

Analysis of methods for estimating the emission rate of odorous compounds from passive liquid surfaces

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Analysis of methods for estimating the emission rate of odorous compounds from passive liquid surfaces

By

Ademir Abdala Prata Junior

A thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy



**School of Civil and Environmental Engineering
Faculty of Engineering**

The University of New South Wales
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The determination of the emission rate of odorous compounds from passive liquid surfaces is critical for the study and management of the environmental impacts associated with odour emissions from wastewater treatment plants (WWTPs). This research analysed two methods widely employed for estimating the emission rate of odorous compounds from such surfaces, namely, predictive emission models and direct sampling with a flux hood. Several theoretical and empirical models for the gas-side (k_G) and liquid-side (k_L) mass transfer coefficients in passive surfaces in WWTPs were evaluated against experimental data. The analysis of the compiled data set led to the development of an alternate approach for estimating k_L which resulted in improved performance, particularly for longer fetches. Since the friction velocity (u_*) is a critical input variable for the modelling of emissions, this work also evaluated different parametrisations of u_* against available wind friction and wave data measured at wind-wave tanks with liquid surfaces of the same scale as WWTP units. For the first time, the most frequently used u_* parametrisation was verified against representative data for WWTPs. Furthermore, new, alternative correlations were derived and combined in an approach that described the u_* data set more accurately and in more detail, incorporating the size of the tanks together with the wind speed in the parametrisation of u_* . A sensitivity analysis was conducted, in order to understand how different emission models are affected by the use of different u_* parametrisations. The mass transfer of compounds inside the US EPA flux hood (one of the enclosure devices most commonly employed for the direct measurement of emissions) was studied by means of experiments that assessed k_G and k_L in the microenvironment created by the flux hood and the effects of concentration build-up in the hood's headspace. The mass transfer of gas phase-dominated compounds inside the US EPA flux hood was found equivalent to conditions of very low wind speeds. A procedure was presented to scale the emission rates of these compounds to conditions of higher winds, by combining the application of emission models and the flux hood measurements.

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Abstract

The determination of the emission rate of compounds from passive liquid surfaces is critical for the study and management of the environmental impacts associated with the atmospheric emissions from wastewater treatment plants (WWTPs), in especial odour annoyance to surrounding communities. Passive liquid surfaces are those without an active gas flow (such as mechanical aeration or intense bubbling), for instance primary and secondary settlement tanks, sequencing batch reactors in decanting phase and stabilisation ponds. This research analysed two methods widely employed for estimating the emission rate of odorous compounds from such surfaces, namely, predictive emission models and direct sampling with a flux hood.

Several theoretical and empirical models for the gas-side (k_G) and liquid-side (k_L) mass transfer coefficients in passive surfaces in WWTPs were evaluated against a compilation of experimental data. Two approaches performed well in describing the available data for k_G for water vapour. One is an empirical correlation whilst the other consists of theoretical models based on the description of the inner part of the turbulent boundary layer over a smooth flat plate. A new, alternative equation for k_G was fitted to the experimental data set, whose performance was comparable to existing ones. However, these three approaches do not agree with each other in the whole range of Schmidt numbers typical for compounds found in emissions from WWTPs.

Regarding k_L , no model was able to satisfactorily explain the behaviour and the scatter observed in the whole experimental data set. Excluding two suspected biased sources, the WATER9 (US EPA, 1994; *Air Emission Models for Waste and Wastewater. North Carolina, USA. EPA-453/R-94-080A*) approach produced the best results among the most commonly used k_L models, although still with considerably high relative errors. For this same sub-set, a new, alternative approach for estimating k_L was proposed, which resulted in improved performance, particularly for longer fetches.

Since the friction velocity (u_*) is a critical input variable for the modelling of emissions, different parametrisations of u_* were evaluated against available wind friction and wave data measured at wind-wave tanks with liquid surfaces of the same scale as WWTP

units (fetches spanning from approximately 3 to 100 m, and equivalent wind speeds at 10 m height from 2 to 17 m s⁻¹). The empirical correlation by Smith (1980; *J. Phys. Oceanogr.* 10, 709-726), which has been frequently adopted in atmospheric emission models (despite the fact that it was originally derived for the ocean), presented a general tendency to overestimate u_* , with significant (although not extreme) relative errors (RMS and maximum errors of 13.5% and 36.6%, respectively). This was the first time that this widely-applied parametrisation has been verified against representative data for WWTPs. The use of Charnock's relation, with Charnock constant 0.010, performed in a very similar manner (RMS and maximum errors of 13.3% and 37.8%, respectively). New, alternative correlations were derived and combined in an approach that described the data set for local u_* more accurately and in more detail (RMS and maximum relative errors of 6.6% and 16.7%, respectively), incorporating the size of the tanks together with the wind speed in the parametrisation of u_* .

A sensitivity analysis was conducted, in order to understand how different emission models are affected by the use of different u_* parametrisations. Three emission models were chosen for the analysis: the model of Mackay and Yeun (1983; *Environ. Sci. Technol.* 17(4), 211-217); the model of Gostelow et al. (2001; *Water Sci. Technol.* 44 (9), 181-188); and the best-performing approaches identified in the present research, which were the theoretical model of Brutsaert (1975; *Water Resour. Res.* 11 (4), 543-550) (based on the description of the inner part of the turbulent boundary layer over a smooth flat plate) for k_G , and the new, alternative approach for estimating k_L proposed herein. The results of these models were compared for three u_* parametrisations, Smith's correlation, use of Charnock's relation (with Charnock constant 0.010) and the parametrisation of u_* devised in this research (averaged throughout the fetch). The analysis was done for a liquid phase-dominated compound (H₂S), a gas phase-dominated compound (butyric acid) and a both phase-dominated compound (2-methylisoborneol, or 2-MIB), for 15000 combinations of fetch (varying from 6 to 120 m) and wind speed at 10 m height (varying from 1.0 to 20.0 m s⁻¹) produced via Monte Carlo simulation. The RMS relative differences among the mass transfer results produced by emission models using different parametrisations of u_* were generally small, smoothed by the process of fetch-averaging u_* . However, relative differences comparing the results from the models using Smith's correlation or Charnock's relation

to the results from the same models using the parametrisation of u_* devised in this research become pronounced for some combinations of fetch and wind speed. Among those, the maximum differences were found at long fetches and wind speed between 5.3 and 6.5 m s⁻¹, for the model of Mackay and Yeun for k_L (critical for the mass transfer rates of liquid phase and both phase-dominated compounds).

The mass transfer of compounds inside the US EPA flux hood, one of the enclosure devices most commonly employed for the direct measurement of emissions from liquid surfaces in WWTPs, was studied by means of experiments comprising the evaporation of water and the volatilisation of a range of compounds. Special attention was given to the evaluation of k_G and k_L in the microenvironment created by the flux hood and the effects of concentration build-up in the hood's headspace. The emission rates of compounds and the water evaporation rates generally increased with the sweep air flow rate, as did the mass transfer coefficients for all compounds. The emission of gas phase and both phase-controlled compounds was greatly affected by concentration build-up, whereas this effect was not significant for liquid phase-controlled compounds. The gas-side mass transfer coefficient k_G estimated inside the US EPA flux hood was of the same order as the respective k_G reported in the literature for wind tunnel-type devices, but the emission rates measured by the flux hood can be expected to be lower, due to the concentration build-up. Compared against an emission model for the passive surfaces in WWTPs, the mass transfer of gas phase-dominated compounds inside the US EPA flux hood was equivalent to conditions of very low wind speeds. A procedure was presented in order to scale the emission rates of these compounds measured with the flux hood to field conditions of higher winds, combining direct measurements with the flux hood and the use of predictive emission models.

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Publications

Peer reviewed journal papers

Paper number	Publication information	Status
1	<u>Prata Jr. A. A.</u> , Santos J. M., Timchenko V., Stuetz R. M., 2014. Use of computational fluid dynamics in the analysis of a portable wind tunnel for sampling of odorous emissions at liquid surfaces. <i>Chemical Engineering Transactions</i> 40, 145-150. DOI: 10.3303/CET1440025	Published
2	<u>Prata Jr. A. A.</u> , Calvo M. J., Boncardo G., Sivret E. C., Santos J. M., Timchenko V., Stuetz R. M. 2016. Influence of the fetch parameter on results from empirical correlations for estimating odorous emissions at passive liquid surfaces. <i>Water Science and Technology</i> 74, 2384-2391. DOI: 10.2166/wst.2016.421	Published
3	<u>Prata Jr. A. A.</u> , Santos J. M., Beghi S. P., Fernandes I. F., Vom Martens L. L. C., Neto L. P., Martins R. S., Reis Jr. N. C., Stuetz R. M. 2016. Dynamic flux chamber measurements of hydrogen sulfide emission rate from a quiescent surface: a computational evaluation. <i>Chemosphere</i> 146, 426-434. DOI: 10.1016/j.chemosphere.2015.11.123	Published
4	<u>Prata Jr. A. A.</u> , Santos J. M., Reis Jr. N. C., Stuetz R. M., 2016. Assessing built-in wind friction parametrisation in WWTP emission models for estimating compound volatilisation. <i>Chemical Engineering Transactions</i> 54, 109-114. DOI: 10.3303/CET1654019	Published
5	<u>Prata Jr. A. A.</u> , Santos J. M., Timchenko V., Reis Jr. N. C., Stuetz R. M. 2017. Wind friction parametrisation used in emission models for wastewater treatment plants: A critical review. <i>Water Research</i> 124, 49-66. DOI: 10.1016/j.watres.2017.07.030	Published
6	<u>Prata Jr. A. A.</u> , Santos J. M., Timchenko V., Stuetz R. M. 2018. A critical review on liquid-gas mass transfer models for estimating gaseous emissions from passive liquid surfaces in wastewater treatment plants. <i>Water Research</i> 130, 388-406. DOI: 10.1016/j.watres.2017.12.001	Published (online)
7	<u>Prata Jr. A. A.</u> , Lucernoni F., Santos J. M., Capelli L., Sironi S., Le-Minh N., Stuetz R. M. Mass transfer inside a flux hood for the sampling of gaseous emissions from liquid surfaces – an experimental assessment. Submitted to <i>Atmospheric Environment</i> .	Under review
8	Lucernoni F., Capelli L., Busini V., Del Rosso R., <u>Prata Jr. A.A.</u> , Stuetz R., Sironi S. Investigation of mass transfer phenomena affecting emission rate of gaseous compounds from porous solid. Submitted to <i>Chemosphere</i> .	Submitted

Conference papers (peer reviewed)

Paper number	Publication information	Status
9	Calvo M. J., <u>Prata Jr. A. A.</u> , Hoinaski L., Santos J. M., Stuetz R. M. Sensitivity analysis of the Water9 model: odorous emissions on passive liquid surfaces present in wastewater treatment plants. Proceedings of the 7th IWA Conference on Odours and Air Emissions (Warsaw, Poland, 25-27 Sep 2017). Submitted to <i>Water Science and Technology</i> .	Accepted for oral presentation
10	<u>Prata Jr. A. A.</u> , Santos J. M., Timchenko V., Stuetz R. M. Including the effect of evaporation in the two-resistance model for liquid-gas mass transfer. Proceedings of the 13th Hydraulics in Water Engineering Conference (Sydney, Australia, 13-16 Nov 2017).	Accepted for oral presentation

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List of symbols

- a : Charnock non-dimensional parameter; $a = gz_0/u_*^2$
- ak_s : significant wave steepness (dimensionless)
- c_p : phase speed (m s^{-1}) of waves at the spectral peak
- C : concentration of the compound (kg m^{-3})
- C_G : compound concentration (kg m^{-3}) in the bulk gas phase
- $C_{G,i}$: compound concentration (kg m^{-3}) adjacent to the gas-liquid interface in the gas side
- $C_{G,0}$: concentration of water vapour (kg m^{-3}) in the inlet air feed
- C_L : compound concentration (kg m^{-3}) in the bulk liquid phase
- $C_{L,i}$: compound concentrations (kg m^{-3}) adjacent to the gas-liquid interface in the liquid side
- C_m : measured gas-phase concentrations (kg m^{-3}) from the flux hood
- C_Z : drag coefficient (non-dimensional), with the reference wind speed U_Z ; $C_Z = (u_*/U_Z)^2$
- C_{10} : drag coefficient (non-dimensional), with the reference wind speed U_{10} ; $C_{10} = (u_*/U_{10})^2$
- d_G : thicknesses (m) of the gas film
- d_L : thicknesses (m) of the liquid film
- D : molecular diffusivity of the compound in the medium ($\text{m}^2 \text{s}^{-1}$)
- D_G : the molecular diffusivity ($\text{m}^2 \text{s}^{-1}$) of the compound in the gas phase
- D_L : the molecular diffusivity ($\text{m}^2 \text{s}^{-1}$) of the compound in the liquid phase
- D^{eff} : effective diffusivity ($\text{m}^2 \text{s}^{-1}$) (the sum of the molecular and eddy diffusivities)
- $D_{L,ether}$: molecular diffusivity ($\text{m}^2 \text{s}^{-1}$) of ethyl ether in water
- f_p : peak frequency (Hz) of the wave spectra
- $\hat{f}_p$: non-dimensional peak wave frequency; $\hat{f}_p = f_p U/g$
- F : non-dimensional group with the form of a Froude number; $F = U_Z/(gZ)^{1/2}$
- g : gravity acceleration (m s^{-2})
- H : water depth (m)
- J : emission rate ($\text{kg s}^{-1} \text{m}^{-2}$)
- J_G : mass flux across the gas film ($\text{kg s}^{-1} \text{m}^{-2}$)
- J_L : mass flux across the liquid film ($\text{kg s}^{-1} \text{m}^{-2}$)
- J_w : evaporation rate ($\text{kg s}^{-1} \text{m}^{-2}$)
- k_G : gas-film mass transfer coefficient (m s^{-1})
- k_G^s : coefficient for the mass transfer (m s^{-1}) between the interface and the height z_s
- k_L : liquid-film mass transfer coefficient (m s^{-1})
- K_H : non-dimensional Henry's law coefficient
- K_L : liquid-phase overall mass transfer coefficient (m s^{-1})
- k_G^{CA} , k_L^{CA} and K_L^{CA} : respectively, k_G , k_L and K_L (m s^{-1}) calculated using u_*^{CA}
- k_G^{Ch} , k_L^{Ch} and K_L^{Ch} : respectively, k_G , k_L and K_L (m s^{-1}) calculated using u_*^{Ch}
- k_G^{Sm} , k_L^{Sm} and K_L^{Sm} : respectively, k_G , k_L and K_L (m s^{-1}) calculated using u_*^{Sm}
- l : turbulent mixing length (m)
- l_B : Batchelor's (1959) length scale (m)

- Q : sweep air flow rate ($\text{m}^3 \text{s}^{-1}$)
- R_G : total resistance to mass transfer (s m^{-1}) in the gas phase; $R_G = 1/k_G$
- R_m : resistance to mass transfer (s m^{-1}) between z_s and z_m
- R_s : resistance to mass transfer (s m^{-1}) between the surface and a height z_s
- Re_X : fetch-based Reynolds number (non-dimensional); $Re_X = U_Z X / \nu$
- u : mean horizontal velocity (m s^{-1}) of the air flow at height z
- u_* : friction velocity (m s^{-1})
- $u_{*,L}$: friction velocity (m s^{-1}) in the liquid phase
- u_*^{CA} : fetch-averaged u_* (m s^{-1}) calculated using the Combined Approach
- u_*^{Ch} : u_* (m s^{-1}) calculated using Charnock's relation
- u_*^{Sm} : u_* (m s^{-1}) calculated using Smith's correlation
- u_*^{Local} : local u_* (m s^{-1}) calculated by the Combined Approach
- u_*^I : fetch-averaged u_* (m s^{-1}) calculated via Equation (5.3)
- u_*^{II} : fetch-averaged u_* (m s^{-1}) calculated via Equation (5.5)
- u_*^{III} : fetch-averaged u_* (m s^{-1}) calculated via Equation (5.7)
- u_1 : instantaneous horizontal component of wind velocity (m s^{-1})
- u_1' : turbulent fluctuation of u_1 (m s^{-1})
- u_3 : instantaneous vertical component of wind velocity (m s^{-1})
- u_3' : turbulent fluctuation of u_3 (m s^{-1})
- U : scaling velocity (m s^{-1}); in most cases, $U = u_*$ or $U = U_{10}$
- U_Z : reference wind speed (m s^{-1}) measured at a reference height Z
- U_0 : velocity (m s^{-1}) of the approaching uniform flow ("free-stream" velocity)
- U_{10} : reference wind speed (m s^{-1}) measured at the reference height of 10 m
- Sc : Schmidt number
- Sc_G : Schmidt number of the compound in the air (gas phase)
- Sc_L : Schmidt number in the liquid phase
- Sc_t : turbulent Schmidt number
- x : horizontal coordinate (m)
- x_1 : horizontal coordinate (m), represented in Einstein's notation
- x_3 : vertical coordinate (m), represented in Einstein's notation
- X : fetch (m)
- $\hat{X}$: non-dimensional fetch; $\hat{X} = Xg/U^2$
- X_f : maximum fetch (m) for which $1.3f_p > 4 \text{ Hz}$
- z : vertical coordinate (m)
- z^+ : normalised height (non-dimensional); $z^+ = u_* z / \nu$
- z_m : height (m) at which the concentration is referenced
- z_s : height (m) corresponding to the bottom of the dynamic sublayer
- z_0 : roughness length parameter (m)
- z_0^+ : aerodynamic roughness Reynolds number (non-dimensional); $z_0^+ = z_0 u_* / \nu$
- $z_{0,g}$: aerodynamic roughness (m) due gravity waves

$z_{0,gc}$: aerodynamic roughness (m) due to gravity-capillary waves

$\hat{\alpha}$: non-dimensional constant so that $z_{0,gc} = \hat{\alpha} u_*^2 / g$

δ_M : thickness of the concentration boundary layer (m)

ε : dissipation rate of turbulent kinetic energy ($\text{m}^2 \text{s}^{-3}$)

κ : von Karman constant (dimensionless)

ν : kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)

ν_G : kinematic viscosity ($\text{m}^2 \text{s}^{-1}$) of the air (gas phase)

ρ : density of the fluid medium (kg m^{-3})

ρ_G : density (kg m^{-3}) of the gas phase (air, in most cases)

ρ_L : density (kg m^{-3}) of liquid phase (water, in most cases)

ω : mass fraction of the compound in the medium (kg kg^{-1})

τ : total stress (momentum flux) ($\text{kg m}^{-1} \text{s}^{-2}$)

τ_W : component of the total stress ($\text{kg m}^{-1} \text{s}^{-2}$) due to the waves

τ_0 : momentum flux ($\text{kg m}^{-1} \text{s}^{-2}$) at the air side of the interface

$\mathcal{T}$: time (s) between successive renewal events

$\bar{\mathcal{T}}$: mean time (s) between renewal events

Abbreviations and acronyms

ANOVA: analysis of variance

CFD: Computational Fluid Dynamics

DMS: dimethyl sulfide

JONSWAP: Joint North Sea Wave Project; also denotes a parametrisation form for f_p

LS&W2008: parametrisation form for f_p proposed by Lamont-Smith and Waseda (2008)

RMS: root mean square

US EPA: United States Environmental Protection Agency

VOCs: volatile organic compounds

WWTP: wastewater treatment plant

2-MIB: 2-methylisoborneol

1. INTRODUCTION

1.1. Background

Atmospheric emissions emanating from wastewater treatment plants (WWTPs) are potentially associated with various environmental impacts. Odour nuisance to local communities often figures as the primary and most widespread of these impacts (Capelli et al., 2009b; Lebrero et al., 2011; Beghi et al., 2012b; Hayes et al., 2014; Godoi et al., 2017), negatively affecting the well-being of the exposed communities and, consequently, their perception towards the development of wastewater treatment projects (Hayes et al., 2014). Other potential environmental impacts of emissions from WWTPs are exposure to harmful substances (Cheng et al., 2008; Yang et al., 2012; Godoi et al., 2017) and greenhouse effect (Daelman et al., 2012; Glaz et al., 2016). The composition of the emissions from WWTPs varies spatially (from site to site) and temporarily; they may contain different volatile organic compounds (VOCs) and some inorganic compounds such as hydrogen sulfide and ammonia.

Passive liquid surfaces are major sources of atmospheric emissions in WWTPs. The classification as “passive” indicates the absence of an active gas flow (such as active aeration or intense bubbling) across the surface (VDI 3475 Bl. 1, 2000; Gostelow et al., 2003; Bockreis and Steinberg, 2005; Capelli et al., 2009b; Lebrero et al., 2011). Examples of passive surfaces normally encountered in urban, rural and industrial WWTPs are primary and secondary settlement tanks, non-aerated sequencing batch reactors and stabilisation ponds. Sometimes, the term “quiescent” is also used to refer to those passive liquid surfaces, although, rigorously, “quiescent” implies an undisturbed surface, which is not the case commonly observed in WWTPs, where the wind is likely to disturb the water surface and generate waves.

Accurate estimates of the emission rates of compounds from passive liquid surfaces in WWTPs (that is, the amount of a given compound emitted per unit time, per unit area) are often required for environmental impact assessments (especially if the atmospheric dispersion of pollutants is to be modelled), emission inventories, management of compliance with regulations and control strategies (see, for instance, the discussions in

Nicell, 2009, Lebrero et al., 2011, Capelli et al., 2013, Schaubberger et al., 2013, 2016, and Brancher et al., 2017, and examples in Atasoy et al, 2004, Beghi et al., 2012b, and Yang et al., 2012). Different approaches have been proposed aiming to determine the emission rate of compounds from passive liquid surfaces, which can be divided into (Gostelow et al., 2001, 2003; Bockreis and Steinberg, 2005; Hudson and Ayoko, 2008b; Santos et al., 2012):

- Using predictive emission models, which contain modelling equations to estimate the emission rates of individual compounds;
- Using an enclosure device (direct methods) to sample emissions directly at the surface;
- Applying reverse dispersion modelling and micrometeorological measurements (indirect methods) to back-calculate the emission rate based on environmental concentrations measured around the source.

Relevant aspects of each of these approaches are briefly discussed in the following items.

1.1.1. Predictive emission models

Emission models allow estimating the emission rate of individual compounds from wastewater treatment units through a mass balance approach, considering characteristics of the gas and liquid phases and modelling production and removal mechanisms by mathematical expressions (Santos et al., 2009). Some emission models, such as the US EPA-endorsed WARTER9 (US EPA, 1994, 2001), TOXCHEM+ (ENVIROMEGA, 2003) and the model proposed by Gostelow et al. (2001), are, in fact, modelling packages comprising a system of equations for various processes and units of WWTPs. The term “emission model” is also commonly used in reference to the specific formulations for the liquid-gas mass transfer process (volatilisation, for passive liquid surfaces). In the present work, which is focused on the study of methodologies for estimating the emission rate of compounds from passive liquid surfaces, this last

meaning will be preferentially adopted, unless where explicitly referring to the mentioned modelling packages.

Emission models have been widely applied in the estimation of atmospheric emissions from WWTPs (Atasoy et al., 2004; Blunden et al., 2008; Cheng et al., 2008; Ro et al., 2008; Rumburg et al., 2008; Santos et al., 2009; Beghi et al., 2012a; Yang et al., 2012; Glaz et al., 2016) and present as main advantages (Santos et al., 2009; Brancher et al., 2017): being a relatively rapid and low-cost approach; and being able to estimate emission rates for environmental impact assessment of proposed WWTPs (before their construction) and of existing plants under hypothetical operational scenarios.

In the context of modelling emissions from passive liquid surfaces in WWTPs, volatilisation is typically described by a core formulation based on the two-resistance hypothesis (see complete development in 2.1.2). In this formulation (Equation (2.6)), the mass transfer rate J (that is, the emission rate, in this case; units $\text{kg s}^{-1} \text{m}^{-2}$) is given straightforward so long as the following values are known: the concentrations of the compound in the liquid (C_L) and gas (C_G) phases; the non-dimensional Henry's law coefficient (K_H); and the overall mass transfer coefficient (K_L), which in turn depends on K_H and the film-specific mass transfer coefficients in the gas (k_G) and liquid (k_L) sides of the gas-liquid interface. The gas-phase concentration is commonly neglected ($C_G \approx 0 \text{ kg m}^{-3}$), considering that the background compounds concentration in ambient air is typically low. The bulk-liquid concentration C_L can be estimated based on the compound mass balance in the liquid phase performed by the modelling packages (as, for example, used by Atasoy et al., 2004, and Santos et al., 2009), which normally use the inlet concentration of the tank and account for all the production and removal pathways, including biological activity and chemical reactions; it can also be directly measured from a liquid sample taken from within the unit (e.g., Blunden et al., 2008; Beghi et al., 2012a; Glaz et al., 2016).

The most challenging aspect for the application of emission models resides in accurately predicting the liquid-film and gas-film mass transfer coefficients (k_L and k_G , respectively). The typical approach to obtain k_L and k_G consists in using expressions to calculate these coefficients based on other variables relevant to the mass transfer process that can be easily measured or estimated. Normally, it involves at least one

variable representing wind forcing and another accounting for the compound molecular diffusion. In practice, the last is taken as the compound molecular diffusivity (in water or air, for k_L or k_G , respectively) (e.g., Springer et al., 1984; Lunney et al., 1985) or the Schmidt number (e.g., Mackay and Matsugu, 1973; Mackay and Yeun, 1983; Gostelow et al., 2001). Wind speed at a certain height (e.g., Mackay and Matsugu, 1973; Springer et al., 1984; Lunney et al., 1985; Liss and Merlivat, 1986; Wanninkhof, 1992; Frost and Upstill-Goddard, 2002; Grant et al., 2013a,b) and the friction velocity (u_*) (e.g., Brutsaert, 1975; Münnich and Flothmann, 1975; Deacon, 1977; Liu et al., 1979; Mackay and Yeun, 1983; Jähne and Haußecker, 1998; Gostelow et al., 2001; Rotz et al., 2014) are the most frequently used in the scaling of the mass transfer coefficients to represent wind forcing. Gostelow et al. (2001) and Wanninkhof et al. (2009) argue that u_* is preferred as a wind parameter compared to wind speed due to its physical significance as it is directly related to the levels of turbulent transport in the fully turbulent part of the boundary layer and appears naturally in theoretical models for near-wall mass transfer over flat air-water interfaces (Brutsaert, 1975; Münnich and Flothmann, 1975; Deacon, 1977). Besides, u_* is often employed in the parametrisation of wind-wave interaction and other water-side phenomena (Janssen, 1991; Csanady, 1997; Fontaine, 2013; Zavadsky et al., 2013; Zakharov et al., 2015; Melville and Fedorov, 2015), which may also influence water-air mass transfer processes. A detailed discussion on the experimental data, and theoretical and empirical models for k_G and k_L is presented in sections 2.2 and 2.3 of the Literature Review (Chapter 2).

1.1.2. Direct methods

Direct methods are characterised by the use of devices that enclosure minimal parts of the emitting surface (enclosure devices) and directly sample the emissions. The local emission rate is calculated based on the concentration values measured in samples collected from the enclosure equipment and the characteristics of the sampling device, such as sweep air flow rate and enclosed surface area. Direct methods have been broadly adopted for the assessment of emissions from area sources (e.g., Muezzinoglu, 2003; Blunden and Aneja, 2008; Beghi et al., 2012a; Rumsey et al., 2012; Hentz et al., 2013; Parker et al., 2013a; Xiao et al., 2014) due to being less costly and easier to handle (Hudson and Ayoko, 2008b; Capelli et al., 2013). Two groups are identified (Hudson and Ayoko, 2008b): dynamic devices, whose headspaces are flushed by a

forced flow (sweep air flow) passing through the device; and static devices (also called “static chambers”), the ones without the flush flow. The dynamic enclosure devices are more common in the assessment of emissions from passive liquid surfaces, and can be further divided into wind tunnels and flux hoods. Wind tunnels (e.g., Jiang et al., 1995; Sohn et al., 2005; Capelli et al., 2009a) are intended to promote a directional air flow, predominantly parallel to the liquid surface, and usually present a nominal air velocity. In contrast, flux hoods (e.g., Klenbusch, 1986; Blunden and Aneja, 2008), alternatively called “dynamic flux chambers”, are normally designed as isolation-mixing chambers, with no representative value of air velocity.

Of particular interest is the flux hood whose design and basic operational conditions were presented by Klenbusch (1986) in a guide endorsed by the United States Environmental Protection Agency (US EPA). This device will be referred hereinafter preferentially as the “US EPA flux hood” (although the names “US EPA dynamic flux chamber” and “US EPA emission isolation chamber” are also frequently adopted in the literature and can be used interchangeably). Hudson and Ayoko (2008b) point out that the US EPA flux hood is suitable if standard, consistent and reproducible conditions are desired. As such, the US EPA flux hood has been widely used for measurement of volatile emissions, not only in the United States but also in many other countries (sometimes with modifications to methodology, as, for example, in Australia). Detailed aspects of the US EPA flux hood are further discussed in section 2.5 of the Literature Review (Chapter 2).

1.1.3. Indirect methods

Indirect methods are based on simultaneous measurements of meteorological conditions and pollutant concentration profiles across the emitted plume and on the use of models for the dispersion of the compound in the atmosphere (Bockreis and Steinberg, 2005; Hudson and Ayoko, 2008a, 2008b; Latos et al., 2011; Capelli et al., 2013). In the most common procedure (used, for example, by Galvin et al., 2004, Latos et al., 2011, Grant et al., 2013a,b, and Schauburger et al., 2011, 2013), a dispersion model is applied backwards to the concentrations measured in the field in order to find the values of the emission rate. Another micrometeorological approach is to measure concentrations and

wind speeds at various points in a “mesh” across the pollutant plume and perform a direct numerical integration of the mass fluxes (Gao et al., 2009).

The main advantages of these methods are that the emitting source is not disturbed and that it allows dispersion model calibration simultaneously with the estimation of the emission rate. However, use of indirect methods can be limited by the large number of downwind measurements required (with associated costs of measurement campaigns or permanent monitoring stations) and constraints of the terrain and surrounding buildings. Because of such limitations, presently, indirect methods are rarely adopted for routine purposes.

1.1.4. Knowledge gaps in the application of predictive emission models and direct methods

This research analysed the two approaches above that are most commonly employed for estimating the emission rate of odorous compounds from passive liquid surfaces in WWTPs, predictive emission models and direct sampling with a flux hood. The scope of the present work does not include the indirect methods. Following, the most challenging aspects and major knowledge gaps regarding the application of these approaches are discussed.

1.1.4.1. Predictive emission models

As mentioned before, the main challenge for the application of emission models is the accurate prediction of film-specific mass transfer coefficients (k_G and k_L): to date, neither a theoretical nor an experimental model for the mass transfer coefficients has been fully established (see Literature Review in Chapter 2). Some theoretical models are physically sound, but their application to the field situation is rather restricted. On the other hand, empirical correlations (e.g., Mackay and Yeun, 1983; Springer et al., 1984; Gostelow et al., 2001) were not validated against experimental data other than the data from which they were derived, and their relation with the theoretical background is not clearly drawn. In this sense, understanding the physical processes underpinning the liquid-air mass transfer of pollutants at passive liquid surfaces is essential not only for the management of the environmental impacts associated with atmospheric emissions

from these sources, but also for the evaluation and improvement of predictive emission models.

It has long been identified that divergent results may be produced if different models are applied to the same situation, which has been attributed to existing differences in the approaches for the calculation of k_G and k_L (Ferro and Pincince, 1996a,b; Gostelow et al., 2001; Santos et al., 2012). Studies about emissions of hydrogen sulfide also report that in many cases these models tend to estimate values of emission rate considerably higher than experimentally-measured emission rates, particularly in comparison to flux hood measurements (Blunden et al., 2008; Beghi et al., 2012a; Santos et al., 2012).

The results of emission models can also be affected by the way their key input variables are determined. For example, Prata Jr. et al. (2016a) investigated the occurrence and significance of systematic deviations in the values of k_G and k_L estimated by WATER9 originating from the use of the effective diameter as fetch parameter in the empirical correlations utilised by the model to estimate emissions from passive liquid surfaces. They concluded that significant deviations may occur in this case, depending on the wind speed, the length-to-width ratio (aspect ratio) and, in the case of k_L , the depth of the tank.

The friction velocity, u_* is another critical input variable for many liquid-gas mass transfer models, as already explained. However, u_* is not as easily measured, normally requiring some degree of sophistication, for instance, high frequency anemometers, or wind speed measurements at different heights (Pond et al., 1971; Sheppard et al., 1972; Kondo, 1975; Smith, 1980; Blake, 1991; Jones and Toba, 2001; Frost and Upstill-Goddard, 2002). Therefore, on-site measurements of u_* are not routinely available (and normally not feasible) in most practical applications in which emission estimates are required. In such cases, u_* has to be inferred on the basis of meteorological records. The common approach consists of using expressions that relate u_* to the wind speed measured at a certain reference height. The correlation developed by Smith (1980) is recurrently adopted (Mackay and Yeun, 1983; Gostelow et al., 2001; Meng et al., 2008; Qiu et al., 2008; Ro et al., 2008); it is frequently recommended in guides for estimating volatilisation of compounds at WWTPs (Gostelow et al., 2001; ENVIROMEGA, 2003; US EPA, 1994, 2001) and is a built-in feature in the code of WATER9 (US EPA, 1994,

2001). Other experimental formulations are also found in the literature, for instance, Wu (1980, 1982) and Csanady (1997).

Nevertheless, these correlations were originally developed from experimental data for wind drag over the ocean, which may present important differences in relation to the wind-wave field over the relatively small liquid surfaces in WWTPs, with short fetch (distance along the liquid surface in the direction of the wind flow). Markedly, the last are characterised by less developed wave spectra, lower macroscale breaking probabilities, smaller wave amplitudes and absence of swell (free-propagating waves) (Donelan et al., 1993; Wüest and Lorke, 2003). Since the characteristics of the wave field are expected to significantly affect the wind flow near the surface and, consequently, the wind drag (Janssen, 1991, 1994, 2004; Kudryavtsev et al., 2014), the friction velocity formulations established for the ocean do not necessarily apply to small liquid surfaces such as tanks and ponds in WWTPs. Despite their widespread application to parametrise u_* in emission modelling, to date, there has never been an attempt to validate or modify these correlations for use in the small fetches and other conditions relevant for WWTPs.

1.1.4.2. *Direct measurements with a flux hood*

Although it has been the subject of several studies (e.g., Gholson et al., 1991; Wang et al., 2001; Leyris et al., 2005; Sohn et al., 2005; Capelli et al., 2009a; Hudson and Ayoko, 2009; Hudson et al., 2009; Woodbury et al., 2011; Parker et al., 2013b; Guillot et al., 2014; Prata Jr. et al., 2014, 2016b), there are still critical unsolved issues regarding the accuracy and applicability of the direct methods, including the US EPA flux hood. A preliminary evidence that the method needs further investigation is the fact that significantly different emission rate measurements are produced if different enclosure devices are used in the same sources at the same time (for instance, pairs of devices are compared in Jiang and Kaye, 1996, Hudson and Ayoko, 2009, Hudson et al., 2009, and Parker et al., 2013b; Guillot et al., 2014, presents a compelling inter-comparison involving several devices). This is an indication that the internal aerodynamics and mass transfer conditions vary among the devices.

A major concern is that the conditions inside enclosure sampling devices do not resemble critical features of the atmospheric flow (and its interaction with the liquid surface) to which the water surface is exposed in the absence of the enclosure device (Gholson et al., 1989, 1991; Hudson and Ayoko, 2008a,b; Parker et al., 2013b), such as the levels of turbulence, boundary layer structure, surface currents and waves. Furthermore, due to the relatively low sweep air flow, some devices may present an artificial increase in the concentration of compounds (concentration build up) in their headspace, which can lead to a reduction of the emission rate during the experiment and an inappropriate measurement of the local emission rate (Hudson and Ayoko, 2008b). These aspects may compromise the accuracy of the emission rate measurements and the composition of odour samples produced by the application of direct sampling devices (Hudson and Ayoko, 2008a,b).

In an attempt to address some of the questions discussed, Parker et al. (2013b) proposed a methodology for the standardisation of direct measurements of the emission rate of compounds in area sources. The approach consisted of quantifying the water evaporative fluxes from containers placed inside the enclosure device (by weighting the container with water before and after a certain time of operation) and using these fluxes to compare the emission rates of poorly volatile compounds measured with different devices and scale up the results to the field situation. This is to be done by means of water evaporative flux ratio correction factors, which are given by the ratio between the evaporation rate measured with a container placed outside (close or on top of the emitting surface) and the evaporation rate measured with an identical container inside the enclosure device. The method is based on the fact that the volatilisation of poorly volatile compounds is controlled by transport processes in the gas side of the gas-liquid interface, which are the same processes responsible for the evaporation of water. Nonetheless, the use of water evaporative flux ratio correction factors and other aspects of this approach are subjected to some important restrictions, especially if the enclosure device presents concentration build up in the headspace. On the other hand, Lucernoni et al. (2017) presented the scaling up of the emission rate measured with a wind tunnel device for compounds with gas phase-controlled volatilisation, using a model for representative values of wind speed that match the emission rate measured by the wind tunnel and allow the recalculation for other values of wind speed. However, the

resulting equations are specific for the wind tunnel and the emission model adopted by those authors, and, therefore, cannot be directly extended to the case of the flux hood.

Other recent studies have applied Computational Fluid Dynamics (CFD) in order to investigate different enclosure devices (Eckley et al., 2010; Saha et al., 2011; Lin et al., 2012; Prata Jr. et al., 2014; di Perta et al., 2016; Lucernoni et al., 2016; Prata Jr. et al., 2016b). The use of CFD enables a detailed representation of the fluid flow pattern and the mass transfer inside the enclosure devices and, thus, provides extremely valuable information for the understanding of their functioning and performance. However, as highlighted by Prata Jr. et al. (2016b), supporting experimental results are essential so as to validate and complement the CFD simulations. Unfortunately, such experimental results are scarce in the literature, in special for flux hood-type devices.

1.2. Research objectives

The overall aim of this research was to analyse the two methods that are most commonly employed for estimating the emission rate of odorous compounds from passive liquid surfaces in WWTPs, namely, predictive emission models and direct sampling with a flux hood.

Considering the challenging aspects and knowledge gaps discussed in item 1.1.4, this research had the following specific objectives:

- i. To evaluate mathematical models for the gas-side (k_G) and liquid-side (k_L) mass transfer coefficients in passive liquid surfaces in WWTPs against experimental data, and develop new, alternative approaches wherever appropriate.
- ii. To test, against experimental data representing liquid surfaces with size and wind conditions similar to those of tanks in WWTPs, different parametrisations for u_* , including the ones conventionally adopted in emission models, and develop alternative approaches to parametrise u_* , based on the analysis of the data set.
- iii. To understand how different mass transfer models are affected by the use of different u_* parametrisations.
- iv. To experimentally assess the mass transfer of compounds inside the US EPA flux hood, with focus on the experimental determination of mass transfer coefficients in the microenvironment created by the flux hood and the effects of concentration build up in the hood's headspace.
- v. To investigate the relation between the emission rates measured with the US EPA flux hood and the estimates from emission models.

1.3. Thesis structure

Considering the research objectives above, this thesis has been structured as follows. Chapter 2 is a literature review, whereas Chapters 3-6 correspond to the original research conducted, for which the methodological details are presented in each chapter, according to their specific objectives.

Chapter 2 contains a literature review focused on the topics that are addressed in the thesis. The main aim of this literature review was to summarise and discuss relevant information that gives support to the methodology and the analysis of the results in the subsequent chapters. In this sense, many equations referring to emission models and parametrisations for u_* are introduced in Chapter 2. Parts of this literature review were included in papers number 5 (Prata Jr. et al., 2017; *Water Res.* 124, 49-66) and 6 (Prata Jr. et al., 2018; *Water Res.* 130, 388-406) in page ix.

Chapter 3 presents the evaluation of mathematical models for the gas-side (k_G) and liquid-side (k_L) mass transfer coefficients, and the development of alternative approaches (research objective (i)). The results in this chapter were included in paper number 6 in page ix (Prata Jr. et al., 2018; *Water Res.* 130, 388-406).

Chapter 4 addresses the analysis of different parametrisations for u_* and the development of alternative approaches, using an experimental data set representing liquid surfaces with size and wind conditions similar to those of tanks in WWTPs (research objective (ii)). Additionally, correlations for determining the peak frequency of the wave spectrum in small bodies of water (which is necessary for the application of the proposed parametrisation of u_*) are fitted. The results in this chapter were included in paper number 5 in page ix (Prata Jr. et al., 2017; *Water Res.* 124, 49-66).

Chapter 5 is dedicated to the sensitivity analysis in order to understand how different emission models are affected by the use of different u_* parametrisations (research objective (iii)). A secondary aim of this chapter was to present the procedure to fetch-average the alternative parametrisation developed in Chapter 4, which is then tested together with other u_* parametrisations in the sensitivity analysis.

Chapter 6 reports the experimental assessment of the mass transfer inside the US EPA flux hood, with focus on the experimental determination of mass transfer coefficients in the microenvironment created by the flux hood and the effects of concentration build up in the hood's headspace (research objective (iv)). The experimental results for the mass transfer of gas phase-dominated compounds inside the US EPA flux hood are compared against an emission model for the passive surfaces in WWTPs (research objective (v)). The results in this chapter are reported in paper number 7 in page ix (Prata Jr. et al., submitted to *Atmospheric Environment*).

Chapter 7 summarises the main conclusions and contributions of the research, and identifies opportunities for future investigations.

The **Appendixes** contain additional results and figures. This thesis also includes an Electronic Annex, with the main computational codes produced.

2. LITERATURE REVIEW

2.1. Volatilisation at passive liquid surfaces

2.1.1. A note on the two-film theory

The two-film theory (also termed, “stagnant film theory”) (Whitman 1923; Lewis and Whitman 1924) is based on the assumption that, at each side of the gas-liquid interface, there is a thin layer (stagnant film) in which the molecules of gaseous compounds are transferred by molecular diffusion only, being the rate of transfer driven by concentration gradients. It is assumed that bulk gas and bulk liquid media are maintained in a well-mixed state (without significant concentration gradients) by turbulence or convective transport so that resistance associated to the stagnant films constitutes the limiting factor to inter-phase mass transfer. Figure 2.1 shows a schematic representation of concentration gradients and mass transfer processes across the films, as postulated by the two-film theory.

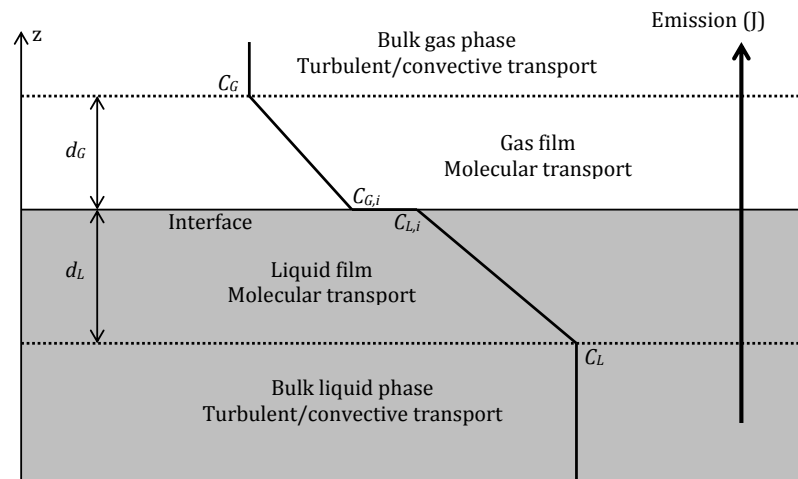


Figure 2.1. Concentration gradients and mass transfer across stagnant films.

Given that molecular diffusion is the major transport mechanism inside the stagnant films, the mass flux J ($\text{kg s}^{-1} \text{m}^{-2}$) of a compound across the films (in the direction normal to the interface) can be described by Fick's law, Equation (2.1).

$$J = -\rho D \frac{\partial \omega}{\partial z} = -D \frac{\partial C}{\partial z} \quad (2.1)$$

where ρ is the density of the fluid medium (kg m^{-3}), here assumed constant; D is the molecular diffusivity of the compound in the medium ($\text{m}^2 \text{s}^{-1}$), also assumed constant; ω is the mass fraction of the compound in the medium (kg kg^{-1}); and C is the concentration of the compound (kg m^{-3}).

It is also assumed that the films are so thin that the concentration distribution inside them can be approximated by linear profiles, which are considered constant along the whole surface, as represented in Figure 2.1. Applying Equation (2.1) along films with linear concentration profiles (which means that the gradient is constant), mass fluxes across the gas and liquid films are given, respectively, by $J_G = -D_G \frac{(C_G - C_{G,i})}{d_G}$ and $J_L = -D_L \frac{(C_{L,i} - C_L)}{d_L}$, where C_L and C_G are the compound concentrations (kg m^{-3}) in the bulk liquid phase and the bulk gas phase, $C_{G,i}$ and $C_{L,i}$ are the compound concentrations (kg m^{-3}) adjacent to the gas-liquid interface, respectively in the gas and liquid sides, and D_L and D_G are the molecular diffusivities ($\text{m}^2 \text{s}^{-1}$) of the compound in the liquid and gas phases, respectively. This is equivalent to model the mass transfer coefficients as $k_G = D_G/d_G$ (m s^{-1}) and $k_L = D_L/d_L$ (m s^{-1}), being d_G and d_L the thicknesses (m) of the gas film and the liquid film, respectively.

The existence of stagnant films with constant physical thickness is not representative of most of the situations of interest, since the layers adjacent to the air-liquid interface of passive liquid surfaces in WWTPs are likely to be sheared turbulent boundary layers, in many cases also subjected to wave-induced stresses (air side) and macro and microscale wave breaking (Brutsaert, 1975; Demars and Manson, 2013; Peirson et al., 2014). However, given its relative simplicity, some concepts used in the two-film theory, such as the notions of “film thickness” and “film resistances”, are incorporated in the representation of other modelling approaches for gas-liquid mass transfer, being also frequently used to report results (e.g., Mackay and Yeun, 1983; Jähne and Haußecker, 1998; Limpt et al., 2005; Chao et al., 2005; Chao, 2009a,b).

2.1.2. Two-resistance models

Two-resistance volatilisation models are based on the assumption that the overall resistance to volatilization or, more generally, to liquid-gas mass transfer, is composed of the resistances associated with two relatively restrict regions/layers, at the gas and liquid phases close to the interface. Inspired by the two-film theory (Whitman, 1923; Lewis and Whitman, 1924), which is in fact a two-resistance model, such regions are normally identified as “liquid film” and “gas film”, but the films do not have to be stagnant nor is the mass transfer solely due to molecular diffusion, as originally assumed in the two-film theory. In this new context, the “films” are the conceptual layers, adjacent to the interface, which present the most important constraints to the mass transfer process. Given the concept of the film-specific mass transfer coefficients, k_G and k_L , the rate of mass transfer of a given compound across each film can be rewritten as Equations (2.2a) and (2.2b).

$$J_G = k_G(C_{G,i} - C_G) \quad (2.2a)$$

$$J_L = k_L(C_L - C_{L,i}) \quad (2.2b)$$

Differences between existing two-resistance mass transfer models (e.g., Lewis and Whitman, 1924; Deacon, 1977; Mackay and Yeun, 1983; Springer et al., 1984; Gostelow et al., 2001) are due to the approaches used to estimate k_L and k_G .

The fact that, in the absence of chemical reactions, the mass flux across the liquid film (J_L) is the same mass flux across the gas film (J_G), corresponding to the overall mass flux between phases (J), makes Equation (2.2a) equals to Equation (2.2b), written as Equation (2.3).

$$J = k_G(C_{G,i} - C_G) = k_L(C_L - C_{L,i}) \quad (2.3)$$

From Henry's law, $C_{G,i} = C_{L,i}K_H$ (where K_H is the non-dimensional Henry's law coefficient); substituting this in Equation (2.3) and rearranging, Equation (2.4) is obtained.

$$C_{L,i} = \frac{k_L C_L + k_G C_G}{k_G K_H + k_L} \quad (2.4)$$

Substituting Equation (2.4) back in Equation (2.3) and rearranging, one arrives at Equation (2.5).

$$J = \frac{k_L k_G}{k_G + \frac{k_L}{K_H}} \left(C_L - \frac{C_G}{K_H} \right) \quad (2.5)$$

Equation (2.5) is the classical equation for liquid-gas mass transfer in terms of the liquid-phase overall mass transfer coefficient (m s^{-1}), K_L , which can be written as:

$$J = K_L \left(C_L - \frac{C_G}{K_H} \right) \quad (2.6a)$$

and

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_G K_H} \quad (2.6b)$$

It is interesting to note that Equation (2.6) describes both volatilisation (positive J) and solubilisation (negative J), depending on whether the difference between C_L and C_G/K_H is positive or negative. The conditions for validity of Equation (2.6) are generally met at the passive liquid surfaces present in WWTPs, unless the air-liquid interface is significantly covered by surface films, scums or other physical barriers (Hudson and Ayoko, 2008a). Scenarios in which chemical reactions occur in the vicinity of the interface may require adaptation of the two-resistance model. The incorporation of chemical reactions and surface films is treated in Schwarzenbach et al. (2003) (for an example including chemical reactions, see Blunden et al., 2008). Additionally, Prata Jr. et al. (2017; paper number 10 in page x) presents a discussion on how evaporation can potentially affect the liquid-gas mass transfer of compounds.

The terms $1/k_L$ and $1/(k_G K_H)$ in Equation (2.6b) can be understood as the resistances to mass transfer associated to the liquid and gas films, respectively; thus, the overall resistance to mass transfer between phases, $1/K_L$, is the sum of these two film

resistances. The way the overall mass transfer coefficient (K_L) is related to K_H , k_L and k_G , as expressed in Equation (2.6b), allows important inferences with practical outcomes, as discussed in 2.1.3. Concerning this last point, it is important to highlight that Equation (2.6b) is not dependent on the formulae by which k_L and k_G are calculated.

2.1.3. Influence of Henry's law coefficient on the volatilisation of compounds

In equilibrium conditions, the spontaneous random motion of molecules from liquid to gas compensates the motion from gas to liquid, with no net mass flux between phases. In such equilibrium cases, the partition between liquid and gas phases is supposed to obey a definite proportion (dependent on temperature) and can be mathematically described by Henry's law, in non-dimensional form $K_H = C_G/C_L$.

If equilibrium is not established, an overall mass transfer will occur. This transfer will be from the liquid to the gas phase (volatilisation) if liquid-phase concentration is higher than the equilibrium concentration; if the liquid-phase concentration is lower than the equilibrium concentration, the flux will be in the opposite direction (solubilisation). In these cases, Henry's law does not describe the relation between concentrations in the bulk of gas and liquid phases. However, it is assumed that equilibrium is reached almost-instantaneously at the gas-liquid interface, so that Henry's law is still a valid means of relating interface concentrations (Jähne and Haußecker, 1998; Chao et al., 2005; Peirson et al., 2014), being expressed as $K_H = C_{G,i}/C_{L,i}$.

Besides determining equilibrium concentrations, Henry's law coefficient also has fundamental influence on whether the mass transfer process is dominated by conditions of liquid-phase, gas-phase or both. By applying Equation (2.6b) for air-water mass transfer and citing considerations of Schwarzenbach et al. (2003) and experimental results from Smith et al. (1980) and Dilling (1977), Hudson and Ayoko (2008a) summarised that:

- In the case of highly volatile compounds, with K_H values significantly higher than 10^{-3} , the term $1/(k_G K_H)$ becomes negligible, so $K_L \approx k_L$, which means that

the overall mass transfer coefficient is limited by conditions of transport in the liquid film (liquid phase-dominated);

- Conversely, in the case of less volatile compounds, with K_H values significantly lower than 10^{-3} , the term $1/k_L$ becomes negligible when compared with $1/(k_G K_H)$, resulting in $K_L \approx k_G K_H$ and, thus, the overall mass transfer coefficient is limited by conditions of transport in the gas film (gas phase-dominated);
- In cases when K_H is about 10^{-3} , no term can be neglected, so both gas-film and liquid-film conditions are relevant to the overall rate of mass transfer.

Jähne and Haußecker (1998) draw attention to the fact that the exact limits of these solubility ranges determining the level of dominance by water, air or both phases are dependent on the Schmidt number, $Sc = \nu/D$ (in which ν is the kinematic molecular viscosity of the medium, units $\text{m}^2 \text{s}^{-1}$), and the surface roughness (which is very well illustrated in the figure 2 of Jähne and Haußecker, 1998). It is important to note that both K_H and Sc (especially in water) vary with temperature (Jähne and Haußecker, 1998; Hudson and Ayoko, 2008a).

