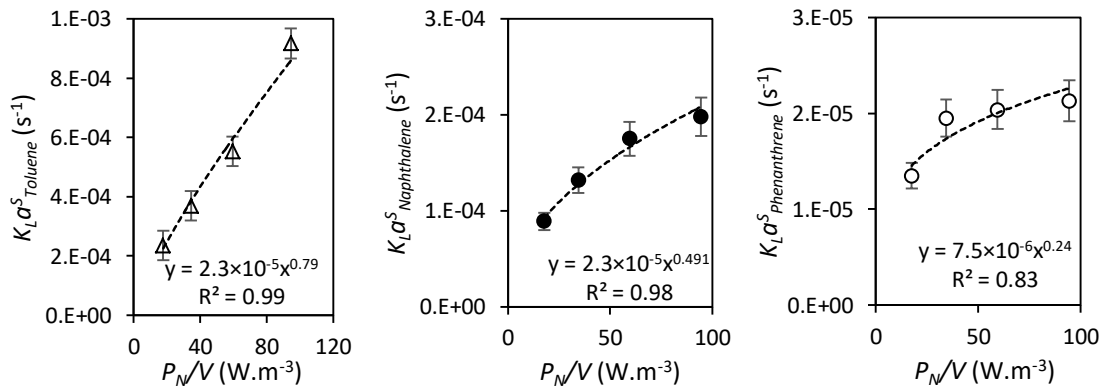
393 4.2.2. HOC

394 In the same way as for water and oxygen transfer, the surface volatilization coefficient of
 395 HOCs depends on the power input. The relation between P_N/V and the mass transfer
 396 coefficient ($K_L a_{HOC}^S$) can be assimilated to a power model in the range of P_N/V tested in this
 397 study (Figure 5).

$$K_L a_{HOC}^S = B \left(\frac{P_N}{V} \right)^p \quad (22)$$

398 Where B and p are empirical constant values.

399



400

401 *Figure 5. Influence of power input on the surface mass transfer coefficient for (Δ) Toluene, (\bullet) Naphthalene and*
 402 *(\circ) Phenanthrene*

403 Moreover, a linear positive dependence of p and the natural logarithm of H_C of the HOCs can
 404 be established (Figure 6). This can be explained by the effect of P_N/V on the mass transfer

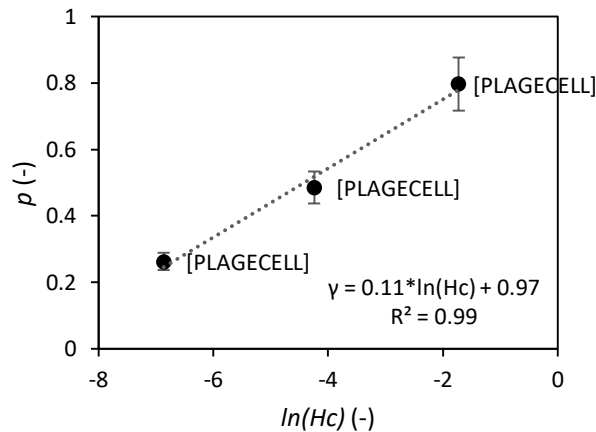
405 coefficient of the liquid side of the interface. In fact, P_N/V has a direct impact on the liquid

406 side and increases at a higher extent the overall mass transfer coefficient of the more volatile

407 compounds. Thus, the volatilization of semi-volatile compounds is less affected by P_N/V ,

408 because the gas-side transfer resistance is comparable or higher than the liquid-side transfer

409 resistance ($R_G \approx R_L$). The correlation proposed in Figure 6 can be used to estimate the extent
410 of the impact of the power input on the volatilization rate for HOCs.



411
412

Figure 6. Correlation between p and $\ln(H_C)$.

413 It is interesting to notice that the p value is higher for toluene than for oxygen, which is
414 probably due to changes in the surface properties of the toluene solution. However, further
415 research is needed on the impact of the modification of surface properties on the film
416 resistances and the mass transfer.

