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)

European Commission DG ENV / RIVM

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This report has been developed in the context of the EU project entitled "Gathering, review and development of environmental emission scenarios for biocides" (EUBEES 2).
The contents have been discussed and agreed by the EUBEES 2 working group, consisting of representatives of some Member States, CEFIC and Commission. The Commissions financial support of the project is gratefully acknowledged (Ref. B4-3040/2001/326154/MAR/C3).

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FOREWORD

The European Parliament and the Council adopted in 1998 the Directive 98/8/EC on the placing of biocidal products on the market (Biocidal Products Directive, BPD). The background for the directive is a need for harmonisation of the legislation of the Member States regarding this type of chemicals, which are intended for exerting a controlling effect on higher or lower organisms. The Directive requires an authorisation process for biocidal products containing active substances listed in positive lists (Annex I and IA). Active substances may be added to the positive lists after evaluation of the risks to workers handling biocides, risks to the general public and risks to the environment. The risk assessments are carried out for the life cycle of the biocide: risks during and resulting from the application, risks associated with (the use of) the treated product and risks resulting from the disposal of the biocide and the treated product.

For the environmental risk assessment the environmental exposure needs to be assessed. As a tool in this assessment emission scenarios are developed specific for the Product Types distinguished in the Directive. Product Type 11 covers Preservatives for liquid cooling and processing systems. This report gives a description of emission scenarios for the preservatives used in liquid cooling systems.

This report has been developed by Royal Haskoning, The Netherlands, in the context of the EU project entitled "Gathering, review and development of environmental emission scenarios for biocides" (EUBEES 2). The contents have been discussed and agreed by the EUBEES 2 working group, consisting of representatives of some Member States, CEFIC and Commission. The Commissions financial support of the project is gratefully acknowledged (Ref. B4-3040/2001/326154/MAR/C3).

SUMMARY

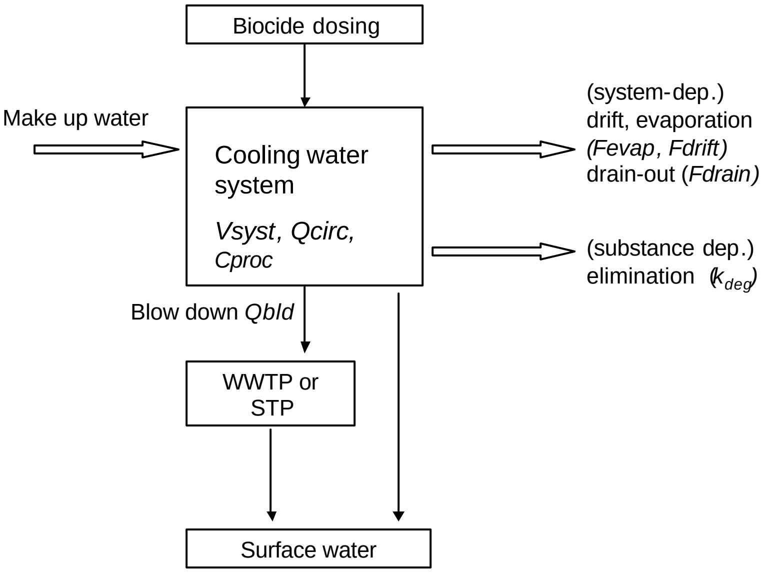
The European Parliament and the Council adopted in 1998 the Directive 98/8/EC on the placing of biocidal products on the market (Biocidal Products Directive). As an implication an environmental risk assessment is to be carried out. For this purpose a method to predict the potential environmental emissions needs to be available. Therefore emission scenario documents are being developed for the various biocidal product types. Product Type 11 under the Biocides Products Directive 98/8/EC covers the following products:

* Preservatives for liquid cooling systems
* Preservatives for liquid processing systems

Liquid cooling systems include once-through cooling systems, open recirculating cooling systems and closed recirculating cooling systems. Liquid processing systems include, e.g., liquids used in oil extraction. The current Emission Scenario Document covers only the use of preservatives for liquid cooling systems.

The report is based on a number of emission scenarios for cooling water systems and on information supplied by some Member States and industry representatives. It was discussed in the Meetings held within the EU project "Gathering, review and development of environmental emission scenarios for biocides (EUBEES 2)".

The available emission scenarios were in varying state of completeness. Some were exposure scenarios for specific biocide substances and others were of a more general theoretical approach. Three types of systems can be distinguished: flow-through or once-through cooling systems, open recirculating cooling systems and closed recirculating cooling systems. The available scenarios were compared and assigned to one or more of these system types. Some scenarios are based solely on system-specific characteristics, whereas others include substance specific characteristics as well. A general scheme of a cooling water system is given below.



Scheme of a cooling water system.
Per system type and per substance, different routes through the system may be relevant

Calculations were carried out for some substances representing different physical-chemical and environmental behaviour to compare the results of the various scenarios. Finally, a generic scenario was identified for a large once-through cooling system, for a large and a small open recirculating system and for a small closed system. The system characterisation is given in the first table and the model calculations are in the next. The model integrates the various approaches into one main model that may be used for all systems. Although the emission should be considered during all stages of the life cycle of the preservatives, this document concentrates mainly on the ‘service life’ stage during the application in the cooling water during use and at blow down. The emission during dosing (application stage) are negligible as compared to the other emissions, whereas the emission at termination of a system (waste stage) is relevant only for closed systems.

Elimination processes may be taken into account by a first-order rate constant kdeg. Using the Hydraulic Residence Time the fraction degraded due to hydrolysis or photodegradation can be calculated. The influence of temperature on kdeg should be taken into account. The effects of biodegradation and removal by sorption in the system cannot be modelled in this way and they are not taken into account.

Readers guide to this document

This document presents a general description of the water cooling process and the application of preservatives and other substances in cooling systems in chapter 2.

For the emission of biocides from water cooling systems various scenarios were found that are described in Annex 2 of this document. These scenarios are analysed and evaluated in chapter 3, using uniform symbols and standard formats. In chapter 3 the scenarios are compared using the same system and substance parameters for each calculation.

Finally, in section 4 a proposal is made for emission scenarios for a once-through or open system, a large and a small recirculating system and a closed system. The systems are characterised by volumes and process parameters and the calculations may be performed with the formulae given.

The Annexes present details, such as the list of abbreviations, examples and characteristics of substances used as cooling water preservatives and considerations on the selection of a biocide.

For quick reference, the proposed scenarios (chapter 4) are presented below.

Proposed scenarios for harmonised emission scenarios for cooling water systems Open places in the table indicate that the parameter is not relevant for the specific system. S: value to be supplied in data set; D: default value; O: output of previous calculations

Characterisation	**Symbol**	**Unit**	**Once-through**	**Open recirc. large**	**Open recirc. small**	**Closed system**	**S/D/O**
Input							
[A] Dose of formulated product	DOSE	kg					S

Characterisation	Symbol	Unit	Once-through	Open recirc. large	Open recirc. small	Closed system	S/D/O
to system							
Fraction of a.i. in product	Fform	-					S
[B] Concentration of active ingredients in system	Cproc	$g.m^{-3}$					S
[C] Initial concentration of active ingredients in system (for continuous dosing) [A/B/C]	$Cproc_{init}$	$g.m^{-3}$					S
Volume of water in system	V_{syst}	m^3	6000	3000	300	30	D
Blowdown flow rate	Qbld	$m^3.h^{-1}$	24000	125	2	0.0004	D
Recirculating cooling water flow rate	Qcirc	$m^3.h^{-1}$	24000	9000	100		D
Dosing interval	Tint	h		24	24		S
Duration of dosing	tdose	h		0.25–0.5	0.25–0.5		S
Fraction evaporated+drift	Fevap+drift	-	0.01	0.01			D
Fraction deposited to soil	Fdepos	-	0.00025	0.00025			D
Degradation rate constant	kdeg	h^{-1}					S
Soil surface where deposition occurs	AREAdepos	m^2	100	100			D
Fraction of a.i. lost during dosing event	$F_{Loss\ dosing}$	-				0.005	D
Fraction of a.i. lost in process due to design	$F_{Loss\ design}$	$month^{-1}$				0.01	D
Fraction of a.i. lost at complete drainage	$F_{Loss\ drain}$	-				1	D
Time	t	h					S
Number of cooling towers per site	N	-	2	2	1		D
Output							
[A] Concentration of active ingredients in system [A/B/C]	Cproc	$g.m^{-3}$					
Concentration of a.i. in blowdown water	Cbld ($t_{0,\ t}$)	$mg.l^{-1}$					
Release to water after time t	$RELEASE_t$	kg					
Max. release after infinite time	$RELEASE_{max}$	kg					
Fraction released to water after infinite time	$Frel_w$	-					
Release from dosing	$RELEASE_{dosing}$	$kg.event^{-1}$					
Release from drainage	$RELEASE_{drainage}$	$kg.event^{-1}$					
Design losses	$RELEASE_{design}$	$kg.h^{-1}$					
Release to air	RELEASEair	$kg.h^{-1}$					
Conc. in surrounding air	Cair	$mg.m^{-3}$					

Characterisation	Symbol	Unit	Once-through	Open recirc. large	Open recirc. small	Closed system	S/D/O
Dose of ai deposited to soil	$DOSE_{pres}$	$g.m^{-2}.h^{-1}$					

Model calculations

$HRT = V_{syst} / Qbld$

Release to water

ONCE-THROUGH, *Shock dosing*

[A] $Cproc = DOSE * 1000 * Fform / (Qbld * tdose)$

No degradation:

$RELEASE_t = N * DOSE$

$Cbld = Cproc$ (maximum, at t = HRT)

With degradation:

$Cbld_t = Cproc * e^{-(kdeg) * HRT}$

$RELEASE = N * DOSE * e^{-(kdeg) * HRT}$ (per event)

ONCE-THROUGH, *Continuous dosing*

[A] $Cproc = DOSE * 1000 * Fform / (Qbld * HRT)$

$Cbld = Cproc_{init} * e^{-(kdeg) * HRT}$

$RELEASE_t = N * Cbld * Qbld * t * 0.001$

OPEN RECIRCULATING, *Shock dosing*

$Cproc = DOSE * 1000 * Fform / Vsyst$

$Qdrift + Qevap = Fevap+drift * Qcirc$

With degradation:

$K_{syst} = (Qbld + Qdrift + Qevap) / V_{syst} + kdeg$

$Cbld_t = Cproc * e^{-(K_{syst}) * t}$

after one shock dose:

$$RELEASE_t = -Cproc * Qbld * \frac{e^{-Ksyst * t} - 1}{Ksyst} * 0.001 * N$$

$RELEASE_{max} = Cproc * Qbld / K_{syst} * 0.001 * N$

$Frel_w = Qbld / (Qbld + kdeg * V_{syst})$

(RIZA 1, adapted for drift or windage and evaporation according to Baur) *with n dosings at intervals of Tint:*

$$Cbld_t = \sum_{i=1}^{n} Cproc * e^{-(t-(i-1)*Tint)*Ksyst} \qquad \text{for } (t - (i-1) * T_{int}) > 0$$

and

$$RELEASE_t = \sum_{i=1}^{n} -Qbld * Cproc * \{e^{-(t-(i-1)*Tint)*Ksyst} - 1\} * N * 0.001 \qquad \text{for } (t - (i-1) * T_{int}) > 0$$

OPEN RECIRCULATING, *Continuous dosing*

[A] $Cproc = DOSE * 1000 * Fform / V_{syst}$

$Cbld = Cproc / (1+K_{syst} * HRT)$

$RELEASE_t = N * Cbld * Qbld * t * 0.001$

Releases to air and soil

ONCE-THROUGH AND OPEN RECIRCULATING

no degradation

$RELEASEair = Fevap+drift * Qcirc * Cproc * 0.001 * N$

$DOSE_{pres} = Fdepos * Qcirc * Cproc / AREAdepos * N$

with degradation: Cproc is to be replaced by Cbld

Release to water

CLOSED SYSTEM

No degradation:

Per biocide dosing event: $RELEASE_{dosing} = F_{Loss\ dosing} * V_{syst} * Cproc$

Design losses per month: $RELEASE_{design} = F_{Loss\ design} * V_{syst} * Cproc$

Complete drainage (per event): $RELEASE_{drainage} = F_{Loss\ drainage} * V_{syst} * Cproc$

Single dosing

$Cproc = DOSE * 1000 * Fform / V_{syst}$

With degradation:

$K_{syst} = Qbld / V_{syst} + kdeg$

$Cbld_t = Cproc * e^{-(K_{syst})*t}$

after one single dose:

$RELEASE_t = Cproc * Qbld * (e^{-(K_{syst}*t)} - 1) / K_{syst} * 0.001$

$RELEASE_{max} = Cproc * Qbld / K_{syst} * 0.001$

$Frel_w = Qbld / (Qbld + kdeg * V_{syst})$

with n dosings, see open recirculating system

CONTENTS

1 INTRODUCTION

Product Type 11 under the Biocides Products Directive 98/8/EC covers the following products:

- Preservatives for liquid cooling systems
- Preservatives for liquid processing systems

Liquid cooling systems include once-through cooling systems, open recirculating cooling systems and closed recirculating cooling systems. Liquid processing systems also include, e.g., liquids used in oil extraction. The current Emission Scenario Document covers only the use of preservatives for liquid cooling systems. Available emission scenarios are evaluated and compared with the aim of producing one harmonised environmental emission scenario.

According to Annex VI of the Biocidal Products Directive the risk assessment shall cover the proposed normal use of the biocidal product together with a ‘realistic worst case scenario’. In this document only the realistic worst case emission scenario was selected. The calculation of a realistic worst case PEC using environmental interactions, for example subsequent movement of emissions to secondary environmental compartments (e.g. from soil to ground water), is considered to be subject to fate and behaviour calculations and models, and outside the scope of the Guideline.

According to the Biocidal Products Directive, Product Type 11 includes products used for the preservation of water or other liquids used in cooling and processing systems for the control of harmful organisms such as microorganisms, algae and mussels which may foul heat exchangers. PT11 also covers the use of preservatives for liquids used in oil extraction. This Environmental Emission Scenario document, however, is limited to preservatives used in liquid cooling systems.

The report is based on:
- emission scenarios developed in different EU countries and
- discussions in the working group for the EU project “Gathering, review and development of environmental emission scenarios for biocides (EUBEES 2)”.

In this report, the emission scenarios are presented in text and tables. In the tables, the input and output data and calculations are specified, and units according to USES are used. The input and output data are divided into four groups:

S	Data Set	parameter must be present in the input data set for the calculation to be executed (no method has been implemented in the system to estimate this parameter; no default value is set, data either to be supplied by the notifier or available in the literature);
D	Default	parameter has a standard value (most defaults can be changed by the user);
O	Output	parameter is the output from another calculation (most output parameters can be overwritten by the user with alternative data;
P	Pick list	parameter values to be chosen from a pick list with values.

1.1 Description of industry or use area

Low temperature heat is often a ‘by-product’ of industrial operations (Donk&Jenner, 1996). Therefore, a heat exchange system is often necessary to maintain optimal operation conditions. In cooling water systems heat exchange takes place from the process stream to water and air. In some cases an intermediate medium takes up the heat and exchanges it to air or water (RIZA, 1995).
The mechanisms of heat exchange are either through exchange by means of conduction (and convection) or by means of evaporation. An example of heat exchange by conduction is the shell & tube heat exchanger in which water and process stream exchange heat through metal pipes (tubes) in a shell. In the case of evaporation the heat is withdrawn from the process stream by direct evaporation of the cooling medium (water), for example, in a cooling tower or an evaporation cooler (RIZA, 1995).
The cooling water is taken in from surface water, ground water or water from river banks, and is, if necessary, pre-treated. Depending on the type of cooling system, the water is discharged immediately to the surface water, or cooled first in a cooling tower and subsequently discharged, or reused after cooling in a cooling tower (recirculation, Van Dokkum, 1998).

A major problem related to process cooling water is the growth of micro-organisms in process cooling water. Examples of industries facing this fouling problem are electrical power generating plants, pulp/paper mills, steel mills, sugar/alcohol plants, refinery/petrochemical plants (Lutey, 1995), food industries and oil recovery operations.

Biological fouling in cooling water systems reduces heta exchange efficiency and consequently the performance of industrial operations. Inadequate control of fouling may have environmental consequences other than excessive use of cooling water additives: it increases the risk of spills by process fluids leaking from heat exchangers. A further risk which arises when fouling is insufficiently controlled is human safety: human pathogens may grow in cooling towers (Donk & Jenner, 1996).

Biocides may be used in the pretreatment of fresh water or in seawater to prevent the growth of (micro) organism. Bacteria, fungi, algae and invertebrates such as mussels can affect the functioning of the cooling water systems (Van Dokkum, 1998).
Biocides may be applied either to control, or to kill micro-organisms:

- control of micro-organisms: biocides are maintained at a sufficient concentration to inhibit microbial growth;
- cleaning of a fouled (dirty) system: first, old algal and fungal residues, and slime and other deposits are removed by mechanical or chemical cleaning. As a second step, it is treated with a high dosage of biocide (shock treatment) (Van Dokkum, 1998).

During oil recovery operations, particularly in the North Sea, seawater is injected into oil reservoirs. During the process, sulphate-reducing bacteria can proliferate underground, and they will produce hydrogen sulphide. This gas is very toxic, highly corrosive to mild steel and also potentially explosive, so it presents a severe hazard if it occurs in the produced water returning to the oil platform. Its presence can also reduce the saleable value of exported gas.

This document is limited to the use of biocides in cooling water systems. The use in oil extraction is not included.

1.2 Cooling water systems

Cooling and process water systems can be divided into three relevant sub-groups (Van Dokkum, 1998; INFU, 2000):

- Flow-through or Once-through cooling systems;
- Open recirculating cooling systems;
- Closed recirculating cooling systems.

The process cycle for biocides used in cooling water systems is depicted in figure 1.

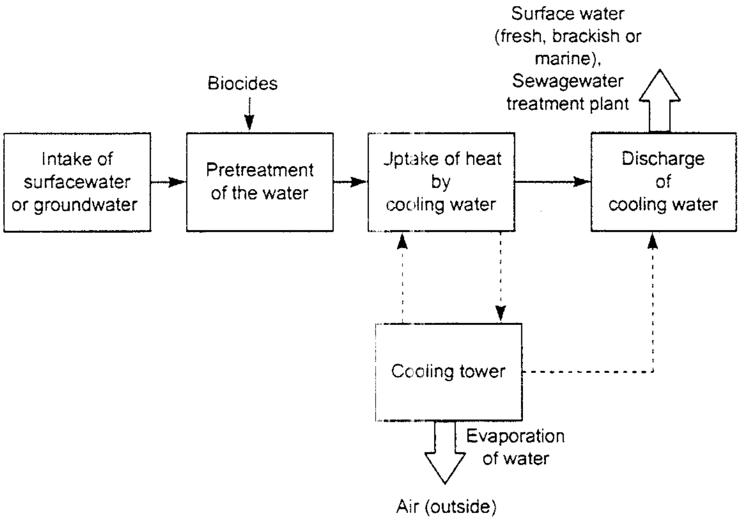


Figure 1. Cooling process, environmental release of preservatives in cooling water to water and air compartments (Van Dokkum, 1998)

The cooling water of recirculating cooling water systems (both open and closed) is removed circa once a year, to clean the system. This is performed by specialised service companies, who treat the (concentrated) cooling water (Van Dokkum, 1998).

Many combinations of the different systems are used. For example, a closed system can be used in combination with a wet cooling system in a cooling tower, to combine the advantages of both systems, or ventilators may be used in wet cooling towers (Van Dokkum, 1998).

The three main system types differ in volume and operating conditions. The problems of microbial contamination in these systems differ as well and therefore the emission scenarios have been evaluated for the three sub-groups.

1.3 Sources of information

Important sources of information that were taken in consideration for the preparation of this document are:

1. *Uniform system for the evaluation of substances 3.0 (USES 3.0)*, National Institute of Public Health and the Environment (RIVM), Ministry of Housing, Spatial Planning

and the Environment (VROM), Ministry of Health, Welfare and Sport (VWS), The Netherlands. **Code: USES 3.0**
Local exposure scenario derived from Luttik et al. 1993. Estimates concentration in receiving wastewater from production and product characteristics. Another documents that refers to this scenario is made by Van der Poel and Bakker 2002;

2. *Water treatment chemicals*, OECD ESD, October 2000, Waiting for entering into official review process, UK -- timing to be decided on 8th meeting of Task Force on Env. Exp. Ass in 2001. **Code: UK TGD**
   Emission scenario document for water treatment chemicals is a summary of the Use Category Document on Water treatment chemicals prepared in 1997 by BRE (Fielden et al, 1997) for the Chemicals Assessment Unit of the Environment Agency (Tgd-e-ex-dr-UK5).

3. *An ecological risk assessment for the use of the biocide, dibromonitrilopropionamide (DBNPA) in industrial cooling systems*, Klaine et al. 1996, Environmental Toxicology and Chemistry Vol. 15, No. 1, 21-30. **Code: US EPA**
   For DBNPA the EPA Exposure Assessment Branch (EAB) developed a conservative calculation of direct discharge exposure from cooling towers. This is based on the Framework for Ecological Risk Assessment as published by the US EPA in 1992 and on the use of a tiered approach for exposure and effects determinations and for risk characterisation the use of probabilistic expressions of effects endpoints and environmental exposure concentrations, as suggested by the Society of Environmental Toxicology and Chemistry (SETAC).

4. *Environmental exposure model for biocide products used in open recycling cooling towers (manuscript),* Baur G, 30 June 2000, Sofia Antipolis 2000, p. 11. **Code: Baur 2000**. Includes also a spreadsheet, Baur 2002.
   A model to predict the environmental risks of biocidal products used in open recirculating cooling towers, which takes into all phenomena happening in the cooling tower. This document also describes a few other existing models, USES 2.0 and 3.0, CEB model (US EPA) and RIZA model 2.

5. *Het gebruik van biociden in recirculatiesystemen* [The use of biocides in recirculation systems], Baltus C.A.M., R.P.M. Berbee, 1996., RIZA report 96.036. **Code: RIZA 1**
   This document describes the use of biocides in recirculating cooling systems, as well as the behaviour of biocides in the systems and sets up a mass balance and a model for the behaviour of biocides in the cooling system.

6. *Development of a concept for environmental risk assessment of biocidal products for authorisation purposes (BIOEXPO)*, Dokkum H.P. van, et al. 1998, TNO report for Umweltbundesamt (UBA): Umweltforschungsplan, UFOPLAN 106 01 065, Berlin, p.213 **Code: TNO**
   In this report emission estimates for several kinds of cooling water preservatives are described. The environmental compartments to which biocides are most likely emitted (the direct exposure compartments) are identified.

7. *Gathering and review of Environmental Emission Scenarios for biocides*, Institute for Environmental Research (INFU), University of Dortmund, UBA Berlin, 2000.

Code: INFU
In this report general information about emissions is described.

8. *Optimisation of biofouling control in industrial cooling water systems with respect to the environment,* Donk, M. van, H.A. Jenner, 1996, KEMA Environment Services, Report nr. 64387. **Code: KEMA**

9. *Process cooling water*, Lutey, R.W., 1997, Chapter 3 in: Handbook of biocide and preservative use, Blackie Academic and Professional, London, p. 50-82.
Code: Lutey

Additional information was obtained from other experts. All documents are given in section 5, References.

A new cooling tower atmospheric emission model is available at Dow Chemical Company. However, due to the current timetable and resource constraints it has not been reviewed. It is recommended to check whether it presents significant improvements at a later occasion.

1.4 Scenarios included

The following models were available for the various cooling systems:

Organisation	Model	System type
US EPA	US EPA Risk assessment model Tier 1 (Klaine, 1996)	Once-through
	US EPA (Cook, 2000)	Once-through
	CEB model (Baur, 2000)	Open recirculating
DOW	DOW Risk assessment model Tier 2 (Klaine, 1996)	Once-through
USES 3.0	EU USES Risk assessment (Luttik, 1993 ; Baur, 2000 ; Van der Poel and Bakker, 2002 ; Poot, 1999)	Once-through Open recirculating
RIZA	RIZA 1 (Baltus & Berbee, 1996)	Open recirculating
	RIZA 2 (Baur, 2000)	Open recirculating
UK TGD	UK model (Fielden, 2000)	Open recirculating Closed recirculating
BAUR 2000	Model Baur (Baur, 2000)	Open recirculating

2 SUBGROUPS AND APPLICATION OF PRESERVATIVES IN LIQUID COOLING WATER SYSTEMS

2.1 Description of various cooling water system types

2.1.1 Once-through cooling

Water, usually pumped from a river, canal or lake, is transported to the heat-exchange module and then discharged directly to the surface water as warmed-up water (INFU, 2000). Sometimes drinking water is used. There is no direct contact between the process stream and the cooling medium except in case of failures of the heat exchanger. The exchange of heat occurs through a separating wall (in the form of pipes or shell & tube or in a plates heat-exchanger (RIZA, 1995).
The increase of the temperature of cooling water is regulated in most countries. Hence cooling towers are used to reduce the temperature of the cooling water before discharge. In the Netherlands , for example, the temperature of the rejected cooling water must not be more than 18°C above the temperature of the recipient water body (INFU, 2000).
In an air-cooling tower, the water is sprayed and flows over a complex structure with a large surface area, thus ensuring intensive contact between water and blown air. Thus, evaporation takes place and the heat is removed from the liquid. During this process, also water droplets may be emitted from the cooling tower (Van Dokkum, 1998).

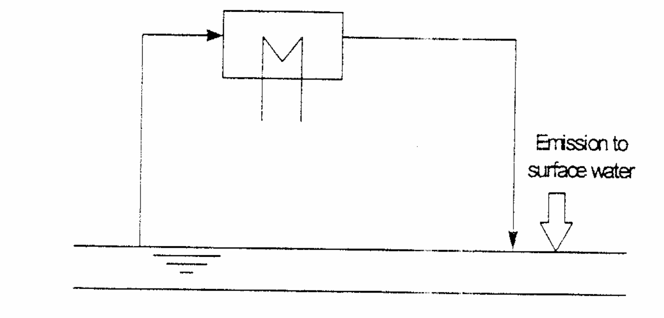


Figure 2. Once-through cooling system (after Held & Schnell, 1994; Van Dokkum, 1998)

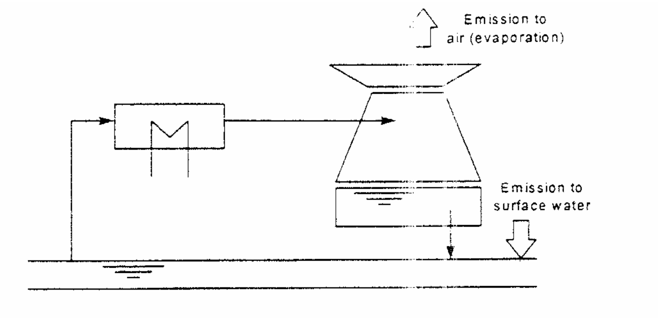


Figure 3. Once-through cooling system with cooling tower (Van Dokkum, 1998)

Most once-through systems have large cooling capacities (>200 MW) and are used by large scale power generators and petrochemical industries, which - for this reason - are often located close to large rivers and lakes (Donk & Jenner, 1996).

a. Open direct cooling system

Process medium and the cooling medium (water) is not separated, e.g. cooling down hot steel. The water is evaporated but may also be contaminated with oil (lubricating oil).

b. Indirect flow-through cooling system

The process/product exchanges heat to cooling water that is in a closed (recirculating) circuit. This secondary cooling water exchanges heat through one (or more) heat-exchangers to surface water that is used only once by this heat-exchangers (primary cooling water) (RIZA, 1995).

The characteristics of a once-through system are:
- there is hardly any evaporation;
- the residence time in the system is very short;
- the water flow varies from 5000 m^3/h to 250,000 $m^3.h^{-1}$ (Adriaensen et al, 2001).

Typical flows for large power plants amount to 30-45 $m^3.s^{-1}$ per1000 MWe and residence times inside the cooling water system typically vary between 2 and 15 minutes (Donk & Jenner, 1996).

Problems that occur are: microbial contamination, corrosion and contamination by suspended matter (Adriaensen et al, 2001).