2.2. The gas-film mass transfer coefficient (k_G)

2.2.1. Theoretical models for k_G

2.2.1.1. *Models based on the developing boundary layer over a smooth flat plate*

The developing boundary layer over a smooth flat plate approached by wind with uniform velocity profile is a classical situation which serves as base for the general study of boundary layers (see Schlichting, 1968). In the laminar case, analytic solutions exist; in the turbulent case, semi-empirical parametrisations for the mass transfer coefficient in the air-side boundary layer have been established. Among those, Thibodeaux and Scott (1985), citing Sherwood and Pigford (1952) and Sherwood et al. (1975), support Equation (2.7) and Equation (2.8), for the laminar and turbulent boundary layers, respectively.

$$k_G = 0.644 \frac{D_G}{X} Re_X^{1/2} Sc_G^{1/3} \quad (2.7)$$

and

$$k_G = 0.036 \frac{D_G}{X} Re_X^{4/5} Sc_G^{1/3} \quad (2.8)$$

where X is the length of the plate (m), the wind fetch in this case; $Re_X = XU_0/\nu_G$ is the fetch Reynolds number, with U_0 the velocity (m s^{-1}) of the approaching uniform flow (or the “free-stream” velocity) and ν_G the kinematic viscosity ($\text{m}^2 \text{s}^{-1}$) of the air (gas phase); $Sc_G = \nu_G/D_G$ denotes the Schmidt number of the compound in the air (gas phase). As highlighted by Thibodeaux and Scott (1985), Equation (2.7) was experimentally verified in aerodynamic wind tunnels for Re_X between 8000 and 20000, while Equation (2.8) for Re_X ranging from 20000 to 300000. It is important to notice that the average k_G along the length of the boundary layer is evaluated from Equations (2.7) and (2.8).

Equation (2.7) is obtained for a laminar boundary layer with velocity profiles described by the classical solution of Blasius (see, for instance, Schetz, 1984). Laminar boundary layers are likely to occur inside some portable wind tunnels used for direct sampling of emissions (Bliss et al., 1995; Capelli et al., 2009a; see also Prata Jr. et al., 2014); however, they are not an appropriate model for the atmospheric boundary layer, which is typically turbulent (Seinfeld, 1986, Jacobson, 1999). Regarding Equation (2.8), although representing a turbulent boundary layer, two main critical points prevent its application for modelling k_G over passive liquid surfaces in WWTPs and other environmental situations: (i) the approaching flow in such cases does not normally have a uniform velocity distribution (a condition for which Equation (2.8) was developed), so that the free-stream velocity U_0 cannot be rigorously defined; and (ii) the flow over passive liquid surfaces in the field does not necessarily resemble the flow over a smooth plate, since waves generated by the wind may induce an effective roughness in the air flow (further discussion in section 2.4).

2.2.1.2. Sutton`s (1953) model based on Taylor`s statistical theory

Sutton (1953) discusses the case of a compound evaporating from a smooth rectangular surface with finite length X in the direction of the wind and virtually infinite width in the cross-wind direction. In the analysed case, the difference $C_{G,i} - C_G$ is taken as constant over the whole surface, with C_G determined far from the surface, so it has the same value as in the air upwind the emitting surface. Also, the mean wind velocity profile over the surface was assumed to be satisfactorily approximated by a power law as $u(z) = U_Z(z/Z)^m$, where $u(z)$ is the wind velocity (m s^{-1}) at any given height z (m), U_Z is the wind velocity measured at a reference height Z , and m is the exponent that fits the approximate profile. Using Taylor`s (1922, 1932, 1935) statistical theory and making additional assumptions, Sutton arrived at an analytical solution for the concentration field above the surface (taking into account advection effects in the wind direction), which, in turn, gives an expression for the evaporation rate per unit of cross-wind length ($\text{kg s}^{-1} \text{m}^{-1}$) that is equivalent to a boundary-layer mass transfer coefficient as in Equation (2.9a).

$$k_G = A U_Z^{(2-n)/(2+n)} X^{-n/(2+n)} \quad (2.9a)$$

where A is a constant dependent on the reference height Z and the kinematic viscosity of air; n , related to m as $m = n/(2 - n)$, is an exponent used by Sutton to parametrise the correlation coefficient between turbulent velocity fluctuations, in the context of Taylor`s statistical theory.

For a wind profile with exponent $m = 1/7$ (corresponding to $n = 1/4$), which is the profile normally attributed to the turbulent flow over a smooth plate (Sutton, 1953), Equation (2.9a) can be written as Equation (2.9b):

$$k_G = A U_Z^{0.78} X^{-0.11} \quad (2.9b)$$

One of the major drawbacks of Sutton`s model is that the molecular diffusivity of the compound, which is particularly relevant for the transport in the viscous sublayer adjacent to the smooth surface, is not explicitly taken into account; one can attempt to incorporate the molecular diffusivity if the constant A is adjusted experimentally, as

done, for example, by Mackay and Matsugu (1973) (see 2.2.3.1). Another limitation is that the model is not suitable for the flow over passive liquid surfaces with aerodynamic roughness, which may be the case if waves are present in WWTPs (section 2.4).

2.2.1.3. *Brutsaert's (1975) model based on the assumption that the "interfacial sublayer" is controlled by renewal mechanisms*

Brutsaert (1975) derived a model for calculating the air-side mass (and heat) transfer over flat surfaces above which a steady-state, turbulent, two-dimensional wind boundary layer is present. Concentration gradients in the along-wind direction are neglected (thus neglecting any advection effects, except the turbulent diffusion in the vertical direction), meaning that the model may not be suitable to describe the very beginning of the concentration boundary layer at the upwind end of the emitting surface (where the boundary-layer thickness and the concentration values change significantly in the wind direction). The model was constructed based on the idea, supported by experimental observations cited by Brutsaert (1975), that the mass transfer in the region very close to the surface (called "interfacial sublayer" in the original paper; in the case of an aerodynamically smooth surface, this comprises the viscous and buffer sublayers of the inner boundary layer of the turbulent flow) is controlled by renewal mechanisms, which, in turn, are imposed by turbulent eddies coming from the fully-turbulent dynamic sublayer ("log sublayer") immediately above the interfacial sublayer. Figure 2.2 schematically illustrates the sublayers considered in the model.

The average renewal frequency was assumed to be proportional to the frequency of the turbulent eddies at the Kolmogorov's scale (frequency scale given by $f = (\varepsilon/\nu)^{1/2}$, being ε the dissipation rate of turbulent kinetic energy, units $\text{m}^2 \text{s}^{-3}$) calculated at the height z_s corresponding to the bottom of the dynamic sublayer (the boundary between the dynamic and interfacial sublayers; see Figure 2.2). For the dynamic sublayer, with logarithmic velocity profile, $\varepsilon = u_*^3/(\kappa z)$, where u_* is the friction velocity (m s^{-1}) and κ is the von Kármán constant. Using this expression, taking $z_s = 30\nu/u_*$ (considered by Brutsaert as the limit of the interfacial sublayer), considering a linear velocity profile in the viscous sublayer and making some additional assumptions about the behaviour of the renewing eddies, Brutsaert (1975) derived the following result (Equation (2.10)) for the mass transfer coefficient over a smooth flat surface:

$$k_G^s = c_s u_* S c_G^{-2/3} \quad (2.10)$$

where c_s is a dimensionless constant to be determined experimentally. Based on a compilation of experimental results, Brutsaert (1975) suggests $c_s = 1/13.6$.

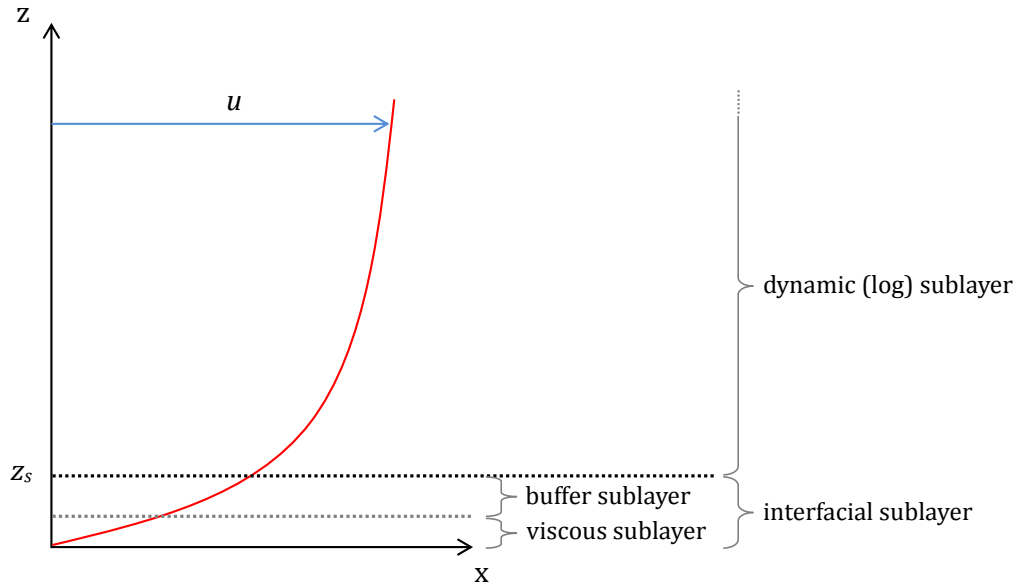


Figure 2.2. Schematic representation of the mean horizontal velocity profile in the inner boundary layer of the smooth turbulent flow over a flat plate, indicating the sublayers considered in Brutsaert's (1975) model.

It is important to highlight that Equation (2.10) gives the coefficient for the mass transfer between the interface (concentration $C_{G,i}$) and the height z_s (in this case, $z_s = 30\nu/u_*$); to denote this, the superscript “s” was included in the representation of the mass transfer coefficient k_G^s . If the bulk concentration C_G is measured at a height $z_m > z_s$, the resistance to mass transfer between the heights z_s and z_m has to be included (discussed in 2.2.1.5).

Brutsaert (1975) also presented a model for rough surfaces; however, as he mentioned in the original paper, this model seems not to be completely appropriate for the mass transfer over waves and, therefore, will not be covered in the present analysis.

2.2.1.4. *Deacon`s (1977) model based on the Reichardt`s (1951) parametrisation for the effective diffusivity in the viscous and buffer sublayers*

Similarly to Brutsaert (1975), Deacon (1977) treats the case of mass or heat transfer over a smooth flat surface in contact with a steady-state, turbulent, two-dimensional wind boundary layer, also neglecting concentration gradients in the along-wind direction (hence, the same restriction applies: the model may not be suitable for the initial stages of the concentration boundary layer at the upwind end of the emitting surface). Deacon`s derivation, however, is based on the Reichardt`s (1951) parametrisation for the effective diffusivity D^{eff} (the sum of the molecular and eddy diffusivities) along the viscous and buffer sublayers of the inner region of the turbulent boundary layer over a smooth flat plate, which is given by $D^{eff} = D\{1 + \kappa Sc \zeta_l [z^+ / \zeta_l - \tanh(z^+ / \zeta_l)]\}$, where $z^+ = u_* z / \nu$ and ζ_l is a constant (Deacon adopts the value $\zeta_l = 11.7$, for $\kappa = 0.41$). The resistance to mass transfer R_s between the surface and a height z_s (the schematic representation in Figure 2.2 also applies here, but, in this case, z_s is located just slightly above the border of the buffer sublayer) is then computed as Equation (2.11a):

$$R_s = \frac{1}{k_G^s} = \int_0^{z_s} \frac{1}{D^{eff}} dz \quad (2.11a)$$

Deacon (1977) numerically computed the integral in Equation (2.11a) for $z_s = 50\nu/u_*$ and proposes an approximation that, for $0.6 < Sc_G < 10$ (which is the typical range of Sc_G for chemicals and also heat in air), can be rewritten in terms of k_G^s as Equation (2.11b) below.

$$k_G^s = \frac{1}{15.2} u_* Sc_G^{-0.61} \quad (2.11b)$$

Similarly to what was said about Brutsaert`s (1975) formulation, the mass transfer coefficient calculated by Equation (2.11b) accounts for the mass transfer between the surface and the height $z_s = 50\nu/u_*$ (that is the reason for the superscript “s” in k_G^s); again, if the bulk concentration C_G is measured at a height $z_m > z_s$, the resistance to

mass transfer between the heights z_s and z_m has to be included, as discussed next (2.2.1.5).

2.2.1.5. *Computing the total resistance to mass transfer in the gas phase*

As mentioned before, both Brutsaert's (1975) and Deacon's (1977) formulations, Equations (2.10) and (2.11b), respectively, calculate the coefficient for mass transfer between the surface (concentration $C_{G,i}$) and a height z_s at the bottom of the dynamic (log) sublayer (where the log sublayer encounters the buffer sublayer; see Figure 2.2), taken as $z_s = 30\nu/u_*$ by Brutsaert and $z_s = 50\nu/u_*$ by Deacon. If the bulk concentration C_G is measured at a height $z_m > z_s$, the gas-film mass transfer coefficient k_G has to account for the total resistance to mass transfer between the surface $z = 0$ and z_m , so Equation (2.2a) can be properly applied. The procedure to do so, following described, is contained in both the works of Brutsaert (1975) and Deacon (1977).

The total resistance to mass transfer in the gas phase (between $z = 0$ and z_m), $R_G = 1/k_G$, can be calculated as the association in series between two resistances, as shown in Equation (2.12): the resistance $R_s = 1/k_G^s$, between $z = 0$ and z_s ; and the resistance R_m , between z_s and z_m .

$$R_G = \frac{1}{k_G} = R_s + R_m \quad (2.12)$$

Following the notation adopted here, k_G^s is given by Equation (2.10), if Brutsaert's formulation is used, and by Equation (2.11b), if Deacon's formulation is used. The resistance R_m can be calculated with ease, if the measurement height z_m is within the fully-turbulent, log sublayer. In this sublayer, the molecular diffusivity can be neglected compared to the turbulent diffusivity, thus the effective diffusivity can be approximated as $D^{eff} = Sc_t^{-1} \kappa u_* z$, where Sc_t is the turbulent Schmidt number and the resistance R_m is given by Equation (2.13).

$$R_m = \int_{z_s}^{z_m} \frac{1}{D^{eff}} dz = Sc_t \frac{1}{\kappa u_*} \ln \left(\frac{z_m}{z_s} \right) \quad (2.13)$$

Figure 2.3 shows a comparison of k_G calculated for water vapour ($Sc_G = 0.61$ in air, at 25 °C; Sc_t taken as 1 for the moment) using Equations (2.12) and (2.13) together with Brutsaert's (Figure 2.3a) and Deacon's (Figure 2.3b) k_G^s formulations, for various u_* and considering different measurement heights z_m . As expected, k_G decreases as z_m increases, since the resistance R_m becomes larger. It is important to observe that the k_G calculated for the same z_m using either Brutsaert's or Deacon's formulations are very similar (generally with difference of order 1% or less); it is remarkable that these formulations, derived through different paths, arrive at practically equivalent results. It can also be noted that, although the curves corresponding to z_m other than z_s are not precisely linear, they can be fairly approximated by a straight line.

The fact that k_G significantly changes with the reference height z_m is critical for the proper determination and use of k_G formulations, otherwise unrealistic resistances would be incorporated. If an actual measurement of C_G is performed, it is imperative that the measurement height z_m is within the dynamic sublayer and also within the limits of the concentration boundary layer. On the other hand, if C_G is approximated by the background concentration upwind the emitting surface, then z_m has to coincide with (or be sufficiently close to) the top limit of the concentration boundary layer.

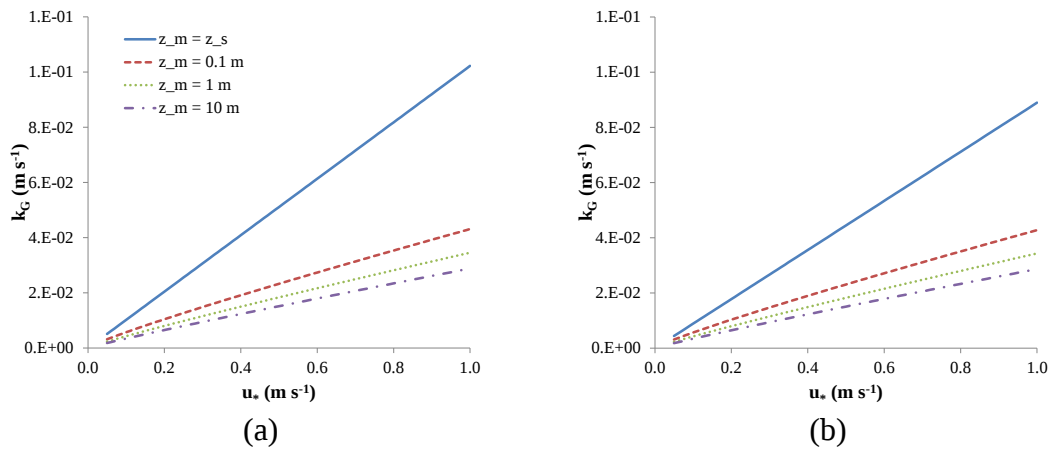


Figure 2.3. Gas-film mass transfer coefficient k_G for water vapour obtained by using Equations (2.12) and (2.13) together with: (a) Brutsaert's (Equation (2.10)) and (b) Deacon's (Equation (2.11b)) k_G^s formulations, for different measurement heights z_m (legend in (a)).

2.2.2. Effects of waves on k_G

Waves on liquid surfaces can affect the dynamics of mass transfer in the air boundary layer by:

- i. Increasing turbulent transport (which means increasing u_*) in the dynamic sublayer, due to the form drag arising from resonant wind-wave interactions (“wave-induced stress”) and air-flow separation at breaking waves (Janssen, 2004; Caulliez et al., 2008; Kudryavtsev et al., 2014; Kudryavtsev and Chapron, 2016);
- ii. Modifying the profile of wind velocity and eddy diffusivity in the proximity of a wavy liquid surface, due to the wind-induced stresses and air-flow separation (Kudryavtsev et al., 2014);
- iii. Generating separation bubbles downwind the air-flow separation (detachment) point at breaking waves.

The increase in turbulent transport listed above as process (i) is automatically taken into account for the modelling of k_G if u_* is measured directly or if an appropriate parametrisation for u_* (i.e., one that satisfactorily incorporates the changes in u_* due to the wind-wave dynamics) is adopted; further discussions on u_* parametrisations applied to emission modelling in WWTP are presented in section 2.4 and Chapter 4. A modified wind velocity profile and the existence of separation bubbles (listed above, respectively, as processes (ii) and (iii)) are much more difficult to describe and to include in a simple theoretical model for liquid-gas mass transfer. A remarkable work was performed by Kudryavtsev et al. (2014), who applied a wind-over-waves coupling model to calculate the heat transfer (which is analogous to mass transfer) over sea waves. Those authors estimated the turbulent fluxes in the air boundary layer by solving a coupled system of conservation equations for momentum in the air side and wave energy in the liquid side, using parametrisations for wave-induced and air flow separation stresses, wave breaking and non-linear wave-wave interactions, among others. They show that, in the region directly influenced by the waves, wind velocity and temperature profiles deviate to some extent from the classical log-linear profile. Moreover, their results suggest that k_G

can be expected to generally increase with the wind speed (due to the increase of u_*), but not at the same rate as u_* , which is explained by the sheltering effect due to the wave-induced stress and the air flow separation.

However, since some of the parametrisations adopted by Kudryavtsev et al. (2014) are based on oceanic data and they do not take into account air-flow separation arising from the breaking of small-scale gravity waves, their results cannot be directly extrapolated to the mass transfer in relatively small liquid surfaces, such as WWTPs, for which a much less developed wind-wave field can be expected (section 2.4). The application of wind-over-waves-coupled models to WWTPs is theoretically possible, although not practical and lacking of preliminary data (as briefly discussed in section 2.4). Thus, the exact extent to which k_G at passive liquid surfaces in WWTPs is influenced by processes (ii) and (iii) is presently not clear, and these remain as open matters for investigation.

Nonetheless, experimental work on the air flow above short gravity waves available in the literature can shed some light on possible effects of process (iii). Before further developing this discussion, it is convenient to recall the two “classes” into which wave breaking events are usually divided, namely *macroscale* and *microscale* breaking. Macroscale breaking refers to the breaking events that manifest as plunging or intense spilling at the breaking front, generally accompanied by significant air entrainment, which leads to the typical “whitecaps” (Banner and Phillips, 1974; Caulliez et al., 2008; Reul et al., 2008; Kudryavtsev et al., 2014). Microscale breaking (or “microbreaking”) corresponds to the breaking of very short gravity waves (wave lengths typically ranging from 0.05 to 0.3 m), with none or almost negligible air entrainment; normally, parasitic capillary waves are generated in this process and travel at a similar speed as the breaking crest (Banner and Phillips, 1974; Peirson and Banner, 2003; Siddiqui and Loewen, 2007).

Air-flow separation can certainly be expected to occur wherever macroscale breaking is present, due to the abrupt surface disruptions (Kudryavtsev et al., 2014). However, in the context of liquid surfaces in WWTPs, where short fetches and low to moderate wind conditions commonly occur, macroscale breaking events are likely to be inexistent or very sparse. Caulliez et al. (2008) observed that the first signs of (sporadic) air

entrainment appeared at wind speeds (referenced at 10 m height) of 10, 9.5 and 8 m s⁻¹, for fetches of 10, 13 and 26 m, respectively. Rhee et al. (2007) estimated that the rate of macroscale breaking is less than 3% for friction velocities up to 0.6 m s⁻¹ along a tank with total length of 40 m. It is important to note that this rate may increase for longer fetches and higher wind speeds.

Microscale breaking waves, on the other hand, are widely observed at low to moderate wind speeds, even for short fetches (Banner and Phillips, 1974; Kawamura and Toba, 1988; Peirson and Banner, 2003; Siddiqui and Loewen, 2007). Air-flow separation from the crests of very short gravity waves has been verified experimentally (Kawai, 1981, 1982; Kawamura and Toba, 1988; Reul et al., Veron et al., 2007; 2008; Shaikh and Siddiqui, 2011b; Buckley and Veron, 2016). Although some of these studies (Kawai, 1981, 1982; Veron et al., 2007; 2008; Shaikh and Siddiqui, 2011b; Buckley and Veron, 2016) do not report if the waves were undergoing microscale breaking, there is a high probability that most of the observed separation events occurred over microscale breaking crests, taking into consideration images of the flow presented in the papers and also indications by other authors who worked under similar conditions (Kawamura and Toba, 1988; Peirson and Banner, 2003; Reul et al., 2008). The occurrence of air-flow separation over short gravity waves appears to be dependent mainly on the local slope at the wave crests: a local surface slope (i.e., the local gradient of the surface) of 0.6 or greater at the leeward face of the wave crest is identified as a sufficient condition for air flow to separate (Kawai, 1982; Reul et al., 2008; Shaikh and Siddiqui, 2011b). In the context of their experiment, Shaikh and Siddiqui (2011b) argued that the air-flow separation observed over waves with smaller gradient was remnant from an earlier stage, at which the slope was equal or greater than 0.6 and triggered the separation; they also report that no separation was verified for slopes less than 0.4. Reul et al. (2008) explain that the large surface slope at the leeward side of the crests produces a large adverse pressure gradient, which leads to air-flow separation. Waves from which the air flow separates are also normally higher than the ones without separation (Kawai, 1982; Reul et al., 2008; Shaikh and Siddiqui, 2011b). As for the frequency at which this process happens, it varies greatly and depends on fetch and wind conditions (both of which certainly influence the maximum slope of the wave crests); for example: Kawai (1982) registered 47 separation events in a total of 79 wave crests examined (59%), for

$u_* = 0.46 \text{ m s}^{-1}$ and fetch 3.7 m; at a fetch of 2.1 m, the results of Shaikh and Siddiqui (2011b) show air-flow separation frequencies of 24 and 64% (this includes the remnant separation bubbles downwind crests with steepness less than 0.6), for corresponding u_* values (extracted from Shaikh and Siddiqui, 2011a) of 0.149 and 0.175 m s^{-1} , respectively; Buckley and Veron (2016) report that less than 20% of the waves presented associated air-flow separation, for $u_* = 0.167 \text{ m s}^{-1}$ and fetch 22.7 m (equivalent 10 m wind speed of 5 m s^{-1}).

Investigations using particle image velocimetry (PIV) reveal important features of the air flow within the separation bubbles downwind the crest of short gravity waves. Generally, the separation bubble develops as a recirculation region, but not as a complete dead zone, with reversed flow in relation to the wave form and often a mildly complex pattern of eddies (Kawai, 1982; Veron et al., 2007; Reul et al., 2008). Flow velocities and vorticity are extremely reduced close to the water surface (Veron et al. 2007; Reul et al., 2008; Shaikh and Siddiqui, 2011b; Buckley and Veron, 2016), as are the near-surface shear stress (Veron et al., 2007; Reul et al., 2008) and the dissipation of turbulent kinetic energy (Shaikh and Siddiqui, 2011b). These particular aspects of the flow can be expected to drastically decrease mass transfer in the boundary layer at the air side of the water surface covered by separation bubbles.

It is important to remember, however, that the separation bubble does not extend along the whole wave form: flow reattachment takes place at some point downwind the wave crest from which the flow detached, before the next wave crest. The location of the reattachment point is highly variable and probably depends on the wind speed, the geometrical characteristics of the wave and the stage of the wave breaking (Kawai, 1982; Kawamura and Toba, 1988; Reul et al., 2008). In their study of mechanically-generated waves swept by wind, Reul et al. (2008) report (in their Figure 12) extents of separation bubble ranging approximately from 10 to 60% of the wave form, for the cases concerning microscale breaking. Adding this to the fact that only a fraction of the short gravity waves present separation bubbles, as discussed in the previous paragraph, one can expect that, in many cases, the majority of the water surface will correspond to regions without air-flow separation. In the non-separated boundary layer and in the boundary layer re-established downwind the reattachment point, the mean flow presents many of the characteristics of a typical turbulent flow over a flat plate, but following the

wave form, except for some distortions and increased shear stress resulting from the wave influence (Kawai, 1982; Veron et al., 2007; Shaikh and Siddiqui, 2011b). Therefore, in the context of the passive liquid surfaces in WWTPs, the significance of air-flow separation for the gas-film mass transfer coefficient, averaged throughout the whole surface, will depend on how much of the surface is covered by separation bubbles and how much the increase in the shear stress outside the separation regions is able to balance the reduction of mass transfer inside the bubbles.

2.2.3. Empirical correlations for k_G

Different empirical correlations, fitted to experimental mass transfers results, have been proposed by several authors with the aim of estimating the gas-film mass transfer coefficient over liquid surfaces. The present analysis focuses on the empirical k_G correlations that are most widely used in the context of emission modelling for WWTPs: the expression proposed by Mackay and Matsugu (1973), which is the one incorporated in the US EPA-endorsed emission model WATER9; the equation by Mackay and Yeun (1983), adopted by the model TOXCHEM+; and the correlation used by Gostelow et al. (2001) in their emission model. The corresponding expressions are presented in Table 2.1, which also summarises relevant auxiliary information. In all three cases, the k_G calculated by the correlations corresponds to the mean value averaged along the whole water surface (fetch-averaged k_G).

Table 2.1. Empirical correlations to calculate k_G used for emission modelling in WWTPs.

Reference	Expression	Additional information
Mackay and Matsugu (1973) ^a	$k_G = 4.82 \times 10^{-3} U_{10}^{0.78} X^{-0.11} S c_G^{-0.67}$ (2.14)	- Follows the general form proposed by Sutton (1953), Equation (2.12b), with molecular diffusivity taken into account by including the factor $S c_G^{-0.67}$. - The value of the constant was obtained by adjusting to cumene evaporation data in small pools (1.2 × 1.2 m and 1.2 × 2.4 m) placed outdoors; the authors did not report the range of wind speeds during the experiments.
Mackay and Yeun (1983)	$k_G = 1 \times 10^{-3} + 46.2 \times 10^{-3} u_* S c_G^{-0.67}$ (2.15)	- Adjusted to experimental data regarding water evaporation and VOCs volatilisation obtained in a laboratory wind-wave tank of fetch 6 m. u_* range: 0.271 – 0.993 m s⁻¹; equivalent U_{10} range: 8.36 – 23.11 m s⁻¹.
Gostelow et al. (2001)	$k_G = 0.04 u_* S c_G^{-0.67}$ (2.16)	- Adjusted to experimental water evaporation data compiled from different sources, all obtained in wind-wave tanks, with fetches ranging from 4.5 to 32.2 m. u_* range: 0.039 – 0.993 m s⁻¹; equivalent U_{10} range: 1.0 – 24.5 m s⁻¹.

^a The value of the constant in Mackay and Matsugu's (1973) correlation given here, 4.82×10^{-3} , is for input variables in SI units, as suggested by US EPA (1994).

2.2.3.1. Mackay and Matsugu (1973)

Mackay and Matsugu (1973) adopted the general theoretical form proposed by Sutton (1953), Equation (2.9b), discussed previously (2.2.1.2), incorporating the factor $Sc_G^{-0.67}$ in order to account for the compounds' molecular diffusivity. In this case, the constant A had to be adjusted experimentally, which was done by using cumene evaporation data obtained in small pools (1.2×1.2 m and 1.2×2.4 m) placed outdoors. The wind speed was not measured on site, but taken from a nearby meteorological station; the authors did not report the range of wind speeds occurring during the experiments. The final equation, Equation (2.14), is shown in Table 2.1, with the constant converted to be consistent with input variables in SI units, as suggested by US EPA (1994).

It is important to mention that Mackay and Matsugu (1973) adjusted Equation (2.14) using the effective diameter (the diameter of a circular pool with the same area as the experimental surface) as the fetch parameter X ; this is also the approach followed by the WATER9 model (US EPA, 1994, 2001). However, as explained in 2.2.1.2, Sutton's (1953) model was derived considering X as the actual physical fetch, i.e., the length across the surface in the direction of the wind. The use of the effective diameter instead of the physical fetch introduces systematic deviations in the calculation of k_G , especially for large length-to-width ratios (which is generally the case of laboratory wind-wave tanks), as discussed in Prata Jr. et al. (2016a).

2.2.3.2. Mackay and Yeun (1983)

Mackay and Yeun (1983) carried out mass transfer experiments in a wind-wave tank with fetch 6 m. By varying the wind speed in the wind tunnel, they obtained friction velocities in the range $0.271 - 0.993 \text{ m s}^{-1}$, corresponding to U_{10} in the range $8.36 - 23.11 \text{ m s}^{-1}$ (calculated based on u_* and roughness length data reported in their paper). Water evaporation rate was measured by knowing the volume of water spent to keep a constant water level in the tank using a “chicken feeder” system; from this, the k_G for water was calculated. The mass transfer coefficients for several volatile organic compounds (VOCs) were determined from the decaying of their concentration in the liquid phase.

Correlations for k_G and k_L , in the form of linear functions of u_* , were adjusted to the mass transfer coefficients obtained experimentally, normalised by powers of the Schmidt number ($Sc_G^{-0.67}$ and $Sc_L^{-1/2}$, respectively). Intercepts of 1×10^{-3} and 1×10^{-6} were introduced in the expressions for k_G and k_L , in order to account for an “still-air” mass transfer coefficient (i.e., the mass transfer coefficient when there is no wind). By doing so, they arrived at Equation (2.15) for k_G . Mackay and Yeun`s (1983) correlation for k_L will be discussed later in this chapter (sub-section 2.3.3.1).

2.2.3.3. Gostelow et al. (2001)

The approach applied by Gostelow et al. (2001) to develop their k_G correlation is explained in detail by Gostelow (2002). These authors compiled a data set regarding u_* and k_G for water vapour, comprising the results reported by three distinct sources: Liss (1973); Mackay and Yeun (1983); and Ocampo-Torres et al. (1994). Overall, the data set used by Gostelow et al. (2001) covered a range of fetches from 4.5 to 32.2 m and u_* from 0.039 to 0.993 m s⁻¹ (equivalent to U_{10} from 1.0 – 24.5 m s⁻¹). These authors were able to adjust a straight line to the data set (with k_G normalised by $Sc_G^{-0.67}$), obtaining Equation (2.16).

2.3. The liquid-film mass transfer coefficient (k_L)

2.3.1. Theoretical models for k_L

Deacon (1977) suggested that the mass transfer at the liquid side of a flat (“unruffled”) air-water interface is dominated by the surface currents produced by the wind and resembles the mass transfer in a smooth turbulent boundary layer over a flat plate. Thus, he again used Reichardt`s (1951) parametrisation for the effective diffusivity D^{eff} and followed the same basic procedure described in 2.2.1.4, but in this case based on the friction velocity and Schmidt number in the liquid phase, $u_{*,L}$ and Sc_L , respectively. The numerical integration of an analogous form of Equation (2.11a) for $z_s = 50\nu/u_{*,L}$ (with ν being the kinematic viscosity of the liquid phase, in this case) led to the

approximation expressed by Equation (2.17), valid for $200 < Sc_L < 5000$ (typical range of Sc_L for chemicals in water).

$$k_L = 0.082 u_{*,L} Sc_L^{-2/3} \quad (2.17)$$

It is interesting to note that, because of the relatively high values of Sc_L for chemicals in water, the thickness of the mass transfer boundary layer is usually of the same order of the depth z_s , in the sheared surface currents considered by Deacon (1977); therefore, the additional resistance to mass transfer at depths larger than z_s can be neglected (this is different in the gas side of the interface, where the boundary layer thickness is much larger than z_s). Since the friction velocity at the gas side, u_* , is normally easier to be measured, the friction velocity in the liquid side can be calculated as $u_{*,L} = u_*(\rho_G/\rho_L)^{1/2}$, which comes from the continuity of the shear stresses at a flat gas-liquid interface, being ρ_G and ρ_L the respective densities (kg m^{-3}) of the gas and liquid phases.

For practical purposes, however, application of Deacon's (1977) approach is considerably limited, since situations with a sheared and at the same time unruffled interface are rare. The presence of surface ripples and waves changes not only the rates of mass transfer in the liquid-side of the interface, but also the dependency of k_L on Sc_L , which shifts from a power $Sc_L^{-2/3}$ to a power $Sc_L^{-1/2}$ (this means that the dependency of k_L on the power of the molecular diffusivity of the compound in the liquid D_L changes from 2/3 to 1/2) (Jähne and Haußecker, 1998; Peirson et al., 2014). This change in the exponent of Sc_L (or D_L) can be explained as a result of surface renewal (Higbie, 1935; Danckwerts, 1951; Münnich and Flothmann, 1975; Banerjee and McIntyre, 2004; Turney and Banerjee, 2013), surface divergence (Banerjee, 1990; Csanady, 1990; Jähne and Haußecker, 1998; Peirson et al., 2014) or the interaction of both (Turney and Banerjee, 2013).

The surface renewal theory, introduced by Danckwerts (1951) building on results of Higbie (1935), considers that the disturbances at the gas-liquid interface promote a periodic renewal of surface elements, bringing fluid from the bulk liquid to the interface, and taking fluid previously in contact with the interface to the bulk of the liquid phase. The theory assumes that, during the time between renewal events, the

(unsteady-state) mass transfer from the interface to each surface element is dominated by molecular diffusion. Considering an statistical distribution of the time $\mathcal{T}$ (s) between successive renewal events (or the time of exposure of the surface elements), Danckwerts (1951) found Equation (2.21), where $\bar{\mathcal{T}}$ is the mean time (s) between renewal events (the mean of the distribution of $\mathcal{T}$).

$$k_L = \left(\frac{D_L}{\bar{\mathcal{T}}} \right)^{1/2} \quad (2.18)$$

In practice, however, determining which are the renewal events and the value of $\bar{\mathcal{T}}$ in a free surface sheared by the wind is not always straightforward. Münnich and Flothmann (1975) evoke the smooth turbulent flow at a flat boundary and propose that $\bar{\mathcal{T}} = 16^2 \nu / u_{*,L}^2$, which makes Danckwerts' (1951) expression for k_L become Equation (2.19).

$$k_L = \frac{1}{16} u_{*,L} S_{C_L}^{-1/2} \quad (2.19)$$

Citing direct numerical simulations and experiments, Banerjee and McIntyre (2004) explore the idea that surface renewal is due to the “sweeps” (or “upwellings”) normally observed in a disturbed water surface. They argue that, if this is the case and $\bar{\mathcal{T}}$ can be taken as the time between sweeps, which in turn scales as $\bar{\mathcal{T}} \sim 100 \nu / u_{*,L}^2$ according to those authors, Equation (2.18) can be rewritten as Equation (2.20).

$$k_L = 0.1 u_{*,L} S_{C_L}^{-1/2} \quad (2.20)$$

There have been a few attempts to experimentally study the renewal events directly. Turney and Banerjee (2013) measured the average age of the surface elements (which corresponds to $\bar{\mathcal{T}}$) by tracking flow-tracing particles using PIV in a wind-wave flume. Garbe et al. (2002) used infrared images of the water surface and digital image processing techniques to derive the probability distribution of the time between renewal events in heat transfer from water to air. In both of these cases, the measurements were restricted to the field of view of the cameras, and the results were very specific for each situation.

The theory of surface divergence, in contrast, postulates that the mechanism controlling mass transfer at the air-water interface is directly related to the existence of divergence (or convergence) of the flow field at the interface plane, which, in turn, is only possible because the air-water interface is not a rigid wall, and the liquid phase can move at the surface-parallel plane (Banerjee, 1990; Jähne and Haußecker, 1998; Banerjee and McIntyre, 2004; Turney and Banerjee, 2013; Peirson et al., 2014). As a consequence, the surface-normal turbulent motions can be much more intense close to the interface (albeit being zero exactly at the interface) than those close to a rigid wall. Combining the non-zero divergent of the surface-parallel motions with some other assumptions, for high Sc_L , a model for the liquid-film mass transfer coefficient is derived, in which k_L is proportional to the square root of the mean square divergence of the surface-parallel turbulent motions, and scales proportionally to $D_L^{1/2}$ (see Banerjee, 1990, Banerjee and McIntyre, 2004, and Turney and Banerjee, 2013). The application of such model requires the value of the root mean square divergence of the surface-parallel turbulent motions, which can be locally measured using PIV (e.g., Turney and Banerjee, 2013; Peirson et al., 2014), or may be parametrised for some cases, based on other bulk variables (e.g., Banerjee, 1990, Banerjee and McIntyre, 2004, and Turney and Banerjee, 2013). However, none of the existing models utilises variables that are all available (or can be reasonably estimated) in the usual situations of modelling atmospheric emissions in WWTPs.

A different take on the surface divergence mechanism was presented by Csanady (1990), who solved simplified transport equations for the flow field and mass transfer in an ideal “model roller”, supposed to represent the basic features of a microscale-breaking wave. With further assumptions, including the idea that the intense divergences are determined by variations of the wind stress, Csanady (1990) was able to simplify the resulting model in the form of Equation (2.21).

$$k_L = \zeta \phi u_{*,L} Sc_L^{-1/2} \quad (2.21)$$

where ζ is a dimensionless constant; and ϕ represents the fraction of the liquid surface effective in mass transfer (i.e., the areas where surface divergence occur and their

surroundings). For these parameters, Csanady (1990) suggests $\zeta = 0.513$ and $\phi = 0.2$ (but he pointed out that ϕ would change depending on the wind-wave field).

A complete different approach relies on dimensional scaling (Lorke and Peeters, 2006; Zappa et al., 2007), proposing that mass transfer in the liquid side of the gas-liquid interface can be modelled by a “film-like” representation (therefore $k_L = D_L/d_L$; see 2.1.1), but with the effective film thickness scaling proportionally to Batchelor’s (1959) length scale l_B , that is $d_L \propto l_B$. Batchelor’s (1959) length scale l_B represents the scale of the smallest turbulent fluctuations of the concentration field; for high Sc_L , l_B is of order $l_B \sim 2\pi(\nu D_L^2/\varepsilon)^{1/4}$ (Batchelor, 1959), with ν being the kinematic viscosity ($\text{m}^2 \text{s}^{-1}$) of the liquid phase and ε the dissipation rate of turbulent kinetic energy ($\text{m}^2 \text{s}^{-3}$) in the liquid-side of the interface boundary layer, in this case. This scaling argument leads to the general k_L form written in Equation (2.22) (Lorke and Peeters, 2006; Zappa et al., 2007), which also contains the Schmidt number dependence with power $-1/2$. It is interesting to note that the proportionality in Equation (2.22) was also obtained by Lamont and Scott (1970) as a result of their “small eddy cell” model, following a different mathematical path.

$$k_L \propto (\varepsilon \nu)^{1/4} Sc_L^{-1/2} \quad (2.22)$$

Similarly to the other approaches discussed above, the practical application of an equation with the form of Equation (2.22) for the estimation of emissions in WWTPs would depend on a reliable parametrisations for one of its key variables, since ε is not normally measured in the field, in this context.

2.3.2. Experimental insights on the mechanisms determining k_L at passive liquid surfaces

The importance of wind friction in determining the velocity of mass transfer at the liquid side of passive liquid surfaces has been repeatedly verified in controlled experimental studies (Liss, 1973; Cohen et al., 1978; Mackay and Yeun, 1983; Jähne et al., 1987; Ocampo-Torres et al., 1994; Rhee et al., 2007; Turney and Banerjee, 2013). Nonetheless, there is not clear agreement in terms of the functional relationships when the results of individual investigations are compiled together, as further analysed in

Chapter 3. The considerable scatter of these data is normally attributed to differences of the experimental conditions and setups, especially wind speed range and wind fetch (differences which also are present in the practical application of emission models for WWTPs), which in turn are certain to influence the underlying physical processes. On the other hand, given the intrinsic difficulties of investigating multi-scale flow features and microscopic chemical transport in the surroundings of a disturbed air-water interface, such physical mechanisms (and their relation with the different theoretical models) are rarely demonstrated in an unambiguous way, and even more difficult is to generalise the conclusions of each study, although relevant insights have been reported in the literature, as following discussed.

Except maybe in cases where the water surface is almost perfectly flat, the description of the liquid-side mass transfer as determined by the development of a smooth turbulent boundary layer in the liquid due to surface currents caused directly by the wind shear, as proposed by Deacon (1977), does not hold once surface waves appear. There is overwhelming experimental evidence indicating that the dynamics of mass transfer changes in the presence of waves, compared to a smooth flat surface. As discussed in 2.3.1, a fundamental change observed with the onset of surface ripples and waves is the shift of the dependence of k_L on Sc_L , nominally from a power $Sc_L^{-2/3}$ to a power $Sc_L^{-1/2}$ (or, equivalently, a shift of the dependence of k_L on D_L from a power $D_L^{2/3}$ to a power $D_L^{1/2}$), which has been consistently verified in experiments (e.g., Jähne et al. 1987; Jähne and Haußecker, 1998; Zappa et al., 2004; Rhee et al., 2007). Albeit showing that, as long as waves are formed, mass transfer is not dominated by a turbulent smooth boundary layer in the liquid side, this does not clarify about the exact mass transfer mechanism, since different proposed mechanisms would lead to the same scaling of k_L with $D_L^{1/2}$ (see 2.3.1).

The presence of surface ripples and waves is shown to enhance the rate of mass transfer of liquid side-controlled compounds. Early evidence of the direct link between mass transfer and wave dynamics was reported by Jähne et al. (1987), who identified that k_L correlated with the mean square slope of the waves (and, in that case, both variables presented an overall correlation with $u_{*,L}$). Those authors hypothesised that “energy put into the wave field by wind is transferred to near-surface turbulence enhancing gas

transfer”, and highlighted the necessity of investigating the way the waves are connected with the near-surface turbulence. In this context, the occurrence of microscale wave breaking has been identified to be of primary importance for the liquid-side mass transfer (Peirson and Banner, 2003; Zappa et al., 2004; Siddiqui and Loewen, 2007; Turney and Banerjee, 2013; Peirson et al., 2014). Using infrared images of the water surface, Zappa et al. (2004) were able to define the dominant areas of enhanced heat transfer as the wakes of microscale breaking waves and have an approximate measure of the fraction of the water surface under the direct influence of microscale breaking. Although measured locally (in the field of view of the infrared imaging camera, nominally at fetches 5.6 and 11.1 m), such fraction showed a non-trivial but significant correlation with k_L for helium (He) and sulfur hexafluoride (SF₆) in the whole tank (18.29 m long). Besides, the fraction of the water surface under the direct influence of microscale breaking also correlated with the mean square slope of the waves, which relates straightforward to the earlier findings of Jähne et al. (1987).

Peirson and Banner (2003) propose that microscale breaking increases the mass transfer rate mainly by the subduction of a thin mass transfer boundary layer at the spilling region of the breaking crests. Siddiqui and Loewen (2007) applied PIV and observed the occurrence of turbulent vortexes (coherent structures) that are formed at the spilling region of the breaking crests and move to the wake of the microscale breaking waves, being able to associate such structures to the thermal wakes captured by infrared imagery. They hypothesise that these vortexes disrupt the mass (and heat) transfer boundary layer in a renewal-like mechanism, enhancing mass transfer. Turney and Banerjee (2013) suggest a model that combines surface divergence and surface renewal and apply it to their PIV measurements of the liquid-phase motions in situations of microscale breaking, identifying that persistent upwelling events in the region upwind the wave crest are significant for mass transfer.

Other experimental studies also point to the relation between k_L and the dissipation rate of turbulent kinetic energy ε . Zappa et al. (2007) showed that a collection of k_L results obtained experimentally under different types of forcing (including, besides wind, cases with tidal currents and rain) could be generally described by a relation of the form of Equation (2.22), but the data is considerably scattered around the fitted line. Vachon et al. (2010) utilised a data set comprising exchange rates of carbon dioxide (CO₂)

measured experimentally in lakes using a floating accumulation chamber simultaneously to measurements of ε in the water. A relation of the form of Equation (2.22) (and similar proportionality constant as found by Zappa et al., 2007) adjusted moderately well to the data set, but was not the best fit. The best fitting equation form was writing k_L as a linear function of the logarithm of ε , which described the overall variation in the data set, also with considerable scatter around the fitted line. It is important to mention that, in both studies, ε was not measured in the immediate vicinities of the gas-liquid interface (as the theoretical models would rigorously require). The PIV results of Siddiqui and Loewen (2007) also provide indirect support for a strong relation between k_L and ε . Besides showing that ε correlated to the mean square slope of the waves, which establishes a link with the findings of Jähne et al. (1987) mentioned before, they identify that the dissipation rate of turbulent kinetic energy near the water surface is highly enhanced in microscale breaking waves, which could explain the substantial increases in the value of k_L in the presence of microscale breaking observed in other studies. Additionally, Siddiqui and Loewen (2007) report that ε depends on $u_{*,L}$, which is in agreement (at least qualitatively) with a large number of controlled experiments of liquid-gas mass transfer that show a correlation between $u_{*,L}$ and k_L .

The effects of macroscale breaking on the liquid-side mass transfer are still to be clarified, in particular, for the wind-wave fields that can be expected at the short fetches that are the typical case in WWTPs. The plunging and intense spilling associated with macroscale breaking certainly produce intense turbulence in the water and, together with the generation of bubbles (whitecaps), will probably enhance local mass transfer. However, macroscale breaking is likely to be sparse in liquid surfaces in WWTPs, as discussed in 2.2.2, hence its effect on the overall mass transfer rates may not be so pronounced. In this sense, Rhee et al. (2007) found that bubbles from whitecaps did not have a significant role in the mass transfer of several compounds in a 40 m long wind-wave tank (the range of air-side friction velocities in their experiments was up to 0.6 m s^{-1}). More studies, covering a broader range of fetches and wind conditions are necessary to conclusively state that macroscale breaking can be neglected in the present context.

2.3.3. Empirical correlations for k_L

Similarly to what happens for k_G , the literature reports a number of correlations for k_L in passive liquid surfaces, derived from empirical data. Many k_L expressions for environmental passive liquid surfaces were recently reviewed by Ro et al. (2007), and we refer the reader to their work for more detail. Therefore, the present review does not aim to cover the variety of the existing correlations, but instead focuses on the k_L correlations that are most widely used in the context of emission modelling for WWTPs, which are explained below: the two complementary equations proposed by Mackay and Yeun (1983), adopted by the model TOXCHEM+; the correlation used by Gostelow et al. (2001) in their emission model; and the approach followed by the US EPA-endorsed emission model WATER9 (US EPA, 1994, 2001).

2.3.3.1. Mackay and Yeun (1983)

The experiments of Mackay and Yeun (1983) were generally described in 2.2.3.2. The mass transfer coefficients for several VOCs were determined from the decaying of their concentration in the liquid phase, and Equation (2.23) was fitted to their data set. Since the minimum u_* in their experiment was 0.271 m s^{-1} , Mackay and Yeun (1983) suggest that the range of application of Equation (2.23) is $u_* > 0.3 \text{ m s}^{-1}$, and that Equation (2.24), modified from Wolff and van der Heijde (1982), should be used for $u_* < 0.3 \text{ m s}^{-1}$. In both cases, they introduced an intercept of 1×10^{-6} to account for a “still-air” mass transfer coefficient.

$$k_L = 1 \times 10^{-6} + 34.1 \times 10^{-4} u_* S_{c_L}^{-1/2} \quad (2.23)$$

$$k_L = 1 \times 10^{-6} + 144 \times 10^{-4} u_*^{2.2} S_{c_L}^{-1/2} \quad (2.24)$$

2.3.3.2. Gostelow et al. (2001)

The correlation of Gostelow et al. (2001) for k_L in passive liquid surfaces, Equation (2.25), was derived in a similar way as their k_G correlation (item 2.2.3.3; more details can also be found in Gostelow, 2002), that is, by fitting a straight line with zero intercept to an experimental data set, in this case assuming k_L to scale with $S_{c_L}^{-1/2}$. The

data set consisted of experimental k_L (for different compounds) and respective u_* compiled from five different sources, which performed their experiments in wind-wave tanks: Liss (1973), oxygen (O_2) and CO_2 ; Cohen et al. (1978), benzene; Mackay and Yeun (1983), benzene and toluene; Wanninkhof and Bliven (1991), SF_6 ; and Ocampo-Torres et al. (1994), CO_2 . Overall, the data set used by Gostelow et al. (2001) covered a range of fetches from 2.4 to 100 m and u_* from 0.047 to 1.046 $m\ s^{-1}$ (equivalent to U_{10} from 1.5 – 26.4 $m\ s^{-1}$).

$$k_L = 3.5 \times 10^{-3} u_* S c_L^{-1/2} \quad (2.25)$$

2.3.3.3. *WATER9 approach*

The scheme adopted by WATER9 (US EPA, 1994, 2001) to model k_L for passive liquid surfaces considers different equations depending on the ranges of wind speed (U_{10}), u_* and the fetch-to-depth ratio (i.e, the ratio X/H , where X is the total fetch and H is the water depth in the tank), as summarised in Table 2.2. In the examples presented by US EPA (1994) and in the source code reported in US EPA (2001), the effective diameter is used as the fetch parameter X (the same situation happens for the calculation of k_G , as explained in item 2.2.3.1). Nonetheless, in the original studies from which Equations (2.26)-(2.28) were built and the application ranges were defined (Springer et al., 1984; Lunney et al., 1985), the fetch X adopted was the actual physical fetch in the experimental setup (the surface length in the wind direction).

Table 2.2. Summary of the scheme adopted by WATER9 (US EPA, 1994, 2001) to calculate k_L for passive liquid surfaces.

Conditions			Reference	Expression ^a	
U_{10}	X/H	u_*			
$U_{10} < 3.25 \text{ m s}^{-1}$	all X/H	-	Springer et al. (1984)	$k_L = 2.78 \times 10^{-6} \left(\frac{D_L}{D_{L,ether}} \right)^{2/3}$	(2.26)
$U_{10} \geq 3.25 \text{ m s}^{-1}$	$X/H < 14$	$u_* > 0.3 \text{ m s}^{-1}$	Mackay and Yeun (1983)	Equation (2.23)	
$U_{10} \geq 3.25 \text{ m s}^{-1}$	$X/H < 14$	$u_* \leq 0.3 \text{ m s}^{-1}$	Mackay and Yeun (1983)	Equation (2.24)	
$U_{10} \geq 3.25 \text{ m s}^{-1}$	$14 \leq X/H \leq 51.2$	-	Springer et al. (1984)	$k_L = \left[2.605 \times 10^{-9} \left(\frac{X}{H} \right) + 1.277 \times 10^{-7} \right] U_{10}^2 \left(\frac{D_L}{D_{L,ether}} \right)^{2/3}$	(2.27)
$U_{10} \geq 3.25 \text{ m s}^{-1}$	$X/H \geq 51.2$	-	Springer et al. (1984)	$k_L = 2.611 \times 10^{-7} U_{10}^2 \left(\frac{D_L}{D_{L,ether}} \right)^{2/3}$	(2.28)

^a $D_{L,ether}$ is the molecular diffusivity of ethyl ether in water (US EPA, 1994, uses the reference value $D_{L,eter} = 8.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

2.4. Wind friction over passive liquid surfaces in WWTPs

2.4.1. Air flow over and waves on passive liquid surfaces in WWTPs

2.4.1.1. Air flow

The air-side friction velocity u_* (m s^{-1}) is defined in Equation (2.29).

$$u_* = \sqrt{\frac{|\tau_0|}{\rho_G}} \quad (2.29)$$

where ρ_G is the air (gas phase) density (kg m^{-3}) and τ_0 is the momentum flux at the air side of the interface ($\text{kg m}^{-1} \text{s}^{-2}$), normal to the surface.