417

418 4.3. Modeling of surface HOC mass transfer coefficient

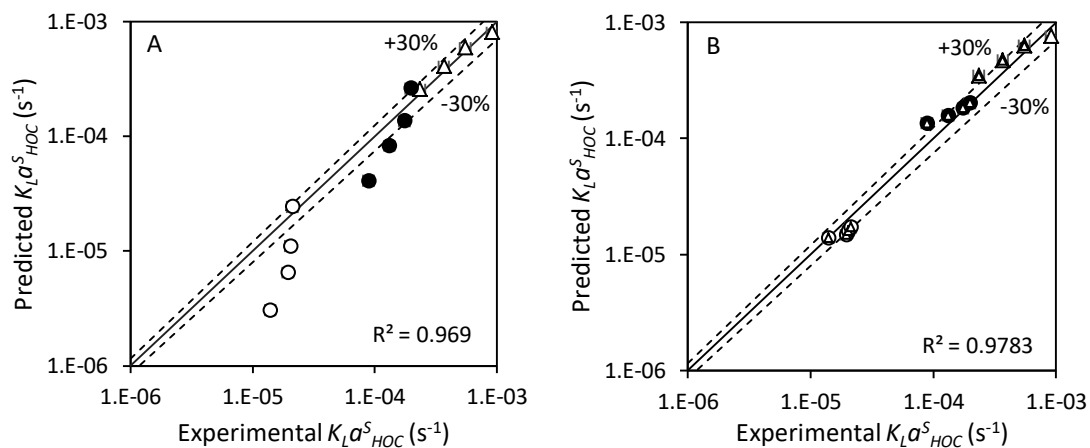
419 The two previously presented models (PCM and 2RCM) were tested employing the
420 experimental data obtained for the surface transfer of HOCs, water and oxygen.

421 The PCM required the use of oxygen as the only reference compound makes possible to
422 neglect the resistance in the gas phase for the reference compound (due to the high H_C value
423 for oxygen). For this model, the ratio of individual volumetric mass transfer coefficients for
424 the oxygen ($k_G a_{O_2}^S / k_L a_{O_2}^S$) is estimated. Since each individual mass transfer coefficient is
425 influenced differently by the mixing in the reactor, their ratio changes with a variation of
426 P_N/V . Therefore, the estimation was made assuming one $k_G a_{O_2}^S / k_L a_{O_2}^S$ for each considered

427 P_N/V .

428 The 2RCM is a more general approach than the PCM for the volatilization modeling of semi-
429 volatile substances [26]. To test the 2RCM, oxygen and water were used as reference
430 compounds for the liquid-side and gas-side mass transfer resistance, respectively. No
431 parameters need to be estimated using this model, since both individual mass transfer
432 coefficient were calculated experimentally, and the diffusivity exponents were fixed.

433 Figure 7 shows the correlation between the experimental and the calculated values for the
 434 overall mass transfer coefficient of the three HOCs tested in this study for the PCM and the
 435 2RCM. The PCM fits rather well to the most volatile compound (toluene), but much higher
 436 error values are obtained for the least volatile ones (naphthalene and phenanthrene).
 437 Moreover, the plot between the calculated and the experimental overall mass transfer
 438 coefficients presents a good correlation ($R^2 = 0.96$). On the other hand, the 2RCM model fits
 439 much better for naphthalene and phenanthrene, but the difference between the experimental
 440 and estimated $K_L a_{HOC}^S$ increase for toluene. Additionally, the goodness of fit is slightly better
 441 than that of the PCM ($R^2 = 0.978$) and most values are within the 30% error. This means that
 442 the 2RCM seems to predict better the overall mass transfer coefficient for the three substances
 443 tested. In addition this result shows that depending on the P_N/V value and thus on the
 444 hydrodynamic conditions the error can vary.



445
 446 *Figure 7. HOC mass transfer coefficients correlation for: (A) the PCM; and (B) the 2RCM; for (Δ) Toluene, (\bullet)*
 447 *Naphthalene and (\square) Phenanthrene in logarithmic scale.*

448 In terms of reference compounds, most authors have used the PCM model due to the
 449 convenience of utilizing oxygen as the only reference compound. Thus, very few studies have
 450 used other substances as reference compounds, much less for estimating the gas-side mass
 451 transfer coefficient. Monteith et al. [35] suggested the use of ammonia for this purpose due to
 452 its low Henry's law constant, but the ionization of this compound in water and the influence
 453 of pH on the mass transfer may complicate the experiments and the analytical processing of
 454 the data. In fact, high ion concentrations and changes in surface tension can modify the mass
 455 transfer coefficient of any compound [36]. In the present paper, we chose to use water as a
 456 reference compound for the surface mass transfer of semi-volatile compounds. This choice
 457 was based on the following advantages (Smith et al. [14]): i) its transfer has virtually no

458 resistance in liquid-phase film; ii) the measurement of water concentration in the gas phase is
 459 relatively easy to perform; and iii) it is an economic and fast method to obtain information for
 460 the gas-side mass transfer.

