National Institute for Public Health
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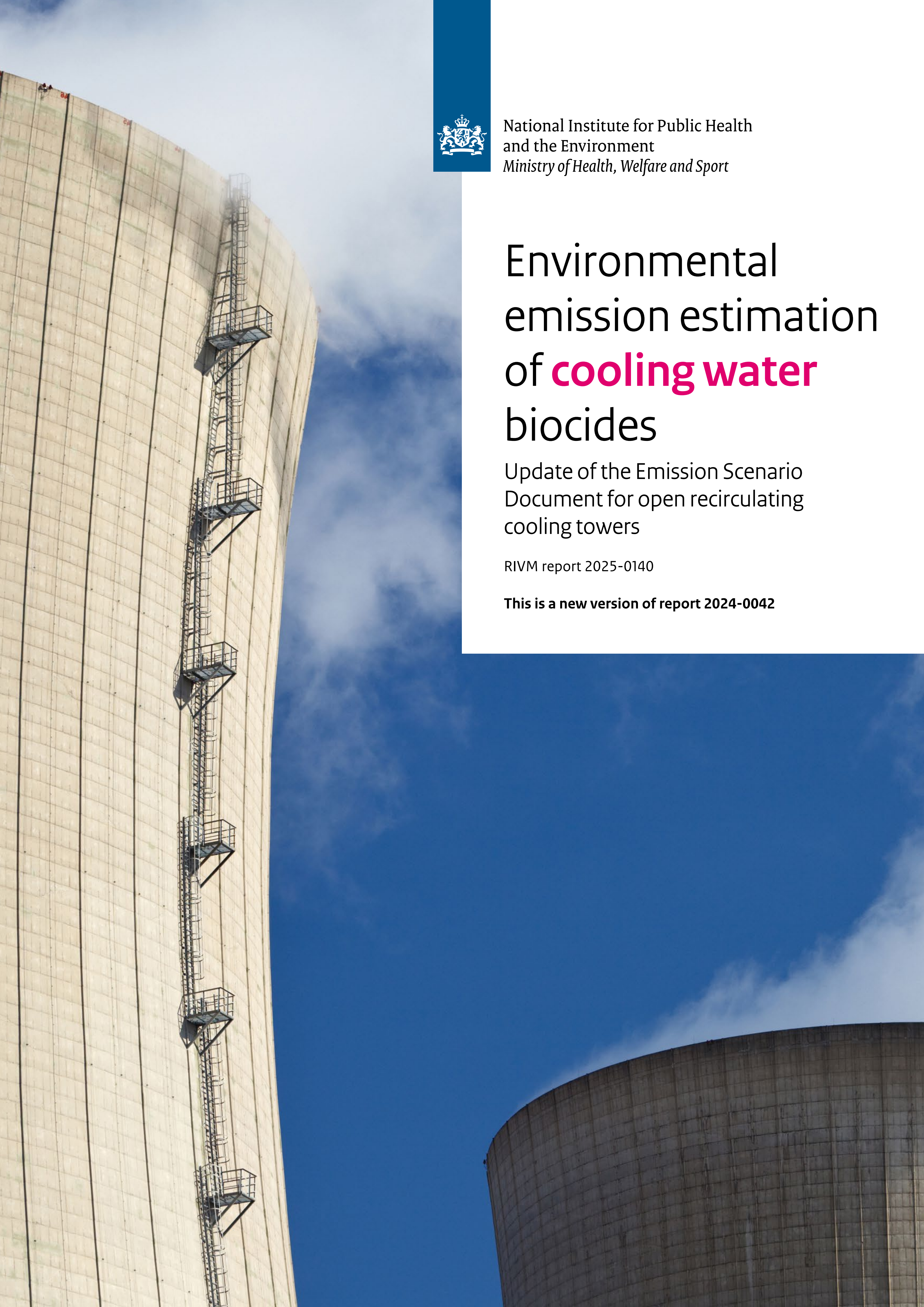
Environmental emission estimation of cooling water biocides

Update of the Emission Scenario Document for open recirculating cooling towers

RIVM report 2025-0140

This is a new version of report 2024-0042



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Colophon

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Synopsis

Environmental emissions of cooling water biocides

Update of the Emission Scenario Document for open recirculating cooling systems

Certain types of industry and power plants use cooling water. The heated cooling water is cooled down in cooling towers and then reused. Organisms such as bacteria and algae may grow in the cooling tower and heat exchangers and hamper the functioning of the installations. To prevent this, the cooling water is treated with biocides. A biocidal product contains one or more active ingredients that are intended to destroy undesired organisms.

Within the EU, biocidal products can be used or traded only if they have been evaluated with regard to their effects on and risks for humans, animals, and the environment. In the Netherlands, the Board for the Authorisation of Plant Protection Products and Biocides (Ctgb) evaluates biocidal products. As part of the evaluation, the Ctgb calculates the amount of active ingredient that ends up in the environment following a certain use. This is carried out by means of emission scenario documents.

RIVM proposes some changes to the emission scenario for the use of biocides in cooling towers. The proposed changes facilitate a more precise calculation of the amount of biocide that will volatilise from the cooling tower to the atmosphere. The changes will improve the estimation of how much active ingredient ends up in the environment and whether this can be harmful.

The active ingredient can end up in the environment via discharged cooling water, but it can also be emitted to air. Emission to air occurs via two routes: via droplets of cooling water that are dragged along by the air flow in the cooling tower, and via volatilisation from the cooling water into the air.

Up to now, the volatilisation was calculated based on a single value. With the proposed changes, the volatilisation can be calculated for each substance separately. The degree of volatilisation depends on certain substance properties.

The proposed changes were prompted by questions raised by the Ctgb and by biocides experts from EU Member States. The proposals have been presented to these experts. The European Chemicals Agency (ECHA) still needs to include them in the calculation method to make them available to all EU Member States.

Keywords: cooling tower, biocide, volatilisation, stripping, mass transfer, emission, air, surface water, modelling

Publiekssamenvatting

Emissieschatting van biociden voor koelwater

Aanpassing van het emissiescenario-document voor open recirculerende koelwatersystemen

Onder andere de industrie en elektriciteitscentrales hebben koelwater nodig. In koeltorens wordt opgewarmd koelwater weer afgekoeld om het opnieuw te kunnen gebruiken. In koeltorens en warmtewisselaars kunnen organismen zoals bacteriën gaan groeien, waardoor de installaties slechter gaan werken. Om dat zo veel mogelijk te voorkomen, wordt het koelwater behandeld met biociden. Een biocide is een middel met een werkzame stof die ongewenste organismen doodt.

Voordat biociden in Europa op de markt mogen komen, wordt beoordeeld of ze schadelijke effecten kunnen hebben. In Nederland doet het College voor de toelating van gewasbeschermingsmiddelen en biociden (Ctgb) dat. Hiervoor berekent het Ctgb hoeveel er van een werkzame stof bij een bepaald gebruik in het milieu terechtkomt. Dit gebeurt met zogeheten emissiescenario's.

Voor het emissiescenario voor gebruik van biociden in koeltorens stelt het RIVM nu enkele aanpassingen voor. Hierdoor kan preciezer worden berekend hoeveel werkzame stof uit de koeltorens naar de lucht vervluchtigt. Met de aanpassingen kan beter worden ingeschat hoeveel werkzame stof er in het milieu terechtkomt en of dat schadelijk kan zijn.

De werkzame stoffen komen in het milieu terecht via het geloosde koelwater. Ook kunnen ze naar de lucht worden uitgestoten. De uitstoot naar lucht gaat via twee routes: via druppeltjes koelwater die door de luchtstroom in de koeltoren worden meegenomen, en doordat de stoffen vanuit het koelwater naar de lucht vrijkomen (vervluchtiging).

Tot nu toe werd de vervluchtiging voor alle chemische stoffen met één waarde berekend. Door de voorgestelde aanpassingen kan dit nu per stof worden berekend. Hoeveel er van een stof vervluchtigt, is afhankelijk van bepaalde eigenschappen van die stof.

Aanleiding voor de voorstellen zijn vragen over de rekenmethode van het Ctgb en biocidenexperts van Europese lidstaten. De aanpassingen zijn met deze experts afgestemd. Het European Chemicals Agency (ECHA) moet ze nog wel in de rekenmethode verwerken, zodat alle lidstaten van de Europese Unie ermee kunnen gaan werken.

Kernwoorden: koeltoren, biocide, vervluchtiging, strippen, stofoverdracht, emissie, lucht, water, modelleren

Contents

Summary

Cooling towers are used to lower the temperature of cooling water that is used as a cooling medium in, for instance, industrial processes or in power plants. The cooling is usually established by bringing a counter-current air flow into contact with the cooling water. Withdrawal of heat is mainly established by evaporation of water. The cooling water system consist of a cooling tower, a collection basin, a heat exchanger, and the piping to transport the cooling water. Biocides are continuously or periodically applied to the cooling system to prevent fouling of the system by aquatic organisms (biofouling) such as bacteria, algae, and higher organisms, e.g. mussels. The cooling water can be re-used after cooling in recirculating systems or discharged directly into so-called once-through systems. Once-through systems may also be equipped with a cooling tower in order to cool down the cooling water before discharge, in view of environmental concerns.

This report deals with the refinement and revision of the current emission scenario document for cooling water biocides. Emission scenario documents are essential to the environmental assessment of biocidal products and active ingredients. Biocidal products are only allowed on the market once their safe use has been demonstrated.

The refinement of the current emission scenario for cooling towers entails the development of a calculation method for the volatilisation of chemicals from the cooling water in the cooling tower. Furthermore, we have evaluated and revised the calculations of the concentration of the biocidal active ingredient in the cooling water in the entire cooling system, and consequently in the discharged cooling water (blowdown), by incorporating the fraction evaporated and the fraction lost via droplet drift as two separate loss processes. From the evaluation it appeared that the current equation for recirculating systems is incorrect. All equations in the emission scenario for cooling systems with a cooling tower need to be replaced by the newly derived ones, which include the volatilisation factor. With that, the erroneous equation is also substituted. Additionally, the parameters that describe the cooling water system are evaluated and new values are proposed where necessary. There appeared to be some inconsistencies in the default values for the smaller cooling systems. Therefore, new default values for small recirculating cooling systems are proposed. Additionally, we introduce parameters for the calculation of the volatilisation addition, such as the average temperature of the cooling water and the air-to-water-ratio for which default values are assigned.

Once the emission to air via volatilisation and droplet drift is properly defined, calculated, and incorporated into the mass balance equation for the cooling system, the concentration in air and the deposition to soil in the vicinity of the cooling tower can be calculated. This can be done by applying suitable air dispersion models. Essential to these calculations is the height of the cooling tower. The height can be calculated and depends on various characteristics of the cooling system. Calculated tower heights are not provided in this report. We recommend modelling

the tower height in a follow-up study and including air dispersion calculations in order to complete the environmental exposure assessment for cooling water biocides.

1 Introduction

1.1 Context of this report

1.1.1 *Emission Scenario Document for cooling water biocides*

The estimation of environmental emissions is an essential part of the environmental risk assessment of biocides in the context of European approval of active substances and national authorisation of biocidal products. Emission Scenario Documents (ESD) for different biocidal product types (PT) were developed in projects issued by the European Commission, OECD, or member states to estimate the initial release of substances from biocidal products (or treated materials) in a harmonised way. All finalised ESDs for biocides are available on the website of the European Chemicals Agency (ECHA).

The environmental emission estimation of cooling water biocides is described in the ESD for PT11 by Groshart *et al.* (2003). The ESD describes the environmental emissions of biocidal active substances when used in liquid cooling systems and it provides generic scenarios for three types of cooling systems:

- once-through systems;
- small and large open recirculating systems; and
- closed recirculating systems.

The ESD provides system characterisations and presents calculations of emissions that are used as input for the calculation of Predicted Environmental Concentrations (PEC) in soil, surface water, groundwater, and air, and where relevant, in sewage treatment plants (STP). The environmental risk of a biocidal active substance follows from a comparison of the PEC with the Predicted No Effect Concentrations (PNEC).

1.1.2 *Questions concerning the calculation of concentrations in soil*

Over the past years, questions arose concerning the calculation of the PEC for soil (PEC_{soil}) for PT11 substances. The main issue is that the ESD provides two methods for calculating the PEC_{soil} for open recirculating systems. The first considers deposition of spray drift droplets and assumes that a fixed fraction of the biocide mass is deposited on a fixed receiving soil area. The second considers the emission of biocides to air from the cooling water and their subsequent distribution to soil using a metamodel of a Gaussian plume model (EC, 2003). Both routes result in a different PEC_{soil} but the ESD provides no clear preference or argumentation, let alone any guidance on how to use these results for further risk assessment (Groshart *et al.*, 2003). This has caused confusion among risk assessors. For cooling towers operating with a once-through system, parts of the ESD imply that emission to air is the only relevant emission route, although a default for the fraction deposited to soil and calculations are provided in the final scenario description. Moreover, in the Technical Agreements on Biocides (TAB), entry ENV 124 refers to an agreement reached in 2013 to perform a risk assessment that includes spray drift though the air and deposition to soil for once-through systems with cooling towers (ECHA, 2022)[1] in line with the ESD. However, in the most recent version of EUSES, the drift route is not implemented for once-through systems and only emission to air is considered (ECHA, 2019).

1.1.3 *Substance-specific approach needed*

Furthermore, the ESD does not seem to distinguish correctly between the evaporation of cooling water and the release of biocidal active substances into air. The default set for release of the biocide is related to the water loss from the system. However, the volatilisation of biocides from water is different from the evaporation of water itself. Therefore, a substance-based approach is needed to address the fact that biocides will behave differently depending on their physical and chemical characteristics. Ionised substances, such as salts or strong acids, will remain in solution and will be emitted via drift droplets, while other compounds will (partially) volatilise and be emitted via air. In other words, the extent to which a biocide is ionised determines how much is lost via drift, and the volatility of the non-ionised fraction determines how much is lost via air through volatilisation.

This issue can be solved, but improvement of the calculation of the fraction emitted to air will not only affect the concentration in soil but also the amount emitted to surface water and consequently PEC_{water}. Specifically, the fraction emitted to air via volatilisation has to be included in the equations for the calculation of the concentration in the blowdown water.

It is noted that PT11 is not the only product type for which a distinction between ionised and non-ionised compounds is relevant. In general, most models and programmes used for fate and behaviour assessment of chemicals were originally developed for neutral organics and are not suited for dissociating substances, e.g. EUSES (EC, 2012), EQC (Hughes *et al.*, 2012), ChemCan (Webster *et al.*, 2004) and CoZMo-POP (Wania *et al.*, 2006). As such, the principles of the approach presented here with respect to the volatilisation of (ionising) chemicals may be applicable to other ESDs as well.

1.2 Aim and scope, reader's guide

The present report provides a new method for deriving substance-specific emission factors to calculate the loss via volatilisation in open-recirculating and once-through cooling systems equipped with a cooling tower and presents updated equations for the calculation of concentrations in the blowdown water.

This report is an updated version of RIVM report 2024-0042. The report was revised based on the received questions and comments from environmental experts (WG ENV) of the ECHA's Biocidal Product Committee (BPC). The changes in the report vary from corrections of typing errors to a further explanation of e.g. the applicability of the proposed methodology to different classes of chemicals, minor

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[1] The agreement is included in the document "Note: Environmental assessment of biocides in PT 11 cooling water systems (TM IV, 2013)" that is available via https://echa.europa.eu/guidance-documents/guidance-on-biocides-legislation/emission-scenario-documents.

adjustments to parameter naming and the revision of selected values of physico-chemical properties. The latter particularly concerns acid-base dissociation constants. Consequently volatilisation factors had to be recalculated. The adaptations in the report did not lead to different insights or major changes in the outcomes of the calculations. The proposed method for the calculation of volatilisation as worked out in the original report and the equations (a few minor exceptions) remain unchanged.

Chapter 2 starts with a brief discussion of the approach taken in the ESD and the current implementation in EUSES. It describes some general aspects of cooling technology, including the loss of cooling water from systems by drift and evaporation.
Chapter 3 further discusses the volatilisation of chemicals from cooling water and describes the estimation of the emission of biocides to air via volatilisation.

Chapter 4 investigates the default values for the new parameters that are needed for the calculation of the substance-specific volatilisation factors.

In Chapter 5, substance-specific volatilisation factors are calculated for biocidal active substances that are currently approved for use in PT11. First, the substance properties and the cooling tower process conditions required for the calculations will be discussed, including calculation methods in case experimental data is not available. This is followed by a detailed description of the data collection. The collected data and calculated volatilisation factors are presented as well.

Chapter 6 discusses the modelling of the emissions of biocides to water for three different dosing regimes: continuous dosing emissions at steady-state, continuous dosing emission at unsteady-state situation, and emissions at interval dosing. The model for calculating the time trend in the emission after starting the dosing has been added to the existing scenarios. A revised set of model calculations will be provided.

Chapter 7 discusses the calculations of the emissions to air and deposition to soil.

Chapter 8 evaluates the default parameters for existing open-recirculating cooling tower scenario and proposes new default values where necessary.

Chapter 9 ends the report with the overall conclusions.

2 Considerations on the approach of the ESD

2.1 Introduction to cooling systems

The emission scenario document for PT11 addresses environmental emissions of biocide-active substances used in liquid cooling systems. Although small-scale systems exist (e.g. in the electronics industry), the ESD on PT11 concerns cooling systems that operate at an industrial scale and deal with low-temperature heat as a by-product. These systems are (usually) equipped with cooling towers, which cool down hot water coming from the heat exchangers, which remove heat from process streams of, for instance, chemical plants, oil refineries or power plants.

Figure 1a shows a schematic presentation of the functioning of a cooling system equipped with a cooling tower. Hot water from the heat exchanger enters the top of the cooling tower through spray nozzles, after which the water (in the form of droplets) moves downwards by gravity and comes into contact with an air flow that is introduced at the bottom of the tower, and cools the water. In cooling towers, cooling is mainly established through evaporation of the cooling water and only for a small part through convective heat exchange between the hot water and the cool air.

With respect to the cooling water flow, three basic types of cooling systems can be distinguished. In open recirculating cooling towers (Figure 1a), the cooled water is collected in the basin of the cooling tower and recirculated into the heat exchangers. In once-through systems (Figure 1b) the cooling water is only used once and discharged after having performed its cooling duty, so that there is no need for a collection basin. In once-through systems, environmental requirements may require cooling of hot cooling water in a cooling tower before release to surface water.

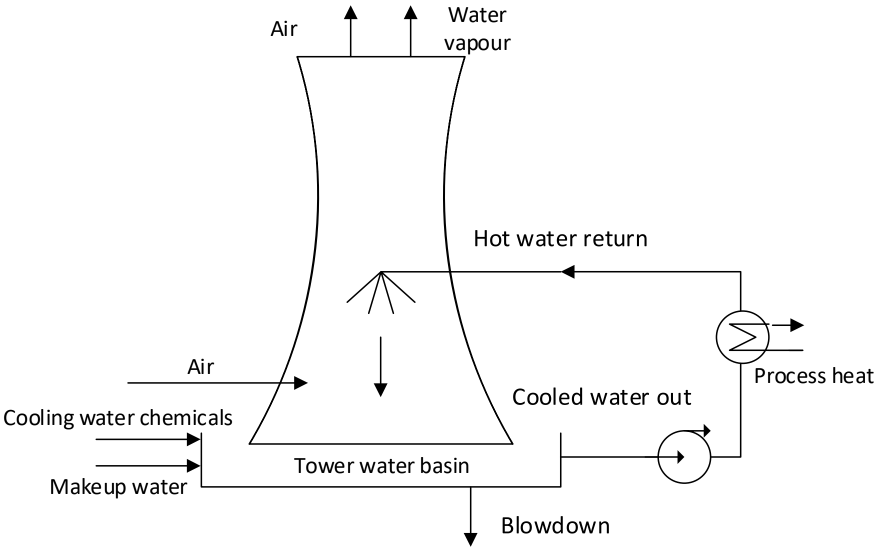
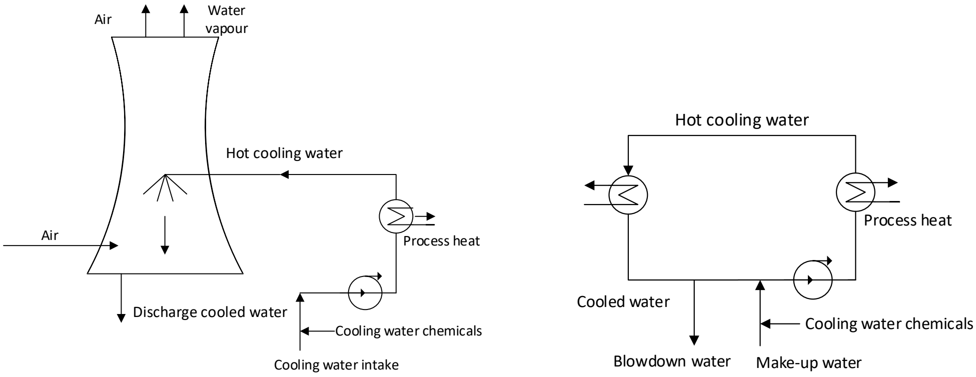


Figure 1a Schematic diagram of a cooling tower.

The third type of system is a closed recirculating system, Figure 1c. In these systems, the hot water circulates in a closed loop. The cooling water is not discharged after cooling. Cooling is established without the use of a cooling tower. Instead cooling is achieved, for instance, by means of plate heat exchangers. Since there is no direct contact with the atmosphere, there is no loss of water and the required amount of make-up water is minimal.



Figures 1b and c Schematic diagram of b) a once through cooling system with cooling tower and c) a closed cooling system.

With respect to the air flow in the cooling tower, as shown in Figure 1a for an open recirculating cooling system, cool ambient air is introduced at the sides or the bottom of the tower, and the heated air exits at the top. In ‘natural draft’ or ‘atmospheric’ cooling towers, the air flow is induced by the air density difference caused by the temperature difference between the less dense heated air at the top of the tower and the denser cool ambient air outside the tower. Air fans can be used to provide a stable and known volume of air to the tower, and therefore a more stable cooling performance. These types of towers are known as ‘mechanical draft’ or ‘forced draft’ cooling towers. Furthermore, cooling towers can be designed in order for the introduced air to travel either horizontally across the direction of the downward moving cooling water (crossflow) or in the opposite direction of the water flow in the cooling tower (counterflow).

Besides evaporation of water, water is lost from open recirculating systems through spray drift (windage). When the hot water coming from the heat exchangers is introduced through pressurised spray nozzles at the top of the tower, a small fraction of the produced droplets is dragged along with the exiting air flow. Furthermore, water is lost via blowdown, which is water-bled from the system to prevent build-up of non-volatile substances such as salts in the system (see also section 2.2).

The ESD for PT11 includes the following three categories of cooling tower systems: once-through cooling systems (also known as flow through cooling systems), open recirculating cooling systems (subdivided into small and large systems) and closed recirculating cooling systems. The ESD indicates that once-through systems do not always have a cooling tower. The reference document on the application of best available techniques to industrial cooling systems also indicates that cooling towers are not common practice for once-through systems (EC, 2001). Whether or not a cooling tower is in place depends on the local situation.

2.2 Emission routes per cooling system type

Figure 3 depicts the possible emission routes. Chemicals, such as biocides, that are introduced into the cooling system can be lost via the air and water streams exiting the cooling system. Volatile compounds can end up in the air stream through the stripping action of the air on the cooling water, also called ‘volatilisation’ or ‘flash-off’. In that respect, the principles for mass transfer of a chemical that hold for stripping columns (see Figure 2) also apply to cooling towers. Contrary to cooling towers, counterflow stripping columns are specifically designed and operated for optimum exchange of a substance between the liquid (water) and the stripping medium (often air) to establish the required substance removal efficiency. In addition, stripping columns are typically not operated as recirculation systems but more generally as once-through systems. Apart from volatilisation, chemicals are removed from the cooling system and emitted to air via spray drift of cooling water droplets also simply called drift, or wind drift, or windage. In addition to the losses via air and drift, cooling water chemicals are lost via the blowdown water. Furthermore, there are losses through chemical reaction such as hydrolysis, reaction with organic material or deposition in the system (scaling).

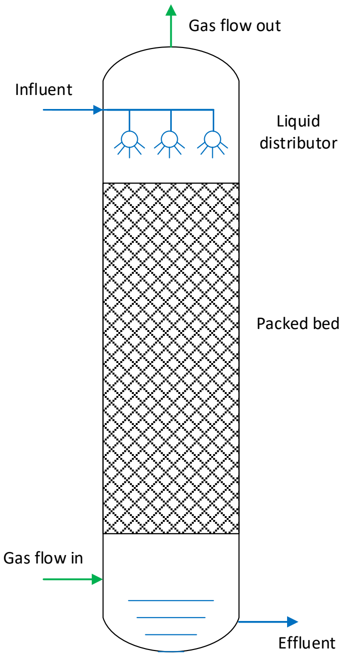
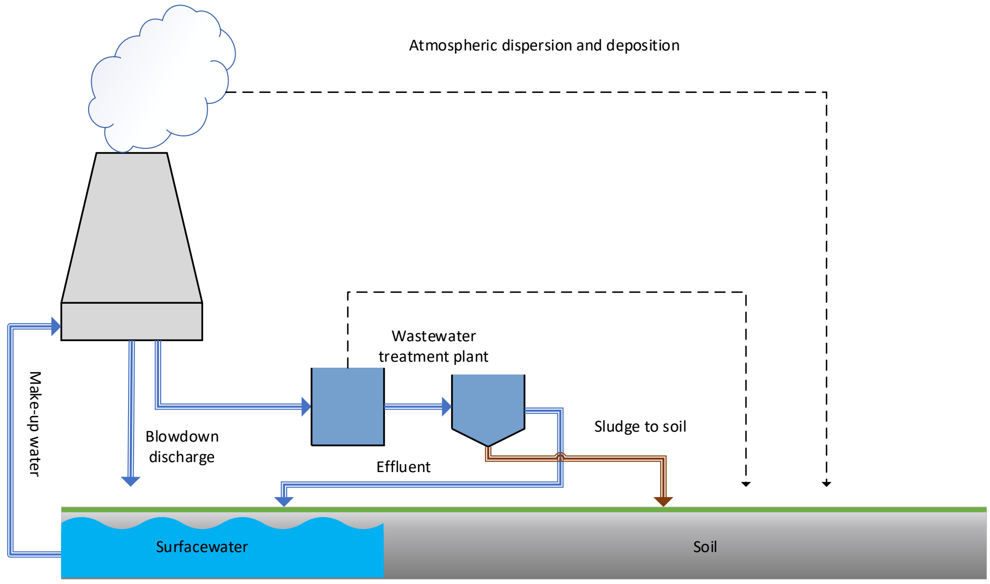


Figure 2 Schematic diagram of a stripping column.

The amount of biocide emitted to air via spray drift and volatilisation will be dispersed in the atmosphere and partly deposited to soil. The blowdown water is discharged directly to surface water, or indirectly via a wastewater treatment plant. Consequently, sewage treatment sludge may be applied (as a fertiliser) to agricultural soil (EEC, 1986, Eurostat, 2021). Table 1 summarises the release routes of cooling water and the relative quantities for the various systems as identified in the ESD, and indicates which emission routes are relevant for soil.



Emission to soil is possible via release to air followed by deposition (both from the tower and from the sewage treatment plant, STP) and via application of sewage sludge onto soil.
Figure 3 PT11 emission routes from cooling towers to the soil compartment.

To clarify Table 1, the relevant emission routes will be further described for each type of cooling system:

- For once-through systems that are operated with a cooling tower, the water loss by evaporation and drift constitutes a small fraction of the total water volume. The rest of the water volume is discharged directly to surface water[2] (blowdown). Due to the large blowdown volume of once-trough systems, the blowdown water is usually discharged directly. There is only indirect emission to soil via air if the once-through system is operated using a cooling tower.
- Open recirculating systems are always operated using a cooling tower, and therefore system water is lost through evaporation and via liquid droplets. Spray drift may lead to direct emissions to and deposition on soil of the biocides dissolved in cooling water. Furthermore, biocides might volatilise in the cooling tower and then be emitted to air followed by atmospheric dispersion and deposition to soil. In addition to the direct atmospheric route, emission to soil may be relevant for open recirculating systems when the blowdown water is discharged via a sewage treatment plant (STP). In the latter case, biocides can reach the soil via sludge application or via air emissions from the STP.
- For closed recirculating systems, spray drift and evaporation are not relevant and no direct emission to soil is assumed. For these systems, the only potential route to soil is indirect emission via the STP when the system is drained for maintenance. Further details on the characteristics of the various systems can be found in the ESD (Groshart *et al.*, 2003). The assumptions made by the

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[2] The Ad Hoc Environmental Exposure Working Group (AHEE WG) agreed that in certain circumstances, a settling pond may be considered as a refinement option. See ECHA (2022).

ESD concerning emission to water resulting from maintenance are left out of consideration in this report and remain unchanged. As indicated in the introduction, other parts of the model calculations have to be revised in order to establish a correct chemical mass balance of the cooling tower.

Table 1 Emission routes for biocides and quantities of water lost from the cooling system, as identified in the ESD for PT11 .

System **Route**	**Once-through**	**Open recirculating**	**Closed recirculating**
Blowdown	+++ (99.9%)	$+^{a}$ (<5%)	- (<2% Q_{circ} or 1% of $V_{syst} \cdot month^{-1}$)
Spray drift	$+^{e}$ (0.1%)	+/- (<0.01% - <0.2%)	n.r.
Evaporation		++ (1%)	n.r.
Volatilisation^{d}	🟩	🟩	
Maintenance	2 years ^{b}	1 year $+^{a,c}$	1 year $+^{a,c}$

The estimated, relative quantity of water lost from the system is indicated using the following criteria: between 0.01% – 0.1%: -, between 0.1% - 1%: +, between 1% - 10%:++ and > 10%: +++. The percentage of water lost, as fraction of the (recirculating) flow rate is presented between brackets. Potential direct emission routes to soil are marked in green, indirect routes in brown. The table is based on Table 2 and 4 of the ESD (Groshart *et al.*, 2003).

n.r. = not relevant.

a: indirect emission only upon discharge to the STP.

b: treatment is stopped, complete drainage and cleaning of the system.

c: under controlled conditions, sometimes de-activation is recommended.

d: the degree of volatilisation is substance dependent.

e: only relevant when a cooling tower is used. Unclear whether this refers to either evaporation, droplet drift or both. The ESD and the original source (Van Dokkum *et al.*, 1998) are unclear about this (see also section 2.3 of this report).

2.3 Fate of biocides in the cooling tower

As described in the previous paragraph, biocides can be emitted to air in two ways: 1) via spray drift of cooling water droplets containing the biocide, and 2) via volatilisation of the substance from the cooling water. In the ESD, the parameter $F_{evap+drift}$ (unitless) describes the fraction of *cooling water* lost through evaporation and drift, but the same parameter is also used for calculating the release of *active substances* to air. However, loss of the active ingredient through volatilisation is not the same as water evaporation. For correctness and clarity with respect to the follow-up calculations, it is necessary to have two different parameters for the atmospheric losses of the chemical. Thus, in order to describe chemical losses from the cooling system, we need a substance-dependent loss factor for volatilisation ($F_{volat,a.i.}$) and a loss factor for spray drift (F_{drift}). Since the fraction lost via drift is related to the recirculating water flow rate and is not substance-dependent, the addition of ‘a.i.’ in the subscript is omitted. As we will show in Chapter 6, the cooling water evaporation factor does not appear in the mass balance for calculating the biocide concentration in the blowdown water, because evaporated water does not contain cooling water chemicals. However, the amount of water evaporated may be helpful in evaluating the cooling tower characteristics (see Chapter 8).