Chlorine and chlorinated compounds are the most common biocide used in open once-through cooling systems (especially sodium hypochlorite). For economic reasons, a discontinuous treatment is used in these systems, e.g. 10 ppm active chlorine or a combination of a dispersant and 1-3 ppm active chlorine (Solvay, sa). Assink (1991) reports 0.2 $mg.l^{-1}$ active chlorine for 10-60 minutes, one or more times a day. Longer treatments (up to days) are required when large mussels have to be removed from brackish or marine cooling water systems.

2.1.2 Open recirculating cooling systems

In an open recirculating cooling water system the cooling water circulates in an open loop. Water that has passed through the heat exchangers is returned to a cooling tower where the temperature is lowered by evaporative cooling. The cooling tower is in contact with outdoor air. The cooled water is collected in a basin, generally located under the cooling tower, from where it is returned to the heat exchangers (Donk & Jenner, 1996).

A tower design can be based on the natural air draft or induced draft (ventilator). There are also systems with depression of the condensation plume (hybrid cooling tower). Water losses are caused by evaporation and drift losses from the top of the cooling tower. Because of evaporation in the tower, minerals and organics in the recirculating water may concentrate to such a level that precipitation can occur, which is called “scaling”. To manage the risk of scaling, and sometimes also corrosion, a certain amount of concentrated recirculating water is purged from the system and water chemicals are used (antiscaling, dispersants…).. This is referred to as “blowdown”. This blowdown depends on the degree of pollution of the system. In order to compensate for water losses due to blowdown, evaporation, drift and leakages, water is added: the so-called “make-up”.

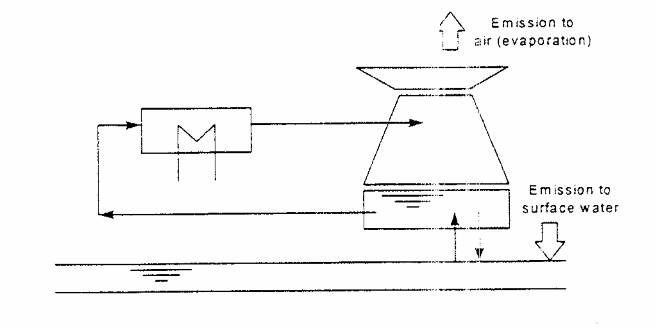


Figure 4. Recirculation cooling system (Van Dokkum, 1998)

Open recirculating systems are mainly used for industrial applications with a heat capacity ranging from 1-100 MWT, but also for power stations with larger capacities if insufficient water is available, or if the temperature of the receiving water is too high, a situation found alongside rivers with low flow in warm summers (Donk & Jenner, 1996).

a. (Direct) dry air cooling

By blowing air (with force (ventilator)) along pipes with process medium, the process medium is cooling off. Large volumes of air are necessary as well as a large heat exchanging surface because of the low heat capacity of air and a small conductivity. There are direct and indirect types: indirect: a intermediate medium (water) is cooled. In the second heat exchanger the intermediate medium is cooled (with air cooler). (RIZA 95.50)

b. Evaporation coolers

In this type of cooler water is spread directly over a pipe or plates collection. Heat is exchanged from a process medium which streams through the pipes, by exchange of heat to water and by evaporation. There is a blowdown stream of cooling water present which may be recirculated. This cooler is also called an evaporative or wet-surface cooler (RIZA, 1995).

c. Hybrid cooling

The “hybrid” cooling tower is a combination of a ‘wet and dry’ cooling tower. The advantages of this method are a relatively low cooling water use and reduction of plume formation above the tower. The heated cooling water first passes through a dry section of the cooling tower, where part of the heat load is removed by an air current, which is often induced by a fan. After passing through the dry section water is further cooled down in the wet section of the tower, which functions similarly to an open recirculating tower. The heated air from the dry section is mixed with the vapour from the wet section in the upper part of the tower, thus lowering the relative humidity before the air current leaves the cooling tower. This reduces plume formation above the tower. Hybrid cooling towers are not yet frequently applied in practice (Donk & Jenner, 1996).

The characteristics of the open recirculating system are:

- by evaporation the concentration of salts increases;
- the concentration of suspended matter (from air) increases;

- suppletion water may be taken from surface water, drinking water, groundwater or purified waste water;
- Often suspended solids may be removed from the water by a side-flow filter
- (Adriaensen et al., 2001).

Problems that may occur are:
- biological contamination and slime forming
- macrofouling
- corrosion of system materials
- contamination/ sedimentation by salts, predominantly lime, iron and mangane
- contamination/sedimentation by sand, sediment and suspended matter
- process leakages
- (Adriaensen et al, 2001).

The water in a recirculating cooling water system can be contaminated by three different sources:
1) the air passing through the tower introduces dust, micro-organisms and exchange of gases,
2) suspended solids in the intake water,
3) sometimes process fluids leaking from heat exchangers.

The first source is unique to open recirculating systems. In a recirculating system both the cooling tower and the heat exchangers are subject to fouling processes. Fouling of the heat exchanger is generally more critical (Donk&Jenner, 1996).

For open recirculating systems both oxidising and non-oxidising biocides are used (INFU, 2000). Most biocide formulations are water-based. Biocides are applied as liquids or sometimes pellets, manually or (in larger systems) with an automatic pumping system (Van Dokkum, 1998). Recirculation systems are mostly treated with shock (intermittent) dosing of biocides in the cooling water supply to the process. Normally biocide is dosed in the system in a period of short time (15-30 min) (Berbee, 1997). The range of the concentrations of non-oxidising active substances goes from 0.5 to 50 mg.l^{-1}, the concentration of the oxidising agents is much lower. Concentrations of oxidising substances are 0.1-0.2 mg.l^{-1}.
In open recirculation systems an important part of heat exchange occurs through evaporation of water. Next to evaporation losses, biocides are are emitted through wind and spray losses and discharged water (Assink, 1991 in Van Dokkum, 1998).

The cooling water can be discharged either directly to the surface water or to a wastewater treatment plant. In the Netherlands, ca 37% of the cooling water containing oxidative biocides is treated in a wastewater treatment plant and ca 35% of the cooling water containing non-oxidative biocides (Van Dokkum, 1998).

Depending on the circulation flow rate, the volume of the system and the dosing rate, a high concentration of active substance will be found in the whole system, after some time (about 15 min). Because of the high circulation flow rate and the dosage time the system concentration will reach a maximum of dosed amount as a.i. / volume of recirculating water + residual concentration before dosing, and the blowdown concentration will not exceed that level. The level in the system and in blowdown will decrease by:
- antifouling action of chlorine;

- reactions of active chlorine with organic substances and Nitrogen in make-up water;
- evaporation losses of HOCl and chlorous amines in the cooling tower;
- the loss of active chlorine by process leakages;
- the addition of make-up water (Berbee, 1997).

2.1.3 Closed recirculating cooling systems

In closed recirculating cooling water systems cooling water recirculates in a closed loop. The cooling water is not discharged after cooling. These systems have minimal loss of water, since there is no direct contact with the atmosphere. Process heat is transferred to the cooling water in one heat exchanger, and in a second heat exchanger the cooling water is cooled of by air or water. The cooled water is then returned to the heat exchanger that cools the process. Closed recirculating cooling water systems mostly use alkalised demineralised water. Residence times in closed cooling water systems can be up to 6 months. Closed cooling water systems are ideal for fouling control, since little or no contamination of the water takes place and the small make-up volumes required allow the use of high quality demineralised water. Problems are known to arise on the air cooled heat exchangers from the accumulation of airborne debris, particularly small insects. Temperatures in the water film at heat exchanger surfaces are up to 5°C higher than the bulk water temperatures typically ranging from 40 to 50°C, although temperatures up to 70-80°C are also encountered in practice (Donk & Jenner, 1996).

When only a limited amount of water is available, dry cooling may be applied in cooling towers instead of the wet cooling described above. The water is not sprayed into the cooling tower, but brought into contact with air by a fine-maze system of tubes. The air is circulated by means of ventilators. These dry recirculating systems have a minimal water loss. Evaporation and wind or spray losses do not occur (Assink, 1991 in Van Dokkum, 1998).

The content of the closed system can be removed from the system, e.g. by periodical refreshment and leakage (Adriaensen, et al, 2001). In the case of refreshment the discharges are predominantly handled by a specialist company.

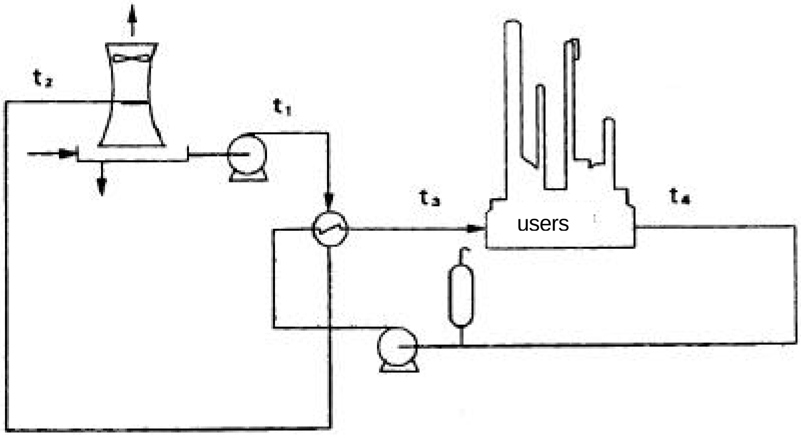


Figure 5. Closed recirculating system (Bloemkolk, 1995)

The characteristics are:

- there is hardly any evaporation;
- the water is hardly refreshed;
- mostly demineralised water is used (Adriaensen, et al, 2001).

The problems that occur are: corrosion and microbial contamination (Adriaensen, et al, 2001).

As water loss in these closed systems is minimal, very low amounts of biocides are used. The most important biocides used in closed recirculation cooling systems are the organic biocides. As the losses are very limited, high concentrations are used (0.5-4 $g.l^{-1}$) (Solvay, SA in Van Dokkum, 1998).

2.2 Description of the technical problems in cooling systems

The biological problems which may affect the functioning of the cooling system are (INFU, 2000; Donk & Jenner, 1996) :

1. development of a biofilm;
2. plugging and fouling of conduits and heat exchangers by micro-, macro-organisms and suspended solids;
3. microbiologically induced corrosion, which may lead to leakages of heat exchangers and spills of process fluids;
4. scaling, predominantly by precipitation of calcium carbonates, sulphates and phosphates;
5. deterioration of wooden components in cooling systems.

2.2.1 Development of biological slime (biofilm)

Slime consists almost entirely of microbial biomass. The main component is formed by heavily encapsulated fast-growing micro-organisms, such as *Aerobacter*, *Arthrobacter*, *Proteus*, *Bacillus*, *Pseudomonae*. Biological slime can develop in very short time scales (e.g. 4-8 hours), especially on heat transfer systems. Quite often the problem exists in high flow velocity environments (Lutey, 1995 in Van Dokkum 1998; Donk & Jenner, 1996). Biological slime problems can occur in open recirculating systems, once-through cooling systems and in closed loop/chill water systems (Lutey, 1995)
The development of biological slime is related to microfouling. There is a planktonic microfouling population, with micro-organisms attached to the surfaces in a matrix of organic material forming a biofilm, a slime layer, in which suspended solids can be caught from the cooling water. The thermal conductivity of biofilm is approx. 25 times lower than that of cast iron (Donk&Jenner, 1996).

2.2.2 Plugging and fouling

Fouling is the development of a mixed microflora of filamentous bacteria, fungi and algae. In contrast to slime, the primary component is non-microbiological organic mass (organic substances, dirt, silt, scale fragments, corrosion by-products, other debris). Filamentous micro-organisms act as ‘binding agent’ for the deposits. The development of a fouling community takes several days to weeks. Fouling and plugging is the most commonly encountered problem in cooling towers, heat transfer systems, screens/filters, etc. In marine environments, extensive macrofouling with barnacles and mussels can occur (Whitehouse et al in Van Dokkum 1998; Lutey, 1995).

In once-through systems the fouling potential is directly associated with the source of water, which may contain particulate matter, various sorts of debris, micro-organisms, macro-organisms and dissolved solids. Sometimes incidental leakages of process fluids play a role. In once-through systems pretreatment of the cooling water is limited to the use of macrofilter. The cooling water treatment program is further mostly limited to dosing of a single biocide, often sodium hypochlorite (Donk&Jenner, 1996).

In open recirculating systems, additional contamination of the cooling water may occur in the tower from contact with atmospheric air. In recirculating cooling systems the fouling control program is usually carried out with a blend of selected cooling water additives. This blend often comprises a cooling water biocide, a corrosion inhibitor, a scaling inhibitor and a dispersant. The concentration of each additive may be in the range of 1-50 $mg.l^{-1}$, as active ingredient, depending on the nature of the fouling problem and its magnitude. In open recirculating systems, pretreatment by macrofiltering, microfiltering, flocculation and/or precipitation are sometimes used to improve water quality (Donk&Jenner, 1996).

Biofouling consists of two types: macrofouling, involving mussels, oysters, barnacles and hydroids; and microfouling or bioslime, consisting of a sessile microbial population, comprising slime producing bacteria and anaerobic sulphate reducing bacteria. Macrofouling is generally confined to once-through systems. Inside recirculating systems, high temperatures and the concentration of salts inhibit macrofouling growth (Donk&Jenner, 1996).
Microfouling related problems occur both in once-through and recirculating systems. There is a planktonic microfouling population, with micro-organisms free in suspension; and a sessile one, with micro-organisms attached to the surfaces in a matrix of organic material forming a biofilm. The most relevant microbial species are *Pseudomonae* (slime formation), *Desulfovibrio* and *Clostridium* (MIC) and Legionella pneumophila (Donk&Jenner, 1996).

2.2.3 MIC: microbiologically induced corrosion

Micro-organisms can induce or accelerate corrosion in cooling water systems, which poses an important problem. Micro-organisms can bind suspended solids and cause scaling. A differential oxygen diffusion gradient in this layer causes corrosion. Specific micro-organisms, important in the context of MIC, are sulphate-reducing bacteria (*Desulphovibrio*, *Desulphotomaculum*), iron-oxidising bacteria (*Gallionella*, *Sphaerotilus*, *Arthrobacter*) and slime-forming micro-organisms (bacteria, algae and fungi). MIC in cooling systems is a relatively new problem, due to changes in process water (Van Dokkum, 1998). Until recently corrosion was controlled by adding an acid (sulphuric acid) to keep the pH low (5.5-6.5) and adding a heavy metal (chromate) to control the growth of the micro-organisms. Due to recent environmental regulation the use of heavy metals is reduced (Lutey, 1995). Furthermore the operating pH of many cooling water systems was raised above pH 7.5. This caused decreased effectiveness of chlorine (reduced to less than 10% of the action at pH>7.5) and lower effectiveness of non-oxidising biocides at alkaline pH ranges (Lutey, 1995).
Corrosion related to the uncontrolled growth of micro-organisms has become increasingly more frequent and more severe in all types of process cooling water systems. In many parts of the world this has become the number one problem in the operation of process cooling water systems (Lutey, 1995).

Corrosion is the electrochemical phenomenon occurring on metal surfaces, where atoms are exposed to an electron acceptor (e.g. O_2) with a higher affinity than that of the potential donor. The result is a metal oxide or other salt having little structural stability, which causes damage to the material. The presence of a biofilm on the metal surface often favours circumstances for corrosion, thus accelerating the process. This is referred to as MIC. *Desulfovibrio* is one of the organism known to cause MIC. This type of corrosion can only be prevented by keeping the heat exchanger surfaces clean or by using high integrity metals (e.g. titanium). In practice corrosion prevention of relatively clean metal surfaces is assured by the application of corrosion inhibitors: cathodic and anodic inhibitors. Cathodic inhibitors prevent the reduction of oxygen at the cathode, by forming a layer of insoluble hydroxides, (bi)carbonates, or oxides. Examples of cathodic inhibitors are: polyphosphates, hydroxyphosphonic acids and zinc salts. Anodic inhibitors form a passivating oxide layer with the metal at the anode, thus limiting the electron flow to the cathode. Examples of anodic inhibitors are: orthophosphates, chromate, nitrite, silicate and molybdate. Blends of inhibitors are employed to improve overall protection (Donk&Jenner, 1996). The choice of a corrosion inhibitor is very much determined by the pH value and type of material used. Corrosion can occur in all cooling water systems and concentrations of corrosion inhibitors in recirculating systems typically range from 2 to 20 $mg.l^{-1}$ as active compound. For some anodic inhibitors (nitrite, molybdate) concentrations are 500 to 1000 $mg.l^{-1}$. In once-through cooling water systems generally no corrosion inhibitors are dosed, with the exception of ferrosulphate dosing in systems with copper alloy heat exchangers, in order to reduce emissions of cupper. Sometimes metal blocks (zinc, aluminium) are fixed in the cooling water systems to prevent corrosion, a method known as aniodic protection (Donk & Jenner, 1996).

2.2.4 Scaling

Evaporation losses from the cooling tower of the recirculating systems concentrate inorganic and organic materials. This concentration process is controlled by adding make-up water and purging blowdown. If the concentrations of salts in the water film near the heat exchanger surface exceed the solubility limits, precipitation occurs, which is referred to as scaling. Scaling reduces the performance of the heat exchanger, since the thermal conductivity of natural calcium carbonate is approximately 25 times lower than that of cast iron. In additional, scaling may cause problems in the cooling tower. The main forms of scale are calcium carbonate and calcium phosphate.
Scale formation is important in once-through and open recirculating systems. In practice scaling is controlled by adjustment of the pH and the application of scaling inhibitors (Donk&Jenner, 1996).

2.2.5 Deterioration of wood

Many wooden components can be present in cooling systems, especially in cooling towers. Two types of deterioration are distinguished: internal or dry rot and soft or surface rot. The microorganisms involved cause the hydrolysis of the cellulose fibres of wood in this way destroying its fibre structure (Lutey, 1995). As this occurs, the wood loses much of its structural strength and becomes soft, punky and cross-checked. The primary organisms associated with wood deterioration in cooling systems are members of the Basidiomycetes and Fungi Imperfecti. Internal or dry rot is commonly found in the plenum and drift eliminators, distribution trays, cell partitions, fan housings and fill supports. Typically, the internal or dry rot fungi need free air (oxygen) to develop to the extent that causes severe wood deterioration (Lutey, 1995). The combatment of the micro-organisms responsible for deterioration of this type of wood falls under this product type insofar it concerns biocides used in cooling water (Van Dokkum, 1998).

2.3 Description of types of substances used and their function

For the prevention or control of the technical problems described in section 2.2, various types of chemical substances are used in cooling systems, including biocides to control micro-organisms, dispersants to remove particulate matter, corrosion inhibitors and anti-scaling agents. In Table 1 substances are listed including the type of cooling system where they find application. A list of active substances currently notified for PT 11 according to the BPD can be found on the ECB Homepage: http://ecb.jrc.it/biocides/.

Mechanism of biocidal action
Biocides inhibit the growth and reproduction of microorganisms in a variety of ways. Some alter the permeability of the cell walls. Heavy metal-based biocides penetrate the cell into the cytoplasm and destroy the protein or complex with other compounds to poison the cell. Others act as enzyme uncouplers which block organic synthesis in the cell, and others block electron transport processes in the cell affecting the utilisation of the energy food sources. Surfactant-types of biocides damage the cell by affecting its differential permeability, disrupting the normal flow of nutrients into the cell and the discharge of wastes from the cell. Cationic surfactant materials (e.g. quarternary ammonium compounds), absorbed on the surface of the cell membrane, chemically react with the negatively charged ions associated with the cell wall. Anionic surfactant compounds reduce cell wall permeability and can eventually dissolve the entire cell membrane. Chlorinated phenolic compounds penetrate the cell wall, forming a colloidal suspension with the cytoplasm. The suspension causes precipitation and denaturation of protein materials within the cell. Other chemicals such as the organo-sulphur compounds complex with an enzyme metabolite, or non-competitively react with an enzyme in place of the normal metabolite, or non-competitively attach to an enzyme at a point different from the normal metabolite and prevent normal enzyme reaction. Oxidising chemicals such as chlorine and bromine in the hypo-acid form, irreversibly oxidise protein and other organic constituents, resulting in a loss of normal enzyme activity, the hydrolysis or organic constituents and subsequently the rapid death of the cell (Lutey, 1995).

Table 1 Types of substances used in cooling systems (Donk & Jenner, 1996; Baltus & Berbee, 1996; Adriaensen et al., 2001; Fielden, 1997; Lutey, 1995; Assink, 1991)

Active substance	Use in once-through systems	Use in open recirculating systems	Use in closed recirculating systems
1. Oxidising Biocides	+	+	
1.1 chlorine/chlorine yielding chemicals	+	+	
1.2 Bromine-yielding chemicals		+	
1.3 Non-halogen oxidising chemicals		+	
2. Non-oxidising biocides		+	+
2.1 Isothiazolones		+	+

Active substance	Use in once-through systems	Use in open recirculating systems	Use in closed recirculating systems
2.2 Quats		+	+
2.3 Ionene polymeric quats		+	
2.4 Organo-sulphur compounds		+	
2.5 Organotin compounds			
2.6 Guanidine compounds			
2.7 Organo-bromo compounds		+	
2.8 Aldehyde compounds		+	+
2.9 Amine/imidazole compounds		+	
2.10 Chlorophenat/ phenolic compounds			
2.11 others		+	
3. Oxygen scavenger			+
4. pH controllers			+
5. Scale control			+
6. Dispersant			+
7. Antifreeze			+
8. Corrosion inhibitors		+	+
9. Scale and deposit inhibitor		+	+
10. Hardness sediment			
11. Other sediment			

See Annex 3 for specific substances belonging to the mentioned groups

Biocides used in cooling water systems include oxidising and non-oxidising biocides. Related to the dosing of biocides is the use of dispersants. The substances of these groups are described below in further detail.

2.3.1 Oxidising biocides

For industrial applications biocides based on active chlorine are normally used. Bromine and iodine are may be used as well. These biocides have a non-specific mode of action: components of the cell or cell wall are oxidised (McCoy, 1980 in Van Dokkum, 1998). These biocides have a rapid action and because of their non-specific reactions have broad spectrum action (Baltus & Berbee, 1996). Due to their rapid toxic action, they are the main biocides for once-through systems (McCoy, 1980 in Van Dokkum, 1998). Oxidising biocides also react with suspended matter and other organic material present in the cooling water which will be oxidised and halogenated. As a result a complex mixture of halogenated by-products is formed (haloamines, haloforms, haloacetonitriles, halogenated amides, halophenoles, haloacetic acids, bromate and chlorate).

1 Chlorine/chlorine-yielding chemicals
Chlorine and chlorine-yielding materials function essentially in the same way. When added to water, a mixture of hypochlorous acid and hypochlorite ions is formed (see also the Environmental Emission Scenario Document for PT 5: Drinking Water disinfectants).

Sodium hypochlorite is the most frequently used biocide. When sodium hypochlorite or chlorine gas are added to water, a mixture (equilibrium) of hypochloric acid and hypochloric ions is formed. The biocide action depends on the concentration of hypochloric acid in the water. Hypochloric acid is a stronger biocide than the hypochloric ions. The equilibrium between hypochloric acid and hypochloric ions strongly depends on the pH. At higher pH the concentration of hypochloric acid decreases and with that the biocide action. The optimum pH is in the range of 6 to 7.5 (Baltus & Berbee, 1996). At pH 8.3-9.5 chlorine becomes less effective as an oxidising biocide (Lutey, 1995). pHs below 6 are not applied in systems because of the potential danger of corrosion. When the cooling water contains ammonium compounds, the hypochloric acid will react with these, to form chloroamines (Baltus & Berbee, 1996).
Chlorine is initially dosed in the system to satisfy the chlorine demand and after that to attain the desired amount of free residual chlorine. The chlorine demand refers to the amount of chlorine that will react with organic contaminants (biomass), tower lumber, sulphur dioxide, hydrogen sulphide and organic nitrogen compounds (Lutey, 1995).
The limitations of chlorine are: ineffectiveness at high pH, inactivation by sunlight and aeration, corrosiveness to metals, adverse effects on wood, expensive feeding equipment and maintenance and hazardous to handle (Lutey, 1995).
The commercial hypochlorite solution is often dosed as 500-2000 mg.l^{-1} Cl_2 of TRO (total residual oxidants) (Donk&Jenner, 1996). Chlorine gas is purchased as a gas and is converted into hypochlorite after injection into the cooling water system typically at 1 mg.l^{-1} but always less than 3.5 mg.l^{-1}.

Bromochlorodimethylhydantoin hydrolyses instantly on contact with water to liberate HOBr, the primary biocide, HOCl and the carrier molecule DMH (Donk & Jenner, 1996).
Chloroisocyanurates are more easily handled as dry products that release chlorine when added to water. Chlorine dioxide does not produce hypochlorous acid immediately when added to water, but remains as ClO_2 in solution. It is more effective at higher pH ranges than chlorine (Lutey, 1995).
Trichloroisocyanuric acid is a stabilised chlorine product, which is thus less reactive than sodium hypochlorite and is used in some smaller systems in the Netherlands (Donk & Jenner, 1996).

2 Bromine-yielding chemicals
Sodium bromide is always used in combination with sodium hypochlorite. In this combination a quantitative conversion of hypochloric acid to hypobromic acid occurs so hypobromic acid becomes the active component. Hypobromic acid is active against bacteria, fungi, yeasts and algae over a larger pH range than hypochloric acid. Furthermore the formed bromoamines have also a biocide action (in contrast to the chloramines) and are less persistent (Baltus & Berbee, 1996).
Sodium bromide and bromine chloride are becoming more widely used. The activated bromide salt or bromine chloride hydrolyses in dilute aqueous solutions to hypobromous acid and hydrochloric acid/sodium chloride. Bromine chloride as a gas is more difficult and hazardous to handle than sodium bromide.
Bromochlorodimethylhydantoine is based on active chlorine and active bromine. In water the substance splits up in the active compounds hypochloric acid and hypobromic acid and the carrier molecule dimethylhydantoin. The hypobromic acid is the primary biocide. The hypochloric acid is converted to hypobromic acid on the moment bromide is formed as a result of the oxidising reactions. The pH is less limiting for the action of bromochlorodimethylhydantoin and also inactivation of the substance by organic pollution is less because of the low dissociation rate. The action mechanism is based on

the inhibition of certain steps in the oxidation of glucoses by the released hypobromic acid. By the interaction with the cell wall, the cell wall is crushed (Baltus & Berbee, 1996).

3 Non-halogen oxidising chemicals

A disadvantage of these substances is that a large part of these substances leaves the system through the cooling tower due to the high volatility. The application of ozone is still in development. A disadvantage of ozone is that it needs relatively clean water and that it is corrosive. An advantage of ozone is that less chlorinated byproducts are formed. The application of hydrogen peroxide is largely limited by safety aspects (Baltus & Berbee, 1996).

Ozone is a strong oxidant, stronger than chlorine dioxide and sodium hypochlorite, and will react with all organic material present. This makes it hard to use in once-through systems (Donk & Jenner, 1996). When ozone is added to a system with a pH > 8 it decomposes to form free hydroxyl radicals, which are stronger oxidising agents than molecular chlorine (Donk & Jenner, 1996). The recommended maximum concentration for continuous exposure is 0.1 $mg.l^{-1}$ (Donk & Jenner, 1996). Ozone leads to less formation of trihalomethanes and extractable organic halogens (EOX) than hypochlorite. Ozonation may lead to the formation of byproducts as bromate and bromohydrins (Donk & Jenner, 1996).

Hydrogen peroxide is sometimes applied as a algicide or biocide in small open and closed recirculating CWS. Hydrogen peroxide disintegrates easily and reacts with some materials. An example is known from the food industry, a recirculating system with demineralised water in which it is dosed at 15 ppm. The motive to choose peroxide is that it does not add salts to the cooling water (Donk & Jenner, 1996).

In the food industry peracetic acid, acetic acid and hydrogen peroxide are applied on a small scale for disinfection (Donk&Jenner, 1996).

