

## Predicting Evaporation Rates from Pools

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A number of simplified approaches, based on semi-empirical models and algebraic formulas, often derived from the correlation of experimental data, are available to predict the evaporation rate of chemicals from pools. In this work they are compared, based on their performances in estimating the evaporation rates determined in some sets of experiments reported in the literature, involving different chemicals, pool geometries, wind velocities, etc. Generally, the models predict correctly the data used in the fitting to determine their own parameters, but most of them fail when applied to other data sets. No model appear capable of predicting all the available sets of literature data with errors within  $\pm 30\%$ : nevertheless, some models application guidelines can be derived. In particular, the model of Heymes et al. (2013), provides reasonable estimates of the evaporation rates of a variety of compounds in rather different operating conditions, for wind speed exceeding 1 m/s, while the simple model of Mackay and Wesembeeck (2014) should be preferred in the absence of ventilation. Other models, such as those of Hummel et al. (1996), Stiver and Mackay (1996) and EPA (1999) can be applied within proper intervals of wind speed, molecular weight and vapour pressure of the chemical.

### 1. Introduction

The knowledge of the evaporation rates of liquids from pools is important in order to properly estimate the consequences possibly associated to the generated vapour cloud, which may include the ignition of flammable vapours (giving rise to a flash fire, or to a VCE) and/or the dispersion of a toxic cloud. The evaporation rate depends on the heat exchange rate of the liquid with the surrounding environment and on the diffusion: the former is more important for liquids with boiling temperature below the ambient one, and the latter in the more common situation of liquids below their normal boiling point, where the vapour pressure of the liquid, its diffusion rate and air velocity are the main variables involved.

The rigorous study of the evaporation of a liquid from a pool will require to solve the proper fluid dynamics equations (Navier-Stoke, Euler, etc.), which can be done using CFD (Computational Fluid Dynamics) techniques: this task is computationally demanding and time consuming. A more rapid, simplified, approach, is based on semi-empirical models and algebraic formulas, often derived from the correlation of experimental data, the fit of which allows to calculate the parameters of the model. Literature data sets refer to different chemicals and ranges of experimental conditions (pool geometry, wind velocity, temperature, etc.) and, in some cases, the values of some relevant variables are not given. Unfortunately, when applying different simplified models to the same liquid pool, rather different evaporation rates are estimated, and this poses the problem of choosing the most reliable approach for the case under exam. In the present work a number of existing simplified pool evaporation models have been tested against the available sets of experimental data, in order to give some guidelines about the ranges where they are capable to provide reliable predictions.

### 2. Simplified models of evaporation rates from pools

In the present section some simplified models for estimating the evaporation rates from pools are very briefly recalled: for all details reference should be done to the respective original papers.

The "Yellow Book" (Van den Bosch and Weterings, 2005) gives the following expression of the evaporation flow, based on heat balance and mass transfer equations:

$$E = k_m \cdot \frac{P_v(T_{ps}) \cdot M_i}{R \cdot T_{ps}} \quad (1)$$

where E is the evaporation rate (kg/m<sup>2</sup>·s), k<sub>m</sub> the mass transfer coefficient (m/s), P<sub>v</sub> the vapour pressure of the chemical (Pa), T<sub>ps</sub> the temperature of the pool surface (K), M<sub>i</sub> the molecular weight of the chemical (kg/kmol), and R the gas constant (m<sup>3</sup>·Pa/K·kmol).

The mass transfer coefficient can be derived from the knowledge of Sherwood number, Sh:

$$Sh = \frac{k_m \cdot L_p}{D_v} \quad (2)$$

where L<sub>p</sub> is the length of the pool along wind direction (m) and D<sub>v</sub> (m<sup>2</sup>/s) is the diffusion coefficient of the vapour in air.

Some expressions allow to calculating Sh as a function of the Schmidt (Sc) and Reynolds (Re) numbers, respectively:

$$Sc = \frac{\mu_a}{\rho_a \cdot D_v} \quad (3)$$

$$Re = \frac{\rho_a \cdot u_w \cdot L_p}{\mu_a} \quad (4)$$

where ρ<sub>a</sub> (kg/m<sup>3</sup>) and μ<sub>a</sub> (Pa·s) are the density and the viscosity of the air, respectively, and u<sub>w</sub> is the wind velocity (m/s), usually measured at the standard height of 10 m.