The speciation and fate of biocides used in cooling towers is depicted in Figure 4. Since dissolved ionised species do not volatilise from the cooling water, the ionised fraction of a biocide will only be emitted via drift of cooling water droplets. Non-ionised biocides may volatilise from the cooling water through the stripping effect. The extent of removal through each of the pathways primarily depends on the substance properties, i.e. Henry's law constant and the acid/base constant, p$K_{a/b}$, which determines the degree of ionisation at the system's pH. In summary, the following three options can be distinguished (see Figure 4):

- Inorganic salts and strong acids, which are completely ionised in the cooling water, only spray drift is relevant.
- Organic (and inorganic) substances that do not ionise, volatilisation is likely to be the most relevant process, but this depends on the volatility of the substance.
- Partly ionisable organic substances, both pathways can be relevant, the relative contribution depending, among others, on substance-specific properties, such as the volatility and the acid/base constant in combination with the pH maintained in the cooling water system.

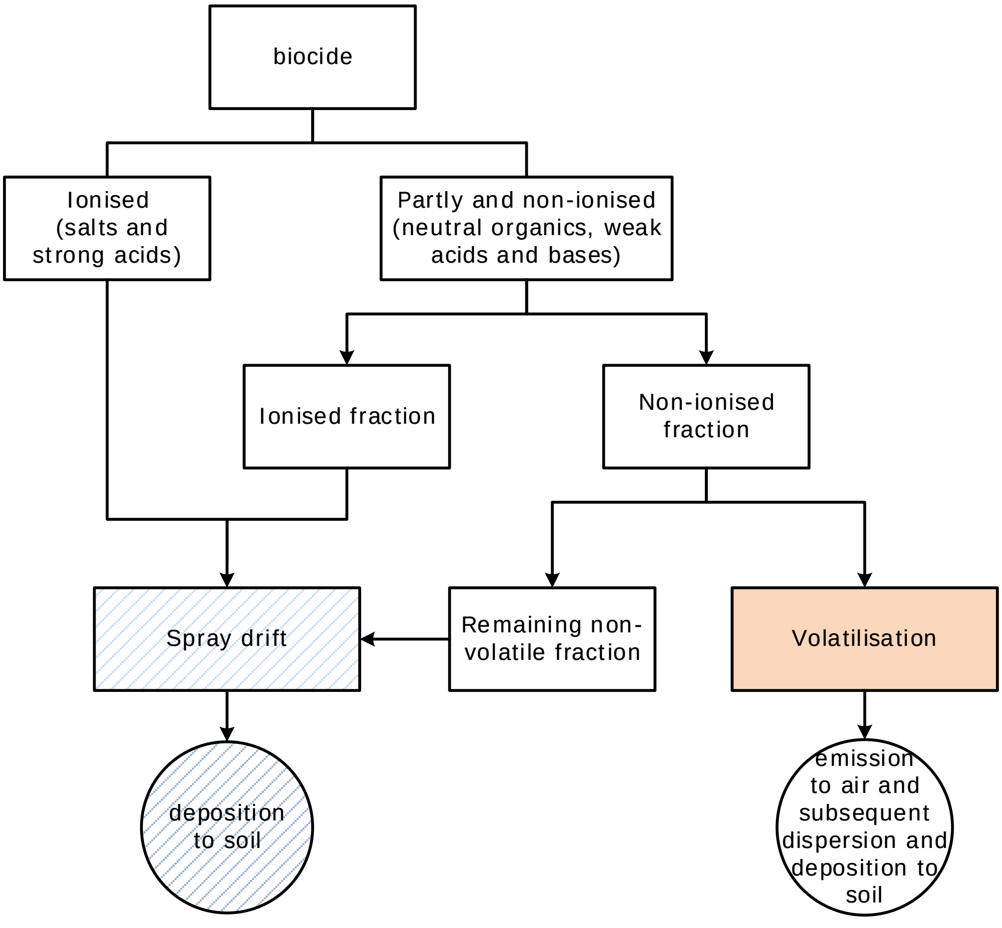


Figure 4 Schematic drawing of the conceptual approach for the emission routes of cooling water biocides from cooling towers to soil.

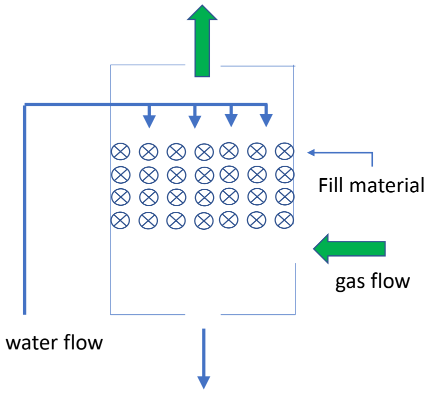
3 Emission of biocides to air by volatilisation

3.1 Introduction

As explained in the previous chapter, chemicals that are introduced into the cooling system can be lost via the air and water streams in the cooling tower. Volatile compounds can end up in the air stream through contact of the air stream with the cooling water. This process is called ‘volatilisation’, ‘flash-off’, or ‘stripping’. The principles that hold for stripping towers also apply to cooling towers. The emission to air through volatilisation ($F_{\text{volat,a.i.}}$) can be estimated by using 1) flash-off factors and 2) substance-specific mass transfer rates.

The flash-off factor (unitless) is defined as the fraction of the substance removed from the liquid stream as it traverses through the cooling tower (Holzwarth *et al.*, 1984). Flash-off factors are calculated using the ratio between liquid and gas flow rate in a cooling tower and the substance-specific Henry’s law constant. The basic assumption of the flash-off method is that a thermodynamic equilibrium between the air leaving the cooling tower and the hot water at the top of the tower is achieved instantly and completely. However, such equilibrium may not be established in practice. Therefore, the current report focuses on substance-specific transfer rates as a more appropriate way to estimate $F_{\text{volat,a.i.}}$.

Substance-specific volatilisation factors may be derived by applying the mass transfer rate approach, which is used in design equations for stripping towers (Billet *et al.*, 1999, Kavanaugh *et al.*, 1980, Srinivasan *et al.*, 2009, Huang *et al.*, 2006, Hand *et al.*, 2011, Cussler, 2009). Although cooling towers are not designed to strip volatile chemicals from water, the physical process that occurs in cooling towers is the same as the one in stripping towers. Like stripping towers, cooling towers are usually equipped with packing material, also called ‘fill’, to enhance the heat exchange between cooling water and air (see Figure 5).



Water and air pass each other in the packing material where a substance is transferred from water to air in the case of stripping or vice versa in the case of absorption.
Figure 5 Schematic drawing of the counterflow in a cooling tower.

The performance of a cooling tower with respect to removing chemicals from cooling water into the air stream is determined by the contact area and the mass transfer rate between cooling water and air. The contact area is determined by the specific interfacial area, which depends on the type of packing material and the volume of the packing section. The overall mass transfer for the water-air interface thus depends on the type of packing, the air and water flow rates, and the diffusion coefficients of a substance in air and water. The interfacial mass transfer is usually described using the two-film model.

By modelling the amount of a substance that is transferred from water to air, the fraction of biocide active substance volatilised from cooling water, $F_{\mathrm{volat,a.i.}}$ can be calculated. In this chapter, the modelling of the mass transfer in a counterflow cooling tower is further elaborated, using the model equations presented in a paper by Hsieh *et al.* (2013). These authors experimentally determined the overall mass transfer coefficient for the stripping of the ionising substance ammonia in a pilot-scale open recirculating cooling tower. While the mass transfer coefficients determined in this study relate to the specific operating conditions (flow rates, temperature, pH) and packing material used, they also provide an indication of the degree of volatilisation in a cooling tower in general The prerequisites for this, however, are that the influence of the operating conditions can be modelled explicitly (pH and temperature) and/or that the conditions can be considered to be representative (flow rates). Furthermore, the experimentally determined mass transfer data needs to be extrapolated to other substances in order to calculate substance-specific emission factors to air. Specifically, when modelling the mass transfer for ionising substances, the degree of ionisation should be taken into account.

In order to calculate the degree of volatilisation for the individual substances, we collected and reported the required data for the active substances that have already been evaluated or are under evaluation for authorisation as cooling water preservatives. The following sections describe the modelling of the mass transfer and the required equations needed in the derivation of the substance-specific volatilisation factors.

3.2 Modelling volatilisation in cooling towers

3.2.1 Mass transfer model for dissociating substances

Hsieh *et al.* (2013) and Safari *et al.* (2014) used the general model for calculating mass transfer rate across the liquid/gas interface that is used for calculating the efficiency of stripping towers. In this model, the mass transfer across the interface is determined by a concentration difference as a driving force and a the resistance ($s \cdot m^{-1}$) to mass transfer across the interface as counteracting force. The inverse of this resistance is the overall mass transfer coefficient ($m \cdot s^{-1}$). Among others, the overall mass transfer (diffusional) resistance can be described according to the two-film theory. According to this model the resistance to the overall mass transfer is viewed as a combined resistance of a liquid and a gas film at the interface. Hsieh *et al.* (2013) and Safari *et al.* (2014) used an adapted version of the general two-film model, suitable for dissociating substances.

The resulting model calculates the concentration in the cooling water that exits at the bottom of the cooling tower ($C_{\mathrm{x,out}}$) from the concentration in the cooling water entering at the top of the cooling tower ($C_{\mathrm{x,in}}$). The loss of substance from the cooling water in a cooling tower, through volatilisation $F_{\mathrm{volat,a.i.}}$, is then calculated as follows:

$$F_{\mathrm{volat,a.i.}} = \frac{C_{\mathrm{x,in}} - C_{\mathrm{x,out}}}{C_{\mathrm{x,in}}} = 1 - \frac{C_{\mathrm{x,out}}}{C_{\mathrm{x,in}}} \qquad \text{Eq. 1}$$

Where

$C_{\mathrm{x,in}}$	concentration in cooling water entering the cooling tower	($\mathrm{kg{\cdot}m^{-3}}$)
$C_{\mathrm{x,out}}$	concentration in cooling water leaving the cooling tower	($\mathrm{kg{\cdot}m^{-3}}$)
$F_{\mathrm{volat,a.i.}}$	fraction of the active ingredient volatilised from the cooling water	(-)

Equations 2 and 3 below show the mass transfer model presented by Hsieh *et al.* (2013) and Safari *et al.* (2014). The equations show how the concentration in the outgoing cooling water can be calculated from the ingoing cooling water on the basis of the cooling tower characteristics, the substance-specific Henry's law constant and the degree of dissociation of the substance in the cooling water. The latter needs to be taken into account for two reasons:

1) the dissociated fraction does not volatilise from the cooling water and
2) the ionised fraction of the substance contributes to the mass transfer across the air-water interface, (see section 3.2.2, Influence of ionisation on mass transfer coefficient).

The ingoing and outgoing concentration in the water of the cooling tower are total concentrations, comprising the dissociated and non-dissociated fraction.

The parameter notation used is the same as in Hsieh *et al.* (2013) and Safari *et al.* (2014), conform to the notation commonly used in text books on gas absorption and stripping. Further details with respect to terminology and parameter notation of Henry's law constant are provided in section 5.2.2 and Annex 5. A full description of the derivation of the model (equations 2 and 3) is provided by Hsieh *et al.* (2013). Background information on deriving the general design equation is provided in Annex 1.

General mass-transfer equation for gas stripping:

$$C_{\mathrm{x,out}} = C_{\mathrm{x,in}} \cdot \frac{\left(\frac{K_{\mathrm{H}}}{Q_x \cdot \alpha} - \frac{1}{Q_y}\right)}{\frac{K_{\mathrm{H}} \cdot e^{\varphi}}{Q_x \cdot \alpha} - \frac{1}{Q_y}} \qquad \text{Eq. 2}$$

Where

$C_{\mathrm{x,in}}$	concentration in cooling water entering to cooling tower	($\mathrm{kg{\cdot}m^{-3}}$)
$C_{\mathrm{x,out}}$	concentration in cooling water leaving the cooling tower	($\mathrm{kg{\cdot}m^{-3}}$)
Q_{x}	water volume flow rate	($\mathrm{m^3{\cdot}s^{-1}}$)
Q_{y}	air volume flow rate	($\mathrm{m^3{\cdot}s^{-1}}$)
K_{H}	Henry's law volatility constant, dimensionless	($\mathrm{m^3_{water}{\cdot}m^{-3}_{air}}$)
φ	term describing the mass transfer efficiency as defined by equation nr. 3	(-)
α	co-diffusion coefficient (see section 3.2.2)	(-)

As presented in equation 3 and 4, the term φ depends on the effective total packing surface area A, which in turn is calculated from the base area of the packing-filled tower (A_b), the volumetric surface area of the packing (a), the packing height (Z_T) and the overall (gas-side) mass transfer coefficient (K_G):

$$\varphi = \left(\frac{K_\mathrm{H}}{Q_\mathrm{x} \cdot \alpha} - \frac{1}{Q_\mathrm{y}}\right) K_\mathrm{G} \cdot A \qquad \text{Eq. 3}$$

$$A = A_\mathrm{b} \cdot a \cdot Z_\mathrm{T} \qquad \text{Eq. 4}$$

Q_x	water volume flow rate	($m^3 \cdot s^{-1}$)
Q_y	air volume flow rate	($m^3 \cdot s^{-1}$)
K_H	Henry’s law volatility constant, dimension less	($m^3_{water} \cdot m^{-3}_{air}$)
α	co-diffusion coefficient (see section 3.2.2)	(-)
K_G	overall (gas-phase) mass transfer coefficient	($m \cdot s^{-1}$)
A	effective overall packing surface area	(m^2)
A_b	base area of the packing filled tower	(m^2)
a	volumetric surface area of the packing	($m^2 \cdot m^{-3}$)
Z_T	height of packing material	(m)

Summarising, the general mass transfer equation as presented in Hsieh *et al.* (2013) shows that the mass of a substance that is transferred from water to air in a counterflow cooling tower is determined by system characteristics, such as air and water flow rates, packing characteristics and packing volume, and by substance properties such as Henry’s law constant, and by the degree of dissociation of the substance (α). The overall mass transfer coefficient K_G is a key parameter, which depends on for instance the geometry of the packing material, properties of the media, the local conditions in the packing and substance properties such as the diffusion coefficient. The next section goes further into the influence of ionisation on the mass transfer coefficient.

3.2.2 *Influence of ionisation on mass transfer coefficient*

According to the two-film theory, the overall resistance to mass transfer depends on the resistance in a thin film on the liquid, in this case water side and a thin film at the gas, in this case air side of the interface. For dissociating substances, the mass transfer is influenced by the degree of ionisation, because diffusion through the liquid boundary layer is enhanced by the charged fraction of the substance. This effect is called co-diffusion. The influence of co-diffusion of the ionised species of the substance on the overall mass transfer coefficient is elaborated by Schwarzenbach *et al.* (2003) for acidic substances.

For each phase, be it the gas side or the liquid side, the overall mass transfer coefficient can be calculated taking speciation into account according to equations 5-8 below[3]. The equations are adopted from Hsieh *et al.* (2013) and Safari *et al.* (2014), who introduced the

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[3] In environmental fate modelling, K_G and K_L are generally referred to as the overall mass transfer coefficient for gas absorption and volatilisation, respectively. This a matter of convention and the naming might suggest a certain direction of the flux, which is not the case. The direction of the net flux is determined by the actual concentrations in the bulk phases and the phase equilibrium partition coefficient.

parameter α for the term that describes the enhancement of the diffusion through the liquid layer for acids and bases, respectively.

$$\frac{1}{K_\mathrm{G}} = \frac{1}{k_\mathrm{G}} + \frac{K_\mathrm{H}}{k_\mathrm{L} \cdot \alpha} \tag{Eq. 5}$$

$$\frac{1}{K_\mathrm{L}} = \frac{1}{K_\mathrm{H} \cdot k_\mathrm{G}} + \frac{1}{k_\mathrm{L} \cdot \alpha} \tag{Eq. 6}$$

For acids:

$$\alpha = 1 + \frac{K_\mathrm{a}}{[\mathrm{H}^+]} \tag{Eq. 7}$$

For bases:

$$\alpha = 1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}} \tag{Eq. 8}$$

Where:

K_G	overall gas-phase mass transfer coefficient	$(\mathrm{m \cdot s^{-1}})$
K_L	overall liquid-phase mass transfer coefficient	$(\mathrm{m \cdot s^{-1}})$
k_G	partial mass transfer coefficient in the gas (air) film	$(\mathrm{m \cdot s^{-1}})$
k_L	partial mass transfer coefficient in the liquid (water) film	$(\mathrm{m \cdot s^{-1}})$
K_H	dimensionless Henry's law volatility constant	$(\mathrm{m^3_{water} \cdot m^{-3}_{air}})$
α	co-diffusion coefficient (accounting for speciation of a substance)	(-)
$[\mathrm{H}^+]$	molar concentration of hydrogen ions	$(\mathrm{mol \cdot dm^{-3}})$
K_a	acid dissociation constant	$(\mathrm{mol \cdot dm^{-3}})$

The co-diffusion coefficient α in the above equations is the inverse of the non-ionised fraction of a dissociating in solution (see Annex 2 for the derivation). The fraction of the chemical that is not ionised is calculated from the acid dissociation constant of a substance, $\mathrm{p}K_\mathrm{a}$ ($-\log_{10} K_\mathrm{a}$) and the pH ($-\log_{10} [\mathrm{H}^+]$) of the solution, i.e. the cooling water. The relation between non-ionised fraction, the pH and $\mathrm{p}K_\mathrm{a}$ is described by the Henderson-Hasselbalch equation (Annex 2). The dissociation constant, K_a, is a quantitative measure of the strength of an acid or base in solution. It is the equilibrium constant for the chemical dissociation of an acid in a hydrogen ion and the conjugated base. By definition, 50 percent of the substance is dissociated when the pH of the solution is equal to the $\mathrm{p}K_\mathrm{a}$. For bases, the acid dissociation constant of the conjugated acid is usually reported and a different equation has to be used in order to calculate the non-ionised fraction.

The acid dissociation constant K_a for monoprotic acids is defined for acids as:

$$K_\mathrm{a} = \frac{[\mathrm{A}^-] \cdot [\mathrm{H}^+]}{[\mathrm{HA}]} \tag{Eq. 9}$$

and the derived Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right) \tag{Eq. 10}$$

The acid dissociation constant of the conjugate acid of a monoprotic base is defined as:

$$K_\mathrm{a} = \frac{[\mathrm{B}]\cdot[\mathrm{H}^+]}{[\mathrm{BH}^+]} \qquad \text{Eq. 11}$$

and the corresponding Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{B}]}{[\mathrm{BH}^+]}\right) \qquad \text{Eq. 12}$$

Referring to Annex 2 for the further derivation, for acids, we arrive at:

$$F_\text{non-ionised} = \frac{1}{1+\frac{K_a}{[H^+]}} = \frac{1}{1+10^{\mathrm{pH}-pK_\mathrm{a}}} \qquad \text{Eq. 13}$$

And for bases, at:

$$F_\text{non-ionised} = \frac{1}{1+\frac{[\mathrm{H}^+]}{K_a}} = \frac{1}{1+10^{\mathrm{p}K_\mathrm{a}-\mathrm{pH}}} \qquad \text{Eq. 14}$$

For neutral compounds that do not dissociate:

$$F_\text{non-ionised} = 1 \qquad \text{Eq. 15}$$

Linking to the parameter α as used by Hsieh *et al.* (2013) and Safari *et al.* (2014) it follows for acids that:

$$\alpha = 1 + \frac{K_\mathrm{a}}{[\mathrm{H}^+]} = 1 + 10^{\mathrm{pH}-\mathrm{p}K_\mathrm{a}} = \frac{1}{F_\text{non−ionised}} \qquad \text{Eq. 16}$$

and for bases:

$$\alpha = 1 + \frac{[\mathrm{H}^+]}{K_\mathrm{a}} = 1 + 10^{\mathrm{p}K_\mathrm{a}-\mathrm{pH}} = \frac{1}{F_\text{non−ionised}} \qquad \text{Eq. 17}$$

With:

pK_a	-log K_a	(-)
pH	-log $[\mathrm{H}^+]$	(-)
$[\mathrm{H}^+]$	molar concentration of hydrogen ions	(mol·dm^{-3})
$[\mathrm{A}^-]$	molar concentration of dissociated acid	(mol·dm^{-3})
[HA]	molar concentration of the non-dissociated acid	(mol·dm^{-3})
[B]	molar concentration of the non-dissociated base	(mol·dm^{-3})
$[\mathrm{BH}^+]$	molar concentration of conjugated acid of a base	(mol·dm^{-3})
α	co-diffusion coefficient (accounting for speciation of dissociating substances)	(-)
$F_\text{non-ionised}$	fraction of the molecules of a dissociating substance being present in neutral form in solution	(-)

Table 2 presents the pK_a and the non-ionised fraction ($F_{\text{non-ionised}}$) for ammonia and a variety of biocides in aqueous solution under different pH conditions. Figure 6 presents graphically the fraction of neutral species of ammonia, hypochlorous acid and some other biocides as a function of pH.

Table 2 Fraction of the substance in the neutral or non-ionised form at different pH values.

Substance	**Type***	**pK_a***	**Fraction non-ionised**				
			pH 5	**pH 6**	**pH 7**	**pH 8**	**pH 9**
MIT	Base	2.81	0.994	0.999	1.000	1.000	1.000
BIT	Acid	7.2	0.994	0.941	0.613	0.137	0.016
Bronopol	Acid	9.91	1.000	1.000	0.999	0.988	0.890
HHT	Acid	6.53	0.971	0.772	0.253	0.033	0.003
Peracetic acid	Acid	8.24	0.999	0.994	0.946	0.635	0.148
NH_3	Base	9.24	0.000	0.001	0.006	0.054	0.365
Reaction products of BCDMH (1-bromo-3-chloro-5,5-dimethylimidazolidine-2,4-dione)							
DMH	Acid	9.19	1.000	0.999	0.994	0.939	0.608
HOCl	Acid	7.53	0.997	0.971	0.772	0.253	0.033
HOBr	Acid	8.65	1.000	0.998	0.978	0.817	0.309

* The value presented here is that of the acid or the conjugated acid of the base. The unit of the K_a is in mol.dm^{-3}. The K_a can also be reported as unitless. The pK_a is usually reported without a unit.
MIT: 2-methyl-2*H*-isothiazol-3-one.
BIT: 1,2-benzisothiazol-3(2*H*)-one.
HHT: hexahydro-1,3,5-tris(2-hydroxyethyl)-*s*-triazine.
DMH: dimethylhydantoin.

From Table 2 and Figure 6, it becomes clear that weak bases such as MIT with a pK_a of 2.81 only adapt hydrogen ions at low pH values and are mainly present as the neutral species under slightly acidic to basic conditions, while stronger bases such as NH_3 with a pK_a of 9.24 require higher pH values to remain in the neutral form. Strong acids are present in the neutral from only at lower pH values. Dissociated acids are present as negatively charged ions, while ionised bases are present as positively charged ions. Figure 6 shows that at neutral conditions, pH=7, ammonia is mainly present as the ammonium ion (NH_4^+) while hypochlorous acid is mainly present as the neutral species (HOCl).

So far, this paragraph discussed the behaviour of monoprotic acids and bases containing one ionisable group. Polyprotic substances however contain more than one acidic or basic functional group. Furthermore, there are also so-called ampholytes, that contain both an acidic and basic functional group such as for instance amino acids and alkylamino carboxylates.

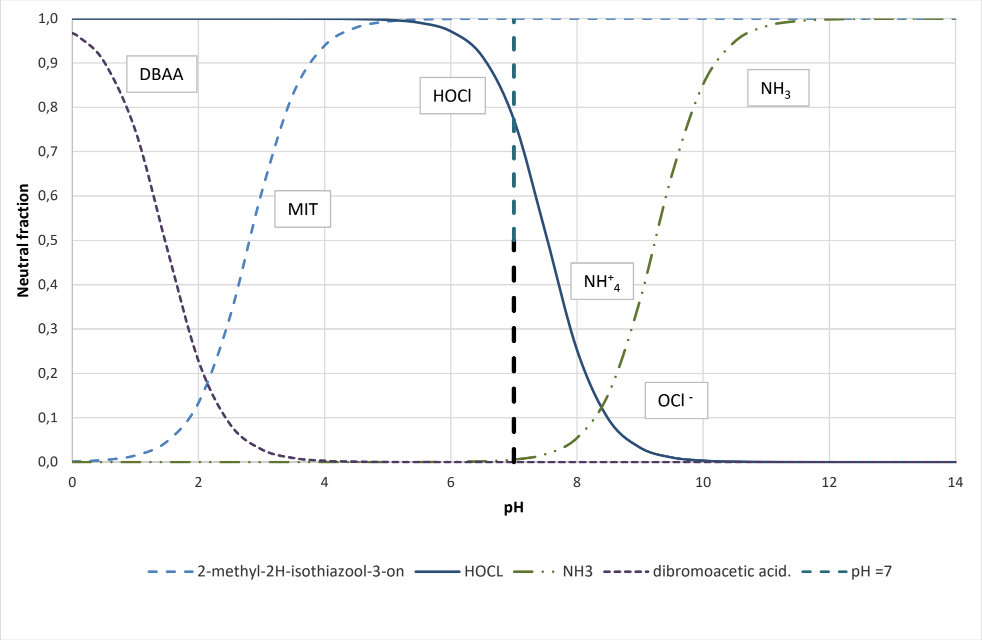

Figure 6 Speciation (neutral fraction) of acids and bases as a function of the pH of the solution.

In the derivation of the non-ionised fractions it is necessary to indicate whether the substance is an acid or base. However, some compounds are amphoteric, which means they possess both acidic and basic properties. Amphoteric compounds referred to as ampholytes are zwitterions, i.e. molecules that contain an equal number of positively and negatively charged functional groups. As such they can exist in either the anionic, cationic and neutral form, but they can also exist with both the acid and the basic functional group simultaneously in the ionised state depending on the pH of the solution.

Betaines also belong to the class of ampholytes, however the quaternary part that does not bear a hydrogen atom is always positively charged. Also quaternary ammonium compounds (quats) are always ionised in aqueous solution independent of the pH of the solution.

It should furthermore be noted that some active substances are used as salts of an acid or base, such as troclosene sodium, potassium dithiocarbamate or dodecylguanidine hydrochloride. Although these substances are used as salts, the pH of the system ultimately determines the fraction of the substance that is dissociated. Consequently, the Henderson-Hasselbalch equation for the original form still applies to calculate the non-dissociated fraction of the substance at a certain pH.

In calculating the parameter α the valence of the different species is not of concern. α can therefore be calculated from the neutral fraction. The above described approach to derive non-ionised fraction only applies for monoprotic acids and bases and is not recommended for amphoteric compounds or polyprotic substances. Instead, methods to calculate the non-ionised fraction of polyprotic acids and bases and amphoteric compounds should be used. These methods can be found in text books such as Dickerson et al. (1979); Skoog et al. (1988) and Zumdahl et al. (2005) and in scientific literature such as Novak (2021). The neutral fraction of a compound (including amphoteric) at a certain pH can also be obtained from structure based chemical property estimating software such as MarvinSketch (2016).

3.2.3 Estimating mass transfer coefficients from a reference substance

3.2.3.1 Partial mass transfer coefficient correlations

Mass transfer coefficients are not physical properties of substances. They depend on the physical properties of the media involved (viscosity), the process conditions (temperature, pressure, flow velocity), packing properties (geometry) and substance properties (diffusion coefficient). They differ from case to case, and even within a system. However, mass transfer coefficients can be predicted using mass transfer correlations. There is quite a large number of publications on predicting the mass transfer coefficients of substances for different types of packing material (Flagiello *et al.*, 2021). From the various (experimentally derived) correlations, it appears that partial mass transfer coefficients show surprisingly uniform variations with fluid velocities and diffusion coefficients, even across different types of packings (random and structured). On the basis of these correlations, experimentally determined mass transfer coefficients of a reference substance (in this case ammonia) can be used to predict the mass transfer coefficients of another substance. Mass transfer correlations are typically expressed as correlations of dimensionless numbers, usually in the following basic form (Kumar *et al.*, 1999, Pratsinis *et al.*, 2022):

$$k \cdot \frac{d}{D} = \mathrm{C} \cdot \left(\frac{d \cdot v^0}{v}\right)^{\mathrm{X}} \cdot \left(\frac{v}{D}\right)^{\mathrm{Y}} \qquad \text{Eq. 18}$$

Or, when using the dimensionless numbers, as

$$\mathrm{Sh} = \mathrm{C} \cdot \mathrm{Re}^{\mathrm{X}} \cdot \mathrm{Sc}^{\mathrm{Y}} \qquad \text{Eq. 19}$$

Where:

k	partial mass transfer coefficient	($m \cdot s^{-1}$)
D	diffusion coefficient	($m^2 \cdot s^{-1}$)
v^0	flow velocity of the medium (gas or liquid)	($m \cdot s^{-1}$)
v	kinematic viscosity	($m^2 \cdot s^{-1}$)
d	nominal packing size of packed bed	(m)
C,X,Y	correlation constants	(-)
Sh	Sherwood number	(-)
Re	Reynolds number	(-)
Sc	Schmidt number	(-)

3.2.3.2 Dependency on the diffusion coefficient

The partial mass transfer coefficient varies with the diffusion coefficient to the 0.5th to 0.7th power in most of the correlations. The liquid-side mass transfer coefficient in a packed tower is generally proportional to the square root of the diffusion coefficient, whereas for the gas side (air), it is proportional to the 2/3rd power of the diffusion coefficient (Cussler, 2009, Kim *et al.*, 2008, Narbaitz *et al.*, 1996, Billet *et al.*, 1999, Hanley *et al.*, 2012, Flagiello *et al.*, 2021). So, in general:

$$k_{\mathrm{L}} \propto D_{\mathrm{L}}{}^{1/2} \quad \text{Eq. 20}$$

$$k_{\mathrm{G}} \propto D_{\mathrm{G}}{}^{2/3} \quad \text{Eq. 21}$$

These proportionalities in the correlations for liquids and gases can be used to translate the experimentally derived partial mass transfer coefficients from one substance to another:

$$\frac{k_{\mathrm{L},1}}{k_{\mathrm{L},2}} = \left(\frac{D_{\mathrm{L},1}}{D_{\mathrm{L},2}}\right)^{\frac{1}{2}} \quad \text{Eq. 22}$$

$$k_{\mathrm{L},2} = k_{\mathrm{L},1} \cdot \left(\frac{D_{\mathrm{L},1}}{D_{\mathrm{L},2}}\right)^{-\frac{1}{2}} \quad \text{Eq. 23}$$

$$\frac{k_{\mathrm{G},1}}{k_{\mathrm{G},2}} = \left(\frac{D_{\mathrm{G},1}}{D_{\mathrm{G},2}}\right)^{\frac{2}{3}} \quad \text{Eq. 24}$$

$$k_{\mathrm{G},2} = k_{\mathrm{G},1} \cdot \left(\frac{D_{\mathrm{G},1}}{D_{\mathrm{G},2}}\right)^{-\frac{2}{3}} \quad \text{Eq. 25}$$

Where:

k_G	partial mass transfer coefficient for the gas (air) film	($m \cdot s^{-1}$)
k_L	partial mass transfer coefficient for the liquid (water) film	($m \cdot s^{-1}$)
D_G	diffusion coefficient in gas (air)	($m^2 \cdot s^{-1}$)
D_L	diffusion coefficient in liquid (water)	($m^2 \cdot s^{-1}$)

Subscripts 1 and 2 denote substance 1 and 2.

In conclusion, partial mass transfer coefficients for air and water can be extrapolated from one substance to another, requiring the diffusion coefficients of both substances in air and water.