2.3.2 Non-oxidising agents

Non-oxidising biocides have a more selective action. The biocides react on specific cel components or act on important reaction steps in the cell. Two mechanisms may be distinguished. Micro-organisms are killed or inhibited because the biocides damage the cell membrane which disturbs the transport of substances into and from the cell. Also the cell components may leach. Next to this biocides may damage the biochemical mechanism that is involved with the energy production or the energy use. By the complex mechanism of action the non-oxidising biocides have a longer reaction time than the oxidising biocides. For an effective reaction a longer contact time between the biocide and the target organism is necessary. Some non-oxidising biocides are not directly lethal but have a rapid biostatic effect, which means that biological growth is inhibited.

Because of the specific action of the non-oxidising biocides, micro-organisms may develop a resistance (Baltus& Berbee, 1996). In The Netherlands they are only applied in recirculating cooling water systems (Donk&Jenner, 1996). They are primarily used when oxidising biocides are not applicable because of the high organic loads in the systems; in a system that is not regularly monitored (daily control) or in a systems where nitrite is used a corrosion inhibitor (Donk&Jenner, 1996). In general non-oxidising biocides are used in relatively high shock doses instead of low continuous doses (Donk&Jenner, 1996).

1 Isothiazolones

These substances are often used as a mixture of isothiazolones. They have a broad spectrum action. The action is based on a rapid interaction of the isothiazolones with proteins in the cell by which the ATP-synthesis is inhibited. The isothiazolones are effective at low concentrations and are stable over a large range of pHs. Isothiazolones are effective against aerobic bacteria, anaerobic (incl. sulphate-reducing) bacteria, fungi, yeasts and algae (Baltus & Berbee, 1996). The activity is only slightly affected by chlorine, amino-nitrogen, hardness, chlorides or suspended solids. Isothiazolones are relatively persistent but can be detoxified readily if necessary (Lutey, 1995) Isothiazolones can be used very well together with corrosion-inhibitors and dispersants. The dispersants intensify the action of isothiazolones (Baltus & Berbee, 1996).

2 Quaternary ammonium compounds

The action of quaternary ammonium compounds (quats) is due to the cationic charge which forms an electrostatic bond with the negatively charged cell wall of the micro-organism. This results in a change of the cell permeability, denaturation of proteins and finally the death of the cell. Quats are effective against algae and bacteria at neutral and alkaline pH. In general quats are not effective against fungi. At low concentrations quats have a biostatic action because the organism can survive some time in a damaged state. At higher concentrations death occurs. The activity of most quats is reduced by high chloride concentrations, oil and other organic contaminations. Polymer quats have a broad spectrum action against micro-organisms. These quats have a longer reaction time than the alkyl quats and the action is limited by the presence of large amounts of suspended particles in water (Baltus & Berbee, 1996).

3 Organo-sulphur compounds

Organo-sulphur compounds include several different types of compounds, widely used, alone or in combination with other chemicals in all types of systems. Their pH ranges of activity differ although the mechanisms of action are similar. They generally require intermediate contact times (4-9h at minimum required concentrations). Most organo-sulphur compounds hydrolyse readily at cooling water temperatures and pHs. With the exception of methylene bisthiocyanate, the organo-sulphur compounds are readily water soluble and relatively convenient to handle and feed. The effectiveness of most organo-sulphur is pH related. The N-methyl and dimethyldithiocarbamates function well at pH 7 and above. Most sulphones and sulphonates are most effective at pH 6.5-7.5 and the thiones function wll at a pH of 7-8.5. Methylene bisthiocyanate hydrolyses rapidly at a pH above 8 and therefore is used at that pH range only in quick kill situations (Lutey, 1995).

4 Organotin compounds

Organotin compounds are biocides that have a specific effectiveness against fungi and certain filamentous algae. They are used primarily in preventing plugging and fouling problems. They have a relatively slow rate of kill, requiring long contact times. They function at best at neutral to alkaline pH ranges. They are not readily biodegradable and persist in the environment (Lutey, 1995).

5 Guanidine compounds (Dodecylguanidine hydrochloride)

Guanidine compounds are used for broad-spectrum control of microorganisms. They function as cationic surfactants that disrupt the extracellular enzyme reactions and the development of bacterial and algal cell walls. They provide some degree of protection to wood from fungal attack. The activity is not pH dependent. High levels of suspended inorganic solids will limit the effectiveness. They can be used in systems containing high levels of hydrocarbon contaminations (oil, greases).

6 Organobromo-compounds

The action of ß-bromo-ß-nitrostyrene is based on the prevention of the energy transport and the energy production in the cell. A consequence of this is that the glucose metabolism (citric acid cycle and glycolysis) is inhibited. This biocide may be used against bacteria, fungi, yeasts and algae. The biocide has a rapid action and hydrolyses quickly with pHs above 8 (Baltus & Berbee, 1996).

Bromonitropropanediol catalyses the formation of disulfide-bonds between sulfhydryl compounds and in this way probably blocks the activity of many enzymes. Thus this biocide may be used against a large range of micro-organisms. The hydrolysis of bromonitroporpanediol at pH 8 and temperatures to 30 °C is very limited (Baltus & Berbee, 1996).

Dibromonitrilopropionamide is a biocide with a broad spectrum action that is effective at low concentrations especially against bacteria. Higher concentrations are necessary to fight the problems caused by algae and fungi. The biocide may be used very well in systems with relatively large amounts of biomass and other organic contaminations. The biocide hydrolyses quickly at pHs above 8 and is used when less expensive non-oxidising substances do not act (Baltus & Berbee, 1996).

Dibromonitrilopropionamide (DBNPA) and bromo-hydroxyacetophenone (BHAP) are broad-spectrum biocides with particular effectiveness in controlling bacteria. DBNPA hydrolyses rapidly at a pH above 8.0 and therefore must be used as a quick kill substance at alkaline pHs. BHAP is not pH dependent. They have low water solubility and must be adequately dispersed (Lutey, 1995).

7 Aldehyde compounds

Glutaraldehyde is effective against both aerobic and anaerobic bacteria under conditions in open recirculating and closed loop systems. It is widely used against troublesome bacteria associated with MIC. It has limited effectiveness against algae, fungi associated with plugging and fouling problems. It is readily neutralised. In once-through systems the relatively short contact times require the material to be used a high concentrations. At alkaline pHs a surfactant may be needed in addition. It functions as a protein cross-linking agent and because of this the application of glutaraldehyde in systems with cooling water containing amino compounds, including ammonia, is not useful. This biocide is primarily used in the food industry. Glutaraldehyde has a good watersolubility (Lutey, 1995 and Baltus & Berbee, 1996).

8 Amine/imidazole compounds

Rosin amines are used at low concentrations to control algae in open recirculating cooling water systems. The activity is limited to algae and some fungi. The activity is not pH dependent, however at alkaline pHs higher concentrations are necessary (Lutey, 1995).

9 Chlorophenate/phenolic compounds

Chlorophenate/phenolic compounds mostly exhibit broad-spectrum activity in cooling water systems, but are most effective against filamentous algae and fungi at slightly acidic to slightly alkaline pHs. Their activity is not affected by high levels of organics or suspended solids in the water. When used in conjunction with dispersants/penetrants, they are particularly effective in controlling plugging and fouling problems. Higher dosages are required when the potential for bacterial slime exists (Lutey, 1995).

10 Other biocides

The action of methylenebisthiocyanate is comparable with the action of ß-bromo-ß-nitrostyrene. It is primarily used against aerobic bacteria, fungi and yeasts. It has a reaction time of about 2 hours. It is therefore applied primarily in recirculation systems. It hydrolyses quickly at pHs > 8 (Baltus & Berbee, 1996).

Organic thiocyano-azole compounds are generally speciality-type biocides that are used when other biocides do not work adequately. An example is 2-(thiocyanomethylthio) benzothiazole (TCMTB). This substance is primarily used as a fungicide to prevent growth of wood-rotting fungi. It is also effective in mitigating severe plugging and fouling and MIC caused by iron-oxidising bacteria. TCMTB has low water solubility and must be adequately dispersed. It requires intermediate contact time. They are used at relatively low concentrations and hydrolyse readily at alkaline pHs (Lutey, 1995).

Organic mercury compound were used as broad-spectrum biocides. Other heavy metal compounds are still used in specific applications. Copper sulphate is widely used for the control of algae in cooling system makeup water from sources such as lakes and reservoirs. Copper is readily precipitated from treated cooling water at alkaline pHs, making it ineffective as an algicide. This way it can also contribute to galvanic corrosion (Lutey, 1995).

Acrolein has been used as a substitute for oxidising biocides. It is easily deactivated by sodium sulphite. It is usually fed as a gas into a pressurized system, using nitrogen as a carrier. A small amount of hydroquinine is added to prevent the formation of the polymer polyacrolein, a water-insoluble deposit-forming substance. Use is limited because of the high toxicity to humans, potentially flammable and violent reaction with strong acids and alkalis (Lutey, 1995).

2.3.3 Dispersants

Dispersants are used to remove particulate matter (microfouling and slime layers) from the heat exchanger surface, to facilitate penetration of the biocide and to keep debris in suspension by lowering the surface tension. It is common practice to dose biocides (oxidising and non-oxidising) in combination with dispersants at levels of 1-10 $mg.l^{-1}$ active ingredient (Donk&Jenner, 1996). The most important dispersants are organic and metal sulphonates, metal phenolates, metal dialkyl dithiophosphates, sodium dialkyl sulphosuccinates, polyethylene alkyl and alicyclic amines and monoethanolamine phosphate salts (Donk&Jenner, 1996).

2.4 Factors influencing emissions

2.4.1 Identification of potential points of release

Emission of cooling water may occur at various places from the system (see figure 6):

Table 2. Possible emission from the various systems

	Once-through system	Open recirculating system	Closed recirculating system
Regular discharge of cooling water (blowdown)	+++	+	-
Spray/wind drift		+	-
Evaporation	+	++	-
Discharge of cooling water for maintenance	[1] (½ yr)	+[2] (1 yr)	+[2] (1 yr)

+ estimate of quantity of water released

[1] treatment is stopped

[2] under controlled conditions, sometimes de-activation is recommended

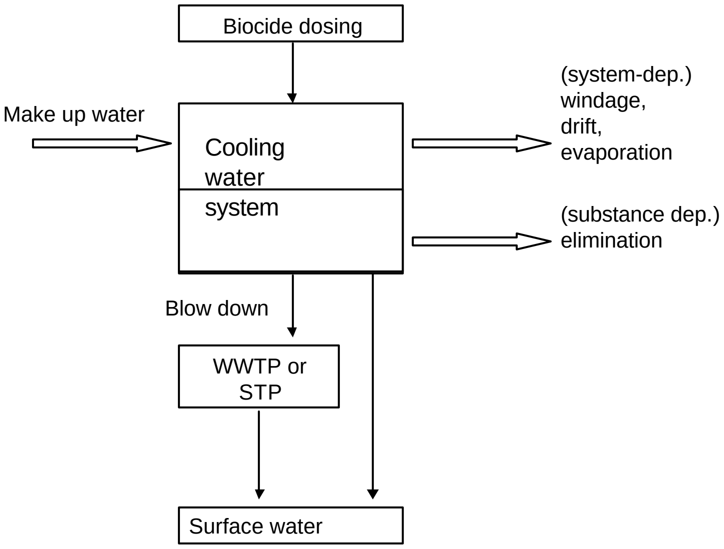


Figure 6. Schematic overview of a cooling water system

Figure 6 presents a schematic overview for all types of cooling water systems. The water is discharged to surface water or to a WWTP or STP. A once-through cooling system has a water flow of 5,000 $m^3.h^{-1}$ to 250,000 $m^3.h^{-1}$ (Adriaensen et al., 2001). When once-through systems have a cooling tower there is also a discharge to air. In modern cooling towers a water discharge of to air of circa of 0.1% of the total water volume may be expected, which would imply 5 $m^3.h^{-1}$ to 250 $m^3.h^{-1}$. In general most once-through systems in Europe do not discharge to a WWTP or a STP, because of the large volumes discharged (Van Dokkum, 1998). In figure 7 the emissions are presented schematically. The substance dependent elimination is relevant for the amount of substance that is discharged. Once-through cooling systems of power stations have a maintenance stop every second year to drain and clean the system (Donk & Jenner, 1996).

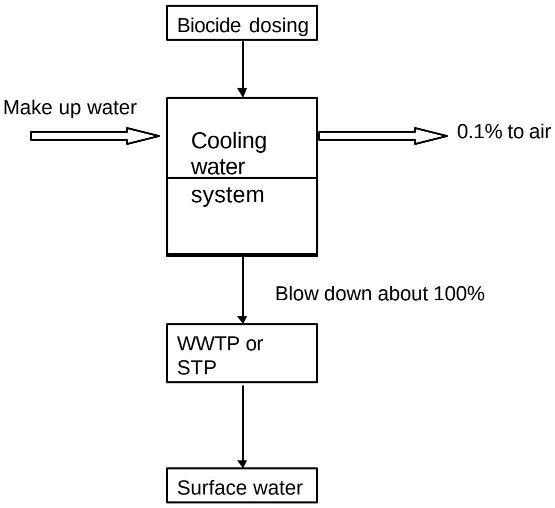


Figure 7. Schematic overview of emission from a once-through cooling system

An open recirculating cooling system blows down water to prevent the concentration of salts and solids. As a result of this the system takes in fresh water to make up for the losses through evaporation and blowdown (make-up water). The blowdown of the system usually is up to 5% of the recirculating volume. Evaporation in an open recirculating system is up to 1% of the recirculating flow per 6-7°C temperature decrease. Furthermore there is a loss to air by spray and wind drift of <0.2% of the recirculating volume for towers with forced air and <0.01% for modern towers (Assink 1991). The make-up water is about 1-3% of the flow of once-through systems with the same cooling capacity (Donk & Jenner, 1996). In figure 8 the emissions are presented schematically. The system is drained and cleaned out every year (Assink, 1991)

In spray and wind drift, very small droplets (~10 µm) are transported over large distances and can be observed as a haze above the cooling tower. The micro-droplets hardly contain any salts (Held & Schell, 1994 in Van Dokkum, 1998). However, larger droplets are also emitted from the cooling towers, despite structures to remove water from the air. These droplets reach the soil within a distance of several hundreds of meters from the cooling tower and (measured in salt) have about the same composition as cooling water (Van Dokkum, 1998).

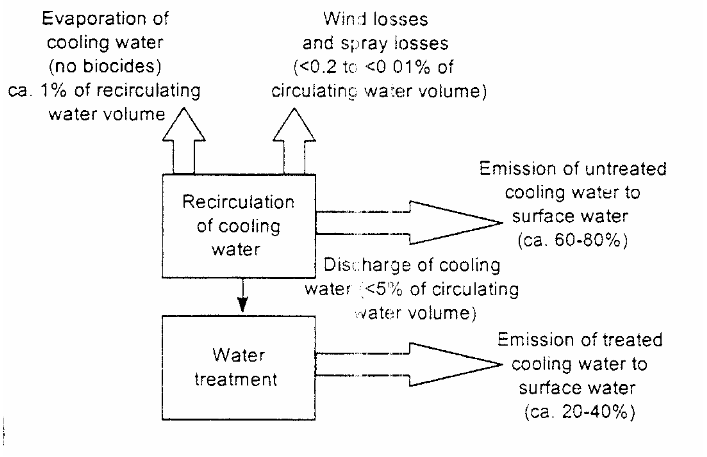


Figure 8. Mass balance of water (and dissolved biocides) in open recirculating cooling water systems (after Assink, 1991 in Van Dokkum, 1998).

In this section the emissions from a single cooling tower are discussed. For a facility with multiple cooling towers, one can extrapolate the results from a single cooling tower. If the cooling towers have a similar capacity and operating mode, the emissions may be multiplied by the number of towers in use. This assumption is more correct on a weekly basis; all the cooling towers are unlikely to be operated similarly on an annual basis.

A closed recirculating cooling system has no evaporation and wind- of spray losses. The amount of cooling water discharged is <2% of the recirculating volume (Van Dokkum, 1998). The systems are drained and cleaned out every year. The discharged water is then usually handled by specialised companies (INFU, 2000). In figure 9 the emissions are presented schematically.
Loss of around 1% of the total system volume per month is anticipated from an existing system being routinely checked and treated. Furthermore there may be spillages or leaks when dosing the formulation (losses during chemical fill). These are estimated to be 0.5% of the finished product. If a system is not checked there will also be a loss of about 1% per month but then the system will need to be emptied and brought back online, earlier (Fielden, 1997).

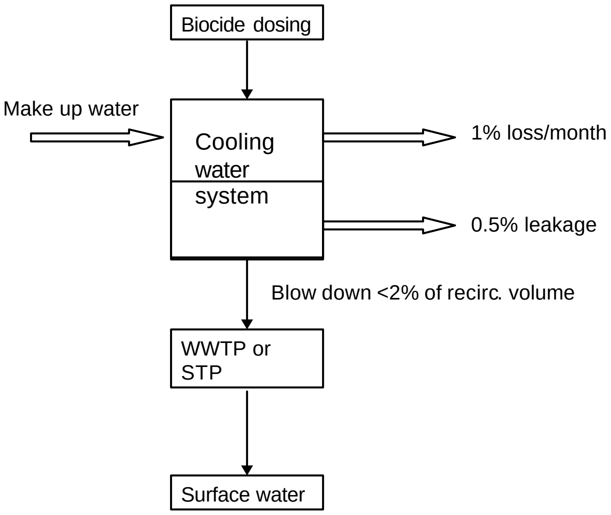


Figure 9. Schematic overview of emission from a closed recirculating cooling system

2.4.2 Estimates of quantity of substance released at these points

The amount of biocide added to the system will be based on the capacity of the system, the minimum effective concentration, the severity of the problem, the required contact time of the biocide, frequency of addition (Lutey,1995).

The frequency of addition may be estimated with:

Frequency: $$\text{days between treatment} = 1.4 \times \frac{\text{volume of water in system}}{\text{volume of blowdown per day}}$$

(However, this varies with the type of biocide).

In extremely high rates of microbiological regrowth it may be 0.7 instead of 1,4 (Lutey, 1995). In closed loop systems, dosages may be at a frequency of once per 1 to 6 months. Additions to once-through systems could be continuous or intermittent (Lutey, 1995).

1. Dosing in an once-through cooling system

In once-through cooling systems a discontinuous treatment of 10 ppm active chlorine is used or a treatment of 1-3 ppm active chlorine in combination with a dispersant. Another report states that 0.2 $mg.l^{-1}$ active chlorine is applied for 10-60 minutes per day, one or more times a day (Van Dokkum, 1998). In Table 3 a few examples of dosing in once-through systems are given. These fall within the range of doses described.

In a clean once-through cooling system with coastal/estuarine water 1.5 to 3 mg Cl_2 l^{-1} is dosed with leads to a concentration of 0.25 to 0.35 mg TRO l^{-1} (TRO= Total residual oxidant) at the heat exchanger after 4-8 minutes.
For macrofouling control in a clean once-through cooling system with seawater during 4-6 weeks in June/July (spat) continuous dosing is used (Donk & Jenner, 1996). Dosing should be aimed at 0.25 – 0.35 mg TRO l^{-1}, measured before the heat exchanger. After spat discontinuous dosing is used during 4 h on, 4 h off. In brackish water the dose should be at least 0.5 mg TRO l^{-1}.
For microfouling control in seawater and brackish water no additional dosing is necessary if an adequate sponge rubber ball system is installed (even in fouled systems). Otherwise 0.5 mg TRO l^{-1} (hypochlorite) for 30 minutes per day is necessary (Donk & Jenner, 1996).
For macrofouling control in freshwater once-through cooling systems continuous treatment of at least 0.35 mg FO l^{-1} (FO is Free Oxidant) (before the condensor) is necessary for 2-3 weeks in autumn.
For microfouling control in fresh water at least 0.40 mg FO l^{-1} is required for 30 minutes per day. In power stations every second year a maintenance stop is held. The second year dosing is 4 h on, 4 h off in early spring with a dose of 0.25-0.35 mg TRO l^{-1}. If settlement has to be prevented completely a dose of >1 mg TRO l^{-1} is necessary. Two extreme examples are: continuous dosing during 1 two-week period with 5 mg TRO l^{-1} chlorine and a two-month continuous dosing of 0.5 mg TRO l^{-1} which still can be survived (Donk & Jenner, 1996).

Chlorine gas is used in a concentration of 1 $mg.l^{-1}$ and always less than 3.5 $mg.l^{-1}$. Ozone is used as 0.1 $mg.l^{-1}$ maximum and hydrogen peroxide as 15 ppm (Donk & Jenner, 1996).
For other doses used see also Table 3.1 in Annex 3.

Table 3 A number of characteristics of shock dosing of active chlorine of 3 once-through systems are given (Berbee, 1997).

Company	**Complexity of system**	**type of water used**	**residence time (min)**	**Cl_2 dosing $mg.l^{-1}$**	**FO in effluent $mg.l^{-1}$**	**TRO in effluent $mg.l^{-1}$**
Electricity plant	Simple	Salt	3	0.8	7	0.31
Chemical site	Complex	Brackish	15 15	2.1 2.56	0.11 0.23	0.18 0.37
Chemical site	Complex	Fresh	10-15	0.5	<0.1	?

Estimated amounts of biocides released
If a continuous dosing of 3 ppm is assumed with a water flow of 5,000-250,000 $m^3.h^{-1}$, an emission of 15-750 $kg.h^{-1}$ is assumed, of which 150-7,500 $g.h^{-1}$ is emitted to air (1%). In this case no elimination of the substance takes place. Chlorine dissociates very quickly: after 4-8 minutes about 10% of the substance remains. Therefore the expected emission will be lower. In dissociating chlorine forms, other products are also emitted to the environment. The emission of these substances should also be evaluated.

2. Dosing in an open recirculating cooling system

In open recirculating cooling systems shock dosing is used: 0.1 – 0.2 $mg.l^{-1}$ active chlorine (from sodium hypochlorite) for 15-30 minutes per day. Non-oxidising biocides are used in concentrations of 1-50 $mg.l^{-1}$ (Baltus & Berbee, 1996). 90% of the recirculating cooling systems are treated with sodium hypochlorite. The ratio of concentrations of any particular solute in cooling water in relation to that in make-up water is referred to as cycles of concentration. These cycles of concentration are 2-3 for large power plants, 8-9 for industrial recirculating cooling systems and 3-5 typical outside the power industry.

In another study it is stated that mostly shock-dosing is used of 1-2 mg FO l^{-1} for 1 $h.d^{-1}$. This is just as effective as a continuous dosing of 0.5 mg FO l^{-1}. Sometimes once a week is enough. Short peak concentrations of 0.8 – 1 mg FO l^{-1} are sufficient. This concentration drops to 0.2 – 0.3 mg FO l^{-1} within 1 h (Donk & Jenner, 1996).

In the UK continuous dosing is required because of concern over insufficient control of human pathogens. Here a continuous dose of 0.3 mg FO l^{-1} hypochlorite is used, while 0.1-0.2 mg FO l^{-1} may be enough to control the system. In a clean system 0.1-0.3 mg FO l^{-1} is used while in a situation with natural variation of the bacteria a concentration of 0.3-0.4 mg FO l^{-1} is used (average 0.2-0.4 mg FO l^{-1}). In a fouled recirculating cooling system a shock dose of 4 mg $FO.l^{-1}$ is used (Donk & Jenner, 1996).

In the risk assessment for hypochlorite a continuous dosing of 0.2 mg TRO l^{-1} at the condensors is given or a discontinuous dose of 0.5 mg TRO l^{-1} for 10 minutes per hour or 1 $h.d^{-1}$. Sometimes 2 mg TRO l^{-1} at the condensor is necessary. The worst case shock injection is 1-20 mg TRO l^{-1} at the inlet for 10-20 minutes every 4-8 hours. This leads to a maximum of 8 mg TRO l^{-1} at the condensor. Chlorine concentrations immediately drop to zero after discharge. Data in discharge plumes in sea water of power stations indicate concentrations of 0 – 0.02 mgTRO l^{-1} (Anonymus, 1999).

Non-oxidising biocides are used in shock treatments. Isothiazolones are dosed as 0.5-2.5 $mg.l^{-1}$ in clean and 2-5 $mg.l^{-1}$ in fouled systems. ß-bromo-ß-nitrostyrene is dosed as 1.5-2 $mg.l^{-1}$ in clean and up to 5 $mg.l^{-1}$ in fouled systems. DBNPA is dosed as 3-15 $mg.l^{-1}$ in clean and 10-25 $mg.l^{-1}$ in fouled systems (Donk & Jenner, 1996). In Table 3.1 in Annex 3 the use concentrations of some substances are given.

Estimated amounts of biocides released
If a daily shock dose of 2 mg FO l^{-1} during one hour is assumed with a blowdown flow of 300 $m^3.h^{-1}$ per 100MWT and a evaporation of 155 $m^3.h^{-1}$ per 100 MWT, a blowdown emission of 600 $g.d^{-1}$ and an evaporation of 310 $g.d^{-1}$ is estimated. The wind drift is then 60 $g.d^{-1}$ (0.2%). In this estimation no elimination of the substance has been taken into account. Chlorine dissociates very quickly: after 4-8 minutes about 10% of the

substance remains. Therefore the emission will be at a maximum 97 g.d^{-1} of which 3.7 g.d^{-1} are emitted to air. If a continuous dose of 0.5 mg FO l^{-1} is assumed, with the same parameters, a blowdown emission of 1800 g.d^{-1}, a evaporation of 924 g.d^{-1} and a wind drift of about 185 g.d^{-1} is estimated. The maximum emission will be 290 g.d^{-1} of which 110 g.d^{-1} is emitted to air.

3. Dosing in a closed recirculating cooling system

In closed recirculating cooling systems mostly organic biocides, as isothiazolones, quats and glutaraldehyde are used (Fielden, 1997). As water losses are very limited high concentrations are used: 0.5-4 g.l^{-1} (Van Dokkum, 1998).
The overall value of active ingredients is 4.3 kg.m^{-3} inhibitor. Quats are used in 10-100 mg.l^{-1}, glutaraldehyde as 5-50 mg.l^{-1} and isothiazolones as 5-50 mg.l^{-1} (Fielden, 1997).

Estimated amounts of biocides released
Assuming a continuous dose of 50 mg isothiazolones l^{-1} with a system volume of 45 m^{3}, an emission of 22.5 g per month is assumed. In this estimation no elimination of the substance is taken into account. It is not clear in how far isothiazolones do associate.

An estimated of the emission from the three system types is given in table 4.

Table 4 Estimated amounts of preservatives emitted.

System	Dosed substance	System characteristics	Emission to compartment	Estimated emission in g (no degradation)
Once-through	3ppm active chlorine [b]	5,000-250,000 m^{3}.h^{-1} [a]	99.9% to water 1% to air [e]	15-750 kg.h^{-1} to water 150 –7500 g.h^{-1} to air
Open recirculating	2mg FO l^{-1} shock dose 1 h.d^{-1} [d]	Blowdown:300 m^{3}.h^{-1}.100MWt^{-1} Evaporation: 155m^{3}.h^{-1}.100MWt^{-1} [d]	Blowdown 5% Evaporation1% Wind drift 0.2% [c]	(per 100 MWT) Blowdown 600 g.d^{-1} Evaporation 310 g.d^{-1} Wind drift 60 g.d^{-1}
	0.5 mg FO l^{-1} continuous [d]	Blowdown:300 m^{3}.h^{-1}.100MWt^{-1} Evaporation: 155m^{3}.h^{-1}.100MWt^{-1} [d]	Blowdown 5% Evaporation1% Wind drift 0.2% [c]	(per 100 MWT) Blowdown 1800 g.d^{-1} Evaporation 924 g.d^{-1} Wind drift 185 g.d^{-1}
	5 mg.l^{-1} isothiazolones shock dose [d]	Blowdown:300 m^{3}.h^{-1}.100MWt^{-1} Evaporation: 155m^{3}.h^{-1}.100MWt^{-1} [d]	Blowdown 5% Evaporation1% Wind drift 0.2% [c]	(per 100 MWT) Blowdown 1500 g.d^{-1} Evaporation 775 g.d^{-1} Wind drift 150 g.d^{-1}
Closed recirculating	50 mg.l^{-1} isothiazolones continuous [f]	45 m^{3} [f]	1% of system volume per month [f]	22.5 g per month

TRO=Total residual oxidant determined by measuring oxidant capacity.
FO=Free oxidant; MWt= MegaWatt (thermic); MWe= MegaWatt (electric)

a Adriaensen et al, 2001
b Solvay SA in Van Dokkum, 1998
c Assink, 1991 in Van Dokkum 1998
d Donk & Jenner (zie blz 22)
e Van Dokkum, 1998
f Fielden, 1997

Effluent concentrations

For 63% of the companies with once-through cooling and active chlorine use for cooling water conditioning effluent concentrations are available. In 25% of these cases the discharged effluent is not higher than 0.25 mg FO l^{-1}. Higher concentrations (in 35% of the cases) are found in cases of shock dosing which are mostly of very short period (5-10% of the time).