A number of different expressions have been proposed to relate Sh to the variables of interest. For example, Bennett and Myers (1974) report the following expressions:

$$\text{laminar flow} \quad Sh = 0.66 \cdot Re^{0.5} \cdot Sc^{0.33} \quad (5)$$

$$\text{turbulent flow} \quad Sh = 0.0365 \cdot Re^{0.8} \cdot Sc^{0.5} \quad (6)$$

Different values of the exponents of the dimensionless numbers, obtained from the fitting of experimental data concerning evaporation from pools have been also suggested, as reported in Eq. (7) (Raj and Morris, 1987) and Eq. (8) (Heymes et al., 2013):

$$Sh = 0.037 \cdot (Re^{0.8} - 15500) \cdot Sc^{0.33} \quad (7)$$

$$Sh = 0.145 \cdot Re^{0.69} \cdot Sc^{0.87} \quad (8)$$

In other cases, specific correlations have been proposed to directly estimate k<sub>m</sub>, such as that of Mackay and Matsugu (1973):

$$k_m = 0.004786 \cdot u_w^{0.78} \cdot D_p^{-0.11} \cdot Sc^{0.67} \quad (9)$$

where D<sub>p</sub> is the diameter of the pool (m), and that, very basic, of Stiver and Mackay (1996), which, however, is not specific for liquid pools exposed to an air stream (Barry, 2005):

$$k_m = 0.000882 \cdot u_w \quad (10)$$

Other more simplified expressions can be used to directly predict the evaporation rate, such as Eq.(11) (Hummel et al., 1996) and Eq. (12) (EPA, 1999):

$$E = 1.47 \cdot 10^{-11} \cdot M_i \cdot P_v \cdot u_w^{0.625} \quad (11)$$

$$E_{eng} = 0.28 \cdot v_{w,eng}^{0.78} \cdot \frac{M_i^{0.667} \cdot P_{v,eng}}{R_{eng} \cdot T_{A,eng}} \quad (12)$$

In Eq. (12) the units are as follows: evaporative flux E<sub>eng</sub> (lb/ft<sup>2</sup>·min), wind speed v<sub>w,eng</sub> (ft/min), vapor pressure of the liquid P<sub>v,eng</sub> (torr), ideal gas constant R<sub>eng</sub> (ft·lb/lbmol·°R), ambient temperature T<sub>A,eng</sub> (°R).

Finally, the simple one-parameter Eq. (13) (Mackay and van Wesenbeeck, 2014) has been proposed for quiescent liquid pools:

$$E = 4.07 \cdot 10^{-10} \cdot M_i \cdot P_v \quad (13)$$

It has to be remarked that the equations listed above do not pretend to cover all the simplified approaches present in the literature; nonetheless they are representative of most of the more commonly adopted models.

### 3. Experimental data on evaporation rates from pools

The sets of available experimental data are not very abundant and, in some cases, the information does not cover all the variables appearing in the simplified expressions.

A first set of data (Kawamura and Mackay, 1987) concerns seven volatile liquids: experiments were carried out in circular pans, 460 mm in diameter, containing 50 mm of liquid, at temperature ranging from 23 to 31°C. The wind velocity is available elsewhere (Fernandez et al., 2012), for 4 experiments involving three different chemicals (n-pentane, n-hexane, toluene): its values were in the range 2.65-5.42 m/s.

Brighton (1990) reports the results of 12 experiments of Hankinson and Murphy on evaporation of n-butane, at temperatures below its boiling point and in the range 275-291 K, from a 1.22 m x 1.22 m pool, at wind velocity in the range 0.5-5.5 m/s, measured at two different heights (0.3 and 9.15 m).

Hummel et al. (1996) report the results of 37 experiments of Braun and Caplan, concerning 13 different chemicals (aliphatic and aromatic compounds, alcohols and ketones) from a pan 25 mm deep by 140 mm square. Pool temperature ranged from 4.4 to 48.9°C, and wind speed from 0.51 to 7.62 m/s; no information is given about air temperature.

Heymes et al. (2013) report data concerning the evaporation rates of some volatile organic compounds (2-propanol, 1-hexene, propionaldehyde, acetone) and water, from a pool 228 mm (length) x 190 mm (width) x 12 mm (depth), at temperatures in the range 271-295 K and wind velocity varying from 1.6 to 4 m/s. The paper reports the evaporation rates in graphs as mass evaporated vs. time: after an initial period, the slope of the curve remains constant, giving the value of the evaporation rate. The total number of experiments is 9, and the values of the evaporation rates derived from the data are reported in the work of Cirocchi (2007).

Mackay and van Wesenbeeck (2014) reported evaporation rates of 51 compounds, at 25°C under quiescent conditions, from a filter paper disk 90 mm in diameter, covered by a liquid film of approximately 0.1 mm: this set of data is different from all the others, since the experiments were performed in absence of ventilation. For this data set, only the experiments referring to 10 compounds, which appear also in one of the other data sets, were considered in order to test the model predictions.

