Sensitivity analysis of the WATER9 model: emissions of odorous compounds from passive liquid surfaces present in wastewater treatment plants

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ABSTRACT

Empirical mathematical models have been frequently used to estimate emissions and to act in the prevention of possible impacts from odorous compounds. Based on the regulatory WATER9 model, the present study had the aim to evaluate the deviations originating from the simplification of using the effective diameter (in contrast to the conceptually appropriate use of the linear physical fetch) as fetch parameter in the calculation of the global mass transfer coefficient at passive liquid surfaces at wastewater treatment plants (WWTPs). The present analysis incorporated the influence of different values of wind velocity, molecular diffusivity and Henry's Law constant. The analyses for the calculation of the mass transfer coefficients were developed for 1,000 wind speeds, chosen using the Monte Carlo method, three WWTPs and three compounds of environmental relevance, spanning different behaviour regarding their volatilisation. The wind speed had a direct influence on the deviations for all types of compounds analysed. However, this parameter was found to be more representative for the compounds whose volatilisation is limited by conditions in the liquid phase. Furthermore, the deviations for the calculation of the mass transfer coefficient arising from the use of the effective diameter as fetch parameter were significantly larger for liquid phase-dominated compounds, compared to gas phase-dominated compounds. Comparison against available experimental data confirm that the use of the effective diameter as the fetch parameter makes the model predictions further depart from the experimental values. The present analysis shows that, for a varied range of wind speed and WWTP configurations, the use of the actual physical fetch shall be preferred over the use of the effective diameter in emission models for WWTPs, so as to avoid the introduction of potentially large systematic deviations.

Key words | fetch parameter, Monte Carlo method, odour emissions, WATER9 model

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INTRODUCTION

The increase of atmospheric pollution and the preventive environmental legislation have boosted the implementation of mechanisms of control by the companies potentially polluting. Environmental sanitation projects, such as industrial and domestic effluent treatment systems, are one of the main urban sources of odorous gas emissions. As a result of increasing urbanization and population growth, wastewater treatment plants (WWTPs), which once offered a large transitional area away from urban centres, are now having a smaller territorial zone between them and the surrounding communities, leading to a high level of annoyance due to the emission of odours (Santos *et al.* 2012). One of the main sources of emissions in WWTPs are the liquid surfaces open to the atmosphere such as sedimentation tanks (primary and secondary), equalization tanks, sequential batch reactors, aerated biological filters and stabilization ponds (Santos *et al.* 2012).

In view of this fact, the use and development of mathematical models to evaluate the impact of odorous emissions have been proposed in order to assist in assessing and minimizing the impacts caused by WWTPs (Atasoy *et al.* 2004; Blunden *et al.* 2008; Cheng *et al.* 2008; Rumburg

et al. 2008; Yang *et al.* 2012; Glaz *et al.* 2016). The most widely applied empirical models of odorous emissions, WATER9 (US EPA 1994, 2001), TOXCHEM + (ENVIROMEGA 2003) and the model proposed by Gostelow *et al.* (2001), allow the estimation, through mass balance, of emissions from these polluting sources considering the characteristics of the liquid (effluent) and gaseous phases. These models are important alternatives for estimating emission rates even during the planning phase of WWTP construction or for a fast and low cost assessment of existing facilities (Santos *et al.* 2009). In addition to this, the empirical models allow the determination of emission values without the need for direct measurements from the sources, which present higher expenses due to the necessity of using materials and labour for analyses. However, there are issues related to the accuracy and representativeness of these models. As pointed out by Prata *et al.* (2016), the difficulties in improving the accuracy of the values calculated by empirical emission models are related to three main factors: the number of variables that may be involved in the modelling; the complex relationships that may exist between them; and the diversity of points that need further investigation at different levels.

In relation to the regulatory model WATER9, the possible deviations related to the calculation of the emission rate of odorous compounds may be related to the use of different expressions by the model. The mathematical expressions are based on three different references: Mackay & Matsugu (1973), Mackay & Yeun (1983) and Springer *et al.* (1984). The experiments considered by these references, for example wind tunnel tank experiments and laboratory scale evaporation tests, consisted of different systems, components and sometimes different theoretical foundations. The procedures used by the WATER9 model to estimate the individual mass transfer coefficients rely mainly on existing mass transfer correlations extrapolated for general application.

For passive liquid surfaces, the total emission per unit time E (kg s^{-1}) of the entire exposed area is estimated by the following equation (US EPA 1994):

$$E = K_L A C_L \tag{1}$$

where K_L is the liquid-phase overall mass transfer coefficient (m s^{-1}); A is the surface area and C_L is the compound concentration (kg m^{-3}) in the liquid phase.

In the two-resistance model considered by WATER9, the inverse overall mass transfer coefficient K_L is a summation of $1/k_L$ and $1/k_G K_H$, which represent, respectively, the resistances to mass transfer associated to the liquid

and gas films/boundary layers adjacent to the gas-liquid interface (US EPA 1994):

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_G K_H} \tag{2}$$

where k_L and k_G are the liquid-film and the gas-film mass transfer coefficients (m s^{-1}), respectively. Table SM1 in the Supplementary Material (available with the online version of this paper) presents the expressions used in the WATER9 model for calculations of the mass transfer coefficients in the liquid and gas phases.