3.2.3.3 Dependency of the mass transfer coefficients on flow velocity

The typical mass transfer correlation (equation 18) shows that besides the diffusion coefficient, the partial mass transfer coefficients also depend on the flow velocity of the medium. Experimentally derived mass transfer coefficients usually apply best within the range of experimental gas or liquid mass flow velocities. As stated by Hsieh *et al.* (2013), the experimental values for ammonia derived in their study can be considered to be typical for counterflow cooling towers. It can therefore be assumed that the derived transfer coefficients are applicable to the same type of cooling towers, featuring gas and liquid mass flows within the same range. In the study conducted by Chien *et al.* (2012) with the same pilot-scale cooling towers, the liquid flow velocity differed by a factor of 1.03 and the gas flow velocities differed by a factor of 1.54. The average water flow velocity of the three towers used by Chien *et al.* (2012) was approximately 7 $m \cdot h^{-1}$ and the average gas velocity was approximately 3800 $m \cdot h^{-1}$. To investigate the influence of the flow conditions on the mass transfer, the product of the overall mass transfer rate and the exchange area (*K.a*) and the volumetric or mass-based liquid-to-gas ratio can be correlated as done by, for instance, Munz *et* *al.* (1984), although using the flow velocity of the respective medium is preferred. As we do not anticipated that the flow velocities within cooling towers will vary to a large extent, we expect that the liquid-to-gas ratio can be used as a proxy for the representativeness as well. The mass-based liquid-to-gas ratios (L/G) for the three towers used in the study conducted by Chien *et al.* (2012) ranged from 1.4 to 2.1. with a reported average value of 1.7. On this basis, and taking into account the variation in collected data on typical liquid to gas ratios for counterflow recirculating cooling towers (see section 4.1.1) as a first estimate, the gas-to-liquid ratio should be within a factor of approximately 2 of the average L/G ratio, with a value of 1.7 for the mass transfer coefficients to apply.

3.2.3.4 From overall to partial mass transfer coefficients

In order to obtain both the liquid-side and the gas-side partial mass transfer coefficient from the overall mass transfer coefficient, many authors have used the two-reference substance approach. This approach requires experimental data for both a substance whose transfer is controlled by the gas phase and a substance whose transfer is controlled by the liquid phase (Douglas et al., 2022). We used a fixed ratio between the partial liquid and gas-side mass transfer coefficient to estimate the value of each single partial mass transfer coefficient from the experimentally derived overall mass transfer coefficient, as proposed by Hsieh *et al.* (2013).

For their pilot-scale cooling tower, Hsieh *et al.* (2013) derived an overall mass transfer coefficient K_G for ammonia of 2.32 x 10^{-3} $m \cdot s^{-1}$. They concluded that, for ammonia, the overall resistance is very close to the partial mass transfer coefficient in the gas film (k_G). They assumed that the overall mass transfer coefficient is constant across all experimental conditions (pH range), since K_G is expected to be dominated by k_G and not k_L. This assumption, however, particularly holds good for the higher pH values (> pH 8) where the influence of co-diffusion is limited. Also, the value of the Henry's law constant influences the degree to which K_G is dominated by k_G. Since a significant share of the experimental results is established around pH 8 or higher, it is expected that there might be a noticeable effect of the pH on K_G at the higher pH values.

For the derivation of k_G and k_L we adopted the method used by Hsieh *et al.* (2013) in estimating K_G. Linear regression was applied to find the value for k_G that provided the best fit for the simulated data with the experimental data. However, the influence of the pH was included by applying equation 5 (equation 3 in Hsieh *et al.* (2013)) – in calculating the ratio of the concentration of ammonia in the cooling water – to that in the make-up water from equation 8 in Hsieh *et al.* (2013). We used the same values for pK_a (8,88) and K_H ($K_{air\text{-}water}$) at 37.5 °C ($1.2 \cdot 10^{-3}$). The value for K_H matches the value recommended by Sander (2015). The value of the pK_a and the temperature dependence originates from Bates *et al.* (1949).

In order to derive values for both k_G and k_L, a value for the ratio of k_G-to-k_L is required. Munz *et al.* (1984) concluded that the ratio might be significantly different from the suggested general value of 150 used to model – among others – counterflow packed columns. They showed that the ratio of mass transfer coefficients differs, depending on the gas-liquid contact process and on the hydrodynamic conditions within a given process. Hsieh *et al.* (2013) mention in their paper that the ratio of k_G-to-k_L generally ranges from 40 to 200 in stripping towers. On the basis of experimental data from three pilot-scale cooling towers, Safari *et al.* (2014) calculated a value for $k_G/k_L = 100$ for CO_2, using the same pilot-scale cooling towers that were used by Hsieh *et al.* (2013). Equation 18 in our report shows that the partial mass transfer coefficient depends on process conditions, characteristics of the packing material, properties of the bulk media and the diffusion coefficients in the respective media. For the same pilot-scale cooling towers that are operated under (approximately) the same conditions, k_G/k_L, however, only varies with the diffusion coefficients of the substance in air and water. From the value for CO_2, a value of $k_G/k_L = 80$ can be calculated for NH_3 using equation 20 and 21. Diffusion coefficients in air and water for NH_3 and CO_2 were adopted from Yaws (2014).

With the k_G/k_L ratio fixed, the best linear fit on the experimental values against the modelled values was found at a k_G of $1.66 \cdot 10^{-3}$ $m \cdot s^{-1}$ with an R^2 (square of the Pearson product-moment correlation coefficient) of 0.92. The resulting value for $k_L = 2.08 \cdot 10^{-5}$ $m \cdot s^{-1}$. The linear fit is slightly better than the R^2 value of 0.90 obtained by Hsieh *et al.* (2013), which is probably due to the introduction of the influence of the pH into our model calculations. The obtained values of k_G and k_L are clearly affected by the values of Henry's law constant and the pK_a, which also shows the importance of applying a temperature correction for this particular purpose.

The partial mass transfer coefficients for ammonia can be used to derive those for other compounds, using equations 23 and 25, where substance 1 is the reference substance ammonia and where, in this study, substance 2 is the biocidal active ingredient under consideration. Diffusion coefficients are temperature-dependent, which needs to be taken into account. However, because the temperature dependence is the same for all substances (see section 5.2.4), in principle, it is sufficient to assume that the diffusion coefficients are based on the same reference temperature.

3.2.3.5 Evaluation of measured overall mass transfer coefficient

In situations where the surface area of mass transfer is unknown, for instance in bubble stripping, only the product of the overall mass transfer coefficient and the specific area ($K.a$) can be obtained from experimental studies. For stripping in a packed column, the volumetric surface area of the packing can be used in calculating K from the experimentally determined $K.a$ values. This allows the comparison of the overall mass transfer rates. As discussed above, the pH influences mass transfer for ionising substances. To exclude the effect of pH in the case of ammonia, ideally, mass transfer rates at water pH values of 11 or higher should be considered, because at a pH value of 11, ammonia exists mainly (for > 99 percent) in the non-ionised form. In addition, process conditions, such as the gas and liquid flow rates and the temperature, need to be considered because they influence the mass transfer rate as well. The value of the overall liquid-side mass transfer rate (K_L) of $1.82 \cdot 10^{-6}$ $m \cdot s^{-1}$ is calculated from the partial mass transfer coefficients for the pilot-scale cooling tower, using equation and assuming no dissociation. This value is consistent with the K_L of $2.86 \cdot 10^{-6}$ m·s^{-1} obtained from a study by Katehis *et al.* (1998) under representative conditions (temperature and pH). The latter is the average of two sets of measurements performed at 36 and 47 °C with a total of nineteen measurements at a pH > 11 in a pilot-scale stripping tower with random packing material (Jaeger Tripack). The liquid-to-gas mass ratio varied from 0.9 to 1.5, with an average value of 1.3. Annex 3 shows the results of three other studies investigating the mass transfer of ammonia in packed stripping columns. The calculated K_L values of the three studies are approximately a factor of ten lower. This can probably be attributed to deviating gas and liquid flow rates and pH values. The L/G ratios in these studies are consistently higher, which means that the air flow rate in relation to the water flow rate is low, which generally would result in a lower mass transfer rate. This trend can also be observed in the data presented in Kim *et al.* (2021). The process conditions in the experiments performed by Ferraz *et al.* (2013) closely match the conditions in the pilot-scale cooling towers, where the L/G ratio is a factor of 3 higher and the temperature 10 degrees lower (Batch 1). Still, the measured liquid-side mass transfer rate is a factor of 10 lower.

The effect of the flowrate regime (gas and liquid flow rates) on the $K.a$ is discussed in Miller *et al.* (1976). For instance, the Ufford-Perona equations, which they mention in their paper, can be used to quantify this effect. This correlation shows that the mass transfer rate depends on the absolute values of the individual flow rates rather than their ratio. Calculating the $K.a$ values on the basis of the experimental flow rates from both the studies described above, using the Ufford-Perona equation, shows that the predicted overall mass transfer coefficient of the experiments performed by Ferraz *et al.* (2013) is expected to be approximately a factor of 2.6 lower. This shows that the flow regime can partly explain the difference, whereas the type of packing used may be another important factor.

3.2.4 *Synthesis: from ammonia to biocidal active substances*

For their pilot-scale cooling tower, Hsieh *et al.* (2013) reported a value for the overall mass transfer coefficient K_G for ammonia of 2.32×10^{-3} m·s^{-1} and concluded that the overall resistance is very close to the partial mass transfer coefficient in the gas film (k_G). In this report the partial mass transfer coefficients for ammonia are re-calculated based on the experimental data provided in Hsieh *et al.* (2013). This resulted in a value of $1.66 \cdot 10^{-3}$ m·s^{-1} for the partial mass transfer coefficient in air ($k_{G,\mathrm{ammonia}}$). For the water side ($k_{L,\mathrm{ammonia}}$), the obtained value is $2.08 \cdot 10^{-5}$ m·s^{-1}. As stated by Hsieh *et al.* (2013), the derived value for K_G is applicable to larger-scale counterflow cooling systems, because the design values of the major process conditions of the pilot towers (cooling water and air flow rates, and cooling water temperature) are representative of large-scale counterflow cooling systems.

The overall liquid-side mass transfer rate (K_L) of $1.82 \cdot 10^{-6}$ m·s^{-1} that results from the recalculated partial mass transfer coefficients is consistent with other data found in literature. For proper comparison, process conditions should be compatible. The influence of, for instance, flow conditions can partly explain differences in measured values, apart from the type of packing used in the experiments.

The derived values for the partial mass transfer coefficients for ammonia can be used to predict the overall mass transfer coefficients for other compounds by applying the following steps:

First: calculate the partial mass transfer coefficients for the biocidal active ingredient using the diffusion coefficients for ammonia and the active ingredient at the cooling system temperature.

Second: derive the co-diffusion coefficient α using the dissociation constant K_a and the pH of the cooling water. Note that different equations apply for acidic and basic substances.

Third: calculate the overall mass transfer rate constant K_G according to equation 5, applying the partial mass transfer coefficients, the co-diffusion coefficient and Henry's law constant K_H of the active substance. Use the K_H value at the relevant temperature.

4 New parameter defaults for calculating $F_{volat,a.i.}$

The model for calculating the emission to air due to volatilisation from the cooling water in the cooling tower requires some new parameters and default settings, i.e. the temperature and the pH of cooling water. The air-to-water flow ratio is also discussed in order to check on the ranges that are observed in practice and to verify the applicability domain of the calculated mass transfer coefficients and volatilisation factors (see Chapter 5).

4.1 New parameters

4.1.1 Water-to-air flow ratio

The ratio of the mass flow of air (*G*) required to cool down a certain mass flow of water (*L*) to a specific temperature, the water-to-air mass flow ratio, is a key parameter in cooling tower design. Apart from being determined by the water and air inlet and outlet temperatures and the ambient conditions, the *L*/*G* ratio is also depends on the contact surface area and contact time for heat exchange, which is determined by the type of fill. Film fills, for instance, are more efficient, having a larger effective surface area compared to, for instance, splash fills. The latter thus require a higher quantity of air, resulting in lower liquid to gas (*L*/*G*) ratios, see Table 3.

*Table 3 Typical L/G ratios for various types of fill media**

Parameter / type of fill	**Splash fill**	**Low-clog film fill**	**Film fill**
Possible *L*/*G* ratio	1.1-1.5	1.4.1.8	1.5-2.0
Effective area ($m^2 \cdot m^{-3}$)	30-45	85-100	150
Fill height required (m)	5-10	1.5-1.8	1.2-1.5
Quantity of air required	High	Low	Very low

* Bureau of Energy Efficiency. Government of India (Anonymous).

Holzwarth *et al.* (1984) indicate that for a refinery cooling tower, the *L*/*G* ratios are in the range of 0.75 – 2.0, typically *L*/*G* = 1.3. Hsieh *et al.* (2013) indicate that the pilot scale towers they used to evaluate the mass transfer rates were designed to represent large-scale counterflow cooling systems. The design value of the *L*/*G* ratio for pilot scale towers was 2.0. While measuring the performance of the pilot-scale cooling towers, the liquid to gas ratios ranged from 1.4 to 2.3, with an average value of 1.7 (Chien *et al.*, 2012). For older types of cooling towers with splash fill, the *L*/*G* ratio typically amounts to 1.3, and for modern types of cooling towers with film fill material, the *L*/*G* ratio is typically 1.7, according to the information provided in Table 3. On the basis of the above information, despite the differences between different types of fills, an *L*/*G* ratio of about 1.5 seems to be representative for a wide range of towers with various types of fills. Furthermore, the range of values measured in the experiments conducted by Chien *et al.* (2012) cover the range of values presented in Table 3. On the basis of this and the typical values, the measured transfer coefficients are thought to be representative for counterflow cooling towers.

4.1.2 *Temperature of the cooling system*

In the pilot study carried out by Hsieh *et al.* (2013), the average recirculating water temperature delivered to the cooling tower was 40.6 °C, and the temperature in the collection basin was 35 °C. The operating temperature for cooling systems may to a large extent depend on the specific process streams to be cooled, and are furthermore determined by local provisions on surface water temperature increase by discharged cooling water. In the Netherlands, for example, the temperature of the released cooling water is bound to be no more than 18 °C above the temperature of the recipient water body (Groshart *et al.*, 2003). Groshart *et al.* (2003) mention bulk temperatures of between 20-30 °C for open recirculating and once-through systems are mentioned. In recirculating systems, the temperature of the bulk water under the cooling tower ranges from 20 to 30 °C, and the temperature of the water entering at the top of the cooling tower is usually between 35 and 40 °C (Baltus *et al.*, 1996). The IPPC BAT Bref document (EC, 2001) reports several examples with average temperatures in the range of 31-35 °C, the average temperature being the average of the tower inlet and exit temperature. Gartiser *et al.* (2002) mention an average cooling water temperature of 35 °C. For recirculating systems, the hot water temperatures are in the range of 35-40 °C, with temperature differences (cooling range) between 5-20 °C (Gartiser *et al.*, 2002). On the basis of this information, a default temperature of 35 °C in the cooling tower seems to be justifiable.

4.1.3 *pH of the cooling water*

Since the degree of ionisation is determined by the pH of the cooling water, this is an important factor to account for. Cooling towers are usually operated at neutral or slightly basic conditions, in order to balance between the risk of corrosion at acidic conditions, and the risk of scaling at more basic conditions. Besides being important with respect to scaling and corrosion, pH is also an important factor for the effectiveness of biocides. Many biocides can be applied within a wide range of pH values, usually between pH 6 and 9 (Annex 4 in Groshart *et al.* (2003). However, specific recommendations apply for various substances. Some biocides, such as dibromo-nitrilopropionamide (DBNPA) and some organosulfur compounds (thiocyanates), show a pH-dependent hydrolysis rate in water, and many show significantly less activity at a pH above 8. On the other hand, some organosulfur (thiones) and quaternary ammonium compounds have a high effectiveness up to and above pH 8.5 (Groshart *et al.*, 2003). Hypochlorous acid is more effective than hypochlorite, favouring slightly acidic or neutral conditions. On the other hand, hypochlorous acid is more volatile under acidic conditions. For this reason, it is recommended to use chlorine-releasing biocides at pH values above 8 in open circulation cooling, despite their lower effectiveness at that pH (Gartiser *et al.*, 2002). The more weakly dissociating hypobromous acid (HOBr) can be used at a pH around 8 or higher, while retaining its effectiveness, because up to pH 9, hypobromous acid dominates over the only weakly biocidal acting hypobromite ion (OBr^-). Gartiser *et al.* (2002) report the pH values of several analysed cooling water samples (*n*=12), with pHs between 7.9 and 9.5. Higher pH values are found for cooling systems using isothiazolines and quaternary ammonium compounds, while slightly lower values were found for systems employing bronopol and

BCDMH. It becomes clear from the above that the pH is a key parameter not only with respect to volatilisation, but also in relation to biocide effectiveness, the rate of hydrolysis and in protecting the cooling tower equipment and functioning from corrosion and scaling. On the basis of the above data, we proposed using a pH of 7.5 for those substances that require neutral to slightly alkaline conditions such as HOCl, ozone, (most) organosulfur compounds and DBNPA. For substances that require or are used at more alkaline conditions, such as BrOH and thiones, a pH of 8.5 is proposed.

4.2 Conclusion

In order to calculate volatilisation factors, default values for the required parameters have to be set, which are the temperature and the pH of cooling water and the air-to-water flow ratio (*L*/*G* ratio).

On the basis of the collected information, an *L*/*G* ratio of 1.5 seems to be representative for a wide range of towers with various types of fills, including splash and film fills. Since the range of values measured in the experiments conducted by Chien *et al.* (2012) cover the typical L/G ratios for various types of fills, the measured (partial) mass transfer coefficients for ammonia are thought to be representative for counterflow cooling towers in general.

For the pH of the cooling water, a default value of pH 8 is proposed. Alternatively, two groups of substances may be defined: one group of active ingredients, which are mainly used at neutral to slightly alkaline conditions, at a pH of approximately 7.5, such as HOCl, ozone and DBNPA, and a group of biocides used at more alkaline conditions (pH of 8.5), such as BrOH, isothiazolines, and quaternary ammonium compounds.

A value of 35 °C for the average temperature in the cooling tower seems to be justifiable, on the basis of the available information.

5 Substance properties and calculated volatilisation factors

5.1 Introduction

In this chapter, substance-specific volatilisation factors are calculated for the biocidal active substances that are currently authorised for use in the PT11 category of biocidal products. First, the substance properties that are required to perform the calculations will be discussed. This will be followed by a detailed description of the data collection process. Furthermore, the default values of the cooling tower process conditions that have been discussed in the previous chapter will be summarised. Finally the data collected on physical-chemical properties and calculated volatilisation factors are presented.

Quaternary ammonium compounds are not included in the list. This class of compounds consists of salts with a positively charged quaternary ammonium group and a negatively charged counter-anion, usually chloride, when dissolved in water. Because of these characteristics quaternary ammonium compounds have an extremely low volatility. They are also rather inert and insensitive to alkaline conditions. Thus the pH of the water does not influence the dissociation. It can therefore be assumed that substances belonging to this class of compounds, will not volatilise from the cooling water in the cooling tower. The only relevant emission route to air for this group of substances is via drift of cooling water droplets.

5.2 Substance properties

The calculation of the volatilisation factors according to the model presented in Chapter 3 requires the dimensionless Henry's law constant (K_H). In environmental fate modelling, K_H is often called the air-water partition coefficient $K_{\text{air-water}}$ ($\text{m}^3_{\text{water}} \cdot \text{m}^{-3}_{\text{air}}$) or K_{aw}, while Sander *et al.* (2022) have recently proposed to rename this parameter as H_v^{cc}. Furthermore, the acid dissociation constant K_a is required to account for dissociation when calculating the overall mass transfer coefficients (see section 3.2.2) to account for the effect of co-diffusion. Furthermore, dissociation in the cooling water has to be accounted for because only the part of non-dissociated fraction will volatilise. Finally, the diffusion coefficients of the active substances in air and water are required in order to estimate the partial mass transfer coefficients for each individual substance. Additional substance properties may be required to allow to estimate the required properties if measured data is not available. As a cooling tower is usually operated at elevated temperatures, the required substance properties have to be adjusted to this temperature. This will be further elaborated when discussing the different substance properties in more detail.

5.2.1 Diffusion coefficients

For many chemicals, diffusion coefficients are available in handbooks, such as the one compiled by Yaws (2014). When measured diffusion coefficients are not available, they can be derived from semi-empirical correlations, such as Fuller's method for the diffusion coefficient in air (Reid *et al.*, 1988, Tang *et al.*, 2014) and the Wilke-Chang correlation for the diffusion coefficient in water (Reid *et al.*, 1988, Schramke *et al.*, 1999, Wilke *et al.*, 1955). A detailed description of the data sources and data selection procedure is provided in Annex 5.

The correlation for the aqueous diffusion coefficient according to Wilke and Chang is:

$$D_{\mathrm{water},T} = \frac{7.4\cdot10^{-12}\cdot\sqrt{x\cdot M_{\mathrm{water}}}\cdot T}{\mu_{\mathrm{water}}\cdot {V_{\mathrm{m,subst}}}^{0.6}} = \frac{7.4\cdot10^{-12}\cdot\sqrt{2.6\cdot18}\cdot T}{\mu_{\mathrm{water}}\cdot {V_{\mathrm{m,subst}}}^{0.6}} = \frac{5.1\cdot10^{-11}\cdot T}{\mu_{\mathrm{water}}\cdot {V_{\mathrm{m,subst}}}^{0.6}} \qquad \text{Eq. 26}$$

Where:

$D_{\mathrm{water},T}$	diffusion coefficient in water at temperature T	($\mathrm{m^2\cdot s^{-1}}$)
x	association constant for water	(-)
M_{water}	molecular weight of water	($\mathrm{g\cdot mol^{-1}}$)
T	temperature	(K)
$\mu_{\mathrm{water,T}}$	dynamic viscosity of water at temperature T	(cP)
$V_{\mathrm{m,subst}}$	molar volume of the compound	($\mathrm{cm^3\cdot mol^{-1}}$)

The association constant x has a value of 2.6 for water and the molecular weight of water (M_{water}) is 18 $\mathrm{g\cdot mol^{-1}}$. At elevated temperatures, the viscosity of liquids generally decreases. The temperature dependence of the viscosity of water is provided by Yaws (2014).

The difficulty in applying this equation lies in the molar volume of the compound. This should actually be the molar volume at the melting point of the substance. That means that the molar volume cannot be calculated from the density of a substance and the molecular weight at standard temperature.

Care needs therefore to be taken to ascertain that the correct molar volume is used from substance properties databases. For many databases, background information on the source or assessment method for the molar volume is difficult to find and rather concise. In the case of data presented in the Chemspider database for instance, it appeared that the molar volume is based on the density at standard (room) temperature and the molecular weight. Alternatively, the molar volume at the melting point can be obtained from correlation equations of which several are presented in Reid *et al.* (1988). None of these methods appeared to be fully applicable to the substances of interest in this report.

Our search for a simple and generally applicable method for calculating the diffusion coefficient finally led to the Stokes-Einstein equation. The Stokes-Einstein equation is used to calculate the diffusion of spherical particles through a liquid.

$$D_{\mathrm{water},T} = \frac{k_{\mathrm{B}}\cdot T}{6\cdot\pi\cdot\mu_{\mathrm{water}}\cdot r} \qquad \text{Eq. 27}$$

Where:

$D_{\mathrm{water},T}$	water diffusion coefficient at temperature T	($m^2 \cdot s^{-1}$)
k_B	Boltzmann constant	($m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$)
T	temperature	(K)
$\mu_{\mathrm{water,T}}$	dynamic viscosity of water at temperature T	($kg \cdot m^{-1} \cdot s^{-1}$)
r	the radius of a spherical particle	(m)

Miyamoto *et al.* (2020) describe the application of the Stokes-Einstein equation in calculating diffusion coefficients using the simple radius, which is calculated from the Van der Waals volume. We used Marvin Sketch (ChemAxon, 2016) in order to calculate the Van der Waals volume V_{VdW} (Å^3). The molecular (simple) radius r_s (m) was calculated as:

$$r_s = \sqrt[3]{\frac{3V_{\mathrm{VdW}}}{4\pi}} \cdot 1^{-10} \qquad \text{Eq. 28}$$

Where:

r_s	simple molecular radius	(m)
V_{vdw}	Van der Waals volume	(Å^3)

The diffusion coefficient for air can be derived with Fuller's method in case experimental values are not available (Al-Malah, 2012, Fogler, 1986, Reid *et al.*, 1988, Tang *et al.*, 2014):

$$D_{\mathrm{air},T} = \frac{1.0111 \cdot 10^{-7} \cdot \sqrt{(M_{\mathrm{air}}+M_{\mathrm{subst}})/(M_{\mathrm{air}} \cdot M_{\mathrm{subst}})} \cdot T^{1.75}}{P \cdot \left(V_{\mathrm{air}}^{\frac{1}{3}} + V_{\mathrm{subst}}^{\frac{1}{3}}\right)^2} \qquad \text{Eq. 29}$$

Where:

$D_{\mathrm{air},T}$	diffusion coefficient in air at a pressure of 1 atmosphere and temperature T	($m^2 \cdot s^{-1}$)
M_{subst}	molecular weight of the substance	($g \cdot mol^{-1}$)
M_{air}	molecular weight of air	($g \cdot mol^{-1}$)
T	temperature	(K)
P	atmospheric pressure	(atm)
V_{air}	dimensionless diffusion volume of air	(-)
V_{subst}	dimensionless diffusion volume of active ingredient	(-)

The molecular weight of air (M_{air}) is 29 $g \cdot mol^{-1}$. If not available, the dimensionless diffusion volume of a compound can be calculated from the sum of the diffusive volumes of the atoms a compound consists of (Reid *et al.*, 1988, Tang *et al.*, 2014, Poling *et al.*, 2001). For air, the dimensionless diffusion volume V_{air} is 19.7.

5.2.2 *Henry's law constant*

Values for Henry's law constant are selected in the following order of preference: measured data including temperature of determination from – among others – literature (Acree *et al.*, 2007) or online databases (Sander, 2015). If no measured data was available, Henry's law constant was calculated from experimentally determined vapour pressure (P_v) and water solubility (S_w) that were not reported as > or < values. If no experimentally determined vapour pressure and water solubility with temperatures of determination were available, the HenryWin estimate (US EPA, 2011) was selected. A detailed description of the data sources and data selection procedure is provided in Annex 5.

Henry's law constant can be calculated from experimentally determined vapour pressure (P_v) and water solubility (S_w) in the following manner:

$$K_{\mathrm{H},T_{\mathrm{test}}} = \frac{P_{\mathrm{v},T_{\mathrm{test}}} \cdot M_{\mathrm{subst}}}{S_{\mathrm{w},\,T_{\mathrm{test}}} \cdot R \cdot T_{\mathrm{test}}} \qquad \text{Eq. 30}$$

Where

K_H	Henry's law volatility constant dimensionless	($m^3_{water} \cdot m^{-3}_{air}$)
P_v	vapour pressure at test temperature, T_{test}	(Pa)
S_w	water solubility at test temperature, T_{test}	($g \cdot L^{-1}$)
R	gas constant	($J \cdot mol^{-1} \cdot K^{-1}$)
T_{test}	temperature at which measured value is determined	(K)
M_{subst}	molecular weight of the substance	($g \cdot mol^{-1}$)

5.2.3 *Acid dissociation constant K_a*

On the basis of chemical structure, it was decided whether a substance does or does not dissociate (d.n.d). For dissociating substances, measured values reported in the CAR or in the literature were preferred, and if these were not available, p*K*a values were calculated using MarvinSketch (ChemAxon, 2016).

5.2.4 *Effect of temperature on substance properties*

Diffusion coefficients, Henry's law constants as well as p*K*a are temperature-dependent. This means that these parameters have to be corrected to the values at the system's operating temperature before using them in the calculation of volatilisation factor ($F_{volat,a.i.}$). The evaluation and selection of the default value for the temperature in the cooling tower (35 °C) is described in section 4.1.2.

Temperature correction of Henry's law constant

The value of Henry's law constant K_H at the average cooling tower temperature can be calculated from K_H at test temperature using the following formula, which is derived from the Van 't Hoff equation:

$$K_{\mathrm{H},T_{\mathrm{system}}} = K_{\mathrm{H},T_{\mathrm{test}}} \cdot e^{-\frac{\Delta H_{\mathrm{volat}}}{R} \cdot \left(\frac{1}{T_{\mathrm{system}}} - \frac{1}{T_{\mathrm{test}}}\right)} \qquad \text{Eq. 31}$$

Where

$K_{H,Tsystem}$	dimensionless Henry's law volatility constant at cooling system temperature	($m^3_{water} \cdot m^{-3}_{air}$)
$K_{H,Ttest}$	Henry's law constant at test temperature	($m^3_{water} \cdot m^{-3}_{air}$)
ΔH_{volat}	molar enthalpy of volatilisation	($J \cdot mol^{-1}$)
R	gas constant	($J \cdot mol^{-1}\ K^{-1}$)
T_{test}	temperature at which K_H is determined	(K)
T_{system}	average temperature of the water in the cooling system	(K)

The molar enthalpy of volatilisation can be obtained from literature (Acree *et al.*, 2007) or online databases (Sander, 2015). Sander et al.

(2015, 2022) provide values for d ln$H$ / d($^1/_T$), i.e. slopes of Van 't Hoff plots, which equals -$\Delta H_{\mathrm{sol}}/R$:

$$\frac{\mathrm{d}\ln H}{\mathrm{d}(1/T)} = \frac{-\Delta H_{\mathrm{sol}}}{R} \qquad \text{Eq. 32}$$

Where

H	molar enthalpy	(J·mol^{-1})
ΔH_{sol}	molar enthalpy of solvation or dissolution	(J·mol^{-1})
R	gas constant	(J·mol^{-1} K^{-1})

Note that the symbol H in the above equation denotes enthalpy. Here, it is not related to Henry's law constant. ΔH_{sol} is the molar enthalpy of solvation. Since the tabulated values in Sander *et al.* (2021) are Henry's law solubility constants, we are using Henry's law volatility constants, which are the reciproke of the solubility constants. The molar enthalpy of volatilisation $\Delta H_{\mathrm{volat}}$ is numerically equal to ΔH_{sol}; they only differ in sign.

Alternatively, the molar heat of volatilisation can be calculated from the molar heat of evaporation (ΔH_{evap}) and solution (ΔH_{soln}) according to:

$$\Delta H_{\mathrm{volat}} = \Delta H_{\mathrm{evap}} - \Delta H_{\mathrm{soln}} \qquad \text{Eq. 33}$$

Where

$\Delta H_{\mathrm{volat}}$	molar enthalpy of volatilisation	(J·mol^{-1})
ΔH_{evap}	molar enthalpy of evaporation	(J·mol^{-1})
ΔH_{soln}	molar enthalpy of solution	(J·mol^{-1})

If a measured value is not available, the value for the chemical class that is assigned by HenryWin, an EpiSuite™ module (US EPA, 2011), can be used.