The overall number of experiments of the above data sets is 73.

### 4. Comparison of models prediction and experimental data

The 9 models listed in Section 2 were applied to estimate the values of evaporation rate obtained from the experiments: this required to accurately calculate some physical properties of the air and of the chemicals, properly taking into account their dependence on the temperature. Fuller correlation (Fuller et al., 1966) was used to estimate diffusion coefficients of the vapours in air, and literature data (Green and Perry, 2008) were used for air density and viscosity as a function of the temperature.

Where some relevant data needed to apply the models (namely, ambient temperature and wind velocity) were not reported, the following hypotheses were assumed. The data of Braun and Caplan (Hummel, 1996) were simulated at different values of the ambient temperature (equal to the pool temperature, or constant, at 288.15, 293.15 and 298.15 °C). The influence of this parameter (which affects the air physical properties) on the model prediction was found to be negligible, due to its limited range of variation: the graphs refer to an ambient temperature of 298.15°C.

For the data set of Mackay and van Wesenbeeck, where ventilation was absent, an arbitrary low value of wind velocity (0.005 m/s) was assumed in order to apply the models requiring the knowledge of this parameter.

Based on the Re values, in all cases the flow regime is turbulent (Re > 10,000), with the only exception of the set of Mackay and van Wesenbeeck (2014) where the flow is laminar. Nevertheless, both Eq. (5) and Eq. (6) were tested against all the available experimental data; the former is expected to provide more accurate predictions in the case of laminar flow and the latter in the case of turbulent flow.

When applying Eq. (7), positive values of the evaporation rate can be obtained only for Re > 173000, which occurs only for most data of Kawamura and Mackay (1987); the predictions of this model (Raj and Morris, 1987) were not reported in the graphs when E<sub>v</sub> values were lower than 0.

Figure 1 shows the trend of the calculated vs. experimental values of the evaporation rate, for all the considered experimental data sets and for all the models reported in Eqs. (5-13): the dotted lines define the zone where the predictions lie within  $\pm 30\%$  of the experimental values.

It can be noticed that model predictions are very scattered, and that most of the tested equations appear to predict evaporation rates remarkably lower than the experimental ones, especially in the low evaporation rate region. Moreover, none of the tested models is capable of predicting the experimental evaporation rates with an error within 30% in the whole range of values of the data sets.

Among the expressions making use of the Sherwood number, both Eq. (5) and Eq. (6), which are not specific for this type of phenomenon, heavily underestimate the evaporation rate; it is rather surprising that, even if most data refer to turbulent flow conditions, the values calculated using Eq. (5), which refers to laminar flow, are slightly closer to the experimental ones than those calculated using Eq. (6), which refers to turbulent flow. Eq. (7), which contains parameters derived from the fitting of some experimental data, also underestimates the (few) data giving rise to very high Re numbers to which it could be applied. Finally, Eq. (8) seems to give the best estimates among all the tested models, both at low and at high evaporation rates, and just in a few cases the difference between calculated and experimental data exceeded  $\pm 30\%$ .