Prata *et al.* (2016) investigated how the mass transfer coefficients calculated by WATER9 for passive liquid surfaces are affected by the choice of the fetch parameter, which constitutes one of the input variables for the model. Physically, the fetch parameter is defined as the linear distance along the liquid surface in the direction of the wind flow; this is the definition considered for the derivation of the empirical equations adopted by the model. However, the approach implemented in WATER9 to calculate the mass transfer coefficients uses as fetch parameter the value of the effective diameter d_e, which represents the diameter of a circular surface with the same area A as the liquid surface being analysed ($d_e = (4A/\pi)^{0.5}$). The use of the fetch parameter by the WATER9 model does not correspond to the definition originally associated with the applied empirical equations and introduces a systematic deviation in the values of the calculated mass transfer coefficients. The study by Prata *et al.* (2016) concluded that, for the WATER9 model, significant deviations in the values of mass transfer coefficients in the liquid and gaseous phases may occur due to the adoption of the effective diameter as the fetch parameter. These authors also point out that such deviations in the mass transfer coefficients vary as a function of wind speed. In addition, deviations in the overall mass transfer coefficient will be dependent, among other factors, on how volatile the compounds are (indicated by the Henry's Law constant) and on the molecular diffusivity of each compound. The preliminary evaluation presented by Prata *et al.* (2016) contemplated only one compound, benzene, and three values of wind speed.

Considering the potential benefits of emissions models, it is highly desirable to investigate possible impacts and the subsequent proposal of feasible improvements. From these considerations and with focus on the WATER9 model, proposed by the United States Environmental Protection Agency (US EPA), the aim of the present study was to evaluate the deviations introduced by the use of the effective diameter as the fetch parameter (in contrast to

the conceptually appropriate use of the linear physical fetch) in the calculation of the global mass transfer coefficient for passive liquid surfaces at WWTPs for three different compounds: hydrogen sulfide, ammonia and acetic acid. In particular, this analysis incorporated the influence of different values of wind speed, generated obeying a uniform distribution, using the Monte Carlo method. The impact of adopting the effective diameter as the fetch parameter was also assessed based on mass transfer data compiled from the literature.

METHODOLOGY

The sensitivity of the WATER9 model with respect to the choice of fetch parameter was evaluated by analysing the differences in the values of the overall mass transfer coefficient (K_L) for passive liquid surfaces calculated by the model, comparing the two approaches for choosing the fetch: using the physical fetch (length or width of the tanks, depending on the orientation of the wind), or adopting the effective diameter as fetch. The comparison was made for several units with geometrical characteristics of actual WWTPs, for a range of values of wind speed (produced via the Monte Carlo method), and three different compounds that represent different behaviours in terms of phase-dependence of the volatilisation process, as explained further on.

Selection of WWTPs

In order to evaluate the influence of the use of the effective diameter as a fetch parameter in the calculation of the values of k_L and k_G by the WATER9 model, the sensitivity analysis was performed using the dimensions of real units in three WWTPs in New South Wales, Australia. The selected plants for this work were: WWTP 1 – Bathurst Sewage Treatment Plant (operated by Bathurst Regional Council); WWTP 2 – Kincumber Water Quality Control Centre (operated by Gosford City Council); WWTP 3 – Young Sewage Treatment Plant (operated by Young Shire Council). All rectangular (or approximately rectangular) open surface units were considered for analysis, including final effluent balance ponds (which are not normally a source of odours) and aeration basins (non-passive liquid surfaces). The reason for the inclusion of such surfaces is due to the fact that in some situations, such as the poor quality of the final effluent or malfunctioning of the aeration system, these surfaces can behave as passive sources of odours.

Table 1 shows the geometric data of the evaluated units of each WWTP in terms of length (L), width (W) and depth (D). The respective aspect ratios, areas, effective diameters and fetch-to-depth ratios (F/D) are also presented, considering the different fetch parameter choices (length, width or effective diameter).