For recirculation system in only 37% of the cases effluent concentrations are available. The concentration in effluent are in 80% of the cases <0.25 mg.l^{-1}. In about 20% of the cases (shock dosing) the concentration > 0.25 mg.l^{-1}. In more than half of the cases the value of 0.1-0.2 mg FO l^{-1} is exceeded. However active chlorine is very reactive and reacts very quickly, in which process other microcontaminants may be formed. (Bijstra, 1999)

2.4.3 Information of the scale or size of the industry area

Power stations make up 75%, the refinery sector uses 4%, the metal sector accounts for 1%, the food sector for 1% and the chemical industry 19% of the total volume of cooling water (Donk&Jenner, 1996).

The average amount of active chlorine used in once-through systems is about 85 kg.MW^{-1} for systems with fresh water as cooling medium and about 400 kg.MW^{-1} for systems with other types of water (ground water, industrial water, steam condensate or demiwater) as a cooling medium. In situations with marine or brackish water as cooling medium in general more biocide is used per MW. For antifouling in cooling water sodium hypochlorite is by far the most used biocide. With recirculation systems other biocides are used next to or instead off sodium hypochlorite. With once-through systems no other biocides are used next to or in stead or sodium hypochlorite.

Consumption of hypochlorite for cooling water applications is estimated at 5.58 ktonnes.yr^{-1} as Cl_2 equivalents and the use of gaseous chlorine is rather similar with 4.8 ktonnes.yr^{-1} in 1994 (Pont, 1999).

In the Netherlands an overall use of about 2100 tonnes Cl_2 yr^{-1} active chlorine is estimated. The greatest part of chlorine is used in once through systems with marine or brackish water as a cooling medium (about 85%, Bijstra, 1999).

Table 5 The estimated use of biocides in recirculation systems in 1994 in the Netherlands (Baltus et al. 1996).

Biocide	**Estimated use of active substance in kg.yr^{-1}**
Oxidative	**510,000**
Sodium hypochlorite	478,000
Sodium bromide	31,400
1-bromo-3-chloro-5,5-dimethylhydantoin	270
Non-oxidative	**1,600**
Isothiazolones	330
ß-bromo-ß-nitrostyrene	540
2,2-dibromo-3-nitrilopropionamide	370
Methylene bisthiocyanate	360

In another study in The Netherlands the use of oxidative biocides in recirculation systems is estimated to be about 510 tonnes active substance in 1994. Of the non-oxidative substances a total use of 1.6 tonnes is estimated in 1994 (see Table 5, Baltus et al. 1996).

The use of active chlorine in the Netherlands leads to an emission of 10 to 20 tonnes halo-organic compounds (reaction products) from cooling water per year (Bijstra, 1989). This concerns primarily the substances chloroform and bromoform. The concentrations of these chemicals vary from about 1-100 $\mu g.l^{-1}$. Next to these substances a discharge of about 500 kg bromate yr^{-1} occurs as a result of cooling water conditioning with active chlorine. The bromate originates from the used active chlorine itself in which it appears as a contamination. The discharge of halo-organic substances in wastewater is approx. 850 $kg.yr^{-1}$ which is significantly lower than the discharge through cooling water (Bijstra, 1999)

The total number of closed systems in the UK is estimated to be 100,000, of which (Fielden, 1997), see table 6:

- Chilled / cooling 25,000
- LTHW/MTHW 60,000
- HTHW 15,000

Of these systems the largest systems (>9,000 l) are usually treated with biocides and uncontrolled losses mostly occur with LTHW/M systems and the smaller systems (<9,000 l).

Table 6 Estimates of numbers within each capacity range (UK) (Fielden, 1997).

System	**Capacity**										**Total**
	0 to 2,000 litres		**2,001 to 4,500 litres**		**4,501 to 9,000 litres**		**9,001 to 20,000 litres**		**20,001 to 45,000 litres**		
	%	*No.*	*%*	*No.*	*%*	*No.*	*%*	*No.*	*%*	*No.*	*%*
Chilled	40	10	40	10	15	3.75	3	0.75	2	0.5	100
LTHW/M	50	30	30	18	10	6	8	4.8	2	1.2	100
HTHW	5	0.75	25	3.75	35	5.25	30	4.5	5	0.75	100

Note: No. = number of systems. expressed in 000’s; LTHW= low temperature heating water; MTHW= medium temperature heating water; HTHW= high temperature heating water.

There are an estimated 50,000 units of open recirculating systems installed in the UK at 25,000 sites (see Table 7), averaging two units per site. It is estimated that around 3000 new units will be installed each year, mostly in the small to medium range (4540 to 227000 litre capacity). Of the installed systems it is estimated that two thirds are on industrial sites and one third on commercial sites (Fielden, 1997).

Table 7 Capacity range of installed base cooling towers (Fielden, 1997)

Capacity in litres	Installed number	Percentage
0 to 4,540	12,500	25
4,540 to 22,700	7,500	15
22,700 to 227,000	25,000	50
227,000 and over	5,000	10
Total	**50,000**	**100**

2.4.4 Information on emission control methods for the industry

Efficiency of dosing
In about 57% of the companies with biocide usage, automatic dosing is used which optimises the use of biocides. The control of biocide use is often done by mussel detection, bacterial counts or measurement of free chlorine (Bijstra, 1999).

Other measures to optimise biocide usage (Bijstra, 1999):
- the removal of causes of current problems with fouling (e.g. leakage)
- introduction/optimisation of a monitoring system
- the use of results of monitoring for the control of the use
- optimisation of dosing (preferably automatic)
- drawing-up reduction plans (including goals)
- take up of measures in the reduction plan in the environmental care system.

Possible measures for the reduction of emissions to surface water are (Bijstra, 1999):
- pretreatment of cooling water (macrofiltration, microfiltration, side-stream filtration)
- optimisation of monitoring and dosing systems
- pulse chlorination and partial stream chlorination
- adjustment of the blowdown regime at recirculation systems
- end of pipe treatment of the cooling water

The cooling water from closed and open recirculating cooling systems when they are drained out, is carried out by specialised companies that handle the discharged water, prevents emissions to the environment.

Alternatives to biocide use for antifouling are thermoshock and mechanical cleaning. These measures are easier to implement in the E-sector than in the more complex process industry. Examples off promising developments are the application of alternating partial current chlorination (process industry) and pulse chlorination (E-sector and process industry) which both result in a decrease of the use of sodium hypochlorite. Mechanical cleaning can be used on-line by circulation of sponge rubber balls and a brush and cage system and can also be used off-line (operation stop). Another alternative can be the use of toxic (TBTO, zinc, copper) and non-toxic coatings and paint to reduce the settlement and growth. Non-toxic coatings may be silicone-based coatings. Other alternatives are the use of ultraviolet light, the use of sonic technology and osmotic shock (Bijstra, 1999).

2.5 Fate during use and in waste disposal

Water streams leaving a cooling water circuit may be received by surface water or a waste water treatment system. Water leaving the system by drift or windage may end up in the air (evaporation), or on the soil. The compartments likely to receive biocides in water leaving the cooling system are indicated in table 8.

Table 8 Receiving compartments from cooling systems (Van Dokkum et al, 1998 in INFU, 2000)

Applications	**fresh surface water**	**marine surface water**	**air indoor and outdoor**	**soil**	**solid waste**	**waste water**
flow-through cooling system	+	+	+	+*	-	-
open recirculating cooling system	+	+	+	+*	-	+
closed recirculating cooling system	-	-	+	-	-	+

+ = relevant'; - = not relevant

* through wind drift.

The fate of the substance in the cooling system during use and in the disposal phase depends both on substance specific characteristics (biodegradability, hydrolysis, reactivity, adsorption) and on the environmental conditions (temperature, pH, hardness, presence of microflora etc.). Table 4.1 in Annex 4 presents some characteristics for a series of biocides used in cooling water systems.

2.6 Characteristics of industrial cooling water systems

Large volumes of water are used, in once-through cooling water systems, which have short residence times, and therefore rapidly reacting oxidising biocides are used. They have a fairly constant inoculum. Mostly shock dosing is used or continuous dosing during specific seasons (spat).

Water in an open recirculation water cooling system is recycled with a longer residence time of 1 to 4 days; therefore, less water is used in these systems than in once-through systems. Because the water remains in the cooling system for some time, microbial pollution may become a problem in the system.

Water in a closed recirculation water cooling system has a residence time of some months. Due to the large residence time corrosion is more likely to occur and therefore corrosion inhibitors are used. There is a lower risk of microbial pollution and thus a lower need for biocides.

In cooling water systems the pH, temperature, dissolved solids, hardness and the presence of H_2S and NH_4 may affect the effectiveness of the biocides. For example, a pH > 8 affects effectiveness of most biocides and a temperature >45°C affects effectiveness of quats. In Table 9 the characteristics of the different types of cooling water systems are summarised.

Table 9. Characteristics of industrial cooling water systems (Source Donk & Jenner, 1996; Fielden, 1997; Adriaensen et al., 2001; Bloemkolk, 1995; Assink, 1991; Baltus,1999).

Characteristic	**Once-through**	**Open recirculating**	**Closed recirculating**
Residence time	2-15 min	1 h – 96 h	up to 12 months
Water type	fresh, brackish, marine	Fresh	fresh demineralised water
Temperature in °C	27-80 surface water 20-80 groundwater 20-80 drinking water	30-80	-
System capacity	Unlimited	1-100 MWT	-
Global water need	30-45$m^3.s^{-1}.1000MWE^{-1}$ 5,000–25,000 $m^3.h^{-1}$ 50-100 $m^3.MW^{-1}$ 170 $m^3.h^{-1}.MW^{-1}.5°C^{-1}$	0.5 – 3 $m^3.h^{-1}.MWT^{-1}$ 2$m^3.MW^{-1}$ 85 $m^3.h^{-1}.MW^{-1}.10°C^{-1}$	-
System volume in m^3		0->227m^3 mostly 4.54 –227m^3 5-3,800 m^3	0-45 m^3
Recirculation flow	-	3.5 x volume	-
Intake flow $m^3.s^{-1}$	2-60	0.1-0.2	0
Temp. of bulk (°C)	max 30	20-30 sometimes higher	30-50 and higher
pH value	7-9	7-9	7-9
Concentration factor	1	3-5 (typical) 2-9 (extremes)	not relevant
Fouling problems	biofouling corrosion scaling	Biofouling corrosion scaling pathogenety	biofouling corrosion
Biofouling organisms	- macrofouling: mussels, oysters, barnacles, hydroids, amphipods, tubeworms - microfouling	Microfouling macrofouling (in conduits): algae, bryozoa, snails	microfouling
Cooling water additives	biocides	Biocides corrosion inhibitors scaling inhibitors dispersants pH adjustment (acid)	biocides corrosion inhibitors dispersants pH adjustment (acid)
Biocides used	oxidising (>90% NaOCl)	oxidising (>90% NaOCl) non-oxidising	non-oxidising

3 EMISSION SCENARIOS FOR THE THREE COOLING SYSTEMS

3.1 Available models

A range of models, ranging from simple to more complex, is available to describe the emission of a biocide product from cooling water systems. The models are analysed and evaluated for their suitability to describe the emission of the three main types of cooling water systems.

In annex 2 the original descriptions of the models are given. In this chapter the models are described, put in a schematic overview and formulas are given. The formulas are described in uniform symbols according to Van der Poel (2000) as far as possible.

3.1.1 US EPA Tier 1 (Klaine,1996)

Tier one is a simple assessment that uses data estimating lowest observed effects levels and highest environmental concentrations. The model was developed in the scope of an exposure assessment for DBNPA (dibromonitrilopropionamide). DBNPA addition to all systems was assumed to be at maximum label rates for once-through systems. Release from electric power plants into waterways was determined under the assumption that no degradation occurred in the cooling systems. Dilution of DBNPA in waterways was estimated from existing low flow and mean flow data. Effluent or blowdown concentrations were calculated using the dose of the active substance, the blowdown flow rate and a dilution factor of the receiving surface water.

For this assessment first the concentration of the active substance in the cooling water system is calculated. This concentration is multiplied by the effluent flow rate and a dilution factor to calculate the stream concentration. The dilution factors for steam electric power plants are 5.48 for rnean stream flow and 1.00 for low stream flow.

Table 10 Emission scenario for calculating the releases from preservatives used in cooling water systems (US EPA Tier 1) Example for DBNPA (Klaine, 1996)

Variable/parameter (unit)	**Unit**	**Symbol**	**Value**	**S/D/O$^{)}$**
Input				
Concentration product in cooling water	$g.m^{-3}$	$C_{product}$	188	A
Fraction of active ingredient in product	-	F_{form}	0.1	A
Concentration active ingredient in cooling water	$g.m^{-3}$		18.8	D/S
Fraction of active ingredient in product	-	F_{form}	10	D/S
Concentration product in cooling water	$g.m^{-3}$	$C_{product}$	188	D/S
Effluent flow rate (Blowdown)	$m^3.d^{-1}$	Qbld	110	D
Dilution factor in surface water	-	DILUTION	1 or 5.48	D
Output:				
Load in discharged cooling water	$kg.d^{-1}$	Release	(2.068)	
Peak concentration in surface water	$g.m^{-3}$	$Cwater_{pres-0}$	(18.8 or 3.43)	

Model calculations:

$C_{proc} = F_{form} * C_{product}$

$Release = C_{proc} * Qbld / 1000$

$Cwater_{pres-0} = C_{proc} / DILUTION$

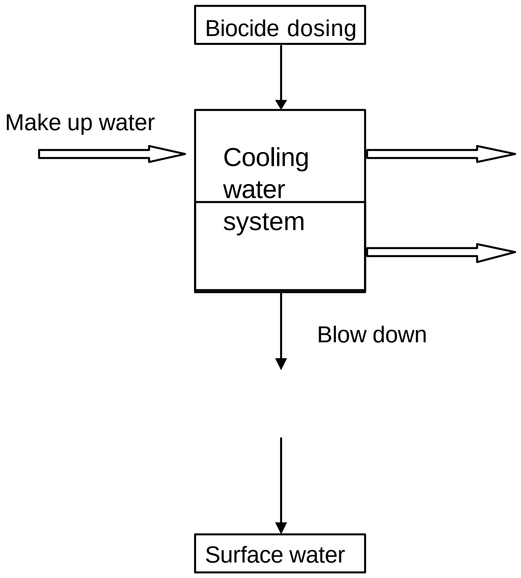


Figure 10 Emission Scenario for EPA Tier 1

This scenario can be applied for once-through cooling systems and can be adjusted to be used for recirculation cooling systems. This scenario only uses a dilution factor in surface water to predict the concentration in water. The amount of biocide released is estimated by multiplication of the blowdown flow rate and the application concentration. No substance dependent parameters are used. A continuous concentration in the system is used.

3.1.2 DOW Tier 2 (Klaine, 1996)

Following Tier 1, in a more complex exposure assessment for DBNPA a simple stream dilution model was used to estimate concentrations in receiving streams. A Monte Carlo sampling technique allowed certain model variables to take on different values for each trial during a series of model trials. The values used were obtained from distributions of possible values defined for each variable. The values were then used to calculate the desired output or “forecasts” based on the model equations.

Five stochastic variables were used as model parameters:
1. DBNPA half-life;
2. Residence time in the cooling system
3. Treatment duration;
4. Flow rate through the cooling system;
5. Stream flow rates.

Probability distributions were created for each variable for use in Monte-Carlo simulations. It was assumed that the cooling system effluent would not contribute more than 50% of the total flow of the receiving stream. Mean and low stream flow rates were obtained from the Stream Dilution Factor Program (SDFP) used by EPA. The mean flow rate was based on a 50th percentile annual average stream flow; the low flow is the lowest 7-d average flow rate recorded during a 10 year period. These were the most conservative data available. Flow conditions for 50th percentile and 10th percentile sites during times of mean and low flow were also obtained from SDFP.

The output from the model included the DBNPA concentration in the discharged cooling water (ppm), DBNPA load in the discharged cooling water (kg) and final in-stream concentration (ppb). Values of each output variable were described by distribution of results from 15,000 trials.

For degradation of DBNPA concentration in the cooling water a first-order decay equation is used. In this simulation, the decay rate cannot be treated as a constant because the half-life of DBNPA is selected from a triangular distribution.

If the cooling system effluent flow rate obtained by random selection from the distribution of possible flow rates, was more than one-half the flow rate of the receiving stream, the selected effluent flow rate was rejected and a new value for that effluent flow rate equal to one-half the stream flow rate was used. This substitution was performed to recognise that effluents do not usually contribute more than half of downstream flow.

Table 11 Emission scenario for calculating the releases from preservatives used in cooling water systems (DOWTier 2) (Klaine, 1996)

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Initial treatment concentration	$g.m^{-3}$	Cproc	24	D/S
Stream flow rate (min, mean, max)	$m^3.d^{-1}$	Qsurf	17.7-37.3-61.0	D
Flow rate through system (min, mean, max)	$m^3.d^{-1}$	Qcirc	3.8-38.2-102.2	D
Residence time (min, mean, max)	h	RT	0.2-6.0-12	D
Time	h	t	-	D
Treatment duration (min, mean, max)	h	Tint	0.2-0.5-3.0	D
Half-life of DBNPA (min, mean, max)	h	DT50	0.1-0.5-10	D/S
Output:				
Decay rate constant	h^{-1}	$kdeg_{pres}$	0.07–0.14–0.69	
Concentration in the effluent (blowdown)	$mg.l^{-1}$	Cbld	(10-650-1530)	
Concentration in surface water	$mg.l^{-1}$	$Cwater_{pres}$	(0.7-3.7-42.4)	

Model calculations:

$kdeg_{pres} = \ln 2/DT50$

$$Cbld_t = Cproc * e^{(-k\ deg_{pres} * t)}$$

or

$$Cbld = Cproc * e^{(-kdeg_{pres} * RT)}$$

if $Qcirc < Qsurf / 2 \rightarrow Cwater_{pres} = Cbld * Qbld / Qsurf$,

else $Cwater_{pres} = 0.5 * Cbld$

Due to the probabilistic approach, it was impossible to track the calculations in the article.

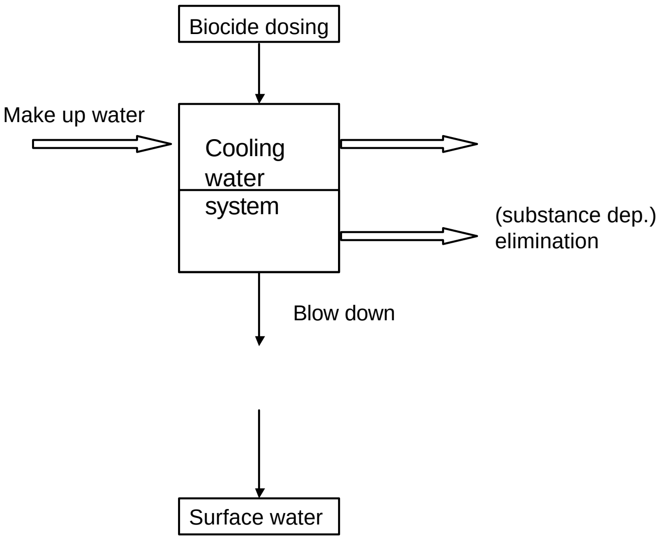


Figure 11. Emission scenario for DOW Tier 2

This scenario can be applied for once-through cooling systems and can be adjusted to use for recirculation cooling systems. This scenario uses the degradation of the biocide to predict the concentration in water. The effluent flow rate and the stream flow rate are used to determine a realistic dilution factor in surface water. Thus only one substance-dependent parameter (half-life for degradation) is used. For dosing, a shock dose is used once a week for 0.2 to 3 h. This method originally is fairly complex because of the number of trials used in it.

3.1.3 US EPA CEB (from Baur, 2000)

The model was developed for open recirculating cooling systems. It takes by default a blowdown of 0.6% of the recirculating water flow rate and a windage of 0.1% of the recirculating water flow-rate.

Table 12 Emission scenario for calculating the releases from preservatives used in cooling water systems (US EPA CEB) (Baur, 2000)

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Concentration of a.i. in cooling water	$g.m^{-3}$	Cproc	1	D/S
Recirculation rate of cooling water	$m^3.h^{-1}$	Qcirc	450	D
Blowdown, fraction	--	Fbld	0.006	D
Windage, fraction	--	Fwind	0.001	D
Output:				
Release of a.i. via blowdown	$kg.d^{-1}$	Release B	(0.065)	
Release of a.i. via windage	$kg.d^{-1}$	Release W	(0.011)	

Model calculations:

Release B = Fbld * Qcirc * Cproc * 24/1000

Release W = Fwind * Qcirc * Cproc * 24/1000

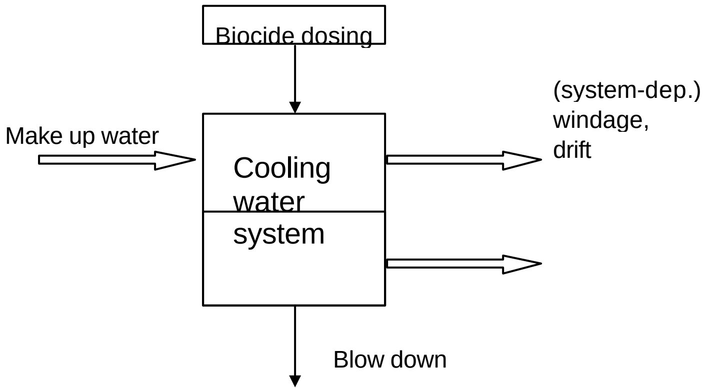


Figure 12. Emission scenario for US EPA CEB

Limitations of the model are that it does not take into account the loss by biotic and abiotic degradation during recirculation in the circuit and loss by evaporation.

This scenario can be applied for open recirculating cooling systems. This scenario only calculates the amount of biocide released. It uses a percentage loss of biocide by blowdown and windage to predict the biocide release to the environment. No substance-dependent parameters are used. This method is essentially the same as the US EPA Tier 1 model but uses a blowdown of 0.6% and a windage of 0.1% of the recirculating water instead of the blowdown flow rate.

3.1.4 USES

USES 3.0 includes an emission scenario for preservatives in cooling water systems. The scenario has been derived from the original scenario described by Luttik et al. (1993). For the risk assessment the concentration in surface water (PEC) is calculated. In the scenario it is assumed that the blowdown is discharged directly into the surface water. The dilution factor in surface water is 3 by default (stagnant water like lakes). The emission takes place throughout the year. The emission is calculated with the dosed concentration, the water flow and a dilution factor.

Loss due to windage is calculated on the basis of 2% recirculating water loss per hour for old cooling towers and less than 0.1% for new cooling systems. A default factor of 0.025% was selected.

Limitations of model are that the model does not take into account the dilution by make-up water, biotic and abiotic degradation in the water circuit, loss by evaporation and windage, possible losses in STP and realistic dilution in rivers.

Table 13 Emission scenario for calculating the releases from preservatives used in cooling water systems (USES). Example for DBNPA

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Concentration of a.i. in recirculating water	$g.m^{-3}$	C_{proc}	0.5	D
Concentration of suspended matter in surface water	$kg.m^{-3}$	$SUSP_{water}$	0.015	D
Solids-water partition coefficient in suspended matter	$m^3.kg^{-1}$	Kp_{susp}	3.8	S
Dilution factor in receiving surface water	-	DILUTION	3	D
Quantity of water in circulation	$m^3.d^{-1}$	Q_{circ}	10000	D
Fraction of water lost due to spray and wind drift	-	F_{depos}	0.00025	D
Soil surface where deposition occurs	m^2	$AREA_{depos}$	100	D
Output:				
Concentration in the effluent (blowdown)	$g.m^{-3}$	Cbld	(0.47)	
Concentration of chemical in surface water	$g.m^{-3}$	$Cwater_{pres}$	(0.16)	
Dosage for one event to soil	$kg.m^{-2}$	$DOSE_{pres}$	(0.0125)	

Model calculations:

$Cbld = C_{proc}/(1+Kp_{susp}*SUSP_{water})$

$Cwater_{pres}=Cbld / DILUTION$

$DOSE_{pres}=Q_{circ}*C_{proc}*F_{depos}/AREA_{depos}$

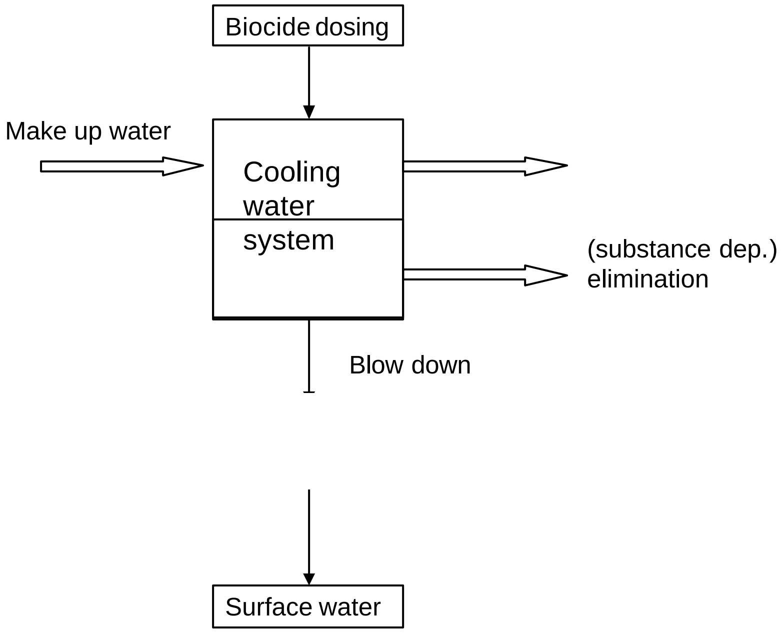


Figure 13. Emission scenario for USES

This scenario can be applied for once-through and open recirculating cooling systems. This scenario calculates the concentration in surface water by using a dilution factor and a substance dependent partition coefficient in suspended matter. A specific amount of the biocide is therefore bound to suspended matter. No degradation of the biocide is taken into account in this scenario.

3.1.5 RIZA 1 (Baltus & Berbee, 1996)

This is a model for a recirculation system. The recirculating system is seen as a continuous flowing reactor with a large recycle. At a certain time a shock dosing is used. By make-up water, blowdown and degradation the concentration in the system will decrease. For such a system a mass balance can be made. Loss mechanisms in this mass balance are degradation, adsorption, evaporation in cooling tower, loss by biocide action and blowdown.

Assumptions:
- Loss by evaporation is limited
- loss by degradation is very limited
- adsorption to the walls of the system is probably limited and therefore neglected
- loss by biocide action is unknown and is neglected
- the temperature in the system is considered to be homogenous and constant (40°C)
- the pH is around 8
- the degradation rate by hydrolysis is described as a pseudo-first order reaction
- it is assumed that after a shock dosing the concentration level in the system will be at the target level C0
- the blowdown volume is much lower than the circulation flow.

Mass balance for the quantity of the substance in the cooling water system:

$$\underbrace{Vsyst * \frac{dCproc}{dt}}_{\text{change}} = \underbrace{-B * Cproc}_{\text{blowdown}} - \underbrace{Vsyst * k * Cproc}_{\text{turnover (degradation)}}$$

For substances that do not degrade, k=0. The contribution of chemical degradation depends on the substance.