An approximation for the wind flow over a liquid surface consists of a steady, incompressible, two-dimensional turbulent flow with negligible pressure gradient in the mean flow direction (horizontal). Although idealised, this approximation is reasonable for most of the cases of interest in the present context, which are the passive liquid surfaces in WWTPs. Under such conditions, an order-of-magnitude analysis leads to the conclusion that there is a layer, from the interface up to a certain height, where the momentum flux τ can be assumed constant; in other words, at any height z inside this layer, $\tau = \tau_0$ (Seinfeld, 1986). This defines the so-called “surface layer” of the atmospheric boundary layer (Seinfeld, 1986), corresponding to the “inner region” of the classical turbulent boundary layer over a flat plate (Schetz, 1984). In the surface layer, but out of the region where the effects of viscous dissipation and the direct influence of waves are important (see Figure 2.3), a dimensional analysis associated with physical intuitive reasoning produces the neutral (adiabatic) wind velocity profile as presented in Equation (2.30) (Seinfeld, 1986).

$$\frac{u}{u_*} = \frac{1}{\kappa} \ln \left(\frac{z}{z_0} \right) \quad (2.30)$$

where $z \equiv x_3$ is the vertical coordinate (m) with its origin at the mean surface level; u is the mean horizontal velocity (m s^{-1}) of the air flow at height z ; $\kappa = 0.4$ is the von Karman constant (dimensionless); and z_0 is a roughness length parameter (m).

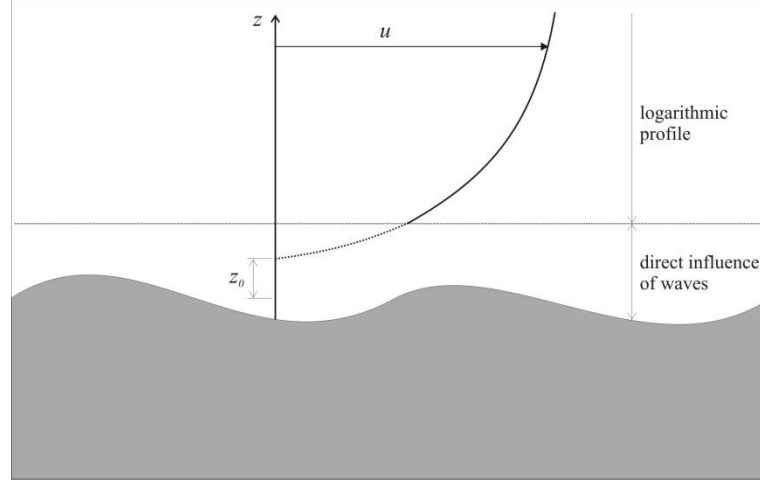


Figure 2.3. Schematic velocity profile over a wavy water surface, for neutral atmospheric condition, with the vertical coordinate z having its origin on the mean surface level. The logarithmic velocity profile, Equation (2.30), applies in the region of the surface layer which is far from the liquid surface, so the direct effects of wave-induced air motion and air flow separation are not detected. The extrapolation of the logarithmic profile in the region under direct influence of the waves is represented as a dotted line.

The region in which Equation (2.30) is valid is called “log layer” and the momentum flux is due to turbulent transport (Reynolds stress), i.e., $\tau = -\rho_G \overline{u_1' u_3'}$, being u_1' and u_3' the turbulent fluctuations of the instantaneous values of the horizontal and vertical wind velocity components u_1 and u_3 , respectively (here, it is considered that the mean wind speed u is aligned with the axis $x \equiv x_1$ and bar denotes the time average). Equation (2.30) implies that the mixing length in the log layer is $l = \kappa z$ (Schetz, 1984). For z approaching the water surface, Equation (2.30) no longer applies, and part (or, sometimes, the totality) of τ is represented by viscous shear stress and, in the case of a wavy surface, also by wave-induced fluctuations of pressure (Janssen, 1991, 1994, 2004; Kudryavtsev et al., 2014). Similarly to cases of flat terrain, the occurrence of a logarithmic velocity profile region has been well verified for water surfaces, both in laboratory (Wu, 1968; Caulliez et al., 2008; Reul et al., 2008; Grare et al., 2013; Peirson et al., 2014) and field studies (Charnock, 1955; Miyake et al., 1970; Hicks, 1972; Sheppard et al., 1972; Garratt, 1977; Wu, 1980). It is important to emphasise that, under unstable or stable atmospheric conditions, Equation (2.30), which is only applicable in

near-neutral situation, has to be modified, using the Monin-Obukhov similarity analysis (Miyake et al., 1970; Hicks, 1972; Sheppard et al., 1972; Garratt, 1977; Jacobson, 1999). The discussion in this thesis addresses only the neutral and near-neutral atmospheric condition, which is a fundamental case and to which the great majority of the available experimental data is referred. However, the cases with non-neutral atmospheric conditions are also important, especially the stable condition, for which dispersion in the atmosphere is limited and the impact of odorous emissions can be even more likely.

For a solid smooth surface, the roughness length z_0 represents the effect of the viscous sublayer adjacent to the interface, where the turbulent fluctuations are damped due to the viscous stress, and can be estimated as $z_0 \approx 0.11\nu/u_*$ (Jacobson, 1999), where ν is the kinematic viscosity of air ($\text{m}^2 \text{s}^{-1}$). This can be an approximation for a smooth water surface, with no waves (Jacobson, 1999). On the other hand, air flow impinges form drag onto the waves surface, through two distinct mechanisms: (i) resonant wave-induced pressure and velocity disturbances in the air flow promote momentum transfer to waves, the so-called “wave-induced stress” (Janssen, 1991, 1994, 2004; Kudryavtsev et al., 2014); (ii) surface discontinuities and protruded elements which occur in an event of wave breaking lead to air flow separation, which, in turn, transfers momentum from air to water (Caulliez et al., 2008; Kudryavtsev et al., 2014; Kudryavtsev and Chapron, 2016). However, as stated before, in the surface layer, but far from the liquid surface, where the direct effects of wave-induced air motion and air flow separation are not detected, the logarithmic profile (Equation (2.30)) is still valid. In this region, the form drag is incorporated in the constant-with-height turbulent stress, viz, $\tau = -\rho_G \overline{u_1' u_3'} = -\rho_G u_*^2$ (Janssen, 1991, 1994, 2004; Grare et al., 2013; Kudryavtsev et al., 2014) and reflected in the effective roughness length z_0 adjusted for the wind profile (Janssen, 1991, 1994, 2004; Grare et al., 2013). It follows, therefore, that z_0 is not a constant, but depends on the wind-wave interactions; as a consequence, the drag coefficient is also dependent on the wind-wave interactions. Caulliez et al. (2008) showed that, for short fetches, the viscous stress is the main component of the shear stress at low wind speeds whereas the form drag component is more important at high wind speeds and accounts for more than 75% of the total wind stress at wind speeds above 9 m s^{-1} . The occurrence of a constant-stress, logarithmic velocity-profile layer, with z_0 dependent on wave

effects, as discussed above, can be expected for the wind flow over passive liquid surfaces encountered in WWTPs. However, there are also aspects concerning the geometrical configuration of the tanks and the liquid surface, such as the abrupt alteration of surface roughness due to the change from surrounding terrain to water and structures which act as backward-facing step at the inlet, which might interact with the inlet flow and result in the development of a new boundary layer structure.

2.4.1.2. Waves

Waves are formed in wastewater treatment unities at which the liquid surface is exposed to wind shear (as shown in Figure 2.4), except for very light winds, sheltered surfaces and/or in the presence of surface films or if scum covers most of the surface. As discussed in 2.4.1.1, waves affect the wind flow and, thus, the wind shear. The primordial differences between the ocean surface and liquid surfaces in WWTP unities are the very short fetches (most commonly, between 5 and 100 m) and the absence of free-propagating waves (swell). Therefore, wind drag and wave data obtained for open sea are not necessarily applicable in the much more constrained environment of a WWTP. On the other hand, detailed wind and wave measurements are not routinely performed in wastewater treatment tanks. To overcome this lack of experimental data, the approach adopted herein is to analyse experimental data obtained in wind-wave tanks and which are available in the literature. The data selected for the analysis is from tanks whose dimensions and conditions resemble the expected physical environment of passive liquid surfaces at wastewater treatment facilities. Unfortunately, these constraints mean that the number of suitable data sets is rather small.

Table 2.3 summarises the maximum and minimum peak frequencies f_p (Hz) of the wave spectra reported by different researchers (Jähne and Riemer, 1990; Caulliez et al., 2008; Grare et al., 2013) for various fetches and wind conditions. As one could anticipate, f_p is much higher for short fetches than those observed in the ocean surface (see the schematic spectra shown in Figure 2.4b). For very short fetches and low wind speed, the waves at the frequency spectral peak are in the gravity-capillary range. It is verified that f_p decreases with increasing fetch and wind speed; the decrease in the frequency of the dominant waves with fetch (indicated by the increase in the wave

length) can also be identified in the sequence of pictures displayed in Figure 2.4c to e. Measured frequencies are also subjected to Doppler effect due to the wind drift current, especially for high frequency waves (Lamont-Smith and Waseda, 2008; Grare et al., 2013); this may explain the fact that the peak phase velocities reported by Caulliez et al. (2008) are larger than the values calculated by directly applying the linear dispersion relation to their f_p values (the difference decreasing as fetch increases). Jähne and Riemer (1990) and Calkoen et al. (1991) indicate that, at a fetch of about 90 m, the linear dispersion relation satisfactorily estimates wave information for lower frequency waves.

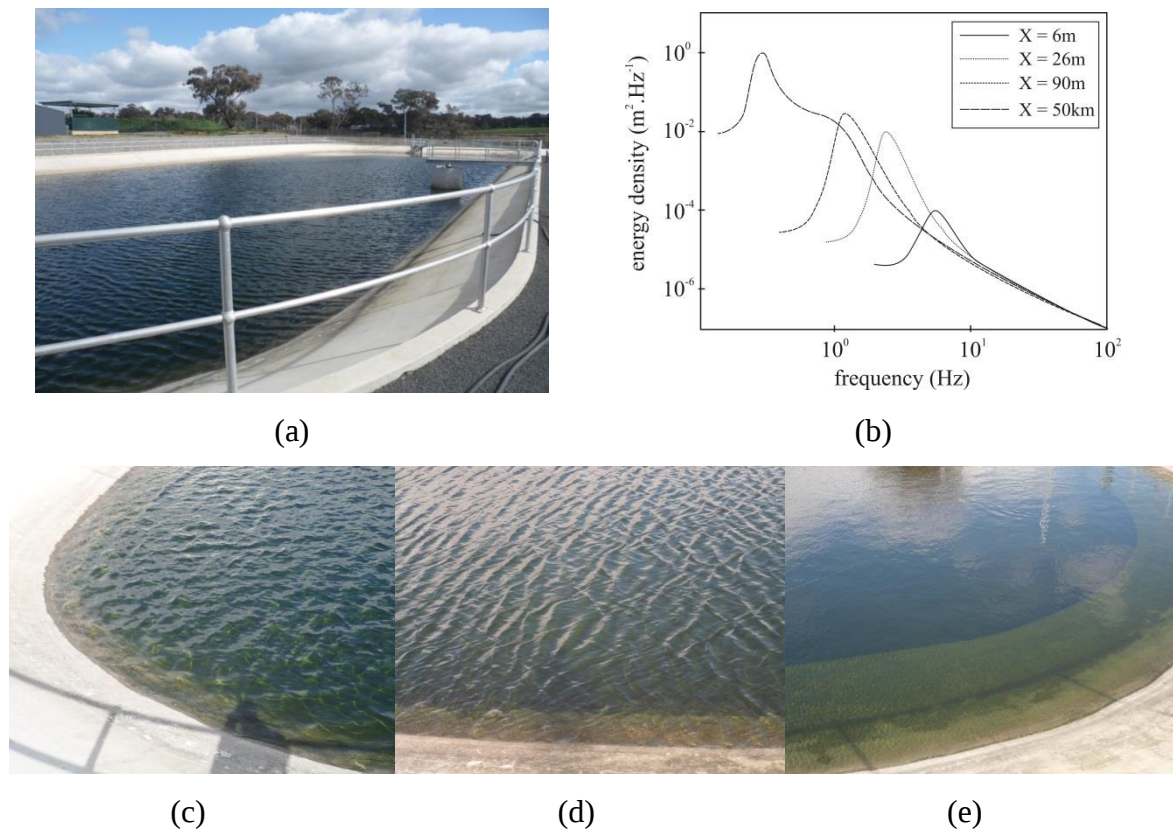


Figure 2.4. Waves in WWTPs. (a) A typical effluent balance pond in a WWTP, with surface waves generated by the wind. (b) Schematic wave energy spectra at typical tank fetches (6, 26 and 90 m) and comparison with an oceanic-scale fetch (50 km). Different regions of the same wave field shown in (a): (c) wavy surface presenting some wave breaking at the downwind end of the tank; (d) wavy surface in the middle part of the tank; and (e) almost-smooth liquid surface, with some capillary disturbances, at the upwind end of the tank. The order of magnitude of the peaks of the wave spectra in (b) are based on results from Jähne and Riemer (1990) and Caulliez et al. (2008), for the short fetches, and Hasselmann et al. (1973), for the oceanic case.

As verified in Table 2.3, for the range of fetches and wind speeds covered in the present compilation, the minimum peak frequency is of the order 1 Hz, for which the wave length calculated using the linear dispersion relation is 1.56 m. Considering that the depths of units in WWTPs are typically larger than 1 m (except close to the margins of lagoons), waves in these environments can be generally expected to be deep-water waves (water depth larger than half of the wave length).

Table 2.3. Peak frequency data from wind-wave tanks.

Reference	Fetch (m)	f_p (Hz)	u_* (m s ⁻¹)	U_{10} (m s ⁻¹)
Jähne and Riemer (1990)	90	max: 2.8	0.07	2.7
		min: ≈ 1	0.72	17.2
Caulliez et al. (2008)	6	max: 9.53	0.12	4.31
		min: 4.75	0.30	9.21
	13	max: 7.51	0.09	3.31
		min: 2.49	0.40	11.10
	26	max: 4.72	0.08	2.69
		min: 1.59	0.67	17.10
Grare et al. (2013) ^a	3.15	7.70	0.23 ^b	6.8
	6.15	5.14	0.23 ^b	6.8
	9.15	3.94	0.26 ^b	7.0
	12.15	3.36	0.27 ^b	7.0
	15.15	2.93	0.27 ^b	6.8
	18.15	2.66	0.28 ^b	6.9
	22.65	2.33	0.28 ^b	7.0
	28	max: 2.66	0.13 ^b	4.3
		min: 1.71	0.38 ^b	10.5

^a Only data regarding pure wind waves (without mechanically generated waves) were selected.

^b u_* values were calculated based on the reported τ .

Lamont-Smith and Waseda (2008) carried out experiments using the wave tank of the Ocean Engineering Laboratory at the University of California, Santa Barbara (UCSB) in the USA and, for peak frequencies lower than 4 Hz, obtained a dimensional relation $f_p \propto (U^{1.25}X)^{-0.43}$ (herein after called LS&W2008 parametrisation form), being X the fetch (m) and U a scaling velocity (in the original work, the authors used the nominal velocity of the wind tunnel). Lamont-Smith and Waseda (2008) tested this parametrisation against experimental data produced by Toba (1972), Donelan et al. (1985) and Rozenberg et al. (1999) and found close agreement with the LS&W2008 parametrisation form.

Combining data from the Joint North Sea Wave Project (JONSWAP) with other field and wind-wave tank experiments, Hasselmann et al. (1973) found a non-dimensional parametrisation $\hat{f}_p = A \hat{X}^{-0.33}$ (herein after called JONSWAP parametrisation form) where $\hat{f}_p = f_p U / g$ is the non-dimensional peak wave frequency, $\hat{X} = Xg / U^2$ is the non-dimensional fetch, g is the gravity acceleration and A is a constant. The equation fitted the JONSWAP data set (excluding capillary waves) either using u_* or U_{10} as scaling velocities. Hasselmann et al. (1973) obtained $A = 3.5$ using U_{10} as the scaling velocity, while Snoeij et al. (1993) found $A = 1.107$ using u_* as the scale velocity.

Wind-wave tank studies also provide valuable insights about other characteristics of the wave energy spectra at short fetches. One of the important features of the spectra is the relative proximity between the peak frequency and the “high frequency tail”, which are much more apart in ocean waves (see the schematic frequency spectra in Figure 2.4b). It means that, at short fetches, wave lengths at peak frequency are of the same order or only one order of magnitude greater than the wave lengths in the high frequency range (Jähne and Riemer, 1990). At low to moderate wind speeds, Jähne and Riemer (1990) noticed that this proximity prevents the establishment of a gravity equilibrium range. Calkoen et al. (1991) point that the tail of the energy spectra does not change significantly with fetch, but depends on the air flow velocity; a similar observation was made by Caulliez et al. (2008) who reported that “the energy level of the equilibrium range is not fetch dependent but increases with wind speed”. Based on experimental evidence, Jähne and Riemer (1990) also hypothesise that the observed capillary waves are generated by steep unstable gravity waves.

Caulliez et al. (2008) modelled the form drag due to waves on relatively small liquid surfaces (short fetches) and the results indicated that, contrarily to ocean surfaces (where most of the form drag is attributed to waves with higher frequency, in the equilibrium wave range), the form drag is mainly caused by the dominant wave range. This is explained by the fact that, at short fetches, dominant waves are steeper and shorter than those in the ocean. However, the partition of the wind stress among viscous, wave-induced and air flow separation stresses was found to be reasonably similar for both large and small fetches.

2.4.2. Estimating the friction velocity over liquid surfaces in WWTPs

2.4.2.1. Empirically-derived correlations for oceans

Several wind drag formulations have been proposed (see, for instance, the reviews contained in Garrat, 1977 and Letchford and Zachry, 2009), normally correlating the friction velocity or the drag coefficient ($C_{10} = (u_*/U_{10})^2$) to the wind speed U_{10} at the height 10 m, sometimes including additional variables (e.g., Blake, 1991). As previously mentioned, the correlation developed by Smith (1980) is the most commonly used as input to mass transfer correlations and is frequently recommended in guides for modelling air emissions from passive surfaces (Gostelow et al., 2001; ENVIROMEGA, 2003; US EPA, 1994, 2001). In addition to Smith's correlation, the expressions proposed by Wu (1980, 1982) and Csanady (1997) were also included in the present analysis, for comparison. The broad data set compiled by Wu (1980, 1982) and used to derive and verify his correlation is associated with developed wind seas (Janssen, 1991). The approach used by Csanady to fit his correlation differs from the one typically adopted and also constitutes an interesting case for comparison. Table 2.4 summarises the main features of these three empirical correlations, which are discussed in the sequence.

Table 2.4. Empirical correlations to estimate the wind friction over oceans.

Reference	Equation	Wind speed range ^a (m s ⁻¹)	Conditions ^a
Smith (1980)	$C_{10} = \left(\frac{u_*}{U_{10}}\right)^2 = 10^{-4}(6.1 + 0.63U_{10})$ (2.31)	$6 \leq U_{10} \leq 22$	neutral atmospheric condition; long wind fetch; deep-water waves.
Wu (1980, 1982)	$C_{10} = \left(\frac{u_*}{U_{10}}\right)^2 = 10^{-4}(8.0 + 0.65U_{10})$ (2.32)	$5 \leq U_{10} \leq 52$	neutral atmospheric condition.
Csanady (1997)	$u_* = 10^{-4}(333.9U_{10} + 4.356U_{10}^2)$ (2.33)	$0 \leq U_{10} \leq 50$	neutral atmospheric condition; long wind fetch.

^a As stated by the authors of the respective empirical expression.

Smith (1980) presented a correlation for the drag coefficient (air phase over the ocean) as a linear function of wind speed at 10 m height under near neutral atmospheric condition (Equation (2.31) in Table 2.4). Smith (1980) used high-frequency wind velocity data measured by an anemometer installed in a floating platform (12.5 m above

water level) to estimate values of U_{10} and directly calculate the eddy fluxes of momentum in the surface layer. U_{10} values were found from 6 m s^{-1} to 22 m s^{-1} , with long wind fetch and waves propagating in deep-water regime.

As pointed out by Smith (1980), in the range between 8 m s^{-1} and 13 m s^{-1} , results from Equation (2.31) practically coincide with the results obtained by Charnock's (1955) relation (Equation (2.36), taking the Charnock parameter as $\alpha = 0.01$ and $\kappa = 0.41$); in fact, the differences between results from these two expressions are very small for wind speeds from 6 m s^{-1} to 15 m s^{-1} . Smith (1980) indicates that deviations compared to Charnock's relation become larger for the highest range of wind speeds studied.

Wu (1980) also proposes an empirical correlation to estimate the drag coefficient at the reference height of 10 m, for near-neutral atmospheric surface layer over oceanic waves (Equation (2.32) in Table 2.4). Initially, this correlation was fit for wind speeds ranging from 1 m s^{-1} to around 22 m s^{-1} (Wu, 1980); later, Wu (1982) showed that Equation (2.32) applied to wind velocities up to 52 m s^{-1} (reaching the range of storm/hurricane conditions). However, more recent data concerning the drag coefficient at low wind speeds (from less than 1 m s^{-1} to 6 m s^{-1}) compiled by Wu (1994) indicate that the correlation is not appropriate for wind velocities lower than 5 m s^{-1} , in which case it was verified that the drag coefficient starts to increase with decreasing wind speed. Wu (1994) attributed this effect to the dominance of the aerodynamic roughness by capillary waves, instead of gravity waves. Hence, the maximum expected validity range of Equation (2.32) is between 5 m s^{-1} and 52 m s^{-1} .

Wu (1980, 1982) compiled drag coefficient values from several studies, some of them obtained at limited fetch, in order to fit Equation (2.32). The compiled data set was organised to avoid the dominance by the data sets with larger number of points by averaging data from the same source (or reference) before averaging all data from all sources. Wu (1982) highlights that C_{10} values predicted by Equation (2.32) agree very closely with Charnock's relation taking $\alpha = 0.0185$ and $\kappa = 0.4$, for wind speeds from 7 m s^{-1} to around 50 m s^{-1} .

Following recommendation from Amorochio and DeVries (1980), Csanady (1997) derived Equation (2.33) (Table 2.4), which correlates friction velocity and wind speed,

instead of presenting a relation for the drag coefficient. According to Csanady (1997), this expression applies to conditions of neutral stability and long fetch and was deduced from the experimental data produced by Garratt (1977), Large and Pond (1981) and Smith (1980) regarding four representative wind speed values (near zero wind, 12 m s^{-1} , 20 m s^{-1} and around 50 m s^{-1}).

2.4.2.2. *Parametrisation using Charnock's non-dimensional group*

Charnock (1955) measured and analysed wind velocity profiles (up to 8 m height) over the liquid surface of a reservoir (dimensions 1.6 km per 1 km), measured with anemometers attached to a mast. Wind fetch was longer than 1 km and the reservoir depth at the mast location was 16 m. Velocity profiles adjusted fairly well to a logarithmic curve (Equation (2.30)), providing values of u_* and z_0 . Charnock (1955) found that z_0 was primarily dependent on u_* , presenting comparatively negligible influence by fetch and atmospheric stability conditions, and proposed a non-dimensional relation described by Equation (2.34).

$$\frac{gz_0}{u_*^2} = a \quad (2.34)$$

where a is constant (later called “Charnock constant” or “Charnock parameter”).

Substituting Equation (2.34) into Equation (2.30), it results in Equation (2.35):

$$\frac{U_Z}{u_*} = \frac{1}{\kappa} \ln \left(\frac{gz}{u_*^2} \right) + B \quad (2.35)$$

with $B = -1/\kappa \ln a$.

This means that, knowing the constant a (or B) and the value of the wind speed U_Z measured at a certain reference height Z , it is possible to determine u_* (by iteratively solving Equation (2.35)) and, therefore, the respective drag coefficient $C_Z = (u_*/U_Z)^2$. This can be considered as a drag coefficient formulation (as pointed by Smith, 1980) based on the assumption that the wind profiles over a wavy liquid surface can be described by Equation (2.35), which implies that the aerodynamic interaction between

the wind and the waves follows Equation (2.34). Wu (1968) pointed out that Charnock's non-dimensional relation could be understood as an "equation of state" that represents a condition of wind-wave equilibrium in which gravity waves are responsible for the aerodynamic roughness in the turbulent boundary layer over the water surface. Furthermore, as pointed, for example, by Wu (1980) and Smith (1980), in the ocean, the gravity waves acting as roughness elements are not necessarily the dominant waves in the wave energy spectrum; instead, the roughness effect would arise from the shorter and steeper waves (which are normally in equilibrium with the local wind, as highlighted by Smith, 1980). Nevertheless, this may not be the case for liquid surfaces in WWTPs, where the dominant waves are responsible for most of the form drag, as already mentioned in 2.4.1.1.

Wu (1969) advocates that a drag coefficient equation based on Charnock's relation should be entirely written in terms of non-dimensional groups, to better relate wind stress data obtained at different scales, suggesting Equation (2.35) to be rewritten as Equation (2.36):

$$\frac{U_Z}{u_*} = \frac{1}{C_Z^{1/2}} = \frac{1}{\kappa} \ln \left(\frac{1}{\alpha C_Z F^2} \right) \quad (2.36)$$

Where: $F = U_Z / (gZ)^{1/2}$ is a non-dimensional group with the same form as a Froude number, but not with the same physical meaning.

Using a large number of results reported by different works found in the literature, encompassing both lab scale and field/oceanic scale, Wu (1969) showed that Equation (2.36) fits considerably well to a plot relating C_Z to the respective F , provided that the adequate reference height (Z) is chosen for each situation. This result was used to support Equation (2.36) as a "general expression" that relates the drag coefficient and the wind speed (both considered with respect to the same reference height Z), supposed to hold for all cases in which the boundary layer over the water surface is aerodynamically rough and the roughness is dominated by gravity waves (Wu, 1969). Determining for which of the practical situations these two conditions are satisfied is not necessarily straightforward. For the oceanic case, Wu (1982) verified that Equation (2.36) describes reasonably well the variation of C_{10} as a function of U_{10} for values of

wind speed in the range between approximately 7 m s^{-1} and 50 m s^{-1} . For wind velocities below 7 m s^{-1} , Wu (1994) suggests that there is a transition from a gravity wave-dominated to a capillary wave-dominated aerodynamic roughness, what would explain why Equation (2.36) was not appropriate to relate C_{10} to U_{10} for lower wind speeds.

Another aspect is that the reference height (or “anemometer height”), Z , has to be chosen so that it does not compromise the validity of Equation (2.36); in practice, this means that Z must be above the direct influence of the waves (or the wave-induced air motion) and within the limits of the logarithmic region of the inner turbulent boundary layer over the water surface (Wu, 1969, 1971). Considering such premises and using approximate correlations for the turbulent boundary layer thickness and the significant wave height (both dependent on the wind fetch), Wu (1971) proposes a set of equations to determine Z (m), for different ranges of a fetch-based Reynolds number, $Re_X = U_Z X / \nu$ (Equations (2.37a)-(2.37c)):

$$Z = 0.1, \text{ for } Re_X < 5 \times 10^7; \quad (2.37a)$$

$$Z = 7.35 \times 10^{-7} Re_X^{2/3}, \text{ for } 5 \times 10^7 < Re_X < 5 \times 10^{10}; \quad (2.37b)$$

$$Z = 10, \text{ for } Re_X > 5 \times 10^{10}. \quad (2.37c)$$

It can be noted that the 10 m reference height usually adopted would only coincide with the recommended reference height for very large fetches: 52 km, 78 km and 156 km, for 10 m wind speeds of 5 m s^{-1} , 10 m s^{-1} and 15 m s^{-1} , respectively. On the other hand, in the range of fetches normally encountered in wastewater treatment units (most certainly, shorter than 300 m), the reference height calculated according to the method would fall between 0.10 m and 0.23 m, for wind speeds varying from 5 m s^{-1} to 15 m s^{-1} . However, it has to be pointed out that, to derive the above expressions (Equations (2.37a)-(2.37c)), Wu (1971) used an approximation for the boundary layer thickness over a flat plate approached by a wind presenting uniform velocity profile. This may not be the exact case in many practical situations (for example, a wind coming from a field towards a lagoon), in which the wind profile approaching the water surface already has a

logarithmic shape. In the last case, the boundary layer thickness is larger and the anemometer height for short fetches could be higher.

Concerning the value of the constant, Charnock (1955) suggested B to be approximately 12.5, which means $a \approx 0.0059$, for $\kappa = 0.41$. However, other values have been indicated in the literature, for instance: Wu (1968) reports $a = 0.0112$ for $\kappa = 0.4$; Garrat (1977) suggests $a = 0.0144$ for $\kappa = 0.41$; Smith (1980), $a = 0.01$ for $\kappa = 0.41$; Mackay and Yeun (1983) find $a = 0.0093$ for $\kappa = 0.4$; Wu (1980) claims $a = 0.0185$ for $\kappa = 0.4$. Wu (1980) presents a discussion about three possible reasons for the existence of different reported values of a : (i) the intrinsic dependence of a on the chosen value of the von Karman constant κ ; (ii) imprecision/errors that naturally occur in drag coefficient data used to derive a are shown to have a much more pronounced effect on the value of a (for example, an error as small as 10 % in C_{10} can introduce a bias of up to 70 % in a , as demonstrated by Wu, 1980); (iii) the value of a can also be influenced by the approach used to fit the experimental data to the Charnock's relation. Addressing the dependence of a on κ , a method for interconversion between a values obtained with different choices of κ is implicit in Wu (1970, 1980); this method works if a is derived directly from drag coefficient data.

In addition to those reasons enumerated by Wu (1980), the physical dependence of the wind drag on the interaction with the wave field can strongly affect the value of a (Janssen, 1991, 1994, 2004; Nordeng, 1991; Donelan et al., 1993; Caulliez et al., 2008). This has been verified experimentally (see, for instance, the collation of experimental data shown by Caulliez et al., 2008, together with their own results) and also evidenced by coupled wind-wave models (Janssen, 1991, 1994, 2004; Nordeng, 1991). Assuming that the “background” aerodynamic roughness due to gravity-capillary waves $z_{0,gc}$ can be described by a Charnock-type relation of the form $z_{0,gc} = \hat{\alpha} u_*^2 / g$, with $\hat{\alpha}$ constant, and the additional effect of the gravity waves in the air flow can be represented by a roughness length $z_{0,g}$, Janssen (1991) proposes that the overall effective roughness length z_0 , for a logarithmic wind profile measured at $z \gg z_{0,g}$, can be parametrised as shown in Equation (2.38) which can be rewritten in terms of the Charnock parameter a as Equation (2.39).

$$z_0 = \frac{z_{0,gc}}{\sqrt{1 - \frac{\tau_w}{\tau}}} \quad (2.38)$$

$$a = \frac{\hat{\alpha}}{\sqrt{1 - \frac{\tau_w}{\tau}}} \quad (2.39)$$

where τ_w is the component of the total stress due to the waves (τ is the total stress in the logarithmic-profile layer far from the water surface, as defined before).

Equation (2.39) shows explicitly the dependence of a on the wind-wave interaction, reflected by τ_w . A comprehensive determination of τ_w , however, is rather complex, requiring the coupled solution of the momentum balance for the wave spectrum (Janssen, 1991, 1994, 2004). Janssen (1991) suggests the constant $\hat{\alpha}$ to be $\hat{\alpha} = 0.0110$, so the coupled modelling produces, for “old wind sea” (i.e., with wave age c_p/u_* of the order 25, being c_p the phase speed at the spectral peak), z_0 values that coincide with the ones obtained from Charnock’s relation with $a = 0.0185$ (for $\kappa = 0.4$). This value of a is the one found by Wu (1980, 1982), who analysed a considerable collection of data, and is regarded as representative of old wind sea (Janssen, 1991). Also, according to this approach, the largest wave stresses (and, consequently, the largest z_0 values) occur for “young wind sea”, with c_p/u_* of the order 10 (Janssen, 1994, 2004). Although the wave age is a good indicator of the stage of wave development and parametrisations for a as a function of c_p/u_* are frequently possible, Janssen (1991, 1994, 2004) argues that c_p/u_* alone may not be sufficient to describe the wind-wave interactions in all situations encountered in the field, especially in a condition of “mixed sea” (when waves in equilibrium with the local wind coexist with swell). On the other hand, the coupled wind-wave model which iteratively solves the momentum balance for the waves and calculates z_0 using Equation (2.39) was shown to estimate wave growth rates and wind stresses in good agreement with experimental observations (Janssen, 1994, 2004).

2.4.2.3. *A note on wind-over-waves coupling*

In addition to the wind-wave coupled model by Janssen (1991), previously cited, other studies have also addressed modelling procedures which involve the coupled solution of momentum conservation in the wind boundary layer and the wave field, for instance: Nordeng (1991), Makin and Kudryavtsev (1999, 2002), Kudryavtsev et al. (2014) and Kudryavtsev and Chapron (2016). In this approach, one attempts to model a range of processes related to momentum transfer and dissipation in a wind-wave field, such as shear stress at the surface, wave-induced and air flow separation stresses, wave breaking, viscous dissipation of wave energy and non-linear wave-wave interactions. The inclusion or not of a given process depends on the model purpose and desired level of complexity.

Concerning short fetches such as the ones present in WWTPs, which is the domain of interest of the present work, it seems appropriate to discuss the modelling performed by Caulliez et al. (2008). Those authors used experimental data regarding the wave frequency spectra and the wind drag measured at the Institut de Recherche sur les Phénomènes Hors Equilibre (IRPHE) Luminy wind-wave tank to test a wind-over-waves coupling model which follows the developments by Kudryavtsev et al. (1999), Makin and Kudryavtsev (1999, 2002) and Kudryavtsev and Makin (2001). In this model, the three components of the wind stress (surface shear, wave-induced and air flow separation) were estimated separately, based on models for the wind boundary layer and, in the case of wave-induced and air flow separation stresses, also parametrisations of the momentum transfer to non-breaking and breaking waves, respectively. The wave-number spectra, which are necessary for the wind-wave coupling, were determined as a combination of two ranges: the low wave number range was reconstructed from the measured frequency spectra; and the high wave number range came from the solution of the energy balance for this range, including models for nonlinear wave interactions, energy input due to the wind and energy dissipation due to viscous effects, wave breaking and the generation of parasitic capillary waves. Comparison between model results and experimental measurements of wind stress and wave properties, which comprised fetches up to 26 m, showed a fairly good agreement, with maximum errors in the wind stress of the order 10% (maximum relative differences in the wave properties were of the order 25%), as long as the wave steepness

limit for wave breaking was adequately adjusted to be consistent with the breaking behaviour at short fetches (Caulliez et al., 2008).

Although requiring further testing with longer fetches, the good results obtained by Caulliez et al. (2008) suggest wind-over-waves coupling as a promising tool to improve wind drag estimation for liquid surfaces at the scale of WWTPs. Two main drawbacks, however, prevent its immediate use for emission modelling purposes. The first of them is the relative complexity of wind-over-waves coupling, which requires the iterative numerical solution of the momentum conservation equation along the spatial domain (and also in time, if non-steady cases are considered) and throughout the wave number spectrum. Thus, a rather complex and computing-costly calculation procedure will have to be included in the framework of the emission models, which normally aim to be simple and practical.

The other critical point is that wind-over-waves coupling requires the complete description of the wave spectra. As one cannot expect to have wave spectra routinely measured at WWTPs (and, in many cases, emission models are to be applied to estimate emissions before a plant is constructed), the only option is to simulate the whole spectra. Concerning this point, it is worth mentioning that, as part of the VIERS-1 program, Calkoen et al. (1991) and Snoeij et al. (1993) describe the effort to build a combined model to predict wave spectra which joints JONSWAP-type spectra for waves in the low frequency range with spectra calculated from the energy balance for the high frequency range. When properly tuned, the combined model performed well in simulating the experimental frequency spectra measured at fetches up to 90 m in the Delft wind-wave flume (Snoeij et al., 1993). The considerably good reproducibility of the spectra reported by Calkoen et al. (1991) for replicate experimental runs done under the same condition suggest that a parametrisation of the wave spectra for short fetches is also a plausible option. One such an attempt is discussed by Snoeij et al. (1993); it was found to predict the spectra accurately only for a range of frequencies (their range of interest), depending on the friction velocity.

2.5. Direct measurement of emissions using the US EPA flux hood

In a guide supported by the US EPA, Klenbusch (1986) presents standards and recommendations for the construction and operation of an “emission isolation flux chamber (also called dynamic flux chamber, or flux hood) for assessment of gaseous emissions from soils. Figure 2.5, reproduced from Klenbusch (1986), shows the original schematic representation of the US EPA flux hood, its main dimensions and supporting equipment.

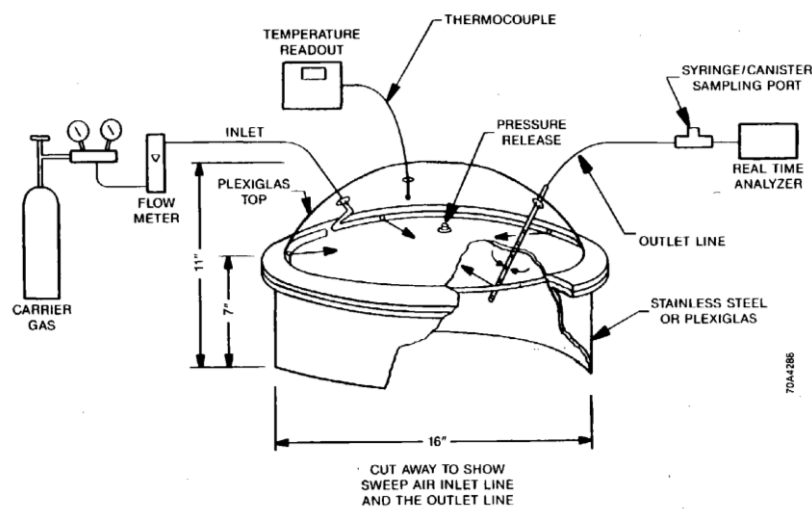


Figure 2.5. Schematic representation of the US EPA flux hood. Source: Klenbusch (1986).

As summarised by Eklund (1992), posterior investigations were carried out in order to extend the use of the US EPA dynamic flux chamber for measurements of volatile emissions from other sources, including passive liquid surfaces. In general, the US EPA flux hood method demonstrated satisfactory results in terms of recovery rate (little losses within the equipment), precision (low variability among replicate measurement from a same individual flux hood) and repeatability (low variability among measurements from different individual flux hoods with identical design, placed side-by-side) (Klenbusch, 1986; Gholson et al., 1989, 1991; Eklund, 1992). Supported by these results and also by the fact that it is a standardised method (Hudson and Ayoko, 2008b), the US EPA flux hood has been widely adopted for measurement of volatile emissions, and its use has expanded to countries other than the United States

(sometimes with modifications to methodology), such as in Australia (AS/NZS 4323.4:2009), where the use of an internal fan was included to promote mixing.

However, the accuracy and applicability of the US EPA flux hood has been questioned. A primary concern regarding the use of a flux hood is an artificial increase in compounds concentration (concentration build up) in the headspace, which may occur in case of insufficient flow rate (Hudson and Ayoko, 2008b). Even if the flow rate is theoretically high, local accumulation may arise if there is not enough mixing in the air phase (Gholson et al., 1989, 1991; Eklund, 1992; Woodbury et al., 2011). An increase in the headspace concentration close to the liquid surface can result in a reduction of the emission rate during the experiment and an inappropriate measurement of the local emission rate (Hudson and Ayoko, 2008b; Parker et al., 2013b). Experimental tracer studies have indicated that the US EPA dynamic flux chamber is likely to have a generally well-mixed air phase when operated within the recommended flow rate range (Gholson et al., 1989; Eklund, 1992; Woodbury et al., 2011), despite evidences of some small zones of local accumulation/stagnation (Gholson et al., 1989; Woodbury et al., 2011). Inaccuracies can also occur if the outlet air that is sampled is not representative of the total exiting air (Gholson et al., 1989).

Another important point is that air flow inside the flux hood may not be able to reproduce relevant features of the atmospheric flow to which the water surface is exposed in the absence of the enclosure device. This can affect directly the mass transfer condition and strongly influence the emission rate of compounds, especially the less volatile ones (Gholson et al., 1989, 1991; Hudson and Ayoko, 2008a, 2008b; Parker et al., 2013b). In an attempt to address this question, Gholson et al. (1989, 1991) used an apparatus that simulates a wind blowing over the surface of a small tank (filled with aqueous solutions of organic compounds) and also allows sampling at the apparatus outlet. By comparing the emission rates obtained directly from the apparatus outlet and the emission rates measured by a US EPA dynamic flux chamber placed inside the apparatus, it was possible to calculate the bias due to the use of the flux hood. The authors found that emission rates quantified by the US EPA flux hood were systematically lower than the “actual” emission rates verified in the simulator, underestimating the emission rates, in average, 68 % for 2-butanone, 38 % for toluene and 21 % for 1,1,1 - trichloroethane. This negative bias was linked to perturbations that

the chamber may impose on the surface currents that are normally induced by the wind at the free liquid surface. Hudson and Ayoko (2008b) also claimed that the results of Gholson et al. (1989, 1991) may present direct relation to the solubility of the compounds: the more soluble suffered higher bias.

Furthermore, different enclosure devices present differences in mass transfer conditions and other details of the internal fluid dynamics. As shown by Guillot et al. (2014), odour measurements carried out at the same time in the same sources can differ largely when different devices are compared. Also, comparative studies performed by Jiang and Kaye (1996), Hudson and Ayoko (2009) and Hudson et al. (2009) found high differences (dependent on the solubility of the compounds) between emission rates of organic compounds obtained with the US EPA flux hood and those obtained with the portable wind tunnel developed at the University of New South Wales, in Australia (UNSW wind tunnel, originally described by Jiang et al., 1995), which presents very different design and operational conditions comparing to the flux hood.

Concerning the above, there are important conceptual differences between the US EPA dynamic flux chamber (and other suchlike flux hoods) and wind tunnels. Wind tunnels are usually designed to allow a directional air flow and, in most cases, present a nominal air velocity (Hudson, 2009), normally controllable (e.g., Jiang et al., 1995; Sohn et al., 2005; Capelli et al., 2009a). Some studies (e.g., Bliss et al., 1995; Capelli et al., 2009a; Lin et al., 2012) also indicate consistency between results obtained with certain wind tunnels and theoretical models of boundary layers. Taking into account the fact that wind tunnels offer the possibility of corrective calculations directly based on air velocity and preliminary evidences of good relations between measurements obtained with wind tunnels and device-independent methods, Hudson and Ayoko (2008b) suggest that wind tunnels are more likely to succeed in the pursuit for realistic emission rate estimates. The US EPA flux hood, on the other hand, is designed as an isolation-mixing chamber, with no representative value of air velocity; as pointed out by Hudson and Ayoko (2008b), such a device is suitable when standard, consistent and reproducible conditions are desired.

3. EVALUATION AND DEVELOPMENT OF MASS TRANSFER MODELS

In this chapter, different models for the gas-film (k_G) and liquid-film (k_L) mass transfer coefficients for passive liquid surfaces in WWTPs are evaluated against a compilation of experimental data, and new alternate approaches are proposed, based on the analysis of the compiled data sets.

3.1. Methodology

3.1.1. Compilation of the data sets

3.1.1.1. Data for k_G

The basic data necessary for the present analysis are values of k_G and the corresponding u_* (and U_{10} , if possible), together with complementary information on average temperatures and size of the water surface. Results from field campaigns were not included, since the variety of factors acting in the field, for instance temperature variations, insolation, contaminants in the water and lack of detailed wind speed information, might increase the scatter of the reported results and, consequently, prevent a clear evaluation of the different approaches. Thus, this analysis focuses on experimental results from laboratory wind-wave tanks. Additionally, the studies reported in the literature were selected observing the following criteria:

- The size, shape and conditions of the experimental setups have to be relevant in relation to the situations of interest for emission modelling in WWTPs; this means, for example, that experiments performed in extremely small tanks and/or without fully turbulent boundary layers were not considered, since the characteristics of the wave field and the air flow would greatly depart from what could be expected for typical liquid surfaces in WWTPs.
- Only studies carried out in rectangular tanks with directional air flow were selected, for which predominantly two-dimensional boundary layers and

directional wave fields can be expected; any situation different from this becomes highly case-specific and, preliminarily, impossible to be treated by any of the theoretical or experimental approaches analysed here.

- Studies with a large number of results clearly affected by experimental flaws were also not included.
- The variables of interest, k_G and u_* , have to be either directly reported (in the body of the text, in a table or in clearly-readable figures) or be able to be derived straightforward from primary information presented in the papers, such as drag coefficients and Dalton numbers.
- Only results concerning cases with neutral or approximately neutral buoyancy in the air flow were considered.

Considering the above constraints, the data for the present analysis were compiled from five independent works, summarized in Table 3.1. Three of these sources coincide with the ones used by Gostelow (2002). The study of Mackay and Yeun (1983) was discussed in 2.2.3.2; the other experiments (Mangarella, 1971; Liss, 1973; Resch and Selva, 1979; and Ocampo-Torres et al., 1994) will be treated in the following paragraphs. In principle, any gas phase-controlled compound is suitable to be included in the data set. However, among the studies considered here, only Mackay and Yeun (1983) reported mass transfer coefficients for compounds other than water; even so, they notice that their results regarding gas phase-controlled VOCs presented large scatter and might have been compromised by the methodology employed to quantify their concentration in the liquid phase. For this reason, the data set used in the present chapter contains only gas-film mass transfer coefficients for water vapour. Water is classically used as a model compound for the study of mass transfer conditions at the air-side of the air-water interface (Schwarzenbach et al., 2003), since it faces virtually no resistance to transport in the liquid-side (therefore it is completely gas-phase controlled).

Table 3.1. Sources composing the data set of k_G for water vapour.

Reference	Fetch (m)	u_* (m s ⁻¹)	U_{10} (m s ⁻¹)	Temperature (°C)	Method for determining k_G	Method for determining u_*
Mangarella (1971)	7.74 – 13.91	0.139 – 0.615	4.6 – 16.5	Air: 14.9 – 21.5 Water: 13.5 – 21.3	Integration in the boundary layer.	Velocity profile.
Liss (1973)	4.50	0.058 – 0.473	2.6 – 13.7	Not available.	Change in salinity of the water with time.	Velocity profile.
Resch and Selva (1979)	2.62 – 37.84	0.293 – 0.345	Not available	Air: 20.0 Water: 20.0	Similarity theory.	Velocity profile.
Mackay and Yeun (1983)	6.0	0.271 – 0.993	8.4 – 23.1	Not available.	Volume of evaporated water measured by “chicken feeder”.	Velocity profile.
Ocampo-Torres et al. (1994)	32.2 ^a	0.039 – 0.973	1.0 – 24.5	Air: 20.91 – 23.94 Water: 17.79 – 21.41	Build-up of humidity in the recirculating air.	Velocity profile.
Whole data set	2.62 – 37.84	0.039 – 0.993	1.0 – 24.5	Air: 14.9 – 23.94 Water: 13.5 – 21.41	-	-

^a The total length of the tank was 32.2 m, but the wave field was divided by an inverted dissipation beach into two sections of 16 m.

The values of U_{10} were either directly reported by or calculated based on other data provided by the original reference (for example, u_* and roughness length; or u_* and the value of the velocity at a different height); U_{10} could not be obtained from the information reported by Resch and Selva (1979). For the sources that do not supply information on the temperature of the experiments, namely Liss (1973) and Mackay and Yeun (1983), a default value of 20 °C was adopted in order to calculate the temperature-dependent properties (air viscosity, molecular diffusivity and Schmidt number of water vapour in air); the deviations in the values of such properties, introduced by choosing this arbitrary value of temperature, are rather small.

Liss (1973) measured water evaporation in a tank, 4.5 m long, mounted inside an aerodynamic wind tunnel. The evaporation rate was obtained by the change in salinity of the water in the tank over time, and k_G was calculated by Liss (1973) using the air humidity at 10 cm above the surface (which, given the size of tank, is a good approximation for the concentration of water vapour in the bulk air). The value of u_* reported for each velocity condition was measured by the velocity profile method at the downwind end of the tank; it will be adopted here as a proxy for the average u_* along the surface.

The experiment of Ocampo-Torres et al. (1994) was carried out in a tank 32.2 m long; the air flow was continuous along the tank, but the wave field was divided by an inverted dissipation beach into two sections of approximately 16 m. The wind tunnel coupled on top of the water tank operated in “circulating mode”, meaning that the air at the outlet of the test section was redirected back to the inlet, in a closed loop, without exchange with the exterior of the tunnel; k_G was then obtained from the curve describing the build-up of water-vapour concentration in the air with time. At each nominal air velocity in the tunnel, u_* was determined by the velocity profile method at three different locations along the surface, and the average of the three (which is the approximated average u_* over the whole surface) was reported in the original paper.

Mangarella (1971) and Resch and Selva (1979) measured detailed velocity and humidity profiles in the air flow at various locations along the water surface, being able to report local values of k_G and u_* at different fetches. Both works employed the profile

method to estimate u_* ; Resch and Selva (1979) also used the velocity and humidity profiles together with similarity theory to estimate k_G . Mangarella (1971) made use of the detailed profiles in a different way, calculating a mass transfer Stanton number (from which k_G can be retrieved) using the so-called “integral method”, based on the change of integral fluxes across the boundaries of control volumes sectioning the mass transfer boundary layer. Only the results regarding the neutral case of Resch and Selva (1979) and the isothermal case without mechanically-generated waves of Mangarella (1971) are considered here. Because the fetch-averaged values of k_G and u_* are necessary for testing the different models evaluated in the present study, they were calculated by simply averaging the respective local values up to the desired fetch, thus obtaining results for multiple fetches. The fact that Mangarella (1971) and Resch and Selva (1979) also report detailed information about the thickness of the mass transfer boundary layer is particularly useful for the present analysis, especially for the evaluation of Brutsaert's (1975) and Deacon's (1977) models, as further explained in sub-section 2.2.2. The results for the three shortest fetches in Mangarella's (1971) work are not included, since that author expressed concern regarding the boundary layer development at those fetches.

3.1.1.2. *Data for k_L*

Analogous to the analysis for k_G , the data for the evaluation of k_L consisted of a compilation of experimental results from laboratory wind-wave tanks regarding the values of fetch-averaged k_L , the corresponding u_* and, wherever possible, U_{10} , together with auxiliary information as average temperatures and dimensions of the tank. The principles and criteria for the selection of the sources of the data set were the same as explained in 3.1.1.1. Observing these, six independent sources were selected, which are summarized in Table 3.2. Five of them were previously used to fit the k_L correlation for the model of Gostelow et al. (2001) (as described by Gostelow, 2002); the sixth is the more recent study of Rhee et al. (2007). Again, for the sources that do not inform on the temperature of the experiments, Liss (1973) and Mackay and Yeun (1983), a default value of 20 °C was adopted to calculate the temperature-dependent properties (density and viscosity of water, and molecular diffusivity and Schmidt number of the compounds

in water); the deviations in the values of such properties, introduced by choosing this arbitrary value of temperature, are rather small.

The basic description of the experimental set-up for the study of Mackay and Yeun (1983) was presented in 2.2.3.2, and for the studies of Liss (1973) and Ocampo-Torres et al. (1994), in 3.1.1.1. The set-up of Cohen et al. (1978) was very similar to the one of Mackay and Yeun (1983), but with a smaller water tank, 2.4 m long. They studied cases of benzene volatilisation with and without agitation in the water; only data for the non-agitated tank was incorporated in the present data set. Wanninkhof and Bliven (1991) used a large wind-wave tank (100 m long) to measure the decaying of the liquid-phase concentration of SF_6 (impinged in the water before the start of the experiments) with time, collecting samples along the length of the tank. Their values of u_* and U_{10} come from a correlation with the reference wind speed, validated by a previous study in the same wind-wave tank. Rhee et al. (2007) investigated the mass transfer of He, SF_6 , nitrous oxide (N_2O), bromomethane (CH_3Br) and dimethyl sulfide (DMS), also working with a relatively large tank, 40 m long. Due to specificities of their apparatus, the calculation of the mass transfer coefficient k_L was done by solving a comprehensive mass balance of the mass of the chemical species simultaneously in the gas and liquid phases. The present data set includes only results for pure wind waves (the studies of Wanninkhof and Bliven, 1991, and Rhee et al., 2007, also had runs with mechanically generated waves, but those results were excluded in the present compilation). In the same way as for k_G , the values of U_{10} used here were either directly reported by or calculated based on other data provided by the original references (such type of data was not available in the paper by Rhee et al., 2007; therefore U_{10} could not be obtained for their data).

Table 3.2. Sources composing the data set of k_L .