Temperature correction for the diffusion coefficient

To extrapolate diffusion coefficients at measurement temperature to the system's temperature, Fuller's method (Tang *et al.*, 2014) can be used to derive the temperature dependence for the diffusion coefficients in air:

$$D_{\mathrm{air},T_{\mathrm{system}}} = D_{\mathrm{air},T_{\mathrm{test}}} \cdot \left(\frac{T_{\mathrm{system}}}{T_{\mathrm{test}}}\right)^{1.75} \qquad \text{Eq. 34}$$

Where:

$D_{\mathrm{air},T\mathrm{system}}$	air diffusion coefficient at system temperature	(m^2.s^{-1})
$D_{\mathrm{air},T\mathrm{test}}$	measured air diffusion coefficient at test temperature	(m^2·s^{-1})
T_{system}	cooling system temperature (35 °C)	(K)
T_{test}	test temperature	(K)

For diffusion in water, the following equation can be used for the temperature correction of measured diffusion coefficients. The temperature correction is based on the temperature dependence that is shown in the Stokes-Einstein equation. In addition, the temperature dependence of the dynamic viscosity should also be accounted for, resulting in the following equation:

$$D_{\mathrm{water},T_{\mathrm{system}}} = D_{\mathrm{water},T_{\mathrm{test}}} \cdot \frac{T_{\mathrm{system}}}{T_{\mathrm{test}}} \cdot \frac{\mu_{\mathrm{water,Ttest}}}{\mu_{\mathrm{water,Tsystem}}} \qquad \text{Eq. 35}$$

Where:

$D_{\mathrm{water},T\mathrm{system}}$	liquid diffusion coefficient at cooling system temperature	($m^2 \cdot s^{-1}$)
$D_{\mathrm{water},T\mathrm{test}}$	measured liquid diffusion coefficient at test temperature	($m^2 \cdot s^{-1}$)
T_{system}	cooling system temperature (35 °C)	(K)
T_{test}	test temperature	(K)
$\mu_{\mathrm{water,Ttest}}$	dynamic viscosity of water at test temperature	(cP)
$\mu_{\mathrm{water,Tsystem}}$	dynamic viscosity of water at system temperature	(cP)

Furthermore, substance specific empirical temperature correlations can be found in handbooks such as Yaws (2014).

5.2.5 *Influence of temperature on the pK_a*

The pK_a is also temperature-dependent. For most acids, dissociation is an endothermic process and the pK_a will increase with rising temperatures. However, the effect of temperature on the pK_a may differ widely between substances and vary from little or no effect to a rather significant effect (Reijenga *et al.*, 2013). For ammonia. for instance, the pK_a is rather sensitive to temperature changes (Bates *et al.*, 1949, Guštin *et al.*, 2011). Unfortunately, data on the temperature dependence of the pK_a is scarce, and for the substances considered in the report, only information on our reference substance ammonia has been found in literature. Therefore, as indicated above, the pK_a is used without further correction for temperature. A detailed description of the data sources and data selection procedure is provided in Annex 5.

5.3 Cooling tower process conditions

The cooling tower process parameters required for calculating the volatilisation factors are the air and water flow rate, the pH of the cooling water and the average temperature of the cooling water in the cooling tower. Default values have been provided in Chapter 4. Other cooling tower characteristics, such as those characterising the packing material equal those for the pilot-scale cooling towers described by Hsieh *et al.* (2013), Chien *et al.* (2012) and Safari *et al.* (2014) (see Table 4). With regard to the air and water flow rates, a literature search has been carried out in order to check whether natural draft counterflow cooling towers operate within the same range as those applying to the pilot-scale cooling towers (see section 4.1.1). It was concluded that for the ratio of these two parameters, the L/G ratio, a value of 1.5 seems to be representative for a wide range of towers with different types of fills. Therefore, the air and water flow rates were set at a value such that the *L*/*G* ratio is 1.5, matching the values for cooling tower B in Chien *et al.* (2012) (see Table 4).

In Chapter 4, we proposed to use a pH of 7.5 for those substances that require neutral to slightly alkaline conditions, such as HOCl, ozone, (most) organosulfur compounds and DBNPA. For substances that require more alkaline conditions, such as BrOH and thiones, a pH of 8.5 is proposed. Without taking into account the chemical class of biocides, the default pH is set at a value of 8 but we calculated the volatilisation factors at the three most common pH values.

Table 4 Default values for the cooling tower process conditions and tower packing characteristics.

Process conditions

Parameter	**Unit**	**Value**	**Source**
G_x	$kg \cdot h^{-1} \cdot m^{-2}$	6940	Chien *et al.* (2012)
G_y	$kg \cdot h^{-1} \cdot m^{-2}$	4642	Chien *et al.* (2012)
T_{system}	K	308.15	Chapter 4, this equals 35 °C
pH	-	8	Chapter 4
Q_x	$m^3 \cdot s^{-1}$	$1.804 \cdot 10^{-4}$	Calculated: $G_x/\rho_{water} \cdot A_b/3600$
Q_y	$m^3 \cdot s^{-1}$	$1.047 \cdot 10^{-1}$	Calculated: $G_y/\rho_{air}\ A_b/3600$
G_x/G_y	-	1.5	calculated

Packing and tower characteristics

Parameter	**Unit**	**Value**	**Source**
a	$m^2 \cdot m^{-3}$	147.8	Chien *et al.* (2012)
A_b	m^2	0.093	Chien *et al.* (2012)
Z_T	m	0.914	Chien *et al.* (2012)

With

a	volumetric surface area of the packing	($m^2 \cdot m^{-3}$)
A_b	base area of the packing filled tower	(m^2)
G_x	water mass velocity	($kg \cdot h^{-1} \cdot m^{-2}$)
G_y	vapour free air mass velocity	($kg \cdot h^{-1} \cdot m^{-2}$)
Q_x	water volume flow rate	($m^3 \cdot s^{-1}$)
Q_y	air volume flow rate	($m^3 \cdot s^{-1}$)
T_{system}	temperature in the cooling tower	(°C)

5.4 Calculation of the volatilisation factors

This section presents the volatilisation factors that are calculated using the model presented in Chapter 3 and the default cooling tower characteristics discussed in Chapter 4 and summarised in Table 4. The required substance properties, including those needed to derive the partial mass transfer coefficients and the calculated partial and overall mass transfer coefficients, are presented in Annex 6. Table 5 summarises the derived values for $F_{volat,a.i.}$.

To facilitate risk assessors in the calculating volatilisation factors the calculation procedure is implemented in an Excel spreadsheet. The Excel spreadsheet is freely available from: https://www.rivm.nl/bibliotheek/rapporten/2025-0140.xlsx

Table 5 Calculated substance-specific volatilisation factors for biocides in cooling water towers based on mass transfer correlations with ammonia.

Substance[a]	**Fraction lost due to volatilisation, $F_{volat,a.i.}$**		
	pH 7.5	**pH 8**	**pH 8.5**
1	9.0E-06	9.0E-06	9.0E-06
2	5.3E-06	5.3E-06	5.3E-06
3	3.0E-07	1.2E-07	4.3E-08
4	7.6E-05	7.5E-05	7.4E-05
5	8.3E-05	8.3E-05	8.3E-05
6	1.6E-03	1.6E-03	1.6E-03
7[b]	0.0E+00	0.0E+00	0.0E+00
8	5.2E-08	5.2E-08	5.2E-08
9	3.6E-07	2.5E-07	1.2E-07
10	2.0E-04	2.0E-04	2.0E-04
11	3.6E-08	3.6E-08	3.6E-08
12	7.9E-08	7.9E-08	7.9E-08
13	0.0E+00	0.0E+00	0.0E+00
14	6.5E-02	6.5E-02	6.5E-02
15	6.6E-14	6.7E-13	6.3E-12
16	7.1E-01	7.1E-01	7.1E-01
17	1.4E-12	4.5E-13	1.4E-13
18	4.3E-10	1.4E-10	4.3E-11
19	1.4E-12	4.6E-13	1.4E-13
20	3.0E-06	3.0E-06	3.0E-06
21	9.4E-15	9.4E-15	9.4E-15
22	4.3E-10	1.4E-10	4.3E-11
23	7.9E-05	7.9E-05	7.9E-05
24	8.3E-03	6.3E-03	3.5E-03
25	6.1E-01	6.1E-01	6.1E-01

[a] Substance names are listed in Annex 6.

[b] This substance is completely ionised when dissolved in water.

Numbers in light grey shaded cells are around or higher than the fraction lost through drift (0.025%). Numbers in dark grey shaded cells are comparable to or higher than the previous default value for evaporation of 1%.

In the emission scenario document for preservatives used in liquid cooling systems, PT11, the default value for the fraction of the substance evaporating to air is 1 percent. The results presented in Table 5 show that for four substances the emission to air via volatilisation is higher than or around 1 percent. For ozone and chlorine dioxide the fraction of the substance that is lost due to volatilisation is substantially higher than 1 percent. For the remainder of the substances, the volatilisation to air is a factor of 10 or more lower. For five substances, the emission to air via volatilisation is comparable or slightly higher than the emission via drift (F_{drift} = 0.00025). Substances with a relatively high Henry's law constant, $K_H > 1.10^{-6}$ ($m^{-3} \cdot m^{-3}$), and which mainly exist in the neutral form at the most common pH values, have the highest tendency for volatilisation. Furthermore, for most of the substances listed in Table 5, the pH has little or no influence on the volatilisation, with the exception of substances 3 (BIT), 9 (BCMDH) and 24 (peracetic acid).

5.5 Conclusion

The volatilisation of biocides used as cooling water preservatives can be estimated from experimental data of other substances, applying the methodology described in this report. Key in this methodology is the prediction of partial mass transfer coefficients from experimental data, based on diffusion coefficients in air and water. Besides the partial mass transfer coefficients, Henry’s law constant and, for ionising substances, the acid dissociation constant are required in order to calculate the volatilisation from the cooling water in the cooling tower. The general model that is applied in calculating stripping tower efficiency, taking ionisation into account, is used to perform the calculations based on process conditions that are typical for counterflow cooling towers.

Cooling towers are operated at elevated temperatures. Therefore, a temperature correction is required for the relevant substance properties. The necessary calculations and data have been provided. The necessary substance properties have been collected from literature and available databases. If measured values are not available, they are estimated. The prediction methods used and the collected and calculated data are presented in this chapter. This results in a complete set of substance properties for all biocides that are currently authorised for use as cooling water preservatives. The outlined methodology and presented data facilitate, if necessary, additional calculations, for instance under other conditions, such as temperature and pH of the cooling water, and support the calculation of the volatilisation factors for new substances to be authorised.

The estimates of the substance-specific volatilisation factors clearly show the importance of a substance-dependent approach and reveal that a single default is inadequate. Depending on the substance properties, emissions to air by volatilisation can exceed the losses from drift multiple times. On the other hand, volatilisation can be much lower compared to drift losses. The same holds when comparing the volatilisation factors to the default value of 1 percent. For many substances, this value is an overestimation with respect to the atmospheric losses, especially for highly water-soluble substances that are largely ionised at the existing pH of the cooling water.

6 Modelling emissions to water via blowdown water

6.1 Introduction

As indicated previously, this document deals with the cooling systems that have a cooling tower in place, the once-through and open recirculating cooling systems. With respect to the emissions to water, the ESD describes two different dosing regimes for both systems, continuous dosing, and shock dosing. Because the degree of volatilisation affects the concentration of the biocide in the cooling system, the volatilisation factor also needs to be implemented in the models for these cooling systems and dosing regimes. This will be elaborated in the following sections for both systems.

6.2 Emissions to water via blowdown: open recirculating system

A schematic representation of the open recirculating cooling system with all ingoing and outgoing flows is provided in Figure 7. Symbols are in line with the ESD for PT11 and adapted where necessary.

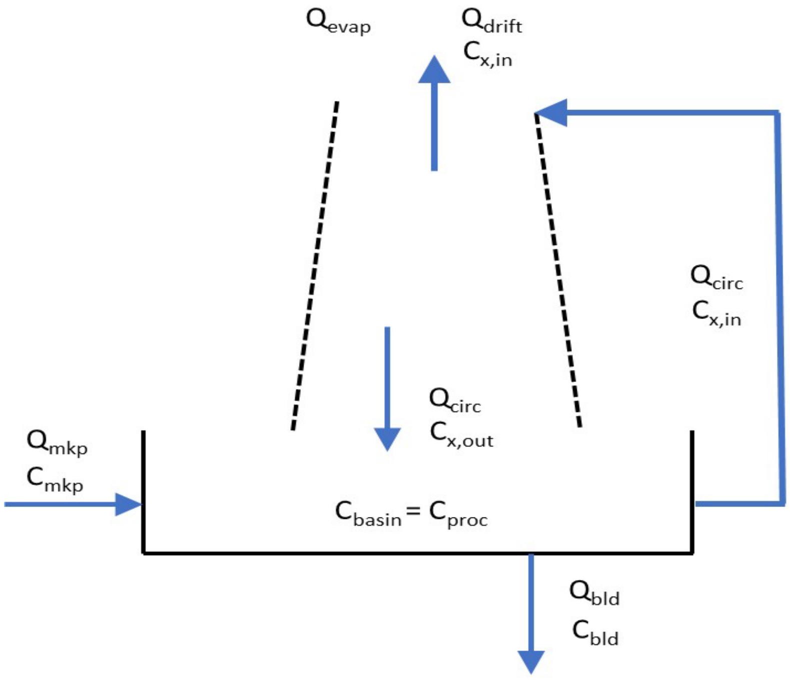

Figure 7 Schematic drawing of the cooling water flows and concentrations in the open recirculating cooling system.

For the recirculating cooling water system, the emission to surface water resulting from the discharge of the blowdown water is calculated from the mass balance of the substance in the cooling water basin.

The general mass balance of a substance is defined as the change in mass per unit of time (dm/dt) in a system being equal to the difference between the ingoing (m_{in}) and outgoing mass flows (m_{out}) plus the amount formed or removed by chemical reaction (m_{react}). When the chemical is reacted away, for instance, due to degradation, m_{react} should be deducted in the mass balance, usually achieved by adding the minus sign to the degradation rate constant:

$$\frac{\mathrm{dm}}{\mathrm{d}t} = m_{\mathrm{in}} - m_{\mathrm{out}} + m_{\mathrm{react}} \qquad \text{Eq. 36}$$

The concentration of the substance in the basin (C_{basin}) can simply be obtained from the mass balance by dividing the mass (of the substance) by the total volume of water, in the basin:

$$V_{\mathrm{basin}} \frac{\mathrm{d}C_{\mathrm{basin}}}{\mathrm{d}t} = m_{\mathrm{in}} - m_{\mathrm{out}} + m_{\mathrm{react}} \qquad \text{Eq. 37}$$

The ingoing and outgoing mass flows, as specified in Figure 7, are determined by the flow rate of the medium and the concentration of the substance in the specific flow. The cooling medium in the system is water, so in Figure 7 all flows denoted by a Q refer to water. Concentrations of the substance, i.e. the active ingredient, in water are denoted by a C. Having noted this, the medium and the substance in subscripts of the symbols for the respective parameters are not further presented in the following equations. Furthermore, although included in Figure 7, the mass balance of the substance should not include the amount of water evaporated from the tower because evaporated water does not contain any chemical substance.

Taking the above into consideration, the mass balance for the basin can be written as follows:

$$V_{\mathrm{basin}} \frac{\mathrm{d}C_{\mathrm{basin}}}{\mathrm{d}t} = Q_{\mathrm{mkp}} \cdot C_{\mathrm{mkp.}} + \ Q_{\mathrm{circ}} \cdot C_{\mathrm{x,out}} - Q_{\mathrm{bld}} \cdot C_{\mathrm{bld}} - Q_{\mathrm{circ}} \cdot C_{x,\mathrm{in}} - k_{\mathrm{deg}} \cdot C_{\mathrm{proc}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 38}$$

Losses via drift are not yet included in order to limit the number of terms in the equations. Although losses via drift are generally small compared to the loss via blowdown (approximately 2 percent of blowdown) these losses should be included to complete the mass balance. We will do so in section 6.2.4.

For the open recirculating cooling tower, two different types of situations can be recognised, according to the ESD. The first one is the situation involving continuous dosing of chemicals in the system via make-up water. The second one is shock dosing, adding a relatively large amount of substance to the system in a short time, resulting in a peak concentration.

6.2.1 *Continuous dosing*

The first situation, involving a constant inlet concentration and all other conditions for the basin constant, results in a steady-state situation. At steady-state, there is no change in concentration in the basin, $\mathrm{d}C/\mathrm{d}t = 0$ and the sum of all ingoing mass flows equals the total of the outgoing mass flows.

$$\frac{\mathrm{d}m}{\mathrm{d}t} = 0 = m_{\mathrm{in}} - m_{\mathrm{out}} \qquad \text{Eq. 39}$$

$$m_{\mathrm{in}} = m_{\mathrm{out}} \qquad \text{Eq. 40}$$

Assuming ideal mixing in the basin, the concentrations in the two flows leaving the basin, the circulating water that is going to the cooling tower and the blowdown, are equal to the concentration in the basin:

$$C_{\mathrm{basin}} \text{ or } C_{\mathrm{proc}} = C_{\mathrm{x.in}} = \ C_{\mathrm{bld}} \qquad \text{Eq. 41}$$

When the recommended concentration to be maintained in the system (C_{proc}) is known, it can be used directly to calculate the emission via blowdown water. For the situation where the substance is added to the system via the make-up water, the mass balance for the steady-state situation has to be arranged:

$$Q_{\mathrm{mkp}} \cdot C_{\mathrm{mkp}} + \ Q_{\mathrm{circ}} \cdot C_{\mathrm{x,out}} = Q_{\mathrm{bld}} \cdot C_{\mathrm{bld}} + Q_{\mathrm{circ}} \cdot C_{\mathrm{x,in}} + k_{\mathrm{deg}} \cdot C_{\mathrm{basin}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 42}$$

As shown earlier in Chapter 3, the outgoing concentration in the cooling tower water and the ingoing concentration are related by the volatilisation factor:

$$1 - F_{\mathrm{volat,a.i.}} = C_{\mathrm{x,out}}/C_{\mathrm{x,in}} \qquad \text{Eq. 43}$$

and

$$C_{\mathrm{x,out}} = C_{\mathrm{x,in}} \cdot \left(1 - F_{\mathrm{volat,a.i.}}\right) \qquad \text{Eq. 44}$$

Using this relationship and knowing that $C_{\mathrm{x,in}}$ = C_{bld} = C_{basin} or C_{proc}, equation 42 can be re-written, resulting in the following equations:

$$Q_{\mathrm{mkp}} \cdot C_{\mathrm{mkp}} + \ Q_{\mathrm{circ}} \cdot C_{\mathrm{proc}} \cdot \left(1 - F_{\mathrm{volat,a.i.}}\right) = Q_{\mathrm{bld}} \cdot C_{\mathrm{proc}} + Q_{\mathrm{circ}} \cdot C_{\mathrm{proc}} + k_{\mathrm{deg}} \cdot C_{\mathrm{proc}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 45}$$

Rearranging the mass balance gives:

$$Q_{\mathrm{mkp}} \cdot C_{\mathrm{mkp}} = Q_{\mathrm{bld}} \cdot C_{\mathrm{proc}} + Q_{\mathrm{circ}} \cdot C_{\mathrm{proc}} - Q_{\mathrm{circ}} \cdot C_{\mathrm{proc}} \cdot \left(1 - F_{\mathrm{volat,a.i.}}\right) + k_{\mathrm{deg}} \cdot C_{\mathrm{proc}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 46}$$

From which the following equation is obtained:

$$Q_{\mathrm{mkp}} \cdot C_{\mathrm{mkp}} = C_{\mathrm{proc}} \cdot \left[Q_{\mathrm{bld}} + Q_{\mathrm{circ}} \cdot F_{\mathrm{volat,a.i.}} + k_{\mathrm{deg}} \cdot V_{\mathrm{basin}}\right] \qquad \text{Eq. 47}$$

Further re-arrangement gives:

$$C_{\mathrm{proc}} = C_{\mathrm{mkp}} \cdot \frac{Q_{\mathrm{mkp}}}{Q_{\mathrm{bld}} + Q_{\mathrm{circ}} \cdot F_{\mathrm{volat,a.i.}} + k_{\mathrm{deg}} \cdot V_{\mathrm{basin}}} \qquad \text{Eq. 48}$$

Which is the steady-state concentration in the cooling tower basin taking into account volatilisation from the cooling tower and degradation of the substance in the cooling basin.

In the above equations,

Q_{mkp}	make-up water flow rate	$(\mathrm{m}^{3}\cdot\mathrm{s}^{-1})$
Q_{bld}	blowdown flow rate	$(\mathrm{m}^{3}\cdot\mathrm{s}^{-1})$
Q_{circ}	water recirculation flow rate	$(\mathrm{m}^{-3}\cdot\mathrm{s}^{-1})$
C_{proc}	concentration of the active ingredient in the system	$(\mathrm{kg}\cdot\mathrm{m}^{-3})$
C_{mkp}	concentration in the make-up water	$(\mathrm{kg}\cdot\mathrm{m}^{-3})$
V_{basin}	water volume in the cooling water basin	(m^{3})
$F_{\mathrm{volat,a.i.}}$	fraction of the active ingredient volatilised from the cooling water	(-)
k_{deg}	First-order degradation rate constant	(s^{-1})

6.2.2 *Shock dosing*

For the second situation, which involves shock dosing, a relatively high amount of chemical is dosed into the system in a short amount of time to cause a peak concentration. The concentration in the system will decline gradually, starting from this initial peak concentration because there is no chemical entering the system anymore. This is a non-steady state situation as the conditions, the concentration, change with time. The change of the concentration in the basin in time is determined on the basis of the same mass balance as shown in equations 36 and 37, but here, the volume of the whole system is used instead of the volume of the basin. This is more correct because, although the bulk of the cooling water volume is in the basin, there is also some hold-up in the transport piping, the heat exchanger and the cooling tower. The change of the concentration in time can be calculated by solving the following differential equation; starting from the mass balance from equation 37 and rewriting to concentrations using the system volume V_{syst}:

$$V_{\mathrm{syst}}\frac{\mathrm{d}C}{\mathrm{d}t} = m_{\mathrm{in}} - m_{\mathrm{out}} + m_{\mathrm{react}} \qquad \text{Eq. 49}$$

In the situation of shock dosing, there is no (continuous) dosing via the make-up water flow after the shock dose is added to the system. Therefore, $C_{\mathrm{mkp}} = 0$ and the mass balance becomes:

$$V_{\mathrm{syst}}\frac{\mathrm{d}C_{\mathrm{proc}}}{\mathrm{d}t} = Q_{\mathrm{circ}}\cdot C_{\mathrm{proc}}\cdot\left(1 - F_{\mathrm{volat,a.i.}}\right) - Q_{\mathrm{bld}}\cdot C_{\mathrm{proc}} - Q_{\mathrm{circ}}\cdot C_{\mathrm{proc}} - k_{\mathrm{deg}}\cdot C_{\mathrm{proc}}\cdot V_{\mathrm{syst}} \qquad \text{Eq. 50}$$

$$V_{\mathrm{syst}}\frac{\mathrm{d}C_{\mathrm{proc}}}{\mathrm{d}t} = C_{\mathrm{proc}}\cdot\left(Q_{\mathrm{circ}}\cdot F_{\mathrm{volat,a.i.}} - Q_{\mathrm{bld}} - k_{\mathrm{deg}}\cdot V_{\mathrm{syst}}\right) \qquad \text{Eq. 51}$$

Rearranging and dividing both sides by V_{syst},

$$\frac{\mathrm{d}C_{\mathrm{proc}}}{C_{\mathrm{proc}}} = \left(\frac{Q_{\mathrm{circ}}}{V_{\mathrm{syst}}}\cdot F_{\mathrm{volat,a.i.}} - \frac{Q_{\mathrm{bld}}}{V_{\mathrm{syst}}} - k_{\mathrm{deg}}\right)\cdot\mathrm{d}t \qquad \text{Eq. 52}$$

To determine C_{proc} as a function of time, the obtained differential equation is solved by integration:

$$\int_{C_0}^{C_t}\frac{\mathrm{d}C_{\mathrm{proc}}}{C_{\mathrm{proc}}} = \int_0^t\left(\frac{Q_{\mathrm{circ}}}{V_{\mathrm{syst}}}\cdot F_{\mathrm{volat,a.i.}} - \frac{Q_{\mathrm{bld}}}{V_{\mathrm{syst}}} - k_{\mathrm{deg}}\right)\cdot\mathrm{d}t \qquad \text{Eq. 53}$$

Which yields:

$$ln\left(\frac{C_{\text{proc},t}}{C_{\text{proc},0}}\right) = -\left(\frac{Q_{\text{circ}}}{V_{\text{syst}}} \cdot F_{\text{volat,a.i.}} + \frac{Q_{\text{bld}}}{V_{\text{syst}}} + k_{\text{deg}}\right) \cdot t \qquad \text{Eq. 54}$$

And finally, after exponentiating both sides:

$$\frac{C_{\text{proc},t}}{C_{\text{proc},0}} = e^{-\left(\frac{Q_{\text{circ}}}{V_{\text{syst}}} \cdot F_{\text{volat,a.i.}} + \frac{Q_{\text{bld}}}{V_{\text{syst}}} + k_{\text{deg}}\right) \cdot t} \qquad \text{Eq. 55}$$

Starting from an initial concentration ($C_{\text{proc,ini}}$) at time 0 and knowing that $C_{\text{proc}} = C_{\text{bld}}$ yields the concentration in the blowdown at time, t:

$$C_{\text{bld,t}} = C_{\text{proc,ini}} \cdot e^{-\left(\frac{Q_{\text{circ}}}{V_{\text{syst}}} \cdot F_{\text{volat,a.i.}} + \frac{Q_{\text{bld}}}{V_{\text{syst}}} + k_{\text{deg}}\right) \cdot t} \qquad \text{Eq. 56}$$

The separate terms in the exponent can be considered as rate constants, all having the unit (s^{-1}) for the various loss processes that add up to the total loss rate for the entire system:

$$K_{\text{syst}} = \frac{Q_{\text{circ}}}{V_{\text{syst}}} \cdot F_{\text{volat,a.i.}} + \frac{Q_{\text{bld}}}{V_{\text{syst}}} + k_{\text{deg}} = k_{\text{volat}} + k_{\text{bld}} + k_{\text{deg}} \qquad \text{Eq. 57}$$

In the ESD for PT 11 (Groshart *et al.*, 2003), the total emission to water during time period $\Delta t = t_i - t_0$ is calculated on the basis of the average concentration over time period Δt after adding the shock dose. Here, we use Δt instead of t to indicate that we are dealing with a time period.

The average concentration during a time period is calculated according to the following equation:

$$C_{\text{bld,avg}} = C_{\text{proc,ini}} \cdot \frac{1 - e^{-K_{\text{syst}} \cdot \Delta t}}{K_{\text{syst}} \cdot \Delta t} \qquad \text{Eq. 58}$$

The total mass released over time period Δt after the shock dose is calculated from the product of the average concentration, and the total amount of blowdown discharged during time period Δt ($Q_{\text{bld}} \cdot \Delta t$):

$$RELEASE_{\text{tot},\Delta\text{t}} = Q_{bld} \cdot \Delta t \cdot C_{\text{proc,ini}} \cdot \frac{1 - e^{-K_{\text{syst}} \cdot \Delta t}}{K_{\text{syst}} \cdot \Delta t} \qquad \text{Eq. 59}$$

After simplification (Δt is cancelled out), this results in

$$RELEASE_{\text{tot},\Delta\text{t}} = Q_{bld} \cdot C_{\text{proc,ini}} \cdot \frac{1 - e^{-K_{\text{syst}} \cdot \Delta t}}{K_{\text{syst}}} \qquad \text{Eq. 60}$$

Equation 58 is obtained by taking the integral of equation 61 below. Equation 61 in turn is obtained from equation 56 by replacing the separate loss terms by K_{syst} (equation 57), resulting in the more general formula:

$$C_{\text{bld,t}} = C_{\text{proc,ini}} \cdot e^{-K_{\text{syst}} \cdot t} \qquad \text{Eq. 61}$$

Integrating equation 61 over the time period Δt and dividing by Δt to obtain the average yields equation 58:

$$C_{\text{bld,avg}} = \frac{1}{\Delta t} \cdot \int_0^{t_i} C_{\text{proc,ini}} \cdot e^{-K_{\text{syst}} \cdot t} \cdot \mathrm{d}t = C_{\text{proc,ini}} \cdot \frac{1-e^{-K_{\text{syst}} \cdot \Delta t}}{K_{\text{syst}} \cdot \Delta t} \qquad \text{Eq. 62}$$

Rather than the total amount (kg) released during a time period Δt, usually the daily emission (kg·d^{-1}) is required in risk assessment. The (average) daily emission during a time period is simply obtained from the product of the average concentration in the blowdown and the (average) blowdown flow rate:

$$RELEASE_{\text{avg,}\Delta\text{t}} = Q_{bld} \cdot C_{\text{proc,ini}} \cdot \frac{1-e^{-K_{\text{syst}} \cdot \Delta t}}{K_{\text{syst}} \cdot \Delta t} \qquad \text{Eq. 63}$$

6.2.3 *Repeated shock dosing*

For repeated shock dosing, the equation calculating the concentration after a number (n) of repeated shock dosings with a time interval of T_{int}, as presented in the ESD (Groshart *et al.*, 2003), can be used, knowing that K_{syst} should be calculated according to equation 57:

$$C_{\text{bld,t}} = \sum_{i=1}^{n} C_{\text{proc,ini}} \cdot e^{-(t-(i-1)\cdot T_{\text{int}})\cdot K_{\text{syst}}} \text{ for } (t-(i-1)\cdot T_{\text{int}} > 0) \qquad \text{Eq. 64}$$

An alternative presentation of the above equation is presented below:

$$C_{\text{bld,max}} = C_{\text{proc,ini}} \cdot \frac{1-\left(e^{-K_{\text{syst}} \cdot T_{\text{int}}}\right)^n}{1-e^{-K_{\text{syst}} \cdot T_{\text{int}}}} \qquad \text{Eq. 65}$$

This equation is similar to the one used in the risk assessment of industrial chemicals and biocides for the application of sewage sludge to soil at the local scale (EC, 2003, ECHA, 2019). It provides the maximum concentration at the last shock dosing.