Table 14 Emission scenario for calculating the releases from preservatives used in cooling water systems (RIZA 1) (Baltus & Berbee, 1996). Example for ß-bromo-ß-nitrostyrene

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Volume of the system	m^3	V_{syst}	4500	D
Concentration of ai in the system	$g.m^{-3}$	Cproc	50	S
Blowdown stream flow rate	$m^3.h^{-1}$	Qbld	203	D
First order rate constant for degradation	h^{-1}	$kdeg_{pres}$	$0.533^{1)}$	S
Time	h	T	-	D
Recirculation flow	$m^3.h^{-1}$	Qcirc	18,000	D
Output:				
Concentration in blowdown (t = 6h)	$mg.l^{-1}$	Cbld	(1.6)	
Load in discharged cooling water (t = 6h)	g	RELEASE	(17.0 * $10^{3)}$	
Fraction of initial dose released	-	Frelease	(0.078)	
Maximum emission of 1 shock dose	g	$RELEASE_{max}$	(17.6 * 10^3)	

Model calculations:

$$Cbld_T = Cproc * e^{-(Qbld/V_{syst}+kdeg_{pres})*T}$$

$$RELEASE = \frac{Cproc*Qbld}{(Qbld/V_{syst}+kdeg_{pres})}*(e^{-(Qbld/V_{syst}+kdeg_{pres})*T}-1)$$

$$RELEASE_{max} = \frac{Cproc*Qbld}{(Qbld/V_{syst}+kdeg_{pres})}$$

$$Frelease = \frac{Qbld}{(Qbld+kdeg_{pres}*V_{syst})} \quad \text{(after infinite time)}$$

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1) ß-bromo-ß-nitrostyrene

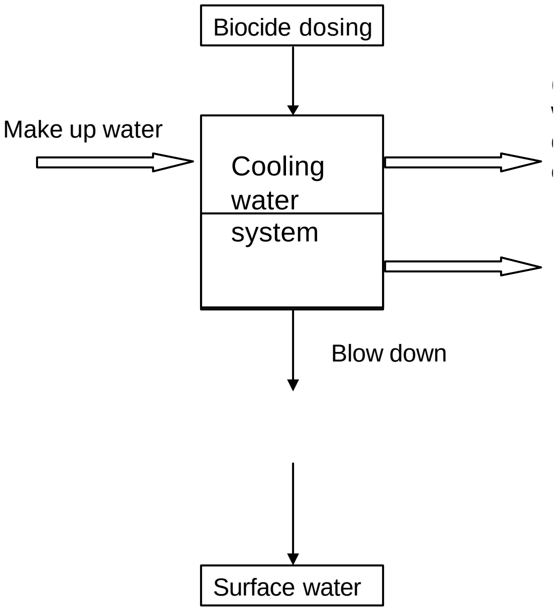

Figure 14. Emission scenario for RIZA 1

The model calculations show that emissions may be limited by refreshing the system before dosing; then dosing and closing the blowdown. After a few hours blowdown must be done because of the salt contents of the system. Biocide action is more efficient without dilution in the system.

The maximum release may be derived after infinite time, as the power in the formula reaches then the value zero. In practice, the maximum emission will be reached after about 60 hours. This maximum emission may be compared to the dosed amount $Cproc*V_{syst}$. From this the fraction released after infinite time may be calculated. The calculations illustrate that some substances are almost completely released through blowdown over a period of time.

Sometimes the pH of the system is somewhat higher which causes the hydrolysis process to be quicker. This does not lead to major differences.

This scenario can be applied for open recirculating cooling systems. This scenario calculates the release and the concentration in surface water using the volume of the system, the blowdown and the first-order degradation rate constant. One substance-dependent parameter is used. The fraction of the substance remaining after use in the cooling system is also estimated. For dosing a shock dose is used.

3.1.6 RIZA 2 (Baur, 2000)

This model was described by Baur (2000) as a RIZA model but the reference is lacking. The model assesses PECair and the release to water for recirculating cooling water systems with forced ventilation and direct discharge. For the water phase the model applies a fixed decay factor in the system of 0.01. The basis of this decay (or dilution) factor and its meaning is not clear. Therefore this part of the RIZA 2 model is not included in the next sections. For the current evaluation only the pathway to air is considered.

Table 15 Emission scenario for calculating the releases from preservatives used in cooling water systems (RIZA 2) (Baur, 2000)

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Volume of recirculating water	$m^3.d^{-1}$	Qcirc	10000	D
Dosage of active ingredients	$g.m^{-3}$	Cproc	1	D/S
Fraction of evaporated water (of Qcirc)		Fevap	0.04	D
Volume of cooling air	$m^3.d^{-1}$	Vair	10,000,000	D
Empirical factor	-	Kair	<1	D
Dilution factor air until reaching the target area	-	DILUTIONair	100	D
Output:				
Theoretical concentration in air of active ingredients at cooling tower outflow	$mg.m^{-3}$	$Cair_{init}$	0.040	
Concentration in air	$mg.m^{-3}$	PECair	0.0004	

Model calculations:

$Cair_{init}$ = Qcirc * Cproc * Fevap * 1000 / Vair

PECair = $Cair_{init}$ * Kair / DILUTIONair

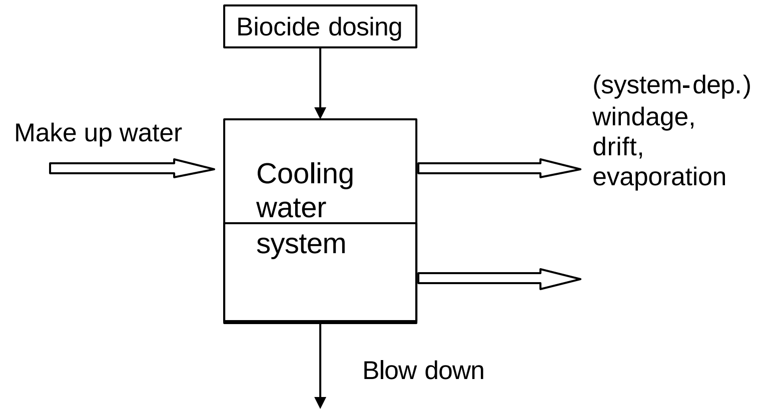

Figure 15. Emission scenario for RIZA 2

This scenario can be applied for open recirculating cooling systems. This scenario also calculates the biocide release to air and PECair. No substance dependent parameters are used. Except for the decay factor of 100 in the system (Dsystem) the model is the same as US EPA Tier 1 and US EPA CEB.

3.1.7 Baur 2000

The model of Baur is based both on biocidal product data (biological and abiotic degradation half-lifes, partition coefficients Kow and Henry's Law Constant) and on cooling tower operating conditions data (a.i. dosage, dosage cycle length, volume of waters, make-up water, blowdown, windage). The model explicitly includes the effects of repetitive dosing.

The model is available as a spreadsheet. It includes the following steps:

1. Calculation of the maximum biocide concentration C_0 (initial concentration);
2. Calculation of C_t (biocide concentrations in recirculating water or blowdown along a full dosage cycle). It takes into account the fate of the biocide during recirculation as it is influenced by biodegradation, hydrolysis and photolysis and by changes in the cooling water volume by blowdown, evaporation and make-up water;
3. Drawing of C_t curves for several consecutive cycles, showing whether a biocide equilibrium concentration can be reached or whether there is a risk of continuing accumulation of active substance in the recirculating loop (optimal operating conditions);
4. (Optional) Calculation of time-dependent a.i. concentrations in the influent and effluent of a WWTP with choice of units. The calculations are based on residence time in the WWTP, adsorption on flocks, biotic and abiotic degradation;
5. The model calculates the time dependent concentration in surface water using a (default) dilution factor.

As biocidal product dosing in open recirculating cooling towers (ORCT) is always done at intervals, there is always a continuous decrease of the concentration during the cycle. This is caused by the combined action of loss of biocide load in circulation water lost through evaporation, windage and blowdown, dilution by make-up water, and possibly by loss of biocide caused by sorption to suspended matter and by degradation during the cycle. Dosage lasts for 15 to 60 minutes while the biocide cycle (time between 2 dosages) may vary from 3-4 hours to several days.

The model calculates the time-related concentration (e.g., figure 17) of active substance in the blowdown water. It produces a new series of concentrations for each dosing interval. The final concentration at time t is determined by summing the concentrations of all dosing series. It produces the maximum and average concentration for the interval.

In the (optional) WWTP, the active substance may be diluted with other streams and may be eliminated by adsorption, (abiotic) degradation, and by biodegradation in the activated sludge unit. The elimination level will depend on the type of WWTP and the substance characteristics.

Table 16 Emission scenario for calculating the releases from preservatives used in cooling water systems (Baur, 2000)

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Cooling tower				
Dose of formulated product	kg	DOSE	25	D/S
Fraction of a.i. in product	--	Fform	0.02	D/S
Volume of water in system	m^3	V_{syst}	300	D
Make-up water flow rate	$m^3.d^{-1}$	Qmkp	48	D
Blowdown flow rate	$m^3.d^{-1}$	Qbld	30	D
Wind drift flow rate	$m^3.d^{-1}$	Qwind	3	D
Evaporation flow rate	$m^3.d^{-1}$	Qevap	15	D
Abiotic degradation rate constant	h^{-1}	$kdeg_{abiot,syst}$	0.038	D/S
Biodegradation rate constant	h^{-1}	$kbiodeg_{syst}$	$6.93*10^{-5}$	D/S
Dosing interval	h	T_{int}	48	
Time	h	t	0 - ∞	D
WWTP				
Partition coefficient in WWTP	$m^3.kg^{-1}$	Kp_{WT}	0.456	D
Density suspended matter in aeration tank	$kg.m^{-3}$	$SUSP_{WT}$	1.3	D
Residence time in first clarifier	h	RT1	5	D
Abiotic degradation rate constant in first clarifier	h^{-1}	$kdeg_1$	0.038	D
Residence time in aeration tank	h	RT2	12	D
Biodegradation rate constant in aeration tank	h^{-1}	$kbiodeg_{WT}$	$6.93*10^{-5}$	D
Residence time in secondary clarifier	h	RT3	0	D
Abiotic degradation rate constant in secondary clarifier	h^{-1}	$kdeg_2$	0.038	D
Volumes of other influents to WWTP	$m^3.d^{-1}$	Qother	270	D
Dilution factor in surface water	-	DILUTION	10	D
Output:				
Cooling Tower				
Concentration of a.i. in cooling water system	$g.m^{-3}$	Cproc	(1.67)	
Dilution loss rate in the sytem	h^{-1}	$kdilut_{syst}$	(0.0067)	
Time constant (for concentration decrease)	h^{-1}	T_{syst}	(22.1)	
Concentration in blowdown water (multiple dosing)	$mg.l^{-1}$	Cbld	(1.8– 0.25)	
WWTP				
Partition coeff. suspended matter – effluent	-	$Ksusp_{WT}$	(0.59)	
Dilution in WWTP	-	$DILUTION_{WT}$	(10)	
Total fraction of a.i. degraded in WWTP	-	$Fdegtot_{WT}$	(0.82)	
Total residence time	h	RT_{tot}	(17)	
Concentration in WWTP effluent	$mg.l^{-1}$	Ceffluent	(0.035 – 0.015)	
Concentration in surface water	$mg.l^{-1}$	$Cwater_{pres}$	(0.0035-0.0015)	

Model calculations:

***Cooling Tower**:*

$$Cproc = DOSE * 1000 * Fform / V_{syst}$$

$$kdilut_{syst} = \frac{(Qbld + Qwind + Qevap) *24}{V_{syst}}$$

$$T_{SYST} = \frac{1}{kbiodeg_{syst} + kdeg_{abiot,syst} + kdilut_{syst}}$$

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O

After one dose:

$$Cbld = Cproc * e^{(-t/T_{syst})}$$

With repeated dosing after T_{int}:

$$Cbld = \sum_{l=1}^{n} Cproc * e^{(-(t-l*T_{int})/T_{syst})} \quad \text{for } (t-l*T_{int}) > 0$$

WWTP:

$Ksusp_{WT} = Kp_{WT} * SUSP_{WT}$

$DILUTION_{WT} = (Qbld + Qother) / Qbld$

$$Fdegtot_{WT} = e^{-(RT1*kdeg_1+RT2*kbiodeg_{WT}+RT3*kdeg_3)}$$

$RT_{tot} = RT1 + RT2 + RT3$

After one dose:

$Ceffluent = Cbld * (1- Ksusp_{WT}) * (1 – Fdegtot_{WT}) / DILUTION_{WT}$

With repeated dosing after T_{int}:

$$Ceffluent = \frac{Cbld*(1-Ksusp_{WT})*(1-Fdegtot_{WT})}{(1-RT_{tot}/T_{syst})*(e^{(-t/T_{syst})}-e^{(-t/RT_{tot})})/DILUTION}$$

$Cwater_{pres} = Ceffluent / DILUTION$

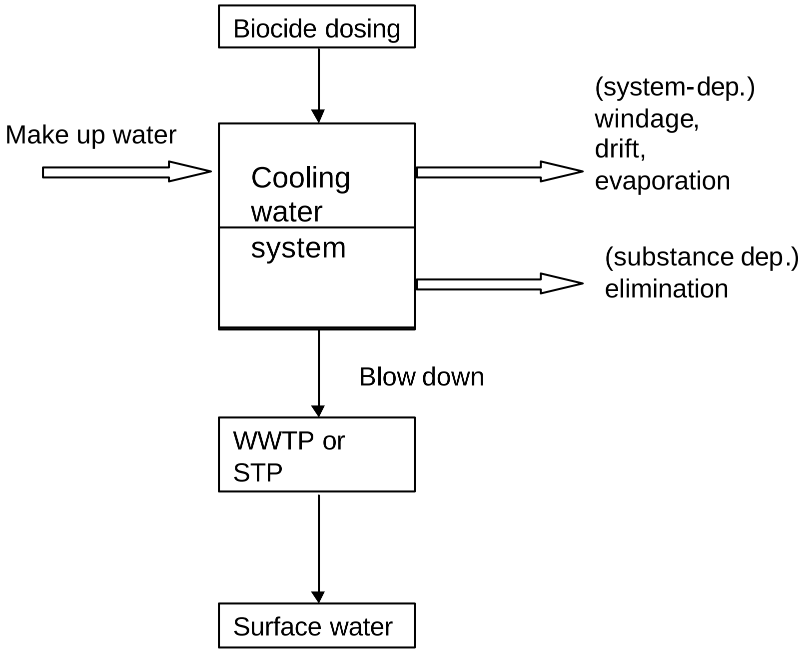

Figure 16. Emission scenario for Baur 2000

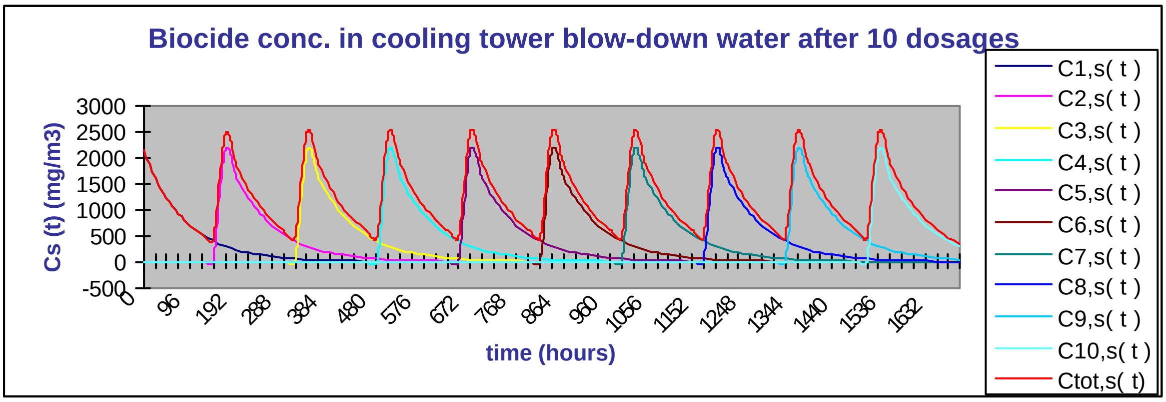

Figure 17. Example of the results for the scenario Baur 2000 (Baur spreadsheet)

This scenario can be applied for open recirculating cooling systems. It calculates the concentration in blowdown, the WWTP and in surface water. As the model is available as a spreadsheet, it can be used to simulate the conditions in any ORCT in order to optimise biocide treatment conditions.
This scenario uses various substance dependent parameters in the calculation. It takes account of:

- the continuous dilution of the active substance in the system by the addition of make-up water;
- the elimination of the substance by degradation in the cooling system;
- (optional) the elimination of the substance by degradation and sorption in the WWTP;
- the effect in time of replicate dosing.

3.1.8 UK TGD 1 (Fielden, 1997)

For open recirculating systems, potential release to the environment will be via blowdown which may be discharged to estuarine waters, routed to an on-site treatment plant or to a local sewage treatment works. The preferred method of blowdown is a continuous low rate bleed using a flow control valve. The setting of the valve depends on the rate of concentration of dissolved solids in the cooling water and is operated to prevent scaling. Blowdown is usually carried out after every 2-5 cycles of water through the tower.

Other potential releases of water treatment chemicals could arise from leakages in the system and a worst-case release scenario would involve complete system failure and the discharge of the water flow from the entire circuit. This may also occur at planned intervals as a result of shut-downs for system maintenance which necessitate the draining of the circuit (Fielden, 1997).

Concentrations in water are calculated for two scenarios in the UK TGD 1:

Scenario 1: Cleaning and disinfection
The system is drained and then cleaned and disinfected by filling and draining the system twice within 24 h. The main chemical lost at cleaning is chlorine.

Scenario 2: Normal operation

During normal operation an evaporation of 1% of the flow is assumed. The amount of substance in the blow down flow is estimated using the evaporation and the concentration cycles[1].

Table 17 Emission scenario for calculating the releases from preservatives used in cooling water systems (UK TGD) (Fielden, 1997)

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Recirculating cooling water flow rate	$m^3.h^{-1}$	Qcirc	350	D
Fraction evaporated	-	Fevap	0.01	
Concentration of ai in cooling system	$g.m^{-3}$	Cproc	6-10 (1) 10 (2)	O
Volume of the system	m^3	Vsyst	100	D
Average cycles of concentration	-	Ncc	3	D
Output				
Evaporation	$m^3.h^{-1}$	Qevap	(3.5)	
Blowdown rate	$m^3.h^{-1}$	Qbld	(1.75)	
Scenario 1: Load in discharged cooling water. a. Drain out b. Cleaning and disinfection	g per life time	RELEASE	(a. 600-1000 (1)) (b. 2000 (2))	
Scenario 2				O
Load in discharged cooling water	$g.h^{-1}$	Release	(10.5 – 17.5 (1))	

Model calculations

Qevap = Fevap * Qcirc

Qbld = Qevap / (Ncc – 1)

Scenario 1

Maintenance: Drain out: Release =V_{syst} * Cproc (1)
Cleaning and disinfection : Release =2* V_{syst}* Cproc (2)

Scenario 2

Normal operation: RELEASE = Qbld * Cproc (1)

1) Alkylbenzyldimethyl ammonium chloride

2) Chlorine

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[1] Evaporation causes the soluble constituents of the water supply to concentrate. The ratio of the maximum concentration of dissolved solids in the recirculating water to the concentration in the make up water is called cycles of concentration.

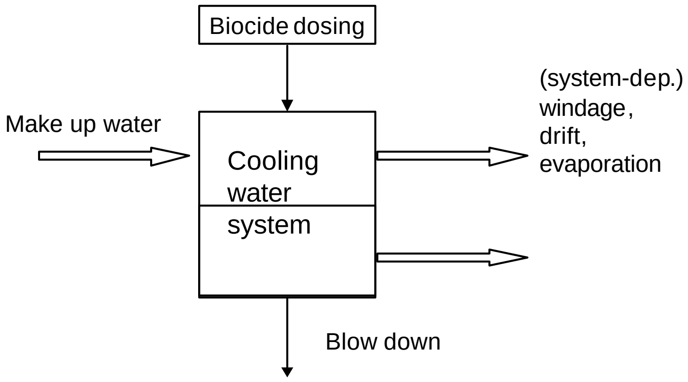

Figure 18. Emission scenario for UK TGD 1

This scenario can be applied for open recirculating cooling systems. It calculates only the amounts of biocide released during the two different processes (cleaning and disinfection and normal operation). No substance dependent parameters are used. For dosing a shock dose is used.

3.1.9 UK TGD 2 (Fielden, 1997)

In closed systems there should be little loss of water, thus requiring small amounts of make up water. A closed system, following routine monitoring and treatment programmes, is expected to lose approximately 1% of the system volume per month.

The larger volumes of losses occur at various stages of the systems life cycle such as commissioning of a new system, changes to an existing system and the uncontrolled losses that occur prior to bringing a system back on line. Each of these stages may result in a total drain of the system volume along with the treatment chemicals. There may also be losses of cleaning agent and spillages of treatment chemicals.

Four scenarios have been identified as potentially occurring during the life cycle of a closed system.
- New system precommission cleaning and filling with treatment chemicals.
- Changes or additions to new or existing systems.
- Design losses from correctly treated and monitored systems.
- Uncontrolled losses equal to or in excess of design loss due to irregular treatment or monitoring.

A diversity of loss factors may be defined to describe the releases from the system. Loss of biocide may be related to (see table 18):
L1 Release during the addition of the formulation to the system (spillage or leaks).
L2 Design losses which are controlled as part of a routine programme.
L3 Draining and uncontrolled losses resulting from lack of a routine programme.

Emissions of specific substances are calculated using the standard emission factor, dose and system capacity.

Table 18. Loss of biocides from a closed cooling system, UK TGD 2 (Fielden 1997)

A complete scenario description is given in Annex 2, including also scenario 3 and processes 9-16. They were excluded here as they do not involved the use of biocides.

Steps in lifecycle	Processes	Emissions UK TGD 2	$kg.m^{-3}$
SCENARIO 1 New Systems Start Up (once during lifetime)	1.Initial flushing		
	2.Chemical cleaning: non-acid cleaning second process (alternative) acid cleaning		
	3.Passivation		
	4.Inhibitor/biocide dosing	L1 Losses during chemical fill (spillage or leaks)	0.5% of 4.3 $kg.m^{-3}$ ([a]) = 0.02 $kg.m^{-3}$
SCENARIO 2 Changes/additions (occasional)	5.Complete or partial drain-down	Complete L3 Chemical inhibitor formulation incl. biocide Partial: loss factor halved	4.3 $kg.m^{-3}$ (100%)
	6.Changes/ additions to the system		
	7.Flushing		
	8.Inhibitor/biocide dosing	L1 Losses during chemical fill (spillage or leaks)	0.5% of 4.3 $kg.m^{-3}$ = 0.02 $kg.m^{-3}$
SCENARIO 4 Existing process-controlled: Maintenance (ongoing)	17.Routine service visits		
	18.Design losses	L2 Design losses from inhibitor and biocide charged system (1% loss per month)	0.043 $kg.m^{-3}$ (=1% of total inhibitor package; 4.3 $kg.m^{-3}$)
	19. Inhibitor/ biocide dosing	L1 Losses during chemical fill (0.5% of finished product) (spillage or leaks)	0.02 $kg.m^{-3}$ (=0.5% of total inhibitor package; 4.3 $kg.m^{-3}$) 1% in existing systems

a total inhibitor package as given in the report, overall value for the active ingredients

L1 Release during the addition of the formulation to the system

L2 Design losses which are controlled as part of a routine programme

L3 Draining and uncontrolled losses resulting from lack of a routine programme

Table 19 Emission scenario for calculating the releases from preservatives used in cooling water systems (UKTGD 2) (Fielden, 1997)

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
Input				
Dose of total inhibitor package to system	$kg.m^{-3}$	DOSE	4.3	
Fraction lost of active ingredient	per cycle	F_{L1}	0.005	D/S
	per month	F_{L2}	0.01	
	per life	F_{L3}	1	
Concentration of a.i. in cooling system	$kg.m^{-3}$	Cproc	4.3	D
Volume of the system	m^3	V_{syst}	30	D
Output:				
Load in discharged cooling water				
Release scenario 1	kgper dosing	RELEASE	(0.645)	

Variable/parameter (unit)	Unit	Symbol	Value	S/D/O
	event			
Release scenario 2	kg per drainage kg per dosing event	RELEASE	(a. 129) (b. 0.645)	
Release scenario 4	$g.h^{-1}$ ($kg.month^{-1}$) kg per dosing event	RELEASE	(a. 1.8) (1.3) (b. 0.645)	

Model calculations:

Scenario 1: New system

Biocide dosing: RELEASE = F_{L1} * DOSE* V_{syst}

Scenario 2: Changes/additions

a. Complete drainage (per event): RELEASE = F_{L3} * V_{syst} * Cproc

b. Biocide dosing (per cycle): RELEASE = F_{L1} * DOSE* V_{syst}

Scenario 4: Existing process - controlled

F_{L2} = 0.01.month^{-1} = 0.0000139 h^{-1}

a. Design losses: RELEASE = F_{L2} * V_{syst} * Cproc

b. Biocide dosing (per cycle) : RELEASE = F_{L1} * DOSE* V_{syst}

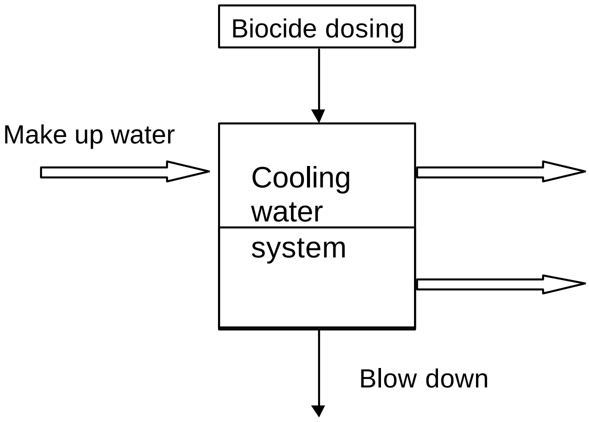

Figure 19. Emission scenario for UK TGD 2

This scenario can be applied for closed recirculating cooling systems. This scenario calculates the amount of biocide released during different processes (dosing; normal operation; and cleaning and disinfection. For these calculations mostly fixed amounts are used. No substance dependent parameters are used.

3.2 Compatibility of parameters with data requirements

In Table 20 the data needed as input in the model(s) and the data provided according to the Biocide Product Directive, are compared.

Table 20. Substance dependent parameters used in the described models

Type of data	Data input into models	Input from Biocide Product directive
Concentration of a.i. in cooling water	Cproc	
Solids-water partition coefficient in suspended matter, adsorption	Kp-susp	Log Kow
Biodegradation rate in cooling system, half-life	$kbiodeg_{syst}$, DT50	Standard tests on Biodegradation (but data are related to test system)
Loss by photodegradation	$kdeg_{photo,syst}$, DT50	Phototransformation
Loss by hydrolysis	$kdeg_{hydro,syst}$, DT50	Hydrolysis

It may seem that the necessary substance data will be provided according to the Biocide Product Directive. However, it should be kept in mind that rates of photodegradation and hydrolysis are greatly influenced by physical-chemical conditions, e.g., temperature, light intensity, pH. Conversion of the standard data will be necessary to obtain the parameters needed for the calculations. Biodegradation rate is not only a substance specific characteristic, but reflects the conditions in the test. Conversion to a rate in a cooling water system (different biomass density and quality) is not possible.

3.3 Qualitative comparison of the methods

The once-through systems and open recirculating systems show a similarity in the fact that they both have a blowdown from the system. Once-through systems typically have a blowdown equivalent to the volume of the system. In open recirculating systems the water is recycled a few times through the system before blowdown occurs. In both systems blowdown may be continuous, although intermittent blowdown is also possible in recirculating systems. In both systems shock dosing is used. Because of the similarity between the systems it is suggested that one model can be used for both systems. In paragraph 3.3.1 models for both systems are compared.

In paragraph 3.3.2 the one model for closed recirculating systems is evaluated. Closed recirculating systems by definition (used here) do not have a (significant) blowdown but do have evaporation losses or accidental losses. In a ‘worst case’ the system looses twice the total volume once a year. Because of the long residence time of the system water degradation of the biocides will be important, although it should be considered that the system is cleaned after drainout. The flushing water will go through the system quickly. However the discharge water of closed systems is mostly collected and handled by specialised companies.

3.3.1 Once-through system and open recirculating systems

The models of US EPA Tier 1, US EPA CEB, RIZA 2 and UK TGD 1 have the same starting points. They use the blowdown to extract release or a concentration in the cooling water effluent. CEB defines blowdown as a specific % of the recirculating water while US EPA Tier 1 and RIZA 2 use a direct blowdown flow rate. The UK TGD1 defines blowdown as a function of the rate of evaporation and the concentration cycles. The background of this relation was not clear and this model has not been included in the comparison in the next sections.