Reference	Compounds	Fetch (m)	u_* (m s ⁻¹)	U_{10} (m s ⁻¹)	Temperature (°C)	Method for determining k_L	Method for determining u_*
Liss (1973)	O ₂ and CO ₂	4.50	0.058 – 0.473	2.6 – 13.7	Not available.	Change in compound's concentration with time.	Velocity profile.
Cohen et al. (1978)	benzene	2.40	0.117 – 0.950	4.46 – 21.10	Air: 20 – 25 Water: 16 – 21	Change in compound's concentration with time.	Velocity profile.
Mackay and Yeun (1983)	benzene, toluene, 1,2-dichloropropane, chlorobenzene, 1,2-dibromoethane and tetrachloromethane	6.0	0.271 – 0.993	8.4 – 23.1	Not available.	Change in compound's concentration with time.	Velocity profile.
Wanninkhof and Bliven (1991)	SF ₆	100	0.086 – 0.977	3.70 – 20.70	Air: 14 Water: 14	Change in compound's concentration with time.	Correlation for the wind-wave tank.
Ocampo-Torres et al. (1994)	CO ₂	16 ^a	0.047 – 1.046	1.47 – 26.42	Air: 23.00 – 26.38 Water: 18.51 – 21.86	Change in compound's concentration with time.	Velocity profile.
Rhee et al. (2007)	He, SF ₆ , N ₂ O, CH ₃ Br and DMS	40	0.090 – 0.610	Not available.	Air: 17.60 – 22.10 Water: 15.40 – 22.30	Mass balance model for the wind-wave tank.	Inertio-dissipative method.
Whole data set	All the above.	2.40 – 100	0.047 – 1.046	1.47 – 26.42	Air: 14 – 26.38 Water: 14 – 21.86	-	-

^aThe total length of the tank was 32.2 m, but the wave field was divided by an inverted dissipation beach into two sections of 16 m.

3.1.2. Evaluation of mass transfer models

3.1.2.1. Models for k_G

The following theoretical and empirical models for k_G for passive liquid surfaces (previously reviewed in section 2.2) were evaluated against the compiled data set for mass transfer of water vapour in air:

- The theoretical models of Brutsaert (1975) (presented in 2.2.1.3) and Deacon (1977) (presented in 2.2.1.4). These models were derived based on the classical description of the inner part of the turbulent boundary layer over a smooth flat plate;
- The empirical correlations of Mackay and Matsugu (1973), Mackay and Yeun (1983) and Gostelow et al. (2001) (presented in 2.2.3).

It is important to mention that Equations (2.7) and (2.8), which are based on the developing boundary layer over a smooth flat plate, were not included in the analysis because they are not suitable for application in the modelling of emissions in WWTPs, given the reasons discussed in 2.2.1.1.

As also discussed in 2.2.1.5, the correct application of Brutsaert's and Deacon's models require the clear definition of a reference height, consistent with the value of the bulk gas-phase concentration C_G that is used to calculate the emission, by means of Equations (2.12) and (2.13) together with Equation (2.10) (Brutsaert's) or (2.11b) (Deacon's). In this sense, if C_G is approximated by the background concentration, as usually done in the context of emission modelling and also in the experimental values used herein, the reference height ideally coincides with the top limit of the concentration boundary layer, δ_M . Because the interest in emission modelling normally resides in the fetch-averaged k_G (and also part of the experimental data set only reports the averaged values of k_G and u_*), the models will be all evaluated against the fetch-averaged values of k_G , using fetch-averaged input variables, u_* and δ_M . The possibility of applying Brutsaert's and Deacon's models with fetch-averaged u_* and δ_M to obtain fetch-averaged k_G was verified for the case of the developing turbulent boundary layer over a smooth flat plate, as further discussed in Appendix A.

Among the sources of the present data set of k_G , only Mangarella (1971) and Resch and Selva (1979) give enough information about the thickness of the mass transfer boundary layer in their experiments. Therefore, the primary evaluation of Brutsaert's and Deacon's models will be based on the data from Mangarella (1971) and Resch and Selva (1979), for which the experimental values of δ_M could be obtained. In order to extend the comparison against the rest of the data, a parametrisation for the average thickness of the mass transfer boundary layer, δ_M , is developed in the present work. Using the data from Mangarella (1971) and Resch and Selva (1979), we were able to satisfactorily correlate the fetch-averaged δ_M to a fetch Reynolds number $Re_* = u_* X / \nu$ and a non-dimensional fetch $X_* = Xg/u_*^2$, via Equation (3.1), being u_* also fetch-averaged. These two non-dimensional groups in the right-hand side of Equation (3.1), Re_* and X_* , represent, respectively, the influences of boundary layer development and wind-wave field, both of which contribute for the thickness of the boundary layer. The constant and exponents were chosen so as to minimize the relative errors in estimating δ_M for Mangarella's (1971) and Resch and Selva's (1979) data, achieving a RMS relative error of 11.8% (with positive and negative maximums of 18.4% and -25.7%).

$$\frac{\delta_M}{X} = 0.751 Re_*^{-0.236} X_*^{-0.138} \quad (3.1)$$

The two models (i.e., Equation (2.10), for Brutsaert's, or Equation (2.11b), for Deacon's, together with Equations (2.12) and (2.13)) were applied with the following input variables, judged as the best representation of the experiments in the data set: fetch-averaged u_* as obtained from the original references; Sc_G for water vapour in air, corrected for the experimental temperatures; von Kármán constant 0.4; turbulent Schmidt number Sc_t equal 0.8; reference “measurement” height z_m equal the fetch-averaged δ_M . For the cases of Mangarella (1971) and Resch and Selva (1979), the values of δ_M were the ones derived from the experimental profile measurements; for the rest of the data set, δ_M was estimated using Equation (3.1).

The empirical models of Mackay and Matsugu (1973), Mackay and Yeun (1983) and Gostelow et al. (2001), Equations (2.14), (2.15) and (2.16), respectively, were also evaluated against the compiled experimental data set. For the application of these correlations, the input variables were considered the same way as in the testing of

Brutsaert's (1975) and Deacon's (1977) models: fetch-averaged u_* (or the equivalent U_{10} , in the case of Mackay and Matsugu's correlation) as obtained from the original references; and Sc_G for water vapour in air, corrected for the experimental temperatures. For the purposes of the present evaluation, X will be always taken as the length of the tank in the direction of the wind, for the reasons discussed in Prata Jr. et al. (2016a).

3.1.2.2. Models for k_L

The experimental data set was used to test the theoretical models of Deacon (1977) (Equation (2.17)), Münnich and Flothmann (1975) (Equation (2.19)) and Banerjee and McIntyre (2004) (Equation (2.20)), and several empirical models for k_L . The model of Csanady (1990) (Equation (2.21)) was not evaluated separately since there is no clear information on how to estimate the parameter ϕ , which represents the fraction of the liquid surface effective in mass transfer and is supposed to change with the wind-wave field. The use of the value of ϕ suggested by Csanady (1990) makes Equation (2.21) practically coincide with Equation (2.20). Among the empirical models, besides the three approaches discussed in 2.3.3 (most commonly used in the context of modelling atmospheric emissions in WWTPs), other models that are frequently cited in the literature were also tested: Lunney et al. (1985); Liss and Merlivat (1986); Wanninkhof (1992); Cole and Caraco (1998); Schwarzenbach et al. (2003); Ro et al. (2007); Wanninkhof et al. (2009); and Vachon and Prairie (2013). The empirical correlations that constitute these additional models and the results of their evaluation are presented in Appendix B. For the models that require the friction velocity in the liquid side, this was calculated based on the friction velocity u_* in the gas side, as $u_{*,L} = u_*(\rho_G/\rho_L)^{1/2}$, where ρ_G and ρ_L are the densities of the air and water, respectively, corrected for the experimental temperatures. Again, the fetch X will be always taken as the length of the tank in the direction of the wind, for the reasons discussed in Prata Jr. et al. (2016a;).

3.2. Results and discussion

3.2.1. Models for k_G

3.2.1.1. Analysis of the experimental k_G data set

Figure 3.1 shows the variation of k_G with u_* and U_{10} , discriminated according to the different sources that compose the data set. Overall, the behaviour of k_G in relation to u_* (or U_{10}) is similar for all the experiments. Nonetheless, a certain degree of scatter is also clearly observed. Part of this scatter can be attributed to the differences in fetch, since the mass transfer boundary layer is expected to increase in thickness with fetch. Differences in the methodologies to estimate k_G and the fetch-averaged u_* and the errors and imprecisions inherent to the experimental practice certainly also contribute to the scatter. Even so, the data from Mackay and Yeun (1983) at large u_* markedly departs from the rest of the data set, and the possibility of a significant experimental bias cannot be ruled out, especially considering the “chicken feeder” apparatus used to quantify the evaporation rates. Therefore, in the following analysis, the different approaches for estimating k_G will be evaluated against the whole data set and against the data set without Mackay and Yeun’s (1983) results.

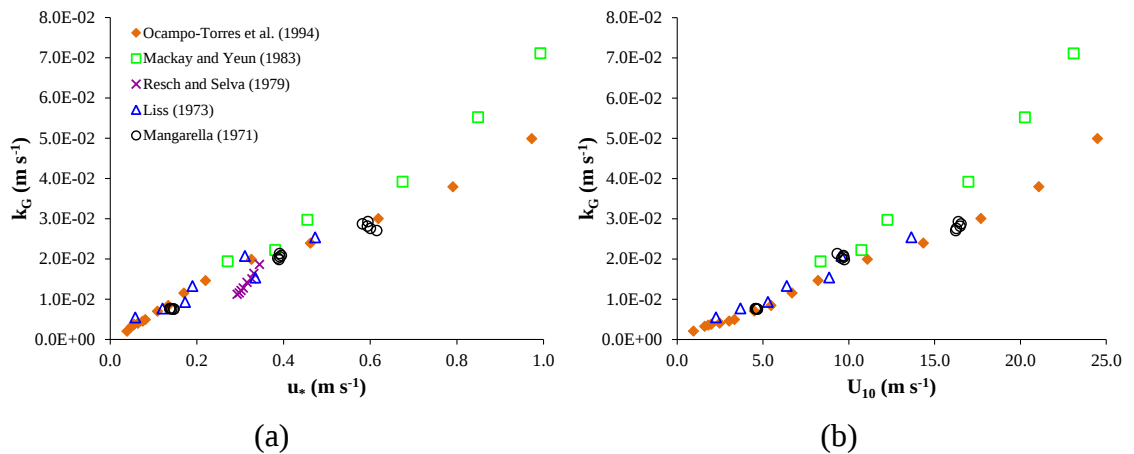


Figure 3.1. Variation of k_G for water vapour with (a) u_* and (b) U_{10} . The sources of the data are identified by the different symbols (legend in (a)).

3.2.1.2. Testing the models of Brutsaert (1975) and Deacon (1977)

The models of Brutsaert (1975) and Deacon (1977) were applied to estimate k_G , following the procedure explained in 3.1.2.1. The comparison between the estimated k_G and the respective experimental k_G from the data set compiled is illustrated in Figure 3.2. The relative errors (RMS, positive extreme and negative extreme) are summarised in Table 3.3, for three sets of data: all data; all data excluding Mackay and Yeun (1983); and only Mangarella (1971) and Resch and Selva (1979).

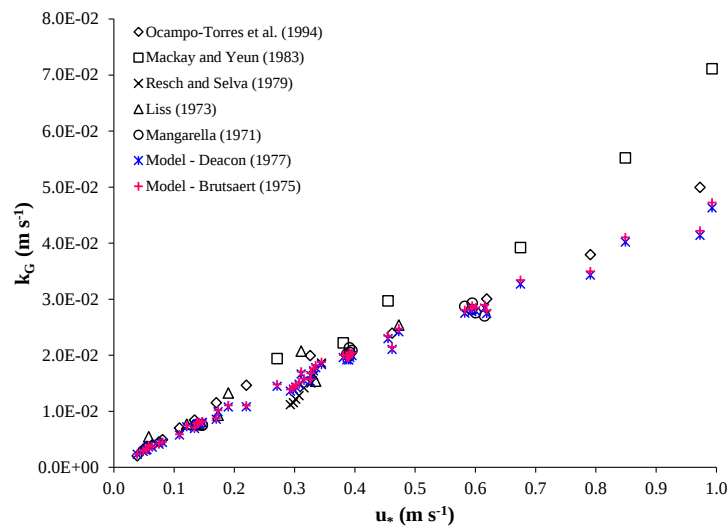


Figure 3.2. Experimental k_G for water vapour from the compiled data set together with respective values estimated by Brutsaert's (1975) and Deacon's (1977) models.

Table 3.3. Relative errors in the k_G estimated by the models of Brutsaert (1975) and Deacon (1977) in relation to the experimental k_G from the compiled data set.

Data set		Brutsaert (1975)	Deacon (1977)
All data	RMS:	14.5%	14.91%
	Positive extreme:	24.0%	21.5%
	Negative extreme:	-33.6%	-34.9%
All data excluding Mackay and Yeun (1983)	RMS:	13.0%	13.2%
	Positive extreme:	24.0%	21.5%
	Negative extreme:	-27.3%	-29.4%
Mangarella (1971) and Resch and Selva (1979)	RMS:	10.5%	9.2%
	Positive extreme:	24.0%	21.5%
	Negative extreme:	-3.8%	-6.0%

The models of Brutsaert (1975) and Deacon (1977) proved to predict the experimental k_G in the data set considerably well, with both models performing in a very similar way. This may be an indication that, for the range of fetches and u_* covered in the present analysis (Table 3.1), the process of mass transfer of compounds in the gas-side of the air-liquid interface does not deviate dramatically from the “classical” picture of the inner layer of a smooth turbulent boundary layer over a flat surface (intrinsic to both models), as long as the appropriate value of u_* is used in the modelling. Although the mass transfer dynamics may be similar, the values of u_* in the experiments are not necessarily the same as expected for a smooth flow, because of the effect of waves on the wind friction (see review and discussion in section 2.4). The relatively good performance of the models is also in accordance with the findings of Merlivat and Coantic (1975), who show that Brutsaert’s model could predict great part of their experimental results regarding isotopic composition of evaporated water vapour in a 40 m long wind-wave tank, with u_* up to 0.228 m s^{-1} .

Because the mass transfer boundary layer thickness δ_M is taken as the reference height (z_m) in this analysis, the models automatically account for the effects of the thickening of the boundary layer as fetch increases and were able to capture part of the scatter in the values of k_G . However, this does not explain the entire scatter, and relative differences between model estimates and experimental values are observed (Figure 3.2 and Table 3.3). Besides the errors and imprecisions that may be associated with the experimental data, possible additional reasons for such differences are:

- The assumption that z_m is inside the dynamic (log) sublayer of the inner part of the turbulent boundary layer, which is inherent to the application of Equation (2.13), is not strictly true for at least part of the experiments; nevertheless, the preliminary testing with the case of the developing turbulent boundary layer over a smooth flat plate (Appendix A) indicated that the errors arising from this assumption would be relatively small.
- The use of Equation (3.1) to parametrise δ_M (i.e., z_m) automatically introduces some degree of error, however smoothed since the logarithm of z_m is taken. Indeed, if the evaluation is done considering only the data of Mangarella (1971)

and Resch and Selva (1979), for which the experimental value of δ_M is adopted, the errors are smaller (Table 3.3).

- The air-flow separation over breaking waves and wave-induced motions in the air flow could have affected to some extent the mass transfer in the boundary layer over the water surface (the mechanisms are discussed in 2.2.2) for some of the experiments, making it deviate from the “classical” smooth flow situation originally described by the models.
- The formation of spray upon wave breaking and the consequent additional evaporation from the spray droplets is not accounted for in the models; spray may have been present in some of the experiments, mainly at high u_* , and resulted in relatively larger experimental k_G . This is a possible explanation to the seemingly likelihood of the models to underestimate k_G for u_* higher than around 0.6 m s^{-1} (which can be seen in Figure 3.2); however, as discussed previously, the data of Mackay and Yeun (1983), for which the largest underestimations are observed, might have been biased by the “chicken feeder” system used to measure the volume of water evaporated.

3.2.1.3. Testing empirical correlations for k_G

The empirical models of Mackay and Matsugu (1973), Mackay and Yeun (1983) and Gostelow et al. (2001), Equations (2.14), (2.15) and (2.16), respectively, were used to estimate k_G , following the procedure explained in 3.1.2.1. The comparison between the estimated k_G and respective experimental k_G is shown in Figure 3.3, and the relative errors (RMS, maximum positive and maximum negative) are summarised in Table 3.4, for the whole data set and for the data set excluding Mackay and Yeun’s (1983) experiment. It is important to note that Mackay and Matsugu’s model is not compared against Resch and Selva’s (1979) data, since no equivalent U_{10} could be retrieved for their experiment.

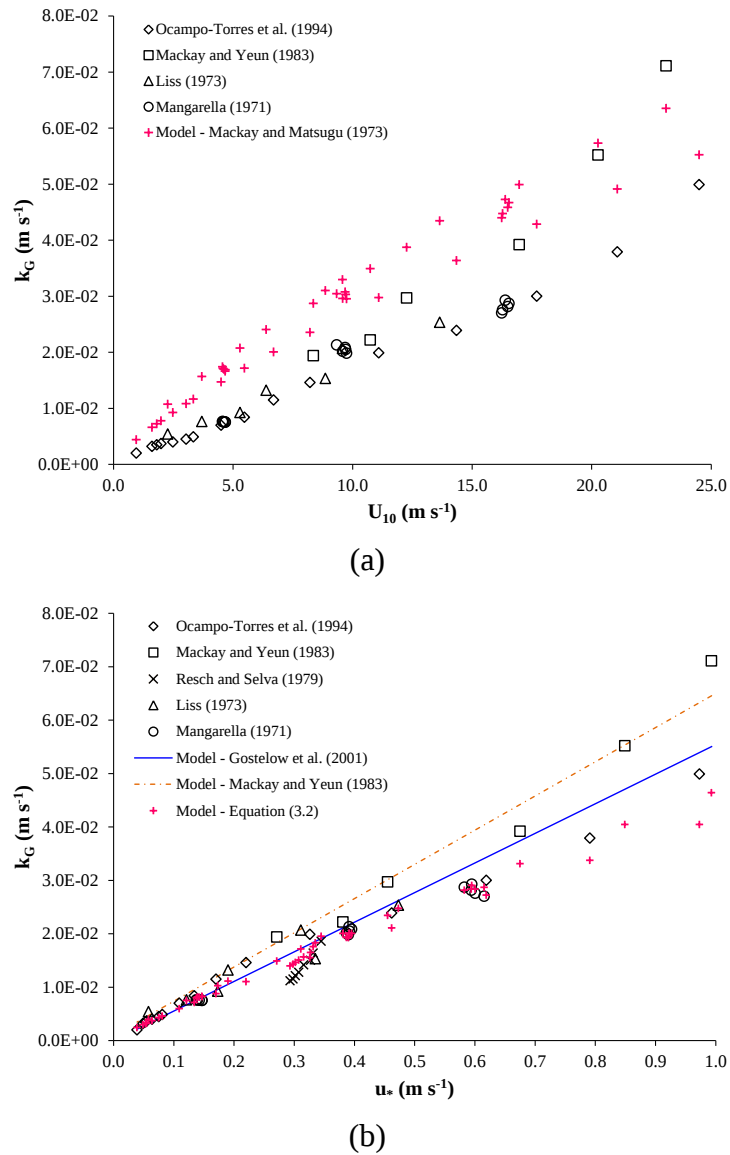


Figure 3.3. Experimental k_G for water vapour from the compiled data set together with respective values estimated by the following model correlations: (a) Mackay and Matsugu (1973); (b) Mackay and Yeun (1983), Gostelow et al. (2001) and Equation (3.2).

Table 3.4. Relative errors in the k_G estimated by empirical correlations in relation to the experimental k_G from the compiled data set.

Data set		Mackay and Matsugu (1973) ^a	Mackay and Yeun (1983)	Gostelow et al. (2001)	Equation (3.2)
All data	RMS:	85.6%	34.7%	18.0%	15.6%
	Positive extreme:	140.8%	76.7%	45.2%	25.0%
	Negative extreme:	-10.7%	-12.9%	-40.6%	-34.7%
All data excluding Mackay and Yeun (1983)	RMS:	91.5%	36.7%	18.2%	13.2%
	Positive extreme:	140.8%	76.7%	45.2%	25.0%
	Negative extreme:	No negative	-12.9%	-40.6%	-27.1%

Mackay and Matsugu's correlation, Equation (2.14) (Table 2.1), performs poorly in describing the experimental data set, with RMS relative error of 85.6%, reaching maximum deviations of order 140%. Furthermore, the behaviour predicted by this correlation does not correspond to the observed experimental variation of k_G with U_{10} , as seen in Figure 3.3a. Together with imprecision of the U_{10} characterizing the data set, one of the probable reasons for errors of such magnitude are methodological shortcomings in the derivation of Mackay and Matsugu's correlation, such as the use of wind speed values not measured on site, but taken from a nearby meteorological station. It may also have been affected by the previously-discussed limitations of Sutton's (1953) model (see 2.2.1.2). The fact that Equation (2.14) is not able to correctly estimate k_G is of particular importance, since this is the equation utilised in the model WATER9 for predicting emissions in liquid impoundments and other types of passive surfaces, which is the model endorsed by the US Environmental Protection Agency (US EPA, 1994, 2001) and is generally accepted as a regulatory model for the assessment of atmospheric emissions in WWTPs.

The model of Mackay and Yeun (1983), Equation (2.15), estimates k_G with smaller errors (RMS relative error of 34.7%) than Mackay and Matsugu's, although extreme deviations as large as 76.7% were still found. Besides, a trend of this correlation to overestimate most of the data set is clearly observable in Figure 3.3b. Nonetheless, the correlation of Gostelow et al. (2001) produces comparatively much better predictions, with smaller RMS relative error (18.0%) and extremes, as seen in Table 3.4 and Figure 3.3b. This can be explained by the fact that part of the present data set was used by Gostelow et al. (2001) to fit their correlation; in other words, for part of this data set, Equation (2.15) actually is the best linear fit in terms of k_G as a function of u_* . A disadvantage of both Mackay and Yeun's and Gostelow's correlations is that they do not respond to differences in fetch.

3.2.1.4. Development of an alternate approach for estimating k_G

In this work, new alternate equation form is fitted to the data set, assuming the normalized k_G , k_G/u_* , to be proportional to powers of Sc_G , Re_* and X_* (the last two defined the same way as in Equation (3.1)). The exponent of Sc_G was set as $-2/3$ (≈ -0.67), a value customarily adopted (e.g., Equations (2.14), (2.15) and (2.16), from Table 2.1); the proportionality constant and the exponents of Re_* and X_* were then chosen so as to minimize the relative errors between the predicted k_G and the k_G in the data set excluding Mackay and Yeun's (1983) data (for the reasons discussed previously). This resulted in Equation (3.2).

$$\frac{k_G}{u_*} = 0.0994 Re_*^{-0.0894} X_*^{0.0178} Sc_G^{-2/3} \quad (3.2)$$

The comparison between the values of k_G estimated by Equation (3.2) and the respective experimental k_G is shown in Figure 3.3, and the relative errors (RMS, maximum positive and maximum negative) are summarised in Table 3.4, for the whole data set and for the data set excluding Mackay and Yeun's (1983) experiment. Equation (3.2) allowed to estimate the experimental k_G with smaller relative errors than the ones obtained with the other correlations (Table 3.4), both for the whole data set and especially for the data set without Mackay and Yeun's (1983) data. On the other hand, as can be noted in Figure 3.3b, Equation (3.2) performed best for u_* up to 0.6 m s^{-1} , seemingly underestimating the values of k_G for higher u_* .

According to Equation (3.2), k_G can be expected to vary proportionally to $u_*^{0.875}$ and $X_*^{-0.072}$. This shows that k_G is much more sensitive to changes in u_* than to changes in the fetch. This also partially explains why a linear fit that does not consider the influence of X , such as Gostelow's correlation, is a relatively good approximation for the variation of k_G with u_* within the data set.

3.2.1.5. *Comparison among the best-performing approaches for estimating k_G in situations of interest to WWTPs*

The present analysis showed that, of the approaches tested against the experimental data set, three produced clearly better results, with the smallest RMS relative errors (and also the smallest positive and negative extremes): the empirical correlation of Gostelow et al. (2001) (Equation (2.17), from Table 2.1); Equation (3.2); and the models of Brutsaert (1975) and Deacon (1977). It is then useful to compare the k_G that would be calculated by these three approaches for conditions beyond the limits of the experimental data set, so as to cover a broader range of situations that are of interest in the modelling of air emissions in WWTPs.

As a starting point, Figure 3.4 illustrates the behaviour of k_G with u_* as estimated by Gostelow's correlation, Equation (3.2) and Brutsaert's model (with z_m equal the fetch-averaged δ_M , estimated by Equation (3.1)), for two values of Sc_G and at three different fetches, with u_* varying from 0.05 to 1.0 m s⁻¹. As expected, the results of Gostelow's correlation do not change with fetch, whereas k_G estimated by Equation (3.2) and Brutsaert's model decreases slightly as X increases, for the same Sc_G (Figures 3.4a, c and e; and Figures 3.4b, d and f). The differences between the results of Equation (3.2) and Gostelow's correlation are normally small for lower u_* , becoming more pronounced for higher u_* and also increasing with X ; the behaviour (and, in fact, the values of the relative differences) does not change significantly with changes in Sc_G , since both equations contain factors of Sc_G to a similar power ($Sc_G^{-2/3} \approx Sc_G^{-0.67}$). The most remarkable aspect that can be observed in Figure 3.4, however, is that Brutsaert's model responds differently to changes in Sc_G compared to the other two approaches (compare the pairs at each fetch in Figure 3.4, a-b, c-d and e-f). This is due to the fact that the resistance R_m along the dynamic sublayer, calculated via Equation (2.13), does not depend on Sc_G ; therefore, changes in Sc_G will have less effect in the total resistance $R_G = 1/k_G$ (Equation (2.12)) and, consequently, in the value of k_G calculated by Brutsaert's model.

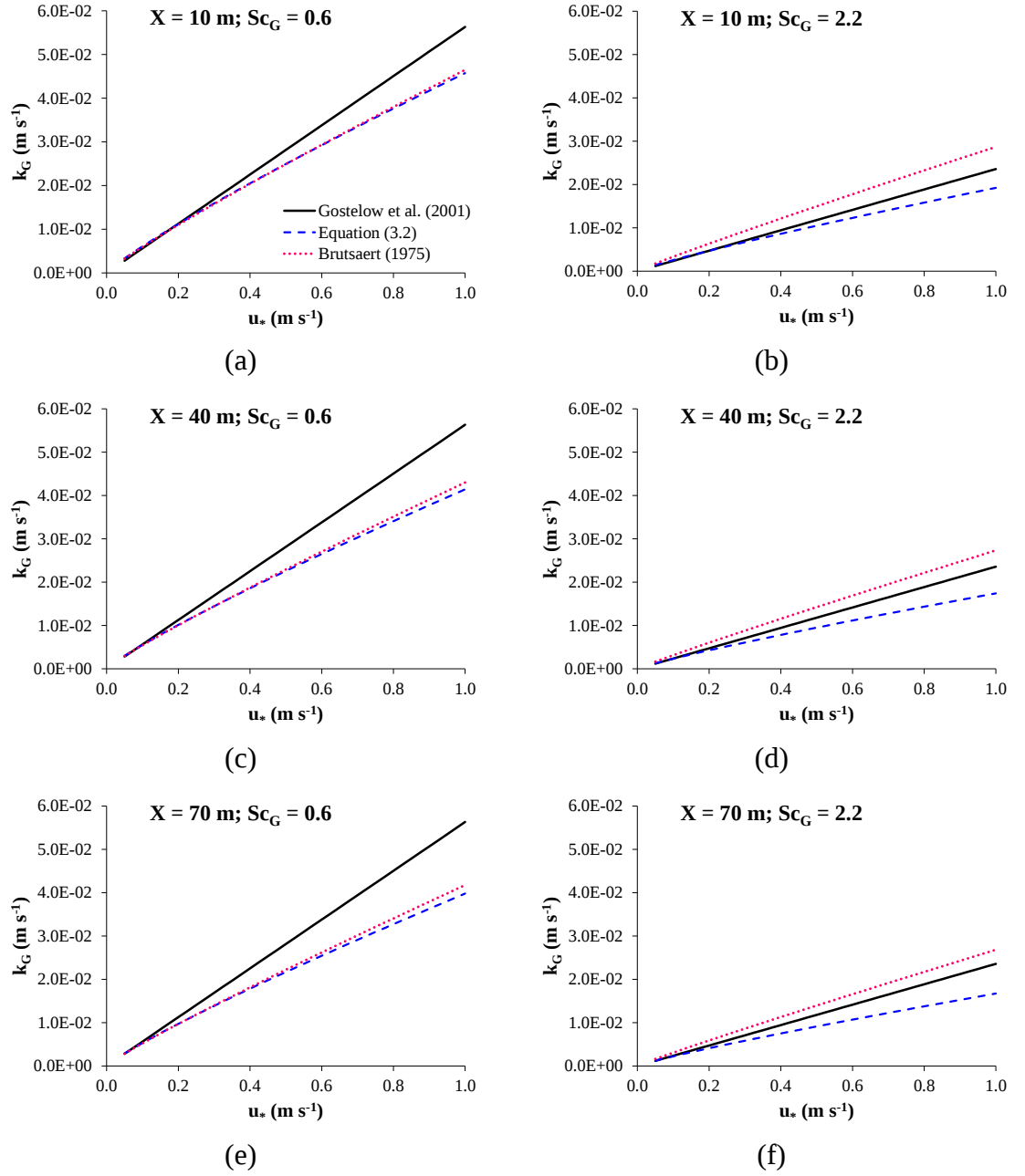


Figure 3.4. Variation of k_G with u_* , at different X and Sc_G , as estimated by three distinct approaches (legend in (a)): the empirical correlation of Gostelow et al. (2001); Equation (3.2); and the model of Brutsaert (1975). The values of X and Sc_G are indicated at the top of each figure. The scales of the axis were kept the same for better comparison.

Having understood how the differences among the results of the three approaches may vary depending on u_* , X and Sc_G , the next step is to estimate such differences in the whole range of situations that are of practical relevance for the modelling of atmospheric emissions in WWTPs. With this purpose, a Monte Carlo simulation was conducted with 30000 combinations of u_* , X and Sc_G , calculating k_G for each of them

applying the three approaches simultaneously: Gostelow's correlation, Equation (2.16); Equation (3.2); and Brutsaert's model, Equation (2.10) together with Equations (2.12) and (2.13), being z_m the fetch-averaged δ_M , estimated via Equation (3.1). The values of u_* , X and Sc_G were randomly chosen within the following ranges, which can be considered typical in the context of air emissions in WWTPs: u_* from 0.05 to 1.0 m s⁻¹; X from 4 to 100 m; and Sc_G from 0.6 to 2.6. Table 3.5 presents the RMS and maximum relative differences between results of each pair of models; it also indicates the percentage of results for which the respective differences were negative. The size of the sample, 30000, was such that these differences do not change significantly if larger sample sizes are adopted.

Table 3.5. Relative differences in the estimated k_G , comparing the empirical correlation of Gostelow et al. (2001), Equation (3.2) and the model of Brutsaert (1975).

	$(k_{G,Eq3.2} - k_{G,G})/k_{G,G}$	$(k_{G,B} - k_{G,G})/k_{G,G}$	$(k_{G,Eq3.2} - k_{G,B})/k_{G,B}$
RMS:	20.0%	17.2%	26.5%
Positive extreme:	25.8%	53.5%	2.2%
Negative extreme:	-31.0%	-26.7%	-40.9%
Percentage of negative differences:	95.3%	23.9%	99.8%

Legend: $k_{G,G}$: k_G calculated by the correlation of Gostelow et al. (2001); $k_{G,Eq3.2}$: k_G calculated by Equation (3.2); $k_{G,B}$: k_G calculated by the model of Brutsaert (1975).

Interestingly, the RMS relative differences between the results of Equation (3.2) and Gostelow's correlation and, especially, between Brutsaert's model and Gostelow's correlation are not extremely large, being of order 20% and 17%, respectively. Nonetheless, it is important to mention that the differences between results of Equation (3.2) and Gostelow's correlation and between results of Equation (3.2) and Brutsaert's model were predominantly negative, whilst the differences between Brutsaert's model and Gostelow's correlation were relatively more distributed and predominantly positive (i.e., for most of the cases, the k_G calculated by Brutsaert's model was larger than the respective k_G calculated by Gostelow's correlation). Also noteworthy are the considerably large extreme positive and negative relative differences which occur, respectively, between Brutsaert's model and Gostelow's correlation (53.5%) and between Equation (3.2) and Brutsaert's model (-40.9%), both cases observed for Sc_G closer to 2.6, the maximum value in the Sc_G range. Overall, the differences between

results of Brutsaert's model and the other approaches can be majorly related to the different dependence on Sc_G , as pointed out previously. On the other hand, the differences between results of Equation (3.2) and Gostelow's correlation are primarily due to the fact that the first has k_G proportional to $u_*^{0.875}$ (besides considering a slight dependence on fetch), while the later takes k_G proportional to u_* . The same analysis was done having Deacon's model in the place of Brutsaert's; the results were very similar.

Although the present analysis shows clearly that each of these approaches would present a different behaviour if applied to the variety of u_* , X and Sc_G that may appear in the practical situations of modelling atmospheric emissions in WWTPs, the testing against the experimental data set, discussed in the previous topic, did not completely indicate which approach shall be favoured, since the magnitude of the relative errors between estimated and experimental k_G was similar for the three of them. In principle, any of the three might be the most accurate; it might also happen that no single approach would perform satisfactorily in all situations, especially if extrapolated beyond the limits of the experimental data set. Of primary importance is the elucidation regarding the appropriate dependence of k_G on u_* (if linear or to a power) and Sc_G (if it scales with $Sc_G^{-2/3} \approx Sc_G^{-0.67}$, or follows a more complex relation as expressed in Brutsaert's model). This will require the conduction of further experimental studies, with large wind-wave tanks and involving gas phase-controlled compounds other than water vapour. In the hypothesis of k_G varying with Sc_G in a way different than the $Sc_G^{-0.67}$ proportion, this could also be related to the relative poor performance of Mackay and Matsugu's (1973) correlation (Equation (2.14), from Table 2.1) in estimating the experimental k_G for water vapour: because this correlation was originally fitted for cumene, the incorrect extrapolation for water vapour's Sc_G would then result in overestimated values of k_G .

Not forsaking the limitations and the necessity of further work cited above, at the present stage, the following points can be made:

- The correlation of Gostelow et al. (2001), Equation (2.16), figures as a reasonable choice if a rapid and simple estimate of k_G is required, keeping in mind its major limitations (not including X and imposing a proportionality to $Sc_G^{-0.67}$).
- The models based on the description of the inner part of the turbulent boundary layer over a smooth flat plate, namely Brutsaert (1975) and Deacon (1977), are also interesting alternatives, especially for research purposes, given their mechanistic character and because they can be incorporated in numerical solutions of coupled wind-wave fields and atmospheric boundary layer. Because of their property of estimating k_G values larger than the k_G obtained by the other approaches (for most of the Sc_G in the range of interest), they can also constitute conservative choices in the assessment of atmospheric emissions in WWTPs. In such context, they have to be used together with an appropriate parametrisation of the boundary layer thickness over the studied surface; Equation (3.1) is presented as a preliminary option, but additional studies on the evolution of the mass transfer boundary layer, for a broader range of u_* , X and Sc_G , are necessary, so as to confirm or adapt this equation.
- Equation (3.2) generally produces the lowest values of k_G ; thus, it may not be the more conservative approach for impact assessment; nonetheless, this equation was fitted by minimising the errors related to the compiled set of data and, therefore, this type of correlation should be further investigated.

3.2.2. Models for k_L

3.2.2.1. Analysis of the experimental k_L data set

Figure 3.5 shows the variation of k_L (normalised for the different compounds by multiplying by $Sc_L^{1/2}$) with u_* and U_{10} , discriminated according to the sources of the data set. Independently of the source, the data present the same overall behaviour of increasing k_L with u_* (or U_{10}), confirming that, under controlled conditions (where interferences such as surface films and bubbling are absent), wind friction constitutes a major forcing for the determination of liquid-side mass transfer. Nevertheless, even

under these controlled conditions, considerable scatter can be observed in the data. Although experimental errors might have naturally contributed for such scatter, it is likely that other factors also affected the behaviour of k_L . A general influence of the wind-wave fetch (X) can be identified, since the results obtained in smaller tanks (Liss, 1973; Cohen et al., 1978; and Mackay and Yeun, 1983) show systematically lower values of k_L compared to the ones from larger tanks (Wanninkhof and Bliven, 1991; Ocampo-Torres et al., 1994; and Rhee et al., 2007). The change of k_L with the wind-wave fetch can be explained by the relation between k_L and certain wave phenomena, in especial microscale breaking (see 2.3.2), which can vary with X .

It can be seen in Figure 3.5a that the data from each source can be reasonably described by linear fits with zero intercept, following the general form of Equation (3.3), where A is a dimensionless proportionality coefficient that changes depending on the source of the data. Table 3.6 summarises the values of A and other statistics regarding the fitted lines.

$$k_L = A u_* S c_L^{-1/2} \quad (3.3)$$

Table 3.6. Linear fit and proportionality coefficient A for each source of the data set.

Source	A	Standard error	99% confidence interval		R^2
			Lower limit	Upper limit	
Liss (1973)	1.332×10^{-3}	8.947×10^{-5}	1.063×10^{-3}	1.602×10^{-3}	0.84439
Cohen et al. (1978)	2.212×10^{-3}	7.788×10^{-5}	1.939×10^{-3}	2.484×10^{-3}	0.97686
Mackay and Yeun (1983)	3.077×10^{-3}	6.379×10^{-5}	2.900×10^{-3}	3.254×10^{-3}	0.90383
Wanninkhof and Bliven (1991)	4.420×10^{-3}	1.003×10^{-4}	4.114×10^{-3}	4.727×10^{-3}	0.99702
Ocampo-Torres et al. (1994)	4.221×10^{-3}	3.825×10^{-5}	4.111×10^{-3}	4.331×10^{-3}	0.98140
Rhee et al. (2007)	5.833×10^{-3}	1.234×10^{-4}	5.495×10^{-3}	6.170×10^{-3}	0.89522
Wanninkhof and Bliven (1991) and Ocampo-Torres et al. (1994)	4.310×10^{-3}	5.026×10^{-5}	4.172×10^{-3}	4.448×10^{-3}	0.99021

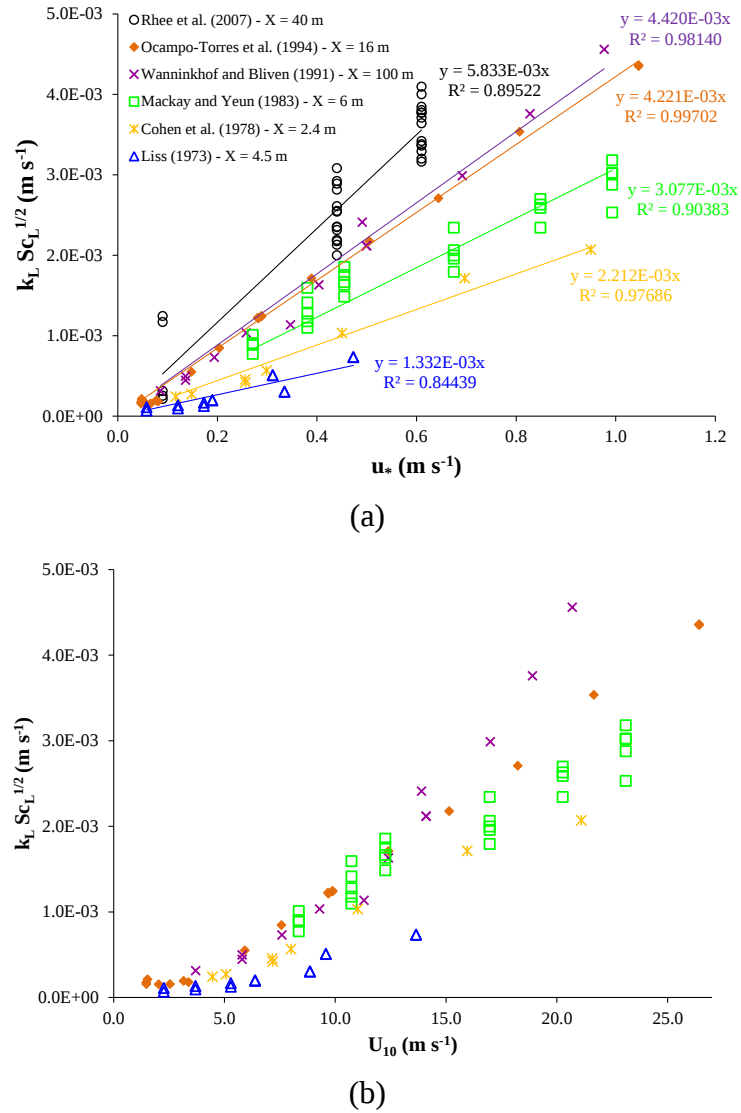


Figure 3.5. Variation of $k_L Sc_L^{1/2}$ with (a) u_* and (b) U_{10} . The sources of the data with their respective fetch are identified by the different symbols and colours (legend in (a)). Linear fits with zero intercept for the data of each source are also shown in (a) (equation colours matching the symbols for the respective source).

Except for the data of Liss (1973) and Rhee et al. (2007), a general pattern of A increasing with fetch is observed. The results of Liss (1973) will be discussed later in this session. Concerning the data of Rhee et al. (2007), two hypothesis are proposed to explain the relatively higher values of A :

- i. The data of Rhee et al. (2007) are free from bias, and there is a physical reason (likely related to the configuration of the wind-wave field) for the liquid-side mass transfer, averaged for the whole fetch, to reach higher values for water

surfaces with fetches of around 40 m and then decrease again for fetches of order 100 m.

- ii. The results of Rhee et al. (2007) are affected by systematic errors. Although the methodology described in the original paper is sound and no evident flaw could be identified, the occurrence of some systematic error cannot be totally discarded. In this sense, it is worth recalling that the calculation of k_L in their study was done by solving a mass balance of the mass of the chemical species simultaneously in the gas and liquid phases, differently from the other studies, which measured k_L more directly from simple decaying curves.

In case hypothesis (i) is true, the variation of the constant of proportionality A will be as represented in Figure 3.6a, for which the tentative quadratic curve shown in the figure fits considerably very well (excluding the data of Liss, 1973). The fitted curve indicates maximum A for a fetch of around 60 m. This hypothesis has to be further investigated in future experimental studies, since the occurrence of maximum liquid-side mass transfer for fetches of order 40 – 60 m would have important consequences for the modelling of emissions in WWTPs.

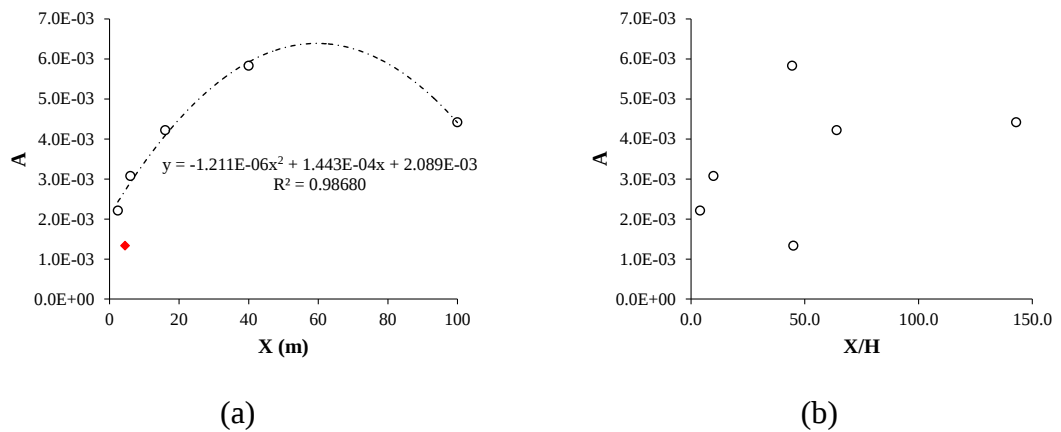


Figure 3.6. Variation of the proportionality coefficient A with (a) the fetch X and (b) the fetch-to-depth ratio X/H . In (a), the red diamond represents the data of Liss (1973).

On the other hand, if hypothesis (ii) is the actual case, the pattern of variation of A with the fetch, now excluding the results from Rhee et al. (2007) and Liss (1973), would be that A increases with X for fetches up to around 16 m and probably reaches a plateau for fetches between 16 and 100 m. The fact that the behaviour of k_L with u_* is similar for

surfaces with fetch of order 16 m and 100 m is indicated by the very close values of A for the data of Ocampo-Torres et al. (1994) and Wanninkhof and Bliven (1991), and better highlighted in Figure 3.7, where the linear fit with zero intercept for the data of Wanninkhof and Bliven (1991) and Ocampo-Torres et al. (1994) combined (Equation (3.4), discussed further in 3.2.2.3) is also plotted. Furthermore, note that the 99% confidence interval for A (Table 3.6) for the data of Wanninkhof and Bliven (1991) and Ocampo-Torres et al. (1994) combined (Equation (3.4)) encompasses the values of A for both Wanninkhof and Bliven (1991) and Ocampo-Torres et al. (1994). The alternate approach for the calculation of k_L investigated in the present work (item 3.2.2.3) builds on this hypothesis.

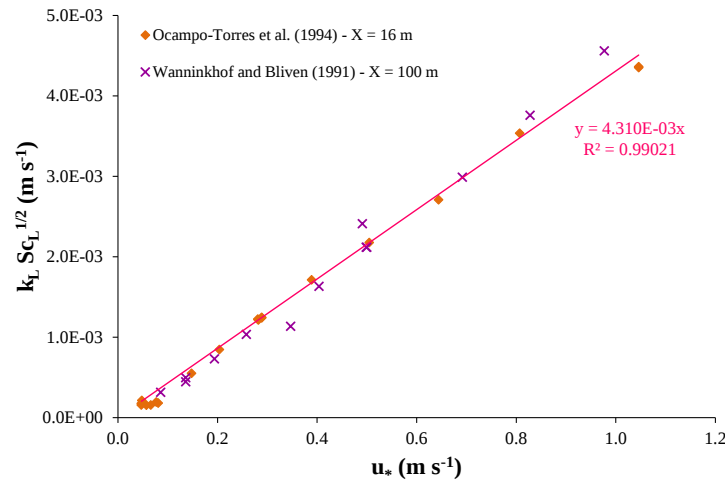


Figure 3.7. Variation of $k_L Sc_L^{1/2}$ with u_* and linear fit with zero intercept for the data of Wanninkhof and Bliven (1991) and Ocampo-Torres et al. (1994) combined (Equation (3.4)). The legend identifies the sources of the data with their respective fetch.

Independently of the hypothesis concerning the data of Rhee et al. (2007), it has to be noticed that the results of Liss (1973) do not follow the behaviour observed for the other experimental sources, presenting relatively low k_L for similar values of u_* . Besides the possibility of systematic errors (which cannot be discarded), this fact could be related to the very small water depth used in the experiments of Liss (1973) (Table 3.7). It can be hypothesised that, with this very small water depth, the patterns of circulation in the liquid phase and the wave field might have developed in a different way compared to the other experiments. It is also important to highlight that the behaviour of the variation of k_L with u_* was generally determined by the absolute values of the fetch X and the

depth H , but does not present any clear relation to the fetch-to-depth ratio X/H (Figure 3.6b), as adopted in the models of Springer et al. (1984) and Lunney et al. (1985).

Table 3.7. Geometric characteristics of the tanks used for the experiments whose results compose the k_L data set.

Source	Fetch X (m)	Depth H (m)	X/H
Liss (1973)	4.5	0.10	45.0
Cohen et al. (1978)	2.4	0.60	4.0
Mackay and Yeun (1983)	6	0.61	9.8
Wanninkhof and Bliven (1991)	100	0.70	142.9
Ocampo-Torres et al. (1994)	16	0.25	64.0
Rhee et al. (2007)	40	0.90	44.4

The analysis above indicates that the data from Liss (1973) and Rhee et al. (2007) might represent biased situations and, if this is the case, have to be treated separately, within their own particularities. In this context, for a better evaluation of the different k_L models (items 3.2.2.2 and 3.2.2.3), the comparison between model predictions and experimental results will consider three sets of data:

- The whole data set;
- Sub-set A: the whole data set for which U_{10} is available (i.e., excluding Rhee et al., 2007);
- Sub-set B: the whole data set except Liss et al. (1973) and Rhee et al. (2007).

3.2.2.2. Testing empirical models for k_L

The theoretical models of Deacon (1977) (Equation (2.17)), Münnich and Flothmann (1975) (Equation (2.19)) and Banerjee and McIntyre (2004) (Equation (2.20)), and three empirical models for k_L were tested against the experimental data set, following the procedure explained in 3.1.2.2. Figure 3.8 shows the comparison between the estimated

k_L and respective experimental k_L (normalised in the graphs by multiplying by $Sc_L^{1/2}$), and the relative errors (RMS, positive extreme and negative extreme) are summarised in Table 3.8, considering the whole data set and the sub-sets A (the whole data set for which U_{10} is available) and B (the whole data set except Liss et al. (1973) and Rhee et al. (2007)), for the theoretical models and for the empirical approaches of Mackay and Yeun (1983), Gostelow et al. (2001) and WATER9 (US EPA, 1994, 2001). Table 5 also contains the relative error statistics regarding the alternate approach (Equations (3.4) and (3.5)), which is discussed later (item 3.2.2.3).

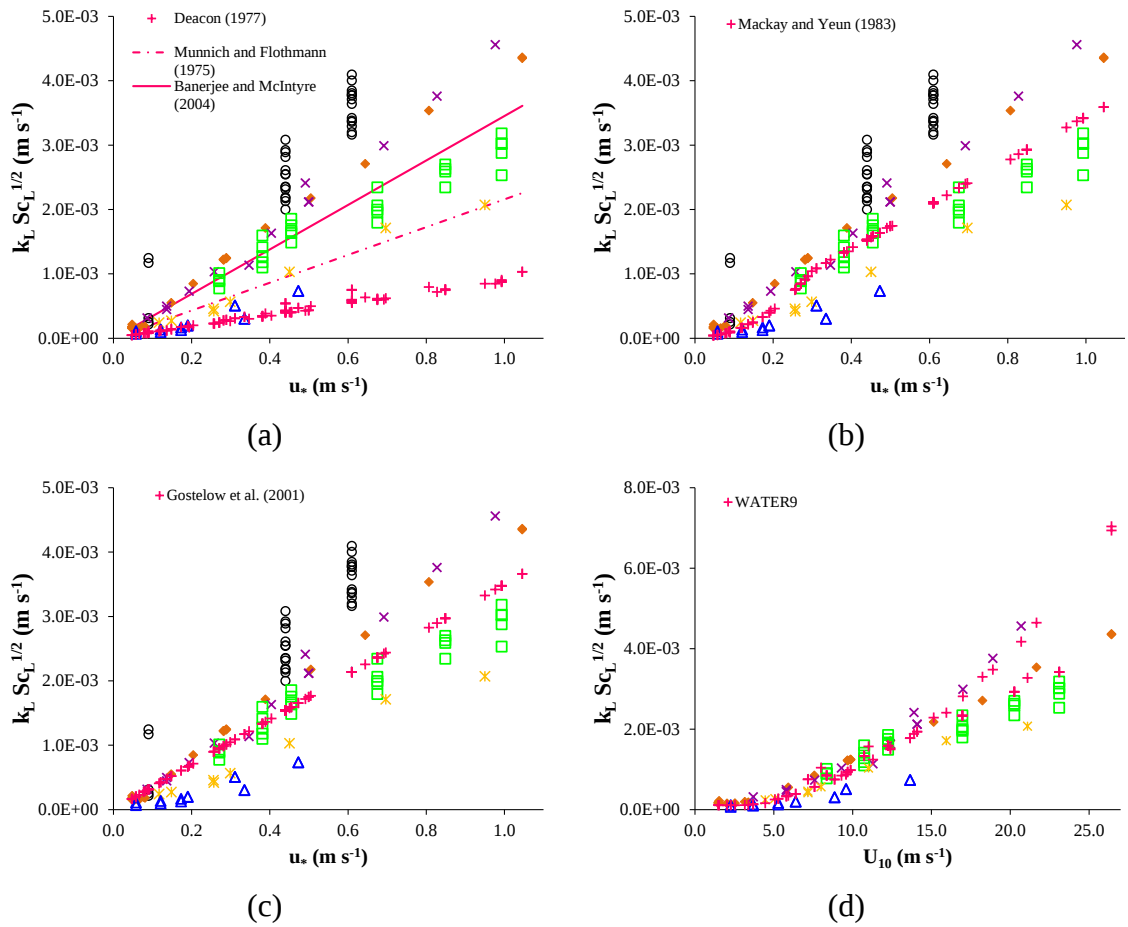


Figure 3.8. Experimental $k_L Sc_L^{1/2}$ from the compiled data set together with respective values estimated by: (a) theoretical models; (b) empirical correlations of Mackay and Yeun (1983); (c) empirical correlation of Gostelow et al. (2001); and (d) WATER9 approach. The sources of the data are identified the same way as in Figure 3.5a.