The average concentration for the time period Δt after the repeated shock dosing has stopped (at $t = n.T_{\text{int}}$) can be calculated analogously to Equation 58 and 62:

$$C_{\text{bld,avg}} = \sum_{i=1}^{n} C_{\text{proc,ini}} \cdot e^{-(t-(i-1)\cdot T_{\text{int}})\cdot K_{\text{syst}}} \cdot \frac{1-e^{-K_{\text{syst}} \cdot \Delta t}}{K_{\text{syst}} \cdot \Delta t} \qquad \text{Eq. 66}$$

6.2.4 *Start dosing during a certain time period*

Additional to the scenarios defined in the ESD for PT 11, there is another possible relevant situation. This is the situation where the concentration in the system will gradually increase after addition of biocides to the system at a constant rate over a certain time period. When dosing starts, there may be no chemical in the system yet or there could be a certain initial concentration. If dosing is maintained long enough, a steady-state concentration will be reached. In order to calculate the change of concentration through time after starting to add the chemical, the mass balance for the cooling system basin has to be solved once again. The difference with the previous situation (shock dosing) is that there is an extra term on the right-hand side of the mass balance, defining the amount added to the system, Q_{mkp} times the concentration in the system C_{mkp}:

$$V_{\text{syst}} \frac{\mathrm{d}C_{\text{proc}}}{\mathrm{d}t} = Q_{\text{circ}} \cdot C_{\text{proc}} \cdot \left(1 - F_{\text{volat,a.i.}}\right) + Q_{\text{mkp}} \cdot C_{\text{mkp}} - Q_{\text{bld}} \cdot C_{\text{proc}} - Q_{\text{circ}} \cdot C_{\text{proc}} - k_{\text{deg}} \cdot C_{\text{proc}} \cdot V_{\text{syst}} \qquad \text{Eq. 67}$$

In this situation, the ingoing and outgoing mass flow rates are not equal and therefore, the equation cannot be simplified. The notation of the equation is simplified by defining $K_{\text{out}} = Q_{\text{out}}/V_{\text{syst}}$ and $K_{\text{in}} = Q_{\text{in}}/V_{\text{syst}}$, which are the sum of the outgoing flows divided by the system volume and the sum of the ingoing flows divided by the system volume, respectively. In analogy with the degradation rate constant, they can be considered as rate constants having the same unit (s^{-1}). First, we will work out the following simple mass balance with one ingoing and one outgoing flow, including degradation. For this situation, the following equation will then be obtained:

$$V_{\text{syst}} \frac{\mathrm{d}C_{\text{proc}}}{\mathrm{d}t} = Q_{\text{in}} \cdot C_{\text{in}} - Q_{\text{out}} \cdot C_{\text{proc}} - k_{\text{deg}} \cdot C_{\text{proc}} \cdot V_{\text{syst}} \qquad \text{Eq. 68}$$

Divide both sides by V_{syst},

$$\frac{\mathrm{d}C_{\text{proc}}}{\mathrm{d}t} = \frac{Q_{\text{in}}}{V_{\text{syst}}} \cdot C_{\text{in}} - \frac{Q_{\text{out}}}{V_{\text{syst}}} \cdot C_{\text{proc}} - k_{\text{deg}} \cdot C_{\text{proc}} \qquad \text{Eq. 69}$$

Introducing K_{in} and K_{out} and rearranging,

$$\frac{\mathrm{d}C_{\text{proc}}}{\mathrm{d}t} = K_{\text{in}} \cdot C_{\text{in}} - K_{\text{out}} \cdot C_{\text{proc}} - k_{\text{deg}} \cdot C_{\text{proc}} \qquad \text{Eq. 70}$$

$$\frac{\mathrm{d}C_{\text{proc}}}{\mathrm{d}t} = K_{\text{in}} \cdot C_{\text{in}} - C_{\text{proc}} \cdot (k_{\text{deg}} + K_{\text{out}}) \qquad \text{Eq. 71}$$

and after integration,

$$\int_{C_0}^{C_t} \frac{\mathrm{d}C_{\text{proc}}}{K_{\text{in}} \cdot C_{\text{in}} - C_{\text{proc}} \cdot (k_{\text{deg}} + K_{\text{out}})} = \int_{t_0}^{t} \mathrm{d}t \qquad \text{Eq. 72}$$

the result is:

$$t = -\frac{1}{k_{\text{deg}} + K_{\text{out}}} \cdot \ln\left[\frac{K_{\text{in}} \cdot C_{\text{in}} - (k_{\text{deg}} + K_{\text{out}}) \cdot C_{\text{proc},t}}{K_{\text{in}} \cdot C_{\text{in}} - (k_{\text{deg}} + K_{\text{out}}) \cdot C_{\text{proc},t_0}}\right] \qquad \text{Eq. 73}$$

or

$$C_{\text{proc},t} = C_{\text{proc},t_0} \cdot e^{-\left(K_{\text{out}} + k_{\text{deg}}\right)} \cdot t + C_{\text{in}} \cdot \frac{K_{\text{in}}}{K_{\text{out}} + k_{\text{deg}}} \cdot \left[1 - e^{-\left(K_{\text{out}} + k_{\text{deg}}\right) \cdot t}\right] \qquad \text{Eq. 74}$$

Here, we also introduce the losses caused by drift. The rate constant for the losses via drift can easily be obtained from the quotient of the amount of water loss via drift ($Q_{\text{circ}} \cdot F_{\text{drift}}$) and the system volume (V_{syst}). So, here we have a new definition of K_{syst} with the losses via drift as an additional loss process added to loss terms in equation 57.

The loss rate, K_{out} (m·s^{-1}) of the substance via the blowdown, volatilisation and droplet drift is then equal to

$$K_{\text{out}} = K_{\text{syst}} = \frac{Q_{\text{bld}}}{V_{\text{syst}}} + \frac{Q_{\text{circ}}}{V_{\text{syst}}} \cdot F_{\text{volat,a.i.}} + \frac{Q_{\text{circ}}}{V_{\text{syst}}} \cdot F_{\text{drift}} \qquad \text{Eq. 75}$$

With Q_{mkp} as the ingoing flow rate, the input rate constant, K_{in} is defined as:

$$K_{\text{in}} = \frac{Q_{\text{mkp}}}{V_{\text{syst}}} \qquad \text{Eq. 76}$$

Equation 73 allows one to calculate the concentration in the system after dosing for a certain time period via the make-up water. The (peak) concentration that is reached can be used as input for the calculation of the change in concentration when the dosing is stopped, equation 56. This model can also be used for repeated dosing at intervals times long enough to prevent build-up in the system, as described for the Baur model (Groshart *et al.*, 2003).

6.3 Model for once-through cooling systems

In the emission scenario for once-though systems, it is assumed that the cooling water is cooled in a cooling tower before discharge. Consequently, emissions to air and soil need to be calculated. In practice, however, once-through systems cooling towers are hardly ever used. One of the reasons is the large amount of cooling water discharged, which would require very large cooling towers. It is therefore suggested to consider two distinct scenarios: one for once-though systems without a cooling tower and one with a cooling tower. For the cooling system without a cooling tower, this would simply mean that only losses due to degradation should be taken into account when calculating emission to surface water, without any other losses to the atmosphere to account for. This is actually what occurs in the calculation of the concentration in the blowdown for the current ESD scenario, which makes it equivocal. The scenario is inconsistent as losses due to volatilisation or drift are not accounted for when calculating the discharge via the blowdown water to surface water, but at the same time, emissions to air are calculated. For consistency’s sake, we therefore suggest considering two distinct scenarios.

6.3.1 Situation without a cooling tower

Because there is no recirculation in once-through systems, we suggest to replace Q_{circ} by Q_{bld} in the current emission scenario for clarity. Apart from that, the current calculation is correct. Below we provide some further explanation on the current equation.

Once-though systems can be modelled as a plug flow reactor, also known as tubular flow reactor. The flow rate through the system is the same as the blowdown flow rate. The travel time required for the fluid to be transported through the cooling system, is called the residence time or the hydraulic retention time (*HRT*). For plug flow reactors, t HRT corresponds to the ratio between the systems’ volume and the blowdown flow rate:

$$HRT = \frac{V_{\mathrm{syst}}}{Q_{\mathrm{bld}}} \qquad \text{Eq. 77}$$

The HRT is also the time allowed for degradation to occur during the passage of the cooling water down the system[4]. Therefore, the concentration in the blowdown after one shock dosing is calculated as:

$$C_{\mathrm{bld}} = C_{\mathrm{proc,ini}} \cdot e^{-\,k_{\mathrm{deg}} \cdot HRT} \qquad \text{Eq. 78}$$

The residence time in once-through systems is short, in the order of 2-15 minutes (Groshart *et al.*, 2003). In the ESD model, a residence time of 15 minutes is used (Groshart *et al.*, 2003).

For continuous dosing, the same equation can be used. The difference between both cases is that for shock dosing, the releases are intermittent, the concentration only applies during the dosing event, while for continuous dosing, the releases are constant throughout the time the installation is in operation.

6.3.2 *Situation with a cooling tower*

In the situation where the blowdown water is first cooled in a cooling tower, the losses to the atmosphere should be taken into account. As the losses occur after the cooling water has left the system and there is no recirculation of the cooling water, the concentration in the blowdown can simply be calculated by directly applying the volatilisation rate of the chemical as a factor that reduces the concentration of the blowdown. In principle, the evaporation of cooling water needs to be accounted for in the calculation of the concentration of the biocide in the blowdown water, as it actually reduces the amount of blowdown, although this effect is small within an evaporation rate of around 1 percent (see section 8.1.1). However, evaporation does not affect the total amount of chemical released. Another way to look at it is, when the amount of blowdown water is reduced by taking evaporation into account, the dilution factor increases simultaneously at the same rate when river flow rate remains the same. These effects cancel each other out and therefore, it is not necessary to include the evaporation of cooling water in the calculations.

In the situation where the used water is cooled in a cooling tower before discharge, the amount of substance discharged is reduced by the amount volatilised from the cooling tower:

$$C_{\mathrm{bld}} = C_{\mathrm{proc,ini}} \cdot e^{-\,k_{\mathrm{deg}} \cdot HRT} \cdot (1 - F_{\mathrm{volat}}) \qquad \text{Eq. 79}$$

Drift losses only reduce the total amount of chemical discharged, by reducing the total flow rate of cooling water discharged, but this does not alter the concentration in the blowdown water. In the emission scenario document, the fraction lost by drift, 0.025 percent, is neglected. Including the fraction drift in the calculation of the emission ($kg.s^{-1}$) to surface water can be achieved using the following equation:

$$Emission = C_{\mathrm{bld}} \cdot Q_{\mathrm{bld}} \cdot (1 - F_{\mathrm{drift}}) \qquad \text{Eq. 80}$$

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[4] The travel time τ (s) is the length of the tube L (m) over the fluid velocity u (m/s), $\tau = L/u$. Multiplying both the denominator and numerator by the flow-through area of the pipe A (m^2) shows that $\tau = \frac{L}{u} \cdot \frac{A}{A} = \frac{V}{Q}$

6.4 Summary of the models for the calculation of the concentration in the blowdown and the emission to water

This section provides an overview of all the different models for calculating the concentration in the blowdown water that have been discussed in this chapter regarding the different dosing regimes for the once-through and open-recirculating cooling towers. It should be remembered that the concentration in the blowdown water equals the concentration in the system $C_{\mathrm{proc}} = C_{\mathrm{bld}}$ because perfect mixing is assumed. For clarity, in the table below, the concentrations in the discharged water are referred to as C_{bld} and not as C_{proc}. Furthermore, the individual loss processes are not included in the equations. Instead, they are replaced by the overall loss rate constant K_{syst}.

Table 6 Summary of the models calculating the concentration in the blowdown discharged to water for once-through and open-recirculating cooling towers for three different dosing regimes.

Open recirculation

Cooling tower type, type of dosing	**Equation**	**Short description**	**Equation nr.**
Continuous dosing	$C_{bld} = C_{\mathrm{mkp}} \cdot \frac{Q_{\mathrm{mkp}}}{K_{\mathrm{syst}} \cdot V_{\mathrm{syst}}}$	Steady-state concentration obtained when dosing at constant rate	48 &57 combined
	$C_{\mathrm{bld},t} = C_{\mathrm{proc},t_0} \cdot e^{-(K_{\mathrm{syst}})} \cdot t + C_{mkp} \cdot \frac{Q_{\mathrm{mkp}}}{K_{\mathrm{syst}} \cdot V_{\mathrm{syst}}} \cdot \left[1 - e^{-(K_{\mathrm{syst}})\cdot t}\right]$	Starting continuous dosing at a certain starting concentration C_{proc,t_0}	74-76 combined
Shock dosing	$C_{\mathrm{bld,t}} = C_{\mathrm{proc,ini}} \cdot e^{-(K_{\mathrm{syst}})\cdot t}$	Concentration at time *t* after adding the shock dose	61
	$C_{\mathrm{bld,avg}} = C_{\mathrm{proc,ini}} \cdot \frac{1 - e^{-K_{\mathrm{syst}}\cdot \Delta t}}{K_{\mathrm{syst}} \cdot \Delta t}$	Average concentration over time period $\Delta t = t_0 + t_i$ after shock dosing is applied	58 and 62
Repeated shock dosing	$C_{bld,max} = C_{proc,ini} \cdot \frac{1 - (e^{-K_{\mathrm{syst}}\cdot T_{int}})^n}{1 - e^{-k\cdot T_{int}}}$	Maximum concentration at adding the last of n shock doses	65
Average concentration after repeated shock dosing	$C_{\mathrm{bld,avg}} = C_{\mathrm{proc,ini}} \cdot \frac{1 - (e^{-K_{\mathrm{syst}}\cdot T_{int}})^n}{1 - e^{-k\cdot T_{int}}} \cdot \frac{1 - e^{-K_{\mathrm{syst}}\cdot \Delta t}}{K_{\mathrm{syst}} \cdot \Delta t}$	Average concentration after *n* repeated shock dosings over time period $\Delta t = t_0 + t_i$ after the last dosing	66

Once-through, shock dosing and continuous dosing

Cooling tower type, type of dosing	Equation	Short description	Equation nr.
Without cooling tower	$C_{\mathrm{bld}} = C_{\mathrm{proc,ini}} \cdot e^{-k_{\mathrm{deg}} \cdot HRT}$	Models holds for the continuous dosing and shock dosing. The difference lies within the exposure duration, i.e. the time period during which the shock dose is applied (minutes) or the prolonged (continuous) dosing time.	78
With cooling tower	$C_{\mathrm{bld}} = C_{\mathrm{proc,ini}} \cdot e^{-k_{\mathrm{deg}} \cdot HRT} \cdot (1 - F_{\mathrm{volat}})$		79

General parameters

Cooling tower type, type of dosing	Equation	Short description	Equation nr.
Systems losses	$K_{\mathrm{syst}} = \frac{Q_{\mathrm{circ}}}{V_{\mathrm{syst}}} \cdot F_{\mathrm{volat,a.i.}} + \frac{Q_{\mathrm{bld}}}{V_{\mathrm{syst}}} + \frac{Q_{\mathrm{circ}}}{V_{\mathrm{syst}}} \cdot F_{\mathrm{drift}} + k_{\mathrm{deg}}$	This parameter includes all streams through which the substance is lost from the system	75
Hydraulic retention time	$HRT = V_{\mathrm{syst}} / Q_{\mathrm{bld}}$	The hydraulic retention time for once-through systems equals the travel time, sometimes also referred to as the passage time	77

6.5 Evaluation of the existing PT11 model for recirculation systems

As we discussed and worked out in the previous chapter, the main issue with Q_{evap} is that it does not contribute to any loss of chemicals from the cooling system. Rather, the volatilisation of the chemical in the cooling tower should be taken into account. However, Q_{evap} is included as a loss process in the current ESD.

Furthermore, the equation used in the current ESD to calculate the steady-state concentration in the outgoing water flow (the blowdown) for open recirculating cooling towers needs further discussion. The equations for the once-through systems do not need further evaluation.

In the ESD, the equation for calculating the outgoing cooling water concentration, i.e. the concentration in the blowdown water, at steady-state is written as:

$$C_{\mathrm{out}} = \frac{C_{\mathrm{in}}}{(1+K_{\mathrm{syst}} \cdot HRT)} \qquad \text{Eq. 81}$$

With K_{syst} being the overall loss rate including degradation:

$$K_{\mathrm{syst}} = K_{\mathrm{dilut}} + k_{\mathrm{deg}} \qquad \text{Eq. 82}$$

In line with the model proposed by Baur (Groshart *et al.*, 2003), K_{dilut} is used in the ESD for the overall loss caused by outgoing water flows in an open recirculating cooling tower with continuous dosing:

$$K_{\mathrm{dilut}} = \frac{Q_{\mathrm{bld}}+Q_{\mathrm{drift}}+Q_{\mathrm{evap}}}{V_{\mathrm{basin}}} = \frac{Q_{\mathrm{out}}}{V_{\mathrm{basin}}} = \frac{1}{HRT} \qquad \text{Eq. 83}$$

There are two issues with the current ESD model. First, starting with the substance mass balance for the cooling system basin:

$$Q_{\mathrm{in}} \cdot C_{\mathrm{in}} = Q_{\mathrm{out}} \cdot C_{\mathrm{out}} + k_{\mathrm{deg}} \cdot C_{\mathrm{basin}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 84}$$

The total outgoing flow (Q_{out}) in equation 84 can be replaced by K_{dilut} when it is defined in accordance with the ESD (equation 83). Proof that the equation presented in the ESD is incorrect is provided by introducing K_{dilut} in the above mass balance, which provides the following result:

From equation 83 Q_{out} is defined as:

$$Q_{\mathrm{out}} = K_{\mathrm{dilut}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 85}$$

Replacing Q_{out} in the simplified mass balance, this results in the final and correct equation:

$$Q_{\mathrm{in}} \cdot C_{\mathrm{in}} = K_{\mathrm{dilut}} \cdot V_{\mathrm{basin}} \cdot C_{\mathrm{out}} + k_{\mathrm{deg}} \cdot C_{\mathrm{basin}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 86}$$

With $C_{\mathrm{out}} = C_{\mathrm{basin}}$,

$$Q_{\mathrm{in}} \cdot C_{\mathrm{in}} = K_{\mathrm{dilut}} \cdot V_{\mathrm{basin}} \cdot C_{\mathrm{out}} + k_{\mathrm{deg}} \cdot C_{\mathrm{out}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 87}$$

$$Q_{\mathrm{in}} \cdot C_{\mathrm{in}} = \left(K_{\mathrm{dilut}} + k_{\mathrm{deg}}\right) \cdot V_{\mathrm{basin}} \cdot C_{\mathrm{out}} \qquad \text{Eq. 88}$$

$$Q_{\mathrm{in}} \cdot C_{\mathrm{in}} = K_{\mathrm{syst}} \cdot C_{\mathrm{out}} \cdot V_{\mathrm{basin}} \qquad \text{Eq. 89}$$

With $Q_{\mathrm{in}} = Q_{\mathrm{out}}$, giving $V_{\mathrm{basin}}/Q_{\mathrm{in}} = HRT$, this results in the following equation:

$$C_{\mathrm{out}} = \frac{C_{\mathrm{in}}}{K_{\mathrm{syst}}} \cdot \frac{Q_{\mathrm{in}}}{V_{\mathrm{basin}}} = \frac{C_{\mathrm{in}}}{K_{\mathrm{syst}} \cdot HRT} \qquad \text{Eq. 90}$$

It resembles the simplified expression of equation 48, which is obtained by applying K_{syst} as defined in equation 57 (see Table 6). This is different from the ESD equation (equation nr. 81), which shows that the ESD model is incorrect.

Second, in the current ESD, the calculation of K_{dilut} according to equation 83 includes the quantity of water lost through evaporation (Q_{evap}), which is correct when we look at the water mass balance. However, because the evaporated water does not contain any dissolved biocide and in fact results in a concentrating effect rather than a loss (of active substance) from the system, it should be left out in making a mass balance for the biocide in the cooling water system. Consequently, K_{dilut} should be calculated as:

$$K_{\mathrm{dilut}} = \frac{Q_{\mathrm{bld}} + Q_{\mathrm{drift}}}{V_{\mathrm{basin}}} \qquad \text{Eq. 91}$$

6.6 Conclusion

Equations for calculating the release of biocide active ingredients to water have been derived for recirculating and once-through cooling towers and for different dosing regimes. The equations include the fraction of the active ingredient that is lost from the cooling system via volatilisation and the drift of cooling water droplets as loss processes.

In addition to the existing dosing regimes, an additional equation is derived to calculate the course of the concentration in time when dosing a biocide for a certain time period.

When deriving the equations, it appeared that the original equation used in the current ESD to calculate the steady-state concentration in the outgoing water flow (the blowdown) for open recirculating cooling towers is incorrect.

7 Emission to air and deposition on soil

7.1 Emissions from spray drift and volatilisation

Chemicals entrained in the cooling water can be emitted from the cooling tower via water droplets that are dragged along with the air flow leaving the cooling tower at the top. This so called ‘spray drift’ or ‘droplet drift’ can be reduced by installing drift eliminators at the top of the cooling tower. The water droplets emitted as spray drift have the same composition as the cooling water. They contain both the dissociated and non-dissociated form of the biocide. Essential to calculating the emissions via drift is the correct calculation of the cooling water concentration, based on the appropriate model for the entire cooling system including relevant loss processes such as volatilisation. The emission to the atmosphere via volatilisation from the cooling water in the cooling tower through stripping is discussed in detail in Chapter 3. The volatilisation can be calculated by modelling the mass transfer of a chemical between air and cooling water in the cooling tower.

As shown in Figure 7 (Chapter 6), the concentration in the blowdown and the concentration in the water entering at the top of the cooling tower are the same. Therefore, the concentration in the blowdown can be used to calculate the emissions to air.

Emissions via spray drift:

$$RELEASE_{\mathrm{air,drift}} = F_{\mathrm{drift}} \cdot Q_{\mathrm{circ}} \cdot C_{\mathrm{bld}} \qquad \text{Eq. 92}$$

In order to calculate the release to air originating through volatilisation, the volatilisation factor is used:

$$RELEASE_{\mathrm{air,volat}} = F_{\mathrm{volat,a.i.}} \cdot Q_{\mathrm{circ}} \cdot C_{\mathrm{bld}} \qquad \text{Eq. 93}$$

7.2 Atmospheric dispersion and deposition on soil

In the current emission scenario, the release to soil is calculated from the fraction that is lost due to spray drift that subsequently deposits on soil, F_{depos}. In fact, the value of F_{depos} appears to be equal to the percentage drift (F_{drift}). In the emission scenario document, based on the descriptions of the original scenario (Luttik *et al.*, 1993, Assink, 1991), $AREA_{\mathrm{depos}}$ is the soil surface area on which deposition occurs. The value of $AREA_{\mathrm{depos}}$, is 100 m^2. On this basis, it seems that the total amount lost via drift deposits on a soil area of 100 m^2. This area of 100 m^2 (10 x 10 m) seems rather small considering the height and diameter of natural draft cooling towers. Large cooling towers can be as high as 130-160 metres, with outlet diameters of 65-68 metres, whereas medium-size cooling towers have heights in the order of 60 metres and a top diameter of approximately 35 metres (Gould *et al.*, 1999). Therefore, the deposition area has been changed to 75,000 m^2 for once-through, large and small recirculating cooling systems (ECHA, 2013). The method used to derive the deposition area shows much similarity with the adapted ASHRAE method described by Harris *et al.* (2017), the latter could be used to verify the current deposition area value.

A way forward for a more thorough estimation of the deposition from air to soil would be to first define cooling tower source characteristics (height, exit velocity, et cetera) for the default once-through and open recirculating cooling tower scenarios. Next, the deposition area or the average deposition on a predefined area could be calculated using an atmospheric dispersion model that preferably is designed to model cooling tower drift dispersion and deposition, such as the SACTI model (EPRI, 2015).

However, models such as the SACTI model usually focus on calculating plume shadowing effects, drift dispersion and drift deposition and do not include dispersion and deposition of chemicals emitted from the cooling tower in the gaseous phase. To that end, Gaussian plume models such as OPS (Sauter *et al.*, 2022) could be used.

As far as we know, there are no models that calculate the dispersion and deposition of both types of emission simultaneously. This would mean that the results of both models need to be combined to determine the concentration in air and the total deposition .

The existing equation used to calculate the deposition on soil as described in the current emission scenario does not require any further update, except for including a factor accounting for the fraction of the drift that deposits on a certain soil area ($F_{\mathrm{depos,area}}$). It is essential, though, to use a representative size deposition area matching the characteristics of the default cooling towers, i.e. height, diameter, exit velocity and heat content of the emitted gas.

An alternative method is to calculate the average deposition on a specific area for a specific cooling tower at a standard source strength, applying an appropriate dispersion model. From the average deposition at the standard source strength, the deposition can be calculated for any source strength similar to the local air distribution model in EUSES (ECHA, 2019).

$$DOSE_{\mathrm{soil,drift/volat}} = RELEASE_{\mathrm{air,drift/volat}} \cdot \frac{F_{\mathrm{depos,area,drift/volat}}}{AREA_{\mathrm{depos}}} \qquad \text{Eq. 94}$$

$$DOSE_{\mathrm{soil,drift/volat}} = RELEASE_{\mathrm{air,\,drift/volat}} \cdot C\mathrm{std}_{\mathrm{depos,drift/volat}} \qquad \text{Eq. 95}$$

To obtain the total deposition, the contribution from both emission routes have to be added up:

$$DOSE_{\mathrm{soil,total}} = DOSE_{\mathrm{soil,drift}} + DOSE_{\mathrm{soil,volat}} \qquad \text{Eq. 96}$$

Where:

$DOSE_{\mathrm{soil,drift}}$	dose a.i. deposited on soil via spray drift	($\mathrm{kg \cdot m^{-2} \cdot s^{-1}}$)
$DOSE_{\mathrm{soil,volat}}$	dose of volatilised a.i deposited on soil	($\mathrm{kg \cdot m^{-2} \cdot s^{-1}}$)
$DOSE_{\mathrm{soil,total}}$	total dose of a.i. deposited on soil	($\mathrm{kg \cdot m^{-2} \cdot s^{-1}}$)
F_{drift}	fraction of water lost via spray drift	(-)
$F_{\mathrm{volat,a.i.}}$	fraction of the a.i. lost via volatilisation	(-)
Q_{circ}	water circulation flow rate	($\mathrm{m^3 \cdot s^{-1}}$)
C_{proc}	concentration of the a.i. in the system	($\mathrm{kg \cdot m^{-3}}$)

$F_{depos,area}$	fraction of drift deposited on predefined soil area	(-)
$AREA_{depos}$	deposition area	(m^2)
$RELEASE_{air,drift}$	release of spray drift to air	($kg \cdot s^{-1}$)
$RELEASE_{air,volat}$	release of a.i. via volatilisation to air	($kg \cdot s^{-1}$)
$Cstd_{depos,drift}$	deposition flux on soil at standard source strength of 1 $kg \cdot s^{-1}$ for a.i. emitted via spray drift	($kg \cdot m^{-2} \cdot s^{-1}$)
$Cstd_{depos,volat}$	deposition flux on soil at standard source strength of 1 $kg \cdot s^{-1}$ for volatilised a.i.	($kg \cdot m^{-2} \cdot s^{-1}$)

7.3 Conclusion

This chapter provides the necessary calculations for the emission to air and provides suggestions on the way forward to assess the concentration in air and the deposition on soil.

A way forward for a more thorough estimation of the deposition on soil would be to first define the source characteristics (height, exit velocity, etc.) for the default once-through and open recirculating cooling towers.

Next, the average deposition on a specific area could be calculated using suitable atmospheric dispersion models. A complicating factor is that, as far as we know, there are no models that calculate the dispersion and deposition of both droplets and substances in the gaseous phase simultaneously.

In order to complete the environmental exposure assessment for cooling water biocides, it is necessary to model the tower height and collect data on other necessary source characteristics, using this as input for air dispersion calculations to determine concentration in air and the deposition on soil.

8 Evaluation of default settings of existing parameters

This chapter evaluates the default values for several characteristics of cooling systems, including those equipped with cooling towers, that are required to model the emissions of biocides from these systems into the environment. The amount of water evaporated and the amount of blowdown is discussed together with drift and retention time. In addition, the number of cycles, which defines the relation between amount of blowdown and the amount of water evaporated, is discussed. Although this parameter (cycles of concentration) is not included in the models it is useful to include it in the evaluation because of its interrelation with the other parameters, such as retention time. Each of these parameters will be discussed in the next paragraphs, mainly for the purpose of evaluating the existing model settings and proposing new default values where necessary. The focus of this chapter is on the open recirculating cooling towers because of the interrelationship between the different parameters.

8.1 Evaluating open recirculating cooling tower scenarios

Table 7 on page 72, provides an overview of the characteristics of the open recirculating systems according to the ESD for PT 11 (Groshart *et al.*, 2003). Table 8 on page 74 contains the changes caused by the newly proposed process parameters for the small recirculating cooling systems. The parameters in question are the evaporation rate, drift, the cycles of concentration, the system volume, and the hydraulic retention time, each of which will be discussed below.

8.1.1 Cooling water evaporation

Usually, the amount of water evaporated is less than 3 percent of the recirculating flow. The emission scenario document for cooling tower preservatives (Groshart *et al.*, 2003) reports a rate of 1 percent for cooling water evaporation. The evaporation rate, Q_{evap} ($m^3 \cdot s^{-1}$) is a function of the difference between temperature of the ingoing and outgoing water flows of the tower and the cooing water circulation flow rate. It can be calculated using the following relationship (Hsieh *et al.*, 2013, Perry *et al.*, 1997):

$$Q_{\mathrm{evap}} = 0.00085 \cdot Q_{\mathrm{circ}} \cdot \Delta T \cdot 1.8 \qquad \text{Eq. 97}$$

Applying the above equation to calculate evaporative loss, an evaporation rate ($Q_{\mathrm{evap}}/Q_{\mathrm{circ}}$) of 1 percent corresponds to a temperature difference of 6-7 °C.

As shown below, the typical temperature differences between in inlet and outlet water of the tower are usually in the range of 5-10 °C. This results in evaporation rates of between 0.8-1.5 percent.

The IPPC BAT BREF document (EC, 2001) reports several examples of cooling tower operating conditions. Reported temperature differences between the ingoing and outgoing water flow range from 6-20 °C. Also, GEA (2015) provides some examples with cooling ranges between 5-10

°C. The cooling range for the cooling towers presented in Annex 4 varies from 7-10 °C. On the basis of the above information, an evaporation fraction of 1 percent, corresponding with a cooling range of 6-7 °C, seems to be somewhat on the low side. However, it can be considered to be an acceptable value.

8.1.2 *Drift*

The drift factor is the fraction of recirculation water that is lost from the cooling system by droplet drift. For modern cooling towers, this factor is small compared to the fraction of recirculation water lost via blowdown and evaporation. Therefore, the drift factor was neglected in the cooling tower model used by Hsieh *et al.* (2013). When considering release to the atmosphere and soil in the vicinity of a cooling tower, droplet drift can be a significant emission route, though.

According to Groshart *et al.* (2003) and EC (2001), cooling water losses caused by spray drift are less than 0.2 percent of the recirculating water volume for towers with a forced air flow. According to EC (2001), drift eliminators that reduce losses to less than 0.01 percent are considered to be the best available technology. In the early 1970s, cooling tower manufacturers were quoting a drift rate value of 0.2 percent, which became an accepted value at that time (Roffman *et al.*, 1974). However, even then, direct measurements of drift enabled the manufacturers to guarantee drift rates of 0.02 percent for fresh water towers and 0.002 percent for salt water cooling towers. The measurements show that drift rates are (slightly) higher for mechanical draft towers because of the higher air flow rate (Roffman *et al.*, 1974). US EPA (1995) reports drift factors ranging from 0.02 percent for induced draft towers to approximately 0.001 percent for natural draft towers. More recent experimentally determined drift factor values for different types of drift eliminators fall within the range of 0.2-0.01 percent (Lucas et al., 2012). Present-day efficient drift eliminators are reported to keep drift losses well below 0.002 percent of the re-circulation water flow rate (Ruiz *et al.*, 2017, TCI, 2021, PUB, 2017).

Drift rates are influenced by several factors, such as the air and water flow rate and the droplet size distribution, which is mainly determined by the cooling water distribution system. Depending on operating conditions, drift rates may vary by as much as an order of magnitude.

In the emission scenario document for the use of biocides in cooling towers, the fraction lost due to spray drift (F_{depos}) is set at 0.025 percent of the recirculation flow rate (Groshart *et al.*, 2003). From the reviewed literature, it appears that drift rates vary considerably depending on the operating conditions and the type of drift eliminator used. Considering the collected data, the default value for the drift factor seems to be an appropriate value especially for older cooling towers equipped with less efficient drift eliminators.

8.1.3 *Build-up of chemicals in recirculating cooling towers, cycles of concentration*

This section discusses the cycles of concentration of the cooling water. Hsieh *et al.* (2013) included the number of cycles in their model in order to be able to calculate the ratio of the concentration in the make-up water and the concentration in the blowdown as a function of the number of cycles. However, as shown in Chapter 6, it is not necessary to introduce the cycles of concentration as a separate parameter as long as all relevant streams are included in the mass balance. However, the concept of the number of cycles is useful in evaluating the parameter values of the recirculating cooling tower as described in the ESD for product type 11.

The cycles of concentration (*N*) is a familiar parameter in cooling tower operation. Some dissolved chemicals which are also referred to as dissolved solids, can build up in evaporative cooling systems because the water that is lost from the cooling system through evaporation, (Q_{evap}) does not contain any of these dissolved substances. Dissolved solids usually include dissolved minerals, salts, metals, cations or anions. Dissolved solids may include suspended (colloidal) solids as well. The number of cycles, often called the cycles of concentration (COC), actually compares the dissolved solids level of the blowdown with that of the make-up water. It can also be interpreted as the number of times the water circulates within the cooling system before being discharged via blowdown.