461 Besides, using Eq. (15) and taking water as a reference compound, it is possible to obtain the
 462 gas-side oxygen mass transfer coefficient ($k_G a_{O_2}^S$) and, thus, to obtain the ratio of individual
 463 oxygen mass transfer coefficients ($k_G a_{O_2}^S / k_L a_{O_2}^S$) by a simple calculation. The estimated
 464 $k_G a_{O_2}^S / k_L a_{O_2}^S$ values for the PCM were then compared to the calculated ones using the 2RCM
 465 model (Table 4). It is important to highlight that the values obtained by both methods are in
 466 the same order of magnitude of those found by Munz and Roberts [13], but much lower than
 467 those found by Hsieh et al. [11]. This can be explained by the different geometry and the
 468 hydrodynamic properties of the reactor in both phases.

469 Moreover, the calculated ratio decreases as the mixing intensity augments. Considering that
 470 the P_N/V was directly applied to the liquid phase and that the gas phase was fed with the same
 471 Q_G throughout all the experiments, the obtained relation seems quite logical. In fact, when
 472 P_N/V increases, the renewal rate at the liquid interface augments, increasing the individual
 473 oxygen mass transfer coefficient in the liquid phase (k_L), while the flow properties in the gas-
 474 side of the interface remains almost unchanged. This can be translated in less important k_G
 475 variations in comparison with k_L variations, particularly for oxygen since its transfer is liquid-
 476 phase controlled. Consequently, $k_G a_{O_2}^S / k_L a_{O_2}^S$ decreases when P_N/V increases.

477 However, for the ratio estimated using the PCM, the ratio increase with P_N/V . This trend
 478 contradicts the results calculated using water as reference compound and it is a direct
 479 consequence of using semi-volatile compounds for fitting the PCM using oxygen. Indeed,
 480 small changes in the gas-phase film can highly influence the transfer of semi-volatile
 481 compounds and this cannot be taken into account by the PCM with oxygen as the sole
 482 reference compound, distorting the relation between power input and $k_G a_{O_2}^S / k_L a_{O_2}^S$.

483

484 *Table 4. $k_G a_{O_2}^S / k_L a_{O_2}^S$ ratio calculated using water as reference compound and estimated for the PCM and*
 485 *calculated*

| $\frac{P_N}{V}$ (W.m ⁻³) | $k_G a_{O_2}^S / k_L a_{O_2}^S$ (-) | |
|--------------------------------------|-------------------------------------|------------|
| | Estimated by the PCM | Calculated |
| | | |

| | | |
|-------|------|------|
| 17.65 | 15.8 | 74.1 |
| 34.37 | 24.1 | 55.9 |
| 59.47 | 29.7 | 43.4 |
| 94.52 | 53.5 | 37.3 |

486

487 In addition, with the purpose of testing the hypothesis made previously on the exponent
 488 values $n = 0.5$ and $m = 1$ and since the 2RCM does not requires the fitting of any parameter,
 489 an estimation of both n and m was done using this model with a minimization of the sum of
 490 the squared errors between the calculated and the experimental mass transfer coefficients. As
 491 a result, the best fitting for n and m was found for values of 0.53 and 1.01, respectively ($R^2 =$
 492 0.98). This confirms the hypothesis behind the choice of these parameter values.