Table 3.8. Relative errors in k_L estimated by different models in relation to the experimental k_L from the compiled data set.

Model	Whole data set			Sub-set A			Sub-set B		
	RMS	Ext+ ^a	Ext- ^b	RMS	Ext+ ^a	Ext- ^b	RMS	Ext+ ^a	Ext- ^b
Deacon (1977)	71.1%	36.2%	-93.1%	66.4%	36.2%	-82.4%	71.9%	-	-82.4%
Münnich and Flothmann (1975)	58.2%	197.9%	-84.3%	56.9%	197.9%	-55.4%	37.4%	32.1%	-55.4%
Banerjee and McIntyre (2004)	87.1%	376.6%	-74.9%	99.6%	376.6%	-28.6%	32.1%	111.3%	-28.6%
Mackay and Yeun (1983)	62.4%	287.1%	-92.1%	67.6%	287.1%	-80.4%	36.8%	84.2%	-80.4%
Gostelow et al. (2001)	88.1%	380.6%	-74.7%	100.9%	380.6%	-28.7%	33.0%	114.2%	-28.7%
WATER9	-	-	-	49.1%	148.5%	-57.6%	30.5%	84.2%	-57.6%
Equations (3.4) and (3.5)	65.6%	292.4%	-68.8%	74.6%	292.4%	-24.1%	22.6%	94.2%	-24.1%

^a Ext+: positive extreme relative error.

^b Ext-: negative extreme relative error.

The data from Liss (1973) was generally overestimated by all models except the theoretical model of Deacon (1977) and the empirical model of Lunney et al. (1985) (results in Appendix B; in especial, see Figure B.1a). This might be due to the very shallow tank used in the experiments of Liss (1973), which would explain the conformity of Lunney's correlation, since Lunney et al. (1985) also made measurements with very shallow water and a short fetch to derive one of their correlations. On the other hand, all the models that could be tested against the data of Rhee et al. (2007) (i.e., the models that do not require U_{10}) tended to significantly underestimate their data, which in turn represent a situation of particularly high k_L , as discussed in 3.2.2.1.

Overall, none of the models was able to satisfactorily explain the behaviour and the scatter observed in the whole experimental data set. For sub-set B, which excludes the two suspected biased situations (results from Liss, 1973, and Rhee et al., 2007), the performance of most models was significantly better, normally falling in the expected range of uncertainty for liquid-gas mass transfer models (which typically varies from a factor of 2 to 10, according to Turney and Banerjee, 2013); however, even in this case, no model performed remarkably well. Among the models most commonly used in the context of estimating emissions in WWTPs (Mackay and Yeun, 1983, Gostelow et al., 2001, and WATER9), the WATER9 approach produced the best results, especially

considering only sub-set B. Of particular concern is the fact that the emission models of Mackay and Yeun (1983) and Gostelow et al. (2001) generally underestimated k_L for the situations with larger fetch (data from Wanninkhof and Bliven, 1991, and Ocampo-Torres et al., 1994; Figure 3.8b and c), which are probably the cases with most critical impact in terms of emissions in WWTPs, since larger emitting areas will be involved.

3.2.2.3. *Development of an alternate approach for estimating k_L*

Based on an analysis of the behaviour of the variation of k_L with u_* in the present data set (item 3.2.2.1), an alternate approach for the calculation of k_L in sub-set B is proposed here. As can be seen in Figure 3.7, the data for longer fetch ($X \geq 16$ m) in sub-set B (that is, the data of Wanninkhof and Bliven, 1991, and Ocampo-Torres et al., 1994) collapse well together, and, in 3.2.2.1, it is shown that these data can be satisfactorily described by Equation (3.4). Additionally, for fetches varying from 2.4 m to 16 m, the data in sub-set B can be modelled via Equation (3.5). Regarding Equation (3.5), it is worth mentioning that Vachon and Prairie (2013) also found a k_L correlation that depends on the logarithm of the fetch; however, their correlation was developed for lakes (most of them with much larger fetches) and do not perform well in the present data set (results in Appendix B). Therefore, the approach devised here consists in the use of Equation (3.4), for $X \geq 16$ m, and Equation (3.5), for $2.4 \text{ m} \leq X < 16 \text{ m}$. In the equations, k_L and u_* are in m s^{-1} , and X is in m. The performance of this new, alternate approach in estimating k_L is depicted in Figure 3.9 and indicated by the relative errors (RMS, positive extreme and negative extreme) reported in Table 3.8.

$$k_L = 4.31 \times 10^{-3} u_* S c_L^{-1/2} \quad (3.4)$$

$$k_L = (1.191 + 2.551 \log_{10} X) \times 10^{-3} u_* S c_L^{-1/2} \quad (3.5)$$

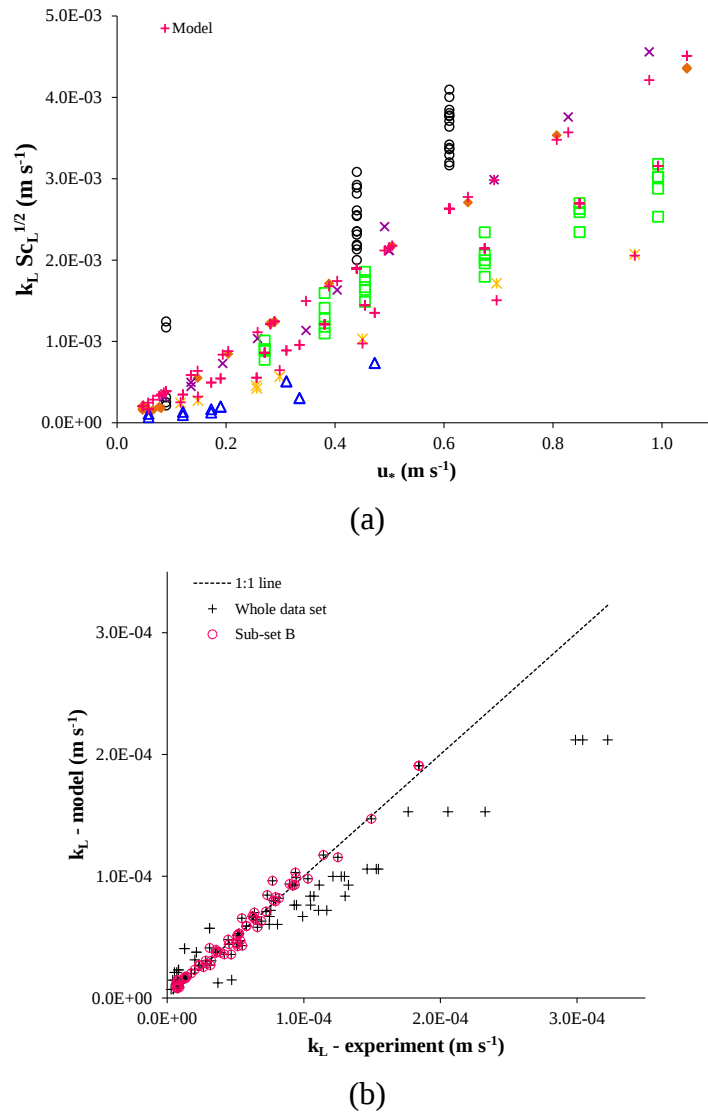


Figure 3.9. Performance of the alternate approach to model k_L : (a) variation of the experimental $k_L Sc_L^{1/2}$ from the compiled data set together with respective values estimated by the model; (b) comparison between empirical and modelled k_L . The sources of the data are identified in (a) the same way as in Figure 3.5a. The legend in (b) indicates the k_L in the whole data set and in sub-set B.

The alternate approach does not describe well the data from Rhee et al. (2007) and, especially, Liss et al. (1973). The results of Liss et al. (1973) are probably representative only of situations of short fetch and extremely shallow water (10 cm deep), which is not a typical situation in WWTPs; for such very shallow depths, the model of Lunney et al. (1985) seems more appropriate, as discussed before. On the other hand, if the data of Rhee et al. (2007) is not affected by systematic errors, which is not presently clear, and the values of k_L are actually higher for tanks with fetch of around 40 – 60 m (see further hypothesis in 3.2.2.1), this would have important consequences for the modelling of emissions in WWTPs. Thus, more studies are desired to clarify the behaviour of k_L for

larger fetches, especially in the range from 40 to 60 m, and to adapt the models, if necessary.

It can be seen that, for sub-set B, the alternate approach generates the best results among all the models, and is particularly accurate for longer fetches (Equation (3.4)). From a fluid dynamics perspective, having u_* as a input variable is more robust than straightforward functions of U_{10} , since u_* has a more direct relation to the phenomena that determine liquid-side mass transfer in passive surfaces (discussion in 2.3.2). Nevertheless, because u_* is not directly measured in the typical situations of use of emission models, an appropriate parametrisation for u_* is necessary, which is explored in Chapters 4 and 5.

4. STUDY OF THE WIND FRICTION PARAMETRISATION USED IN EMISSION MODELS

Given the importance of the friction velocity (u_*) in the calculation of the mass transfer coefficients (highlighted in the literature review and, especially, in Chapter 3), the aims of this chapter are:

- to test the wind friction parametrisations conventionally used to estimate u_* in the context of liquid-gas mass transfer models, against a compilation of experimental data representing liquid surfaces with size and wind conditions similar of those of tanks in WWTPs;
- to develop alternative approaches to parametrise u_* , based on the analysis of the compiled data set;
- and to fit correlations for determining the peak frequency of the wave spectrum in small bodies of water, which is necessary for the application of the proposed parametrisation of u_* .

4.1. Methodology

4.1.1. Compilation of the u_* data set

The data set used in present analysis is constituted by the experimental results from van Haselma et al. (1989), Caulliez et al. (2008) and Grare et al. (2013). Those authors report measurements of the wind stress over liquid surfaces in the presence of wind-generated waves, with fetch size and wind speed ranges comparable to the ones encountered in WWTPs. Van Haselma et al. (1989) performed their experiments at the Delft wind-wave flume, in the context of the VIERS-1 Project, with fetches varying from 25 m to 100 m. The results from Caulliez et al. (2008) and Grare et al. (2013) were obtained at the Institut de Recherche sur les Phénomènes Hors Equilibre (IRPHE)

Luminy wind-wave tank, with fetches ranging from 3.15 m to 28 m. Only data regarding pure wind waves (without mechanically generated waves) were included in the present analysis. For all the cases, the waves were propagating in deep-water regime, except for the highest wind speeds at fetch 100 m, for which the waves can be expected to be nominally at the borderline between deep-water and transitional regimes. As reference wind speed, the values of U_{10} originally reported by the experimental works (which, in turn, were extrapolated based on their measured u_* and z_0) were adopted. Neutral or approximately neutral buoyancy in the air flow can be assumed for these results. As mentioned in Chapter 2, it is important to notice that the cases with non-neutral atmospheric conditions are also relevant, and it is greatly desirable that future experimental work gathers data for such cases.

4.1.2. Evaluation of conventional wind friction parametrisations

The following “conventional” wind friction parametrisations (reviewed in 2.4.2) were evaluated: the empirical correlations of Smith (1980), Wu (1980, 1982) and Csanady (1997) (respectively, Equations (2.31), (2.32) and (2.33), Table 2.4), which were derived based on data for the ocean; and Charnock’s relation (Equation (2.36)). As mentioned before, Smith’s (1980) correlation is the most commonly used as input to mass transfer models and is frequently recommended in guides for modelling air emissions from passive surfaces (Gostelow et al., 2001; ENVIROMEGA, 2003; US EPA, 1994, 2001), whilst the data set used to derive Wu’s (1980, 1982) correlation is associated with developed wind seas (Janssen, 1991), and the approach used by Csanady (1997) constitutes an interesting case for comparison. On the other hand, Charnock’s relation was developed based on a dimensional argument and is favoured in some contexts (see, for example, Jacobson, 1999).

Estimates of u_* resulting from the empirical correlations and Charnock’s relation are tested against the experimental data set (described in the previous item, 4.1.1), having the values of U_{10} as the single input.

4.1.3. Development of alternative approaches for parametrising u_*

Based on the data set described in 4.1.1, alternative approaches to parametrise u_* are developed and analysed. The first alternative approach is to make use of a result obtained by Caulliez et al. (2008), who were able to correlate, at fetch 26 m, the aerodynamic roughness Reynolds number $z_0^+ = z_0 u_* / \nu$ with two distinct wave parameters, the significant wave steepness ak_s and the inverse wave age (also called “wind forcing”) u_*/c_p , obtaining, respectively, the power law dependencies $z_0^+ \propto (ak_s)^{8.1}$ and $z_0^+ \propto (u_*/c_p)^{4.0}$. Those authors did not report the constants of proportionality, since their theoretical discussion was on the expected relation between the two exponents: the exponent of ak_s was predicted to be the double of u_*/c_p exponent, as verified. We performed the same curve-fitting to their 26 m fetch data, yielding Equations (4.1) and (4.2).

$$z_0^+ = 6.724 \times 10^4 (ak_s)^{7.8} \quad (4.1)$$

$$z_0^+ = 2.316 \times 10^2 (u_*/c_p)^{3.9} \quad (4.2)$$

To fit Equation (4.2), the lowest wind speed, corresponding to $U_{10} = 2.69 \text{ m s}^{-1}$ (which did not conform with the remaining points, as also indicated by Caulliez et al., 2008), was not considered. The power law forms fit substantially well to the analysed data, and exponents very similar to those reported by Caulliez et al. (2008) were found, also following the predicted relation of one being the double of the other. The ability of such correlations to estimate z_0^+ and their adaptation so as to be used in a practical parametrisation of u_* are analysed in 4.2.3.

Inspired by the good results produced by the use of wave-related parametrisations, a second, final alternative approach is developed and analysed in item 4.2.4.

4.1.4. Fitting correlations for the peak wave frequency

In order to complement the evaluation of the wind friction parametrisations, it is convenient (and necessary, for the application of the final, Combined Approach) to have a preliminary description of the wave field (at least, an estimate of the peak wave frequency f_p) in the passive liquid surfaces for which u_* is to be estimated. As discussed in 2.4.1.2, there are simple correlation forms to parametrise f_p as a function of the fetch X and some scaling wind velocity, namely, the parametrisation forms proposed by Lamont-Smith and Waseda (2008) (denoted here as LS&W2008 parametrisation form) and Hasselmann et al. (1973) (denoted here as JONSWAP parametrisation form). However, as explained in 2.4.1.2, Lamont-Smith and Waseda (2008) do not report the constant of proportionality, whereas the available values for the constant in the JONSWAP form come from data measured in the ocean.

Therefore, before proceeding with the evaluation and development of the parametrisations of u_* , we fit these two f_p correlation forms using the wave measurements of Jähne and Riemer (1990) (herein after referred as VIERS-1 Project, referring to the broader project in which the investigation was included), Caulliez et al. (2008) and Grare et al. (2013), which is described in 4.2.1. These experimental results were obtained in wind-wave tanks with fetch size and wind speed ranges comparable to those normally found in WWTPs. From the work of Grare et al. (2013), only data regarding pure wind waves (without mechanically generated waves) were included in the present analysis.

4.2. Results and discussion

4.2.1. Fitting correlations for the peak wave frequency

A summary of the adjusted equations is presented in Table 4.1. Figure 4.1a and b show the dimensional values of f_p plotted against $(u_*^{1.25}X)^{-0.43}$ and $(U_{10}^{1.25}X)^{-0.43}$, respectively. Figure 4.1c presents the plot of the non-dimensional peak frequency $\hat{f}_p = f_p u_*/g$ against the power of the non-dimensional fetch $(Xg/u_*^2)^{-0.33}$. For f_p lower than 4 Hz, a straight line fits well to the data, as shown in Figure 4.1a, b and c. Figure 4.1d shows that all parametrisation forms produce fairly good estimates of f_p , within a maximum relative error generally of the order 20%; the RMS relative errors were 11.0%, 8.3% and 11.7%, respectively, for LS&W2008 form with u_* , LS&W2008 form with U_{10} and JONSWAP form with u_* . This indicates that both the LS&W2008 and the JONSWAP parametrisation forms are suitable for modelling the wave peak frequency for the range of wind speed and fetch considered (Table 2.3), as long as f_p is lower than 4 Hz, supporting the propositions made by Lamont-Smith and Waseda (2008) and Hasselmann et al. (1973).

Table 4.1. JONSWAP and LS&W2008 parametrisation forms fitted to experimental data from Jähne and Riemer (1990) (VIERS-1 Project), Caulliez et al. (2008) and Grare et al. (2013), for $f_p < 4$ Hz and fetch and velocity scale ranges shown in Table 2.3.

Parametrisation form	Velocity scale	Equation		A^a	b	c	RMS relative error
JONSWAP	u_*	$f_p u_*/g = A(Xg/u_*^2)^c$	(4.3a)	0.91	–	-0.33	11.0%
LS&W2008	U_{10}	$f_p = A(U_{10}^b X)^c$	(4.3b)	27.07	1.25	-0.43	8.3%
LS&W2008	u_*	$f_p = A(u_*^b X)^c$	(4.3c)	4.40	1.25	-0.43	11.7%

^a Adjusted coefficient.

As seen in Table 4.2, if u_* is used as scaling velocity, the values found in other studies for the constant A in the JONSWAP parametrisation form $\hat{f}_p = A \hat{X}^{-0.33}$ are close to the values found in the present work, in which the parametrisation was tested against the data sets from Jähne and Riemer (1990), Caulliez et al. (2008) and Grare et al. (2013), with few discrepancies. On the other hand, it is important to notice that the original

JONSWAP proportionality constant $A = 3.5$, with U_{10} as reference velocity, does not fit properly to the present data set. Thus, it can be concluded that the JONSWAP parametrisation should be used only with u_* as scaling velocity for the range of fetches and wind speeds analysed here.

Table 4.2. Values of the constant A for the JONSWAP parametrisation form $\hat{f}_p = A \hat{X}^c$.

Reference	Experimental data set	Velocity scale	A	c
Hasselman et al. (1973)	JONSWAP	U_{10}	3.5	-0.33
Mituyasu and Honda (1974)	Mituyasu and Honda (1974)	u_*	1.00	-0.33
Snoeij et al. (1993)	JONSWAP	u_*	1.11	-0.33
Snoeij et al. (1993)	VIERS-1 Project	u_*	0.73	-0.325 ^a
Present work	Jähne and Riemer (1990) (VIERS-1 Project), Caulliez et al. (2008) and Grare et al. (2013)	u_*	0.91	-0.33

^a The exponent adjusted by Snoeij et al. (1993) was found very close to the one originally associated to JONSWAP form.

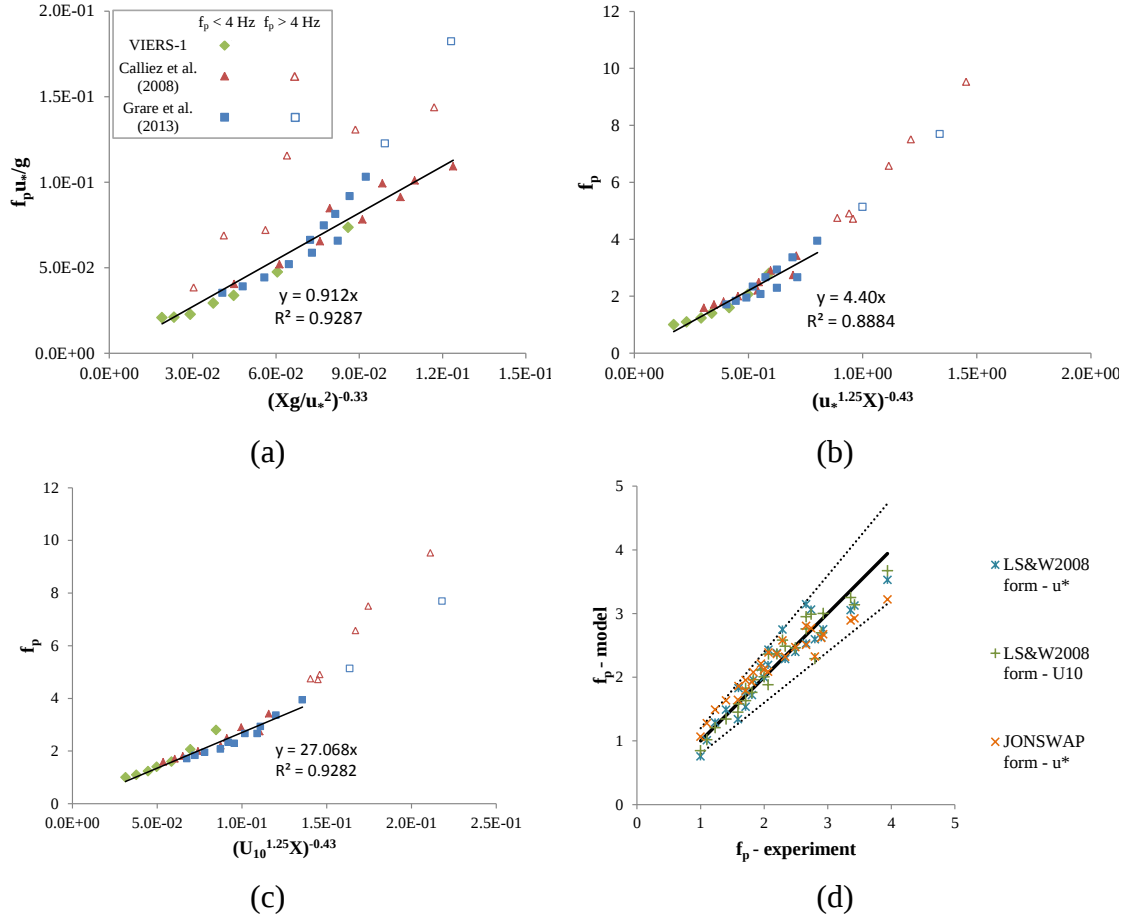


Figure 4.1. Curve-fitting of parametrisations for wave peak frequency: (a) JONSWAP form using u_* ; (b) LS&W2008 form using u_* ; (c) LS&W2008 form using U_{10} ; and (d) comparison of the f_p estimated by the three models against the experimental data set. Symbols in (a), (b) and (c) identify the source of the data (legend in (a)). Curves were fit only to frequencies lower than 4 Hz; higher frequencies are indicated by empty symbols in (a), (b) and (c). The thick solid line in (d) is the 1:1 line, and the dotted lines delimit the 20% relative error range.

4.2.2. Evaluation of conventional wind friction parametrisations

4.2.2.1. Empirically-derived correlations for oceans

The comparison among the results estimated by the three empirical correlations for oceans discussed before, Smith (1980), Wu (1980, 1982) and Csanady (1997), and against experimental data from wind-wave tanks is shown in Figure 4.2 and their performance in predicting u_* is presented in Table 4.3. In general, the three correlations tend to overestimate the friction velocity at the small fetches analysed. The one by

Smith (1980) presented the best performance among the three, with RMS and maximum errors of 13.5% and 36.6%, respectively.

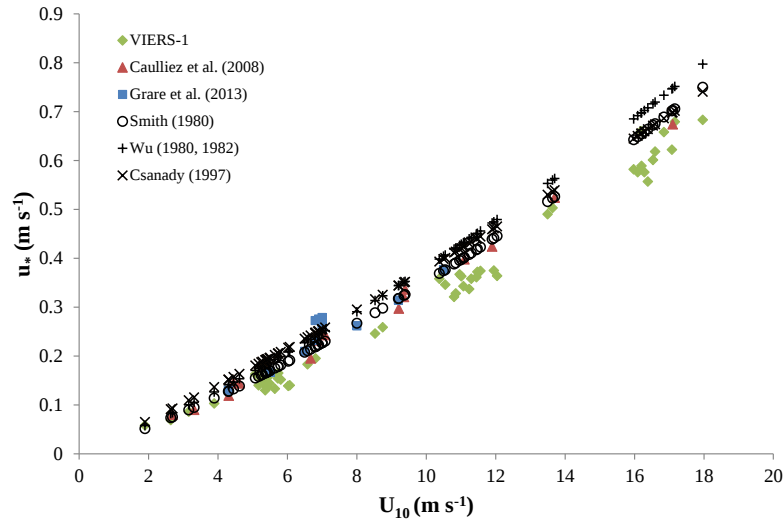


Figure 4.2. Comparison of the friction velocities calculated via empirical correlations derived for oceans against experimental results from wind-wave tanks. Full symbols identify the source of the data (legend in the figure). The u_* values calculated via the empirical correlations of Smith (1980), Wu (1980, 1982) and Csanady (1997) are represented as hollow circles, plus signs, and “×” signs, respectively.

Table 4.3. Performance of the empirical correlations derived for oceans in estimating the friction velocity for the experimental data set.

Correlation	Relative errors in u_*		
	RMS	Maximum	0.95-percentile
Smith (1980)	13.5%	36.6%	22.9%
Wu (1980, 1982)	20.5%	49.9%	35.3%
Csanady (1997)	22.3%	56.2%	42.5%

The observed tendency to overestimate u_* is probably due to the fact that the enhancement in momentum transfer due to wind-wave interactions is expected to be larger for the wave conditions in the ocean than for very short fetches (very young wind-wave field) (Nordeng, 1991; Donelan et al., 1993; Janssen, 1994, 2004; Caulliez et al., 2008). Results produced by Wu’s (1980, 1982) correlation are always larger (thus, more overestimated) than the corresponding ones by Smith (1980), which is explained by the fact that these two expressions have the same form, but Wu’s correlation has larger coefficients (Table 2.3). As mentioned before, in the wind speed

range from 7 m s^{-1} to 50 m s^{-1} , estimates by Wu's correlation agree closely with results from Charnock's relation taking $a = 0.0185$ (for $\kappa = 0.4$), which, in turn, is regarded as representative of mature wind seas (Janssen, 1991). For very young wind-wave fields, as the ones observed at the short fetches considered herein, the representative Charnock coefficient a is expected to be smaller (Nordeng, 1991; Janssen, 1994, 2004; Caulliez et al., 2008). As will be discussed next (4.2.2.1), the analysed experimental data can be reasonably described by the Charnock's relation with coefficient $a = 0.010$ (for $\kappa = 0.4$), which produces u_* estimates only slightly smaller than the ones by Smith (1980), for wind speeds between 7 m s^{-1} and 15 m s^{-1} . The correlation by Csanady (1997) presents a different behaviour compared to the other two, but also produces overestimated values of u_* .

4.2.2.2. Charnock's relation

The iterative solution of Equation (2.36), which is based on the Charnock's relation, taking $a = 0.010$ (for $\kappa = 0.4$), conforms in a reasonable manner to the present compilation of experimental results for wind-wave tanks, especially for fetches of size 28 m or less, as seen in Figure 4.3. The RMS relative error for the whole domain was 14.0%, with maximum relative error of 39.2% and 0.95-percentile relative error 25.2% (for 95% of the data points, the relative error was less than 25.2%).

The value $a = 0.010$ is similar to those reported by Wu (1968) ($a = 0.0112$, for $\kappa = 0.4$), Smith (1980) ($a = 0.01$, for $\kappa = 0.41$) and Mackay and Yeun (1983) ($a = 0.0093$, for $\kappa = 0.4$). Wu (1968) and Mackay and Yeun (1983) performed their experiments at small wind-wave tanks, with wind speeds in the range of the ones considered here, which probably explains the similarity of the a values; the reason why the oceanic data evaluated by Smith (1980) produced a a value in the range of the ones typical of short fetches is not clear. It is also interesting that the Charnock coefficient obtained in the present analysis is very close to the value $\hat{a} = 0.0110$ suggested by Janssen (1991) for the constant proposed to parametrise the “background” aerodynamic roughness due to gravity-capillary waves ($z_{0,gc}$) via a Charnock-type relation of the form $z_{0,gc} = \hat{a}u_*^2/g$ (see item 2.4.2.2). Assuming that the parametrisation by Janssen (1991, 1994, 2004), Equation (2.39), is able to describe the general features of the

aerodynamic roughness in the sea, such a proximity between a and $\hat{a}$ for the present case may be a reflection of the fact that, for small liquid surfaces, the wave spectra are mainly composed by very short gravity waves and gravity-capillary waves (see item 2.4.1.2), which would constitute only the “background” aerodynamic roughness in the oceanic case.

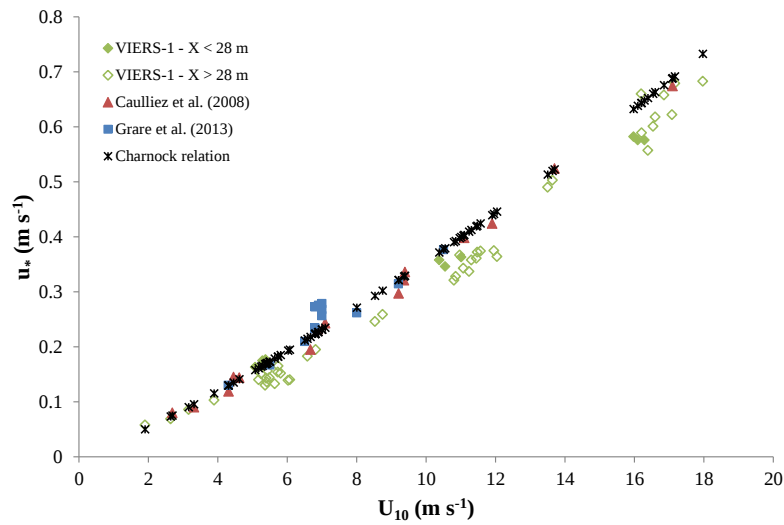


Figure 4.3. Comparison of the friction velocities estimated via Charnock’s relation with $a = 0.010$ (for $\kappa = 0.4$) against experimental results from wind-wave tanks. The source of the data is identified in the legend. Hollow symbols indicate fetches larger than 28 m. The u_* values calculated via Charnock’s relation are represented as “*”.

Given the similar results produced by the Charnock’s relation with $a = 0.010$ (for $\kappa = 0.4$) and by the empirical correlation found by Smith (1980), for wind speeds between 6 m s^{-1} to 15 m s^{-1} , it is important to compare the advantages and disadvantages of each one of these approaches. The main advantage of using Smith’s correlation is its simplicity, since, differently from the Charnock’s relation, it does not require solution via iterations. On the other hand, the Charnock’s relation performed slightly better for higher wind speeds. Moreover, it is not bounded to the use of U_{10} as reference wind speed, which is the major limitation of Smith’s correlation (adapting this correlation to some arbitrarily chosen reference height would also require iterations). Such a feature allows the simple application of the approach based on Charnock’s relation with any reference height, which may be required in more detailed studies of the wind boundary layer over liquid surfaces (e.g., Smith, 1988).

4.2.3. Evaluation of an approach based on wave-related parameters

As explained in 4.1.3, Equations (4.1) and (4.2), which correlate $z_0^+ = z_0 u_* / \nu$ with two distinct wave parameters, ak_s and u_*/c_p , were obtained by performing the same curve-fitting done by Caulliez et al. (2008) to their 26 m fetch data. The ability of such correlations to estimate z_0^+ was tested against the whole data set reported by Caulliez et al. (2008). At the fetch 26 m and in the range of wind speeds for which they were fit, Equations (4.1) and (4.2) predicted z_0^+ with RMS relative errors of 37% and 16%, respectively. This performance can be considered good for practical purposes, since u_* relates to z_0^+ in a logarithmic scale (as will be discussed below), and also because the errors in the experimental determination of z_0 are normally large. Outside the range of fetch and wind speeds used for fitting the correlations, the errors in predicting z_0^+ were larger, especially for Equation (4.2).

Having an estimated value for z_0^+ , obtained by means of one of the correlations above, and the wind speed U_Z measured at a height Z , the friction velocity can be calculated via iterations with Equation (2.30): starting with a guess for u_* , one can derive z_0 from z_0^+ ; in sequence, use z_0 , Z and U_Z to calculate a new value for u_* from Equation (2.30); this new u_* is then used again to obtain a new z_0 , and the process is repeated until convergence for u_* is reached. In Figure 4.4, the values of u_* calculated by this process, using the z_0^+ estimated via Equations (4.1) and (4.2) applied to the data from Caulliez et al. (2008), are compared to their respective experimental u_* . At the fetch 26 m and in the range of wind speeds for which the correlations were fit, the model produced very good estimates for u_* , with root mean square relative errors of 4% and 3% and maximum errors of the order 6% and 5%, for the modelling with Equations (4.1) and (4.2), respectively. The calculation based on Equation (4.1) predicted u_* reasonably well also at the fetch 13 m, for U_{10} greater than 4 m s^{-1} , with maximum error of 8.6%. It is clear that relative differences between modelled and experimental values are smaller in the estimation of u_* than in the respective prediction of z_0^+ ; this is explained by the fact that z_0 relates to u_* via the logarithmic scale in Equation (2.30), which buffers the response of u_* to differences in z_0^+ . About the relatively good suitability of ak_s as a parameter to calculate the wind friction, it is interesting to note that Grare et al. (2013)

found the wave steepness (in their case, the average steepness) to be correlated to the wind energy input to the waves and the turbulent attenuation of wave energy.

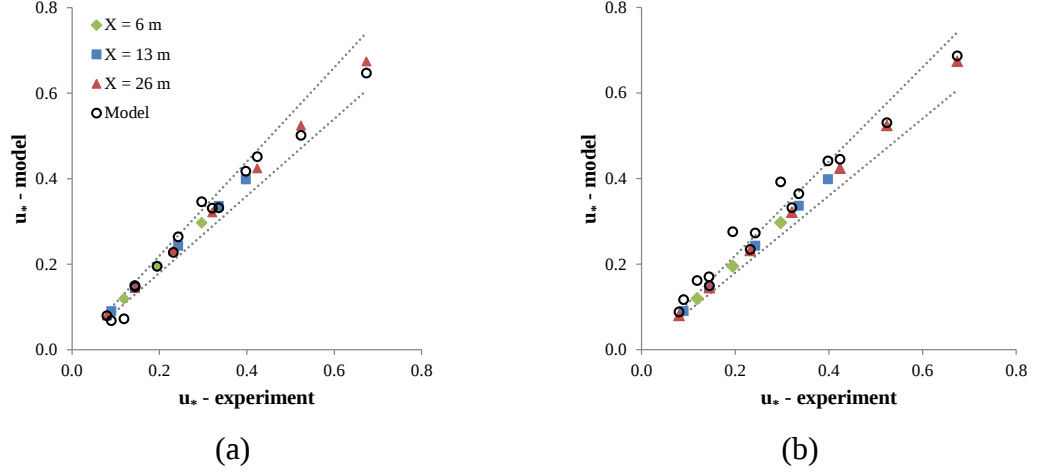


Figure 4.4. Comparison of u_* (m s⁻¹) modelled using z_0^+ estimated by (a) Equation (4.1) and (b) Equation (4.2) against the experimental values from Caulliez et al. (2008). The open circles represent the modelled results; the full symbols indicate experimental results at fetches of 6 m, 13 m and 26 m (legend shown in (a)). The dotted lines delimit the 10% relative error range.

The above-described approach to estimate u_* based on correlations between z_0^+ and wave variables requires the knowledge of the values of either ak_s or c_p . However, these are normally not known in most of the situations of interest for the present work, i.e., the estimation of u_* with the purpose of modelling atmospheric emissions from passive liquid surfaces in WWTPs. To overcome such a hindrance, one may attempt to devise correlations for ak_s and/or c_p as a function of other available variables. Performing a curve-fitting to the experimental results from Caulliez et al. (2008), we obtained correlations for ak_s as a function of the non-dimensional fetch $\hat{X} = Xg/U^2$ (being U a scaling wind velocity), Equation (4.4).

$$ak_s = A \left(\frac{Xg}{U^2} \right)^m \quad (4.4)$$

The values of the best-fit coefficients, A and m , for the scaling velocities $U = u_*$ and $U = U_{10}$, are presented in Table 4.4, together with their respective performance in estimating ak_s . To fit Equation (4.4), the cases with f_p higher than 4 Hz were not considered, since they did not conform to a power law of the non-dimensional fetch.

The remaining data are described well by Equation (4.4), as indicated in Table 4.4 and Figure 4.5. Correlations for c_p as the product of powers of the non-dimensional fetch and of the fetch Reynolds number were also tested, but their performance, although not poor, was not as good as Equation (4.4); for this reason, the correlations involving ak_s will be used in the sequence of the present analysis.

Table 4.4. Coefficients for Equation (4.4) fit to Caulliez et al. (2008) data.

Scaling velocity	Coefficients	R^2	Estimated v.s. experimental ak_s^a	
			RMS relative error	Maximum relative error
u_*	$A = 7.562 \times 10^{-1}$ $m = -0.127$	0.89	4.5%	9.8%
U_{10}	$A = 3.226 \times 10^{-1}$ $m = -0.142$	0.88	4.3%	8.6%

^a Comparison only for the cases with $f_p < 4$ Hz.

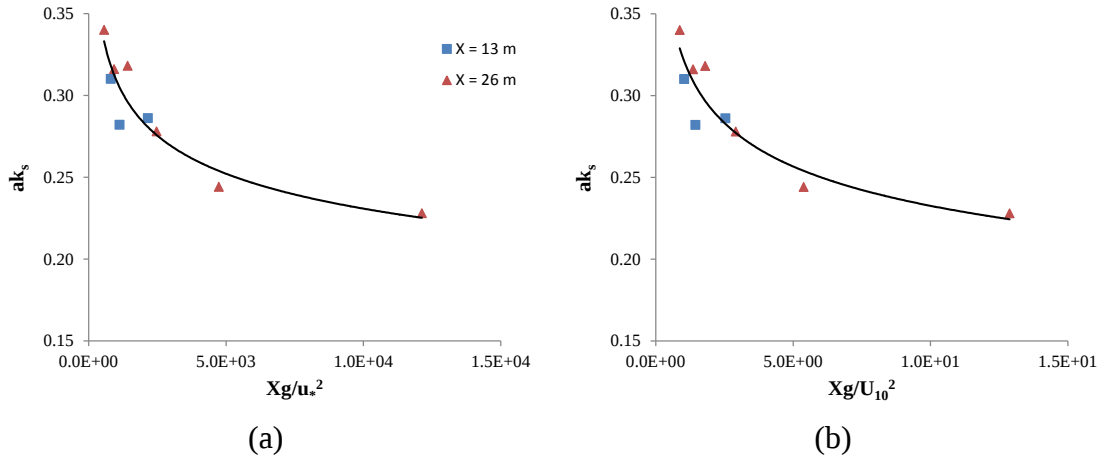


Figure 4.5. Significant wave steepness ak_s versus (a) Xg/u_*^2 and (b) Xg/U_{10}^2 . Results for the fetches of 13 m and 26 m are indicated according to the legend in (a). The solid lines represent the power law fits (a) $ak_s = 7.562 \times 10^{-1}(Xg/u_*^2)^{-0.127}$ and (b) $ak_s = 3.226 \times 10^{-1}(Xg/U_{10}^2)^{-0.142}$.

The correlation for ak_s as a function of Xg/u_*^2 or Xg/U_{10}^2 can be used in combination with Equation (4.1), in order to obtain u_* having as input the fetch X and the wind speed U_Z measured at a height Z , through the following steps: (i) with X and a first guess of u_* (or the value of U_{10} , if the reference height Z is 10 m), obtain the non-dimensional fetch Xg/u_*^2 (or Xg/U_{10}^2); (ii) use Equation (4.4), with appropriate coefficients (Table 4.4) to estimate ak_s ; (iii) apply Equation (4.1) to estimate z_0^+ and then obtain the corresponding z_0 ; (iv) with z_0 , Z and U_Z , calculate a new value for u_*

from Equation (2.30); (v) check the convergence for u_* and repeat the process with the updated value of u_* until convergence is reached.

The iterative procedure described above, combining the use of Equation (4.4) to calculate ak_s as a function of Xg/u_*^2 or Xg/U_{10}^2 and Equation (4.1) to correlate ak_s to z_0^+ , thus obtaining u_* , was applied to the data set from van Haselma et al. (1989), Caulliez et al. (2008) and Grare et al. (2013), encompassing results for longer fetches and different wind velocities. For Equation (4.4), both scaling velocities, $U = u_*$ and $U = U_{10}$, were tested, with the coefficients from Table 4.4. Figure 4.6 presents the comparison between the results from this approach and the u_* values measured experimentally, plotted versus U_{10} . It is verified that the approach using the wave-related parameters is able to estimate generally well the values of u_* . Nonetheless, there are some clear cases for which the largest discrepancies between modelled and experimental u_* occur, which can be grouped in the following ranges:

- Range A: cases with the peak frequency of the wave spectra higher than 4 Hz; for this range, as stated before, Equation (4.4) does not apply.
- Range B: cases with wind speeds U_{10} from 5.3 m s^{-1} to 6.5 m s^{-1} ; in this region, most of the experimental u_* are less than the ones calculated even for a smooth surface (result not shown). Interestingly, examining data measured in the sea, Wu (1994) identifies that the sea reaches its smoothest state when wind speeds are around 5 m s^{-1} , and Caulliez et al. (2008) also mention an “ultrasmooth” condition, but for lower wind speeds. No satisfactory explanation for this phenomenon has been offered in the present context; however, Sirovich and Karlsson (1997) showed that protrusions randomly positioned on the floor of a channel were able to reduce the shear stress to values smaller than the ones observed in a smooth flow, and attributed this effect to a relative reduction in the occurrence of bursts and sweeps (which are major sources of aerodynamic drag at a smooth wall).

- Range C: cases with wind speeds U_{10} higher than 13 m s^{-1} at fetches larger than 50 m. Under such conditions, the approach treated here tends to underestimate u_* . This is probably due to the intensification of wave macroscale breaking with higher wind speeds and longer fetches, which interferes to some extent with the dependencies expressed by Equations (4.1) and (4.4). Those equations were derived based on results of the experiment of Caulliez et al. (2008), in which macroscale wave breaking was limited.

The part of the data that does not fall into one of the above ranges will be named Range D, hereinafter, for which the application of correlations using wave-related parameters is appropriate; those data points are represented by full diamonds, triangles and squares and by black hollow circles and plus signs in Figure 4.6. The performance of the combined use of Equation (4.4) and Equation (4.1) in modelling the friction velocity for the whole experimental data set and only for data inside Range D is shown in Table 4.5. For Range D, the parametrisation of u_* based on wave-related parameters results in the best estimates among the three approaches discussed so far (that is, in comparison to empirical correlations derived for oceans and Charnock's relation). Furthermore, this approach is able to capture some particular features of the experimental u_* versus U_{10} plot (for instance, the “plateau” when U_{10} is between 7 m s^{-1} and 9 m s^{-1}) which reflect the influence of the fetch on the wind drag. It is also remarkable that these correlations, which were derived using only data from Caulliez et al. (2008), conformed well to results from other two independent data sets (van Haselma et al., 1989, and Grare et al., 2013). Inspired by the good results produced by the use of wave-related parametrisations, we next explore the possibility of obtaining even more simplified correlations with comparable performance.

Table 4.5. Performance of the combined use of Equation (4.4) and Equation (4.1) in modelling the friction velocity for the experimental data set.

Velocity in Equation (4.4)	Relative errors in u_*					
	All data set			Range D only		
	RMS	Maximum	0.95-percentile	RMS	Maximum	0.95-percentile
u_*	15.5%	41.6%	33.7%	9.0%	19.3%	16.0%
U_{10}	14.1%	37.2%	32.1%	7.9%	17.4%	14.3%

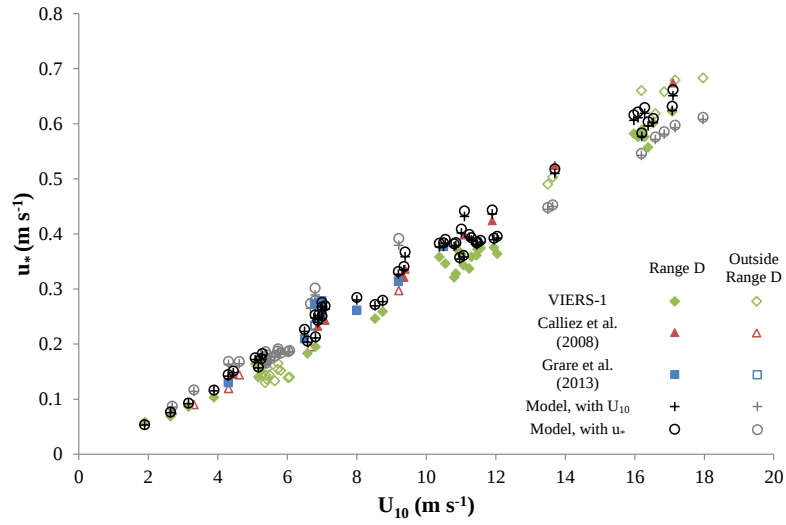


Figure 4.6. Comparison of the friction velocities estimated by the combined use of Equation (4.4) and Equation (4.1) against experimental results from wind-wave tanks. The source of the data is identified by the legend in the figure. The u_* values calculated by the combined use of Equation (4.4) and Equation (4.1) are indicated by hollow circles and plus signs, which identify, respectively, the scaling velocities $U = u_*$ and $U = U_{10}$. Points outside Range D are denoted by grey hollow circles and grey plus signs and by hollow diamonds, hollow triangles and hollow squares.

4.2.4. Development of a new alternative approach with simplified correlations

4.2.4.1. Correlations for Range D

The use of Equation (4.4) together with Equation (4.1) to obtain u_* can be simplified by condensing the two-step calculation as a single overall correlation between C_Z or z_0^+ and the non-dimensional fetch Xg/u_*^2 or Xg/U_{10}^2 . Using the experimental data set in Range D, Equations (4.5a,b) and (4.6a,b) can be derived.

$$C_{10} = 3.009 \times 10^{-3} \left(\frac{Xg}{u_*^2} \right)^{-0.121} \quad (4.5a)$$

$$C_{10} = 1.334 \times 10^{-3} \left(\frac{Xg}{U_{10}^2} \right)^{-0.127} \quad (4.5b)$$

and

$$z_0^+ = 9.469 \times 10^3 \left(\frac{Xg}{u_*^2} \right)^{-1.084} \quad (4.6a)$$

$$z_0^+ = 6.901 \left(\frac{Xg}{U_{10}^2} \right)^{-1.193} \quad (4.6b)$$

Equation (4.5b) is explicit for u_* ; the other three require iterative solution for the friction velocity. Figure 4.7 depicts the behaviour of u_* estimated by means of the Equations (4.5a,b) and (4.6a,b) versus U_{10} , plotted together with the experimental results for the same conditions of fetch and wind speed. The performance of the equations above in predicting u_* is shown in Table 4.6. Generally, all the four correlations produced similar results, being able to estimate u_* considerably well, especially for data in Range D. Similarly to when Equations (4.1) and (4.4) were used together, particular features of the experimental u_* versus U_{10} plot are also modelled by Equations (4.5a,b) and (4.6a,b), indicating that they are able to incorporate the influence of the fetch on the wind drag. In fact, Equations (4.5a,b) and (4.6a,b) performed, in general, even slightly better than Equations (4.1) and (4.4) used together, which may be explained because the use of a single correlation avoids the accumulation of errors that may occur if two equations are used in sequence.

Table 4.6. Performance of the simplified correlations in modelling the friction velocity for the experimental data set.

Equation	Relative errors in u_*					
	All data set			Range D only		
	RMS	Maximum	0.95-percentile	RMS	Maximum	0.95-percentile
(4.5a)	10.4%	27.2%	23.1%	6.8%	18.1%	15.6%
(4.5b)	10.7%	28.6%	22.7%	6.8%	16.7%	15.6%
(4.6a)	12.1%	34.3%	26.3%	6.1%	14.6%	13.1%
(4.6b)	11.8%	32.0%	26.4%	6.2%	15.0%	13.4%

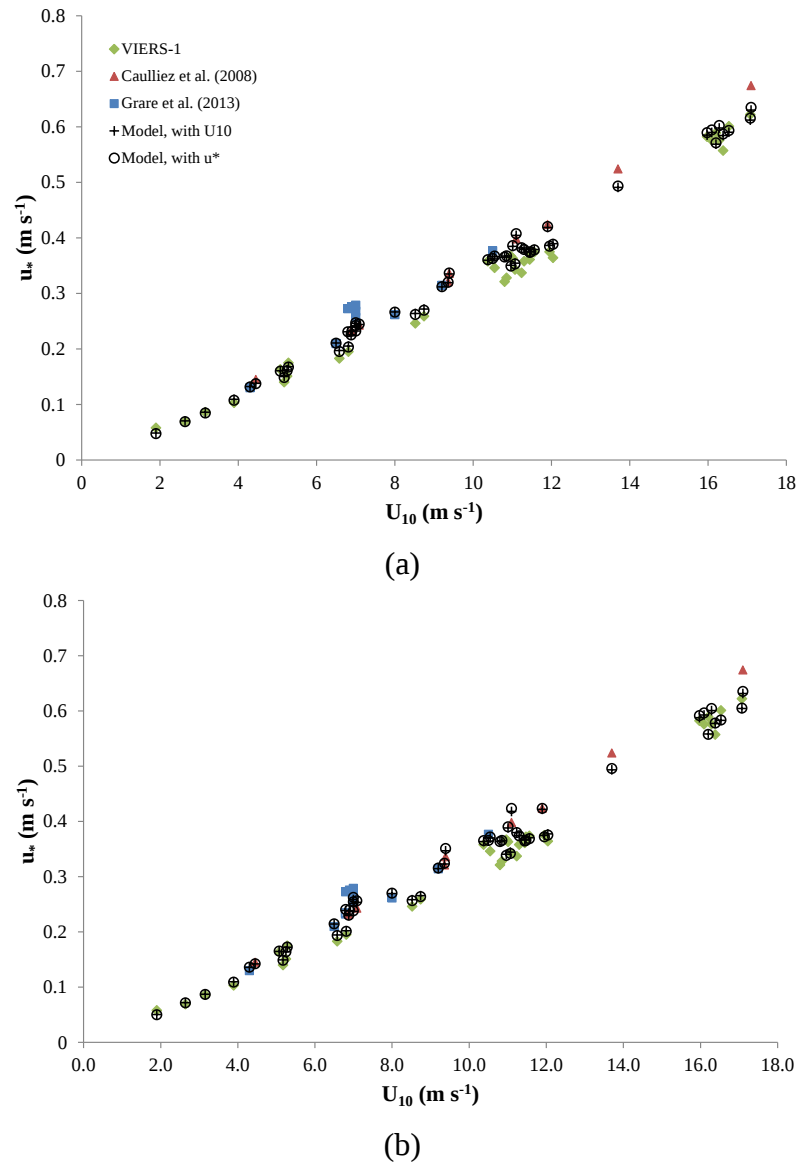


Figure 4.7. Comparison of the friction velocities estimated by (a) Equation (4.5a,b) and (b) equation (4.6a,b) against experimental results from wind-wave tanks, for cases in Range D. Legend is shown in (a); the u_* values calculated by the correlation equations are indicated by hollow circles and plus signs, which identify, respectively, the scaling velocities $U = u_*$ (Equations (4.5a) and (4.6a)) and $U = U_{10}$ (Equations (4.5b) and (4.6b)).

4.2.4.2. Addressing the remaining ranges

If an approach to estimate the wind friction at small liquid surfaces is to be proposed, it is desired that such an approach is able to treat the whole variety of situations of interest for emission modelling in WWTPs. Therefore, we tested if alternative approaches could be satisfactorily applied to Ranges A, B and C. Table 4.7 summarizes the suggested approaches, found to be the best compromise between simplicity and small relative

errors. The following correlations adjusted well in Range B (cases with $5.3 < U_{10} < 6.5 \text{ m s}^{-1}$):

$$C_{10} = 2.369 \times 10^{-3} \left(\frac{Xg}{U_{10}^2} \right)^{-0.416} \quad (4.7)$$

$$z_0^+ = 2.764 \times 10^9 \left(\frac{Xg}{u_*^2} \right)^{-2.471} \quad (4.8)$$

Table 4.7. Alternative approaches for Ranges A, B and C.

Range	Conditions	Suggested approach	Relative errors in u_* ^a	
			RMS	Maximum
A	$f_p > 4 \text{ Hz}$	Charnock's relation with $a = 0.010$ (for $\kappa = 0.4$)	7.2%	11.8%
B	$5.3 < U_{10} < 6.5 \text{ m s}^{-1}$ ^b	Equation (4.7) ^c	5.2%	11.8%
C	$U_{10} > 13 \text{ m s}^{-1}, X > 50 \text{ m}$	Charnock's relation with $a = 0.010$ (for $\kappa = 0.4$)	4.7%	7.3%

^a In the respective range (A, B or C).

^b Only fetches larger than 25 m were available for this condition; errors may be larger for smaller fetches.

^c Equation (4.7) was preferred to Equation (4.8) because of its simplicity.

4.2.4.3. Proposed approach

The discussion in this section points towards the proposal of a “Combined Approach”, which comprises different expressions, each one for a specific range of conditions, in order to parametrise the wind friction to be used for the modelling of atmospheric emissions at passive liquid surfaces in WWTPs. Based on the analysis in 4.2.4.1 and 4.2.4.2, a combined procedure to obtain u_* for a given fetch X is proposed, as explained below. It is important to notice that this will give a local friction velocity, which has to be integrated along the total fetch, as further studied in Chapter 5.