By definition the degree of build-up expressed by number of cycles (*N*) is the concentration of dissolved solids in the feed water over concentration in the cooling water. For dissolved solids that do not evaporate, the number is cycles is calculated as:

$$N = Q_{\text{mkp}}/Q_{\text{bld}} \qquad \text{Eq. 98}$$

From the water balance of the cooling system, the blowdown can be related to the evaporation rate. Assuming that the share of spray drift is very small compared to the blowdown, it can be omitted in making the water balance:

$$Q_{\text{mkp}} = Q_{\text{bld}} + Q_{\text{evap}} \qquad \text{Eq. 99}$$

Introducing *N*, the blowdown flow rate is related to the evaporation rate as follows:

$$Q_{\text{bld}} = \frac{Q_{\text{evap}}}{N-1} \qquad \text{Eq. 100}$$

Knowing the evaporation rate, the number of cycles determines the make-up and blowdown flow rate. Q_{mkp} and Q_{bld} are thus defined by the temperature difference over the cooling tower, the flow rate of the recirculation water (section 8.1.1, equation 96) and the number of cycles, *N*.

Thus, the cycles of concentration constitute an important parameter, which relates the blowdown flow rate to the cooling water evaporation rate. In order to prevent unrealistic combinations, the values for these two parameters should not be chosen independently.

The number of cycles very much depends on the quality of the make-up water, for instance with respect to hardness. The number of cycles is approximately 3 in hard water locations, 6 in soft water locations but may be as high as 20 when applying cooling water conditioning, such as water filtration (Morris, 2022). Assink (1991) states that the concentration factors above a factor of 4 are seldom useful from a company's point of view, mainly because of the decrease in relative water savings at a higher number of cycles. However, from an environmental point of view, higher factors may be advantageous.

For large power plants, the number of cycles is between 2 and 3; for industrial recirculating systems, between 8 and 9; and outside the power industry, they typically range from 3 to 5 (Groshart *et al.*, 2003). For three industrial cooling towers, the process parameters of which are presented in Annex 4, the number of cycles vary from 6 to 9 (NFL, 2017). This is in agreement with the numbers provided by Groshart *et al.* (2003). During the testing of the pilot scale cooling tower in the ammonia stripping study conducted by Hsieh *et al.* (2013), the number of cycles ranged from 3 to 6 with an average value of 4. According to Bloemkolk (1995) the number of cycles may even vary from 1 to 20. Bloemkolk further states that a common practical value is between 2 and 5 and that a number of cycles higher than 5 is hardly useful, since at higher values, the amount of make-up water approaches the amount of water evaporated. In the model defined by Fielden *et al.* (1997) a value of 3 was used. The number of cycles used by Baltus *et al.* (1996) is 3. For the Baur model the number of cycles is 1.6, calculated from the data provided by Groshart *et al.* (2003).

For the small and large open recirculation towers as defined in the ESD for PT 11, the cycles of concentration are below 2, which seems to be rather low considering the information presented in this section. A lower number of cycles results in a higher blowdown rate and a shorter residence time. On the basis of the information presented here, a value of 3 or higher is considered to be more realistic and more in line with the models defined by Fielden *et al.* (1997) and Baltus *et al.* (1996) that were discussed by Groshart *et al.* (2003).

8.1.4 Retention time

The hydraulic retention time (*HRT*) of the cooling water should be limited in order to prevent biological fouling and build-up of minerals in the system that cause deposition of minerals on the equipment (scaling), which may also contribute to corrosion. Furthermore, the *HRT* is an important parameter as it determines the response time of the system whilst dosing cooling water chemicals. Longer response times are beneficial because concentrations of biocides decrease more slowly following, for instance, shock dosing, exerting a longer exposure time and limiting the amount of biocide to be added.

In cooling tower evaluations, the hydraulic time index (*HTI*) is used as a measure to indicate the residence time of chemicals in the system. The *HTI* is defined as the time required to reduce the concentration in the system by 50 percent. The *HTI* is calculated from the *HRT,* usually neglecting the loss of chemicals by drift and thus depending solely on the quotient of the system volume and the blowdown flow rate: $HTI = \ln(2) \times V/Q_{\mathrm{bld}}$ with $V/Q_{\mathrm{bld}} = HRT$. Most industrial systems operate with an

HTI of 48 hours or less (Hoots *et al.*, 2001), which corresponds to an *HRT* of 69 hours.

In section 8.1.3, we discussed that the blowdown flow rate depends on the cycles of concentration and the amount of water evaporated. Thus, besides indicating the degree of build-up of chemicals in the cooling system, the number of cycles also provides a (relative) indication of the residence time. That is, a high number of cycles means a relatively low blowdown rate and thus a high residence time (at the same system volume). Conversely, a low number of cycles means a relative high blowdown and a shorter residence time. As mentioned in the previous section, the cycles of concentration for the ESD models for open recirculating systems are below 2 (Table 7), which is rather low considering the information presented in section 8.1.3. As a result, the blowdown flow rate is relatively high. At the same system volume, a higher blowdown flow rate causes the hydraulic retention time to be shorter or else, when a high residence time is desired, the system volume needs to be raised accordingly.

The HRTs for the large system and the small system, as defined in the ESD, differ substantially: 24 hours versus 150 hours. As Groshart *et al.* (2003) indicated, residence times may vary widely, from 1 to 96 hours. Usually, the retention time for open recirculating systems is between one and two days. In the outlined example provided by Baltus *et al.* (1996), the *HRT* is 22 hours, which was indicated to be representative for the Dutch situation on the basis of a comparison of data from different cooling systems. From the description of the characteristics of three industrial cooling systems provided by NFL (2017), the hydraulic retention time calculated as V/Q_{bld}, ranged from 100 to 150 hours, and the number of cycles between 6 and 8, which are both (due to their interrelationship) relatively high. The information on these cooling systems is provided in Annex 4.

In the scenario drafted by Baur, the *HRT* is 150 hours, while in the scenario drawn up by Fielden *et al.* (1997), the *HRT* is 57 hours (Groshart *et al.*, 2003). Due to the combination of a high blowdown flow rate and a high residence time, the volume for the small system is high also in comparison with the large system.

In conclusion, HRTs may vary considerably in reality depending on the system’s design. The ESD scenarios are representative of this wide range of HRTs. But it is unclear whether they actually meant to represent a wide range of possible situations. The model presented by Fielden *et al.* (1997), with a residence time of 57 hours, seems to have served as the basis for small systems (HRT = 150 hours), whereas the Baur scenario served as the basis for large systems. The system volume for the small cooling systems seems to be on the high side.

Table 7 Default scenario evaluation: Parameter values for large and small cooling tower systems taken from the ESD for PT11.

parameter	**description**	**unit**	**Large system**	**Small system**
Original values from the emission scenario document[a]				
V_{syst}	Water volume in the cooling water system	m^3	3000	300
Q_{circ}	Water recirculation flow rate	$m^3 \cdot h^{-1}$	9000	100
F_{evap}	Fraction of evaporated cooling water	-	0.01	0.01
F_{drift} (in ESD F_{depos})	Fraction of cooling water lost via spray drift	-	0.00025	0.00025
F_{bld}	Fraction lost via blowdown	-	0.014	0.02
Q_{evap}	Evaporation loss rate	$m^3 \cdot h^{-1}$	90	1
Q_{drift}	Drift loss	$m^3 \cdot h^{-1}$	2.25	0.025
Q_{bld}	Blowdown flow rate	$m^3 \cdot h^{-1}$	125	2
Q_{mkp}	Make-up water flow rate	$m^3 \cdot h^{-1}$	217.25	3.025
HRT	Hydraulic retention time $V_{\text{syst}}/(Q_{\text{bld}}+Q_{\text{evap}}+Q_{\text{drift}})$	h	14	99
Additional cooling tower parameters used in the evaluation				
N	Cycles of concentration $(Q_{\text{evap}}+Q_{\text{bld}})/Q_{\text{bld}}$	-	1.7	1.5
R_{rec}	Recycle ratio $Q_{\text{circ}}/Q_{\text{bld}}$	-	72	50
HRT	Hydraulic retention time ($V_{\text{syst}}/Q_{\text{bld}}$)	h	24	150

a) Groshart *et al.* (2003)

8.1.5 *Relation between the system volume and the recirculation rate*

The system volume depends on many parameters and there is no clear design equation to calculate it. There are several rules of thumb that can be applied to giving a first indication. Possible measures include the number of minutes of the recirculation rate in cubic meters per minute, or the fraction of the recirculation rate in cubic meters per hour.

As an explanation to these two measures, we provide two examples.

First, the system volume is said to be 15 minutes of the water recirculation flow rate. In this case, the system volume is the amount of water collected from the recirculation flow rate (Q_{circ}) during a time period (t_{circ}) of 15 minutes, with Q_{circ} in m^3 min^{-1}. A value of 100 $m^3 \cdot min^{-1}$ for Q_{circ} results in a system volume of:

$$V_{\text{system}} = t_{circ} \times Q_{\text{circ}} = 15 \times 100 = 1500 \text{ m}^3$$

Second, the system volume is indicated to be 25 percent (F_{circ}) of the recirculation flow rate. The recirculation flow rate (Q_{circ}) in this case should be in cubic meters per hour. With a value of 6000 $m^3 \cdot h^{-1}$ for the recirculation flow rate, the system volume can be calculated as follows:

$V_{\mathrm{system}} = F_{\mathrm{circ}} \text{ x } Q_{\mathrm{circ}} = 0.25 \text{ x } 6000 = 1500 \text{ m}^3$

The example shows that these two measures can easily be converted into one or the other by multiplication (fraction into minutes) or division (minutes into fraction) by 60 (minutes per hour).

Recommended values are between 3 and 10 minutes of the recirculation rate in cubic metre per minutes. On the basis of the recirculation rate in hours, recommended values ranging from 25 up to 65 percent have been found, which correspond to values in the range of 15-39 minutes. In the example situation provided by Baltus *et al.* (1996), the system volume is 25 percent of the recirculation flow rate (in cubic meters/hour). For the three industrial cooling systems described in NFL (2017), the system volume expressed as the fraction of the recirculation rate in cubic meters per hour range from 23 to 36 percent.

It can be concluded that the range of recommended system volumes is rather large, with more than a factor of 3 between the lowest and highest recommended values. Recommended values of 5 to 17 percent (3 to 10 minutes) seem to be on the low side. Values of 25-33 percent (15 -20 minutes) seem to be more common.

The value of 33 percent for the large open recirculating cooling system from the ESD is in line with the information found. The value for the small system, as described in the ESD, appears to deviate a lot from the recommended values, having a value of 300 percent. if we take a closer look at the ESD default values, it looks as if the system volume and recirculation rate for the small system have been inadvertently switched. If that is the case, the correct numbers would also result in a value of 33 percent or 20 minutes.

8.2 Conclusion

The evaporation fraction of 1 percent used in the ESD seems to be a feasible value that is corresponding to a cooling temperature range of approximately 7 °C (section 8.1.1).

Also, the default value of 0.025 percent for the drift factor seems to be a representative value considering the ranges found in the studied literature.

The characteristics of the large cooling system, as described in the ESD, do not need to be updated. The number of cycles for the large system is on the low side, a value of 2 to 3 being more realistic. Changing the number of cycles to a value of 2 or 3 would result in a hydraulic retention time of 33 hours or 67 hours, respectively, instead of the current value of 24 hours. The latter is close to the hydraulic retention time of 22 hours in the model described by Baltus *et al.* (1996). The current value of 24 hours for the large system can be maintained.

With respect to the characteristics of the small cooling system, as described in the ESD, the scenario developed by Fielden *et al.* (1997) seems to have served as the starting point. However, the values for the system volume and the recirculation rate appear to have been switched. We propose to correct the characteristics of the small cooling system accordingly. Furthermore, we propose to change the cycles of concentration to a value of 3. With fixed fractions for the amount of water evaporated (1 percent) and the amount of water lost via drift (0.025 percent), and applying equation 100 to calculate the amount of blowdown, this results in a reduced hydraulic retention time of 67 hours instead of 150 hours. By comparison, in the Fielden *et al*. scenario, the *HRT* is 57 hours. Table 8 shows the differences between the current and the proposed parameters for small open recirculating cooling towers.

Table 8 Current and newly proposed parameter values for the small open recirculating cooling tower systems.

parameter	**description**	**unit**	**Small system**	**Small system updated**
Original values from the emission scenario document[a]				
V_{syst}	Water volume in the cooling water system	m^3	300	100
Q_{circ}	Water recirculation flow rate	$m^3 \cdot h^{-1}$	100	300
F_{evap}	Fraction of evaporated cooling water	-	0.01	0.01
F_{drift}	Fraction cooling water lost through drift	-	0.00025	0.00025
F_{bld}	Fraction of cooling water lost via blowdown	-	0.02	0.005
Q_{evap}	Evaporation loss rate	$m^3 \cdot h^{-1}$	1	3
Q_{drift}	Drift loss	$m^3 \cdot h^{-1}$	0.025	0.075
Q_{bld}	Blowdown flow rate	$m^3 \cdot h^{-1}$	2	1.5
Q_{mkp}	Make-up water flow rate	$m^3 \cdot h^{-1}$	3.025	4.575
HRT	Hydraulic retention time $V_{syst}/(Q_{bld}+Q_{evap}+Q_{drift})$	h	99	22
Additional cooling tower parameters used in the evaluation				
N	Cycles of concentration $(Q_{evap}+Q_{bld})/Q_{bld}$	-	1.5	3
HRT	Hydraulic retention time (V_{syst}/Q_{bld})	h	150	67

[a] Groshart *et al.* (2003)

9 Conclusions

Emission factors for air that are based on the flash-off factor can be derived from Henry’s law constant in a relatively simple manner. The key assumption is that there is complete thermodynamic equilibrium between the air stream leaving and the cooling water entering at the top of the cooling tower. However, equilibrium between the two streams may not be established at the top of the cooling tower and therefore, this method may not represent the real situation.

The actual situation with respect to the atmospheric emission from cooling towers resulting from the volatilisation of a chemical from the cooling water is more realistically described and estimated on the basis of experimentally derived mass transfer rates, such as those published by Hsieh *et al.* (2013). Mass transfer correlations are applied to predict mass transfer rates for a substance on the basis of the experimentally determined values of another substance, using the diffusion coefficients of both substances in air and water. These estimates apply best to the specific design and operating conditions of the (pilot scale) cooling towers that were used in the experiments. Hsieh *et al.* (2013) stated that their experimentally derived mass transfer coefficients should be applicable to larger-scale counterflow cooling systems because the pilot scale towers were designed to be representative of large-scale counterflow cooling towers.

In order to calculate emission factors for the volatilisation to air, the model published by Hsieh *et al.* (2013) is applied. For biocides that are acids or bases, the degree of ionisation is an important factor to take into account. The degree of ionisation depends on the pH of the cooling water and the acid dissociation constant (pK_a) of the substance.

To be able to calculate the substance-specific release factors, substance properties, such as the Henry’s law constant, pK_a, the enthalpy of volatilisation and the diffusion coefficients are required. This information has been collected for most of the biocides that are approved for use as cooling water preservatives. Volatilisation factors are calculated for these substances using default cooling tower conditions, such as the pH, cooling water temperature and the air and water flow rate. The proposed defaults for the cooling tower conditions are based on a literature study that has been conducted in order to gain further insight into the general operating conditions of open recirculating cooling towers and to see whether the experimental conditions are representative. It can be concluded that this is the case and that the statement made by Hsieh *et al.* (2013) can be confirmed. New default values for additional process parameters are proposed, such as for the cooling water temperature in the cooling tower and the pH value of cooling water.

Experimental values for mass transfer rates of the reference substance ammonia that are found in literature corroborate the experimental values used in this study. The collected data shows there is a substantial range in the values found in literature, which can be explained to some extent by the differences in operating conditions. However, the mass transfer rates obtained under conditions most similar to those in the experimental cooling towers most closely match the reference values used in this study.

Applying the methodology described in this report, the volatilisation of biocides used as cooling water preservatives can be estimated from experimental data on one substance. The estimates of the substance-specific volatilisation factors clearly show the importance of a substance-dependent approach and also show that a single default is inadequate. Depending on the substance properties, emissions to air by volatilisation can exceed the losses from drift multiple times. On the other hand, volatilisation can be much lower compared to drift losses. The same holds when comparing the volatilisation factors to the default value of 1 percent. For many substances, this value is an overestimation with respect to the atmospheric losses, especially for highly water-soluble substances that are largely ionised at the existing pH of the cooling water.

Besides the active ingredients that are authorised for use as cooling water preservatives, by-products, such as those resulting from the chlorine- and bromine-releasing hydantoins and the reaction products resulting from halogenated (chlorine and bromine) oxidising biocides, can be relevant as well with respect to atmospheric emissions because they tend to be volatile compounds. This category of compounds was not considered in this report.

In addition to the methodology to calculate the volatilisation of biocides from cooling towers, the existing models for calculating the emissions to water from the open recirculating cooling towers, as described in the emission scenario for product type 11, were evaluated and rewritten to include the volatilisation factor. It was shown that the steady-state models used to calculate the concentration of the biocide in the blowdown water for the recirculating cooling system is incorrect.

With regard to the emissions to air, the necessary calculations and suggestions are provided on the way forward to assessing the concentration in air and the deposition to soil. In order to complete the environmental exposure assessment for cooling water biocides, it is necessary to model the tower height and collect data on other necessary source characteristics, using this as input for air dispersion calculations to determine the concentration in air and the deposition to soil.

Existing cooling tower characteristics, as described in the current ESD, were evaluated. From the evaluation, it appeared that the characteristics of the small open recirculating cooling tower deviate from common practice, especially with respect to the relation between the system volume and the recirculation rate. On the basis of the collected information it was suggested to update the current scenario for small open recirculating cooling towers, which is more in line with the models discussed in the ESD.

References

The reference list includes references in the Annexes.

Acree WE, Mintz C, Clark M, Abraham MH. 2007. Enthalpy of Solvation Correlations for Gaseous Solutes Dissolved in Water and in 1-Octanol Based on the Abraham Model. J Chem Inf Model 47: 115-121.

Al-Malah KI. 2012. Exemplification of the Concept of Diffusivity in Mass Transfer. Int J Chem Eng Appl Sci 2: 24-26.

Anonymous. Bureau of Energy Efficiency. Government of India. Ministry of Power. Syllabus Chapter 7. https://beeindia.gov.in/sites/default/files/3Ch7.pdf. Accessed: 05/04, 2023.

Assink JW. 1991. Industiële koelsystemen: Milieuaspecten en kosten (in Dutch). Apeldoorn, The Netherlands: Instituut voor Milieu- en Energietechnologie TNO (IMET). Report nr. TNO IMET and RIZA Report 91-301, 1991. RIZA notanummer 92.005. TNO-Milieu en Energie. 55 pp. https://www.google.nl/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwjNi5HfyPn8AhVf8rsIHah6CRAQFnoECAoQAQ&url=https%3A%2F%2Fpuc.overheid.nl%2FPUC%2FHandlers%2FDownloadDocument.ashx%3Fidentifier%3DPUC_63870_31%26versienummer%3D1&usg=AOvVaw1ApTKXa40lVf6ndjUju9SX.

Atkins P, De Paula J. 2006. Atkins' Physical Chemistry. 8th ed. New York, U.S.A.: W.H. Freeman and Company. ISBN: 0-7167-8759-8.

Baltus CAM, Berbee RPM. 1996. Het gebruik van biociden in recirculatiesystemen (in Dutch). Lelystad, The Netherlands: Rijksinstituut voor afvalwaterzuivering (RIZA). Report nr. 96.036. 93 pp.

Bates RG, Pinching GD. 1949. Acidic Dissociation Constant of Ammonium Ion at 0 to 50 °C, and the base Strenght of Ammonia. Journal of Research of the National Bureau of Standards 42: 419-430.

Billet R, Schultes M. 1999. Prediction of Mass Transfer Columns with Dumped and Arranged Packings. Update Summary of the Calculation Method of Billet and Schultes. Chem Eng Res Des 77, Part A (6): 498-504.

BioByte. 2006. BioLoom for Windows (computer program). Version 1.5. Claremont, CA, USA, BioByte Corporation.

Bloemkolk JW. 1995. Industriële Koelwaterlozingen, koelsytemen en emissies. Rijksinstituut voor integraal Zoetwaterbeheer en Afvalwaterbehandeling. Report nr. RIZA Notanr.: 95.050.

ChemAxon. 2016. MarvinSketch (computer program). Version 16.10.24.0. Budapest, Hungary, ChemAxon Ltd. http://www.chemaxon.com/.

Chien S-H, Hsieh M-K, Li H, Monnel J, Dzombak DA, Vidic RD. 2012. Pilot-scale cooling tower to evaluate corrosion, scaling, and biofouling control strategies for cooling system makeup water. Rev Sci Instrum 83: 024101. doi: https://aip.scitation.org/doi/10.1063/1.3680563.

Cussler EL. 2009. Fundamentals of Mass Transfer. In: Diffusion Mass Transfer in Fluid Systems. 3rd Ed. Cambridge, United Kingdom: Cambridge University Press. Chapter 8. p. 237-273.

Dickerson RE, Gray HB, Haight GP. 1979. Chemical principles. 3rd ed. Menlo Park, CA, U.S.A.: The Benjamin/Cummings Publishing Company, Inc. ISBN: 0-8053-2398-8.

EC. 2001. Integrated Pollution Prevention and Control (IPPC). Reference Document on the application of Best Available Techniques to Industrial Cooling Systems. December 2001. https://eippcb.jrc.ec.europa.eu/reference: European IPPC Bureau. 313 pp. https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/cvs_bref_1201.pdf.

EC. 2003. Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, Part II. Ispra: European Commission.

EC. 2012. EUSES, the European Union System for the Evaluation of Substances, version 2.1.2 (computer program). Version 2.1.2. Bilthoven, The Netherlands, Prepared for the European Chemicals Bureau by the National Institute for Public Health and the Environment (RIVM). https://ec.europa.eu/jrc/en/scientific-tool/european-union-system-evaluation-substances.

ECHA. 2013. Note on the environmental assessment of biocides in PT11 cooling water systems. https://echa.europa.eu/documents/10162/983773/pt11_note_env_assessment_biocides_cooling_water_en.pdf/d90ce922-28bd-4e85-b3a8-d3740cb91127.

ECHA. 2017. Guidance on Biocidal Products Regulation: Volume IV Environment - Assessment and Evaluation (Parts B+C). Agency EC. https://echa.europa.eu/documents/10162/2324906/bpr_guidance_ra_vol_iv_part_b-c_en.pdf/e2622aea-0b93-493f-85a3-f9cb42be16ae.

ECHA. 2019. EUSES - European Union System for the Evaluation of Substances version 2.2.0 (computer program). Version Helsinki, Finland, European Chemicals Agency (ECHA). https://echa.europa.eu/support/dossier-submission-tools/euses.

ECHA. 2022. Technical Agreements for Biocides Environment (ENV). October 2022. 180 pp. https://webgate.ec.europa.eu/s-circabc/w/browse/65ed457b-535f-41e5-a559-aa8b168d1558.

EEC. 1986. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal (L181): 0006-0012.

EPRI. 2015. Seasonal/Annual Cooling Tower Impacts (SACTI) (computer program). Version Version 2.0 with Source Code. Electric Power Research Institute (EPRI). https://www.epri.com/research/products/3002006350.

Eurostat. 2021. Sewage sludge production and disposal - agricultural use. https://ec.europa.eu/eurostat/databrowser/view/ENV_WW_SPD__custom_7642047/default/table?lang=en. Accessed: October 2, 2023, 2023.

Ferraz FM, Povinelli J, Vieira EM. 2013. Ammonia removal from landfill leachate by air stripping and absorption. Environ Technol 34 (15): 2317-2326. doi: 10.1080/09593330.2013.767283.

Fielden T, Idden M, Hobbs G. 1997. Use category document – water treatment chemicals (draft). Wallingford, United Kingdom: Environmental Agency. 75 pp.

Flagiello D, Parisi A, Lancia A, Di Natale F. 2021. A review on the Gas-Liquid Mass Transfer Coefficient in Packed-Bed Columns. ChemEngineering, 5(3), 43 5 (43). doi: 10.3390/chemengineering5030043.

Fogler HS. 1986. Elements of Chemical Reaction Engineering. New Jersey, U.S.A.: Prentice-Hall, Inc. ISBN: 0-13-263666-2. 769 p.

Fuller EN, Schettler PD, Giddings JC. 1966. A new method for prediction of binary gas-phase diffusion coefficients. Ind Eng Chem 58 (5): 18-27.

Gartiser S, Urich E. 2002. Environmentally compatible cooling water treatment chemicals. Berlin, Germany: Environmental Research of the Federal Ministry of the Environment. Report nr. UBA-FB 200 24 233. Hydrotox GmbH. 197 pp. https://www.hydrotox.de/fileadmin/user_upload/pdfs/forschungen/projekte/UBA_cooling_water_text_05-11-02.pdf.

GEA. 2015. Het koeltorenboekje, versie 1. GEA Polacel Cooling Towers B.V. https://www.yumpu.com/nl/document/view/51387619/koeltorenboekje-gea-heat-exchangers.

Gould PL, Krätzig WB. 1999. Cooling Tower Structures. Wai-Fah C (Ed.) In: Structural Engineering Handbook. Boca Raton, U.S.A.: CRC Press LLC. Chapter 14.

Groshart C, Balk F. 2003. Supplement to the methodology for risk evaluation of biocides. Harmonisation of Environmental Emission Scenarios for biocides used as preservatives for liquid cooling systems (product type 11). Nijmegen, the Netherlands: Haskoning Nederland B.V. Report nr. 4L1784.A1/R015/FBA/TL/Nijm. European Commission. 93 pp.

Gu W, Cheng P, Tang M. 2018. Compilation and evaluation of gas phase diffusion coefficients of halogenated organic compounds. Royal Society open science 5 (7): 171936.

Guštin S, Marinšek-Logar R. 2011. Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. Process Safety and Environmental Protection 89 (1): 61-66. doi: https://doi.org/10.1016/j.psep.2010.11.001.

Hand DW, Hokanson DR, Critenden JC. 2011. Gas-liquid processes: principles and applications. Edzwald JK (Ed.) In: Water quality and treatment, a handbook on drinking water. 6 Ed. New York: McGraw Hill. Chapter 6. p. 1-66.

Hanley B, Chen C. 2012. New Mass-Transfer Correlations for Packed Towers. AIChE Journal 58 (1): 132-152. doi: 10.1002/aic.12574.

Harris W, Kadiayi AK, Macdonald K, Witow D. 2017. Environmental discharge criteria and dispersion estimation for mine ventilation exhaust stacks. In Hudyma M, Potvin Y (Eds.) UMT 2017: Proceedings of the First International Conference on Underground Mining Technology. Sudbury, 11-13 October. Australian Centre for Geomechanics p. 103-113.

Holzwarth G, Balmer RG, Soni L. 1984. The fate of chlorine and chloramines in cooling towers. Wat Res 18 (11): 1421-1427.

Hoots JE, Johnson DA, Lammering JD, Meier DA. 2001. Correctly Operate Cooling Towers at High Cycles of Concentration. http://lib3.dss.go.th/fulltext/Journal/Chemical%20Engineering%20Progress/no.3/2001v97n3p29-36.pdf.

Hsieh M-K, Walker ME, Safari I, Chien S-H, Abbasian J, Vidic RD, Dzombak DA. 2013. Ammonia Stripping in Open-Recirculating Cooling Water Systems. Environ Prog Sustain Energy 32 (3): 489-495. doi: https://doi.org/10.1002/ep.11648.

Huang J-C, Shang C. 2006. Air Stripping. Wang LK, Hung Y-T, Shammas NK (Eds.) In: Advanced Physicochemical Treatment Processes. Totowa, NJ: Humana Press. p. 47-79. https://doi.org/10.1007/978-1-59745-029-4_2.

Hughes L, Mackay D, Powell DE, Kim J. 2012. An updated state of the science EQC model for evaluating chemical fate in the environment: Application to D5 (decamethylcyclopentasiloxane). Chemosphere 87 (2): 118-124. doi: https://doi.org/10.1016/j.chemosphere.2011.11.072.

Katehis D, Diyamandoglu V, Fillos J. 1998. Stripping and recovery of ammonia from centrate of anaerobically digested biosolids at elevated temperatures. Wat Environ Res 70 (2).

Kavanaugh MC, Trussell RR. 1980. Design of aeration towers to strip volatile contaminants from drinking water. Research and Technology. J Am WATER Work Assoc 72 (12): 684-692.

Kim EJ, Kim H, Lee E. 2021. Influence of Ammonia Stripping Parameters on the Efficiency and Mass Transfer Rate of Ammonia Removal. Applied Sciences 11 (1): 441. doi: 10.3390/app11010441.

Kim S, Deshusses MA. 2008. Determination of mass transfer coefficients for packing materials used in biofilters and biotrickling filters for air pollution control—2: Development of mass transfer coefficients correlations. Chem Eng Sci 63: 856-861. doi: 10.1016/j.ces.2007.10.021.

Kumar A, Hartland S. 1999. Correlations for Prediction of Mass Transfer Coefficients in Single Drop Systems and Liquid–Liquid Extraction Columns. Chem Eng Res Des 77 (5): 372-384. doi: https://doi.org/10.1205/026387699526359.

Luttik R, Emans HJB, Van der Poel P, Linders JBHJ. 1993. Evaluation systems for pesticides (ESPE): 2. Non-agricultural pesticides to be incorporated into the Uniform System for the Evaluation of Substances (USES). Bilthoven, The Netherlands: National Institute for Public Health and the Environment. Report nr. 679102021. 66 pp. https://www.rivm.nl/publicaties/evaluation-system-for-pesticides-espe-2-non-agricultural-pesticides-to-be-incorporated.

Miller JD, Rehm TR. 1976. Packed column mass transfer coefficients for concurrent and countercurrent flow: an analysis of recent work. Chemical Engineering Education 10 (2).

Miyamoto S, Shimono K. 2020. Molecular modeling to estimate the diffusion coefficients of drugs and other small molecules. Molecules 25 (22): 5340. doi: https://doi.org/10.3390/molecules25225340.

Morris B. 2022. Make-up / Blow down | Cycles of Concentration. https://constructandcommission.com/makeup-blow-down-cycles-of-concentration/. Accessed: 03/30, 2023.

Munz C, Roberts PV. 1984. The Ratio of Gas-Phase to Liquid-Phase Mass Transfer Coefficients in Gas-Liquid Contacting Processes. Brutsaert W, Jirka GH (Eds.) In: Gas Transfer at Water Surfaces. Dordrecht: Springer Netherlands. p. 35-45. https://doi.org/10.1007/978-94-017-1660-4_4.

Narbaitz RM, Djebbar Y. 1996. Nonparametric modeling of mass transfer coefficients for air stripping packed towers. Can J Civ Eng 23: 549-559. doi: https://doi.org/10.1139/l96-059.

NFL. 2017. Technical Section of Tender Documents for Cooling Water Treatment Package at National Fertilizers Limited. Bathinda, India: 22 pp. https://nationalfertilizers.com/NFL/admin_tender/upload/20171011151517_Tech%20Part%20of%20CWT-NIT.pdf.

Novak I. 2021. An idea to explore: Visualization of ionization of amino acids using Mathematica. Biochem Mol Biol Educ 49 (3): 333-345. doi: https://doi.org/10.1002/bmb.21470.

Perry RG, Green DW, Maloney JO. 1997. Perry’s Chemical Engineers’ Handbook. 7th ed. New York, U.S.A.: McGraw-Hill, Inc. ISBN: 0-07-049841-5. 2582 p.

Poling BE, Prausnitz JM, O'Connel JP. 2001. The properties of gases and liquids. 5th ed. New York, U.S.A.: McGraw-Hill. doi: DOI: 10.1036/0070116822.