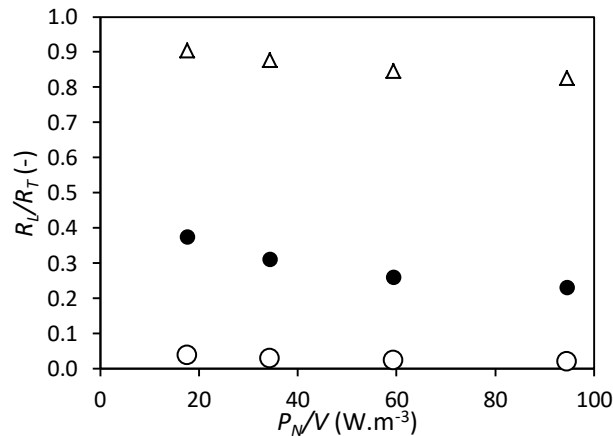
493

494 **4.4. (Semi-)Volatile nature of HOCs**

495 Many authors consider that the “volatile” characteristic of a dissolved compound in terms of
 496 mass transfer is mainly given by its Henry’s law constant. Although there is no definitive
 497 consensus on the matter, in general, compounds with $H_C \geq 0.19$ are considered volatile and
 498 thus their mass transfer is considered to be liquid-phase controlled [37]. Besides, some
 499 authors consider that the liquid-side resistance is only completely negligible for compounds
 500 with $H_C \geq 0.55$ [26]. According to these definitions, toluene is placed around the limit of the
 501 “volatile” category ($H_C = 0.178$). Low-molecular-weight PAHs (i.e. naphthalene and
 502 phenanthrene) are generally considered “semi-volatile” compounds [14,38], presenting a
 503 much more important gas-phase resistance [39]. Nevertheless, some authors also consider
 504 naphthalene as a volatile compound [11,40]. This proves that the limit between the two
 505 categories is not well-defined, mainly because the rate of volatilization of a dissolved
 506 compound does not only depends on H_C , but also on the hydrodynamic properties of the
 507 phases where the transfer occurs as highlighted by the present study.

508 Using the results of the 2RCM, the relative liquid resistance (R_L/R_T) for each molecule as a
 509 function of P_N/V was calculated. This parameter represents the proportion of the total mass
 510 transfer resistance that is due to the liquid-phase transfer resistance. The calculation is based
 511 on Eq. (8) and the results are depicted in Figure 8. For toluene, more than 90% of the
 512 resistance correspond to the liquid side, which admits classifying it as a “volatile” compound,
 513 as expected. On the other hand, phenanthrene (less than 10% of liquid-side resistance) and
 514 naphthalene (between 20% and 40% liquid-side resistance) can be confirmed as “semi-
 515 volatile” substances at the conditions tested in this study. This means that, since three

516 substances tested are comprised within a wide R_L/R_T range, the conclusions of this research
517 work may be applicable to most volatile and semi-volatile substances.



518

519 *Figure 8. Relative liquid resistance for (Δ) Toluene, (\bullet) Naphthalene and (\circ) Phenanthrene*

520

521 **4.5. Relevance and limitations of the models**

522 Traditionally, in VOCs surface volatilization and stripping modeling, the gas-side resistance is
523 considered negligible [4,6]. However, this assumption is not always correct because of the
524 variability of the “volatile” condition of the compounds according to the process
525 characteristics and its operating conditions as highlighted by the present study. Therefore, for
526 semi-volatile compounds, using models that consider the gas-side resistance is a better option.
527 Moreover, in many aerobic processes, oxygen represents a useful reference compound.
528 Indeed, numerous oxygen mass transfer measurements methods and scale-up correlations
529 based on oxygen exist in the literature [21]. Thus, the PCM, usually based on this molecule, is
530 one of the most frequently used in the literature. Although the use of only one reference
531 compound is an easy and practical way to calculate the mass transfer coefficient of other
532 compounds, this method has several limitations. For example, only the parameters affecting
533 exclusively the liquid phase are considered (since the gas-side resistance is negligible for this
534 compound). In addition, several parameters should be either assumed or estimated for the
535 specific system, i.e. the ratio of individual mass transfer coefficient and the exponents of the
536 liquid and gas diffusivity ratio. Hsieh et al. [11] explain that the mass transfer coefficient ratio
537 is generally assumed to be ranged between 50 and 300 (with an average of 150), which is a
538 wide range. Besides, this parameter varies according to the hydrodynamic conditions as
539 shown in section 4.3. In the same way, the values of m and n can significantly vary. All this
540 may lead to wrong estimations of the mass transfer coefficient.

541 One may reduce the uncertainties or the estimations errors by developing an approach to
542 calculate the gas-side resistance using the 2RCM. By directly estimating the individual mass
543 transfer coefficients with the help of two reference compounds, this model leads to a more
544 robust way to obtain the gas-liquid mass transfer coefficient of any compound, volatile or not.
545 This research work has proved that, for surface volatilization, the use of water as a reference
546 compound produces better results than the traditional PCM for semi-VOCs. The use of the
547 2RCM avoids the introduction of errors associated to assumptions made for the ratio of
548 individual mass transfer coefficients. Knowing both oxygen and water transfer behaviors in
549 the system allows accounting for liquid-film and gas-film changes, respectively. Moreover, by
550 means of simple equipment, basic experiments on water transfer can be performed in almost
551 any system to obtain the necessary information regarding the gas-side resistance. This implies
552 that, if the reference compounds' gas-liquid transfer is characterized, the transfer of any
553 volatile or semi-volatile compound can be obtained by extrapolation.