The US EPA Tier 1, US EPA CEB and UK TGD 1 models represent a simple worst case approach by assuming no degradation of substances in the system. RIZA 2 applies a fixed decay factor in the system of 0.01. As the basis of this decay (or dilution) factor and its meaning was not clear, this part of the RIZA 2 model has not been included in the next sections. None of these models uses substance dependent parameters.

The models of DOW Tier 2, BAUR 2000, RIZA 1 are also essentially the same. They all include degradation as a substance dependent parameter in the form of a first order rate constant (k_{deg}). The method of DOW Tier 2 directly uses the hydraulic residence time (HRT) as system-specific parameter, whereas the methods of RIZA 1 and BAUR 2000 use the quotient of the system volume and the blowdown rate (this is in fact HRT). In once-through systems, the total system volume is blown-down in a very short time, so the quotient HRT becomes very small. This indicates the methods RIZA 1 and BAUR 2000 could be used for both systems. The method of BAUR 2000 gives the most complete description of the system, including system-specific processes like evaporation and windage as well as substance specific processes like degradation.

The model of USES distinguishes itself by using adsorption as a substance dependent removal mechanism. The model does not include degradation of the biocides. The adsorption of the model USES could be added to the model of BAUR.

Generally, once-through systems are characterised by a large water flow and a very short residence time. Therefore degradation in the system has probably very limited influence on the concentration of the biocide except in cases where the substance is degraded very quickly. However, in once-through systems the biocide used most frequently is chlorine which does degrade very rapidly. In open recirculating systems degradation may play an important role.

The emission to air is described by in four models: USES, US EPA CEB, RIZA 2 and UK TGD 1. US EPA CEB simply suggests a percentage (0.1%) loss of the recirculating volume to air and determines a release. The UK TGD 1 method uses a percentage (1%) loss of the recirculating volume as well but includes also a concentration factor to correct for the recirculation and refreshment of the system. The RIZA 2 method suggests a percentage (4%) loss of the recirculating volume to air but also calculates a concentration in air in the cooling system and in surrounding air by dilution. USES also uses a fraction of water lost to air (0.025%) and does not calculate the concentration in air but an expected concentration in soil.

In table 21 the scenarios for once-through and open recirculating cooling water systems are compared.

Table 21 Comparison of the scenarios for open and open recirculating systems

Factor	**US EPA Tier 1**	**DOW Tier2**	**US EPA CEB**	**USES**	**RIZA 1**	**RIZA 2**	**Baur 2000**	**UK TGD**
Existing system (Cleaning and disinfection)								
Cleaning and disinfection								+
Existing system (normal operation)								
Dilution in cooling						+	+	

Factor	**US EPA Tier 1**	**DOW Tier2**	**US EPA CEB**	**USES**	**RIZA 1**	**RIZA 2**	**Baur 2000**	**UK TGD**
system								
Blowdown	+	+	+		+	+	+	+
Spray and wind drift			+	+			+	
Evaporation						+	+	+
Adsorption				+				
Abiotic degradation: hydrolysis		+			+	+	+	
Abiotic degradation: photolysis							+	
Biodegradation							+	
Leakage in system								
Air								
Dilution factor						+		
Soil								
Deposition				+				

3.3.2 Closed recirculating systems

Only one scenario is available for the closed recirculating system: model Fielden. This model hardly uses any calculations for the determination of the emission but rather uses determined emission factors for specific parts of the system's life cycle. Closed recirculating systems are characterised by a long residence time of the substance in the system; thus degradation in the system will be important for the concentration of the substance. If large amounts of water are emitted during refreshment of the system, the discharged water is often disposed off by a specialised company and not brought into the environment. For risk assessment purposes, however, a conservative approach should be taken and therefore the refreshment scenario was included as well.

3.4 Detection of similarities and differences, comparison and examples

To illustrate the differences between the calculation methods for different scenarios, an example is elaborated in detail for four substances: DBNPA, bronopol, sodium hypochlorite and ß-bromo-ß-nitrostyrene. Bronopol is a slowly degrading biocide, whereas sodium hypochlorite and ß-bromo-ß-nitrostyrene are degrading fast. DBNPA hydrolyses quickly at pH 8.

In table 22 and 23 the different models for once-through and open recirculating cooling water systems are compared by using the same input values. In Table 22 the models of US EPA Tier 1 and US EPA CEB that include only system-specific characteristics, are compared. Table 23 compares the models of DOW Tier 2, RIZA 1, BAUR 2000 and USES. These models include also substance-specific parameters. For the models without degradation of the substances, the calculations of C_{bld}, $Cwater_{pres}$ and Release are added if they were not included in the original method. In view of the dynamics of the systems including degradation, the Release could not easily be added to those models.

The input values are listed in table 22 and 23, where the parameters are indicated as 'S' (substance characteristic to be supplied by the applicant), 'D' default or 'O' result or output. A default is a value given in the original scenarios or methods. Results are calculated for dummy values for the substance characteristics (not validated values) and defaults.

Table 22 Input values for the calculation of RELEASE, Cbld and Cwater$_{pres}$ of the models of US EPA Tier 1 and US EPA CEB [once-through, substance – independent]

Methods

US EPA Tier 1 : RELEASE = Cproc * Qbld * 24/1000
Cbld = Cproc
US EPA CEB: RELEASE= Fbld * Qcirc * Cproc *24/1000 (Fbld = 0.006)
Cbld = Cproc

	Symbol	Unit	Value Substance X	S/D/O
Input				
Conc. of a.i in system	Cproc	$mg.l^{-1}$	25	D/S
Volume of water in system	Vsyst	m^3	4500	D
Dilution in surface water	DILUTION	-	0.1	D
Blowdown flow rate	Qbld	$m^3.h^{-1}$	110	D
Recirculating cooling water flow rate	Qcirc	$m^3.h^{-1}$	18333	D
Evaporation rate	Qevap	$m^3.h^{-1}$	3.5	D
Output				
Method US EPA Tier 1	RELEASE	$kg.d^{-1}$	66	
	Cbld	$mg.l^{-1}$	25	
Method US EPA CEB	RELEASE	$kg.d^{-1}$	66	
	Cbld	$mg.l^{-1}$	25	

When the results of the different models with similar input values are compared, it is concluded that the results are the same. The difference in the calculation is that US EPA Tier 1 uses Qbld, whereas in US EPA CEB, Qbld is first derived as a fraction of the circulation flow rate.

Table 23 Input values for the calculation of RELEASE, Cbld and Cwater$_{pres}$ for the models of DOW Tier 2, USES, RIZA 1 and BAUR 2000 (include substance-dependent parameters)

Methods

DOW Tier 2:

$$Cbld = Cproc * e^{-kdeg * t}$$

with $t = HRT = V_{syst} / Qbld$

For comparison: t = 24 h

USES: $Cbld = Cproc / (1 + Kp_{susp} * SUSPwater)$

with $Kp_{susp} = foc * Koc$

$Koc = 0.33 \log Kow + 1.25$ (2)

$foc = 0.015$

RIZA 1: $RELEASE = Cproc * Qbld * (e^{-(Qbld/V_{syst}+kdeg)*t} - 1)/(Qbld/V_{syst}+kdeg)$

$$Cbld = Cproc * e^{-(Qbld/V_{syst}+kdeg)*t}$$

BAUR 2000:

$$Cbld = Cproc * e^{(-t/T_{syst})}$$

with $T_{syst} = 1 / \{ kbiodeg + kdeg + (Qbld+Qwind+Qevap) / V_{syst} \}$

BAUR 2000 with addition of adsorption from USES

$Cbld = Cproc * e^{(-t/Tsyst)} / (1 + Kp_{susp} * SUSPwater)$ (dissolved concentration)

with $T = 1 / \{ kbiodeg + kdeg + (Qbld+Qwind+Qevap) / V_{syst} \}$

	Symbol	**Unit**	**DBNPA**	**Bronopol**	**Sodium hypo-chlorite**	**ß-bromo-ß-nitrostyrene**	**S/D/O**
Input							
Conc. of a.i. in system	Cproc	$mg.l^{-1}$	24	25	3	5	S
Volume of water in system	V_{syst}	m^3	4500	4500	4500	4500	S
Recirculating cooling water flow rate	Qcirc	$m^3.h^{-1}$	350	350	350	350	S
Blowdown flow rate	Qbld	$m^3.h^{-1}$	113	113	113	113	S
Evaporation rate	Qevap	$m^3.h^{-1}$	3.5	3.5	3.5	3.5	S
Wind drift rate	Qwind	$m^3.h^{-1}$	1,1	1,1	1,1	1,1	S
Conc. of suspended matter in surface water	SUSP	$kg.m^{-3}$	0.015	0.015	0.015	0.015	D
Octanol/water part. coeff,	Log Kow						S
Solids-water partition coeff. in suspended matter	Kp_{susp}	$m^3.kg^{-1}$	3.8	1.093	0.13	10.52	O
biodegradation rate constant	kbiodeg 1)	h^{-1}	$6.9*10^{-5}$	$6.9*10^{-5}$	$6.9*10^{-5}$	$6.9*10^{-5}$	S
abiotic degradation rate constant	$kdeg_{abio}$	h^{-1}	0.07	$6*10^{-5}$	23	0.533	S
total degradation rate constant	$kdeg_{total}$	h^{-1}	0.07	$12.9*10^{-5}$	23	0.533	S
Time	t	h	24	24	24	24	D

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[2] QSAR for amides in the EU-TGD

Output						
Hydraulic retention time	HRT	h^{-1}	40	40	40	40
Method DOW Tier2	Cbld	$mg.l^{-1}$	1.5	24.98	0.00	0.0083
Method USES	Cbld	$mg.l^{-1}$	22.7	24.6	2.99	4.3
Method RIZA 1	RELEASE	kg	25.2	49.9	0.014	0.99
	Cbld	$mg.l^{-1}$	2.53	13.9	0.00	$7.7*10^{-6}$
Method BAUR 2000	Cbld	$mg.l^{-1}$	4.43	24.3	0.00	$1.35*10^{5}$
Method BAUR with addition of adsorption from USES	Cbld	$mg.l^{-1}$	4.19	23.9	0.00	$1.16*10^{5}$

1 kbiodeg is set to zero (DT50 10000 h)

A summary of the calculations is given in table 23. In this table, the concentration in the blowdown flow Cbld of the methods DOW Tier 2, USES, RIZA 1 and BAUR 2000 is calculated for four biocides with different degradability. One shock dose is given and the concentration after 24 h is calculated.

All methods use substance dependent parameters. The calculations show that the degradation of the substance has a distinct influence on the predicted concentration in the blowdown. USES includes sorption but no degradation. The absorption factor to suspended matter, however, has little influence on the outcome of the calculations. This is logically considering that the amount of suspended matter will be limited in the system. Moreover, with the low logKow values, the tendency to sorb is low. In the last row the absorption term formulated in USES has been added to the method of BAUR 2000. This again only slightly alters the value of Cbld. It should also be taken into account that Cbld (adsorption included) represents the dissolved concentration. The blowdown water will included the material sorbed to suspended matter, in other words, Cbld total does not change. Therefore it is not considered necessary to include this parameter in the final method.

The results for the models of Dow Tier 2, RIZA 1 and Baur are at the same level (per substance). The RIZA 1 model seems to be the intermediate.

As the concentration of a.i. in the blowdown water will decrease in time, calculation of the release (load) per day involved the summation of the (decreasing) release in time. The RIZA 1 model is the only model that includes the calculation of the release (cumulated during the day).

For closed recirculation cooling water systems only one method is available: UK TGD 2. This method uses a standard emission which is not substance dependent. An example of the calculations is given in table 19. Different scenarios estimated the emission from losses:

- due to spills and leakage during dosing (0.5% of the dosed amount);
- due to the normal process operations (1% of V_{syst} per month, design losses);
- due to termination of the cycle when the system is drained (100% of biocide present).

The calculations in table 19 illustrate that the release at termination (draining) may be more important than the release caused by design losses. However, in this case the degradation of the substances will be especially important because of the long residence time of the substance in the system. This process is not included in the calculations. It is therefore suggested to add a step to this model to take degradation into account. For this use could be made of the loss term defined in the BAUR 2000 method (T_{syst}). In this case the quotient ((Qbld+Qwind+Qevap)/V_{syst}) is set to 0.

Three models include the release to air. Table 24 shows the modules of the pathway to air of the models US EPA CEB, USES and RIZA 2. The three methods give different output: the release (converted to 24h), the deposition on soil ($g.m^{-2}.d^{-1}$) and the concentration in air (after degradation) assuming default dilution volumes, respectively. Therefore the values cannot be compared among each other. These calculations are substance-independent.

Table 24 Input values for the calculation of RELEASE to air and soil for the models of US EPA CEB, USES, RIZA 2 and UK TGD 1 (substance independent)

Methods

US EPA CEB: RELEASE= Fwind * Qcirc * Cproc * 24/1000

USES: DOSEpest = Fdepos * Qcirc * Cproc * 24/ AREAdepos

RIZA 2: Cair = Fevap * Qcirc * Cproc * 1000 / Vair
PECair = Cair * Kair / DILUTIONair

	Symbol	**Unit**	**Substance X**	**S/D/O**
Input				
Conc. of a.i. in recirculating water	Cproc	$g.m^{-3}$	25	D/S
Volume of the system	V_{syst}	m^3	4500	D
Recirculating water flow rate	Qcirc	$m^3.h^{-1}$	18333	D
Windage	Fwind	-	0.006	D
Deposition to soil	Fdepos	-	0.00025	D
Evaporation	Fevap	-	0.04	D
Soil surface area	AREAdepos	m^2	100	D
Volume of cooling air	Vair (cooling air)	m^3	10^7	D
Dilution factor air	DILUTIONair	-	100	D
Empirical factor	Kair	-	1	D/S
Output				
US EPA CEB	RELEASE	$kg.d^{-1}$	66.0	
USES				
Dosis to soil	$DOSE_{pres}$	$g.m^{-2}.d^{-1}$	27.5	
RIZA 2	Cair	$mg.m^{-3}$	1.8	
	PECair	$mg.m^{-3}$	0.018	

4 DISCUSSION AND CONCLUSIONS

4.1 Process description

The fate of a biocidal active ingredient in the effluent (blowdown flow) of a cooling water system is determined by the characteristics of the system and by substance specific characteristics.

Most models discussed in this document use shock dosing. Only in the method of BAUR 2000 (spreadsheet) an interval between two doses is taken into account. The other models consider the results after just one dose. When repeated dosing is applied, the concentration in the system will come to a steady state after an initial stage. The estimation of the daily emission becomes more complicated when on the one hand elimination of a.i. causes a decrease in time whereas additional dosing at intervals might cause a built-up of the concentration.

4.1.1 Characteristics of the system

In the evaluation in the previous sections the addition of the biocide was always assumed to be intermittent, as a shock dose during a short period (e.g., 15 minutes, once or twice per day). The behaviour and fate in the cooling system depends on the type of system, where the two extremes are the once-through system on the one hand and the closed system and the open recirculating system on the other hand. A once-through system may be considered as a so-called plug-flow reactor where the bulk flow proceeds through the system in an orderly, uniform manner. Assuming that there is no mixing in the longitudinal direction, the biocide dosed in the water passes as a ‘plug’ (with concentration $C_{proc} = DOSE / (Qcirc*t)$; symbols are described in table 25) through the system and will leave the system after the residence time HRT. Thus the effluent will see no biocide untill the plug reaches the outlet and then the concentration will be elevated for short time and return to zero when the plug has passed. It should be noted that this is a conservative approach, as in practice no bulk flow will proceed through any system in an "orderly uniform manner". Some mixing will result in an initial high concentration in the outflow when the bulk reaches the exit point followed by a rapidly decreasing concentration, but with a certain tailing depending on the dimensions of the system.

An open recirculating system or a closed system is to be considered as a completely mixed flow reactor. In this type of reactor the dosing is rapidly diluted throughout the system and thus the system absorbs shock loadings: $C_{proc} = DOSE / V_{syst}$. The concentration of in the system equals the concentration in the blowdown: $C_{bld} = C_{proc}$. The concentration in the effluent will be maximal just after dosing and decreases in time (by dilution and degradation) until the next dosing takes place.

With continuous dosing in a recirculating system, the fluctuations disappear and the concentration in the blowdown is constant. This is also the case in a once-through system with continuous dosing: the short ‘plug’ changes into a continuous stream.

4.1.2 Substance specific characteristics

The active ingredient may be partially eliminated in the cooling water circuit. Elimination processes are hydrolysis, photodegradation, biodegradation and adsorption, in addition to blowdown, evaporation and windage.

Hydrolysis and photolysis take place in the water phase and can be considered as a first order reaction related to the concentration of the biocide. This implies that the fraction degraded by hydrolysis and/or photolysis can be calculated based on a first-order reaction rate constant $k_{hydrolysis}$ and/or $k_{photodeg}$ and time or the Hydraulic Residence Time (HRT).

In a once-through system, degradation can take place during the time the plug passes the system. When the plug passes the outlet the concentration is:
$C_{bld} = C_{proc} * e^{-k * HRT}$.
With continuous dosing in a once-through system, the short ‘plug’ changes into a continuous stream and the fluctuation over the system disappears. The concentration at the outlet will be continuous at the level described above.

In an open recirculating system or a closed system degradation processes take place during the time the water recirculates in the system.
For a shock dose: $C_{bld,\,t} = C_{proc} * e^{-k * t}$.
With continuous dosing in a recirculating system, the fluctuations in time disappear and the concentration in the blowdown is constant as described by the following equation (Weber 1972):
$C_{bld} = C_{proc} / (1 + k * HRT)$.

It should be noted that these reaction rates are highly dependent on the temperature and pH. However, it is inherent to cooling water systems that the temperature fluctuates throughout circulation. The value entered for $k_{hydrolysis}$ and/or $k_{photodeg}$ should reflect this effect. As a conservative approach the rates for the minimum temperature could be used. For a number of active substances the influence of pH and temperature on hydrolysis rate are given in Annex 4 of this report.

A problem is posed by the description of the biodegradation process. Usually biomass is already present in a cooling water circuit in the form of slime or foulings. The major part of the biodegradation capacity of the system will be located in the residential biomass in the system. The more surface area suitable for slime formation and/or fouling, the greater the degrading capacity. This implies that the biodegradation rate is a function of the amount of biomass in the system and not a function of the HRT as described in many models. As a consequence, the biocide concentration in the blowdown flow cannot be predicted. Another aspect is that the biocide is added to prevent growth of micro-organisms and therefore the biodegradation capacity will be greatly inhibited. When biodegradation starts to take place, the specific biocide lost its function and the cooling water system will need a refreshment or a change of biocide type. Therefore it is reasonable to neglect the effect of biodegradation.

The removal by sorption to organic matter in the system is also impossible to predict on the basis of the HRT, for the same reason as for biodegradation. On the other hand, if it is assumed that over time, the sorption capacity of the immobile organic phase in the system is saturated, sorption can only take place on the newly added material in the make-up water (SUSP: 15 $mg.l^{-1}$). Due to the generally low log Kow of the active ingredients, the impact of sorption will be negligible. Moreover it should be taken into account that the substance sorbed to suspended matter will still be discharged in the blowdown water. A calculation of sorption to the newly added suspended material would merely distinguish the fraction sorbed and dissolved in the blowdown water. Therefore, it is not considered necessary to include this parameter in the final method.

4.1.3 Other aspects

The distribution in the environment is not taken into account in most of the methods. The pathway to air is included in USES, US EPA CEB and RIZA 2. In USES this results in a deposition to soil. These approaches could be added to the proposed scenarios. These models include no substance dependent parameter, although the volatility of substance may be very important in this respect.

The releases to air and water may be used as input in EUSES for further modelling of the distribution in the environment. Procedures to describe the fate in an STP and further distribution in the environment are included in the EU Technical Guidance Documents (TGD) for risk assessment. According to inforrmation given by service companies, current practice in Europe is to minimize drift and to control the chemistry of cooling towers with blowdown.

The dilution of the cooling water system effluent in the surface water is often calculated using a fixed dilution factor of 1:10. Final dilution into surface water is usually very important because cooling tower system blowdown flow-rates may range between 10 and $2.5 * 10^6$ $m^3.h^{-1}$. Assuming the EUSES standard water flow rate of 18000 $m^3.d^{-1}$ or 750 $m^3.h^{-1}$, the actual dilution varies from 75:1). The latter is not realistic as large cooling water systems will never be located on small waterways. The emission scenarios for biocides in cooling water systems estimate the concentration in the blowdown or the load. The dilution into surface water is currently not included.

All models estimate an emission per time-unit during the normal procedure of the cooling system. The method UK TGD 1 and 2 also take the start-up and ending of the system into account. Especially in closed recirculating cooling systems the emission from start-up and ending the system may be significantly higher than emissions during the working stage (that is, if no degradation is assumed). In open recirculating cooling systems the emission during the working stage is the most relevant.

The degradation of the a.i. in a closed system may be added to the UK TGD2 model using the loss term in RIZA 1 or in Baur.

4.2 Proposal for emission scenarios

Based on the previous discussions a generic scenario can be identified for a large once-through cooling water system, for a large and a small open recirculating system and for a small closed system. A distinction is made between shock dosing and continuous dosing. The characteristics are given in table 25. The calculation methods are summarised in table 26.

Table 25. Proposal for harmonised emission scenarios for PT11: Once-through systems, open recirculating and closed systems. Characterisation of the systems.
S: value supplied in data set; D: default value; O: output of previous calculations

Characterisation	Symbol	Unit	Once-through	Open recirc. large	Open recirc. small	Closed system	S/D/O
Input							
[A] Dose of formulated product to system	DOSE	kg					S
Fraction of a.i. in product	Fform	-					S
,[B] Concentration of active ingredients in system	Cproc	$g.m^{-3}$					S
[C] Initial concentration of active ingredients in system (for continuous dosing) [A/B/C]	$Cproc_{init}$	$g.m^{-3}$					S
Volume of water in system	V_{syst}	m^3	6000	3000	300	30	D
Blowdown flow rate	Qbld	$m^3.h^{-1}$	24000	125	2	0.0004	D
Recirculating cooling water flow rate	Qcirc	$m^3.h^{-1}$	24000	9000	100		D
Dosing interval	Tint	h		24	24		S
Duration of dosing	tdose	h		0.25–0.5	0.25–0.5		S
Fraction evaporated+drift	Fevap+drift	-	0.01	0.01			D
Fraction deposited to soil	Fdepos	-	0.00025	0.00025			D
Degradation rate constant	kdeg	h^{-1}					S
Soil surface where deposition occurs	AREAdepos	m^2	100	100			D
Fraction of a.i. lost during dosing event	$F_{Loss\ dosing}$	-				0.005	D
Fraction of a.i. lost in process due to design	$F_{Loss\ design}$	$month^{-1}$				0.01	D
Fraction of a.i. lost at complete drainage	$F_{Loss\ drain}$	-				1	D
Time	t	h					S
Number of cooling towers per site	N	-	2	2	1		D
Output							
[A] Concentration of active ingredients in system [A/B/C]	Cproc	$g.m^{-3}$					
Concentration of a.i. in blowdown water	Cbld ($t_{0,\ t}$)	$mg.l^{-1}$					
Release to water after time t	$RELEASE_t$	kg					
Max. release after infinite time	$RELEASE_{max}$	kg					
Fraction released to water after infinite time	$Frel_w$	-					
Release from dosing	$RELEASE_{dosing}$	$kg.event^{-1}$					

Characterisation	Symbol	Unit	Once-through	Open recirc. large	Open recirc. small	Closed system	S/D/O
Release from drainage	$RELEASE_{drainage}$	$kg.event^{-1}$					
Design losses	$RELEASE_{design}$	$kg.h^{-1}$					
Release to air	RELEASEair	$kg.h^{-1}$					
Conc. in surrounding air	Cair	$mg.m^{-3}$					
Dose of ai deposited to soil	$DOSE_{pres}$	$g.m^{-2}.h^{-1}$					

Table 26. Proposal for harmonised emission scenarios for PT11, calculation methods.

Model calculations

$HRT = V_{syst} / Qbld$

Release to water

ONCE-THROUGH, *Shock dosing*

[A] $Cproc = DOSE * 1000 * Fform / (Qbld * tdose)$

No degradation:

$RELEASE_t = N * DOSE$

$Cbld = Cproc$ (maximum, at t = HRT)

With degradation:

$Cbld_t = Cproc * e^{-(kdeg) * HRT}$

$RELEASE = N * DOSE * e^{-(kdeg) * HRT}$ (per event)

ONCE-THROUGH, *Continuous dosing*

[A] $Cproc = DOSE * 1000 * Fform / (Qbld * HRT)$

$Cbld = Cproc_{init} * e^{-(kdeg) * HRT}$

$RELEASE_t = N * Cbld * Qbld * t * 0.001$

OPEN RECIRCULATING, *Shock dosing*

$Cproc = DOSE * 1000 * Fform / Vsyst$

$Qdrift + Qevap = Fevap+drift * Qcirc$

With degradation:

$K_{syst} = (Qbld + Qdrift + Qevap) / V_{syst} + kdeg$

$$Cbld_t = Cproc * e^{-(K_{syst}) * t}$$

after one shock dose:

$$RELEASE_t = -Cproc * Qbld * \frac{e^{-Ksyst * t} - 1}{Ksyst} * 0.001 * N$$

$RELEASE_{max} = Cproc * Qbld / K_{syst} * 0.001 * N$

$Frel_w = Qbld / (Qbld + kdeg * V_{syst})$

(RIZA 1, adapted for drift or windage and evaporation according to Baur) *with n dosings at intervals of Tint:*

$$Cbld_t = \sum_{i=1}^{n} Cproc * e^{-(t-(i-1)*Tint)*Ksyst} \quad \text{for } (t-(i-1)*T_{int}) > 0$$

and

$$RELEASE_t = \sum_{i=1}^{n} -Qbld * Cproc * \{e^{-(t-(i-1)*Tint)*Ksyst} - 1\} * N * 0.001 \quad \text{for } (t-(i-1)*T_{int}) > 0$$

OPEN RECIRCULATING, *Continuous dosing*

[A] Cproc = DOSE *1000 * Fform / V_{syst}

Cbld = Cproc / (1+K_{syst} * HRT)

$RELEASE_t$ = N * Cbld * Qbld * t * 0.001

Releases to air and soil

ONCE-THROUGH AND OPEN RECIRCULATING

no degradation

RELEASEair = Fevap+drift * Qcirc * Cproc * 0.001 * N

$DOSE_{pres}$ = Fdepos * Qcirc * Cproc / AREAdepos * N

with degradation: Cproc is to be replaced by Cbld

Release to water

CLOSED SYSTEM

No degradation:

Per biocide dosing event:	$RELEASE_{dosing} = F_{Loss\ dosing} * V_{syst} * Cproc$
Design losses per month:	$RELEASE_{design} = F_{Loss\ design} * V_{syst} * Cproc$
Complete drainage (per event):	$RELEASE_{drainage} = F_{Loss\ drainage} * V_{syst} * Cproc$

Single dosing

Cproc = DOSE *1000 * Fform / V_{syst}

With degradation:

K_{syst} **=** Qbld / V_{syst} + kdeg

$$Cbld_t = Cproc * e^{-(K_{syst})*t}$$

after one single dose:

$$RELEASE_t = Cproc*Qbld*(e^{-(K_{syst}*t)}-1)/K_{syst}*0.001$$

$RELEASE_{max}$ = Cproc * Qbld / K_{syst} * 0.001

$Frel_w$ = Qbld / (Qbld + kdeg*V_{syst})

with n dosings, see open recirculating system

5 REFERENCES

Assink J.W., 1991. Industiële koelsystemen: Milieuaspecten en kosten. TNO IMET en RIZA Report 91-301, 1991. RIZA nota nr 92.005, 1992

Baur G, 30 June 2000. Environmental exposure model for biocide products used in open recycling cooling towers (manuscript). Rohm and Haas European Laboratories Sophia Antipolis 2000, p. 11.

Baltus C.A.M., R.P.M. Berbee, 1996. Het gebruik van biociden in recirculatiesystemen RIZA report nr 96.036.