Pratsinis SE, Mavrantzas V. 2022. Mass Transfer. Lecture 7: Mass Transfer Coefficients II. https://studylib.net/doc/8076979/correlations-of-mass-transfer-coefficients. Accessed: 27-06-2022,

PUB. 2017. Technical Reference for Water Conservation in Cooling Towers. 1 st Edition, Nov 2017. Singapore: Public Utilities Board (PUB), Singapore's National Water Agency. 35 pp. https://www.pub.gov.sg/Documents/TechnicalReference_WaterConservation_CoolingTowers.pdf.

Reid RC, Prausnitz JM, Poling BE. 1988. The properties of gases and liquids. 4th ed. New York, U.S.A.: McGraw-hill, Inc. ISBN: 0-07-051799-1. 753 p.

Reijenga J, van Hoof A, van Loon A, Teunissen B. 2013. Development of Methods for the Determination of pK_a Values. Analytical Chemistry Insights 8: ACI.S12304. doi: 10.4137/ACI.S12304.

Roffman A, Vleck LD. 1974. The State-of-the-Art of Measuring and Predicting Cooling Tower Drift and Its Deposition. Journal of the Air Pollution Control Association 24 (9): 855-859. doi: 10.1080/00022470.1974.10469982.

Royal Society of Chemistry. 2023. ChemSpider. Search and share chemistry. Version 2022.0.72.0. https://www.chemspider.com/.

Ruiz J, Kaiser AS, Lucas M. 2017. Experimental determination of drift and PM10 cooling tower emissions: Influence of components and operating conditions. Environ Pollut 230: 422-431. doi: https://doi.org/10.1016/j.envpol.2017.06.073.

Safari I, Hsieh M-K, Chien S-H, Walker ME, Vidic RD, Dzombak DA, Abbasian J. 2014. Effect of CO_2 stripping on pH in open-recirculating cooling water systems. Environ Prog Sustain Energy 33 (1): 275-282. doi: https://doi.org/10.1002/ep.11769.

Sander R. 2015. Compilation of Henry's law constants (version 4.0) for water as solvent. Atmos Chem Phys 15: 4399–4981. doi: 10.5194/acp-15-4399-2015.

Sander R, Acree Jr. WE, De Visscher A, Schwartz SE, Wallington TJ. 2021. Symbols, names, and units used for Henry's law constants in the literature. doi: https://doi.org/10.5281/zenodo.5543555.

Sander R, Acree WE, De Visscher A, Schwartz SE, Wallington TJ. 2022. Henry's law constants (IUPAC Recommendations 2021). Pure and Applied Chemistry 94 (1): 71-85. doi: doi:10.1515/pac-2020-0302.

Sauter F, Sterk M, van der Swaluw E, Wichink Kruit R, de Vries W, van Pul A. 2022. The OPS-model. Description of OPS 5.1.0.2. National Institute for Public Health and the Environment (RIVM). https://www.rivm.nl/sites/default/files/2023-01/ops_documentation_0.pdf.

Schramke JA, Murphy SF, Doucette WJ, Hintze WD. 1999. Prediction of aqueous diffusion coefficients for organic compounds at 25 °C. Chemosphere 38 (10): 2381-2406.

Schwarzenbach RP, Gschwend PM, Imboden DM. 2003. Environmental organic chemistry. 2nd ed. Hoboken, NJ, U.S.A.: John Wiley & Sons, Inc. ISBN: 0-471-35750-2.

Skoog DA, West DM, Holler F. 1988. Fundamentals of Analytical Chemistry. Vol. International edition. 5th ed. Saunders College Publishing. ISBN: 0-03-14828-6.

Srinivasan A, Chowdhury P, Viraraghavan T. 2009. Air Stripping in Industrial Wastewater Treatment - A. In: Water and waste water treatment technologies. Vol. 1, https://www.eolss.net/Sample-Chapters/C07/E6-144-03.pdf.

Tang MJ, Cox RA, Kalberer M. 2014. Compilation and evaluation of gas phase diffusion coefficients of reactive trace gases in the atmosphere: volume 1. Inorganic compounds. Atmos Chem Phys 14: 9233-9247. doi: 10.5194/acp-14-9233-2014.

TCI. 2021. Cooling Tower Basics – Drift Eliminator. https://www.towercomponentsinc.com/cooling-tower-basics-drift-eliminator. Accessed: August 4, 2021,

US EPA. 1995. Wet Cooling Towers. Office of Air Quality Planning And Standards (Ed.) In: AP–42: Compilation of Air Pollutant Emission Factors. 5th Ed. Research Triangle Park, NC, U.S.A.: Vol. Volume 1, Stationary Point and Area Sources, Chapter 13 (Misceallaneous Sources), section 4. https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors and https://www3.epa.gov/ttnchie1/ap42/ch13/final/c13s04.pdf.

US EPA. 2011. HenryWin. An EpiSuite model for estimating the Henry's Law Constant of organic compounds. (computer program). Version 3.20. Washington, DC, U.S.A., U.S. Environmental Protection Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC).

US EPA. 2012. EPI Suite™ (computer program). Version 4.11. Washington, DC, U.S.A., U.S. Environmental Protection Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC).

Van Dokkum HP, Bakker DJ, Scholten MCT. 1998. Development of a concept for environmental risk assessment of biocidal products for authorisation purposes (BIOEXPO), Part 2: Release estimation for 23 biocidal product types. Umweltbundesamt, Forschungsbericht 106 01 065 UBA IV 1.4. Report nr. TNO-MEP - R 97-443.

Wania F, Breivik K, Persson NJ, McLachlan MS. 2006. CoZMo-POP 2 – A fugacity-based dynamic multi-compartmental mass balance model of the fate of persistent organic pollutants. Environmental Modelling & Software 21 (6): 868-884. doi: https://doi.org/10.1016/j.envsoft.2005.04.003.

Webster E, Mackay D, Di Guardo A, Kane D, Woodfine D. 2004. Regional differences in chemical fate model outcome. Chemosphere 55 (10): 1361-1376. doi: https://doi.org/10.1016/j.chemosphere.2003.10.061.

Wilke CR, Chang P. 1955. Correlation of diffusion coefficients in dilute solutions. AIChE Journal 1 (2): 264-270. doi: dx.doi.org/10.1002/aic.690010222.

Yaws CL. 2014. Transport Properties of Chemicals and Hydrocarbons. 2nd ed. Amsterdam, the Netherlands: Elsevier. ISBN: 978-0-323-28658-9. 715 p.

Zangeneh A, Sabzalipour S, Takdastan A, Jalilzadeh Yengejeh R, Abdullatif Khafaie M. 2021. Mass transfer coefficient of ammonia in the air stripping process for municipal wastewater: An experimental study. Advances in Environmental Technology 7 (4): 289-304. doi: 10.22104/aet.2022.5345.1447.

Zumdahl SS. 2005. Chemical Principles. 5th ed. Boston, U.S.A.: Houghton Mifflin Company. ISBN: 0-618-37207-5.

Annex 1 Derivation of the design equation

In this annex the derivation of the design equation for the stripping tower will be explained by elaborating the mass balance for the liquid phase in the stripping column (Kavanaugh *et al.*, 1980, Huang *et al.*, 2006, Hand *et al.*, 2011).

For the mass balance a differential volume, dV is considered. In stripping tower design usually the height of the tower is calculated. Therefore the differential height, dZ is considered, assuming a fixed base area (A_b) of the stripping column, with dV=A_b·dZ, see also Figure 8.

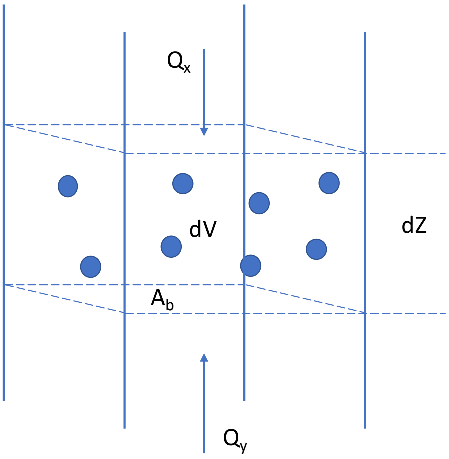

Figure 8 Contact between a gas and liquid in a stripping column

In the situation of contact between a liquid flow (Q_x) and air flow (Q_y) passing through the column in counterflow, first the change in mass (M_x) per unit volume of the packing or concentration of the substance with the time is considered:

$$J = \frac{1}{V} \cdot \frac{dM_x}{dt} = \frac{dC_x}{dt} \qquad \text{Eq. 1}$$

The differential height is introduced through calculating the time required for the liquid flow Q_x to pass the volume V:

$$dt = \frac{A_b \cdot dZ}{Q_x} \qquad \text{Eq. 2}$$

Applying the equation for dt in the mass balance results in:

$$J = \frac{dC_x}{dt} = \frac{dC_x \cdot Q_x}{A_b \cdot dZ} \qquad \text{Eq. 3}$$

The mass transfer or the change in concentration equals the mass transfer rate per unit volume of packing (J) across the air-water interface.
The mass transfer rate (J) across the air-water interface (per unit volume of packing) is the product of the driving force, which is the

difference between the actual concentration in one phase and the equilibrium concentration that the substance would have in the other phase ($\mathrm{C_x} - C_\mathrm{x}^*$), the inverse of the resistance to transport across the interface (*R*) and the available mass transfer surface area, in this case the specific area per volume of fill material, a. It is common to express the inverse of the resistance as the overall mass transfer coefficient ($K = 1/R$). When the liquid phase is considered, *K* is the overall mass transfer coefficient based on the liquid phase K_L.

For transfer from the liquid (water) to the gas (air)phase (air stripping) the mass transfer rate per unit volume of packing is defined as:

$$J = K_L \cdot a \cdot (C_x^* - C_x) \qquad \text{Eq. 4}$$

Combining equation 3 and 4:

$$J = K_L \cdot a \cdot (C_x^* - C_x) = -\frac{dC_x \cdot Q_x}{A_b \cdot dZ} \qquad \text{Eq. 5}$$

and after rearranging:

$$Q_x \cdot dC_x = (C_x - C_x^*) \cdot K_L \cdot a \cdot A_b \cdot dZ \qquad \text{Eq. 6}$$

the equation for the differential height of the column is obtained

$$\frac{dC_x}{C_x - C_x^*} \cdot \frac{Q_x}{K_L \cdot a.A_b} = dZ \qquad \text{Eq. 7}$$

The required column height is obtained by integrating the above equation, see also Safari *et al.* (2014):

$$\int_{C_{x,out}}^{C_{x,in}} \frac{dC_x}{C_x - C_x^*} \cdot \frac{Q_x}{K_L \cdot a.A_b} = \int_0^{Z_T} dZ \qquad \text{Eq. 8}$$

The first integral part on the left hand side of the equation is dimensionless and is defined as the number of transfer units (NTU). The second term at the left hand side is the height of a transfer unit (HTU).

$$NTU \cdot HTU = Z_T \qquad \text{Eq. 9}$$

In analogy with the liquid phase, the design equation for the gas phase, Q_y can be derived:

$$Q_\mathrm{y} \cdot \mathrm{d}C_\mathrm{y} = \left(C_\mathrm{y} - C_\mathrm{y}^*\right) \cdot K_\mathrm{G} \cdot a \cdot A_\mathrm{b} \cdot \mathrm{d}Z \qquad \text{Eq. 10}$$

$$\int_{C_\mathrm{y,out}}^{C_\mathrm{y,in}} \frac{\mathrm{d}C_\mathrm{y}}{C_\mathrm{y} - C_\mathrm{y}^*} \cdot \frac{Q_\mathrm{y}}{K_\mathrm{G} \cdot a.A_\mathrm{b}} = \int_0^{Z_\mathrm{T}} \mathrm{d}Z \qquad \text{Eq. 11}$$

To solve the integral part (*NTU*) the mass balance of the differential volume is required in order to get the equilibrium concentration C_x^*:

$$NTU = \int_{C_\mathrm{x,out}}^{C_\mathrm{x,in}} \frac{\mathrm{d}C_\mathrm{x}}{C_\mathrm{x} - C_\mathrm{x}^*} \qquad \text{Eq. 12}$$

From the mass balance the equilibrium concentration can be determined.
The amount of substance going to the gas phase equals the amount leaving the liquid phase:

$$Q_y \cdot (C_y - C_{y,in}) = Q_x \cdot \left(C_x - C_{x,out}\right) \qquad \text{Eq. 13}$$

With
$$C_y = C_x^* \cdot K_{\mathrm{H}} \qquad \text{Eq. 14}$$

and the ingoing air concentration considered to be negligible or zero:

$$C_{y.in} = 0 \qquad \text{Eq. 15}$$

the following equation is obtained

$$Q_y \cdot C_x^* \cdot K_{\mathrm{H}} = Q_x \cdot \left(C_x - C_{x,out}\right) \qquad \text{Eq. 16}$$

Defining the stripping factor, *S*:

$$S = K_{\mathrm{H}} \cdot Q_y / Q_x \qquad \text{Eq. 17}$$

The equilibrium concentration can be calculated as follows:

$$C_x^* = \frac{Q_x \cdot (C_x - C_{out})}{Q_y \cdot K_{\mathrm{H}}} = \frac{(C_x - C_{out})}{S} \qquad \text{Eq. 18}$$

Combining equation 18 and 12:

$$\int_{C_{x,out}}^{C_{x,in}} \frac{dC_x}{C_x - \frac{(C_x - C_{x,out})}{S}} = \int_{C_{x,out}}^{C_{x,in}} \frac{S dC_x}{S \cdot C_x - C_x + C_{x,out}} \qquad \text{Eq. 19}$$

Integrating equation 19:

First the differential equation is simplified by defining *u* and then solved:

$$u = S \cdot C_x - C_x + C_{x,out} \qquad \text{Eq. 20}$$

$$\frac{du}{dx} = S - 1 \; and \; dx = \frac{1}{S-1} \cdot du \qquad \text{Eq. 21}$$

$$\frac{S}{S-1} \int \frac{1}{u} du = \frac{S}{S-1} \cdot ln\, u = \frac{S}{S-1} \cdot ln\left(S \cdot C_x - C_x + C_{x,out}\right) \qquad \text{Eq. 22}$$

$$\frac{S}{S-1} \int_{C_{x,out}}^{C_{x,in}} \frac{d\left(S \cdot C_x - C_x + C_{x,out}\right)}{\left(S \cdot C_x - C_x + C_{x,out}\right)} = \frac{S}{S-1} \cdot ln\left(\frac{S \cdot C_{x,in} - C_{x,in} + C_{x,out}}{S \cdot C_{x,out}}\right) \qquad \text{Eq. 23}$$

Rearranging the term in the natural logarithm:

$$\frac{S \cdot C_{x,in} - C_{x,in} + C_{x,out}}{S \cdot C_{x,out}} = \frac{S \cdot C_{x,in}}{S \cdot C_{x,out}} - \frac{C_{x,in}}{S \cdot C_{x,out}} + \frac{C_{x,out}}{S \cdot C_{x,out}} = \frac{\frac{C_{x,in}}{C_{x,out}} S - \frac{C_{x,in}}{C_{x,out}} + 1}{S} = \frac{\frac{C_{x,in}}{C_{x,out}}(S-1) + 1}{S}, \qquad \text{Eq. 24}$$

yields the final result of the integral:

$$\int_{C_{x,out}}^{C_{x,in}} \frac{dC_x}{C_x - C_x^*} = \frac{S}{S-1} ln \frac{\frac{C_{x,in}}{C_{x,out}}(S-1)+1}{S} \qquad \text{Eq. 25}$$

Substituting equation 25 in equation 8:

$$\frac{S}{S-1} \cdot ln\left(\frac{\left[C_{x,in}/C_{x,out} \cdot (S-1)\right]+1}{S}\right) = \frac{K_L \cdot a.A_b}{Q_x} \cdot Z_T \qquad \text{Eq. 26}$$

defining φ,

$$\varphi = \frac{K_L \cdot a.A_b}{Q_x} \cdot Z_T \qquad \text{Eq. 27}$$

this results in:

$$\varphi \cdot \frac{S-1}{S} = ln\left(\frac{\left[C_{x,in}/C_{x,out} \cdot (S-1)\right]+1}{S}\right) \qquad \text{Eq. 28}$$

$$S \cdot e^{\varphi \frac{S-1}{S}} = C_{x,in}/C_{x,out} \cdot (S-1) + 1 \qquad \text{Eq. 29}$$

$$S \cdot e^{\varphi \frac{S-1}{S}} - 1 = C_{x,in}/C_{x,out} \cdot (S-1) \qquad \text{Eq. 30}$$

$$C_{x,out} = \frac{C_{x,in} \cdot (S-1)}{S \cdot e^{[\varphi \cdot (S-1)/S]} - 1} \qquad \text{Eq. 31}$$

$$F_{volat,a.i.} = 1 - \frac{C_{x,out}}{C_{x,in}} = 1 - \frac{(S-1)}{S \cdot e^{[\varphi \cdot (S-1)/S]} - 1} \qquad \text{Eq. 32}$$

Annex 2 Fraction non-ionised for acids and bases

Acids

Departing from the equilibrium reaction HA ⇆ A^- + H^+, the acid dissociation constant K_a is defined by:

$$K_\mathrm{a} = \frac{[\mathrm{A}^-]\cdot[\mathrm{H}^+]}{[\mathrm{HA}]} \qquad \text{Eq. 1}$$

from which follows:

$$\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \frac{K_\mathrm{a}}{[\mathrm{H}^+]} \qquad \text{Eq. 2}$$

Taking negative logarithms from equation 100:

$$\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a} = -\log\left(\frac{[A^-]\cdot[H^+]}{[HA]}\right) \qquad \text{Eq. 3}$$

From equation nr. 102, the Henderson-Hasselbalch equation is derived:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right) \qquad \text{Eq. 4}$$

Which can be rewritten as:

$$\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = 10^{\mathrm{pH}-\mathrm{p}K_\mathrm{a}} \qquad \text{Eq. 5}$$

The fraction non-ionised (=fraction acid = fraction neutral) for an acid, $F_\text{non-ionised}$ is (e.g. Schwarzenbach *et al.* (2003):

$$F_\text{non-ionised} = \frac{[\mathrm{HA}]}{[\mathrm{HA}]+[\mathrm{A}^-]} = \frac{1}{1+\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}} \qquad \text{Eq. 6}$$

Combining equation nr. 101, 104 and 105 results in multiple expressions to calculate the non-ionised or neutral fraction ($F_\text{non-ionised}$) of an acidic substance in aqueous solution:

$$F_\text{non-ionised} = \frac{[\mathrm{HA}]}{[\mathrm{HA}]+[\mathrm{A}^-]} = \frac{1}{1+\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}} = \frac{1}{1+\frac{[K_a]}{[H^+]}} = \frac{1}{1+10^{\mathrm{pH}-pK_\mathrm{a}}} \qquad \text{Eq. 7}$$

(Safari *et al.*, 2014) defined α*,* the co-diffusion coefficient, to account speciation of an acid (in their paper CO_2):

$$\alpha = 1 + \frac{[K_a]}{[H^+]} \qquad \text{Eq. 8}$$

Using equation nr. 106, it follows that

$$\alpha = \frac{1}{F_{non-ionised}} \qquad \text{Eq. 9}$$

Bases

The equilibrium reaction for the dissociation of the conjugate acid of a base is given as BH$^+$ ⇆ B + H$^+$, resulting in the dissociation constant:

$$K_\mathrm{a} = \frac{[B]\cdot[\mathrm{H}^+]}{[BH^+]} \qquad \text{Eq. 10}$$

from which it follows that:
$\frac{[\mathrm{B}]}{[\mathrm{BH}^+]} = \frac{K_\mathrm{a}}{[\mathrm{H}^+]}$ and

$$\frac{[\mathrm{BH}^+]}{[\mathrm{B}]} = \frac{[\mathrm{H}^+]}{[K_\mathrm{a}]} \qquad \text{Eq. 11}$$

Taking negative logarithms from equation nr. 111:

$$\mathrm{p}K_\mathrm{a} = -\log\left(\frac{[B]\cdot[H^+]}{[BH^+]}\right) \qquad \text{Eq. 12}$$

Resulting in (Henderson-Hasselbalch):

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{B}]}{[\mathrm{BH}^+]}\right) \qquad \text{Eq. 13}$$

And

$$\mathrm{pH} - \mathrm{p}K_\mathrm{a} = \log\left(\frac{[\mathrm{B}]}{[\mathrm{BH}^+]}\right) \Leftrightarrow \mathrm{p}K_\mathrm{a} - \mathrm{pH} = \log\left(\frac{[\mathrm{BH}^+]}{[\mathrm{B}]}\right) \qquad \text{Eq. 14}$$

Which can be written as:

$$\frac{[\mathrm{BH}^+]}{[\mathrm{B}]} = 10^{\mathrm{p}K_\mathrm{a} - \mathrm{pH}} \qquad \text{Eq. 15}$$

The fraction non-ionised (=fraction base, =fraction neutral) for a base is:

$$F_\text{non−ionised} = \frac{[\mathrm{B}]}{[\mathrm{B}]+[\mathrm{BH}^+]} = \frac{1}{1+\frac{[\mathrm{BH}^+]}{[\mathrm{B}]}} \qquad \text{Eq. 16}$$

Combining equations nr. 110, 114 and 115 results in multiple expressions to calculate the non-ionised or neutral fraction ($F_\text{non-ionised\_b}$) of a conjugate base in aqueous solution:

$$F_\text{non-ionised} = \frac{[\mathrm{B}]}{[\mathrm{B}]+[\mathrm{BH}^+]} = \frac{1}{1+\frac{[\mathrm{BH}^+]}{[\mathrm{B}]}} = \frac{1}{1+\frac{[\mathrm{H}^+]}{K_a}} = \frac{1}{1+10^{\mathrm{p}K_\mathrm{a}-\mathrm{pH}}} \qquad \text{Eq. 17}$$

Hsieh *et al.* (2013) defined α, the co-diffusion coefficient, to account for speciation of bases:

$$\alpha = 1 + \frac{[H^+]}{[K_a]} \qquad \text{Eq. 18}$$

Using equation nr. 116, it follows that:

$$\alpha = \frac{1}{F_{non-ionised}}$$ Eq. 19

Neutral substances

This applies to substances without dissociating moieties:

$$F_{\text{non-ionised}} = 1$$ Eq. 20

With:

$\mathrm{p}K_\mathrm{a}$	$-\log K_\mathrm{a}$	(-)
pH	$-\log [\mathrm{H}^+]$	(-)
$[\mathrm{H}^+]$	molar concentration of hydrogen ions	$(\mathrm{mol \cdot dm^{-3}})$
$[\mathrm{A}^-]$	molar concentration of dissociated acid	$(\mathrm{mol \cdot dm^{-3}})$
[HA]	molar concentration of the (non-dissociated) acid	$(\mathrm{mol \cdot dm^{-3}})$
[B]	molar concentration of the (non-dissociated) base	$(\mathrm{mol \cdot dm^{-3}})$
$[\mathrm{BH}^+]$	molar concentration of conjugated acid of a base	$(\mathrm{mol \cdot dm^{-3}})$
α	co-diffusion coefficient	(-)
$F_{\text{non-ionised}}$	fraction of the molecules of a dissociating substance (acidic or base) in the neutral form in solution	(-)

Annex 3 Measured overall mass transfer coefficients

Table A3.1 Measured mass transfer rates for ammonia in packed (random) stripping columns at different conditions.

$K_L \cdot a$ (h^{-1})	Temperature (°C)	L/G (kg_{water}/kg_{air})	pH	K_L ($m \cdot s^{-1}$)	Type of packing	Packing surface area ($m^2 \cdot m^{-3}$)	Reference
0.079	34.3	14.4	9.7	3.0E-08	Kaldness 3	725	Zangeneh *et al.* (2021)
0.322	38.6	12.5	10.9	1.2E-07			
0.466	40.5	11.0	11.9	1.8E-07			
0.19	70	4.3	8.5	1.8E-07	18 mm PP Pall rings	296[a]	Kim *et al.* (2021)
0.22		25.5		2.1E-07			
0.17		50.9		1.6E-07			
0.10		101.9		9.3E-08			
0.18	25	5.5	11	1.7E-07	15 mm PE Rashing rings	300	Ferraz *et al.* (2013)

[a] this is the average of the interpolated values. The interpolated values are calculated from the reported surface areas of 16 mm and 25 mm rings from five different manufacturers.

Annex 4 Industrial cooling tower parameters, examples

Reported parameters for three industrial cooling towers (NFL, 2017), including calculated cycles of concentration (*COC*), Hydraulic Time Index (ln2 x *V*/*B*) and Hydraulic retention time (V/B). Also included are the system volume as minutes of recirculation flow = *V*/(*CR*/60) and the hold-up to circulation flow rate ratio, *V*/*CR*.

Reported Parameters

	Ammonia CT	**Urea CT**	**CPP CT**
No. of Cells	10	4	3
Temperature in/out (°C)	44/34	44/36	42/35
Cooling water circulation, *CR* (m^3/h)	16500	8000-10,000	8000
Drift loss, *D* (m^3/h) 0.1% of circulation water	17	10	8
Evaporation loss, *E* (m^3/h)	300	148	102
Blowdown rate approx., *B* (m^3/h)	40	30	15
System volume approx., *V* (m^3)	6000	3000	1800

Calculated parameters

	Ammonia CT	**Urea CT**	**CPP CT**
COC (*D*+*E*+*B*)/(*D*+*B*)	6.3	4.7	5.4
COC (*E*+*B*)/(*B*)	8.5	5.9	7.8
HTI (h)	74	52	54
HTI (d)	3.1	2.2	2.3
System Volume (*V*=minutes x *CR* in m^3/min, min)	21.8	18.0	13.5
Hold-up to circulation (*V*/*CR, h*)	0.36	0.30	0.23
HRT (h)	150	100	120

Annex 5 Collection of substance properties

This Annex provides the data sources, data selection and the calculation of parameters needed to calculate the overall mass transfer rate coefficient in air (K_G) for active substances and the fraction volatilised from the cooling tower.

Substance identity and basic molecular properties

The list of substances including CAS registry numbers was compiled by extracting all PT11 actives listed in ECHAs Biocial active substances database. Excluded were salts, since these dissolve and do not evaporate.

The chemical property parameters: molecular weight, molecular formula and SMILES code were retrieved from the ECHA database if possible. If no assessment was yet available, the REACH registration dossier was checked. If not, the parameters were generated by the substance databases of ChemAxon's Marvin Sketch (ChemAxon, 2016), Bioloom (Biobyte, known for e.g. ClogP (BioByte, 2006) or EPISuite (US EPA, 2012). Structural and molecular formulas and SMILES code were cross checked using these data sources, if possible.

Dimensionless diffusion volume

Dimensionless diffusion volume was derived using Fuller's method (Fuller *et al.*, 1966) using the species volumes published by Gu *et al.* (2018). For molecules that are acids or bases their volume was calculated for the undissociated (neutral) form, as this is the species that will evaporate. For substances that are negatively charged, the counter ion (e.g. K^+) was replaced by one hydrogen atom to calculate the molecular diffusion volume.

Van der Waals volume and molecular radius

Van der Waals volume V_{VdW} (Å^3) was calculated using Marvin Sketch (ChemAxon, 2016). The molecular (simple) radius r_s (m) was calculated as $r_s = \sqrt[3]{\frac{3V_{VdW}}{4\pi}} \cdot 1^{-10}$ (Miyamoto *et al.*, 2020). The molecular radius is used to calculate the diffusion coefficient in water using the Stokes-Einstein equation.

V_{VdW}	Van der Waals volume	(Å^3)
r_s	simple molecular radius	(m^3·s^{-1})

pK_a

Based on chemical structure it was decided whether a substances does or does not dissociate (d.n.d). For dissociating substances the following sources were checked to retrieve pK_a values, in the following order of preference:

1. Published AR (LoEP) from the ECHA database on biocidal active substances. Only data from published LoEPs were used, draft CARs were not used since data therein are not yet public.

2. Registered substances database ECHA (REACH).
3. MarvinSketch (ChemAxon, 2016).

Since temperatures of experimental determination for pK_a values are often not reported, and the temperature dependence often not known, we pragmatically assumed no influence of temperature on pK_a and used the values without further correction for temperature.

Henry's law constant

Sources were checked/used in the following order of preference.

1. Published AR (LoEP) on ECHA database on biocidal active substances.
   Only data from published LoEPs were used when a temperature of determination (or calculation) was also provided. Draft CARs were not used since data in these are not yet made publicly available.
2. Sander. 2015. Atmos Chem Phys, 15: 4399–4981. The database version was used: http://satellite.mpic.de/henry. Measured (M) values and values from literature review (L) were preferably selected and compared. However, these are often not available, which means that sometimes QSPR values (Q) from other databases or values calculated from vapour pressure and water solubility (V) were selected.
3. Registered substances database ECHA (REACH).
4. H calculated from -preferably- experimentally determined vapour pressure (P_v) and water solubility (S_w) that were not reported as > or < values. The temperatures of determination of P_v and S_w should be reported as well.
5. HenryWin module (v 3.20) from EPISUite (US EPA, 2011). Values calculated using the bond estimation method were used since group contribution method values were often not available.
   In the situation that no experimentally determined H or P_v and S_w were available in BPR or REACH, or temperatures of determination were missing for these parameters or values are reported as < or >, the HenryWin estimate was selected.

Temperature correction of Henry's law constant

In this annex we follow the recently adopted IUPAC nomenclature of Henry's law constants, see Sander *et al.* (2022).

Enthalpy of volatilisation

This paragraph concerns the database on Henry's law constants provided by Sander (http://www.henrys-law.org/henry/) that have been quality assessed. In this paragraph we therefore use the same notation. In this database, values for H_s^{cp} are tabulated at 25°C, in some cases accompanied with values for $\frac{d \ln H_s^{cp}}{d(1/T)}$, which describe temperature dependence of H_s^{cp}.

H_s^{cp} is Henry's law solubility constant, i.e. H is defined as the ratio of aqueous phase concentration c, and partial pressure p. We are interested in temperature dependence of Henry's volatility law constant, H_v^{pc} which is the inverse: i.e. the ratio of aqueous phase concentration and partial pressure. Both are thus related as $H_s^{cp} = 1/\ H_v^{pc}$, section 2.5.1 (Sander, 2015).

Temperature dependence of equilibrium constants is described by the Van 't Hoff equation. Applied to Henry's solubility law constant this is: $\frac{d \ln H_s^{cp}}{d(1/T)} = \frac{-\Delta H_{sol}}{R}$ (e.g Sander, 2015, Atkins *et al.*, 2006, Schwarzenbach *et al.*, 2003). ΔH_{sol} is the molar enthalpy of dissolution, which should not be confused with the enthalpy of solution, the amount of heat that is released or absorbed during the dissolving process, ΔH_{soln} used in this report. Since we are interested in the molar enthalpy of volatilisation (ΔH_{volat}), we can substitute $H_s^{cp} = 1/\ H_v^{pc}$ (see above), giving

$$\frac{d \ln \left(1/H_v^{pc}\right)}{d(1/T)} = \frac{-\Delta H_{volat}}{R} \Rightarrow \frac{d \ln H_s^{cp}}{d(1/T)} = \frac{\Delta H_{volat}}{R}$$

Thus:

$$\Delta H_{volat} = \frac{d \ln H_s^{cp}}{d(1/T)} \cdot R$$

In case no value for ΔH_{volat} was available, the slope ($-\Delta H_{volat}/R$) from the temperature dependence of Henry's law constant assigned by HenryWin v3.20 from EPISuite (US EPA, 2011) was used to calculate ΔH_{volat}.