554 In this sense, the approach proposed in this paper can be used in wastewater treatment plants,
555 slurry reactors, soil washing processes or any process in which HOC volatilization is non-
556 negligible to quantify the gas-liquid mass transfer of compounds susceptible to volatilize.
557 Nonetheless, the major limitation of this practice is that air saturation can be reached easily
558 and rapidly, especially in systems with low or no gas-phase circulation. The same limitation
559 applies for aerated systems using bubble diffusers within the liquid phase in which, depending
560 on the bubble size and the physicochemical properties of the compound, few centimeters may
561 be sufficient to reach the mass transfer equilibrium. For these cases, a similar approach, but
562 using other substances allowing higher equilibrium concentrations in the gas phase can be
563 used.

564 It is important to highlight that the extrapolation of the results of this paper for larger scales
565 should be considered thoroughly regarding the specific conditions of the mass transfer. For
566 instance, in large tanks open to the atmosphere, gas-side mass transfer at the surface will be
567 largely controlled by the wind action, which will not be necessarily homogeneous along the
568 surface of the reactor. Moreover, theoretical expressions proposed in Table 1, in which the
569 models studied in this article are based allow an accurate representation of the mass transfer
570 phenomena in conditions similar to the reactor condition. However, in the case of fully
571 turbulent gas-films, modifications to the theoretical expressions should be included (e.g.
572 eddies dynamics in the interfacial layer), which would produce complex correlations between
573 the diffusivity and the k_{Ga} , hindering the application of the 2RCM [41,42].

574 **5. Conclusions**

575 On one hand, this study demonstrated the impact of the mechanical power input (P_N/V) on
576 the surface volatilization. A power-type correlation was found between water, oxygen and
577 HOC surface overall mass transfer coefficients and P_N/V . A correlation between the Henry's
578 law constant and the exponent of the mentioned power-type correlation for the HOCs was
579 established. These correlations can be used to estimate the extent of the impact of P_N/V on the
580 volatilization rate for HOCs.

581 On the other hand, the role of the reference compounds on the modeling of the mass transfer
582 coefficient on volatile and semi-volatile compounds has been clarified. The 2RCM can predict
583 the gas-liquid mass transfer coefficient with a reasonable error using only the hypothesis for
584 fixing the diffusivity n and m . In addition, the use of the 2RCM avoids the error introduced
585 by the estimation of the ratio of individual mass transfer coefficients if the PCM is used for
586 semi-VOCs. This means that the former is preferable for the cases where a reference
587 compound with gas-side controlled mass transfer can be used, due to its higher robustness and
588 its extrapolatable characteristics regarding hydrodynamic changes in both gas-side and liquid-
589 side interfaces.

590

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596

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723

724 **Appendix A. Theoretical considerations for Henry's law constant determination**

725 The mass transfer rate by bubble volatilization is given by Eq. (A.1.) In this case, the transfer
 726 area is the interface between the dispersed bubbles in the liquid phase and the liquid phase
 727 itself (A_B).

$$V_G \frac{dC_G}{dt} = K_L A^B (C_L^{*,B} - C_L) \quad (\text{A.1})$$

728 Where V_G the total gas phase volume in the bubbles and the superscript is B refers to bubbles.
 729 Under certain conditions, it is possible to assume that the variation of C_L is negligible in
 730 relation to the variation of C_G inside a single bubble rising through the reactor. Therefore, C_L
 731 can be considered constant for the integration of Eq. (A.1). Then, using Eq. (3) and
 732 integrating in time from the moment in which a bubble enters into the reactor ($C_G = 0$) to the
 733 moment it exits ($C_G = C_G^{out}$) (i.e. the gas residence time) and for all the bubbles dispersed in
 734 the gas phase, Eq. (A.2) is obtained.

$$\ln \left| 1 - \frac{C_G^{out}}{H_C \cdot C_L} \right| = - \frac{K_L \alpha^B V_L}{H_C V_G} t_r \quad (\text{A.2})$$