Baltus, C.A.M., L.C.M. Kerkum, P.G.M. Kienhuis. Acute toxiciteit van koelwaterlozingen uit recirculatiekoelsystemen. RIZA rapport 99.025.

Berbee, R.P.M. 1997. Hoe omgaan met actief chloor in koelwater? RIZA rapport 97.077

Bijstra, D. 1999. Verantwoord omgaan met biociden in koelwater. FWVO-nota (Rijkswaterstaat) (chloorbleekloogverbruik)

Bijstra, D., 2000. FWVO workshop koeling 2000. Cool of niet…? dat is de vraag, Syllabus

Bloemkolk, J.W., 1995. Industriële koelsystemen en emissies. RIZA Nota nr. 95.050, Rijkswaterstaat/RIZA.

Cook, 2000. Cook.Norm@epamail.epa.gov, Model of EPA

Dokkum H.P. van, D.J. Bakker, M.C.Th. Scholten, TNO-Report, 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.

Donk, M. van, H.A. Jenner, 1996. Optimisation of biofouling control in industrial cooling water systems with respect to the environment. KEMA Environment Services, Report nr. 64387-

Fielden T., M. Idden, G. Hobbs 1997. Use category document – water treatment chemicals (draft). Environmental Agency (UK). Wallingford 1997, p. 75.

Herrchen M., M. Müller, H. Rüdel, 1997. Methodology for an ecological assessment of offshore products, Frauenhofer-Institute for Environmental Chemistry and Ecotoxicology, Schmallenberg, research Report Umweltbundesamt, December 1997

INFU, 2000, Gathering and review of Environmental Emission Scenarios for biocides, Institute for Environmental Research (INFU), University of Dortmund, UBA Berlin, 2000.

Klaine, S.J., G.P. Cobb, Dickerson, R.L., Dixon, K.R., Kendall, R.J., Smith, E.E., Solomon, K.R., 1996, An ecological risk assessment for the use of the biocide, dibromonitrilopropionamide (DBNPA) in industrial cooling systems, Environmental Toxicology and Chemistry Vol. 15, No. 1, 21-30.

Lutey, R.W., 1997, Process cooling water, Ch.3 in Handbook of biocide and preservative use, Blackie Academic and Professional, London, p. 50-82.

Luttik R., H.J.B. Emans, P. v.d. Poel, J.B.H.J. Linders, 1993. Evaluation systems for pesticides (ESPE): 2. Non-agricultural pesticides to be incorporated into the Uniform System for the Evaluation of Substances (USES). RIVM Report 679 102 021.

OECD ESD: Water treatment chemicals, October 2000
Waiting for entering into official review process, UK -- timing to be decided on 8th meeting of Task Force on Env. Exp. Ass in 2001

Van der Poel, P, 2000. Supplement to the methodology for risk evaluation: Proposal for the formats of names, parameters, variables, units and symbols to be used in emission scenario documents, RIVM report 601450 007

Van der Poel, P., and J. Bakker, 2001. Emission scenario documents for biocides, RIVM report 601450009.

Poot, 1999, Draft Risk Assessment report for sodium hypochlorite.

Weber Jr, W.J., 1972. Physicochemical processes for water quality control. Wiley-Interscience Series of Texts and Monographs. Wiley & Sons, Inc. ISBN 0-471-92435-0.

USES 2.0 (existing scenario for biocides) / VdPoel en Bakker 2001

ANNEX 1. LIST OF ABBREVIATIONS

ai	active ingredient
AREAdepos	soil surface
Cair	theoretical concentration of active ingredients at cooling tower outflow
Cbld	concentration in the effluent of the cooling water system (blowdown)
Cinit	initial concentration of ai in cooling water
Conc-cycl	concentration cycles
Cproc	concentration active ingredient in cooling water in kg or $g.m^{-3}$
$Cwater_{pres}$-0	the peak concentration in surface water in $g.m^{-3}$
$Cwater_{pres}$-t	the average concentration in surface water in t days in $g.m^{-3}$
DILUTION	dilution factor in surface water
Dose-pest	dosage for one event in $kg.m^{-2}$ to soil
Dsoil	Daily dosage of 1 m^2 soil surface with ai ($mg.m^{-2}.d^{-1}$)
Dsystem	dilution factor, closed system, 24 h (hydrolysis, decay time) - 100
Qevap	evaporation in $m^3.d^{-1}$
EEC	estimated exposure concentrations
Fdepos	the amount of water lost by spray and wind drift
FO	Free oxidant
DT50	the half-life of ai
k	decay rate constant
Kair	factor estimated in test
Kp-susp	solids-water partition coefficient in suspended matter in $m^3.kg^{-1}$
Qmkp	flow of make-up water
MWE	MegaWatt (electric)
MWT	MegaWatt (thermic)
Nappl	number of applications in 1 year
PECair	concentration in air
Qbld	blowdown in $m^3.d^{-1}$
Qcirc	circulation of water or water flow rate in cooling water system in $m^3.d^{-1}$ or $m^3.h^{-1}$
Qsurf	surface water flow in $m^3.d^{-1}$
RT	residence time (time it takes for water to pass through the cooling system).
SUSPwater	concentration of suspended matter in cooling water in $kg.m^{-3}$
t	time
Tair	dilution factor until reaching the target area
Tint	period between 2 emissions
TRO	Total residual oxidant determined by measuring oxidant capacity
Vair	Volume of cooling air (m^3)
Vsyst	volume in system in m^3
Wind	release ($kg.site^{-1}.d^{-1}$) via windage

ANNEX 2. ORIGINAL DESCRIPTIONS OF METHODS

US EPA Tier 1 (Klaine, 1996)

For DBNPA, the EPA Exposure Assessment Branch (EAB) developed a conservative calculation of direct exposure from cooling towers. DBNPA addition to all systems was assumed to be at maximum label rates for once-through systems. Release of DBNPA from electric power plants into waterways was determined under the assumption that no degradation occurred in the cooling systems. Dilution of DBNPA in waterways was estimated from existing low flow and mean flow data. This assessment produced the following calculation of in-stream DBNPA concentrations.

Calculation of application concentration (EAB used the highest concentration in the range):
10% active ingredient *10 lb of formulation liquid per gallon*0.095 gallons of liquid per 1000 gallons of water*0.373 $kg.lb^{-1}$*10^{9} µg/kg*1 gallon per 3.785 l = 18,800 $g.l^{-1}$ or 18,800 ppb (1 8.8 ppm)

Calculation of the chemical release in $kg.site^{-1}.d^{-1}$: The chemical concentration calculated in the effluent flow in $µg.l^{-1}$ (above) is multiplied by the effluent flow rate in $l.d^{-1}$. For cooling towers, the typical flow is 110 million liters per day (MLD):

18,800 $µg.l^{-1}$* 1.1*10^{8} $l.d^{-1}$* 10^{-9} $kg.µg^{-1}$ =2.068 $kg.d^{-1}$ (5,544 $lbs.d^{-1}$)

Calculation of stream concentration in $µg.l^{-1}$ (ppb): The chemical concentration in the effluent flow ($µg.l^{-1}$) is divided by a stream dilution factor to produce estimated exposure concentrations (EECs). The dilution factors for steam electric power plants (SIC code 4911) are 5.48 for rnean stream flow and 1.00 for low stream flow.

Mean stream flow:
18,800 $µg.l^{-1}$/5.48 = 3,430 $µg.l^{-1}$, (3.43 ppm)

Low stream flow:
18,800 $µg.l^{-1}$/I.00 = 18,800 $µg.l^{-1}$ (18.80 ppm)

These EECs were then compared with the toxicity results for the most sensitive species. In this case a 96-h flow-through study performed with *Crassostrea virginica* (eastern oyster) resulted in significant reduction of shell deposition (lowest-observed-effect concentration (LOEC) at 0.07 $mg.l^{-1}$.

Conclusion: This model can be applied for once-through cooling systems and can be adjusted to be used for recirculation cooling systems. This scenario only uses a dilution factor in surface water to predict the concentration in water. The amount of biocide released is estimated by multiplication of the effluent flow rate and the application concentration. No substance dependent parameters are used.

DOW Tier 2 (Klaine, 1996)

A simple stream dilution model was used to estimate DBNPA concentration in receiving streams. A Monte Carlo sampling technique allowed certain model variables to take on different values for each trial during a series of model trials. The values used were obtained from distributions of possible values defined for each variable. The values were then used to calculate the desired output or "forecasts" based on the model equations. These outputs were collected into distributions of the instantaneous peak DBNPA concentration in the receiving stream as welt as the total DBNPA input into the stream. This was done for flows corresponding to the Standard Industrial Classification (SIC) code 4911, steam electric power plants. These flows were chosen to be representative of streams that receive once-through cooling system effluent. Stream concentrations and loadings were calculated using Gaussian distributions for both mean and low flow rates. These distributions represented mean and low flows for streams receiving effluent from all facilities in the SIC code. These calculations were repeated 15,000 times using models written for commercially available software. Resultant distributions of predicted aqueous concentrations were used in risk assessment scenarios.

Model parameters

Five stochastic variables were used as model parameters: (1) DBNPA half-life; (2) residence time in the cooling system (3) treatment duration; (4) flow rate through the cooling system; and (5) stream flow rates. Probability distributions were created for each variable for use in Monte-Carlo simulations. For the first three variables, a triangular distribution was formed using values of the minimum, mean, and maximum to form the triangle. Without more data, a triangular distribution is the simplest form of probability distribution warranted. The minimum, mean, and maximum values for each triangular distribution are used. The fourth variable, flow rate through the cooling system, was described using a beta distribution with $\alpha = 3.0$ and $\beta = 5.0$. The minimum, maximum, and mean values were 3.8, 102.2, and 38.2 (MLD), respectively. We assumed that the cooling system effluent would not contribute more than 50% of the total flow of the receiving stream because if it did, additional National Pollutant Discharge Elimination System (NPDES) permit requirements would be imposed. Mean and low stream flow rates were obtained from the Stream Dilution Factor Program (SDFP) used by the EAB of the EPA. Data from the steam electric power plant (SIC 4911) were chosen to represent the flows of receiving streams for cooling system effluent. The 50th and 10th percentile were used to generate at Gaussian distribution for low flow conditions. This procedure was repeated for high flow conditions, The mean flow rate was based on a 50th percentile annual average stream flow; the low flow is the lowest 7-d average flow rate recorded during a 10-y period. These were the most conservative data available. Flow conditions for 50th percentile and 10th percentile sites during times of mean and low flow were obtained from SDFP.

A constant treatment concentrations of 24 ppm was used for all simulations because it represents the maximum recommended concentration of DBNPA (as active ingredient) for bacterial treatments.

The output from the model included the DBNPA concentration in the discharged cooling water (ppm), DBNPA load in the discharged cooling water (kg) and final in-stream concentation; (ppb). Values of each output variable were described by distributrion of results from 15,000 trials.

Model equations

DBNPA concentration in the cooling water after it had passed through the system was calculated using the first-order decay equation shown below:

$$Cf\ (mg.l^{-1}) = Ci\ (mg.l^{-1})(e^{kt})$$

Where Cf is defined as the DBNPA concentration in the effluent at discharge into the stream and Ci is the initial treatrnent concentration. The decay rate constant is defined as k and time is t. In this simulation, the decay rate cannot he treated as a constant because the half-life of DBNPA is selected from a triangular distribution. Defining t =

t1/2 where Cf = C/2 and solving for the unknown constant k, we obtain k = ln2/t1/2. Substituting for the unknown k, we obtain DBNPA concentrations in the discharged cooling water based on known parameters: initial concentration, half-life, and residence time. This was calculated according to the equation:

$$\text{Cf (rng[L)} = \text{Ci (rng.l}^{-1}\text{)e}^{(-\ln 2/\text{HL (h) RT (h))}}$$

where HL is defined as the half-life of DBNPA and RT is the residence time (the amount of time it takes for water to pass through the cooling system).
Final in-stream concentrations, the output of greatest biological interest, were determined using the following equation:

if FR < SF/2,

$$\text{SC (µg.l}^{-1}\text{) = Cf (mg.l}^{-1}\text{).FR (MLD)/SF(MLD).1,000 µg.mg}^{-1}$$

where FR is defined as the effluent flow rate, SF as the stream flow rate, and SC as the in-stream concentration.

If the cooling system effluent flow rate obtained by random selection from the distribution of possible flow rates was more than one-half the flow rate of the receiving stream, the selected effluent flow rate was rejected and a new value for that effluent flow rate equal to one-half the stream flow rate was used. This substitution was performed to recognise that effluents do not usually contribute more than half of downstream flow.

Conclusion: This scenario can be applied for once-through cooling systems and can be adjusted to use for recirculation cooling systems. This scenario uses the degradation of the biocide to predict the concentration in water. The effluent flow rate and the stream flow rate are used to determine a realistic dilution in surface water. Thus only one substance dependent parameter (half-life) is used.

US-EPA CEB (Baur, 2000)

The model takes by default a blowdown of 0.6% of recirculating water flow rate per hour and a windage of 0.1% of the recirculating water flow-rate per hour.

$B = 0.6\% * Cas * Q * 24/1000 = 0.07 * Cas$

Cas	concentration of as in cooling water ($g.m^{-3}$)
Q	recirculation rate of cooling water ($m^3.h^{-1}$) - 450
B	as release ($kg.site^{-1}.d^{-1}$) via blowdown

$W = 0.1\% * Cas * Q * 24/1000 = 0.01 * Cas$

Cas	concentration of as in cooling water ($g.m^{-3}$)
Q	recirculation rate of cooling water ($m^3.h^{-1}$) - 450
W	as release ($kg.site^{-1}.d^{-1}$) via windage

Limitations of the model" it does not take into account for the calculation a.s. released amounts biotic and abiotic degradation in recirculation circuit, loss by evaporation, loss in STP (option).

Conclusion: This scenario can be applied for open recirculating cooling systems. This scenario only calculates the amount of biocide released. It uses a percentage loss of biocide by blowdown and windage to predict the amount of biocide release to the environment. No substance dependent parameters are used.

USES

The following assumptions have been made in this model:
- water blowdown is discharged to surface water (no STP treatment)
- concentration of biocide in system is constant and equal to dosed concentration (no dilution, no degradation, no loss)
- final dilution factor is by default 3

$$C_{waterpest\text{-}0} = C_{as,\ cooling}/((1+Kp_{susp}*SUSP_{water})*DILUTION_{cooling}$$

$C_{waterpest\text{-}0}$	concentration of chemical in surface water (PEC)
$C_{as,\ cooling}$	concentration of as in recirculating water (dosed concentration)
Kp_{susp}	solids-water partition coefficient in suspended matter
$SUSP_{water}$	concentration of suspended matter
$DILUTION_{cooling}$	dilution factor in receiving surface water (default dilution factor 3 - stagnant water like lakes)

As loss due to windage is also calculated on basis of 2% recirculating water loss per hour for old ORCT and less than 0.1% for new ORCT with a default factor of 0.025%.

$$DOSE_{pest} = Q_{circ}*C_{as,cooling}*F_{depos}/AREA_{soil,cooling}$$

$DOSE_{pest}$	dosage for one event ($kg.m^{-2}$)
Q_{circ}	quantity of water in circulation ($m^3.d^{-1}$) - 10000
$C_{as,cooling}$	concentration of as in recirculating water ($kg.m^{-3}$) - 0.0005
F_{depos}	fraction of water lost due to spray and wind drift - 0.00025
$AREA_{soil,cooling}$	soilsurface where deposition occurs (m^2) - 1000

Limitations of model: that model does not take into account large dilution by make-up water, biotic and abiotic degradations in the water circuit, losse by evaporation and windage, possible losses in STP and realistics dilution in rivers.

Conclusion: This scenario can be applied for once-through and open recirculating cooling systems. This scenario calculates the concentration in surface water by using a dilution factor and a substance dependent partition coefficient in suspended matter. A specific amount of the biocide us therefore bound to suspended matter. No degradation of the biocide is taken into account in this scenario.

RIZA 1 (Baltus & Berbee)

This is a model for a recirculation system. This model is not meant to be used for inclusion in the current methodes for evaluation of substances.

For the model the recirculation system is seen as a continuous flowing reactor with a large recycle. At a certain time a shock dosing is used. By makeupwater / blowdown and degradation the concentration in the system will decrease. For such a system a mass balance can be made. Terms of loss in this mass balance are degradation, adsorption, evaporation in cooling tower, loss by biocide action and blowdown.

Assumptions:

- Loss by evaporation is limited
- loss by degradation is very limited
- adsorption to the walls of the system are probably limited and are neglected
- loss by biocide action is unknown and is neglected
- the temperature in the system is considered to be homogenous and constant (40°C)
- the pH is around 8
- the degradationrate by hydrolysis is described as a pseudo first order reaction
- assumed is that at shock dosing the concentration level in the system will be at the target level C0
- the blowdown stream is much lower than the circulation flow stream

Mass balance:

$$\underbrace{V \frac{dCb}{dt}}_{\text{change}} = \underbrace{-Q_v * C_b}_{\text{blowdown}} - \underbrace{V*k*C_b}_{\text{turnover}}$$

V	volume of the system (m^3)
Cb	percentage of biocide in the system at point of time t
Qv	blowdown stream ($m^3.h^{-1}$)
k	first order rate constant
t	time (h)

The solution of the mass balance is:

$$C_b = C_0 * e^{-(Qv/V + k)t}$$

For substances that don’t degrade k=0.

For a existing situation the mass balance is further elaborated:

Volume 4500 m^3
blown down stream 203 $m^3.h^{-1}$
circulation stream 18000 $m^3.h^{-1}$
concentration factor 3
concentration at t=0 is 50 ppm

The contribution of the chemical degradation depends on the substance.

From the figure it follows that emissions may be limited by:
- refreshing the system before dosing; then dosing and closing the blowdown. After a few hours blowdown must be done because of the salt contents of the system. Biocide actiob is more efficient without dilution in the system.
The emission through blowdown is:

$E = Q_v \, {}_0\int^t C_0 * e^{-(Qv/V + k)t} * dt$ or $E = \frac{-C_0 \, Q_v}{(Q_v/V + k)} (e^{-(Qv/V + k)\,t} - 1)$

From the emission formule the maximum emission may be derived after infinite time. De e power reaches than the value zero. The maximum emission will be reached after about 60 hours. The maximum emission is

$$E_{max} = \frac{C_0 \, Q_v}{(Q_v/V + k)}$$

This maximum emission may be compared to the dosed amount C_0*V

From this the fraction that comes free after infinite time may be calculated:

$$\text{Fraction (\%)} = \frac{Qv}{(Qv + k*V)} * 100\%$$

Sometimes the pH of the system is somewhat higher which causes the hydrolyses to be quicker. This does not lead to mayor differences.

From the calculations it seems that some substances are almost completely released through blowdown over a period of time.

Conclusion: This scenario can be applied for open recirculating cooling systems. This scenario calculates the concentration in surface water using the volume of the system, the blowdown stream and the first order degradation rate constant. Only 1 substance dependent parameter is used. The release is calculated using the same parameters. Also the fraction of the substance remaining after use in the cooling system is also estimated.

RIZA 2 (Baur, 2000)

This model is to assess PECair and PECwater for recirculating cooling water, with forced ventilation and direct discharge

Cair = A*I*S/V
where

A	Volume of circulating cooling water (m^3) - 10000
I	dosage of active ingredients ($g.m^{-3}$) - 1
S	loss of evaporated water (%) - 4
V	Volume of cooling air (m^3) - 10000000

PECair=Cair*T*K
where

C	theoretical concentration of active ingredients at cooling tower outflow - 40 $ug.m^3$
K	factor estimated in test - <1
T	dilution factor until reaching the target area - 0.01

PECwater = B * I * D * U
where
B bleach off volume (m^3) - 500
I maximum content of active ingredients ($g.m^{-3}$) - 1
D dilution factor, closed system, 24 h (hydrolysis, decay time) - 100
U dilution factor - 10

Limitations of the model:
It does not take inot account for the calculation of PECwater dilution by make-up water, biotic and abiotic degradations in recirculating water circuit, losses by evaporation and windage, possible treatment in STP (option)

Conclusion: This scenario can be applied for open recirculating cooling systems. This scenario calculates the amount of biocide released to surface water using a dilution factor in the cooling system and in surface water and the amount of water blown down. No substance dependent parameters are used.

Baur 2000

This model is based on true biocidal product data (physico-chemical properties, degradation half-lifes, Kow) and on true cooling tower operating conditions data (a.s. dosage, dosage cycle length, volume of waters, make-up water, blowdown, windage).

1. The model calculates the max. biocide concentration C0 (initial dosed concentration)
2. From dilution with make-up water (M) and taking into account biocide fate in recirculating loop (Eb, Fads, Bdeg, Hdeg and Pdeg) it calculates C(t) (=biocide concentrations in recirculating water or blowdown along full dosage cycle)
3. It draws automatically C(t) curves for several consecutive cycles what is useful to know whether a biocide concentration equilibrium (flat part) can be reached (good operating conditions) or whether there is a risk of a.s. concentration build-up in the recirculating loop.
4. It offers the option to add a STP treatment with choice of STP units. The a.s. concentrations in STP influent and effluent is calculated taking into account residence time in STP, a.s. adsorption on flocs, biotic and abiotic degradation. The model assesses also the risks tot STP micro-organisms.
5. The model calculates PEC and PEC/PNEC for the water compartment taking into account a.s. dilution, degradation and adsorption
6. The model can be used to run on each ORCT simulation programs in order to optimize biocide treatment conditions at desired levels of risks.

The model is based on basic equations listed but it contains a higher level of mathematics to simulate continous dilution, a.s. degradation, evaporation.

Dosed concentration $Cai.d^{-1} = M/V$
M amount of biocide (a.s.) per dosage (gr)
V volume of recirculating water (m^3)

Average dosed concentration over a dosage cycle: $Cai/av=M/(V+U)$
U volume of make-up water over a cycle (m^3)

Average concentration in blowdowns: Cai/bl= Cai/av*f1*f2*f3*f4*..

f1	% a.s. loss by biodegradation
f2	% a.s. loss by abiotic degradation
f3	% a.s. loss by adsorption on suspended matter
f4	% a.s. loss by evaporation

Concentrations after STP: Cai/stp= Cai/bl* f5*f6*f7*..

f5	% a.s. loss by adsorption on flocs
f6	% a.s. loss by degradation in activated sludge unit
f7	rate of dilution in STP

Concentration in river: PEC= Cai/bl or Cai/stp* f8

f8	rate of dilution in receiving medium

In ORCT cooling water continuously recirculates through an heat exchanger where it picks up calories and subsequently through and evaporator where it release calories. Biocide is used to control biolfouling or recirculating water. Make-up water is added to balance water losses via blowdown, evaporation and windage.
Biocidal product dosage in ORCT is always done using intermittent mode, there is always a continuous dilution of biocide concentration along biocide cycle (time between 2 consecutive dosages), always losses of biocide by windage in evaporator and possibly by evaporation and often losses due to biotic and abiotic degradations. Other biocide losses may also occurr in sewage treatment plant (STP) by adsorption and degradation.

In open recirculating cooling towers, water continuously recirculates through heat exchanger and evaporator. Hot water leaving heat exchanger circulates to evaporator where heat is removed due to water evaporation. Cooled water is then recirculated to heat exchanger. To control chemistry of recirculating water a blowdown must be carried out and consequently make-up water must be added to balance water loss due to blow down. Fresh water must also be added to balance losses via evaporation and windage. Biofouling (bacteria and algae) in recirculating water comes from contamination by air contaminants in evaporator and in make-up water, Because biofouling causes reduction of heat exchange efficiency it is necessary to preserve recirculating water with biocidal products
Biocidal products is always added to recirculating water by using intermittent dosage mode. Dosage lasts for 15 to 60 minutes while biocide cycle (time between 2 dosages) may vary from 3-4 hours to several days, Biocide dosage must be well to avoid biocide concentration build-up in ORCT circuit.
Biocide concentration in water circuit is not constant along dosage cycle. Active substance (a.i.) concentration decreases continuously along dosage cycle because of dilution with make-up water added to balance water losses in blowdown-evaporation-windage, because of possible a.s. losses by adsorption and because of possible a.s. degradation.

<u>Important parameters inORCT</u>

V	Volume of water in CT circuit	m^3	300-10000
Q	recirculation flow rate	$m^3.h^{-1}$	100-20000
ΔT	temperature difference between hot and cooled water	C	5-10
E	water evaporation flow rate	$m^3.h^{-1}$	0.5-3% of Q

Wd	water windage flow rate	m^3.h^{-1}	0.2-0.3% of Q (natural)
	m^3.h^{-1}	0.3-0.5% of Q (forced)	
Bd	water blowdown flow rate	m^3.h^{-1}	0.6% of Q
Bdt	water losses flow rate	m^3.h^{-1}	0.8-0.9% *Q (natural) 0.9-1.1% * Q (forced)
M	Make-up water flow rate	m^3.h^{-1}	36-720
F	concentration rate factor	-	3-5
T	residence time in circuit	h	1-96
Bpd	biocidal product	kg.dosage^{-1}	
Asd	Active substance	% in product	
T’	Δ hours between 2 dosages	h	3-168

<u>Fates biocidal product</u>

H	Henry’s law constant	-	
Eb	Biocide evaporation	m^3.h^{-1}	
Fads	adsorbed fraction	-	
DT50 Bdeg		a.s. biodegradation half-life	d
DT50 Hdeg		a.s. hydrolysis half-life	d
DT50 Pdeg		a.s. photolysis half-life	d

As is released to surface water via blowdown waste direct discharge or after treatment in STP. In STP a.s. is diluted with other streams and may be eliminated by adsorption in flocculation-sedimentation unit and degraded in activated sludge unit. As elimination level will depend on STP type.
Final dilution is usually very important because ORCT blowdown flow-rates which range between 1 and 10 m^3.h^{-1} are very small compared to river flow-rates.

Dilution in cooling tower effluents after a single dosage: dilution with 1.04% blowdown.h^{-1}, 1.04% evaporation.h^{-1} and 0.2% windage.h^{-1}.

Model Equations
Cactive substance= (dose* %a.s)/V= (25750 * 0.025)/300 =2.1 ppm active substance

Cai/d = M/V 25750/300 = 85,833

Cai/av= M/(V+U) 25750/(300+696)= 26,573 gr/m^3

F1 = ln(2)/DT50 Bdeg
F2 = ln (2)/DT50 Hdeg
F3 = F1 + F2
F4 =(Bd+Wd+E)/(V*24)
T = 1/(F4+ F3)
Ceffluent = Cai/d*e$^{(-t/T)}$

Model in STP :
F6 = KP_{STP} * $SUSP_{STP}$
F7 = ln (2)/HL_{STP}
F8 = ln (2)/HLa_{STP}
F9 = ln (2)/HL_{STP}
F10 = Bd / (Bd +Qother)

$\mathrm{Degtot}_{STP} = (e^{(-RT1STP * F7)} * e^{(-RTaSTP *F8)} * e^{(-RT2STP * F9)})$
$RT_{tot} = RT1_{STP} + RTa_{STP} + RT2_{STP}$

$$\mathrm{Cstp}= \frac{\mathrm{Ceffluent} * F10 * (1- F6) * \mathrm{Degtot}_{STP}}{(1- RT_{tot} / T) * (e^{(-t/T)} - e^{(-t/RT\ tot)})}$$

$\mathrm{Cwater}_{pest-0}=\mathrm{Cstp}*\mathrm{DILUTION}$

The following parameter values are used in the model
Dosed at 2.1 ppm a.s.
V = 300 m^3
E = 15 $m^3.d^{-1}$
Wd = 3 $m^3.d^{-1}$
Bd = 30 $m^3.d^{-1}$

Bpd = 25.75 $kg.dosage^{-1}$
Asd = 2.5% in product
T’’= 12-48-168 h

DT50 Bdeg =18 h
DT50 Hdeg = 10000 h

Fraction of as adsorbed sewage sludge = Partit. coeff water-susp*density susp. matter

$RT1_{STP}$	Residence time in the primary clarifier = 5 h
HL_{STP}	Abiotic degradation coefficient in 1rst clarifier= 0 h^{-1}
RTa_{STP}	Residence time in aerated basin of STP= 12 h
HLa_{STP}	Biodegradation coefficient in STP = 0.7 h^{-1}
$RT2_{STP}$	Residence time in the secondary clarifier = 20 h
HL_{STP}	Abiotic degradation coefficient in 2nd clarifier= 0 h^{-1}

Conclusion: This scenario can be applied for open recirculating cooling systems. This scenario calculates the concentration in effluent, in STP and in surface water. This scenario uses 5 substance dependent parameters in the calculation. The method is however not completely clear. It is the most releastic scenario. It is not clear if it is necessary to take all these substance dependent parameters into account.