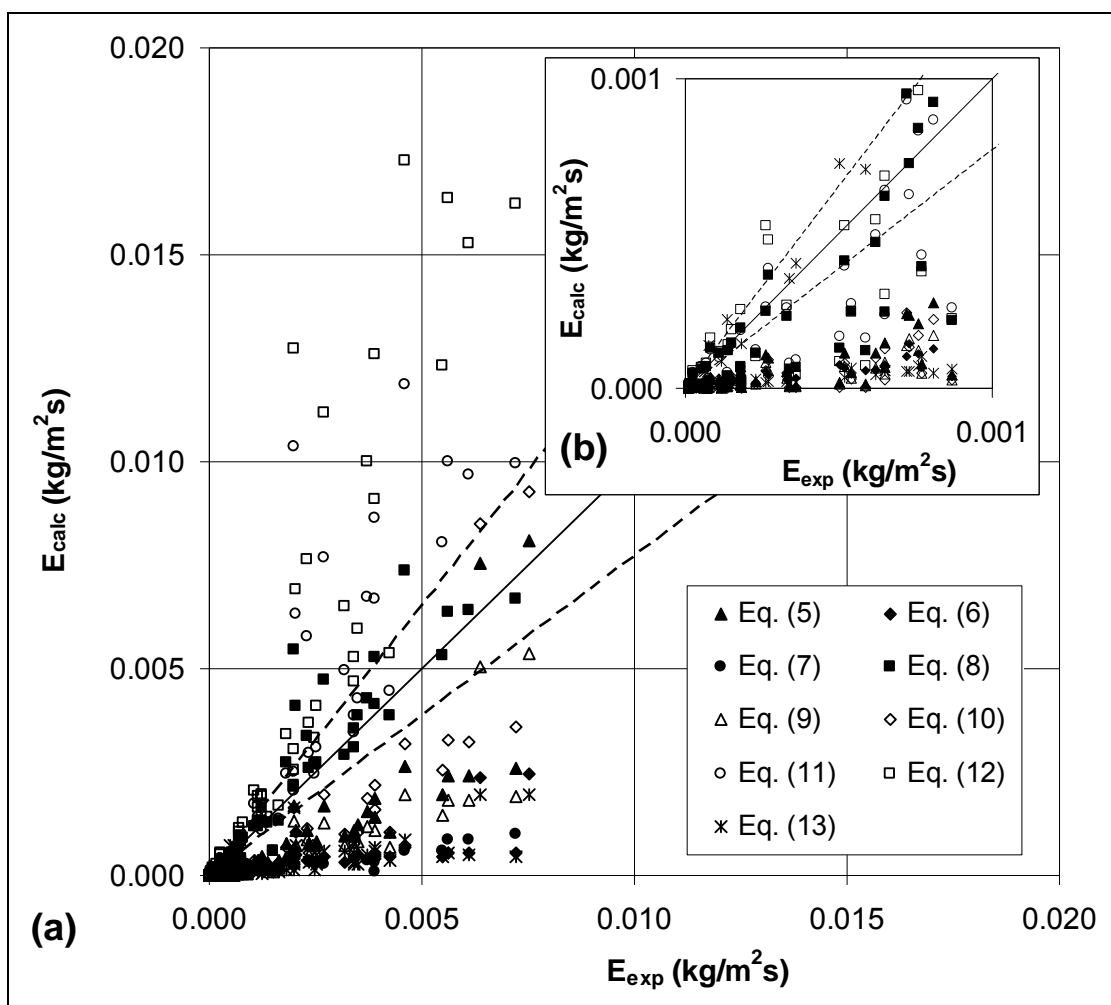


Figure 1: Calculated vs. experimental values of the evaporation rate: a) all data; b) enlarged scale for evaporation rates lower than  $0.001 \text{ kg/m}^2 \text{ s}$ .

Eqs. (9) and Eq. (10), which provide expressions for the mass transfer coefficient, on an average, appear to inadequately describe the phenomenon: despite its more complex dependence on the involved variables, Eq. (9) gives worse estimates with respect to Eq. (10), the former underestimating and the latter overestimating the experimental evaporation rates.

Eq.(11), which directly predicts the evaporation rate, accurately estimate the data belonging to the set of Braun and Caplan (Hummel, 1996) which, indeed, were used to derive its parameters, but fails with the other data sets, especially with that reported by Brighton (1990). The results obtained applying Eq. (12), which also directly predicts the evaporation rate, are partially scattered, and it greatly overestimates the evaporation rates in the high values range. Finally, Eq. (13), which does not include any influence of wind velocity, gives acceptable predictions in the very low range of evaporation rates, underestimating the phenomenon at higher rates: anyway, it seems remarkable that the differences between calculated and experimental data, at rather high wind velocity, are similar to those obtained applying more complex equations.

## 5. Discussion

Based on the comparison reported above, only the model by Heymes et al. (2013), Eq. (8), appears capable of estimating rather reasonably the evaporation rates for all the available experimental data sets. However, taking into account that the phenomenon is influenced by variables related to the ambient (wind velocity), the chemical (molecular weight) and their interactions (vapour pressure, which depends on the temperature and on the chemical), further investigation was devoted to assess whether some of the proposed models are capable of providing better estimates than others in some specific ranges of these variables.

At very low wind velocity ( $u_w < 0.6$  m/s) all models generally underestimate the evaporation rate: Eq. (13) gives good predictions in the absence of ventilation, but underestimates the data at a wind speed of 0.51 m/s ( $E$  values above  $0.0005$  kg/m<sup>2</sup>s in Figure 2a). Eq. (11), which is based also on the fitting of such data, still underestimates the evaporation rate, similarly to Eq. (8) and Eq. (12); the other equations provide very poor estimates. By increasing the wind velocity above 1 m/s, Eq. (8) provides good estimates (as shown in Figure 2b), followed by Eq. (11) and Eq. (12) which both overestimate the intensity of the phenomenon, and by Eq. (10), which underestimates it (see Figure 1a, for comparison); for wind velocity above 3 m/s the predictions of Eq. (10) become closer to the experimental data with respect to those of Eq. (11) and Eq. (12). It has to be remarked that the exponent of the wind velocity in Eqs. (8, 11-12) ranges between 0.62 and 0.78, while in Eq. (10) is higher, and equal to 1.