Table 1 | Geometric characteristics of liquid surfaces for each WWTP

| Units | | | Dimensions | | | | | | F/D ratio | | | d_e/F ratio | |
	No.	Identification	L (m)	W (m)	D (m)	$r = L/W$	A (m²)	d_e (m)	L/D	W/D	d_e/D	d_e/L	d_e/W
WWTP 1	1	Anaerobic chamber	5.0	4.0	4.5	1.3	20.0	5.0	1.1	0.9	1.1	1.0	1.3
	2	IDEA tank – min[a]	37.5	12.5	3.2	3.0	468.8	24.4	11.7	3.9	7.6	0.7	2.0
	3	IDEA tank – min[a]	69.0	31.5	3.20	2.2	2,173.5	52.6	21.6	9.8	16.4	0.8	1.7
	4	IDEA tank – max[b]	69.0	31.5	4.27	2.2	2,173.5	52.6	16.2	7.4	12.3	0.8	1.7
	5	Balance pond, shallow section – max[b]	107.2	60.6	2.21	1.8	6,492.5	90.9	48.5	27.4	41.1	0.8	1.5
WWTP 2	1	Primary sedimentation tank	61.2	22.6	2.58	2.7	1,383.1	42.0	23.7	8.8	16.3	0.7	1.9
	2	Aeration tank, anoxic zone	70.8	6.0	4.83	11.8	424.5	23.2	14.7	1.2	4.8	0.3	3.9
	3	Aeration tank, anoxic/aerobic zone	74.6	6.0	4.77	12.4	447.6	23.9	15.6	1.3	5.0	0.3	4.0
	4	Aeration tank, aerobic zone	74.6	12.8	4.53	5.8	954.9	34.9	16.5	2.8	7.7	0.5	2.7
WWTP 3	1	Sludge lagoon	45.6	32.7	3.6	1.4	1,436.7	43.6	12.7	9.1	12.1	0.9	1.3
	2	IDEA tank – min[a]	61.8	24.3	3.5	2.5	1,475.0	43.7	17.7	6.9	12.5	0.7	1.8
	3	IDEA tank – max[b]	61.8	24.3	4.0	2.5	1,475.0	43.7	15.4	6.0	10.9	0.7	1.8
	4	Balance pond	65.4	28.7	2.0	2.3	1,818.3	48.9	33.5	14.7	25.1	0.7	1.7

L, W and D indicate the length, width and depth of the tanks respectively; r the aspect ratio; A the surface area; d_e the effective diameter; and F the fetch parameter.
[a]min – denotes the minimum water level in the unit.
[b]max – denotes the maximum water level in the unit.

Inclusion of wind speed in the sensitivity analysis

Liquid-gas mass transfer from passive liquid surfaces greatly depends on the wind shear and associated disturbances at the gas-liquid interface; hence, the wind speed is typically one of the main input variables used to model emissions from such surfaces (see review in Prata *et al.* (2018)). The effect of wind on emissions is related to the level of turbulence within the gas phase and the liquid phase, including the formation of waves. The turbulence, in turn, directly affects the values of the mass transfer coefficients k_L and k_G.

Since the wind speed is one of the input variables for the WATER9 model, the deviations in the values of mass transfer coefficients due to the adoption of the effective diameter as the fetch parameter will also vary with the wind speed, as mentioned before. The Monte Carlo method was employed in order to include the variation of wind speed in the present sensitivity analysis. A sample of 1,000 random wind velocities (U_{10}) (reference at 10 m height), between 3.25 m s^{-1} and 15 m s^{-1}, was generated obeying a uniform distribution. The Matlab® routine used for the generation of the wind speeds is attached in the Supplementary Material (available with the online version of this paper). The minimum wind speed was determined according to the wind velocity ranges proposed by the WATER9 model. The Springer *et al.* (1984) model, incorporated by WATER9, implies that k_L is constant for wind speeds in the range of 0 to 3.25 m s^{-1}; therefore, values below 3.25 m s^{-1} do not influence the deviations of results for the mass transfer coefficients in the liquid phase and also do not depend on the F/D ratio, focus of this work. The wind speed of 15 m s^{-1} was considered reasonable for a maximum limit value to be evaluated in the sensitivity analysis, since the occurrence of wind speeds above this value is atypical for the region where the plants are located.

Analysis with different compounds of environmental relevance

The compounds were selected based on the significance of their impacts in relation to the odours from WWTPs and their different behaviours with respect to the volatilization process. The phase dominance of the compound, influenced by the Henry constant value, has a direct effect on the result of the global mass transfer coefficient (K_L) and how significantly it will be influenced by the formulations used to calculate the mass transfer coefficients in the liquid and gaseous phases. For highly volatile compounds, K_L is dominated by the transport conditions in the liquid phase; for poorly volatile compounds, K_L is dominated by the gas phase. Compounds with dominance in the liquid phase have the global mass transfer coefficient approximated by the value of k_L; on the other hand, for compounds dominated by the gas phase, the global coefficient is approximated by $k_G K_H$. For the analysis of the sensitivity of the WATER9 model to different fetch parameter choices, three potentially odour-causing substances were evaluated and divided into the following categories: 1. Compound dominated by liquid phase, represented by hydrogen sulfide; 2. compound dominated by the gas phase, represented by acetic acid; and 3. compound with dominance in both phases, represented by ammonia. Table SM2 in the Supplementary Material (available online) presents the respective values of the Henry's Law constant (dimensionless) and diffusivity in air and water (m² s^{-1}) for the compounds adopted for the analysis.

Calculation of mass transfer coefficients and sensitivity analysis

The mass transfer coefficients were calculated following the equations, the wind speed ranges and fetch-to-depth ratio adopted by WATER9 (see Introduction and Supplementary Material, Table SM1). From the WWTP geometries, the coefficients were estimated considering the cases with the wind aligned to the length and to the width of the surfaces, for which L and W constitute the physical fetch parameter, respectively. The coefficients were also estimated assuming the effective diameter as the fetch parameter, resulting in altered values, k'_L, k'_G and K'_L. From these results, it was possible to calculate the relative deviation values for the mass transfer coefficients in the liquid phase $(k'_L - k_L)/k_L$, in the gas phase $(k'_G - k_G)/k_G$ and for the overall mass transfer coefficient $(K'_L - K_L)/K_L$.