If U_{10} is to be used as reference wind speed, the calculation follows the sequence:

- First, check for cases with f_p higher than 4 Hz; use U_{10} and X in Equation (4.3b) (LS&W2008 form), to estimate f_p ; if $1.3f_p$ is higher than 4 Hz, apply Charnock's relation with $a = 0.010$ (for $\kappa = 0.4$) to calculate u_* . The factor 1.3 is introduced to

account for the possibility of error in the f_p estimate; on the other hand, it does not produce unnecessary inaccuracies in the estimates of u_* , since Charnock's relation also adjusts well for peak frequencies slightly lower than 4 Hz.

- ii. Else, if U_{10} is between 5.3 m s^{-1} and 6.5 m s^{-1} , use Equation (4.7) to calculate C_{10} and, then, estimate u_* .
- iii. Else, if the fetch is larger than 50 m and U_{10} is above 13 m s^{-1} , use Charnock's relation with $a = 0.010$ (for $\kappa = 0.4$) to calculate u_* .
- iv. Finally, if none of the above occurs, use Equation (4.5b) to calculate C_{10} and, then, estimate u_* .

If the wind speed at a height Z other than 10 m is to be used, two options are available. Based on the original data set used for the present analysis, one can derive a new set of correlations, the same way it was done for the reference velocity U_{10} in the present work. In case the reference height is constant and is expected to be used in several calculations, this might be worth of the effort, in order to have a set of equations explicitly for u_* . The other option is to obtain u_* via an iteration process, for which a sequence is presented in Appendix C.

In Figure 4.8, the variation of u_* with U_{10} , estimated for the whole domain using the Combined Approach (with correlations having U_{10} as scaling velocity), is shown together with the respective experimental u_* versus U_{10} curve. For the whole data set, the proposed approach was able to model the general behaviour and many particular features of the experimental curve. The RMS relative error for the whole domain was 6.6%, with maximum relative error of 16.7%; for 95% of the data points, the relative error was less than 13.9%.

If one desires an approach which is completely explicit for u_* (as a function of U_{10}), Smith's (1980) correlation, Equation (2.31), can be used as a linear approximation for Charnock's relation in the Combined Approach (for Ranges A and C), thus eliminating the necessity of iterations. This would introduce a rather small deviation in the results (tested against the experimental data set considered in this work, the RMS relative error

for the whole domain was 6.8%, with maximum relative error of 16.7% and 0.95-percentile relative error 15.3%).

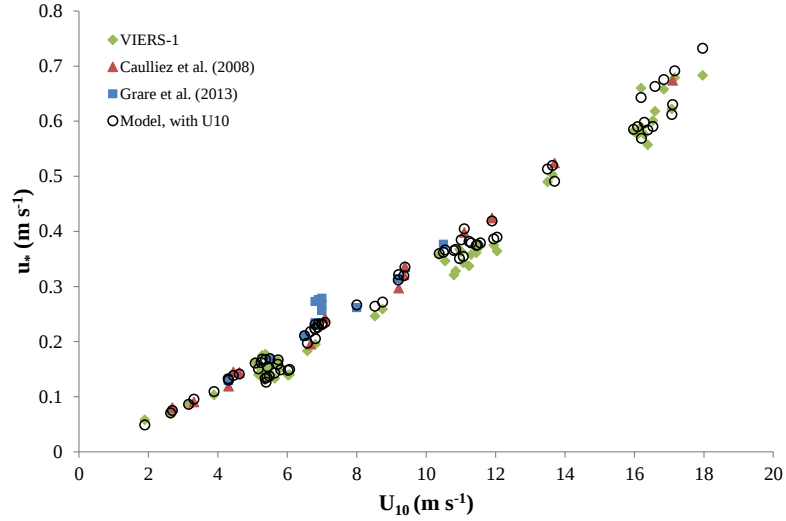


Figure 4.8. Comparison of the friction velocities estimated by the Combined Approach, with correlations having U_{10} as scaling velocity, against experimental results from wind-wave tanks, for the whole domain. The source of the data is identified by the legend in the figure; the u_* values calculated by the Combined Approach are indicated by hollow circles.

5. SENSITIVITY OF MASS TRANSFER MODELS TO THE PARAMETRISATION OF WIND FRICTION

As shown in Chapters 2 and 3, many liquid-gas mass transfer models require the wind friction, represented by the friction velocity u_* , as a critical input variable (including the models derived in the present research, Chapter 3). However, as also discussed, u_* is not directly measured in the typical situations where emission models are applied and, therefore, has to be parametrised based on other available variables (different parametrisation approaches were analysed in Chapter 4). This chapter aims to understand how different emission models are affected by the use of different u_* parametrisations. One of the parametrisations tested is the new, alternative approach proposed in 4.2.4. Because this approach gives a local friction velocity and the emission models normally consider a fetch-averaged u_* , a secondary aim of this chapter is to present the procedure to fetch-average the proposed approach, which is then tested together with other u_* parametrisations in the sensitivity analysis.

5.1. Methodology

5.1.1. Parametrisations of u_* tested

The results of different emission models were compared for three u_* parametrisations: the correlation of Smith (1980), Equation (2.31); the iterative solution of Equation (2.36), based on the Charnock's relation, taking $\alpha = 0.010$ (for $\kappa = 0.4$); and the new, alternative approach proposed in 4.2.4, which will be denoted here as “Combined Approach”.

As highlighted before, Smith's correlation is widely employed to estimate u_* as an input to mass transfer models, being frequently recommended in guides for modelling air emissions from passive surfaces (e.g., Gostelow et al., 2001; ENVIROMEGA, 2003; US EPA, 1994, 2001) and constituting a built-in feature in the US EPA-endorsed model WATER9 (US EPA, 1994, 2001). As also mentioned, Charnock's relation was developed based on a dimensional argument and is favoured in some contexts (see, for

example, Jacobson, 1999) and has the advantage of not being bounded to the use of U_{10} as reference wind speed, which is a useful aspect in more detailed studies of the wind boundary layer over liquid surfaces (e.g., Smith, 1988).

In Chapter 4, the alternative approach proposed in 4.2.4 was shown to describe the data set for local u_* considerably more accurately and in more detail than both Smith's correlation and Charnock's relation, incorporating the wind fetch together with the wind speed in the parametrisation of u_* . If U_{10} is used as reference input wind speed, the calculation of the local u_* follows the sequence outlined in 4.2.4.3. Since the emission models evaluated require the value of u_* averaged along the fetch, a procedure is presented in section 5.2 to fetch-average the u_* calculated with the Combined Approach, so it can be tested together with other u_* parametrisations in the sensitivity analysis.

A Matlab© function ,used in the sensitivity analysis to simultaneously calculate u_* via Smith's correlation, Charnock's relation and the Combined Approach (fetch-averaged), having as input the wind speed U_{10} and the total fetch X , is provided in the Electronic Annex.

5.1.2. Mass transfer models evaluated

Three emission models were chosen for the analysis:

- The model of Mackay and Yeun (1983): this includes Mackay and Yeun's correlation for k_G (Table 2.1 and item 2.2.3.2), Equation (2.15); and their complementary correlations for k_L (item 2.3.3.1), Equation (2.23) (for $u_* > 0.3 \text{ m s}^{-1}$) and Equation (2.24) (for $u_* < 0.3 \text{ m s}^{-1}$).
- The model of Gostelow et al. (2001): Equation (2.16) for k_G (Table 2.1 and item 2.2.3.3), and Equation (2.25) for k_L (item 2.3.3.2).
- The best-performing approaches identified in Chapter 3 (which will be denoted here as “Alternative Approach”, for simplicity): the theoretical model of Brutsaert (1975) for k_G (item 2.2.1.3); and the alternate approach for estimating

k_L developed in the present research (3.2.2.3), which consists in the use of Equation (3.4), for $X \geq 16$ m, and Equation (3.5), for $2.4 \text{ m} \leq X < 16 \text{ m}$.

In the present sensitivity analysis, the bulk gas-phase concentration C_G is approximated by the background concentration, assumed to be negligible ($C_G \approx 0$), as usually done in the context of emission modelling. In this case, as discussed in 2.2.1.5, for the correct application of Brutsaert's model for k_G , the reference “measurement” height (z_m) ideally coincides with the top limit of the concentration boundary layer, δ_M , and Equations (2.12) and (2.13) have to be applied together with Equation (2.10), so as to account for the total resistance to mass transfer in the gas phase, from the interface up to the height z_m . For the sensitivity analysis, the fetch-averaged $z_m = \delta_M$ was estimated using Equation (3.1). Also, a value of 0.4 for the von Kármán constant and turbulent Schmidt number Sc_t equal 0.8 were used in Equation (2.13) (same values tested in 3.2.1.2).

5.1.3. Monte Carlo simulation and sensitivity analysis

The analysis was done for a liquid phase-dominated compound (H_2S), a gas phase-dominated compound (butyric acid) and a both phase-dominated compound (2-methylisoborneol, or 2-MIB). The three compounds chosen are of interest for the study of odorous emissions from wastewater treatment, although the critical characteristic of the compounds is their behaviour regarding the phase dominance of the volatilisation process (therefore, any compound with the same dominance would lead to very similar results, in each case). The values of the relevant properties of the compounds, K_H , Sc_G and Sc_L , shown in Table 5.1, were taken for the temperature of 20 °C.

Table 5.1. Properties of the compounds used in the sensitivity analysis.

Compound	K_H	Sc_G^a	Sc_L^a
H_2S	$3.578 \times 10^{-1}{}^b$	0.96	594
Butyric acid	$5.718 \times 10^{-6}{}^b$	1.81	1228
2-MIB	$2.8 \times 10^{-3}{}^c$	2.71	1863

^a Obtained based on the diffusivities estimated by the US EPA online diffusivity estimator (<https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion-ext.html>, accessed Jun 2017).

^b From Sander (2015).

^c Measured by Ömür-Özbek and Dietrich (2005).

The sensitivity of the emission models to the parametrisation of u_* was evaluated for 15000 combinations of X , randomly varying from 6 to 120 m, and U_{10} , randomly varying from 1.0 to 20.0 m s⁻¹, produced via Monte Carlo simulation. These ranges can be considered typical for the wind speeds and the size of the liquid surfaces in situations of modelling atmospheric emissions from passive liquid surfaces in WWTPs. For each combination of X and U_{10} , the following procedure was repeated:

- Three options of u_* were calculated using the three parametrisations tested (item 5.1.1): u_*^{Sm} (from Smith's correlation), u_*^{Ch} (from Charnock's relation) and u_*^{CA} (from Combined Approach, fetch-averaged according the procedure in section 5.2).
- Each of the emission models analysed (item 5.1.2) was then applied to calculate the mass transfer coefficients, k_G , k_L and K_L (the last obtained using Equation (2.6b)) for each of the compounds, comparing these three options of u_* , which resulted in mass transfer coefficients: k_G^{Sm} , k_L^{Sm} and K_L^{Sm} (calculated using u_*^{Sm}); k_G^{Ch} , k_L^{Ch} and K_L^{Ch} (calculated using u_*^{Ch}); and k_G^{CA} , k_L^{CA} and K_L^{CA} (calculated using u_*^{CA}). Note that the fetch X is also a direct input variable for the models for k_G and k_L in the Alternate Approach.
- The relative differences between pairs of mass transfer coefficients obtained using different u_* parametrisations were calculated, for each compound, model and transfer coefficient. For example, for a given compound, emission model and combination (X, U_{10}) , $(K_L^{Sm} - K_L^{CA}) / K_L^{CA}$ is the relative difference in K_L comparing the result using u_*^{Sm} in relation to the use of u_*^{CA} .

Statistics of such relative differences (RMS, positive extreme and negative extreme) calculated over the 15000 combinations of X and U_{10} were used as a primary assessment of the sensitivity of the emission models to different parametrisations of u_* . The number of combinations, 15000, was chosen so that these statistics change negligibly for larger numbers.

It is important to highlight that the discussion in this chapter treats mainly of the sensitivity of the predicted overall mass transfer coefficient, K_L . However, for any given set of conditions, the relative deviations in K_L represent exactly the relative deviations in the emission rate J , since, according to Equation (2.6a), K_L can be understood as the emission rate per unit concentration difference (that is, $K_L = J/(C_L - C_G/K_H)$).

5.2. Fetch-averaging u_* estimated by the Combined Approach

The Combined Approach, developed in 4.2.4, estimates the local u_* at a given fetch, having as input the fetch and a the wind speed U_Z (measured at some reference height Z). If U_{10} (reference height of 10 m) is used as the input, the calculation of the local u_* follows the sequence outlined in 4.2.4.3. As explained before, the emission models evaluated require the value of u_* averaged along the fetch, which will be given by Equation (5.1).

$$u_*^{CA} = \frac{1}{X} \int_0^X u_*^{Local} dx \quad (5.1)$$

Where u_*^{CA} is the fetch-averaged u_* from the Combined Approach; X is the total fetch of the liquid surface; u_*^{Local} is the local u_* calculated by the Combined Approach as described in 4.2.4 at a position x along the liquid surface (written here in lower case to distinguish from the total fetch X ; in this case, the liquid surface extends in the direction of the wind from $x = 0$ to $x = X$).

Following the sequence outlined in 4.2.4.3, the equation by which u_*^{Local} is calculated depends on the ranges of fetch, wind speed and peak frequency of the wave spectrum (f_p). Therefore, the result of Equation (5.1) will be calculated in different ways, depending on the case, as explored next. Before analysing the different cases, it is important to notice that in the Combined Approach, if $1.3f_p > 4$ Hz at any fetch x , u_*^{Local} is calculated via Charnock's relation (with $a = 0.010$, for $\kappa = 0.4$), that is $u_*^{Local} = u_*^{Ch}$. Considering that f_p is given by Equation (4.3b), this is equivalent to say

that $u_*^{Local} = u_*^{Ch}$ for any $x < X_f$, where X_f is given by Equation (5.2) (with X_f in m, and U_{10} in m s^{-1}). If the total fetch X is smaller than X_f , $u_*^{Local} = u_*^{Ch}$ along the whole surface and, thus, Equation (5.1) will result in $u_*^{CA} = u_*^{Ch}$.

$$X_f = \left(\frac{4}{1.3 \times 27.07} \right)^{-1/0.43} U_{10}^{-1.25} \approx 157.1 U_{10}^{-1.25} \quad (5.2)$$

Case I: $X > X_f$ and $5.3 \leq U_{10} \leq 6.5 \text{ m s}^{-1}$

The situation represented by Case I is schematically illustrated in Figure 5.1. From $x = 0$ to $x = X_f$, $u_*^{Local} = u_*^{Ch}$, thus the average u_* in this interval is u_*^{Ch} . From $x = X_f$ to $x = X$, u_*^{Local} is given by Equation (4.7) (this corresponds to the Range B, as defined in 4.2.3), and the average u_* in this interval (denoted as u_*^I) is calculated by Equation (5.3).

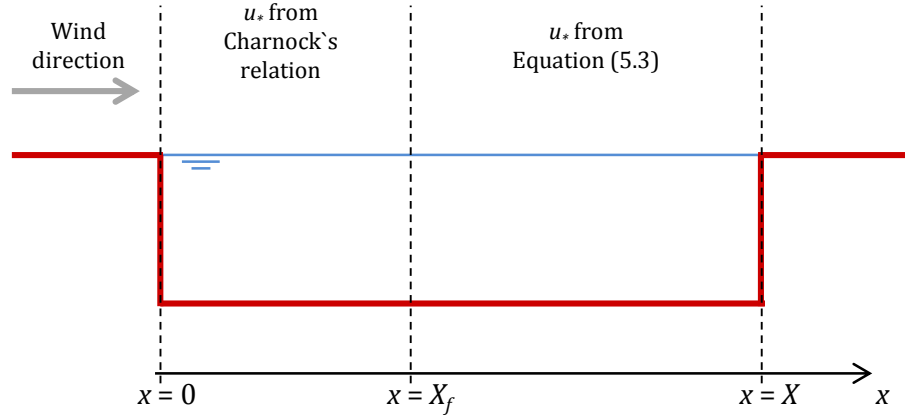


Figure 5.1. Schematic representation of Case I.

$$u_*^I = \frac{1}{X - X_f} \int_{X_f}^X u_*^{Local} dx = \frac{(2.369 \times 10^{-3})^{1/2}}{0.792(X - X_f)g^{0.208}} U_{10}^{1.416} (X^{0.792} - X_f^{0.792}) \quad (5.3)$$

Considering the above, the value of u_* averaged along the total fetch, calculated generically by Equation (5.1), will be given by Equation (5.4) for Case I.

$$u_*^{CA} = \frac{1}{X} \left(\int_0^{X_f} u_*^{Local} dx + \int_{X_f}^X u_*^{Local} dx \right) = \frac{X_f u_*^{Ch} + (X - X_f) u_*^I}{X} \quad (5.4)$$

Case II: $X > X_f$, U_{10} not in the range from 5.3 to 6.5 $m s^{-1}$, and one of the following:
 (i) $X < 50$ m, any U_{10} ; or (ii) $X > 50$ m, for $U_{10} \leq 13$ $m s^{-1}$

The situation represented by Case II is schematically illustrated in Figure 5.2. The same as in Case I, from $x = 0$ to $x = X_f$, $u_*^{Local} = u_*^{Ch}$, thus the average u_* in this interval is u_*^{Ch} . From $x = X_f$ to $x = X$, u_*^{Local} is given by Equation (4.5b) (that is, Range D), and the average u_* in this interval (denoted as u_*^I) is calculated by Equation (5.5).

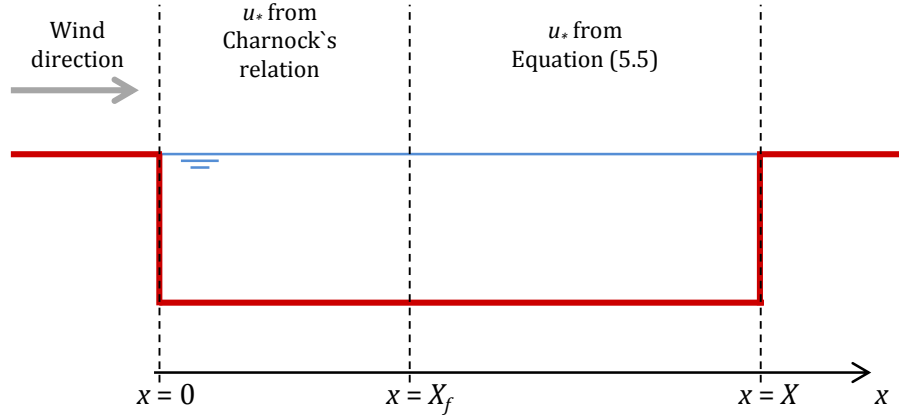


Figure 5.2. Schematic representation of Case II.

$$u_*^I = \frac{1}{X - X_f} \int_{X_f}^X u_*^{Local} dx = \frac{(1.334 \times 10^{-3})^{1/2}}{0.9365(X - X_f)g^{0.0635}} U_{10}^{1.127} (X^{0.9365} - X_f^{0.9365}) \quad (5.5)$$

Then, the value of u_* averaged along the total fetch, calculated generically by Equation (5.1), will be given by Equation (5.6) for Case II.

$$u_*^{CA} = \frac{1}{X} \left(\int_0^{X_f} u_*^{Local} dx + \int_{X_f}^X u_*^{Local} dx \right) = \frac{X_f u_*^{Ch} + (X - X_f) u_*^I}{X} \quad (5.6)$$

Case III: $X > 50 \text{ m}$ and $U_{10} > 13 \text{ m s}^{-1}$

The situation represented by Case III is schematically illustrated in Figure 5.3. In this case, there are three intervals: from $x = 0$ to $x = X_f$, $u_*^{Local} = u_*^{Ch}$, thus the average u_* in this interval is u_*^{Ch} ; for $X_f < x < 50 \text{ m}$, u_*^{Local} is given by Equation (4.5b) (Range D), and the average u_* in this interval (denoted as u_*^{III}) is calculated by Equation (5.7); for $x > 50 \text{ m}$, $u_*^{Local} = u_*^{Ch}$, and the average u_* in this interval is u_*^{Ch} (this corresponds to Range C).

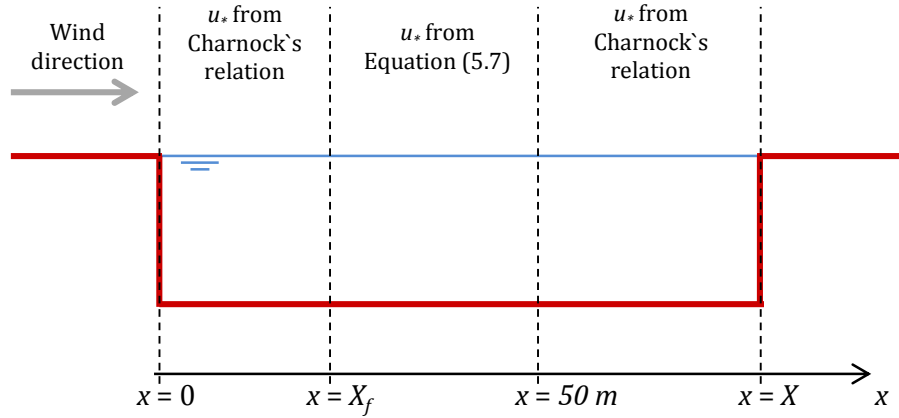


Figure 5.3. Schematic representation of Case III.

$$u_*^{III} = \frac{1}{50 - X_f} \int_{X_f}^{50} u_*^{Local} dx = \frac{(1.334 \times 10^{-3})^{1/2}}{0.9365(50 - X_f)g^{0.0635}} U_{10}^{1.127} (50^{0.9365} - X_f^{0.9365}) \quad (5.7)$$

For Case III, the value of u_* averaged along the total fetch, calculated generically by Equation (5.1), will be given by Equation (5.8).

$$\begin{aligned} u_*^{CA} &= \frac{1}{X} \left(\int_0^{X_f} u_*^{Local} dx + \int_{X_f}^{50} u_*^{Local} dx + \int_{50}^X u_*^{Local} dx \right) \\ &= \frac{(X + X_f - 50)u_*^{Ch} + (50 - X_f)u_*^{III}}{X} \end{aligned} \quad (5.8)$$

5.3. Results and discussion

5.3.1. Fetch-averaged u_* estimated by different parametrisations

Before studying the sensitivity of the three emission models to different parametrisations of u_* , it is convenient to analyse how the values of u_*^{Sm} , u_*^{Ch} and u_*^{CA} deviate from one another, for the same set of input combinations (X , U_{10}). Table 5.2 presents the summary of the relative differences (RMS, positive extreme and negative extreme) among the values of u_* calculated over the 15000 combinations of X and U_{10} .

Table 5.2. Relative differences in the estimated u_* , comparing the results from Smith's correlation (u_*^{Sm}), Charnock's relation (u_*^{Ch}) and the Combined Approach (u_*^{CA}).

	$\frac{u_*^{Ch} - u_*^{Sm}}{u_*^{Sm}}$	$\frac{u_*^{Ch} - u_*^{CA}}{u_*^{CA}}$	$\frac{u_*^{Sm} - u_*^{CA}}{u_*^{CA}}$
RMS:	1.85%	4.27%	5.02%
Positive extreme:	1.89%	16.9%	14.8%
Negative extreme:	-7.38%	-3.25%	-5.02%
Percentage of negative differences:	51.5%	11.1%	20.4%

Figure 5.4 compares the estimates from Smith's correlation and Charnock's relation over the range of U_{10} used in the sensitivity analysis (u_*^{Sm} and u_*^{Ch} do not depend on the fetch). It is clear that the results from both approaches are generally very similar (RMS relative difference of 1.87%), with the largest relative differences occurring for low wind speeds (Figure 5.4b). This similarity between the outcomes of Charnock's relation and Smith's correlation, and the advantages and disadvantages of each have been already discussed in 4.2.2.2.

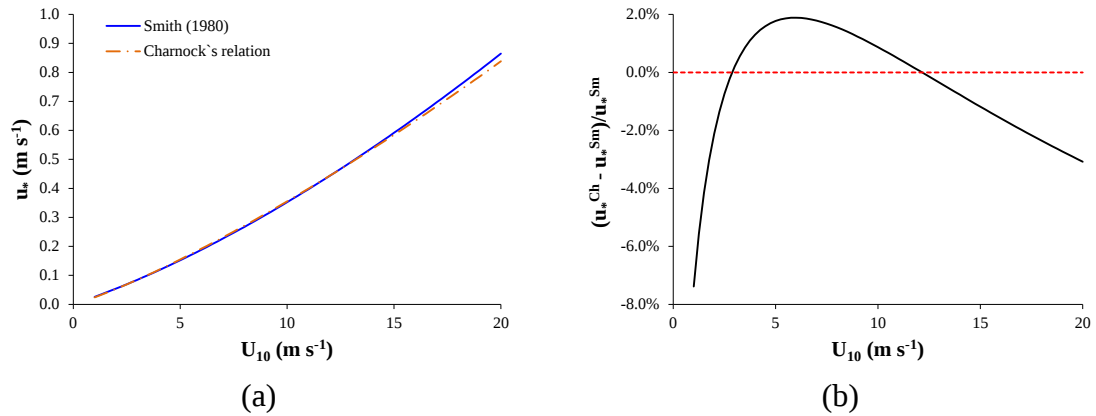


Figure 5.4. (a) Estimates of u_* from Smith's correlation and Charnock's relation; and (b) relative differences between u_*^{Ch} and u_*^{Sm} . The red dashed line in (b) indicates the 0% relative difference.

Figure 5.5 shows how the relative differences between either u_*^{Ch} or u_*^{Sm} and u_*^{CA} vary throughout the ranges of X and U_{10} used in the sensitivity analysis. As seen in Figure 5.5, comparing the values of u_*^{Ch} and u_*^{Sm} against the results of the Combined Approach (u_*^{CA}), the relative differences are generally small (but not as small as the differences between u_*^{Ch} and u_*^{Sm}), which is also indicated by the calculated RMS relative differences reported in Table 5.2. Nonetheless, although limited to a maximum of 16.8% for u_*^{Ch} and 14.7% for u_*^{Sm} , relative differences of over 10% are observed for some combinations of fetch and wind speed (Figure 5.5), particularly: (i) fetch around 50 m and large U_{10} ; (ii) long fetches and moderate U_{10} ; and (iii) long fetches and U_{10} between 5.3 and 6.5 m s^{-1} . The occurrence of larger relative differences in these regions of the domain is explained by the specificities of the Combined Approach, which in turn try to capture the behaviour of u_* described in the experimental data (see Chapter 4). In especial, the largest relative differences occur for the situation (iii), which is the case with a large proportion of the liquid surface presenting the “ultrasmooth” condition (related to the Range B, defined in Chapter 4), discussed in 4.2.3.

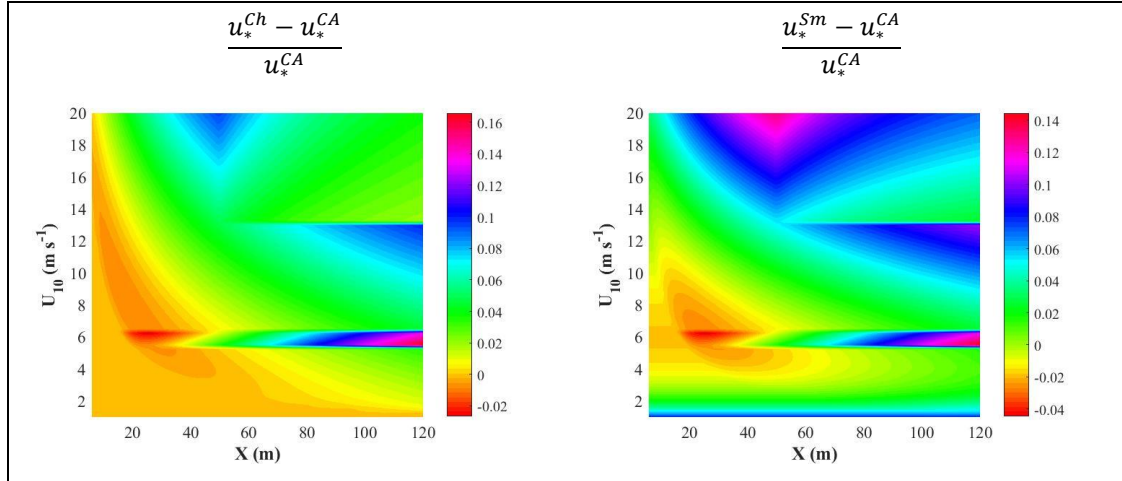


Figure 5.5. Relative differences between u_*^{Ch} (left) or u_*^{Sm} (right) in relation to u_*^{CA} throughout the ranges of X and U_{10} used in the sensitivity analysis. The colour scale indicates the value of the relative differences.

It is also important to note that the relative differences discussed above are given in relation to u_*^{CA} , the fetch-averaged u_* estimated by the Combined Approach (section 5.2), which is the one required to be used in the mass transfer models evaluated. On the other hand, the relative differences between u_*^{Local} (that is, the local value of u_* produced by the Combined Approach) and u_*^{Ch} or u_*^{Sm} can be considerably larger, reaching extreme values of 38.7% for u_*^{Ch} and 36.1% for u_*^{Sm} (but these, however, are not relevant for the emission models analysed here).

5.3.2. Liquid phase-controlled compound – H₂S

Table 5.3 presents the summary of the relative differences (RMS, positive extreme and negative extreme) among the values of K_L for H₂S obtained using different u_* parametrisations for each mass transfer model, calculated over the 15000 combinations of X and U_{10} . Corresponding results for the film-specific mass transfer coefficients, k_G and k_L , can be found in Appendix D. Given the value of K_H for H₂S (Table 5.1), its volatilisation is controlled by the conditions in the liquid phase, that is, K_L is dominated by the value (and the behaviour) of k_L .

Table 5.3. Relative differences in the value of K_L for H_2S estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (K_L^{Sm}), Charnock's relation (K_L^{Ch}) and the Combined Approach (K_L^{CA}).

Emission model	Error statistics	$\frac{K_L^{Ch} - K_L^{Sm}}{K_L^{Sm}}$	$\frac{K_L^{Ch} - K_L^{CA}}{K_L^{CA}}$	$\frac{K_L^{Sm} - K_L^{CA}}{K_L^{CA}}$
Mackay and Yeun (1983)	RMS:	2.29%	6.00%	5.95%
	Positive extreme:	3.93%	36.63%	31.67%
	Negative extreme:	-3.06%	-6.68%	-10.19%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.85%	4.26%	5.02%
	Positive extreme:	1.88%	16.93%	14.81%
	Negative extreme:	-7.38%	-3.25%	-5.01%

First, let us compare the results of K_L using Smith's correlation and Charnock's relation, for which the relative differences over the range of U_{10} used in the sensitivity analysis are illustrated in Figure 5.6. Following the pattern observed for the values of u_* , the relative differences in K_L are small, that is, the values of K_L for liquid-phase controlled compounds calculated by any of the three models do not differ much if u_* is parametrised by Smith's correlation or Charnock's relation.

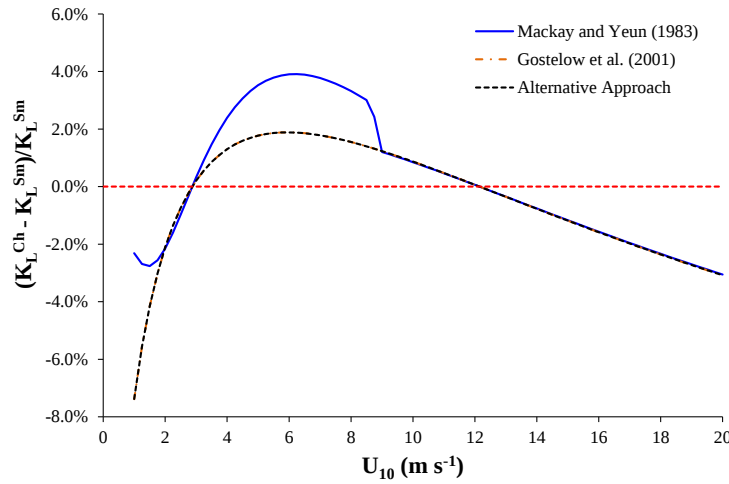


Figure 5.6. Relative differences between K_L^{Ch} and K_L^{Sm} for H_2S from the three emission models (legend in the figure). The red dashed line indicates the 0% relative difference.

Figure 5.7 shows the variation of the differences between either K_L^{Ch} or K_L^{Sm} and K_L^{CA} in the domain of X and U_{10} , for the three emission models evaluated. For the model of Gostelow et al. (2001) and the Alternative Approach, the values and pattern of relative differences in K_L are practically identical to the relative differences in u_* (5.3.1), which is explained by the fact that, for liquid phase controlled compounds, $K_L \approx k_L$, and by the form of Equations (2.25) and (3.4)-(3.5), in which k_L is proportional to u_* . Analogously to u_* , overall relative differences were not pronounced, however large differences (over 10%) occur for some combinations of fetch and wind speed (Figure 5.7), the same situations (i), (ii) and (iii) discussed in item 5.3.1. For the situation (iii) (long fetches and U_{10} between 5.3 and 6.5 m s⁻¹), the values of K_L estimated by the model of Mackay and Yeun (1983) were much more sensitive to the different parametrisations of u_* , compared to the other two models, resulting in maximum relative differences $(K_L^{Ch} - K_L^{CA})/K_L^{CA}$ and $(K_L^{Sm} - K_L^{CA})/K_L^{CA}$ of, respectively, 36.6% and 31.7%. This

contrasting behaviour of Mackay and Yeun's model is due to the fact that u_* is raised to a power 2.2 in Equation (2.24), which is the equation adopted by Mackay and Yeun (1983) for k_L ($\approx K_L$, for H_2S and other liquid phase-controlled compounds) in the range between $5.3 < U_{10} < 6.5$ m s⁻¹.

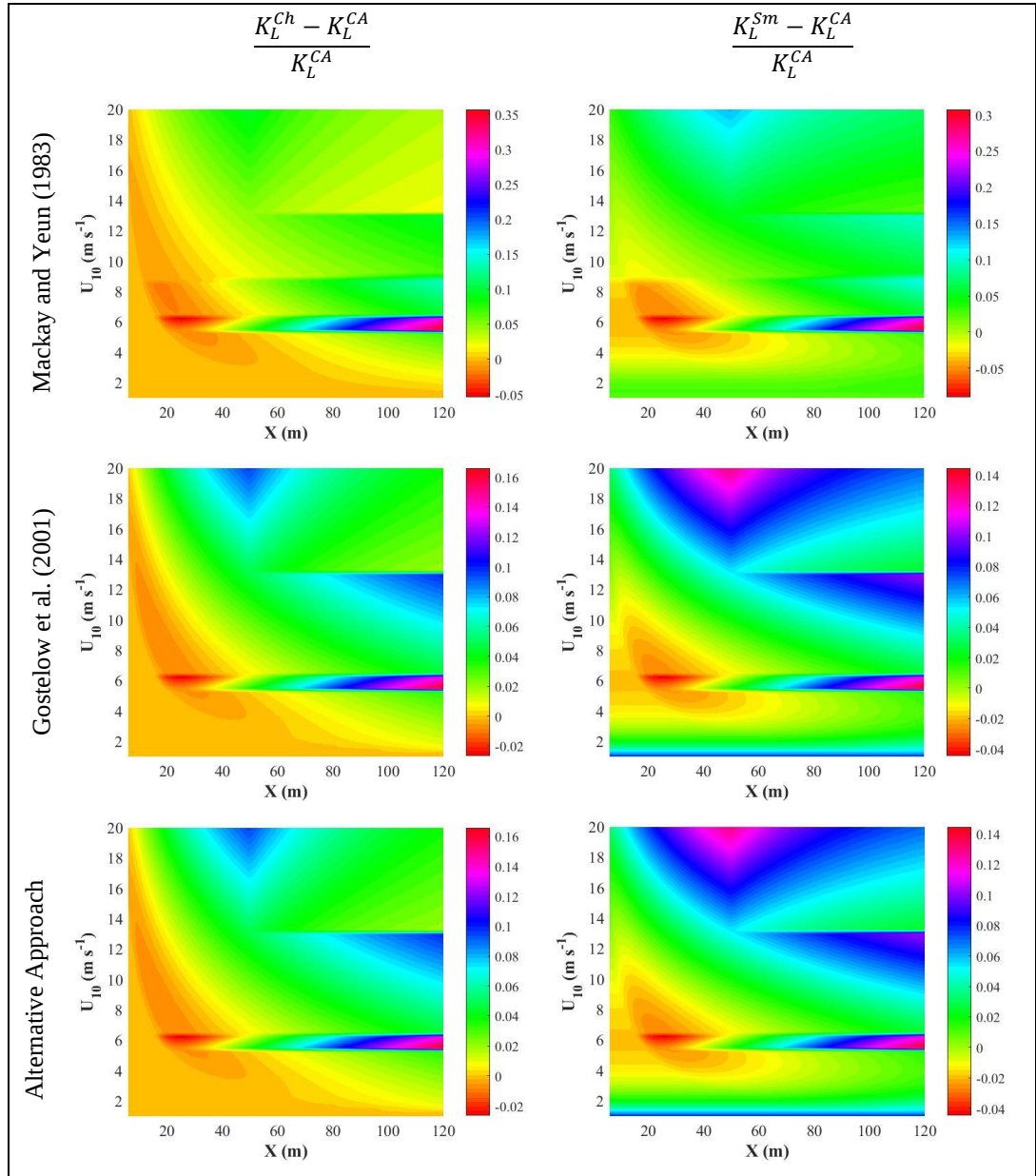


Figure 5.7. Relative differences between K_L^{Ch} (left) or K_L^{Sm} (right) in relation to K_L^{CA} for H_2S throughout the ranges of X and U_{10} used in the sensitivity analysis. The colour scale indicates the value of the relative differences.

5.3.3. Gas phase-controlled compound – butyric acid

Table 5.4 presents the summary of the relative differences (RMS, positive extreme and negative extreme) among the values of K_L for butyric acid obtained using different u_* parametrisations for each mass transfer model, calculated over the 15000 combinations of X and U_{10} . Corresponding results for the film-specific mass transfer coefficients, k_G and k_L , can be found in Appendix D. The value of K_H for butyric acid (Table 5.1) implies that its volatilisation is controlled by the conditions in the gas phase, which means that K_L follows the behaviour of k_G (in this case, $K_L \approx k_G K_H$).

Table 5.4. Relative differences in the value of K_L for butyric acid estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (K_L^{Sm}), Charnock's relation (K_L^{Ch}) and the Combined Approach (K_L^{CA}).

Emission model	Error statistics	$\frac{K_L^{Ch} - K_L^{Sm}}{K_L^{Sm}}$	$\frac{K_L^{Ch} - K_L^{CA}}{K_L^{CA}}$	$\frac{K_L^{Sm} - K_L^{CA}}{K_L^{CA}}$
Mackay and Yeun (1983)	RMS:	1.50%	3.91%	4.60%
	Positive extreme:	1.62%	13.94%	12.42%
	Negative extreme:	-3.28%	-2.85%	-4.39%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.73%	3.99%	4.69%
	Positive extreme:	1.76%	15.74%	13.78%
	Negative extreme:	-6.84%	-3.03%	-4.68%

Comparing the results of K_L using Smith's correlation and Charnock's relation (relative differences shown in Figure 5.8), it is observed that the relative differences $(K_L^{Ch} - K_L^{CA}) / K_L^{CA}$ are generally small for all the three models evaluated.

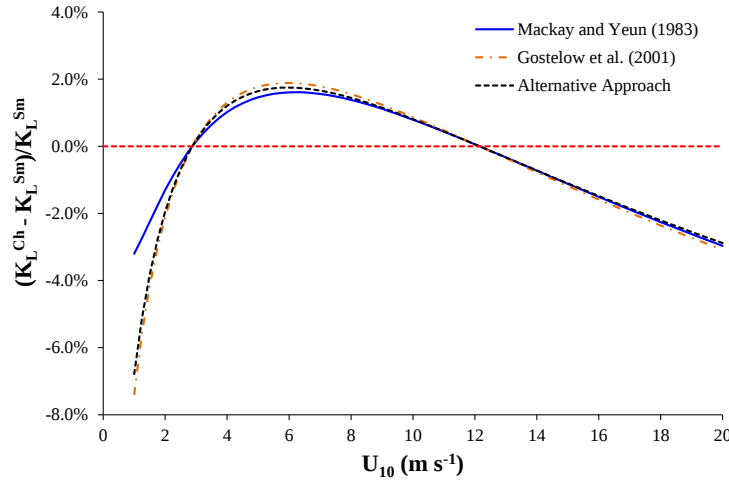


Figure 5.8. Relative differences between K_L^{Ch} and K_L^{Sm} for butyric acid from the three emission models (legend in the figure). The red dashed line indicates the 0% relative difference.

Figure 5.9 shows the variation of the relative differences between either K_L^{Ch} or K_L^{Sm} and K_L^{CA} in the domain of X and U_{10} , for the three emission models evaluated. In the case of butyric acid, a gas phase-controlled compound, the relative differences in K_L follow the same pattern as the relative differences in u_* (5.3.1), for the three mass transfer models. Slight discrepancies among the models are due to the fact that each model treats u_* in a different manner in the equation for k_G (which, in turn, controls the value of K_L): in the model of Gostelow et al. (2001), Equation (2.16), k_G is proportional to u_* ; in Mackay and Yeun's (1983) model, k_G varies linearly with u_* with a non-zero intercept (Equation (2.15)); and in the Alternative Approach, k_G (calculated by Brutsaert's model) is a non-linear function of u_* , but almost proportional to u_* (see Figure 2.3). Similarly to what happens for u_* , the relative differences were not pronounced in most of the domain (which is verified by the small RMS values in Table 5.4), although large differences (over 10%) appear for the situations (i), (ii) and (iii) discussed previously (item 5.3.1).

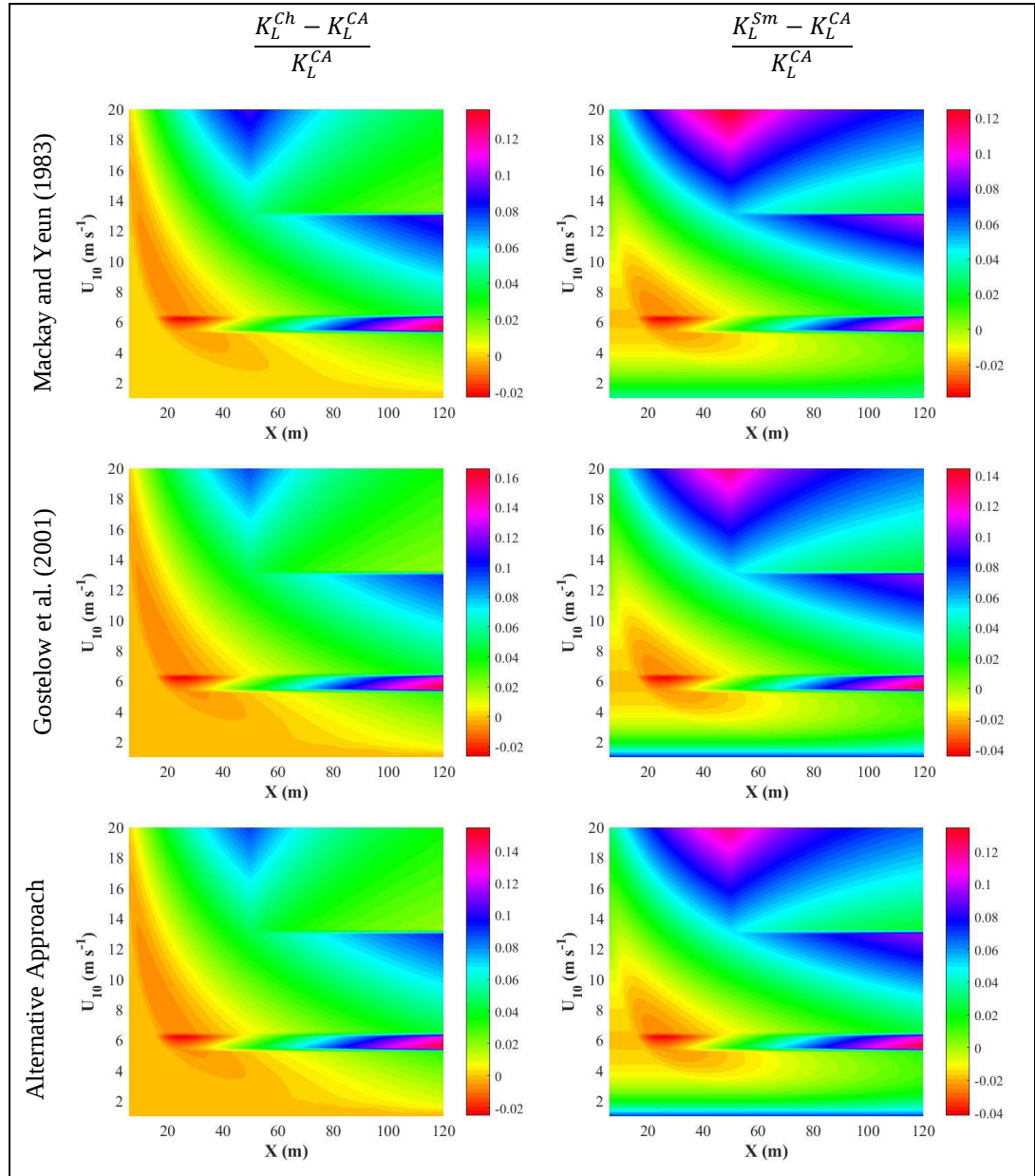


Figure 5.9. Relative differences between K_L^{Ch} (left) or K_L^{Sm} (right) in relation to K_L^{CA} for butyric acid throughout the ranges of X and U_{10} used in the sensitivity analysis. The colour scale indicates the value of the relative differences.

5.3.4. Both phase-controlled compound – 2-MIB

Being 2-MIB a compound whose volatilisation is controlled by both phases (considering the value of K_H), the behaviour of K_L will be significantly affected by both k_G and k_L . Table 5.6 presents the summary of the relative differences (RMS, positive extreme and negative extreme) among the values of K_L for 2-MIB obtained using different u_* parametrisations for each mass transfer model, calculated over the 15000 combinations of X and U_{10} . Corresponding results for the film-specific mass transfer coefficients, k_G and k_L , can be found in Appendix D.

Table 5.5. Relative differences in the value of K_L for 2-MIB estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (K_L^{Sm}), Charnock's relation (K_L^{Ch}) and the Combined Approach (K_L^{CA}).

Emission model	Error statistics	$\frac{K_L^{Ch} - K_L^{Sm}}{K_L^{Sm}}$	$\frac{K_L^{Ch} - K_L^{CA}}{K_L^{CA}}$	$\frac{K_L^{Sm} - K_L^{CA}}{K_L^{CA}}$
Mackay and Yeun (1983)	RMS:	1.83%	4.89%	5.17%
	Positive extreme:	2.90%	26.56%	23.10%
	Negative extreme:	-2.99%	-4.91%	-7.55%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.80%	4.13%	4.86%
	Positive extreme:	1.83%	16.37%	14.33%
	Negative extreme:	-7.14%	-3.15%	-4.86%

Comparing the results of K_L for 2-MIB obtained by using the values of u^* from Smith's correlation and Charnock's relation (relative differences shown in Figure 5.10), it is observed that, similarly to the other cases analysed before, the relative differences $(K_L^{Ch} - K_L^{Sm}) / K_L^{Sm}$ are small for all the three models evaluated. The maximum relative differences occur at low wind speeds.

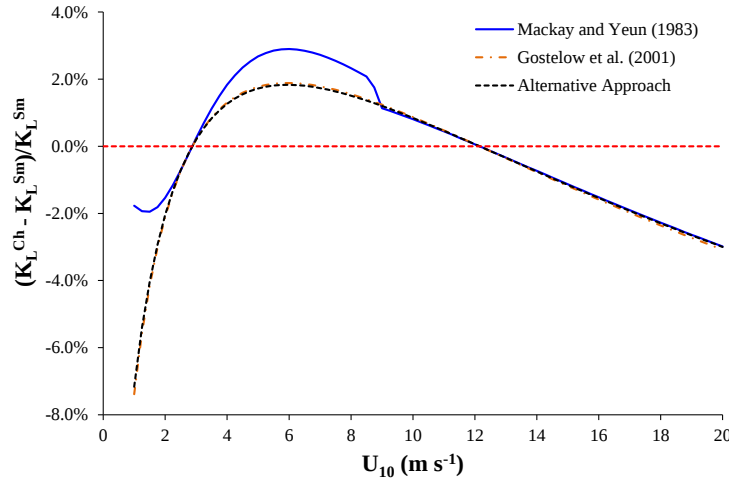


Figure 5.10. Relative differences between K_L^{Ch} and K_L^{Sm} for 2-MIB from the three emission models (legend in the figure). The red dashed line indicates the 0% relative difference.

Figure 5.11 illustrates the variation of the relative differences $(K_L^{Ch} - K_L^{CA})/K_L^{CA}$ and $(K_L^{Sm} - K_L^{CA})/K_L^{CA}$ in the domain of X and U_{10} , for the three emission models

evaluated. As expected for a compound whose K_L is dominated by both phases, the values and the behaviour of the relative differences in K_L are intermediate between what is observed for a liquid phase-controlled compound (item 5.3.2) and a gas phase-controlled compound (item 5.3.3). For the model of Gostelow et al. (2001) and the Alternative Approach, the values and pattern of relative differences in K_L follow very closely the relative differences in u_* (5.3.1). Consistently with the results discussed in the previous sections, the overall relative differences were not pronounced, but larger differences (over 10%) are verified for the same situations (i), (ii) and (iii) discussed in item 5.3.1. For long fetches and U_{10} between 5.3 and 6.5 m s⁻¹ (situation (iii)), the values of K_L estimated by the model of Mackay and Yeun (1983) were oversensitive to the different parametrisations of u_* , compared to the other two models, although these extreme relative differences were not as large as the ones for H₂S. As explained before, this behaviour of Mackay and Yeun's model arises from the fact that u_* is raised to a power 2.2 in the equation for k_L (Equation (2.24)) in the range between 5.3 < U_{10} < 6.5 m s⁻¹; however, in the case of both phase-controlled compounds, the response of K_L is partially buffered by the significant contribution from k_G , which is not as sensitive as k_L in the model of Mackay and Yeun (1983).

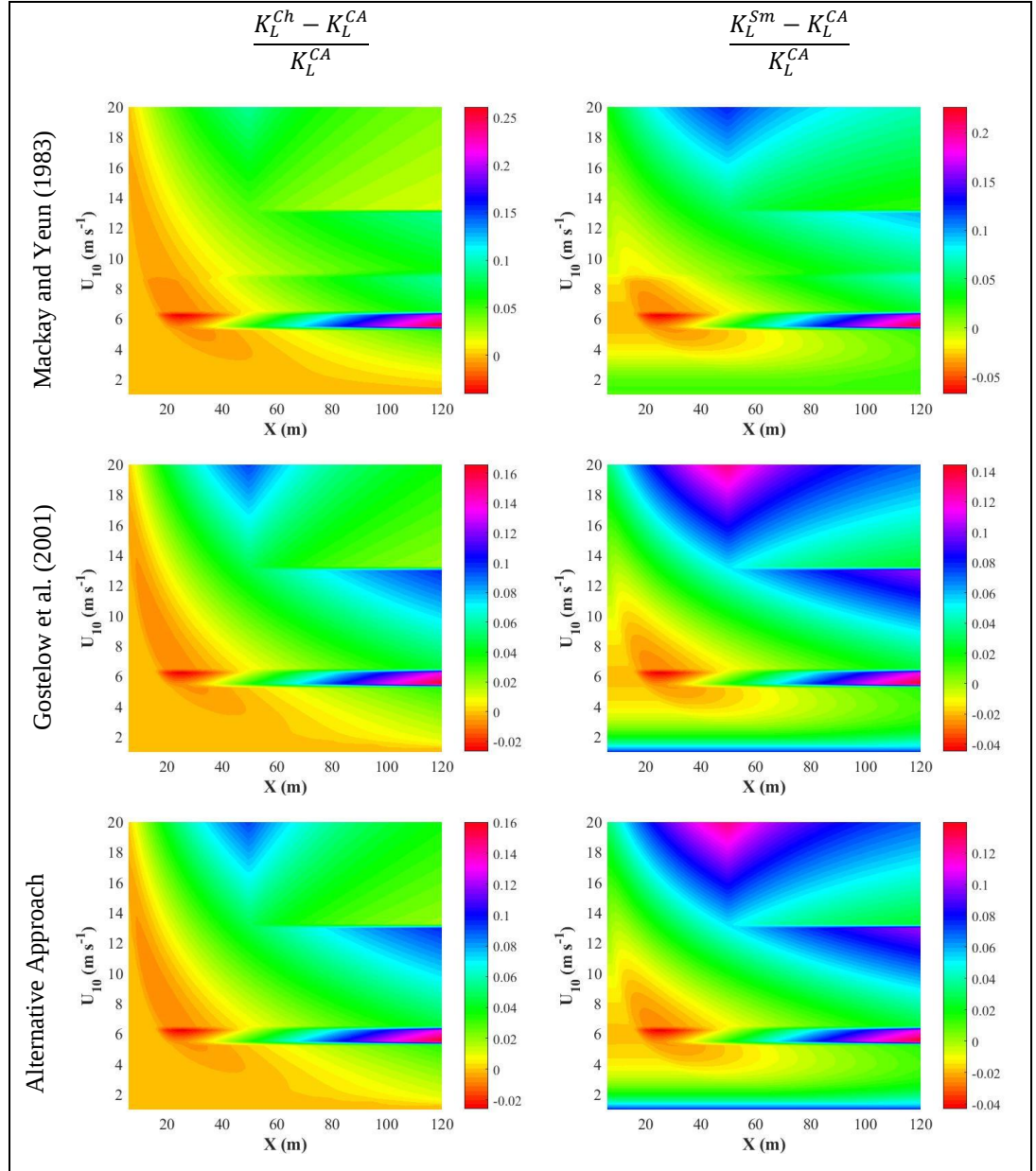


Figure 5.11. Relative differences between K_L^{Ch} (left) or K_L^{Sm} (right) in relation to K_L^{CA} for 2-MIB throughout the ranges of X and U_{10} used in the sensitivity analysis. The colour scale indicates the value of the relative differences.