The evaporation rate linearly depends on the vapour pressure of the chemical in all models: the experimental values of vapour pressure are in the range 0.013 - 69 kPa. At low vapour pressure ( $P_v < 0.7$  kPa), Eq. (8), Eq. (11) and Eq. (12) provide similar reliable estimates; by increasing the vapour pressure, Eq. (8) still provides reliable predictions, while Eq. (11) and, especially, Eq. (12) overestimate the evaporation rates, progressively becoming less accurate; Eq. (10), always underestimates the evaporation rates, but its accuracy increases with increasing the vapour pressure of the chemical.

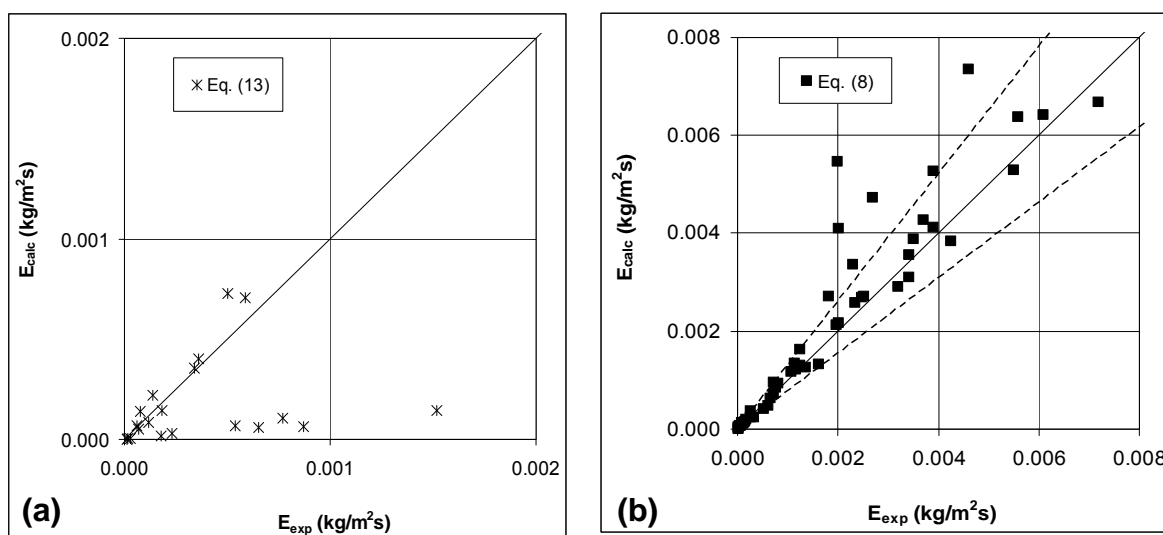


Figure 2: Calculated vs. experimental value of the evaporation rate: a) at wind velocity below 1 m/s; b) at wind velocity above 1 m/s.

For the two chemicals with molecular weight lower than or comparable with that of air (29 kg/kmol), i.e. water and methanol, Eq. (8) and Eq. (11) give a reasonable fitting of the data, and this parameter does not appear to

present a remarkable influence, also for chemicals with  $M_i$  in the range 58-72 kg/kmol, and above 78 kg/kmol. In both Eq. (8) and Eq. (11) the molecular weight of the chemical appears with an exponent equal to 1.

In conclusion, it is confirmed that the phenomenon is mainly ruled by chemical vapour pressure and by wind velocity: as might be expected, at very low wind velocity, this parameter shows a limited influence, and the evaporation rate is proportional to the vapour pressure of the chemical; by increasing wind velocity, the influence of this variables increases, too, according to an exponent slightly lower than unity.

## 6. Conclusions

A number of different approaches and equations are reported to predict the evaporation rates of chemicals from liquid pools. Those derived from generalized approaches, with no adjustable parameter obtained from the fitting of experimental data, have demonstrated to be inadequate, but also those including fitting parameters, in most cases, correctly predict only the experimental data used for this fitting. Wind velocity proved to be the main variable which might be used as a key parameter to properly choose the most adequate simplified model capable of giving reasonable estimates of the evaporation rates under the adopted ambient conditions: in the absence of ventilation (for example, indoor), the very simple model proposed by Mackay and van Wesembeeck (2014) proved to be the most reliable; when wind velocity exceeds 1 m/s the model reported by Heymes et al. (2013) provides the best estimates.

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