This same analysis was repeated for each compound for each of the 1,000 random wind speed values. The additional parameters used as input for the estimation of the mass transfer coefficients were kinematic viscosity of air and water, and diffusivity of ethyl ether in water. The ethyl ether was chosen by Springer *et al.* (1984) for the desorption rate measurements and included in the equation that they proposed. The values adopted are listed in Table SM3 in the Supplementary Material (available online).

RESULTS AND DISCUSSION

The values of the individual coefficients k_L and k_G were calculated following the formulations proposed by the

WATER9 model, for two alternatives of wind direction: in the length direction (fetch = L) and in the width direction (fetch = W). k_L and k_G were also calculated using the effective diameter as the fetch parameter. For each choice of the fetch parameter, the F/D ratios were calculated by dividing the fetch parameter chosen by the depth of the tank. The overall coefficient was estimated for each case by Equation (2) based on the values of the resulting liquid and gas-film mass transfer coefficients.

From the results of k_L, k_G and K_L, the relative deviations were calculated by comparing the actual fetch usage (this being the length or width of the tank, respectively, in the case of longitudinal or transverse wind direction alignment) and the use of the effective diameter (procedure adopted by WATER9). The same analysis was repeated for each compound in all units of the WWTPs listed in Table 1, for each of the 1,000 random wind speed values.

The analysis of the relative deviations for K_L, for the different geometries and for each compound, are presented in Table 2, containing, for each case, the mean, maximum and minimum of the distribution of the relative deviations.

Compound with dominance in the liquid phase

Hydrogen sulfide allows us to analyse the response of the WATER9 model for compounds with dominance in the liquid phase. The overall mass transfer coefficient (K_L) for this compound is predominantly influenced by the mass transfer coefficient of the liquid phase (k_L). It is observed that the deviations of k_L occur in the following circumstances: (i) when the fetch parameter selection leads to different F/D ratio ranges, resulting in the calculation of k_L by different formulations; or (ii) when the calculated F/D ratio for the effective diameter and the actual fetch is in the range of 14 to 51.2, since in this case the F/D ratio is a linear parameter in the correlation (Equation SM4).

Table 2 presents the statistical analysis of the relative deviations of K_L for hydrogen sulfide, considering the results referring to 1,000 wind speed values, randomly sampled according to the Monte Carlo method. The greatest relative deviations for hydrogen sulfide were 119.52% for WWTP 1, 124.80% for WWTP 2 and 122.24% for WWTP 3. The cases of greater deviations are related to the change of equation in the k_L calculation according to the ranges of F/D ratio (situation (i) described above). For example, unit 4 of WWTP 1 can be highlighted, for which k_L was calculated by Equations SM1 and SM2 when using the effective diameter (F/D = 12.3) and the width (F/D = 7.4) as the fetch parameter, since the F/D ratios are less than 14 (Table SM1).

Table 2 | Relative deviations due to the simplification of using the effective diameter as fetch parameter for the values of for hydrogen sulfide, acetic acid and ammonia