5.3.5. Additional considerations

The analysis in items 5.3.1 – 5.3.4 reveals that the parametrisation of the wind friction via Smith's correlation and Charnock's relation produces very similar values of u_* and, consequently, the resulting mass transfer coefficients (k_G , k_L and K_L) estimated by all the models analysed are also very close. In this sense, for the range of wind speeds evaluated, Smith's correlation and Charnock's relation (taking $\alpha = 0.010$ and $\kappa = 0.4$) can be used interchangeably for practical purposes; the choice of one or the other will depend on how convenient they are in each specific situation, as discussed in 4.2.2.2.

The relative differences between either u_*^{Ch} or u_*^{Sm} in relation to u_*^{CA} vary throughout the ranges of X and U_{10} used in the sensitivity analysis, but are generally small (smoothed by the fact that u_*^{Ch} is the fetch-averaged u_* produced by the Combined Approach), albeit larger relative differences, of over 10%, can occur for some combinations of fetch and wind speed, the situations (i), (ii) and (iii) discussed in item 5.3.1. Comparing the mass transfer coefficients (k_G , k_L and K_L) estimated using u_*^{Ch} or u_*^{Sm} against the use of u_*^{CA} , in most of the cases analysed, the magnitude and behaviour of the relative deviations in the resulting mass transfer coefficients are similar to the corresponding deviations in u_* . An important exception is the calculation of k_L by the model of Mackay and Yeun (1983), particularly for long fetches and U_{10} in the range between 5.3 and 6.5 m s⁻¹ (situation (iii)); in this case, the relative deviations in k_L are considerably larger than the corresponding deviations in u_* , which has consequences for the value of the overall mass transfer coefficient K_L for liquid phase and both phase-controlled compounds. This aspect of the model of Mackay and Yeun (1983) is especially important, since this model is adopted, together with Smith's parametrisation of u_* , in the US EPA-endorsed model WATER9 and in the model TOXCHEM+, and has been employed in many scientific studies (e.g., Atasoy et al., 2004; Blunden et al., 2008; Cheng et al., 2008; Qiu et al., 2008; Rumburg et al., 2008; Tao et al., 2017).

In Chapter 4, the Combined Approach was shown to better describe the data set for local u_* . Therefore, it can be expected that the fetch-averaged estimates of u_* produced by this approach are also more accurate than the parametrisations of Smith (1980) and Charnock's relation, and, in principle, should be preferred to be used in the modelling of

liquid-gas mass transfer in WWTPs. Nonetheless, compared to simpler approaches such as Smith's correlation and Charnock's relation, the Combined Approach presents increased complexity, requiring the use of the fetch as an input parameter. On that topic, it is important to notice that the deviations are mostly positive, meaning that, in this case, the emission values modelled using Smith's correlation or Charnock's relation, even if biased, will tend to represent conservative estimates. Ultimately, the choice of the wind friction parametrisation (and the intrinsic compromise between accuracy and simplicity) is a very case-specific decision, depending on the purpose of the application of the emission models and the consequences involved. The analysis in the present chapter assessed the response of mass transfer models to the choice of different u_* , which can help guide the user of emission models in this decision, identifying the situations in which the most critical differences occur and their magnitude.

6. EXPERIMENTAL ASSESSMENT OF THE FLUX HOOD METHOD

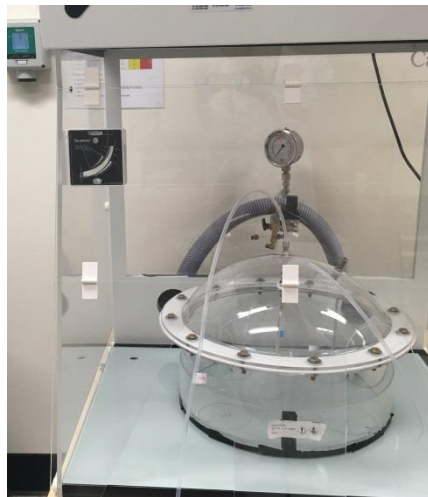
This chapter reports the experimental assessment of the mass transfer inside the US EPA flux hood, with focus on the experimental determination of mass transfer coefficients in the microenvironment created by the flux hood and the effects of concentration build up in the hood's headspace. The experimental results for the mass transfer of gas phase-dominated compounds inside the US EPA flux hood are compared against an emission model for the passive surfaces in WWTPs. The evaluation of the US EPA flux hood as a method is of great relevance, given the widespread application of this device, and the methodological and theoretical considerations presented here can be adopted for the assessment of other enclosure devices, in particular of flux-hood type.

6.1. Methodology

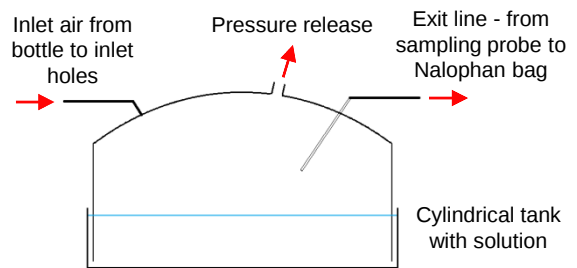
6.1.1. Flux hood design and operation

The flux hood used in this study, which can be seen in Figure 6.1a, was made of Plexiglas® and followed the design proposed by Klenbusch (1986), endorsed by the United States Environmental Protection Agency (US EPA). The standard design specifies a cylindrical body, with diameter of 40.6 cm and height of 17.8 cm, and a dome-shaped top whose highest part (at its central point) is 10.2 cm above the cylindrical body; our flux hood reproduces these dimensions with ± 1.3 cm difference. Also following the recommendations of Klenbusch (1986), there were four equidistantly-positioned holes on the top, one of which was an opening, with diameter 2.1 cm, for pressure equilibration and flow release. The other three had diameter 1.3 cm and were used to fit 1/4" stainless steel bulkheads with the following purposes: one connected the sweep gas feed line to the internal inlet distribution tube; another connected the internal sampling probe to the outer sampling line; and the other was kept capped during most of the time of the runs, being used occasionally for checking the pressure differential between the interior of the hood and the external environment of

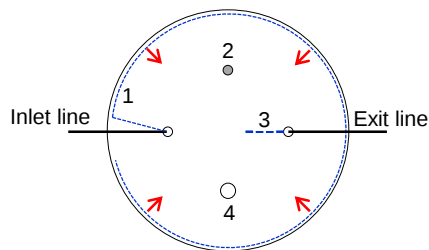
the laboratory. The sweep gas distribution tube was made of stainless steel, ¼” OD, and fixed to the cylindrical body internal wall, at the height where the dome meets the body. It contained four equidistant inlet orifices, positioned horizontally (so as to produce horizontal inlet jets), the one closest to the inlet bulkhead connection having diameter 2.0 mm, and the other three, diameter 2.4 mm. Figure 6.1c illustrates the relative positioning of the inlet orifices and the holes at the top.



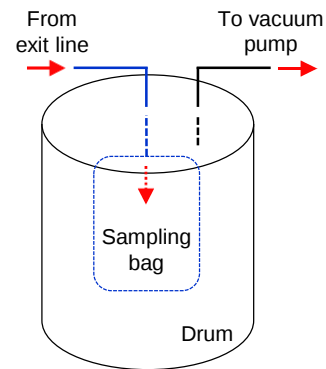
(a)



(b)



(c)



(d)

Figure 6.1. Experimental setup: (a) US EPA flux hood, fit to the cylindrical tank; and (b) schematic representation of Figure 6.1a, identifying the inlet and outlet lines, and the pressure release; (c) schematic top view of the flux hood, showing the holes and connections at the dome-shaped top and their positioning in relation to the internal inlet orifices (inlet jets represented by the red arrows); and (d) schematic representation of the “lung system” used to collect the samples in the Nalophan® bags. The numbers in (c) identify the following: 1 - sweep gas distribution tube; 2 - capped hole at the top, used occasionally for checking the pressure differential between the interior of the hood and the external environment of the laboratory; 3 - internal sampling probe; 4 - opening for pressure equilibration and flow release.

The sampling probe consisted of a 6" long tube, capped at the tip, perforated with two rows of holes, each row containing five holes with diameter 2.4 mm. The holes were separated 1" from each other along the tube length and positioned orthogonally in the radial direction. A Teflon® outlet line, ¼" OD, connected to the sampling probe via one of the bulkheads, conveyed the sampled flow to Nalophan® bags, which were filled using a "lung system" (Figure 6.1d) for the runs with sampling. The sweep air feed line, connecting the supplying gas bottle to the inlet distribution tube, was also Teflon® tubing, ¼" OD.

The basic operation of the flux hood system was conducted according to the standard sampling procedure described by Kienbusch (1986), observing the additional recommendations of Eklund (1992) concerning sampling on liquid surfaces. The sweep air feed was supplied by instrument-grade air bottles, with maximum humidity content of 25 ppm (which can be approximated as completely dry air, for practical purposes). The desired flow rates were adjusted by valve rotameters and checked using an electronic flow rate meter (Mesa Labs – Defender 510). Two groups of experiments were carried out (items 6.1.2 and 6.1.3), which also present details of the operation of the flux hood system specific for each group.

6.1.2. Volatilisation of compounds

The flux hood sampling system was used to measure the rate of volatilisation from aqueous solutions of compounds with different values of Henry's law coefficient (a broad compilation of Henry's law coefficients for various compounds of environmental interest is presented by Sander, 2015, which is used in the present work), so as to cover the range of behaviours regarding the dominance of the volatilisation process (see item 2.1.3): acetic acid, with volatilisation dominated by conditions in the gas phase; chloroform and hydrogen sulfide (H_2S), with liquid phase-dominated volatilisation; and 1-butanol, whose volatilisation, in the present experiment, was significantly dependent on both phases. The compounds were assessed individually, in separate sets of experiments, for three nominal values of sweep air flow rate, 2, 5 and 10 L min^{-1} ; at each flow rate, runs were conducted in triplicate for each VOC and in duplicate for H_2S .

Additional triplicate runs were carried out for acetic acid and chloroform, at a nominal flow rate of 5 L min^{-1} and under conditions similar to the other runs, except by using humidified sweep air in this case (all the other runs used instrument-grade dry air, which is the default condition).

VOC solutions were prepared by simply mixing a predefined volume of the pure compound (50 mL for acetic acid, 2.5 mL for 1-butanol and 590 μL for chloroform) per litre of milliQ® water; the temperature of the laboratory was recorded at the time of the mixing, making it possible to use the pure compounds' density to obtain the value of their concentration in the solutions. The preparation of the H_2S solutions followed a different procedure. An initial solution was produced, with sulfide (S^{2-}) concentration of 100 mg L^{-1} , by adding 0.375 g of solid sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) in 500 mL of milliQ® water; 10 mL of this solution were then diluted in 2 L of milliQ® water, achieving a nominal final concentration of $0.5 \text{ mg L}^{-1} \text{ S}^{2-}$. Just before the start of each run, the S^{2-} solution was acidified to a pH lower than 4 using sulfuric acid, making all sulfide be in the non-dissociated form H_2S (Santos et al., 2012).

The preparation of all the solutions took place shortly before the beginning of each experiment, so as to avoid significant losses of the compounds. For each experimental run, 1.7 L of the solution was transferred to a cylindrical tank made of Plexiglas®, with diameter 41.0 cm and height 8.5 cm; the depth of the liquid in the tank was approximately 1.3 cm. The flux hood was then fit to the cylindrical tank (Figure 6.1a,b), and the sampling and sweep air flow started immediately. The sweep air flow rate was then finely-adjusted to the desired value with the help of the in-line electronic flow meter. The flow rate in the sampling line was 200 mL min^{-1} for all the runs, guaranteed by previous calibration of the lung system. After the adjustment of the sweep air flow rate, the so-called stabilisation time started, following the recommendation of Klenbusch (1986) that valid samples should be collected only after waiting some time (minimum of four residence times) so the internal air flow and mass transfer achieve a stabilised condition. The stabilisation times adopted in the present study were: 30 min for the flow rates of 5 L min^{-1} and 10 L min^{-1} , and 60 min for the flow of 2 L min^{-1} . After the stabilisation time, the bag in the lung system was replaced, starting then the valid sampling time, which varied between 20 to 30 min for each run; the sample collected during the stabilisation time was discarded.

The internal pressure in the flux hood was equilibrated with the pressure in the laboratory environment, which was systematically monitored using a differential manometer. The temperatures of the liquid in the tank and of the laboratory environment were measured at the beginning and the end of the sampling time. The laboratory temperature was 19.0 ± 1.0 °C, whilst the temperature of the liquid ranged from 17.9 to 21.5 °C among the runs, with average 20.0 °C. The sweep air flow rate was also verified at the end of the sampling time, the value being recorded (together with the initially adjusted value) to be used in the subsequent calculations. Since part of the H₂S was expected to escape during the acidification step (thus the nominal concentration when the solution was prepared would significantly differ from the actual concentration in the experiment), for the experiments with H₂S, samples of the solution in the tank were collected at the beginning and end of the valid sampling time, by inserting a pipette through the pressure-equilibration opening at the top of the flux hood. The sulfide concentration in these liquid samples (dissolved S²⁻) was determined via the methylene blue method coupled with spectrophotometry (equivalent to APHA, 2005, method 4500-S²⁻ D), using a HACH spectrophotometer (HACH – DR1900) and analysis kit.

For all compounds, the gas samples collected in the Nalophan® bags during the valid sampling time (sampling flow rate of 200 mL min⁻¹) were analysed within maximum one hour of the time of sampling, thereby preventing any possible significant losses of the compounds via diffusion through the bags. The concentration of H₂S was measured using a H₂S analyser (Jerome – 631-X, Arizona Instrument, USA). The concentrations of the VOCs were quantified by gas-chromatography (GC) – 7890A (Agilent Technologies, USA), equipped with a micro-cell electron capture detector (μECD) and a flame ionisation detector (FID), employing a capillary column Agilent Plot Q, 30 m × 535 μm × 40 μm, with He as carrier gas. The gas samples were manually injected using a gas-tight syringe. Acetic acid and 1-butanol were detected by the FID, with detector temperature 250 °C and N₂ make-up flow of 25 mL min⁻¹; injector temperature was 250 °C, operating in “splitless” mode, and the carrier gas flow of 9 mL min⁻¹ in the column. Chloroform was analysed by the μECD, with detector temperature 150 °C and N₂ make-up flow of 30 mL min⁻¹; injector temperature was 250 °C, operating in “split” mode (split ratio 100:1), septum purge flow of 3 mL min⁻¹, and carrier gas flow of 3.5 mL

min^{-1} in the column. The oven temperature programme was different for each compound: for acetic acid, an initial temperature of 180 °C was hold for 1 min, then increased at a rate of 100 °C min^{-1} to 220 °C, then maintained for 7 min; for 1-butanol, the initial temperature was also 180 °C, hold for 1 min, then increased at a rate of 20 °C min^{-1} to 200 °C, maintained for 0.7 min, and increasing again, at a rate of 100 °C min^{-1} to a final temperature of 210 °C, maintained for 3 min; for chloroform, the initial temperature was 150 °C, hold for 0.5 min, then increased at a rate of 30 °C min^{-1} to a final temperature of 250 °C, maintained for 1 min. Calibration curves for each compound were established using gas samples at five known concentrations, produced by evaporating different amounts of pure standard solutions of the compounds into Nalophan® bags flushed with fixed volumes of sweep air (preparation method adapted from Wang et al., 2015).

Following the standard procedure for the use of the US EPA flux hood (Klenbusch, 1986), the measured gas-phase concentrations $C_m(\text{kg m}^{-3})$ were used in Equation (6.1) to estimate the volatilisation rate of the compounds J ($\text{kg s}^{-1} \text{m}^{-2}$), being Q the sweep air flow rate ($\text{m}^3 \text{s}^{-1}$) and A the area (m^2) of the surface enclosed by the hood (“footprint area”). Implicit in Equation (6.1) is the idea that the concentration in the samples collected via the sampling probe represents the mean concentration in the total outlet flow (which comprises the small fraction that is sampled plus the majority of the flow that is released by the pressure equilibration hole at the top of the flux hood). This, in turn, would be guaranteed by a completely-mixed bulk gas phase inside the hood. Preliminary CFD simulations by Prata Jr. et al. (2016b) indicated differences between the sampled flow and the total outlet flow of order 7%, for flux hood configuration and operational conditions slightly different from the present study. Differences for the present case can be expected to be of the same order, thus the volatilisation rates calculated using Equation (6.1) can be assumed satisfactorily accurate in the context of the mass transfer experiments treated herein.

$$J = \frac{QC_m}{A} \quad (6.1)$$

Additional tests were conducted with acetic acid and chloroform, at a nominal flow rate of 5 L min^{-1} , in order to assess the influence of high humidity in the sweep air flow on

the volatilisation rate of these compounds. The procedure for these tests were the same as previously described, except that the sweep air flow was passed through a bubbling column before entering the flux hood inlet distribution line. The bubbling column was filled with milliQ® water, 30 cm deep, and had a relatively large diameter, which avoided significant changes in the depth of the water column during the course of a run, therefore avoiding significant changes in the head losses along the feed line, consequently stabilising the flow rate. The relative humidity in the sweep air flow exiting the bubble column was approximately 90%, measured by an electronic relative humidity sensor before and after each run. Volatilisation rates were also calculated using Equation (6.1).

6.1.3. Water evaporation

Water evaporation experiments were performed aiming to adapt and assess the use of the water evaporative rate method (Parker et al., 2013b) applied to the US EPA flux hood to characterise the overall mass transfer inside the flux hood, under different operational conditions. Because the mass transfer conditions are not uniform along the surface enclosed by the hood (Parker et al., 2013b; Prata Jr. et al., 2016b), it is important that the evaporation source corresponds to the whole footprint area. Following this premise, the Plexiglas® cylindrical tank (same as described in 6.1.2) was employed as the evaporation pan for the water evaporation experiments. The evaporation rates were evaluated for nine different set of conditions: three nominal values of sweep air flow rate, 2, 5 and 10 L min⁻¹, times three nominal humidity contents in the sweep air, relative humidity of 0% (dry air), 45% and 90%. For each set of conditions, triplicate runs were conducted.

The humidity contents in the sweep air were achieved using the bubbling column system (described in 6.1.2). For the relative humidity of 90%, all the feed air flow was passed through the bubbling column. For the relative humidity of 45%, the feed air flow was split in two parallel lines, with only one of them (i.e., approximately half of the total flow) passing through the bubbling column; the two lines joined again by means of a T-joint and the resulting single line connected to the inlet distribution system of the flux hood (Figure 6.2). In each run, the actual humidity content in the sweep air feed line differed slightly from the nominal values, depending mainly on temperature and

flow rate, and was measured by an electronic relative humidity sensor before and after the run.

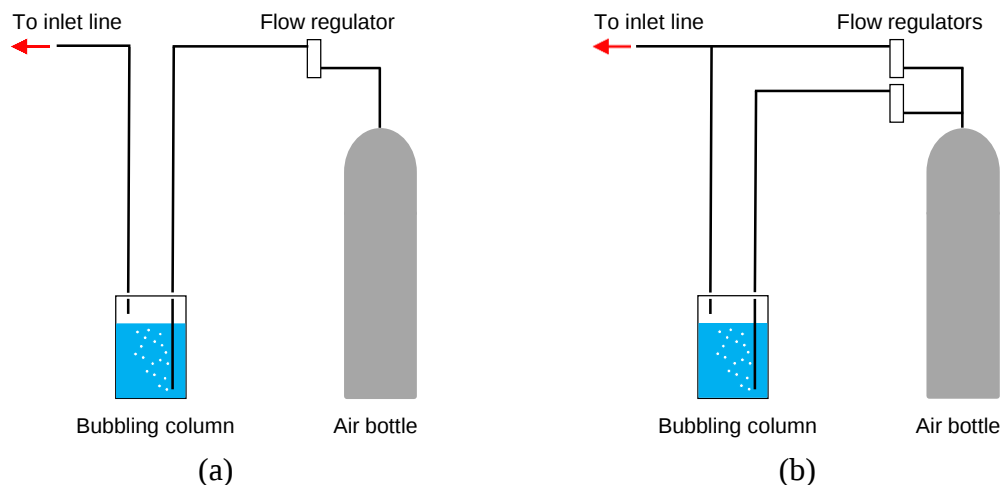


Figure 6.2. Two configurations of the humidification system, in order to produce inlet air with nominal relative humidity of (a) 90% and (b) 45%.

Before the start of a run, the tank was filled with 1.7 L of milliQ® water, and the precise mass of the filled tank was recorded using a laboratory scale with precision of 0.1 g. After weighting the tank, the flux hood was fit to it, and the small gaps between the hood and the tank walls sealed with Parafilm® (fixed with adhesive tape) to avoid evaporation losses through the gaps; this was necessary, since it was verified that the undesired collateral evaporation could affect significantly the measured evaporation rate. The feed gas line was then connected to the hood, starting the experimental run, and the sweep air flow rate was finely-adjusted to the desired value with the help of the in-line electronic flow meter; the value of the flow rate was also checked at the end of each run. There was no sampling in the evaporation experiments, and the sampling outlet line was kept sealed and inactive. The flux hood operated under isobaric condition. The laboratory temperature was 19.0 ± 1.0 °C, and the temperature of the water ranged from 17.2 to 19.0 °C among the runs, with average 18.3 °C.

For the experiments with dry sweep air, the run time was 2 h, for which the change in the mass of the water in the tank was well above the precision of the scale whereas the water level in the tank was not significantly affected; it was also verified that the measured evaporation rates did not change if longer runs were performed. The duration of the runs for the experiments with humid sweep air was longer, so as to allow for an

amount of evaporation that would promote a detectable change in the mass of the water in the tank. At the end of the run, the feed gas line was disconnected, the Parafilm® seal removed, and the mass of the tank with water was again weighted on the scale. The evaporation rates J_w ($\text{kg s}^{-1} \text{m}^{-2}$) were calculated via Equation (6.2), where m_0 and m_f are the initial and final mass (kg) of the filled tank, and Δt is the duration of the run (s). If desired, the evaporation rate can be straightforward converted in mm d^{-1} by using the water density (which is function of the water temperature) and converting units.

$$J_w = \frac{(m_0 - m_f)}{A \Delta t} \quad (6.2)$$

6.2. Theoretical support and calculations

6.2.1. Obtaining the mass transfer coefficients from the experimental results

In conceptual terms, it can be considered that the headspace of the US EPA flux hood, under typical operational configurations, offers a condition of approximately complete mixing, with an almost homogeneous concentration in the bulk of the gas phase. In fact, experimental evidence provided by Gholson et al. (1989) and Woodbury et al. (2011) and CFD results by Prata Jr. et al. (2016b) support this general picture, except for restricted points of possible local accumulation of compounds close to the chamber walls (Prata Jr. et al., 2016b). In this case, the main resistance to mass transfer (and, consequently, the major concentration gradients) in the gas phase can be expected to develop in the region adjacent to the gas-liquid interface. Based on this consideration, it is appropriate to describe the mass transfer conditions in the gas phase by means of the gas-film mass transfer coefficient k_G (m s^{-1}), so that the mass flux of a given compound through the gas-film can be expressed by Equation (2.2a). It is important to note that Equation (2.2a) is applicable in the description of the evaporation process, since the transport of water in the gas phase is not different from the transport of other compounds; in this case, J_G would correspond to the evaporation rate J_w , and $C_{G,i}$ would be the concentration of water in the saturated air in immediate contact with the water

surface (which can be obtained from the vapour pressure of water, dependent on the surface temperature).

Analogously, the liquid-film mass transfer coefficient k_L (m s^{-1}) can be defined, and the mass flux of a given compound through the region of major resistance in the liquid phase (the “liquid film”) expressed by Equation (2.2b). Differently from the situation of the flux hood headspace, the condition of almost complete mixing in liquid column enclosed by the hood has not been fully investigated in previous studies and is treated here as a preliminary hypothesis. For a situation of liquid-gas mass transfer such as the one assumed herein, with resistances associated only to the liquid and gas films, the volatilisation rate J of a given compound ($J = J_L = J_G$, in this case) can be expressed by Equation (2.6), in terms of the (liquid phase-based) overall mass transfer coefficient K_L (m s^{-1}) and the bulk concentrations, C_G and C_L (complete derivation presented in 2.1.2).

Assuming a completely-mixed gas phase in the flux hood’s headspace (which is a reasonable assumption for the US EPA flux hood, as discussed before), the concentration of the compounds in the bulk of the gas phase C_G can be approximated by the concentration C_m sampled in the Nalophan® bags in the experiments of compounds’ volatilisation (item 6.1.2). The bulk liquid-phase concentration of the compounds C_L is known beforehand in the experiments, based on the amount of the pure compound used to prepare the aqueous solutions, in the case of the VOCs, and directly measured for H_2S (item 6.1.2). The values of the compound’s K_H corrected for the experimental temperatures are taken from the literature (Sander, 2015). Using these values of K_H , C_L and C_G ($\approx C_m$) together with the experimental volatilisation rate J (calculated via Equation (6.1)), Equation (2.6a) can be solved for the experimental overall mass transfer coefficient K_L .

Because both H_2S and chloroform are highly volatile ($1/k_L \gg 1/(k_G K_H)$), their volatilisation will be liquid phase-dominated, and therefore the experimental K_L will represent an approximation of their liquid-side mass transfer coefficients, that is $k_L \approx K_L$. In contrast, acetic acid presents $1/(k_G K_H) \gg 1/k_L$, meaning that its volatilisation will be gas phase-controlled and $k_G \approx K_L/K_H$. In other words, the experiments with a highly volatile compound provide experimental values for its k_L ,

and the experiments with a poorly volatile compound allow its k_G to be assessed. Having k_G or k_L for a given compound, say $k_{G,1}$ or $k_{L,1}$, the respective mass transfer coefficients $k_{G,2}$ or $k_{L,2}$ for another compound can be estimated using appropriate powers of their Schmidt numbers, as in Equations (6.3a) and (6.3b).

$$k_{G,2} = k_{G,1} \left(\frac{Sc_{G,2}}{Sc_{G,1}} \right)^{-2/3} \quad (6.3a)$$

$$k_{L,2} = k_{L,1} \left(\frac{Sc_{L,2}}{Sc_{L,1}} \right)^{-2/3} \quad (6.3b)$$

Where $Sc_{G,1}$ and $Sc_{L,1}$ are the Schmidt numbers (in the gas and liquid phase, respectively) of the compound for which k_G and k_L are known; and $Sc_{G,2}$ and $Sc_{L,2}$ are the Schmidt numbers (in the gas and liquid phase, respectively) of the compound for which k_G and k_L are unknown. The exponent -2/3 in Equations (6.3a) and (6.3b) was adopted since this value has been pointed as characteristic of undisturbed boundaries (without waves or ripples) (Jähne and Haußecker, 1998), which was the observed situation in the experiments.

In theory, a similar procedure can be applied to obtain k_G from water evaporation experiments. In this case, Equation (2.2a) can be solved for k_G of water vapour, having $J_G = J_w$ and the interface concentration $C_{G,i}$ being the concentration of water vapour in the saturated air (calculated for the experimental temperature conditions). The bulk concentration of water vapour in the headspace of the hood C_G can be estimated via Equation (6.4), which is derived from a mass balance as follows. Supposing a well-mixed air phase, the total outlet mass flux can be written as $Q \times C_G$ (i.e., the total mass of water vapour leaving the headspace of the hood, per unit time). For a steady-state condition, this outlet flux will correspond to the sum of two inputs of water vapour to the gas phase inside the hood: (i) the total flux of water vapour evaporating from the water surface, which is given by $J_w \times A$; (ii) and the water vapour that comes in the sweep air flow, which will be given by $C_{G,0} \times Q$, being $C_{G,0}$ the concentration of water vapour in the inlet air feed (= 0 for dry air; varied values for the experiments with humid sweep air, calculated based on the measured relative humidity). Therefore, the

mass balance of water vapour for the headspace of the flux hood under steady-state condition will be expressed by $Q \times C_G = J_w \times A + C_{G,0} \times Q$, which, rearranged, results in Equation (6.4).

$$C_G = C_{G,0} + \frac{J_w A}{Q} \quad (6.4)$$

6.2.2. Effects of compounds accumulation in the headspace

Besides the effects of conditions such as concentration in the liquid phase, temperature and concentration in the inlet gas, the volatilisation rate of a given compound (or the evaporation rate of water) in the interior of the flux hood will depend fundamentally on the mass transfer coefficients for the compound and its accumulation in the headspace, which, in turn, may change with the sweep air flow rate. For the case of water vapour, substituting Equation (6.4) in Equation (2.2a) and rearranging, Equation (6.5) is obtained. This equation is valid as long as the approximation of a well-mixed gas phase applies.

$$J_w = \frac{1}{\frac{1}{k_G} + \frac{A}{Q}} (C_{G,i} - C_{G,0}) \quad (6.5)$$

An analogous mass balance can be performed for compounds other than water vapour, using Equation (2.6) instead of Equation (2.2a); in this case, the inlet concentration was always $C_{G,0} \approx 0$, since clean air was used as feed in all the experiments (which is the typical situation for the operation of the flux hood). This results in Equation (6.6a).

$$J = \frac{1}{\frac{1}{k_L} + \frac{1}{K_H} \left(\frac{1}{k_G} + \frac{A}{Q} \right)} C_L \quad (6.6a)$$

In the case of poorly volatile compounds, for which $1/(k_G K_H) \gg 1/k_L$ and $C_{G,i} \approx C_L K_H$, Equation (6.6a) can be rewritten as Equation (6.6b). Equation (6.6b) corresponds to Equation (6.5) with $C_{G,0} \approx 0$, reflecting the fact that the volatilisation of poorly volatile compounds resembles the evaporation of a pure liquid.

$$J = \frac{1}{\frac{1}{k_G} + \frac{A}{Q}} C_{G,i} \quad (6.6b)$$

Writing the evaporation and volatilisation rates in the form of Equations (6.5) and (6.6) allows the effect of the accumulation in the hood's headspace to be more directly visualised. It can be noticed that the accumulation of the compound in the headspace manifests as an apparent additional resistance ($=A/Q$) in the gas phase and is expected to diminish as the sweep air flow rate increases. For highly volatile compounds, $1/k_L \gg 1/(k_G K_H) + A/Q K_H$, and therefore the effect of compounds' accumulation can be expected to be negligible, provided that the headspace of the hood is well mixed.

Equations (6.5) and (6.6b) also show that the rates of water evaporation and volatilisation of gas phase-controlled compounds do not necessarily change proportionally with k_G (this would only happen in particular cases, for example, if k_G is proportional to Q or if $1/k_G \gg A/Q$). From a rigorous point of view, this violates one of the conditions for the use of the water evaporation method (Parker et al., 2013b) to inter-convert between volatilisation rates measured with the US EPA flux hood and the ones measured with other devices (or with the US EPA flux hood under different operational conditions). However, approximations may still be possible, as further examined in section 6.3. It is also worth mentioning that the water evaporation method can be suitable to inter-convert between results of two wind tunnel-type devices (which normally operate with higher specific sweep air flow rates and present a directional flow), provided that the flow inside the wind tunnels is high enough in order to avoid accumulation in their headspace, making the concentration at the edge of the mass transfer boundary layer equal to the inlet concentration.

The build-up of the concentration of water vapour and other compounds in the headspace of the flux hood also clearly prevents the general application of a straightforward water evaporative flux ratio correction factor as proposed by Parker et al. (2013b) to scale up the measurements to field conditions. That is because the values of concentration of water vapour and other gas phase-controlled compounds in the headspace of the flux hood, C_G , present no direct relation to the background values in the field. Moreover, the evaporation rates in the field depend on the humidity content in

the atmospheric air, whilst the volatilisation of other compounds does not; this is one of the major drawbacks of the scaling up of emission rates using water evaporative flux ratio correction factors, independently of the sampling device employed.

6.3. Results and discussion

6.3.1. Volatilisation and evaporation rates under different sweep air flow rates

Figure 6.3 presents the variation of the volatilisation rates J of the VOCs and H_2S with the sweep air flow rate (Q). As a trend, the emission rates of all compounds increased with the flow rate. The behaviour of the measured emission rate of acetic acid and 1-butanol, for which the volatilisation is controlled by conditions in the gas phase and in both phases, respectively, is similar to the reported by Rhoades et al. (2005) for the flux of ammonia, whose volatilisation is controlled by both phases, measured with the US EPA flux hood in a lagoon. The increase in the volatilisation rates of chloroform and H_2S , both liquid phase-controlled, contrasts with the results of Gholson et al. (1989), who found that the emission rates of 1,1,1-trichloroethane (also liquid phase-controlled) measured with the US EPA flux hood did not present any clear pattern of variation with the flow rate. This difference may be attributed to the fact that, in the present study, the only dynamical forcing in the liquid phase was the friction produced by the sweep air flow on the water surface whereas in the experiments of Gholson et al. (1989) the flux hood was placed inside an apparatus that simulates a wind blowing over the surface of a small tank, which generated surface currents. It is possible that the interaction of these surface currents with the edge of the flux hood was the main source of turbulence and the main driver for mass transfer in their case, surpassing the effects of any changes in the relatively weak friction of the sweep air inside the hood.

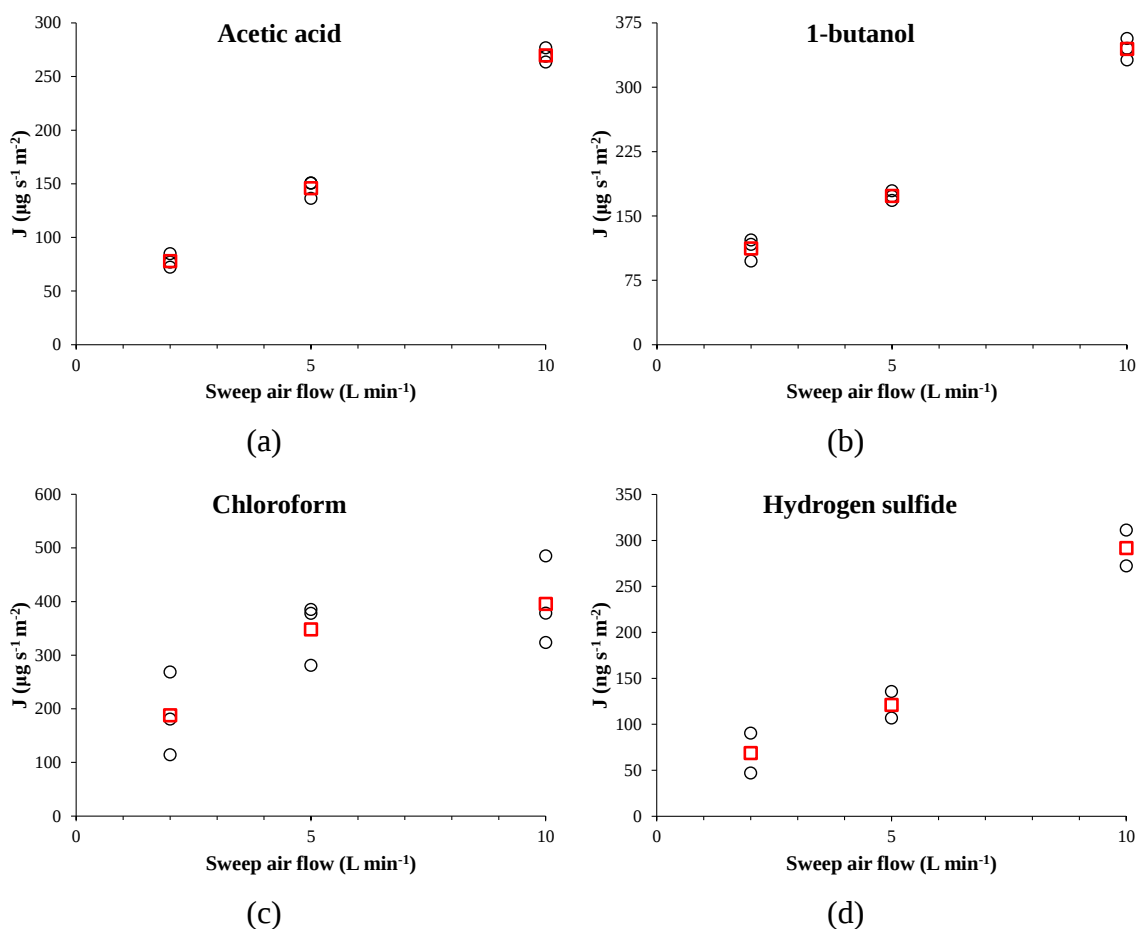


Figure 6.3. Volatilisation rates of VOCs and hydrogen sulfide measured by the flux hood operating with different sweep air flow rates. Black circles represent results of individual experimental runs, and the red squares indicate the average volatilisation rate at each nominal flow rate.

The variation of the volatilisation rates with the sweep air flow, observed in Figure 6.3, reflects the combined effect of the changes in the mass transfer coefficients and in the accumulation of compounds in the hood's headspace. The experimental mass transfer coefficients are examined in more detail in 6.3.2. Being C_L and C_G the concentration of the compound (kg m^{-3}) in the bulk of the liquid and the gas phases, respectively, and K_H the non-dimensional Henry's law coefficient, the importance of accumulation can be preliminarily assessed by examining the relative magnitude of C_G/K_H compared to C_L (Equation (2.6a)). For a well-mixed headspace, as in the present case, C_G can be approximated by the concentration C_m measured for the sample collected in the Nalophan® bags. For acetic acid, C_G/K_H was between 46% to 81% of the corresponding C_L , and for 1-butanol, C_G/K_H ranged from 54% to 92% of C_L . This confirms that concentration build up inside the flux hood is significant for the mass transfer of compounds whose volatilisation is affected by the gas phase (gas phase or

both phase-controlled volatilisation). Conversely, for chloroform and H_2S , C_G/K_H was less than 1% of C_L in all the experiments, indicating that the accumulation in the hood's headspace was not relevant for the compounds with liquid phase-controlled volatilisation, consistent with the theoretical considerations made previously (6.2.2).

Figure 6.4a shows how the water evaporation rate inside the flux hood varies with the sweep air flow rate, for different values of humidity content in the inlet air. Similarly to the volatilisation rate of compounds, J_w generally increases with Q . As expected, at a given sweep air flow rate, J_w is smaller for higher humidity content in the inlet air. For dry inlet air ($\text{RH} = 0\%$), the behaviour (and, to a certain degree, the values) of J_w is similar to the results of Parker et al. (2013b) for an evaporation source covering the whole footprint of the flux hood, which is an evidence of the relatively good repeatability of the US EPA flux hood, an attribute classically associated with this device.

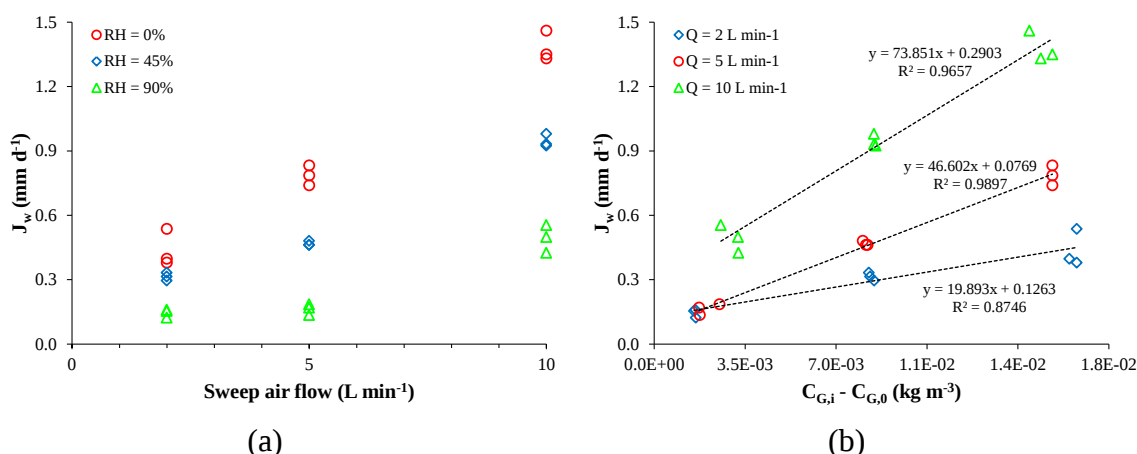


Figure 6.4. Variation of the water evaporation rate J_w with: (a) the sweep air flow rate, for three nominal inlet relative humidity values (legend in (a)); and (b) the difference between $C_{G,i}$ and $C_{G,0}$, for the three nominal sweep air flow rates (legend in (b)).

In Figure 6.4b, it can be observed that, for a given Q , the water evaporation rate J_w increases as the difference between the concentration (kg m⁻³) of water vapour at the gas side of the gas-liquid interface ($C_{G,i}$) and in the inlet air ($C_{G,0}$) becomes larger. The seemingly linear fashion with which J_w varies as a function of the difference $C_{G,i} - C_{G,0}$ is consistent with Equation (6.5), except for the existence of a non-zero, positive intercept in the experimental lines (in contrast, according to Equation (6.5), J_w should

be strictly proportional to the difference $C_{G,i} - C_{G,0}$). Possibly, the main reason for this deviation is the difficulty of accurately determining the temperature at the water surface, which is necessary to estimate $C_{G,i}$ (Parker et al., 2013b, also points out the same difficulty); in the present experiments, the bulk temperature of the water in the Plexiglas® tank is used. An additional factor that may have contributed is the uncertainty in the measurement of the relative humidity in the inlet air, which is converted into $C_{G,0}$. On the other hand, although the experimental procedure was designed in order to avoid losses of water by collateral evaporation, the possibility of minor losses contributing to the positive offset identified in Figure 6.4b cannot be totally discarded.

It is worth mentioning that, with dry inlet air, the average volatilisation rates J are positively correlated with the corresponding water evaporation rates J_w ; the plots of J against J_w for the four VOCs are presented in Figure 6.5. For acetic acid (gas phase-controlled volatilisation), the variation of J with J_w appears to be almost linear (but not exactly proportional), although more values are necessary to verify if linearity actually holds. As discussed in 6.2.2, the water evaporation method (Parker et al., 2013b) is not necessarily applicable to inter-convert between volatilisation rates measured with the US EPA flux hood under different operational conditions. However, the almost-linearity observed for acetic acid (Figure 6.5a) suggests that the water evaporation method may be used in order to approximate relative changes in the magnitude of the volatilisation rate of gas phase-dominated compounds due to changes in the sweep air flow rate. It can also be useful to qualitatively compare the overall mass transfer conditions in the headspace of the US EPA flux hood under different operational conditions.

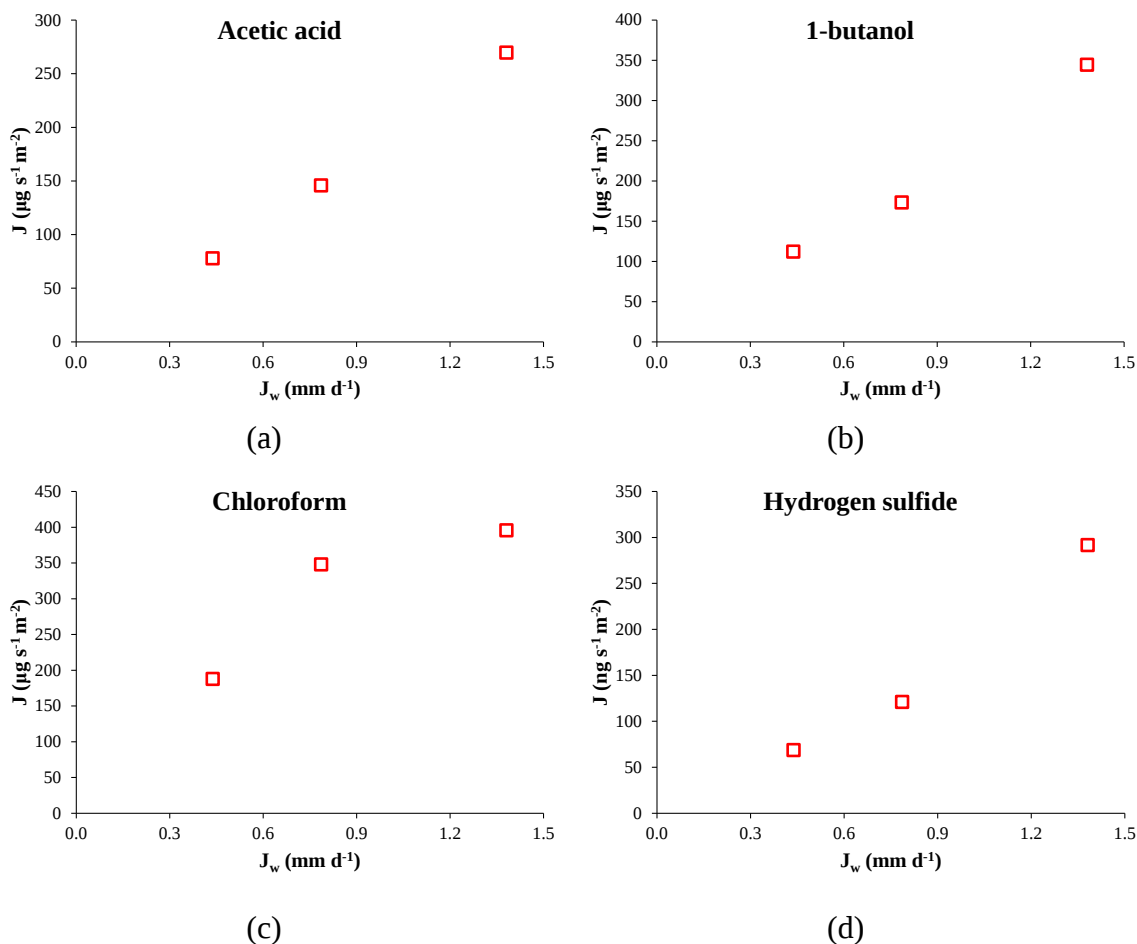


Figure 6.5. Variation of the average volatilisation rates J of (a) acetic acid, (b) 1-butanol, (c) chloroform and (d) hydrogen sulfide with the corresponding average water evaporation rate J_w for dry inlet air.

6.3.2. Mass transfer coefficients inside the flux hood

Table 6.1 presents the average, minimum and maximum of the experimental values of the overall mass transfer coefficient K_L for all compounds, the liquid-film mass transfer coefficient k_L for chloroform and H_2S (liquid phase-controlled volatilisation) and the gas-film mass transfer coefficient k_G for acetic acid (gas phase-controlled volatilisation), obtained by the procedure explained in 6.2.1. The variation of the experimental k_G and k_L with Q is illustrated in Figure 6.6a-c. The mass transfer coefficients generally increased with the sweep air flow rate, reflecting the enhancement of the near-interface turbulence that is expected to occur as Q rises. The only case that appears not to conform to this overall trend is the K_L for 1-butanol at $Q = 2 \text{ L min}^{-1}$. This is probably due to the difficulty of determining the temperature at the water surface, as mentioned before, and the uncertainty in the value of the Henry's law

coefficient K_H (also noticing that this case presented a particularly large difference between minimum and maximum values).

Table 6.1. Experimental mass transfer coefficients.

Compound	Coefficient								
	$K_L (10^{-9} \text{ m s}^{-1})$								
	$Q = 2 \text{ L min}^{-1}$			$Q = 5 \text{ L min}^{-1}$			$Q = 10 \text{ L min}^{-1}$		
	average	min	max	average	min	max	average	min	max
Acetic acid	7.1	5.5	9.1	7.4	6.4	7.9	13.5	12.3	15.3
1-butanol	470.6	183.5	794.0	200.0	185.4	224.7	451.2	447.1	453.3
Chloroform	242.7	154.0	337.3	431.6	364.1	469.5	507.1	434.3	600.4
Hydrogen sulfide	249.2	198.4	300.0	363.4	352.9	374.0	1076.9	825.2	1328.5
	$k_L (10^{-7} \text{ m s}^{-1})$								
	$Q = 2 \text{ L min}^{-1}$			$Q = 5 \text{ L min}^{-1}$			$Q = 10 \text{ L min}^{-1}$		
	average	min	max	average	min	max	average	min	max
Chloroform	2.427	1.540	3.373	4.316	3.641	4.695	5.071	4.343	6.004
Hydrogen sulfide	2.492	1.984	3.000	3.634	3.529	3.740	10.769	8.252	13.285
	$k_G (10^{-3} \text{ m s}^{-1})$								
	$Q = 2 \text{ L min}^{-1}$			$Q = 5 \text{ L min}^{-1}$			$Q = 10 \text{ L min}^{-1}$		
	average	min	max	average	min	max	average	min	max
Acetic acid	1.001	0.802	1.253	1.059	0.945	1.122	2.103	1.808	2.454

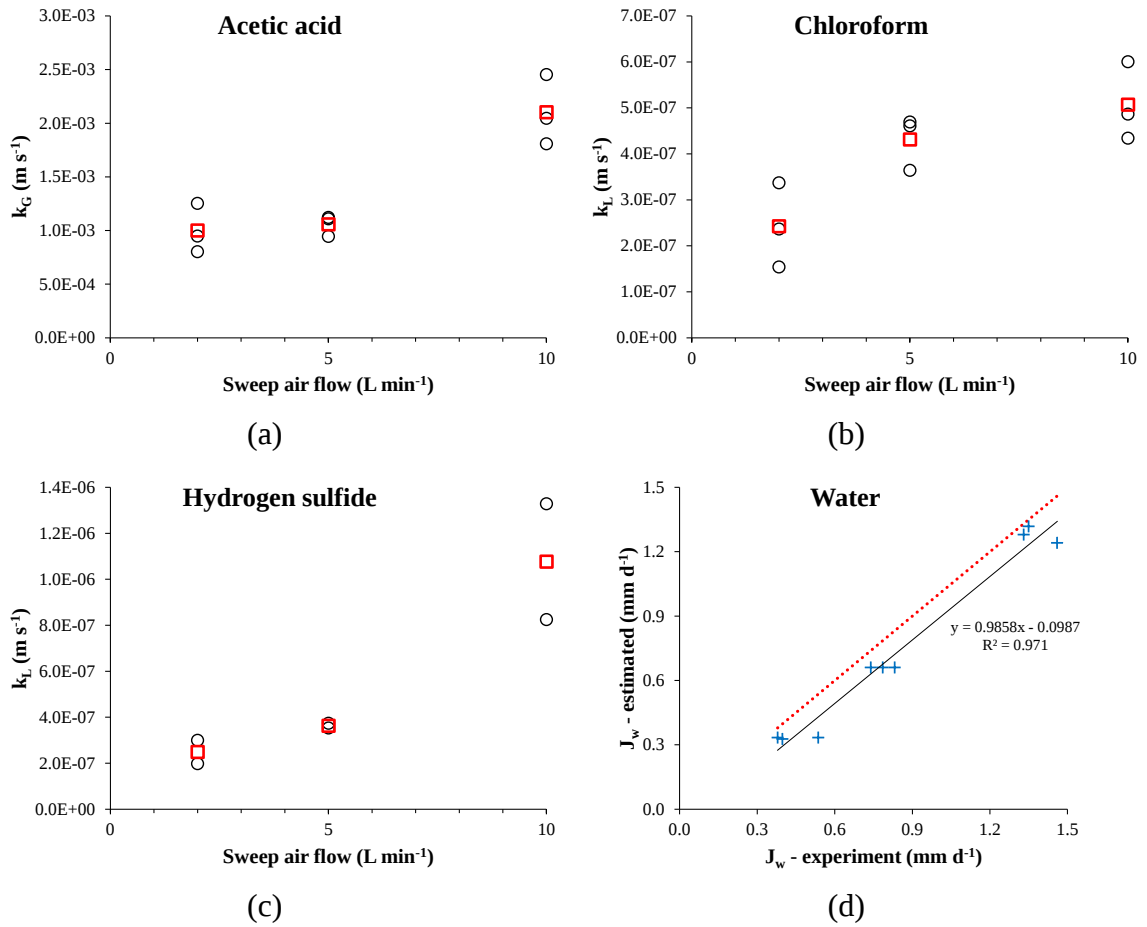


Figure 6.6. Variations with the sweep air flow rate of the experimental (a) gas-film mass transfer coefficient k_G for acetic acid and the liquid-film mass transfer coefficients k_L for (b) chloroform and (c) H₂S inside the US EPA flux hood; and (d) comparison between the experimental water evaporation rate J_w and the J_w estimated by applying Equation (6.5) with k_G for water calculated based on k_G for acetic acid, using Equation (6.3a). In (a)-(c), the black circles represent results of individual experimental runs, and the red squares indicate the respective average at each nominal flow rate; in (d), the red dotted line is the 1:1 line, and the black line is the linear fit to the results (equation shown in the figure).