736
 737 Where t_r is the residence time of the gas in the reactor and is defined as $t_r = \frac{V_G}{Q_G}$. If Eq. (A.2)
 738 is rearranged by using the relations established in Eq. (A.3) derived from Henry's law (which
 739 defines the saturation degree), it is possible to obtain the concentration of the desired
 740 compound in the bubble when it reaches the surface of the liquid as a function of the mass
 741 transfer coefficient, the Henry's law constant and the operational parameters of the reactor V_L
 742 and Q_G (Eq. (A.4)).

$$\frac{C_G^{out}}{C_G^{*,B}} = S_d \quad (\text{A.3})$$

$$S_d = 1 - e^{-\frac{K_L \alpha^B V_L}{H_C Q_G}} \quad (\text{A.4})$$

743
 744 According to Matter-Müller et al. [36], a mass balance in the liquid phase of a reactor in
 745 which only bubble volatilization occurs would lead to Eq. (A.5). Invoking Henry's law (Eq.
 746 (3)) and using Eq. (A.3) it is possible to obtain Eq. (A.6).

$$V_L \frac{dC_L}{dt} = -Q_G C_G^{out} \quad (\text{A.5})$$

$$C_G^{out} = S_d H_C C_L \quad (\text{A.6})$$

747

748 By combining and rearranging Eq. (A.5) and Eq. (A.6), it is possible to obtain Eq. (A.7).
 749 Then, if the concentration of the volatile compound in the liquid phase is recorded in time, a
 750 first order curve may be plotted, from which it can be possible to calculate the saturation
 751 degree and, hence, the diffused mass transfer coefficient. A linear correlation may be found
 752 between the natural logarithm of the normalized concentration of the volatilized product and
 753 time, and the slope of this correlation, Sp^B , can be defined by Eq. (A.8).

$$\frac{dC_L}{dt} = - \left(\frac{Q_G H_C}{V_L} S_d \right) C_L \quad (\text{A.7})$$

$$Sp^B = - \frac{Q_G H_C}{V_L} S_d \quad (\text{A.8})$$

754

755 Hsieh et al. [36] consider three cases regarding the saturation degree in the bubble: i) when
 756 $S_d \leq 0.1$, the slope, Sp^B is approximately equal to the bubble mass transfer coefficient; ii)
 757 when $S_d \geq 0.99$, the bubbles exit the liquid phase near saturation and the slope will
 758 approximate $-\frac{Q_G H_C}{V_L}$ and iii) when $0.1 \geq S_d \geq 0.99$, the mass transfer coefficient can be
 759 calculated using the expressions in Eq. (A.4) and Eq. (A.8). When bubble saturation (case ii)
 760 is reached in a range of air flows, a linear correlation between Sp^B and Q_G can be obtained
 761 and, using the slope of this correlation, it is possible to calculate accurately the Henry's law
 762 constant of a particular compound using Eq. (A.8) and assuming $S_d = 1$ [17].

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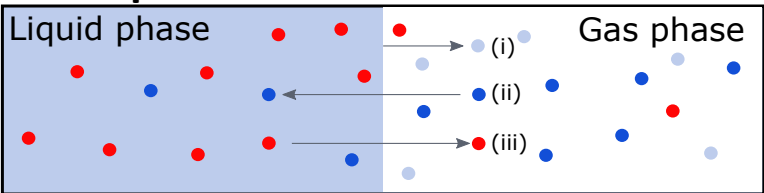
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Gas-liquid mass transfer



Resistance to transfer:

- Water - Gas side
- Oxygen - Liquid side
- HOC - Both sides



Volatilization modeling

PC model

2RC model



- Reference compounds
- ✓ Performance for: Volatile
- ✗ Performance for: Semi-volatile

Reference compounds

Performance for:

Volatile

Semi-volatile

- Reference compounds
- ✓ Performance for: Volatile
- ✓ Performance for: Semi-volatile

$$\psi = \frac{K_L a_{HOC}^S}{K_L a_{O_2}^S} = \frac{1}{\frac{1}{\left(\frac{D_{L,HOC}}{D_{L,O_2}}\right)^n} + \frac{1}{H_C (k_G a_{O_2}^S / k_L a_{O_2}^S) \left(\frac{D_{G,HOC}}{D_{G,O_2}}\right)^m}}$$

$$\frac{1}{K_L a_{HOC}^S} = \frac{1}{k_L a_{O_2}^S \left(\frac{D_{L,HOC}}{D_{L,O_2}}\right)^n} + \frac{1}{H_C k_G a_W^S \left(\frac{D_{G,HOC}}{D_{G,W}}\right)^m}$$