	Unit	Hydrogen sulfide						Acetic acid						Ammonia					
		Length-wise wind			Width-wise wind			Length-wise wind			Width-wise wind			Length-wise wind			Width-wise wind		
		Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	Min
WWTP1	1-Anaerobic chamber	0.00%	0.00%	0.00%	-0.01%	-0.01%	0.00%	-0.10%	-0.10%	-0.10%	-2.51%	-2.51%	-2.47%	-0.07%	-0.08%	-0.04%	-1.69%	-1.96%	-0.90%
	2-IDEA tank-min[a]	0.02%	0.03%	0.01%	-0.03%	-0.05%	-0.01%	4.80%	4.81%	4.74%	-7.07%	-7.08%	-6.98%	3.41%	3.88%	1.93%	-5.02%	-5.72%	-2.83%
	3-IDEA tank-min[a]	-7.23%	-7.25%	-7.21%	-43.34%	-54.26%	-32.11%	2.93%	2.98%	2.75%	-5.88%	-6.45%	-5.62%	-1.04%	-3.93%	0.00%	-20.05%	-24.64%	-11.78%
	4-IDEA tank-max[b]	79.53%	119.52%	47.88%	-0.03%	-0.04%	-0.01%	3.47%	4.12%	3.18%	-5.46%	-5.47%	-5.39%	22.88%	31.29%	10.86%	-3.96%	-4.48%	-2.30%
	5-Balance pond. shallow section-max[b]	-7.50%	-7.53%	-7.47%	17.87%	17.94%	17.80%	1.76%	1.80%	1.65%	-4.22%	-4.30%	-3.94%	-1.11%	-3.69%	0.00%	2.63%	8.77%	0.00%
WWTP2 WWTP3	1.Primary sedimentation tank	-10.21%	-10.24%	-10.18%	-43.49%	-54.39%	-32.30%	4.09%	4.17%	3.83%	-6.98%	-7.55%	-6.71%	-1.58%	-5.65%	0.00%	-21.00%	-25.28%	-12.78%
	2.Aeration tank. anoxic zone	85.83%	124.80%	51.45%	-0.07%	-0.10%	-0.02%	13.48%	14.11%	13.17%	-13.77%	-13.80%	-13.60%	32.41%	39.20%	20.17%	-9.76%	-11.13%	-5.51%
	3.Aeration tank. anoxic/aerobic zone	81.05%	121.40%	49.16%	-0.07%	-0.10%	-0.02%	13.78%	14.38%	13.49%	-14.01%	-14.05%	-13.84%	31.80%	38.54%	19.97%	-9.94%	-11.33%	-5.61%
	4.Aeration tank. aerobic zone	78.73%	118.55%	47.24%	-0.05%	-0.08%	-0.01%	9.15%	9.76%	8.86%	-10.38%	-10.41%	-10.26%	27.34%	33.73%	15.65%	-7.45%	-8.46%	-4.26%
	1.Sludge lagoon	0.00%	0.00%	0.00%	-0.02%	-0.02%	0.00%	0.49%	0.50%	0.49%	-3.09%	-3.09%	-3.05%	0.36%	0.40%	0.21%	-2.23%	-2.53%	-1.29%
	2.IDEA tank-min[a]	75.48%	114.57%	44.56%	-0.03%	-0.05%	-0.01%	4.30%	4.92%	4.02%	-6.23%	-6.24%	-6.16%	22.67%	29.87%	11.08%	-4.50%	-5.10%	-2.59%
	3.IDEA tank-max[b]	81.75%	122.24%	49.71%	-0.03%	-0.05%	-0.01%	4.34%	5.02%	4.04%	-6.23%	-6.24%	-6.16%	24.39%	32.99%	12.03%	-4.50%	-5.10%	-2.59%
	4.Balance pond	-10.21%	-10.25%	-10.18%	16.17%	16.22%	16.11%	3.14%	3.20%	2.92%	-5.50%	-5.61%	-5.15%	-1.74%	-5.54%	0.00%	2.41%	8.58%	0.00%

Ave, Max and Min indicate the average, maximum and minimum relative deviation values, respectively.

On the other hand, the value of k_L was estimated by Equation SM4 when the length of the tank (F/D = 16.2) was used as the actual fetch, since the ratio is in the range 14 < F/D < 51.2. Although smaller, deviations occurring in cases where F/D is between 14 and 51.2 for different fetch parameter choices (situation (ii)) can reach significant values, as in the case of unit 5 of WWTP 1, for example. Units 1 and 2 of WWTP 1 and unit 1 of WWTP 3 did not show any deviation since, in these cases, all fetch parameter choices result in F/D ratios less than 14; consequently, for all cases, k_L was calculated by the correlations of Mackay & Yeun (1983), which are independent of the F/D ratio.

It can be seen that the greatest positive relative deviations are greater than 100%, often with an average relative deviation of about 80% for hydrogen sulfide, which implies a severe overestimation of the final value of the emission of the compound. On the other hand, it is important to note the occurrence of extreme negative deviations greater than −50% (e.g. −54.26% and −54.39% for units 3 of WWTP 1 and 1 of WWTP 2, respectively). The negative deviations mean that the use of the effective diameter produced an underestimation of the calculation. These values of relative deviation greater than 50% negative represent less than half of the values that would be estimated if the actual fetch (in these cases, the width of the tank) was used.

Compounds with dominance in the gas phase

The compounds dominated by the gas phase have the overall mass transfer coefficient (K_L) approximated by $k_G K_H$, whereas k_L becomes negligible in the expression. Thus, the final value of the mass transfer coefficient to determine the emission of the compound is predominantly dependent on the correlation of Mackay & Matsugu (1973) (Equation SM6). It is noticed from the results that there are relative deviations depending on the choice of the fetch parameter, given that this is an input for the calculation of k_G; however, the relative deviations are not as expressive as those for the compounds dominated by the liquid phase. This situation is related to the fact that k_G is calculated by only one equation, in which the fetch parameter is raised to the power −0.11, smoothing the effects of differences in the fetch.

Table 2 presents the statistical analysis of the relative deviations of K_L for acetic acid, considering the results referring to the 1,000 wind speed values, randomly sampled according to the Monte Carlo method. The largest relative deviations of K_L occurred in unit 3 of WWTP 2. This value represented 14.38% in the length-wise wind and

−14.05% in the width-wise wind. For WWTP 1 and WWTP 2, there were no significant relative deviations (all of an order less than 10%) for the compounds dominated by the gas phase. As explained by Prata *et al.* (2016), the relative deviations in the calculation increase with the aspect ratio of the tank; this explains the reason why units 2, 3 and 4 of WWTP 2 were the only ones with relative deviations greater than 10%: these units present larger aspect ratios.