Dimensionless Henry's law constant, temperature correction

The selected value for Henry's law (volatility) constant H_s^{cp} was recalculated into the dimensionless Henry's law volatility constant, which is known as K_H, $K_{air\text{-}water}$ or K_{AW}. In this report we still use the symbol K_H although we are well aware that recent IUPAC terminology has deprecated the use of those symbols, which should be replaced by H_v^{cc}:

$$H_v^{cc} = \frac{H_v^{pc}}{RT}\ (= K_H = K_{air-water} = K_{AW})$$

The Henry's law constant we selected for calculations – for each substance –, may be available at different temperatures. E.g. EPISuite and Sander provide values at 25°C (T_1 = 298.15 K), but a value from a CAR could be available at 20°C. If our selected H_v^{pc} was calculated from solubility and vapour pressure, these were first corrected first to 25°C (298.15 K) using the equations and default values for molar enthalpy given in BPR Vol IV, Part B&C (ECHA, 2017). All Henry's law constants were corrected to 35°C (T_2 = 303.15 K), the default value chosen in this report for the water temperature in the cooling tower.

ΔH_{sol}	molar enthalpy of dissolution	($J \cdot mol^{-1}$)
ΔH_{volat}	molar enthalpy of volatilisation	($J \cdot mol^{-1}$)
H_v^{cc}	dimensionless Henry's law volatility constant	(-)
H_s^{cp}	Henry's law solubility constant	($mol \cdot m^{-3} \cdot Pa^{-1}$)
H_v^{pc}	Henry's law volatility constant	($Pa \cdot m^3 \cdot mol^{-1}$)
$K_{air\text{-}water}$	dimensionless Henry's law constant	($m^3_{water} \cdot m^{-3}_{air}$)
R	gas constant	($Pa \cdot mol \cdot m^{-3}$)
T	temperature	(K)

Annex 6 Substance properties

This annex shows the values of the collected and calculated substance properties that are needed to derive the overall mass transfer rate coefficient in air (K_G) and that are required to estimate the volatilisation in the cooling tower for all active substances currently listed for use in PT11 in ECHAs active substance database. Besides the substance properties, the calculated values of the partial mass transfer coefficients and the overall mass transfer coefficient are included.

Since lengthy chemical names hinder easy tabular display, the active substances were numbered (Table A6.1). These numbers were used as substance identifier in Tables A6.2 to A6.4. The embedded Excel files below show the chemical name, the alternative name usually an abbreviation, the CAS number and all selected and calculated property values.

Table A6.1 Identification and numbering for substances in Tables A6.2 to A6.4

Subtance number	**Chemical name**	**Alternative name**	**CAS**
1	(ethylenedioxy)dimethanol		3586-55-8
2	2-methyl-2*H*-isothiazol-3-one	MIT	2682-20-4
3	1,2-benzisothiazol-3(2*H*)-one	BIT	2634-33-5
4	2,2-dibromo-2-cyanoacetamide	DBNPA	10222-01-2
5	2-octyl-2H-isothiazol-3-one	OIT	26530-20-1
6	4,5-dichloro-2-octyl-2*H*-isothiazol-3-one	DCOIT	64359-81-5
7	tetrakis(hydroxymethyl)phosphonium sulphate (2:1)	THPS	55566-30-8
8	2-bromo-2-nitro-1,3-propanediol	Bronopol	52-51-7
9	bromochloro-5,5-dimethylimidazolidine-2,4-dione	BCMDH	32718-18-6
10	1,5-pentanedial	Glutaraldehyde	111-30-8
11	hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine	HHT	4719-04-4
12	ɑ, ɑ′, ɑ''-trimethyl-1,3,5-triazine-1,3,5(2*H*,4*H*,6*H*)-triethanol	HPT	25254-50-6
13	2-dodecylguanidine monohydrochloride	DGH	13590-97-1
14	monochloramine	NH2Cl	7783-20-2; 10599-90-3
15	*N*-(3-aminopropyl)-N-dodecylpropane-1,3-diamine	Diamine	2372-82-9
16	ozone		10028-15-6
17	potassium dimethyldithiocarbamate	KDDC	128-03-0
18	sodium dichloroisocyanurate dihydrate	Troclosene sodium dihydrate	51580-86-0
19	sodium dimethyldithiocarbamate	NDDC	128-04-1
20	1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione	Symclosene	87-90-1
21	tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazole-2,5 (1H,3H)-dione; tetramethylol acetylenediurea	TMAD	5395-50-6
22	sodium dichlorocyanurate	troclosene sodium	2893-78-9
23	hydrogen peroxide		7722-84-1
24	peracetic acid		79-21-0
25	chlorine dioxide		10049-04-4

Table A6.2 Collected and calculated molecular properties and overall mass transfer coefficients for currently listed PT11 active substances, nrs. 1-7. Substance numbers shown in Table A6.1.

Parameter	**Symbol**	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Molecular weight	M_w	$[g \cdot mol^{-1}]$	122.12	115.16	151.19	241.87	213.34	282.20	406.28
Dimensionless diffusion volume	V_i	[-]	111.1	109.1	119.8	111.3	234.0	271.4	139.8
Dissociation constant	$pK_{a1,2,3}$	[-]	d.n.d.	d.n.d.	7.2	10.2	d.n.d.	d.n.d.	f.i.
acid, base, ionised, neutral		[-]	n	n	A	a	n	n	i
Co-diffusion factor $(1/F_{neutral})^a$	α	[-]	1.00	1.00	1.63	1.00	1.00	1.00	100000
Henry's law constant	H	$[Pa \cdot m^3 \cdot mol^{-1}]$	1.55E-04	8.19E-05	1.45E-05	1.92E-03	1.63E-03	3.30E-02	1.72E-18
Temperature H	T	[°C]	20	20	20	25	20	20	25
Enthalpy of volatilisation	ΔH_{volat}	$[J \cdot mol^{-1}]$	49887	54876	54876	49887	54876	54876	49887
Dimensionless Henry's law volatility constant at 35°C	K_H	$[m^3 \cdot m^{-3}]$	1.72E-07	1.01E-07	1.78E-08	1.49E-06	2.00E-06	4.05E-05	1.33E-21
Van der Waals volume	V_{vdW}	$[Å^3]$	114.75	94.08	119.82	112.06	212.81	240.79	325.16
Simple radius	r_s	[m]	3.01E-10	2.82E-10	3.06E-10	2.99E-10	3.70E-10	3.86E-10	4.27E-10
D_{air} at 35°C	D_{air}	$[m^2 \cdot s^{-1}]$	8.40E-06	8.51E-06	7.98E-06	7.98E-06	5.77E-06	5.31E-06	7.07E-06
D_{water} at 35°C	D_{water}	$[m^2 \cdot s^{-1}]$	1.05E-09	1.12E-09	1.04E-09	1.06E-09	8.55E-10	8.21E-10	7.43E-10
partial mass transfer coefficient in air film	$k_{G,2}$	$[m \cdot s^{-1}]$	7.91E-04	7.98E-04	7.64E-04	7.64E-04	6.16E-04	5.82E-04	7.05E-04
partial mass transfer coefficient in water film	$k_{L,2}$	$[m \cdot s^{-1}]$	1.42E-05	1.47E-05	1.41E-05	1.43E-05	1.28E-05	1.26E-05	1.19E-05
overall mass transfer coefficient air ^{a}	K_G	$[m \cdot s^{-1}]$	7.91E-04	7.98E-04	7.64E-04	7.64E-04	6.16E-04	5.81E-04	7.05E-04
overall mass transfer coefficient water ^{a}	K_L	$[m \cdot s^{-1}]$	1.36E-10	8.02E-11	1.36E-11	1.14E-09	1.23E-09	2.35E-08	9.40E-25

Notes

d.n.d. = does not dissociate, f.i. = fully ionised. ^{a} at pH 7.

Table A6.3 Collected and calculated molecular properties and overall mass transfer coefficients for currently listed PT11 active substances, nrs. 8-14. Substance numbers are shown in Table A6.1.

Parameter	**Symbol**	**Unit**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Molecular weight	M_w	$[g\cdot mol^{-1}]$	199.99	241.47	100.11	219.28	261.41	263.86	51.48
Dimensionless diffusion volume	V_i	[-]	112.4	139.3	110.2	205.3	254.6	287.3	30.2
Dissociation constant	$pK_{a1,2,3}$	[-]	12.9;13.7	8.1;10.1	d.n.d.	1.1;1.8; 4.1	1.4;1.5; 4.5	11.8	1.6
acid, base, neutral		[-]	a	a	n	b	b	b	b
Co-diffusion factor $(1/F_{neutral})^a$	α	[-]	1.00	1.08	1.00	1.00	1.00	63097	1.00
Henry's law constant	H	$[Pa\cdot m^3\cdot mol^{-1}]$	1.32E-06	1.14E-05	3.33E-03	1.09E-06	2.56E-06	8.98E-12	8.24E-01
Temperature H	T	[°C]	25	25	25	25	25	25	20
Enthalpy of volatilisation	ΔH_{volat}	$[J\cdot mol^{-1}]$	49887	54876	76493	49887	49887	37415	49887
Dimension less Henry's law volatility constant at 35°C	K_H	$[m^3\cdot m^{-3}]$	1.02E-09	9.43E-09	3.66E-06	8.45E-10	1.98E-09	5.91E-15	9.16E-04
Van der Waals volume	V_{vdW}	[Å^3]	120.43	144.48	100.71	218.25	269.47	261.61	37.30
Simple radius	r_s	[m]	3.06E-10	3.26E-10	2.89E-10	3.73E-10	4.01E-10	3.97E-10	2.07E-10
D_{air} at 35°C	D_{air}	$[m^2\cdot s^{-1}]$	8.04E-06	7.25E-06	8.60E-06	6.12E-06	5.49E-06	5.18E-06	1.57E-05
D_{water} at 35°C	D_{water}	$[m^2\cdot s^{-1}]$	1.03E-09	9.73E-10	1.10E-09	8.48E-10	7.91E-10	7.99E-10	1.53E-09
partial mass transfer coefficient in air	$k_{G,2}$	$[m\cdot s^{-1}]$	7.68E-04	7.17E-04	8.03E-04	6.41E-04	5.96E-04	5.73E-04	1.20E-03
partial mass transfer coefficient in water	$k_{L,2}$	$[m\cdot s^{-1}]$	1.41E-05	1.37E-05	1.45E-05	1.28E-05	1.23E-05	1.24E-05	1.71E-05
overall mass transfer coefficient air ^{a}	K_G	$[m\cdot s^{-1}]$	7.68E-04	7.17E-04	8.03E-04	6.41E-04	5.96E-04	5.73E-04	1.13E-03
overall mass transfer coefficient water ^{a}	K_L	$[m\cdot s^{-1}]$	7.83E-13	6.76E-12	2.94E-09	5.41E-13	1.18E-12	3.39E-18	1.03E-06

Notes

d.n.d. = does not dissociate, f.i. = fully ionised. ^{a} at pH 7.

Table A6.4 Collected and calculated molecular properties and overall mass transfer coefficients for currently listed PT11 active substances, nrs. 15-21. Substance numbers are shown in Table A6.1.

Parameter	**Symbol**	**Unit**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Molecular weight	M_{w}	$[\mathrm{g \cdot mol^{-1}}]$	299.55	48.00	159.31	197.96	143.21	232.40	262.22
Dimensionless diffusion volume	V_{i}	[-]	394.5	[a]	114.2	105.7	114.2	124.4	177.8
Dissociation constant	$\mathrm{p}K_{\mathrm{a1,2,3}}$	[-]	6.5; 9.3; 10.4	d.n.d.	4.2	3.6	4.2	d.n.d.	d.n.d.
acid, base, neutral		[-]	b	n	a	a	a	n	a
Co-diffusion factor $(1/F_{\mathrm{neutral}})^{c}$	α	[-]	755960	1.00	618	2400	618	1.00	1.00
Henry's law constant	H	$[\mathrm{Pa \cdot m^3 \cdot mol^{-1}}]$	1.40E-07	9.21E+03	6.30E-08	5.13E-05	6.30E-08	4.93E-05	2.59E-13
Temperature H	T	[°C]	20	25	20	20	20	20	25
Enthalpy of volatilisation	$\Delta H_{\mathrm{volat}}$	$[\mathrm{J \cdot mol^{-1}}]$	37415	23281	37415	54876	37415	54876	54876
Dimensionless Henry's law volatility constant at 35°C	K_{H}	$[\mathrm{m^3 \cdot m^{-3}}]$	1.21E-10	5.04E+00	5.46E-11	6.29E-08	5.46E-11	6.05E-08	2.14E-16
Van der Waals volume	V_{vdW}	[Å^3]	354.58	29.70	104.93	121.30	104.93	136.02	210.96
Simple radius	r_{s}	[m]	4.39E-10	1.92E-10	2.93E-10	3.07E-10	2.93E-10	3.19E-10	3.69E-10
D_{air} at 35°C	D_{air}	$[\mathrm{m^2 \cdot s^{-1}}]$	4.43E-06	1.89E-05[b]	8.11E-06	8.26E-06	8.18E-06	7.63E-06	6.47E-06
D_{water} at 35°C	D_{water}	$[\mathrm{m^2 \cdot s^{-1}}]$	7.22E-10	1.65E-09	1.08E-09	1.03E-09	1.08E-09	9.93E-10	8.58E-10
partial mass transfer coefficient in air	$k_{\mathrm{G},2}$	$[\mathrm{m \cdot s^{-1}}]$	5.16E-04	1.36E-03	7.73E-04	7.82E-04	7.77E-04	7.42E-04	6.65E-04
partial mass transfer coefficient in water	$k_{\mathrm{L},2}$	$[\mathrm{m \cdot s^{-1}}]$	1.18E-05	1.78E-05	1.44E-05	1.41E-05	1.44E-05	1.38E-05	1.28E-05
overall mass transfer coefficient air [c]	K_{G}	$[\mathrm{m \cdot s^{-1}}]$	5.16E-04	3.52E-06	7.73E-04	7.82E-04	7.77E-04	7.42E-04	6.65E-04
overall mass transfer coefficient water [c]	K_{L}	$[\mathrm{m \cdot s^{-1}}]$	6.24E-14	1.78E-05	4.22E-14	4.92E-11	4.24E-14	4.49E-11	1.42E-19

Notes

d.n.d. = does not dissociate, f.i. = fully ionised. [a] Parameter not needed since D_{air} was taken from a handbook. [b] D_{air} taken from Yaws (2014). [c] at pH 7.

Table A6.5 Collected and calculated molecular properties and overall mass transfer coefficients for currently listed PT11 active substances, nrs. 22-25. Substance numbers are shown in Table A6.1.

Parameter	**Symbol**	**Unit**	**22**	**23**	**24**	**25**
Molecular weight	M_w	$[g\cdot mol^{-1}]$	197.96	34.00	76.05	67.45
Dimensionless diffusion volume	V_i	[-]	105.7	[a]	59.4	[a]
Dissociation constant	$pK_{a1,2,3}$	[-]	3.6	11.5	8.2	d.n.d.
acid, base, neutral		[-]	a	a	a	n
Co-diffusion factor $(1/F_{neutral})^c$	α	[-]	2400	1.00	1.06	1.00
Henry's law constant	H	$[Pa\cdot m^3\cdot mol^{-1}]$	5.13E-05	1.10E-03	2.17E-01	1.00E+02
Temperature H	T	[°C]	20	25	25	25
Enthalpy of volatilisation	ΔH_{volat}	$[J\cdot mol^{-1}]$	54876	54876	44067	29101
Dimensionless Henry's law volatility constant at 35°C	K_H	$[m^3\cdot m^{-3}]$	6.29E-08	9.09E-07	1.56E-04	5.90E-02
Van der Waals volume	V_{vdW}	$[Å^3]$	121.30	28.43	64.89	39.46
Simple radius	r_s	[m]	3.07E-10	1.89E-10	2.49E-10	2.11E-10
D_{air} at 35°C	D_{air}	$[m^2\cdot s^{-1}]$	8.26E-06	1.89E-05[b]	1.15E-05	1.55E-05[b]
D_{water} at 35°C	D_{water}	$[m^2\cdot s^{-1}]$	1.03E-09	1.67E-09	1.27E-09	1.50E-09
partial mass transfer coefficient in air	$k_{G,2}$	$[m\cdot s^{-1}]$	7.82E-04	1.36E-03	9.74E-04	1.19E-03
partial mass transfer coefficient in water	$k_{L,2}$	$[m\cdot s^{-1}]$	1.41E-05	1.79E-05	1.56E-05	1.70E-05
overall mass transfer coefficient air [c]	K_G	$[m\cdot s^{-1}]$	7.82E-04	1.36E-03	9.65E-04	2.32E-04
overall mass transfer coefficient water [c]	K_L	$[m\cdot s^{-1}]$	4.92E-11	1.24E-09	1.50E-07	1.37E-05

Notes

d.n.d. = does not dissociate, f.i. = fully ionised. [a] Parameter not needed since D_{air} was taken from a handbook. [b] D_{air} taken from Yaws (2014). [c] at pH 7.

Annex 7 Nomenclature and default values

Parameter	Description	Unit
α	co-diffusion coefficient (accounting for speciation of an acid or a base)	(-)
ΔH_{evap}	molar enthalpy of evaporation	$(\mathrm{J\cdot mol^{-1}})$
ΔH_{soln}	molar enthalpy of solution	$(\mathrm{J\cdot mol^{-1}})$
ΔH_{sol}	molar enthalpy of dissolution	$(\mathrm{J\cdot mol^{-1}})$
$\Delta H_{\mathrm{volat}}$	molar enthalpy of volatilisation	$(\mathrm{J\cdot mol^{-1}})$
$\mu_{\mathrm{water,Tsystem}}$	dynamic viscosity of water at system temperature	(cp) = $(\mathrm{mPa\cdot s})$
$\mu_{\mathrm{water,Ttest}}$	dynamic viscosity of water at test temperature	(cp) = $(\mathrm{mPa\cdot s})$
$\mu_{\mathrm{water,T}}$[a]	dynamic viscosity of water at temperature T	(cp) = $(\mathrm{mPa\cdot s})$
φ	term describing the mass transfer efficiency (defined by equation nr. 3)	(-)

[a] The unit of dynamic viscosity differs by what the author gives preference to. The historic unit is centipoise (cp). and 1 cp equals 1 mPa.s. The unit of dynamic viscosity in SI units is $\mathrm{kg\cdot m^{-1}\cdot s^{-1}}$.

Parameter	Description	Unit
a	volumetric surface area of the packing	$(\mathrm{m^{2}\cdot m^{-3}})$
A	effective overall packing surface area	$(\mathrm{m^{2}})$
A_{b}	base area of the packing filled tower	$(\mathrm{m^{2}})$
$[\mathrm{A^{-}}]$	molar concentration of dissociated acid	$(\mathrm{mol\cdot dm^{-3}})$
$AREA_{\mathrm{depos}}$	deposition area	$(\mathrm{m^{2}})$
$[\mathrm{B}]$	molar concentration of the (non-dissociated) base	$(\mathrm{mol\cdot dm^{-3}})$
$[\mathrm{BH^{+}}]$	molar concentration of conjugated acid of a base	$(\mathrm{mol\cdot dm^{-3}})$
C	correlation constant (equation nr. 18)	(-)
$C_{x.\mathrm{in}}$	concentration in water entering the cooling tower	$(\mathrm{kg\cdot m^{-3}})$
C_{mkp}	concentration in the make-up water	$(\mathrm{kg\cdot m^{-3}})$
$C_{x.\mathrm{out}}$	concentration in water leaving the cooling tower	$(\mathrm{kg\cdot m^{-3}})$
C_{basin}	concentration of the biocidal product in the cooling water basin	$(\mathrm{kg\cdot m^{-3}})$
$C_{\mathrm{bld.t}}$	concentration at time t after adding the shock dose	$(\mathrm{kg\cdot m^{-3}})$
$C_{\mathrm{bld.max}}$	maximum concentration in the cooling water blowdown at adding the last of n shock doses	$(\mathrm{kg\cdot m^{-3}})$

Parameter	Description	Unit
$C_{bld.avg}$	average concentration in the cooling water blowdown after shock dosing over time period Δt	$(kg\cdot m^{-3})$
C_{proc}	concentration of the active ingredient (a.i.) in the system	$(kg\cdot m^{-3})$
$C_{proc.t0}$	starting concentration of the active ingredient (a.i.) in the system	$(kg\cdot m^{-3})$
$C_{proc.ini}$	initial concentration of the active ingredient (a.i.) in the system at shock dosing	$(kg\cdot m^{-3})$
$C_{proc.t}$	concentration of the active ingredient (a.i.) in the system at time t	$(kg\cdot m^{-3})$
$Cstd_{depos.drift}$	deposition flux to soil at standard source strength of 1 $kg\cdot s^{-1}$ for a.i. emitted via spray drift	$(kg\cdot m^{-2}\cdot s^{-1})$
$Cstd_{depos.volat}$	deposition flux to soil at standard source strength of 1 $kg\cdot s^{-1}$ for volatilised a.i.	$(kg\cdot m^{-2}\cdot s^{-1})$
C_x	concentration of the substance in the water phase of the cooling tower	$(kg\cdot m^{-3})$
C_x^*	substance equilibrium concentration in the water phase	$(kg\cdot m^{-3})$
$C_{y.in}$	concentration air entering the cooling tower	$(kg\cdot m^{-3})$
C_y	substance concentration in the air phase of the cooling tower	$(kg\cdot m^{-3})$
C_y^*	substance equilibrium concentration in the air phase	$(kg\cdot m^{-3})$
$C_{y.out}$	concentration in air cleaving the cooling tower	$(kg\cdot m^{-3})$
d	nominal packing size of packed bed	(m)
D	diffusion coefficient	$(m^2\cdot s^{-1})$
D_G	diffusion coefficient in gas (air)	$(m^2\cdot s^{-1})$
D_L	diffusion coefficient in liquid (water)	$(m^2\cdot s^{-1})$
$D_{air.T}$	diffusion coefficient in air at a pressure of 1 atmosphere and temperature T	$(m^2\cdot s^{-1})$
$D_{air.Tsystem}$	air diffusion coefficient at (average) cooling system temperature	$(m^2\cdot s^{-1})$
$D_{air.Ttest}$	measured air diffusion coefficient at test temperature	$(m^2\cdot s^{-1})$
$DOSE_{soil.drift}$	dose of a.i. deposited to soil via spray drift	$(kg\cdot m^{-2}\cdot s^{-1})$
$DOSE_{soil.volat}$	dose of volatilised a.i. deposited to soil	$(kg\cdot m^{-2}\cdot s^{-1})$
$DOSE_{soil.total}$	total dose of a.i. deposited to soil	$(kg\cdot m^{-2}\cdot s^{-1})$
$D_{water.Tsystem}$	liquid diffusion coefficient at the average cooling system temperature	$(m^2\cdot s^{-1})$
$D_{water.Ttest}$	measured liquid diffusion coefficient at test temperature	$(m^2\cdot s^{-1})$
$D_{water.\ T}$	diffusion coefficient in water at temperature T	$(m^2\cdot s^{-1})$
F_{bld}	fraction of cooling water lost via the blowdown	(-)
F_{circ}	system volume expressed as a fraction of the recirculation flow rate	(-)
F_{depos}	fraction lost due to spray drift and deposited to soil from Groshart *et al.* (2003)	(-)
$F_{depos.area}$	fraction of drift depositing on predefined soil area	(-)
F_{drift}	fraction of cooling water lost via spray drift	(-)

Parameter	Description	Unit
$F_{evap+drift}$	fraction of cooling water lost due to evaporation and drift from Groshart *et al.* (2003)	(-)
F_{evap}	fraction of cooling water lost through evaporation	(-)
$F_{non\text{-}ionised}$	fraction of the molecules of an ionising substance being present in neutral form in solution	(-)
$F_{volat.a.i.}$	fraction of the active ingredient volatilised from the cooling water	(-)
G_x	water mass velocity	($kg \cdot h^{-1} \cdot m^{-2}$)
G_y	Vapour-free air mass velocity	($kg \cdot h^{-1} \cdot m^{-2}$)
H	molar enthalpy	($J \cdot mol^{-1}$)
H_v	Henry’s law volatility constant	($Pa \cdot m^3 \cdot mol^{-1}$)
H_v^{cc}	dimensionless Henry’s law volatility constant	(-)
H_s^{cp}	Henry’s law solubility constant	($mol \cdot m^{-3} \cdot Pa^{-1}$)
H_v^{pc}	Henry’s law volatility constant	($Pa \cdot m^3 \cdot mol^{-1}$)
$[H^+]$	molar concentration of hydrogen ions	($mol \cdot dm^{-3}$)
[HA]	molar concentration of the (non-dissociated) acid	($mol \cdot dm^{-3}$)
HRT	hydraulic retention time	(h)
J	mass flow rate of the substance (J) across the air-water interface per unit volume of packed column	($kg \cdot m^{-3} \cdot s^{-1}$)
k	partial mass transfer coefficient	($m \cdot s^{-1}$)
k_B	Boltzmann constant	($m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$) = ($J \cdot K^{-1}$)
k_{deg}	first order degradation rate constant	(s^{-1})
k_G	partial mass transfer coefficient for the gas (air) film	($m \cdot s^{-1}$)
k_L	partial mass transfer coefficient for the liquid (water) film	($m \cdot s^{-1}$)
K_a	acid dissociation constant	($mol \cdot dm^{-3}$)
$K_{air\text{-}water}$	dimensionless Henry’s law constant (often used as such in environmental fate modelling)	($m^3_{water} \cdot m^{-3}_{air}$)
K_G	overall gas-phase mass transfer coefficient	($m \cdot s^{-1}$)
K_H	Henry’s law volatility constant (dimensionless) as used in this report	($m^3_{water} \cdot m^{-3}_{air}$)
K_L	overall liquid-phase mass transfer coefficient	($m \cdot s^{-1}$)
$K_{H.Tsystem}$	Henry’s law constant at the cooling system temperature (35 °C)	($m^3_{water} \cdot m^{-3}_{air}$)
$K_{H.Ttest}$	Henry’s law constant at test temperature	($m^3_{water} \cdot m^{-3}_{air}$)
M_{air}	molecular weight of air	($g \cdot mol^{-1}$)
M_{subst}	molecular weight of the substance	($g \cdot mol^{-1}$)
M_{water}	molecular weight of water	($g \cdot mol^{-1}$)

Parameter	Description	Unit
N	cycles of concentration (sometimes indicated as COC)	(-)
P	atmospheric pressure	(atm)
pH	$-\log [H^+]$	(-)
pK_a	$-$log of the acid dissociation constant	(-)
P_v	vapour pressure at test temperature. T_{test}	(Pa)
Q_{bld}	blowdown flow rate	($m^3 \cdot s^{-1}$)
Q_{evap}	evaporation loss rate rate	($m^3 \cdot s^{-1}$)
Q_{mkp}	make-up water flow rate	($m^3 \cdot s^{-1}$)
Q_{circ}	water recirculation flow rate	($m^{-3} \cdot s^{-1}$)
Q_x	water volume flow rate	($m^3 \cdot s^{-1}$)
Q_y	air volume flow rate	($m^3 \cdot s^{-1}$)
r	the radius of a spherical particle	(m)
r_s	simple molecular radius	(m)
R	gas constant	($J \cdot mol^{-1}$ K^{-1})
Re	Reynolds dimensionless number	(-)
R_{rec}	Recycle ratio	(-)
$RELEASE_{air.volat}$	release of a.i. via volatilisation to air	($kg \cdot s^{-1}$)
$RELEASE_{air.drift}$	release of spray drift to air	($kg \cdot s^{-1}$)
S	stripping factor	(-)
Sc	Schmidt dimensionless number	(-)
Sh	Sherwood dimensionless number	(-)
S_w	water solubility at at test temperature. T_{test}	($g \cdot L^{-1}$)
T	temperature	(K)
t_{circ}	volume of the cooling system expressed as the number of minutes of the recirculation flow rate	(min)
T_{test}	temperature at which measured values are determined	(K)
T_{system}	average temperature of the water in the cooling system	(K)
v	kinematic viscosity	($m^2 \cdot s^{-1}$)
v^0	flow velocity of the medium (gas or liquid)	($m \cdot s^{-1}$)
V_{air}	dimensionless diffusion volume of air	(-)
V_{basin}	water volume in the cooling water basin	(m^3)

Parameter	Description	Unit
$V_{m.subst}$	molar volume of the substance (active ingredient)	($cm^3 \cdot mol^{-1}$)
V_{subst}	dimensionless diffusion volume of substance (active ingredient)	(-)
V_{syst}	water volume in the cooling water system	(m^3)
V_{vdw}	Van der Waals volume	(Å^3)
x	association constant for water	(-)
X	correlation constant (equation nr. 18)	(-)
Y	correlation constant (equation nr. 18)	(-)
Z_T	height of packing material	(m)

Parameters from the above table and their associated (default) values used in model calculations.

Parameter	Value	Unit	Remark
μ_{water}	0.712299685	(cp)	at 35°C
k_B	1.38048×10^{-23}	($m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}$)=($J \cdot K^{-1}$)	
M_{air}	19	($g \cdot mol^{-1}$)	
R	8.314472	($J \cdot mol^{-1}$ K^{-1})	
T_{system}	308.15	(K)	
V_{air}	19.7	(-)	
x	2.6	(-)	

Parameters with more than one default value. derived for ESD update.

Parameter	Description	Default value		Unit
		Large system	Small system	
F_{bld}	fraction lost via blowdown	0.014	0.02	(-)
F_{evap}	fraction of evaporated cooling water	0.01	0.01	(-)
F_{drift}	fraction of cooling water lost via spray drift	0.00025	0.00025	(-)
HRT	hydraulic retention time (V_{syst}/Q_{bld})	24	150	(h)
HRT (ESD)	hydraulic retention time $V_{syst}/(Q_{bld}+Q_{evap}+Q_{drift})$	14	99	(h)
N	cycles of concentration $(Q_{evap}+Q_{bld})/Q_{bld}$	1.7	1.5	(-)
pH	-log of H^+ concentration	8	8	(-)
Q_{bld}	blowdown flow rate	125	2	($m^3 \cdot h^{-1}$)
Q_{circ}	water recirculation flow rate	9000	100	($m^3 \cdot h^{-1}$)

Parameter	Description	Default value		Unit
		Large system	Small system	
Q_{drift}	drift loss	2.25	0.025	$(m^3 \cdot h^{-1})$
Q_{evap}	evaporation loss rate	90	1	$(m^3 \cdot h^{-1})$
Q_{mkp}	make-up water flow rate	217.25	3.025	$(m^3 \cdot h^{-1})$
R_{rec}	recycle ratio Q_{circ}/Q_{bld}	72	50	(-)
V_{syst}	water volume in the cooling water system	3000	300	(m^3)

Default values for the cooling tower process conditions and tower packing characteristics used to calculate substance-specific values for $F_{volat.a.i.}$.

Parameter	Value	Unit	Source
G_x	6940	$(kg \cdot h^{-1} \cdot m^{-2})$	Chien *et al.* (2012)
G_y	4642	$(kg \cdot h^{-1} \cdot m^{-2})$	Chien *et al.* (2012)
T_{system}	308.15	(K)	Chapter 4
pH	7.5. 8. 8.5	(-)	Chapter 4
Q_x	$1.79 \cdot 10^{-4}$	$(m^3 \cdot s^{-1})$	calculated: $G_x/\rho_{water} \cdot A_b/3600$
Q_y	$1.05 \cdot 10^{-2}$	$(m^3 \cdot s^{-1})$	calculated: $G_y/\rho_{air} \cdot A_b/3600$
G_x/G_y	1.5	-	calculated from the values in this table
a	147.8	$(m^2 \cdot m^{-3})$	Chien *et al.* (2012)
A_b	0.093	(m^2)	Chien *et al.* (2012)
Z_T	0.914	(m)	Chien *et al.* (2012)

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