Despite being feasible in theory (see 6.2.1), the calculation of k_G for water vapour directly from the experimental evaporation rates J_w was not possible in the present circumstances, producing unreasonable values of k_G (some of which negative). This is a result of two factors: again, the imprecision of the measurements of the temperature at the water surface, which, as a consequence, makes the estimate of $C_{G,i}$ not precise; and the apparent offset verified in J_w (see 6.3.1) this would lead to an overestimation of C_G , as per Equation (6.4). For water vapour and other gas phase-controlled compounds, the accumulation in the headspace significantly interferes with the emission rates, as identified before (6.3.1), since the differences between $C_{G,i}$ and C_G (or, alternatively,

between C_L and C_G/K_H) are relatively small. This same fact may also affect the calculation of K_L (or k_G , for water vapour) for such compounds by solving Equations (2.6a) (or (2.2a)), given that the difference $C_L - C_G/K_H$ (or $C_{G,i} - C_G$) will be very sensitive to the uncertainties in the values of C_G and K_H (or $C_{G,i}$ and J_w , for water vapour), which is observed in some of the cases reported herein (K_L for 1-butanol at $Q = 2 \text{ L min}^{-1}$ and k_G for water vapour).

This highlights some of the challenges inherent to the experimental determination of mass transfer coefficients for gas phase-controlled compounds in a mixed-headspace device such as the US EPA flux hood, if the a ratio A/Q is not large enough to avoid significant accumulation in the gas phase. In special, the necessity of appropriate values of K_H and high-precision measurements of the temperature at the water surface is clear, both of which are not always straightforward available. The difficulty of having accurate temperature values at the water surface, preventing the satisfactory calculation of k_G based on the water evaporation rates, was already noted by Parker et al. (2013b) when the water evaporation method was originally devised. The effects of accumulation in the headspace can be minimised by adopting water tanks with smaller surface area; for instance, Parker et al. (2013b) propose the use of Petri dishes as evaporation sources. However, this practice is not suitable for the study of the US EPA flux hood because the mass transfer conditions are not uniform along the hood's footprint, as evidenced by Parker et al. (2013b) and Prata Jr. et al. (2016b). Thus, for the correct assessment of the mass transfer inside the US EPA flux hood, the simulated emission source has to encompass the whole footprint of the flux hood.

In order to verify the accuracy of the k_G values for acetic acid, Equation (6.3a) was applied to estimate k_G for water vapour based on the average experimental k_G of acetic acid at the three sweep air flow rates. The estimated water vapour's k_G is then used in Equation (6.5) to obtain estimates of J_w (considering dry inlet air), which are compared against the experimental J_w in Figure 6.6d. As seen in this figure, the estimated k_G produced J_w values in relatively close agreement with the experimental ones (average relative error of -15.1%) and also correctly represented the pattern of variation of J_w with Q , indicated by the good linear fit with slope close to 1 (black line and equation in Figure 6.6d). The slight underestimation in J_w are consistent with the apparent offset

reported (6.3.1). These results validate the experimental values of k_G for acetic acid and show that they can be used to characterise the magnitude of mass transfer in the gas phase inside the US EPA flux hood, under the studied operational conditions. Furthermore, they support the use of Equation (6.3a) to estimate k_G for other compounds based on the experimental k_G for acetic acid.

Table 6.2 presents experimental values of k_G reported by different authors that used wind tunnel-type devices. Since the compounds used in the studies were not the same, for better comparison, Table 6.2 also includes the expected k_G for each compound in the US EPA flux hood operating with sweep air flow of 5 L min^{-1} (which is the typical operation), estimated using the average k_G for acetic acid in the flux hood found in the present experiments (for $Q = 5 \text{ L min}^{-1}$) and Equation (6.3a). It is interesting to notice that, except for the highest nominal velocity tested by Parker et al. (2008), k_G in the flux hood is of the same order as the respective k_G observed in the wind tunnels, sometimes higher. However, due to the concentration build-up in the flux hood's headspace (which normally is inexistent or very small in wind tunnels), the emission rates measured by the US EPA flux hood may be significantly lower than the emission rates measured by wind tunnels. An assessment of this effect is also shown in Table 6.2, which contains the ratio between the volatilisation rate that can be expected to happen in the wind tunnel (which can be estimated by Equation (2.2a), using the wind tunnel's k_G and considering $C_G \approx 0$) and the volatilisation rate that would take place inside the flux hood (calculated by Equation (6.6b), using the estimated k_G for the compound in the flux hood), considering the same concentration $C_{G,i}$ at the gas-liquid interface. The ratios varied from 1.69 to 19.23, and depend on the compound, the type of wind tunnel and its operational conditions.

Table 6.2. Mass transfer coefficients reported in the literature for wind tunnel devices and comparison with the US EPA flux hood (operating with sweep air flow of 5 L min⁻¹).

Reference	Compound	Nominal velocity in the wind tunnel	k_G (m s ⁻¹)	k_G (m s ⁻¹) in the flux hood ^a	Ratio for J in wind tunnel/flux hood ^b
Bliss et al. (1995)	Ammonia	0.33 m s ⁻¹	1.788×10 ⁻³	1.726×10 ⁻³	3.64
Parker et al. (2008)	Water	0.003 m s ⁻¹	9.167×10 ⁻⁴	2.601×10 ⁻³	1.69
		0.133 m s ⁻¹	1.045×10 ⁻²	2.601×10 ⁻³	19.23
Capelli et al. (2009a)	1-butanol	0.138 m s ⁻¹	7.754×10 ⁻⁴	1.233×10 ⁻³	1.76
		0.6 m s ⁻¹	9.892×10 ⁻⁴	1.233×10 ⁻³	2.24

^a k_G for the same compound, calculated using the experimental k_G for acetic acid in the flux hood found in this research and Equation (6.3a).

^b Ratio between the volatilisation rate that would be measured by the wind tunnel (calculated by Equation (2.2a), using the wind tunnel's k_G and considering $C_G \approx 0$) and the respective rate that would be measured by the US EPA flux hood (calculated by Equation (6.6b), using the estimated k_G for the compound in the flux hood), considering the same $C_{G,i}$.

Regarding the liquid-film mass transfer coefficient k_L , the results for chloroform and H₂S showed that k_L increased with Q , suggesting that the small motions induced in the liquid by the friction of the sweep air flow above (which is expected to be more intense for larger Q) were the main drivers of mass transfer in the liquid side, as anticipated in 6.3.1. Nevertheless, if surface currents are present, the interaction of these currents with the edge of the flux hood will likely dominate the mass transfer in the liquid, as also discussed before. Comparing Figures 6.6b and 6.6c, it can be seen that the proportional changes in k_L with Q did not follow the same pattern for chloroform and H₂S, which can be attributed to unavoidable small losses of these highly volatile compounds that may have occurred during the preparation of the solutions and when the solutions were transferred to the tank. Because such losses would happen in a rather random way, this is consistent with the relatively large difference between minimum and maximum values of k_L observed for these compounds, especially for $Q = 10$ L min⁻¹. However, the results for both chloroform and H₂S agree in terms of the order of magnitude of k_L in the micro environment under the sole influence of the US EPA flux hood, and this can be used for the analysis in following item (6.3.3).

Tests were also performed with acetic acid and chloroform, with $Q = 5$ L min⁻¹, aiming to assess the sensitivity of, respectively, k_G and k_L to changes of humidity in the sweep air flow. With relative humidity of approximately 90% in the inlet air, the average k_G

for acetic acid inside the flux hood was $7.500 \times 10^{-4} \text{ m s}^{-1}$ (minimum $6.050 \times 10^{-4} \text{ m s}^{-1}$, maximum $9.470 \times 10^{-4} \text{ m s}^{-1}$), and the average k_L for chloroform was $4.372 \times 10^{-7} \text{ m s}^{-1}$ (minimum $4.199 \times 10^{-7} \text{ m s}^{-1}$, maximum $4.628 \times 10^{-7} \text{ m s}^{-1}$). Considering a level of significance of 10%, an analysis of variance (ANOVA) indicates that k_G is affected by the humidity in the inlet air (p-value = 0.058), whilst k_L is not (p-value = 0.885). It can be hypothesised that one or both of the following mechanisms account for the slight difference in k_G between the cases with dry and humid inlet air. (i) Being a poorly volatile compound, part of the volatilised acetic acid in the headspace of the chamber may have been absorbed in the little droplets of water that condensed on the flux hood's walls when humid inlet air was employed, leading to an apparent reduction of k_G . (ii) It may be possible that additional turbulence generated by buoyancy due to the difference in density between the lighter, saturated air close to the water surface and the heavier, dry inlet air contribute to the near-interface mass transfer (i.e., to k_G); with humid inlet air, this buoyancy would be greatly reduced, making k_G smaller. It is important to highlight that the volatilisation rates of acetic acid are relatively less sensitive to the change in the sweep air humidity, buffered by the effect of accumulation in the headspace: while the average k_G decreased by 29%, the average J was only 14% smaller.

6.3.3. Relating measurements obtained with the flux hood and modelled field emission rates

By knowing the values of the mass transfer coefficients in the interior of the flux hood, it is possible to estimate the bias in the measured emission rate, compared to the values that could be expected in the field in the absence of the sampling device, especially for compounds with volatilisation controlled by conditions in the gas phase. For simplicity, in the present analysis, the k_G calculated by the volatilisation model proposed by Gostelow et al. (2001) (Equation (2.16)) for passive liquid surfaces is adopted as a proxy for the k_G values in the field, with the friction velocity estimated based on the wind speed at 10 m height (U_{10}) by applying the correlation of Smith (1980) (Equation (2.31)). Figure 6.7a shows k_G for acetic acid estimated by the model for U_{10} varying from 0 to 10 m s^{-1} . For comparison, the respective average k_G inside the US EPA flux hood obtained in our experiments for the sweep air flow rates of 2, 5 and 10 L min^{-1} are

also indicated in Figure 6.7. It is clear that the k_G in the flux hood represent conditions of low wind speeds; more specifically, for the flow rates of 2, 5 and 10 L min⁻¹, the k_G for acetic acid equal the model estimates for $U_{10} = 1.18, 1.25$ and 2.36 m s⁻¹, respectively. Figure 6.7b presents the ratios between the k_G calculated by the model and the experimental k_G in the flux hood, for acetic acid at various U_{10} .

Nevertheless, because of the build-up of concentration in the headspace of the hood (an effect that does not occur for open surfaces in the field), the volatilisation rates inside the flux hood will be lower than the corresponding volatilisation rates in the field, for the same k_G . To illustrate this, Figure 6.7c shows the emission rates J of acetic acid predicted by applying Gostelow et al.'s (2001) model, considering the concentration in the liquid $C_L = 10$ g L⁻¹ and U_{10} ranging from 0 to 10 m s⁻¹. For the same C_L , the volatilisation rates inside the flux hood were estimated by using the experimental k_G together with Equation (6.6b) (considering $C_{G,i} \approx C_L K_H$, which is valid for poorly volatile compounds such as acetic acid) and are indicated by the traced lines in Figure 6.7c. Figure 6.7d presents the ratios between the J calculated by the model for the field and the expected J in the flux hood, for the same concentration C_L of acetic acid at various U_{10} . It is interesting to notice that the emission rates of acetic acid that would be observed in the flux hood operating with $Q = 2, 5$ and 10 L min⁻¹ are equivalent to the field J at $U_{10} = 0.27, 0.51$ and 0.99 m s⁻¹, respectively (the estimates for J and the respective field-to-flux hood ratio in the low wind speed range is shown in detail in Figures 2.7e and f). Such equivalencies for J will change depending on the compound (different k_G).

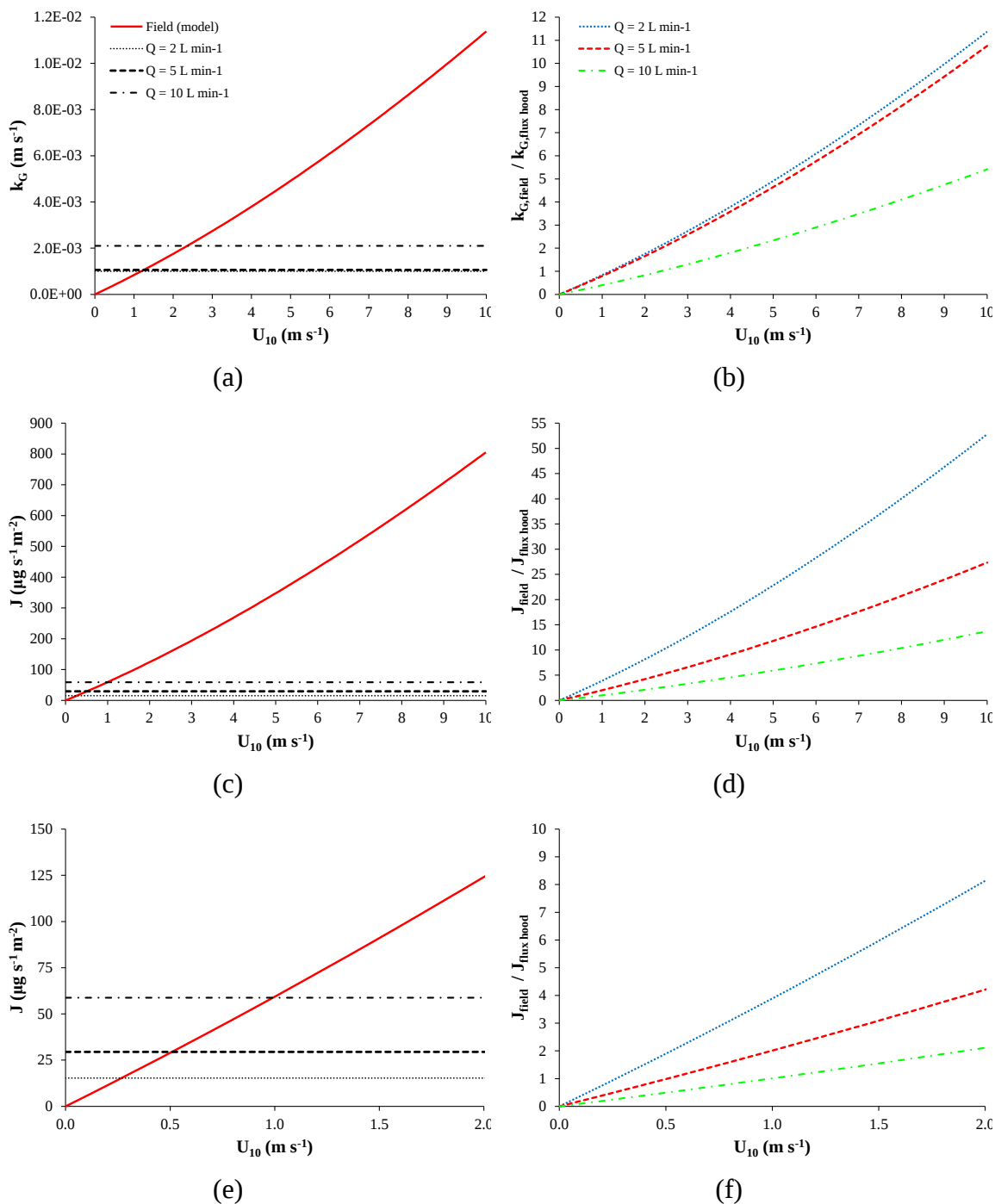


Figure 6.7. Comparison between the mass transfer of acetic acid inside the US EPA flux hood and a modelled field situation (model of Gostelow et al., 2001), for wind speeds at 10 m (U_{10}) varying from 0 to 10 m s^{-1} , showing the values for (a) the gas-film mass transfer coefficient k_G and (c) the emission rates J , and the respective field-to-flux hood ratios (b and d). The low wind speed range of (b) and (d) is shown in detail in (e) and (f). Legend for (a), (c) and (e) in (a), and for (b), (d) and (f) in (b).

The procedure summarised in the previous paragraph allows the emission rates of gas-phase controlled compounds measured with the US EPA flux hood to be scaled (at least in order of magnitude) to field conditions different than the mass transfer conditions

imposed by the micro-environment inside the flux hood. By back-calculating $C_{G,i}$ using Equation (6.6b), it takes into account the effects of the concentration build-up in the hood's headspace, which is a feature not present in other proposed scaling methods such as the water evaporative flux ratio correction factor (Parker et al., 2013b) (see discussion in 6.2.2). The following aspects are important to be observed:

- The flux hood has to present a well-mixed headspace, so that Equation (6.6b) is valid, which is the typical case for the US EPA flux hood; for wind tunnel devices, Equation (2.2a) shall be used instead, requiring that the bulk gas-phase concentration C_G is known.
- Proper recording of the sweep air flow rate Q is necessary for the back-calculation of $C_{G,i}$; this can be done by using calibrated rotameters or in-line electronic flow meters.
- If k_G for the desired compound inside the flux hood is to be determined experimentally, the discussion in sub-section 6.3.2 points out the importance of repetitions and cross-checks in the experiments, to avoid that the k_G retrieved from the experimental results are not significantly affected by the uncertainty in the temperature at the liquid surface and other sources of inaccuracy. Besides, either with k_G determined directly from experiments or calculated based on other compound, it is critical that the operational conditions of the flux hood for which k_G was assessed are as similar as possible to the ones used during the sampling in the field (for instance, same Q , sampling rate and depth of insertion in the liquid); if scums and slick microfilms are present over the liquid surfaces in the field, this may compromise the reproduction of the conditions.
- The accuracy of the scaling approach is directly dependent on the application of a suitable emission model to approximate the field k_G , and this may vary from case to case (see Chapter 3).
- The procedure is applicable for scaling emission rates of individual compounds; if the sample is analysed via dynamic olfactometry to obtain odour emission rates, the calculation is not possible, unless the odour is always dominated by a

single compound (or group of compounds). As highlighted by Hudson and Ayoko (2008b), since the volatilisation rates of different compounds may respond differently to the mass transfer conditions created by the flux hood, the composition of the odour samples may be altered in relation to the emissions in the absence of the hood, leading, in some cases, to non-representative olfactometry results.

Virtually, the analysis developed in this sub-section could also be adapted to compounds with liquid phase-controlled volatilisation, provided that the value of k_L in the area enclosed by the flux hood is known and an appropriate emission model is available to approximate the field situation. However, surface currents are expected to be present in the field (and will vary with the wind speed), and the turbulence arising from the interaction of these currents with the edge of the flux hood will make the mass transfer conditions in the liquid differ from the conditions of the laboratory experiments where the reference k_L for the flux hood is obtained. Moreover, some WWTP units may present bubbling, which can significantly affect the emission rates of more volatile compounds (Grant et al., 2013b). For these reasons, we will refrain from extending the complete analysis to liquid phase-controlled compounds. Nonetheless, as a preliminary comparison, it is worth mentioning that Rhee et al. (2007), performing experiments in a large wind-wave tank, with size and wind conditions that partially approximate the conditions of the liquid surfaces in a wastewater treatment tank, measured k_L of the order 10^{-5} to 10^{-4} m s⁻¹, for compounds with similar Sc_L as chloroform and H₂S, and friction velocities ranging from 0.09 to 0.61 m s⁻¹ (equivalent U_{10} from 3.15 to 15.5 m s⁻¹). This means that the k_L observed inside the US EPA flux hood in the absence of surface currents (results in 6.3.2) are one to more than two orders of magnitude lower than the k_L typical of the field.

7. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1. Conclusions and final remarks

In **Chapter 3**, different theoretical and empirical models for k_G and k_L in passive surfaces in WWTPs were evaluated against relevant experimental data sets. Regarding the gas-film mass transfer coefficient k_G , among the empirical models, the correlation of Gostelow et al. (2001) was the one that resulted in the smallest relative errors; keeping in mind its major limitations (not including the fetch and imposing a proportionality to $Sc_G^{-0.67}$), it figures as a reasonable choice for rapid and simple estimates of k_G . The models of Brutsaert (1975) and Deacon (1977), which are based on the description of the inner part of the turbulent boundary layer over a smooth flat plate, are also interesting alternatives, especially for research purposes, and may constitute conservative choices in the assessment of atmospheric emissions in WWTPs. To be applied for practical purposes, however, these models have to be used together with an appropriate parametrisation of the boundary layer thickness over the studied surface (Equation (3.1) proposed as a preliminary option). Equation (3.2), developed by minimising the errors related to the compiled set of data, generally resulted in the lowest values of k_G ; thus, it may not be the more conservative approach for impact assessment. A very concerning outcome of the evaluation of the emission models is that the model of Mackay and Matsugu (1973), which is the equation utilised in the model WATER9 (endorsed by the US EPA and generally accepted as a regulatory model for the assessment of atmospheric emissions in WWTPs), performed poorly in describing the experimental data set.

With respect to the models for k_L , none was able to satisfactorily explain the behaviour and the scatter observed in the whole experimental data set. Excluding the two suspected biased situations (results from Liss, 1973, and Rhee et al., 2007), among the most commonly used emission models, the WATER9 approach produced the best outcomes, although still with considerably high relative errors. For this same sub-set, we proposed an alternate approach (Equations (3.4) and (3.5)), which presented

considerably improved performance compared to the other models, particularly for longer fetches.

The analysis of different parametrisations for u_* , reported in **Chapter 4**, revealed that, at the short fetches analysed, consistent with the size of liquid surfaces in WWTPs, the three wind drag correlations originally derived for the oceanic case, by Smith (1980), Wu (1980, 1982) and Csanady (1997), tended to systematically overestimate u_* for most of the cases, with the one by Smith (1980) presenting a better performance than the other two. This is the first time that Smith's correlation has been evaluated against experimental data for this range of relatively short fetches, although this correlation has long been adopted for emission modelling at short fetches. In general, the u_* values estimated by the Charnock's relation with coefficient $a = 0.010$ (for $\kappa = 0.4$) were only slightly smaller than the ones resulting from Smith (1980) expression.

The estimation of u_* based on wave-related parameters produced comparatively accurate values of u_* and was able to resemble particular features of the experimental u_* versus U_{10} plot, for a considerable range of the data set (Range D). An approach was devised, combining the use of Charnock's relation and of new, simplified correlations (relating the non-dimensional fetch and the wind drag). For the whole data set, the proposed approach was able to predict u_* with considerably better accuracy, when compared with the other parametrisations evaluated. It was also able to incorporate the influence of the fetch in the wind drag, reflected as some particular features of the variation of u_* with U_{10} .

Chapter 5 presented a sensitivity analysis comparing how different emission models respond to the use of different u_* parametrisations. The analysis shows that the parametrisation of the wind friction via Smith's correlation and Charnock's relation produces very similar values of u_* and, consequently, the resulting mass transfer coefficients (k_G , k_L and K_L) estimated by all the models analysed were also very close. In this sense, for the range of wind speeds evaluated (1.0 to 20.0 m s⁻¹), Smith's correlation and Charnock's relation (taking $a = 0.010$ and $\kappa = 0.4$) can be used interchangeably for practical purposes. The RMS relative differences comparing the results from the models using Smith's correlation or Charnock's relation to the results

from the same models using the parametrisation of u_* were generally small, smoothed by the process of fetch-averaging u_* in the alternative approach. However, larger relative differences, of over 10%, can occur for some combinations of fetch and wind speed. Among those, the maximum differences were found at long fetches and wind speed between 5.3 and 6.5 m s⁻¹, for the model of Mackay and Yeun for k_L (critical for the mass transfer rates of liquid phase and both phase-dominated compounds). This aspect of the model of Mackay and Yeun (1983) is especially important, since this model is adopted, together with Smith's parametrisation of u_* , in the US EPA-endorsed model WATER9 and in the model TOXCHEM+, and has been employed in many scientific studies.

In **Chapter 6**, the mass transfer inside the US EPA flux hood was assessed by means of experiments of water evaporation and volatilisation of different VOCs, covering different behaviours regarding the dominance of the volatilisation process. Supported by a theoretical analysis, the results were processed in order to obtain the gas-film (k_G) and liquid-film (k_L) mass transfer coefficients in the microenvironment created by the flux hood. The VOCs emission rates J and the water evaporation rates J_w generally increased with the sweep air flow rate Q . As expected, at a given Q , J_w was smaller for higher humidity content in the inlet air. Concentration build up in the hood's headspace was found to significantly affect the mass transfer of compounds whose volatilisation is influenced by the gas phase (acetic acid, 1-butanol and water, in this case), but was not relevant for the compounds with liquid phase-controlled volatilisation (chloroform and H₂S), consistently with the theoretical considerations.

The mass transfer coefficients for all compounds inside the flux hood tended to increase with the sweep air flow rate, reflecting the enhancement of the near-interface turbulence that is expected to occur as Q rises. The values of k_G for acetic acid were shown to be accurate and could be converted using Equation (6.3a) so as to satisfactorily estimate water evaporation rates inside the hood. This is the first time that the mass transfer coefficients (k_G and k_L) for different compounds have been systematically assessed inside the US EPA flux hood under typical operational conditions (Prata Jr. et al., 2016b, had previously measured k_L for H₂S with stirring in the liquid phase). The knowledge of the mass transfer coefficients, together with other results reported in

Chapter 6, allowed a clear evaluation of this device and a more informed comparison against other enclosure devices. Comparatively, k_G inside the US EPA flux hood under typical operational conditions was found to be of the same order as the respective k_G reported in the literature for wind tunnel-type devices. However, due to the concentration build-up in the flux hood's headspace (which normally is inexistent or very small in wind tunnels), the emission rates measured by the flux hood may be significantly lower than the emission rates measured by wind tunnels. Furthermore, the present results can be used in support and complementarily to CFD studies involving the US EPA flux hood.

The k_G for acetic acid in the interior of the US EPA flux hood was compared against the k_G calculated by the volatilisation model proposed by Gostelow et al. (2001) for passive liquid surfaces (adopted here as a proxy for the k_G values in WWTPs, in the absence of the sampling device). This establishes an approach for the estimation of the magnitude of the potential bias in the emission rate of gas phase-controlled compounds (in this case, acetic acid) introduced by the placement of the flux hood. The k_G in the US EPA flux hood were shown to represent conditions of low wind speeds: for the flow rates of 2, 5 and 10 L min⁻¹, the k_G for acetic acid equal the model estimates for $U_{10} = 1.18$, 1.25 and 2.36 m s⁻¹, respectively. Nonetheless, because of the concentration build-up in the headspace, J inside the flux hood will be lower than the corresponding emission rates in the field, for the same k_G ; for acetic acid, J observed in the flux hood operating with $Q = 2, 5$ and 10 L min⁻¹ are equivalent to the field J for $U_{10} = 0.27, 0.51$ and 0.99 m s⁻¹, respectively. Therefore, measurements of the emission rate of gas phase-controlled compounds made with the US EPA flux hood can be expected to be underestimated for wind speed conditions higher than those (the greater the wind speed, the greater the bias). The general lines of a procedure were devised in order to scale (at least in order of magnitude) the emission rates of gas-phase controlled compounds measured with the US EPA flux hood to field conditions different than the mass transfer conditions imposed by the micro-environment inside the hood. This procedure is subjected to the restrictions highlighted in 6.3.3.

Since other fields of study such as modelling the fate of chemicals in natural environments also make use of liquid-gas transfer models (e.g., Meng et al., 2008; Qiu et al., 2008; Reese et al., 2008; Kong et al., 2013), it is worth mentioning that the discussion presented here can potentially find broader application, as far as the same ranges of fetch and wind speed are concerned. Moreover, it is important to notice that the emission models discussed here represent simplified situations, and other factors, such as surface films (Broecker et al., 1978), bubbling (Grant et al., 2013b) and influence of atmospheric stability condition, may be present in the field and have the potential to increase the deviations between model predictions and actual emission rates.

7.2. Recommendations for future work

The evaluation of emission models conducted in the present work points out that additional research is required for accomplishing further improvements and validation of mass transfer models for passive liquid surfaces in WWTPs. In especial, the following knowledge gaps are recommended to be addressed:

- Investigations on the evolution of the mass transfer boundary layer over liquid surfaces, in order to elucidate the appropriate dependence of k_G on u_* and Sc_G (if it scales with $Sc_G^{-2/3} \approx Sc_G^{-0.67}$, or follows a more complex relation as expressed in Brutsaert's model);
- Investigations on the influence of microscale breaking on k_G ;
- Models of the type of Equation (3.2) should be further explored;
- And experimental studies are needed to clarify the behaviour of k_L for larger fetches, especially in the range from 40 to 60 m, and its relation to microscale breaking.

In regards to the parametrisation of the friction velocity for short fetches, as liquid surfaces in WWTPs, more experiments are desired in order to continue the study of the

approach proposed in 4.2.4, and further elucidate the behaviour of u_* , in particular, for the following conditions:

- Long fetches and high wind speeds, where macroscale breaking may start to play a more significant role;
- Long fetches and U_{10} between 5.3 and 6.5 m s⁻¹, which corresponds to the liquid surface presenting the “ultrasmooth” condition;
- And situations with stable or unstable atmospheric flow.

Additionally, it is suggested that the scope of the sensitivity analysis be extended, to include the evaluation of how the results of dispersion modelling respond to different emission models and parametrisations of u_* .

Based on the outcomes of the present research, the following recommendations are made concerning future studies with the direct methods and, especially, the use of the US EPA flux hood:

- Continue experiments with different configurations and operational conditions of the US EPA flux hood, including the incorporation of a fan, as in the Australian Standard AS/NZS 4323.4:2009; also, extend the methodological approach to other enclosure devices, including portable wind tunnels;
- Use the experimental results to validate and complement CFD studies of the US EPA flux hood;
- Investigate the ways in which different humidity contents in the inlet air affect the mass transfer of gas phase-controlled compounds;
- Study the liquid-film mass transfer coefficient k_L inside the flux hood in the presence of waves and surface currents;

- And, for field situations, compare emission rates estimated by direct methods (raw measurements and scaled-up values, using the methodology proposed in 6.3.3) against emission rates estimated by indirect methods.

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Appendix A – Testing Brutsaert's and Deacon's models with fetch-averaged u_* and δ_M

The possibility of applying Brutsaert's (1975) and Deacon's (1977) models with fetch-averaged u_* and δ_M to obtain fetch-averaged k_G was verified for the case of the developing turbulent boundary layer over a smooth flat plate approached by a uniform velocity profile. As discussed in 2.2.1.1, for this case, there is a semi-empirical parametrisation for k_G , Equation (2.8), which is valid for Re_X ranging from 2×10^4 to 3×10^5 (Thibodeaux and Scott, 1985). There are also semi-empirical parametrisations for the fetch-averaged u_* and the local momentum boundary layer thickness δ , Equations (A.1) and (A.2), respectively, which are valid for Re_X of order 10^5 to 10^8 (Schlichting, 1968). As in Equation (2.8), $Re_X = XU_0/\nu_G$ is the fetch Reynolds number, being X the plate length (m) (that is, the fetch), U_0 the velocity (m s^{-1}) of the approaching uniform flow and ν_G the kinematic viscosity ($\text{m}^2 \text{s}^{-1}$) of the air (gas phase).

$$\frac{u_*^2}{\frac{1}{2}U_0^2} = 0.074 Re_X^{-1/5} \quad (\text{A.1})$$

$$\frac{\delta}{X} = 0.38 Re_X^{-1/5} \quad (\text{A.2})$$

Considering that, for the situation treated here, the thickness of the mass transfer boundary layer can be reasonably approximated by the thickness of the momentum boundary layer δ , whose local values is given by Equation (A.2), the fetch-averaged δ_M can be calculated by Equation (A.3).

$$\delta_M = \frac{1}{X} \int_0^X \delta dX = \frac{0.38}{1.8} Re_X^{-1/5} \quad (\text{A.3})$$

The results of Equation (2.8) are compared against the results of Brutsaert's and Deacon's models in a Monte Carlo simulation with 10000 combinations of X and U_0 , with X varying from 1.5 to 3.0 m, and U_0 from 0.5 to 3.0 m s^{-1} . These ranges of X and U_0 resulted in Re_X from 4.97×10^4 to 5.96×10^5 , which is close to the range of validity for

Equation (2.8). The kinematic viscosity of air was taken as $\nu_G = 1.51 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (temperature of 20 °C), and the analysis was repeated for two values of Sc_G , 0.61 (water vapour in air at 20 °C) and 2.20 (approximately the upper limit of the typical range in environmental applications). The two models (i.e., Equation (2.10), for Brutsaert’s, or Equation (2.11b), for Deacon’s, together with Equations (2.12) and (2.13)) were applied with: fetch-averaged u_* as obtained from Equation (A.1); reference “measurement” height z_m equal the fetch-averaged δ_M , calculated via Equation (A.3); von Kármán constant 0.4; and turbulent Schmidt number Sc_t equal 0.8.

Table A.1 presents the relative deviations between the results of the models and the respective k_G calculated by Equation (2.8). The similarities between the k_G obtained via both approaches were considerably good throughout the whole range. It has to be noticed that the comparison is made here for the most critical case, that is, the first meters of the developing boundary layer. For longer fetches, the relative change in u_* and δ along X will be smother, thus the impacts of using fetch-averaged u_* and δ_M on the estimation of k_G can be expected to be even less important. Therefore, the analysis developed here indicates that the use of fetch-averaged u_* and δ_M to obtain fetch-averaged k_G does not introduce appreciable systematic errors for the evaluation of the models, especially for $Sc_G = 0.61$, which was the case for the evaluation in 3.2.1.2.

Table A.1. Relative errors between k_G estimated by the models and the respective k_G calculated by Equation (2.8).

Model	$Sc_G = 0.61$		$Sc_G = 2.20$	
	RMS	Extreme	RMS	Extreme
Brutsaert (1975)	4.5%	-4.7%	15.0%	20.2%
Deacon (1977)	7.5%	-7.6%	12.8%	17.9%

Appendix B – Evaluation of additional empirical models for k_L

Among the empirical models, besides the three approaches discussed in sub-section 3.2.2.2 (most commonly used in the context of modelling atmospheric emissions in WWTPs), other models that are frequently cited in the literature were also tested: Lunney et al. (1985); Liss and Merlivat (1986); Wanninkhof (1992); Cole and Caraco (1998); Schwarzenbach et al. (2003); Ro et al. (2007); Wanninkhof et al. (2009); and Vachon and Prairie (2013). The empirical correlations that constitute these additional models are presented in Table B.1. Figure B.1 shows the comparison between the estimated k_L and respective experimental k_L (normalised in the graphs by multiplying by $Sc_L^{1/2}$), and the relative errors (RMS, positive extreme and negative extreme) are summarised in Table B.2, considering the sub-sets A and B, for the additional empirical models tested.

Table B.1. Summary of the additional empirical models to calculate k_L for passive liquid surfaces evaluated. k_L and U_{10} in m s^{-1} unless stated otherwise.

Reference	Conditions	Expression ^a	
Lunney et al. (1985)	$U_{10} < 5 \text{ m s}^{-1}$, all X/H	$k_L = 2.788 \times 10^{-6} \left(\frac{D_L}{D_{L,ether}} \right)^{2/3}$	(B.1a)
	$U_{10} \geq 5 \text{ m s}^{-1}$, $14 \leq X/H \leq 51.2$	$k_L = 2.60 \times 10^{-9} \left(\frac{X}{H} \right) + 1.277 \times 10^{-7} U_{10}^2 \left(\frac{D_L}{D_{L,ether}} \right)^{2/3}$	(B.1b)
	$U_{10} \geq 5 \text{ m s}^{-1}$, $X/H > 51.2$	$k_L = 2.611 \times 10^{-7} U_{10}^2 \left(\frac{D_L}{D_{L,ether}} \right)^{2/3}$	(B.1c)
Liss and Merlivat (1986)	$U_{10} \leq 3.6 \text{ m s}^{-1}$; resulting k_L in cm h^{-1}	$k_L = 0.17 U_{10} \left(\frac{Sc_L}{600} \right)^{-2/3}$	(B.2a)
	$3.6 < U_{10} \leq 13 \text{ m s}^{-1}$; resulting k_L in cm h^{-1}	$k_L = (2.85 U_{10} - 9.65) \left(\frac{Sc_L}{600} \right)^{-1/2}$	(B.2b)
	$U_{10} > 13 \text{ m s}^{-1}$; resulting k_L in cm h^{-1}	$k_L = (5.9 U_{10} - 49.3) \left(\frac{Sc_L}{600} \right)^{-1/2}$	(B.2c)
Wanninkhof (1992)	Resulting k_L in cm h^{-1}	$k_L = 0.31 U_{10}^2 \left(\frac{Sc_L}{660} \right)^{-1/2}$	(B.3)
Cole and Caraco (1998)	Resulting k_L in cm h^{-1}	$k_L = (2.07 + 0.215 U_{10}^{1.7}) \left(\frac{Sc_L}{600} \right)^{-0.67}$	(B.4)
Schwarzenbach et al. (2003)	Resulting k_L in cm s^{-1}	$k_L = 10^{-4} \times (4 + 0.4 U_{10}^2) \left(\frac{D_L}{D_{L,oxygen}} \right)^{-0.57}$	(B.5)

Table B.1 (continued). Summary of the additional empirical models to calculate k_L for passive liquid surfaces evaluated. k_L and U_{10} in m s^{-1} unless stated otherwise.

Reference	Conditions	Expression ^a	
Ro et al. (2007)		$k_L = 170.6 U_{10}^{1.81} Sc_L^{-1/2} \left(\frac{\rho_G}{\rho_L} \right)^{1/2} \times 2.78 \times 10^{-6}$	(B.6)
Wanninkhof et al. (2009)	Resulting k_L in cm h^{-1}	$k_L = (3 + 0.1 U_{10} + 0.064 U_{10}^2 + 0.011 U_{10}^3) \left(\frac{Sc_L}{660} \right)^{-1/2}$	(B.7)
Vachon and Prairie (2013) ^c	X in km; resulting k_L in cm h^{-1}	$k_L = \left[2.13 + 2.18 U_{10} + 0.82 U_{10} \left(\log_{10} X - \frac{1}{\ln(10)} \right) \right] \left(\frac{Sc_L}{600} \right)^{-1/2}$	(B.8)

^a $D_{L,ether}$ is the molecular diffusivity of ethyl ether in water (Lunney et al., 1985, adopt the reference value $D_{L,eter} = 8.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$); $D_{L,oxygen}$ is the molecular diffusivity of oxygen in water (Schwarzenbach et al., 2003, adopt the reference value $D_{L,oxygen} = 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

^b Assuming that k_L scales with $Sc_L^{-1/2}$.

^c Equation (B.8) results from fetch-averaging (integrating in X and dividing by the total fetch) the model of Vachon and Prairie (2013) and assuming that k_L scales with $Sc_L^{-1/2}$.

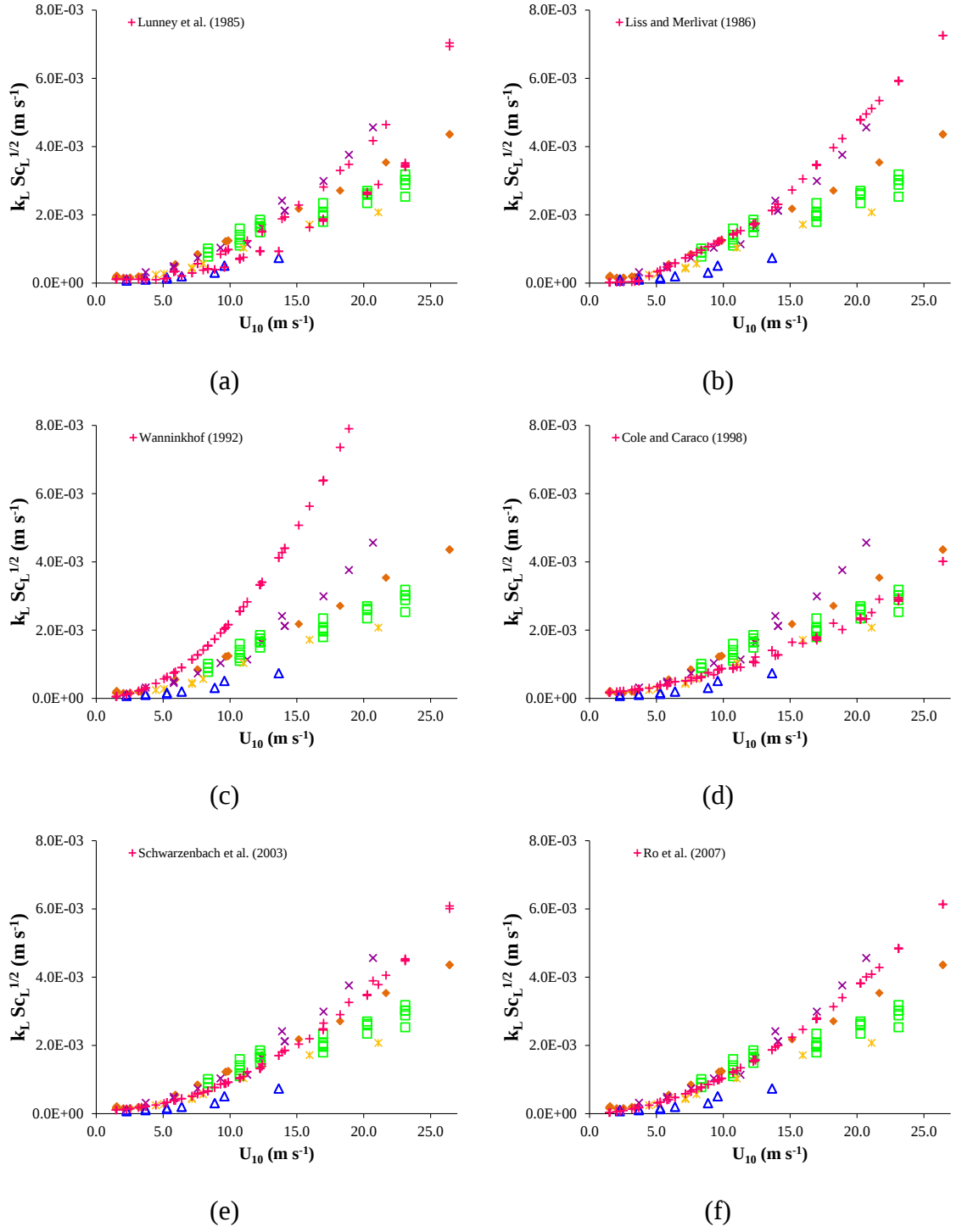


Figure B.1. Experimental $k_L Sc_L^{1/2}$ together with respective values estimated by the additional models evaluated. The sources of the data are identified the same way as in Figure 3.5a, and the models are indicated in each figure.

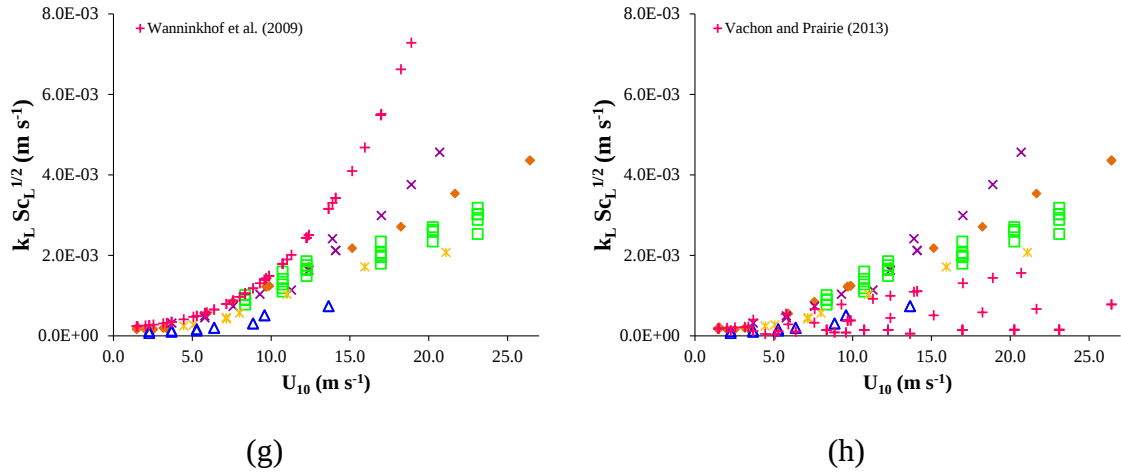


Figure B.1 (continued). Experimental $k_L Sc_L^{1/2}$ together with respective values estimated by the additional models evaluated. The sources of the data are identified the same way as in Figure 3.5a, and the models are indicated in each figure.

Table B.2. Relative errors in k_L estimated by the additional empirical models evaluated.

Model	Sub-set A			Sub-set B		
	RMS	Ext+ ^a	Ext- ^b	RMS	Ext+ ^a	Ext- ^b
Lunney et al. (1985)	32.6%	61.4%	-70.2%	34.1%	61.4%	-70.2%
Liss and Merlivat (1986)	86.1%	252.3%	-91.6%	58.4%	147.3%	-91.6%
Wanninkhof (1992)	203.7%	476.2%	-75.7%	162.7%	376.1%	-75.7%
Cole and Caraco (1998)	62.4%	212.9%	-48.9%	26.9%	44.7%	-48.9%
Schwarzenbach et al. (2003)	54.2%	161.1%	-50.2%	29.4%	82.6%	-50.2%
Ro et al. (2007)	61.7%	183.3%	-83.4%	37.4%	97.5%	-83.4%
Wanninkhof et al. (2009)	170.1%	394.1%	-	148.7%	394.1%	-
Vachon and Prairie (2013)	75.1%	89.7%	-115.5%	77.2%	30.8%	-115.5%

^a Ext+: positive extreme relative error.

^b Ext-: negative extreme relative error.

Appendix C – Sequence for applying the Combined Approach if the wind speed U_Z at an arbitrary height Z is used

- i. Start by applying the Charnock's relation with $\alpha = 0.010$ (for $\kappa = 0.4$) to produce a first guess for u_* .
- ii. Use u_* and X in Equation (4.3c) (LS&W2008 form), to estimate f_p and check for f_p higher than 4 Hz; if $1.3f_p$ is higher than 4 Hz, the value of u_* calculated based on Charnock's relation is the final u_* .
- iii. Else, if the fetch is larger than 50 m, use u_* , Z and U_Z in the logarithmic profile (Equation (2.30)) to obtain an candidate U_{10} ; if the candidate U_{10} is above 13 m s^{-1} , the value of u_* calculated based on Charnock's relation is the final u_* .
- iv. If none of the above occur, apply Equation (4.6a) to estimate z_0^+ and then obtain the corresponding z_0 ; with z_0 , Z and U_Z , calculate a new value for u_* from Equation (2.30); check the difference between the new u_* and the previous one; if the relative difference is larger than the tolerable error, use the new u_* back in Equation (4.6a) and repeat this procedure until convergence is reached; after convergence, use Equation (2.30) to obtain U_{10} ; if U_{10} is not between 5.3 m s^{-1} and 6.5 m s^{-1} , the calculated u_* is the final value.
- v. If U_{10} is between 5.3 m s^{-1} and 6.5 m s^{-1} , use Equation (4.7) together with the values of Z and U_Z in the logarithmic profile (Equation (2.30)), iterating to obtain simultaneously u_* and a refined value of U_{10} .

In step (v), Equation (4.8) can be used instead of Equation (4.7), following a procedure analogous to step (iii), with practically equivalent performance.

Appendix D – Sensitivity analysis of the film-specific mass transfer coefficients

Liquid phase-controlled compound – H₂S

Table D.1. Relative differences in the value of k_G for H₂S estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (k_G^{Sm}), Charnock's relation (k_G^{Ch}) and the Combined Approach (k_G^{CA}).

Emission model	Error statistics	$\frac{k_G^{Ch} - k_G^{Sm}}{k_G^{Sm}}$	$\frac{k_G^{Ch} - k_G^{CA}}{k_G^{CA}}$	$\frac{k_G^{Sm} - k_G^{CA}}{k_G^{CA}}$
Mackay and Yeun (1983)	RMS:	1.57%	4.02%	4.72%
	Positive extreme:	1.70%	14.79%	12.94%
	Negative extreme:	-4.08%	-2.97%	-4.58%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.69%	3.91%	4.60%
	Positive extreme:	1.73%	15.39%	13.48%
	Negative extreme:	-6.65%	-2.96%	-4.57%

Table D.2. Relative differences in the value of k_L for H₂S estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (k_L^{Sm}), Charnock's relation (k_L^{Ch}) and the Combined Approach (k_L^{CA}).

Emission model	Error statistics	$\frac{k_L^{Ch} - k_L^{Sm}}{k_L^{Sm}}$	$\frac{k_L^{Ch} - k_L^{CA}}{k_L^{CA}}$	$\frac{k_L^{Sm} - k_L^{CA}}{k_L^{CA}}$
Mackay and Yeun (1983)	RMS:	2.29%	6.01%	5.96%
	Positive extreme:	3.94%	36.72%	31.75%
	Negative extreme:	-3.06%	-6.69%	-10.21%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%

Gas phase-controlled compound – butyric acid

Table D.3. Relative differences in the value of k_G for butyric acid estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (k_G^{sm}), Charnock's relation (k_G^{ch}) and the Combined Approach (k_G^{CA}).

Emission model	Error statistics	$\frac{k_G^{ch} - k_G^{sm}}{k_G^{sm}}$	$\frac{k_G^{ch} - k_G^{CA}}{k_G^{CA}}$	$\frac{k_G^{sm} - k_G^{CA}}{k_G^{CA}}$
Mackay and Yeun (1983)	RMS:	1.50%	3.91%	4.60%
	Positive extreme:	1.61%	13.85%	12.42%
	Negative extreme:	-3.29%	-2.83%	-4.37%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.73%	3.99%	4.69%
	Positive extreme:	1.76%	15.74%	13.78%
	Negative extreme:	-6.84%	-3.03%	-4.67%

Table D.4. Relative differences in the value of k_L for butyric acid estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (k_L^{sm}), Charnock's relation (k_L^{ch}) and the Combined Approach (k_L^{CA}).

Emission model	Error statistics	$\frac{k_L^{ch} - k_L^{sm}}{k_L^{sm}}$	$\frac{k_L^{ch} - k_L^{CA}}{k_L^{CA}}$	$\frac{k_L^{sm} - k_L^{CA}}{k_L^{CA}}$
Mackay and Yeun (1983)	RMS:	2.20%	5.88%	5.84%
	Positive extreme:	3.85%	35.08%	30.32%
	Negative extreme:	-3.05%	-6.56%	-10.01%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%

Both phase-controlled compound – 2-MIB

Table D.5. Relative differences in the value of k_G for 2-MIB estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (k_G^{sm}), Charnock's relation (k_G^{ch}) and the Combined Approach (k_G^{CA}).

Emission model	Error statistics	$\frac{k_G^{ch} - k_G^{sm}}{k_G^{sm}}$	$\frac{k_G^{ch} - k_G^{CA}}{k_G^{CA}}$	$\frac{k_G^{sm} - k_G^{CA}}{k_G^{CA}}$
Mackay and Yeun (1983)	RMS:	1.44%	3.81%	4.50%
	Positive extreme:	1.55%	13.11%	12.27%
	Negative extreme:	-2.94%	-2.73%	-4.20%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.75%	4.03%	4.74%
	Positive extreme:	1.78%	15.94%	13.95%
	Negative extreme:	-6.94%	-3.07%	-4.73%

Table D.6. Relative differences in the value of k_L for 2-MIB estimated by different emission models, comparing the use of three u_* parametrisations: Smith's correlation (k_L^{sm}), Charnock's relation (k_L^{ch}) and the Combined Approach (k_L^{CA}).

Emission model	Error statistics	$\frac{k_L^{ch} - k_L^{sm}}{k_L^{sm}}$	$\frac{k_L^{ch} - k_L^{CA}}{k_L^{CA}}$	$\frac{k_L^{sm} - k_L^{CA}}{k_L^{CA}}$
Mackay and Yeun (1983)	RMS:	2.16%	5.79%	5.77%
	Positive extreme:	3.78%	33.92%	29.32%
	Negative extreme:	-3.04%	-6.47%	-9.86%
Gostelow et al. (2001)	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%
Alternative Approach	RMS:	1.85%	4.27%	5.02%
	Positive extreme:	1.89%	16.95%	14.83%
	Negative extreme:	-7.38%	-3.25%	-5.02%