Compounds with dominance in both phases

For the compounds dominated by both the liquid and gas phases, the equation for the calculation of the mass transfer coefficient (Equation (2)) is used without neglecting any of the terms. Therefore, the conditions of both phases significantly influence the final value to be used in the calculation of the compounds' emission. Table 2 shows the statistical analysis of the relative deviations of K_L for ammonia, considering the results referring to the 1,000 wind speed values, randomly sampled according to the Monte Carlo method. The largest relative deviations occurred in units 4 of WWTP 1, 2 of WWTP, and 2 and 3 of WWTP 3. Similarly to the compounds dominated by the liquid phase, the major deviations in this case are a consequence of the changes of formulation for the estimation of the mass transfer coefficient in the liquid phase (k_L), depending on the F/D ratio range. As the value of k_L is incorporated significantly in the value of the overall coefficient K_L, large deviations in k_L may result in considerable deviations in K_L. The largest deviation for ammonia (39.20%) in tank 2 of WWTP 2, for the length-wise wind, is due to K_L being calculated by Equation SM1 or SM2 if the effective diameter is used as the fetch parameter, and being calculated by Equation SM4 if the length of the tank is taken as the fetch.

Wind speed analysis

In order to illustrate the influence of the wind speed on the deviations resulting from the fetch parameter choice, two different liquid surface geometries were analysed for hydrogen sulphide, acetic acid and ammonia. Figure 1 shows, for unit 5 of WWTP 1 and unit 1 of WWTP 2, the different results of K_L within the wind speed range used in this work. This figure is constructed taking 25 wind speeds between 3.25 and 15 m s^{-1} with spacing of 0.5 m s^{-1} between them.

For the analysis with hydrogen sulfide, unit 5 of WWTP 1 falls within the circumstance (ii), where Equation SM4, of
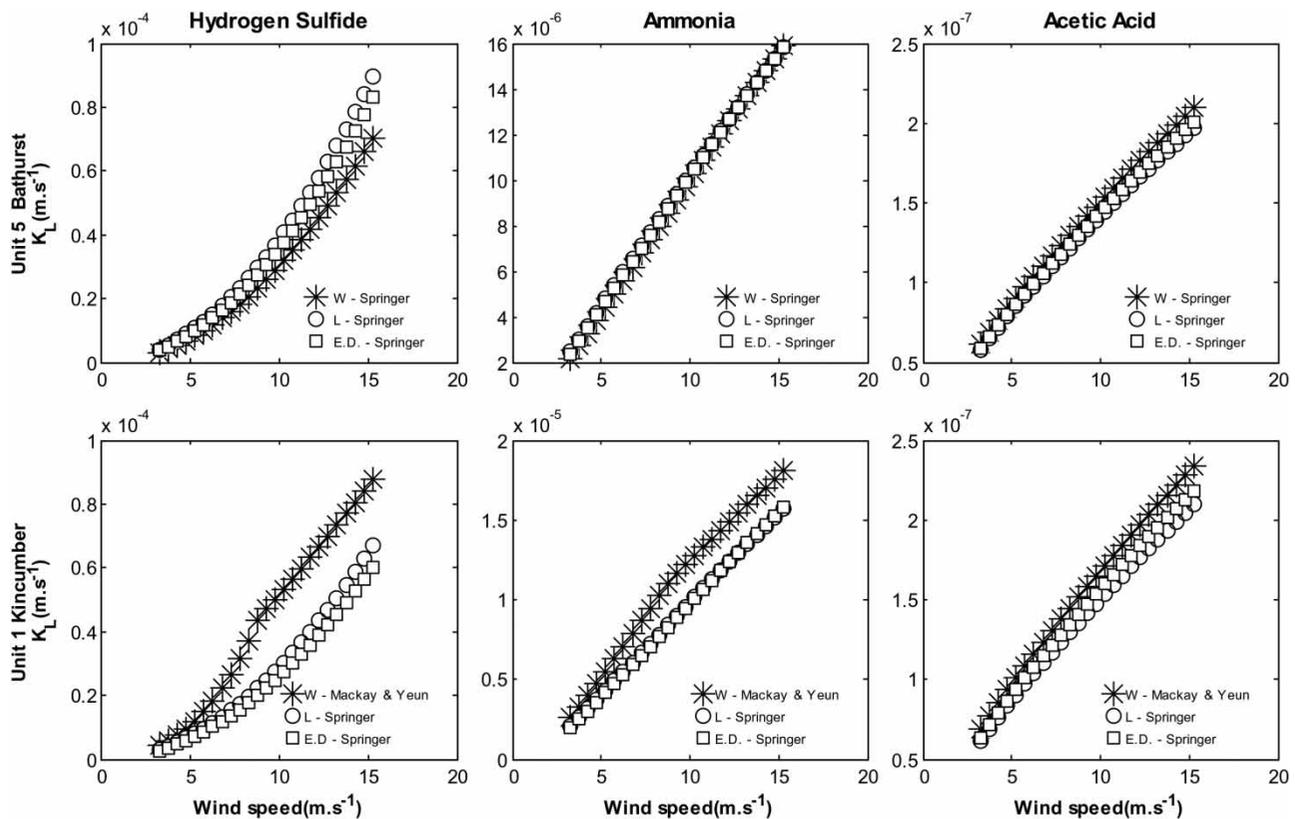
Figure 1 │ Analysis of K_L for wind speed range between 3.25 and 15 m s^{-1} for hydrogen sulfide, ammonia and acetic acid in selected units. The symbols in the figures indicate the choice of fetch parameter (length L, width W or effective diameter E.D.) and the respective formulation used to calculate k_L.

Springer *et al.* (1984), was applied for the calculation of k_L (which dominates the value of K_L) for the three fetch parameter choices. Thus, the profiles of the generated curves followed the same format, varying according to the choice of the fetch parameter as previously discussed: lower values of K_L if the fetch parameter is approximated by the width (smaller fetch) and higher values of K_L if adopting the tank length (longer fetch); with the effective diameter, the value was intermediate. Still, in Figure 1 it is possible to notice the increase of the absolute deviations in the value of K_L for higher wind speeds. For unit 1 of WWTP 2, the deviations occurred for both circumstances (i) and (ii). It is possible to notice the significant difference in K_L values for the cases where the change of equation (circumstance (i)) occurs. For the situations in which Equations SM1 and SM2 of Mackay & Yeun (1983) were used, the values were much higher when compared to the values generated by Equation SM4 of Springer *et al.* (1984). However, even where calculated by the equation of Springer *et al.* (1984), the deviations in the values of K_L were higher with the wind speed increase, since the fetch and wind speed variables are input parameters for the calculation of k_L.

In the analysis with ammonia, the values of K_L presented distinct profiles as a result of the both phase dominance of the compound. For unit 5 of WWTP 1, the values of k_L were calculated using the same Equation SM4 (circumstance (ii)), of Springer *et al.* (1984), for the three choices of fetch parameter. On the other hand, unit 1 of WWTP 2 had the values of k_L calculated by the equations of Mackay & Yeun (1983) or Springer *et al.* (1984), depending on the choice of fetch (circumstance (i)), since the fetch parameter selection leads to different ranges of F/D ratio. The use of different equations resulted in deviations in the values of k_L; the values of k_L are normally higher if the equations of Mackay & Yeun (1983) are used.

It can be seen from the graphs that the deviations for compounds dominated by the gas phase are less significant compared to those generated for compounds with dominance in the liquid phase, due to the use of only one formula for the calculation of k_G and the fact that the fetch parameter is raised to the power −0.11, smoothing the effects of differences in the fetch, as pointed out before. However, it is worth noting the increase of the

absolute difference in the values of k_G with increasing wind speed, especially for WWTP 2. The highest K_L values for the analysis with acetic acid were generated by choosing the width as the actual fetch. This result can be explained by the fact that, for the gas side of the air-water interface, the greater the actual fetch, the greater the boundary layer thickness, consequently causing a higher concentration of pollutant near the surface. With the accumulation of pollutants at the liquid-gas interface, the pollutant transfer to the atmosphere is lower and the emission of the compounds decreases.
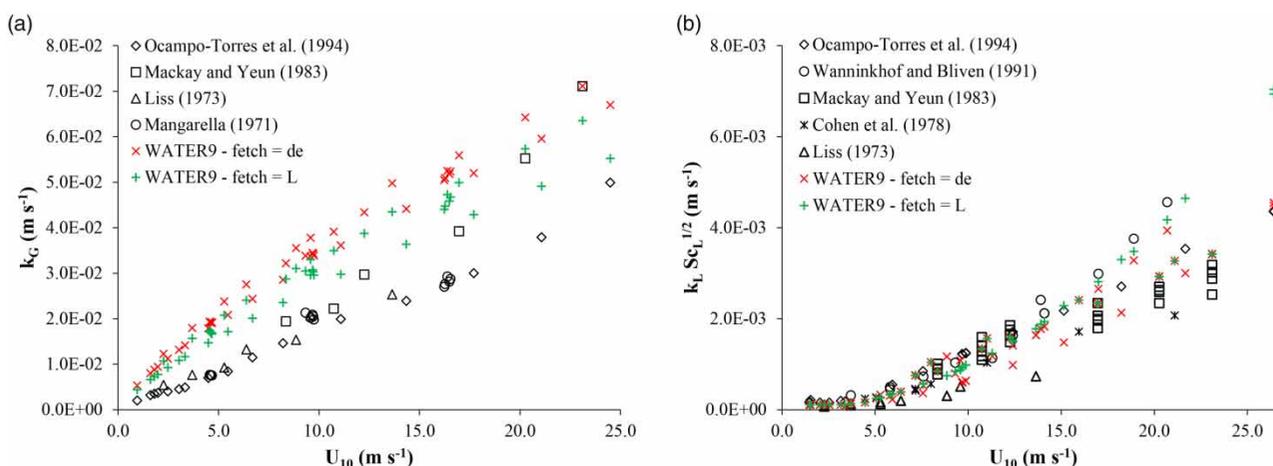
Comparison against experimental data

Extending the discussion in the previous subsections, an assessment of the implication of the choice of fetch parameter against experimental emission data is in order to complement the present study. In the current literature, only results obtained in laboratory wind-wave tanks can be traced to conditions which are controlled enough so as to allow a scrutinised testing of mass transfer equations for passive liquid surfaces (Prata *et al.* 2018). For the present analysis, the data sets of experimental values of k_G and k_L compiled by Prata *et al.* (2018) is used (please, refer to Prata *et al.* (2018) for discussion about the compilation process and details of the data set). The data set for k_G is composed only of results of water evaporation, whilst the k_L data are for various compounds. Table 3 indicates the sources of the data and summarises the geometric characteristics of the wind-wave tanks. In these experiments, the wind was always aligned with the length of the tanks; therefore the length is taken as the physical fetch.

The WATER9 model was applied to the various experimental cases that compose the data set, using the geometric characteristics of the wind-wave tanks, the equivalent U_{10} and the properties of the compounds. The results for the two choices of fetch parameter, fetch = L and fetch = d_e, are compared against the experimental data, as illustrated in Figure 2. The root mean square (RMS) relative error for k_G is 85.6%, if fetch = L, against 115.3%, if fetch = d_e; the RMS relative error for k_L is 49.1%, if fetch = L, and 65.9%, if fetch = d_e. This comparison shows that, whereas the estimates of k_G and k_L made by WATER9 do not represent very accurately the data set, even if L is taken as the fetch, the use of d_e as the fetch parameter makes the model predictions further depart from the experimental values.

Table 3 | Geometric characteristics of the wind-wave tanks used in the studies compiled in the k_G and k_L data sets

Source	Coefficient	Compounds	Dimensions						F/D ratio	
			L (m)	W (m)	D (m)	r = L/W	A (m²)	d_e (m)	L/D	d_e/D
Mangarella (1971)	k_G	Water vapour	7.74 to 13.91	0.91	0.97	8.5 to 15.3	7.04 to 12.66	2.99 to 4.01	7.98 to 14.34	3.08 to 4.13
Liss (1973)	k_G	Water vapour	4.5	0.3	0.1	15	1.35	1.31	45	13.1
Mackay & Yeun (1983)	k_G	Water vapour	6.0	0.6	0.61	10	3.6	2.14	9.84	3.51
Ocampo-Torres et al. (1994)	k_G	Water vapour	32.2	0.76	0.25	42.4	24.47	5.58	128.8	22.32
Liss (1973)	k_L	O_2 and CO_2	4.5	0.3	0.1	15	1.35	1.31	45	13.1
Cohen et al. (1978)	k_L	Benzene	2.4	0.6	0.60	4	1.44	1.35	4.0	2.25
Mackay & Yeun (1983)	k_L	Benzene, toluene, 1,2-dichloropropane, chlorobenzene, 1,2-dibromoethane and tetrachloromethane	6.0	0.6	0.61	10	3.6	2.14	9.84	3.51
Wanninkhof & Bliven (1991)	k_L	SF_6	100	8	0.70	12.5	800	31.92	142.9	45.6
Ocampo-Torres et al. (1994)	k_L	CO_2	16	0.76	0.25	21.1	12.16	3.93	128.8	22.32

Figure 2 | Estimates of (a) k_G and (b) k_L (normalised by the 1/2 power of the liquid-phase Schmidt number, Sc_L) made by WATER9, for two choices of fetch parameter, fetch = L and fetch = d_e, compared against experimental data.

CONCLUSIONS

This study had the purpose of analysing the relative deviations in the calculated mass transfer coefficients generated by the use of the effective diameter as a fetch parameter on passive liquid surfaces present in WWTPs by WATER9 (US EPA 1994, 2001), taking into account the parameters wind speed, liquid surface geometry, Henry's Law constant and molecular diffusivity of the compounds. The relative deviations calculated were found to be considerably large in some cases, and may represent serious underestimates or overestimates of emission of odorous compounds. Wind speed had a direct influence on the values of the relative deviations for all compounds analysed; however, this parameter was more representative for compounds dominated by the liquid phase. The phase dominance of the compounds directly influenced the values of the relative deviations in the calculation of the mass transfer coefficient (K_L). For the more volatile compounds, dominated by the liquid phase, the relative deviations were more significant, especially if the different choices of fetch lead to different ranges of F/D ratio, where WATER9 uses different correlations for the calculation of k_L. The present analysis and comparison against experimental data shows that, for a varied range of wind speed and WWTP configurations, the use of the actual physical fetch shall be preferred over the use of the effective diameter in emission models for WWTPs, so as to avoid the introduction of potentially large systematic deviations. By including compounds with various mass transfer behaviours, a range of wind speeds and comparing against experimental data, this study expands and complements the initial work of Prata *et al.* (2016), providing further compelling evidence against the adoption of the effective diameter as the fetch parameter in emission models for WWTPs. It is also important to remember that the use of the correct physical choice of fetch is not alone sufficient to guarantee accuracy of the predictions made by emission models, since other sources of inaccuracy may be present (see, for instance, the analysis in Prata *et al.* (2018)).

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