UK TGD 1 (Fielden, 1997)

Steps in lifecycle	Processes
Cleaning and disinfection	Drain out of system 100 m^3 * dosage
	Cleaning and disinfecting main chemical lost is chlorine system is filled and drained 2x within 24h and average free chlorine is 10 $mg.l^{-1}$ 200 m^3* 10 $mg.l^{-1}$= 2 kg chlorine
Normal operation	blowdown=evaporation/(concentration cycles -1) *dose-pest

	$1.75\ m^3.h^{-1}$= $1.75\ l.h^{-1}$ * dosage Evaporation 1% of flow rate Drift (<0.01% of flow rate in cooling towers fitted with drift eliminators) Windage ?
	leakage in the system: unknown

Assumptions:average system volume 100 m^3
average water flow rate 350 $m^3.h^{-1}$ (=3.5 times the capacity)
average cycles of concentration 3
average evaporation loss 1% of flow rate
average tower operation 24 $h.d^{-1}$; 360 $d.yr^{-1}$
blowdown usually after every 2-5 cycles of water through the tower
(Fielden, 1997)

Conclusion: This scenario can be applied for open recirculating cooling systems. This scenario calculates only the amounts of biocide released during the two different processes (cleaning and disinfection and normal operation). No substance dependent parameters are used.

UK TGD 2 (Fielden, 1997)

In closed systems there should be little loss of water, thus requiring small amounts of make up water. A closed system, following routine monitoring and treatment programmes, is expected to lose approximately 1% of the system volume per month.

The larger volumes of losses occur at various stages of the systems life cycle such as commissioning of a new system, changes to an existing system and the uncontrolled losses that occur prior to bringing a system back on line.

Each of these stages may result in a total drain of the system volume along with the treatment chemicals. There may also be losses of cleaning agent and spillages of treatment chemicals.

Four scenarios have been identified as potentially occurring during the life cycle of a closed system.

- New system precommission cleaning and filling with treatment chemicals.
- Changes or additions to new or existing systems.
- Design losses from correctly treated and monitored systems.
- Uncontrolled losses equal to or in excess of design loss due to irregular treatment or monitoring.

Generally releases from the system can be summarised under the following loss factors:

L1	Release during the addition of the formulation to the system.
L2	Design losses which are controlled as part of a routine programme.
L3	Draining and uncontrolled losses resulting from lack of a routine programme.
L4	Losses from the flushing process.
L5	Losses from the chemical cleaning process.
L6	Losses from the passivation process.
L7	Losses arising from acid descale of the boiler.

Losses during formulation of the chemical treatment are estimated to be up to 2 % of the finished product. This would be released through the cleaning out of equipment at the formulator’s site, not on the site where a closed system is installed.

Emissions of specific substances are calculated using the standard emission factor, dose and system capacity.

Steps in lifecycle	**Processes**	**Emissions** **UK TGD 2**	**mg.l^{-1}**
SCENARIO 1 New Systems Start Up (once during lifetime)	1.Initial flushing	L4 insoluble iron oxides	500-1000 mg.l^{-1}
	2.Chemical cleaning: non-acid cleaning second process (alternative) acid cleaning	L5a organic cleaning agent L5b iron corrosion products L5c Neutralised acid product[1] L5d Soluble iron+copper salt	30000-50000 mg.l^{-1} 500-2000 mg.l^{-1} 100-200 kg.m^{-3} 500-2000 mg.l^{-1}
	3.Passivation	L6 High nitrite passivation	1000-2000 mg.l^{-1}
	4.Inhibitor/biocide dosing	L1 Losses during chemical fill	0.5% of 4.3 kg.m^{-3} = 0.02 kg.m^{-3}
SCENARIO 2 Changes/additions (occasional)	5.Complete or partial drain-down	Complete L3 Chemical inhibitor formulation incl. biocide Partial: loss factor halved	4.3 kg.m^{-3}
	6.Changes/ additions to the system		
	7.Flushing	L4 insoluble iron oxides	500-1000 mg.l^{-1}
	8.Inhibitor/biocide dosing	L1 Losses during chemical fill	0.5% of 4.3 kg.m^{-3}= 0.02 kg.m^{-3}
SCENARIO 3 Existing process-uncontrolled Ongoing (up to 15 years)	9.No routine service visits	L3 chemical inhibitor formulation including biocide	0.043 kg.m^{-3} (=1% of total inhibitor package; 4.3 kg.m^{-3})
	10.Uncontrolled/continuous losses		
Problem solving as a result of 9 and 10 (infrequent)	11.System flushing		
	12.Chemical cleaning of boiler	L7 chemical clean of boiler plant (inhibited Hcl; followed by neutralisation with sodium hydroxide)	a 30 kg mixture used every 5 years for a boiler of 5000 l
	13.Chemical cleaning of system	L5c Neutralised acid product L5d Soluble iron and copper	100-200 kg.m^{-3} 500-2000 mg.l^{-1}

		salts	
	14.Flushing	L4 Insoluble iron oxides	500-1000 mg.l^{-1}
	15.Passivation	L6 High nitrite passivation	1000-2000mg.l^{-1}
	16.Dosing inhibitor/ biocide	L1 Losses during chemical fill	0.02 kg.m^{-3} (=0.5% of finished product) 1% in existing systems
SCENARIO 4 Existing process-controlled: Maintenance (ongoing)	17.Routine service visits		
	18.Design losses	L2 Design losses from inhibitor and biocide charged system (1% loss per month)	0.043 kg.m^{-3} (=1% of total inhibitor package; 4.3 kg.m^{-3})
	19. Inhibitor/ biocide dosing	L1 Losses during chemical fill (0.5% of finished product)	0.02 kg.m^{-3} (=0.5% of total inhibitor package; 4.3 kg.m^{-3}) 1% in existing systems
Final draining (once during lifetime)	20.Final draining when system life concluded		

Conclusion:

This scenario can be applied for closed recirculating cooling systems. This scenario calculates only the amounts of biocide released during two different processes (cleaning and disinfection and normal operation). For these calculations mostly fixed amounts are used. No substance dependent parameters are used.

ANNEX 3. TYPES OF SUBSTANCES

Table 3.1 Types of substances used for cooling systems in the Netherlands (nd = no data; na is not applicable) Donk, 1996

	Active substance	Use conc. in once-through systems	Use conc. in open systems	Use conc. in closed system	Target organism
1. Oxidising biocides					
1.1 chlorine/chlorine yielding chemicals					
	Sodium hypochlorite[6] CAS nr 7681-52-9 NaOCl		1-5[2] 0.1-0.2[1] 0.5-5 F0 after 5min[3] 0.5-5 maint.dose		aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)
	Calcium hypochlorite		1-5[2]		
	Sodium dichloro isocyanurate		1-5[2]		
	Trichloro isocyanuric acid		1-5[2]		
	Chlorine gas[4] CAS nr 7782-50-5 Cl_2				
	Chlorine hydroxide[6] CAS nr		0.2		
	Chlorine dioxyde[1] CAS nr 10049-04-4		*[2]		
	Ca(ClO)2.4H2O[4] CAS nr 7778-54-3				
	Na dichloro-s-triazine trione[4] CAS nr 51580-86-0				
	Trichloro-s-triazinetrione[4] CAS nr 87-90-1				
	1,3-Dichloro-5,5-dimethylhydantoin[4] CAS nr 118-52-5				
	1,2 bromine-yielding chemicals				
	Bromine chloride[4] CAS nr 13863-41-7				
	1-bromo-3-chloro-5,5-dimethylhydantoine[6] CAS nr 32718-18-6[3] CAS nr 16079-88-2[4] C5H6BrClN2O2[3]		2-7[1]		aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)
	1-Bromo-3-chloro-5-methyl-5-ethylhydantoin[4] -		0.2-5[2]		
	1,3-dichloro 5,5 dimethylhydantoin		0.2-5[2]		

	Active substance	**Use conc. in once - through systems**	**Use conc. in open systems**	**Use conc. in closed system**	**Target organism**
	Hypobromous acid/ hypobromite		1[2]		
	sodium bromide NaBr[6] CAS nr 7647-15-6 only active in combination with sodium hypochlorite[3]		1-5[2]; conc. depends on Cl dosing[1]		aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)
1.3 Non-halogen oxidising chemicals					
	ozone[6] CAS nr 10028-15-6		0.02-0.2[2] 0.015-0.2[1]		aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)
	hydrogenperoxide[6] CAS nr 7722-84-1		1-5[2]		
	Iodine/hypoiodous acid		0.3-1.5[2]		
	Iodophors		*[2]		
	Peracetic acid		1-5[2]		
	2. Non-oxidising biocides				
2.1 Isothiazolones					
	Isothiazolon mix[3] C4H5NOS/ 2682-20-4 + C4H4ClNO5/ 26172-55-4		1-5 (isothiazolones)[1] 1.5-5 $g.m^{-3}$ init.dose[3] 1.3 $g.m^{-3}$ maint.dose		
	2-methyl-4-isothiazolon-3-on[6] CAS nr 2682-20-4		1-30[2]	5-50 (isothiazolones)[2]	aerobic bacteria, fungi, yeast algae(1)
	5-chloro-2-methyl-4-isothiazolon-3-on[6] CAS nr 26172-55-4		1-30[2]		aerobic bacteria, yeast algae(1)
	5-chloro-2-methyl-3-(2H)-isothiazolone[4] CAS nr 26172-55-4				
	2-methyl-3(2H)-isothiazolone[4] CAS nr 2682-20-4				
	1,2-benzoisothiazolon-3-on[6] CAS nr 2634-33-5				
2.2 Quats					
	Alkyl trimethyl ammonium chloride		6-10[2]		
	dialkyl dimethyl ammonium chloride		6-10[2]		
	Alkyldimethylbenzylammoniumchloride[6] CAS nr 8001-54-5 (60% C14,30% C16,5%		6-10[2] 3-50 (quats)	5-50 (quats)[2]	aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)

	Active substance	**Use conc. in once - through systems**	**Use conc. in open systems**	**Use conc. in closed system**	**Target organism**
	C18,5%C12)Lutey CAS nr 53516-76-0 Lutey				
	alkyldimethylethylbenzylammoniumchloride^{6} (68%C12, 32% C14) Lutey CAS nr 85409-23-0 Lutey		3-50 (quats)		aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)
	Dialkylmethylbenzylammonium chloride^{4} (60%C14, 30%C16, 5%C18,5%C12)lutey CAS nr 73049-75-9				
	Dodecyl dimethyl ammonium chloride^{4} CAS nr 7173-51-5				
	didecyldimethylammoniumchloride^{6} CAS nr 7173-51-5		3-50 (quats)^{1}		aerobic bacteria, anaerobic bacteria, fungi, yeast algae
	Alkyldimethylbenzylammoniumchloride^{4} (50%C14, 40%C12, 10% C16) CAS nr 68424-85-2				
	oxydiethylenebis alkyldimethylammonium chloride^{4} (40%C12, 50%C14, 10%C16) CAS nr 68607-28-3				
2.3 Ionene polymeric quats					
	poly(oxyethylene-(dimethyliminio)-ethylene-(dimethyliminio)-ethylenedichloride^{6} CAS nr 31075-24-8		3-50 (quats)		aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)
	poly(oxyethylene-(dimethylimino)-ethylene-(dimethylimino)-ethylenedichloride^{4} CAS nr 31512-74-0		3-50^{2}		
2.4 Organo-sulphur compounds					
	disodium ethylenebis (dithiocarbamate) ^{4} CAS nr 142-59-6		11-20^{2}		
	Sodium dimethyldithio carbamate^{4} CAS nr 128-04-1		11-20^{2}		
	bis-dimethylthiocarbomoyl disulphide		nd^{2}		

	Active substance	Use conc. in once - through systems	Use conc. in open systems	Use conc. in closed system	Target organism
	Potassium N-methyl dithiocarbamate[4] CAS nr 137-41-7				
	Disodium cyanodithio imidocarbamate CAS nr 138-93-2				
	2-(thiocyanomethylthio)benzothiazole[4] CAS nr 21564-17-0				
	Methylenebis (thiocyanate)[4] CAS nr 6317-18-6		0.75-5[2] 2-6[1]		
	Potassium N-hydroxymethyl-N-methyldithiocarbamate[4] CAS nr 51026-28-9				
	Potassium dimethyl dithiocarbamate[4] CAS nr 128-03-0				
	Bis(trichloromethyl)sulphone[4] CAS nr 3064-70-8				
2.5 Organotins compounds					
	Bis(tributyltin)oxide[4] CAS nr 56-35-9				
2.6 Guanidine compounds					
	Dodecylguanidine hydrochloride[4] CAS nr 112-65-2				
	Dodecylguanidine acetate[4] CAS nr 2439-10-3				
2.7 Organo-bromo compounds					
	methyl 2,3 dibromo propionate[4] CAS nr 1729-67-5				
	2-bromo-4-hydroxy acetophenone[4] CAS nr 2491-38-5				
	ß-bromo- ß- nitrostyrene[6] CAS 7166-19-0		1-5[1]		aerobic bacteria, anaerobic bacteria, fungi, yeast algae(1)
	2-bromo-2-nitro-(1,3)-propanediol (bronopol)[6] CAS nr 52-51-7		200-1500[2] 1-25[1]		aerobic bacteria, anaerobic bacteria, fungi and algae
	2,2-dibromo-3-nitrilopropionamide (DBNPA)[6] CAS nr 10222-01-2 C3H2ON2Br2		1-50[2] 4-10[1] 6-12 g.m^{-3}. init.dose[3]		aerobic bacteria, fungi, yeast algae(1)

	Active substance	Use conc. in once - through systems	Use conc. in open systems	Use conc. in closed system	Target organism
			3-12g.m^{-3} maint.dose[3] Algae/fungi 6-12 g.m^{-3} init.dose[3] 3-12 g.m^{-3} maint.dose[3]		
2.8 aldehyde compounds					
	glutaraldehyde[6] CAS nr 111-30-8 $C_5H_8O_2$		1-50[2] 25-50[1] 15-50 g.m^{-3} init.dose[3] 5-30 g.m^{-3} maint.dose[3]	5-50[2]	aerobic bacteria, anaerobic bacteria(1)
	glutaraldehyde bis (sodium sulphite) [4] CAS nr 7420-89-5				
2.9 Amine/imidazole compounds					
	1-(alkylamino)-3-amino-propane monoacetate[4] CAS nr 61791-64-8				
	1-(2-hydroxyethyl)-2-alkyl-2-imidazoline[4] CAS nr 61791-39-7				
2.10 Chlorophenat/phenolic compounds					
	pentachlorophenol, sodium salt[4] CAS nr 131-52-2				
	Sodium 2,4,5-trichlorophenate[4] CAS nr 136-32-3				
	Chlorinated phenols		50[2]		
2.11 Other biocides					
	methylenebisbenzamide[6] CAS nr		2-6[1]		
	Methylenebisthiocyanate[1] CAS nr 6317-18-6				aerobic bacteria, fungi, yeast (1)
	2,2-dithiobisbenzamide[6] CAS nr 2527-57-3				
	N-(1,2-dimethylpropyl)-N-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine[4] CAS nr 22936-75-0				
	Nonylphenoxypolyethoxyethanol-iodine complex[4] CAS nr 11096-42-7				

	Active substance	Use conc. in once - through systems	Use conc. in open systems	Use conc. in closed system	Target organism
	Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2 thione[4] CAS nr 149-30-4				
	Copper sulphate[4] CAS nr 7758-99-8				
	Ortho-phenylphenol		nd[2]		
	2-thiocyanomethylthio-benzothiazole (TCMTB)		nd[2]		
	Formaldehyde release agents		nd[2]		
	Alkyl 1,3-propylene diamine salt		nd[2]		
	Poly(hexamethylene-biguanide) hydrochloride		21-50[2]		
	tributyl tetradecylphosphonium chloride		nd[2]		
3. Oxygen scavenger					
	Sodium sulphite			50-100[2]	
	Hydrazine			1-10[2]	
	Diethylhydroxylamine			1-10[2]	
	Methylethylketoxime			1-10[2]	
	Tannins			50-150[2]	
4. pH controllers					
	Cyclohexylamine			5-20[2]	
	Morpholine			5-20[2]	
	sodium hydroxide			300-500[2]	
5. Scale control					
	disodium phosphate			30-100[2]	
	trisodium phosphate			30-100[2]	
6. Dispersants					
	sodium polyacrylate			50-150[2]	
	sodium polymethacrylate			50-150[2]	
	polymaleic acid			50-150[2]	
	polymaleic acid-sulphonated styrene copolymer			50-150[2]	
7. Antifreeze					
	Ethylene glycol			25-33%[2]	
8. Corrosion inhibitors					
	sodium nitrite		5-150[2]	800-1200[2]	
	sodium borate		na	50-500[2]	
	sodium molybdate		2-15 molybdate[2]	100-500[2]	
	sodium silicate		5-25[2]	10-50[2]	
	triethanolamine phosphate		na	100-500[2]	aluminium[2]
	Mercaptobenzthiazole		1-5[2]	2-10[2]	copper[2]
	tolyltriazole		1-5[2]	2-10[2]	copper[2]
	benzotriazole		1-5[2]	2-10[2]	copper[2]

	Active substance	**Use conc. in once - through systems**	**Use conc. in open systems**	**Use conc. in closed system**	**Target organism**
	Sodium phosphate		5-25 (ortho and poly) ^{2}		
	zinc chloride or sulphate		5-20^2 2-10 zinc ^{2}		
	phosphonobutane-1,2,4-tricarboxylic acid		5-20^2		
	hydroxyethylidene diphosphonic acid		5-20^2		
	hydroxyphosphonoacetic acid		2-10^2		
	amino tri(methylene phosphonic acid)		5-20^2		
	amino tri(methylene phosphonic acid)		2-10^2		
	Chromate				
	Zinc				
	Molybdate				
	Silicates				
	polyphosphates				
	phosphonates				
	all organics				
9. Scale and deposit inhibitors					
	phosphonobutane-1,2,4-tricarboxylic acid		2-10^2		
	Tannins		10-100^2		
	Polymaleic acid		5-20^2		
	amino tri(methylene phosphonic acid)		5-20^2		
	amino tri(methylene phosphonic acid)		2-10^2		
	Polyacrylic acid		5-20^2		
	Polymethacrylic acid		5-20^2		
	Polyethylene glycol		5-20^2		
	Maleic acid-styrene copolymer		5-20^2		
	Maleic -methylvinylether		5-20^2		
	Maleic - ethylacrylate - vinylacetate		5-20^2		
	Phosphino polyacrylates		5-20^2		
	Hydroxyethylidene diphosphonic acid		2-10^2		
	Phosphate esters		2-10^2		
	Amino tri(methylene phosphonic acid)		2-10^2		
	diamine tetra(methylene phosphonic acid)		2-10^2		
	diethylene triamine		2-10^2		

	Active substance	**Use conc. in once-through systems**	**Use conc. in open systems**	**Use conc. in closed system**	**Target organism**
	penta(methylene phosphonic acid)				
	Sulphonated polystyrene		5-20[2]		
	Sulphonated styrene - acrylate copolymer		5-20[2]		
	Sulphonated styrene - maleic copolymer		5-20[2]		
	Allyl sulphonate - maleic copolymer		5-20[2]		
	Lignosulphonates		10-100[2]		
	Hydroxy phosphono acetic acid		2-20[2]		
	Polyacrylamide		5-20[2]		
	Partially hydrolysed polyacrylamide		5-20[2]		
	Polyethylene imines		2-10[2]		
	Poly isopropanyl phosphonic acid		2-10[2]		
	Polyesters				
10	**Hardness sediment**				
	Phosphonates				
	all organics				
	Synthetic polymers				
11	**Other sediment**				
	all organics				
	natural organic substances				
	Synthetic polymers				

1 Baltus & Berbee, 1996; 2 Stuk UK; 3 Adriaensen, 2001; 4 Lutey, 1995; 5 Assink, 1991; * ppm Fo

ANNEX 4. PHYSICAL AND CHEMICAL CHARACTERISTICS OF SUBSTANCES USED.

Table 4.1 Physical and chemical characteristics of substances used for cooling systems in the Netherlands

	Active substance	pH-area	Reaction rate	Hydrolysis rate
1. Oxidising Biocides				
1.1 chlorine/chlorine yielding chemicals				
	Sodium hypochlorite CAS nr 7681-52-9 NaOCl	6.0-8.5[1]	rapid[1]	short[1]
	Sodium dichloro isocyanurate C_3HCl_2N3Na[6]		fast[6]	
	Chlorine dioxyde CAS nr 10049-04-4 ClO_2[6]		very fast[6]	
1.2 Bromine-yielding chemicals				
	Bromine chloride CAS nr 13863-41-7 NaBr		fast (together with NaOCl) [6]	
	1-bromo-3-chloro-5,5-dimethylhydantoine CAS nr 32718-18-6[3] CAS nr 16079-88-2[4] C5H6BrClN2O2[3,6]	6.5-9.5[1]	rapid[1]	short[1]
	sodium bromide NaBr CAS nr 7647-15-6 only active in combination with sodium hypochlorite[3]	6.0-9.5[1]	rapid[1]	short[1]
Non-halogen oxidising chemicals				
	ozone CAS nr 10028-15-6 O3	6.5-9.5[1]	rapid[1], very fast[6]	-
	hydrogenperoxide CAS nr 7722-84-1 H2O2		fast, unless stabilized[6]	
	Peracetic acid C2H4O3[6]		fast[6]	
2. Non-oxidising biocides				
2.1 Isothiazolones				
	Isothiazolon mix[3] C4H5NOS/ 2682-20-4 + C4H4ClNO5/ 26172-55-4			100 d:pH 4-4.5+T=7C 83 d: pH 8 + T= 7C 11.4d: pH 8 + T=25C 6.8d: pH 8 + T=30C 2.6d: pH 8 + T=40C 92.9d: pH 9 + T=7C 4.6d: pH 9 + T=40C 8.2d: pH 11 + T=7C 0.072d: pH 11+T=40C

	Active substance	pH-area	Reaction rate	Hydrolysis rate
				Krzeminski, et al, 1975a in Balthus et al, 1999
	2-methyl-4-isothiazolon-3-on CAS nr 2682-20-4 C4H5NO5[6]	6.0-9.0[1]	slow [1,6]	long[1,6]
	5-chloro-2-methyl-4-isothiazolon-3-on CAS nr 26172-55-4 C4H4ClCNO5[6]	6.0-9.0[1]	slow [1,6]	long[1,6]
	1,2-benzoisothia-zolin-3-on CAS nr 2634-33-5 C9H6N2S3[6]		slow [6]	long[6]
2.2 Quats				
	Alkyldimethylbenzylammoniumchloride CAS nr 8001-54-5 (60% C14,30% C16,5% C18,5%C12)Lutey CAS nr 53516-76-0 Lutey	7.0-8.5[1]	average[1]	average[1]
	alkyldimethylethylbenzylammoniumchloride (68%C12, 32% C14) Lutey CAS nr 85409-23-0 Lutey R(CH3)2(C8H9)NCl[6]	7.0-8.5[1]	average[1,6]	average[1,6]
	didecyldimethylammoniumchloride CAS nr 7173-51-5 C22NH48Cl[6]	7.0-8.5[1]	average[1,6]	average[1,6]
	alkyldimethylbenzylammoniumchloride (50%C14, 40%C12, 10% C16) CAS nr 68424-85-2 R(CH3)2(C7H7)NCl[6]		average[6]	average[6]
ionene polymeric (quats)				
	poly(oxyethylene-(dimethyliminio)-ethylene-(dimethyliminio)-ethylenedichloride CAS nr 31075-24-8 (C10H24N2O.Cl_2)n[6]	7.0-8.5[1]	average[1,6]	average[1,6]
	poly(oxyethylene-(dimethylimino)-ethylene-(dimethylimino)-ethylenedichloride CAS nr 31512-74-0			
Organo-sulphur compounds				
Organotin compounds				
Guanidine compounds				

	Active substance	pH-area	Reaction rate	Hydrolysis rate
Organo-bromo compounds				
	ß-bromo- ß- nitrostyrene CAS 7166-19-0 C8H6NO2Br[6]	6.0-8.5[1]	rapid[1,6]	short[1,6] 6 h:pH 5 + T=25C 0.6 h: pH 6 + T= 50C 4.8 h: pH 8 + T=25C 0.6 h: pH 8 + T=50C 0.3 h: pH 8.5 + T=50C 1.5 h: pH 9 + T=25C <0.1h: pH 11 + T=50C in Balthus et al, 1996 en 1999
	2-bromo-2-nitro-(1,3)-propanediol (bronopol) CAS nr 52-51-7 C3H6NO4Br[6]	6.0-9.5[1]	average[1,6]	long[1,6] >> 5 y:pH 4-4.5+T=5C >>5 y:pH4-4.5+T=22-25C > 2 y:pH 4-4.5+T=40C 2 w: pH 4-4.5+ T=60C > 6 y: pH 6 + T=5C 6 y: pH 6 + T=22-25C >4 m: pH 6 + T=30C 4 m: pH 6 + T=40C 36 h: pH 6 +T=60C 6 m: pH 8 +T=5C 4 m: pH 8 +T= 22-25C 14 d: pH 8 + T=30C 8 d: pH 8 + T=40C 3 h: pH 8 + T=60C in Balthus et al, 1996 en 1999
	2,2-dibromo-3-nitrilopropionamide (DBNPA) CAS nr 10222-01-2 C4H2ON2Br2[6]	6.0-8.5[1]	rapid[1,6]	short[1,6] 38 d:pH 6 + T=10C 12 d: pH 6 + T= 20C 3 d: pH 6 + T=30C 20 h: pH 6 + T=40C 4 d: pH 7 + T=10C 30 h: pH 7 + T=20C 9 h: pH 7 + T=30C 2 h: pH 7 + T=40C 13 h: pH 8+T=10C 3 h:pH 8 +T=20C 1 h: pH 8 + T=30C 0.2 h: pH 8 + T=40C 1.5 h: pH 9 + T=10C 0.5 h: pH 9 + T=20C 0.15 h: pH 9 + T=30C in Balthus et al, 1996 en 1999
aldehyde compounds				
	glutaraldehyde CAS nr 111-30-8	6.0-9.0[1]	average[1,6]	average[1,6]

	Active substance	pH-area	Reaction rate	Hydrolysis rate
	C5H8O2 CHO-(CH2)3-CHO[6]			
Amine/imidazole compounds				
Chlorophenat/phenolic compounds				
Chlorinated phenols				
others				
	methylenebisthiocyanate CAS nr 6317-18-6 CH2(SCN)2	6.0-8.0[1]	rapid[1,6]	short[1,6] stabile:pH 5+T=24C 12 d: pH 6 + T= 24C 21 d: pH 7 + T=24C 5 d: pH 8 + T=24C 2 d: pH 8 + T=24C in Balthus et al, 1999
Oxygen scavenger				
pH controllers				
Scale control				
Dispersant				
Antifreeze				
Corrosion inhibitors				
Scale and deposit inhibitor				
Hardness sediment				
Other sediment				

1 Baltus & Berbee, 1996; 2 Stuk UK; 3 Adriaensen, 2001; 4 Lutey, 1995; 5 Assink, 1991; 6 Donk & Jenner, 1996;
* ppm Fo

ANNEX 5: SELECTION OF A BIOCIDE

Selection of biocide
In the choice of the most suitable biocide for the treatment of cooling water systems the following aspects are important: type of cooling water system, chemical and microbiological parameters of the cooling water and other additives that are added to the system like corrosion inhibitors or dispergants.
The water in once-through systems have a short residence time. For this reason the rapid reacting oxidising biocides will be used for the treatment of these systems. Furthermore it is economicly not interesting to use non-oxidising biocides because of the large quantities of water that are used in these once-through systems and this would also mean an environmentally important load by discharge. (Baltus & Berbee, 1996).

In both once-through as recirculating systems the first choice will be made for sodium hypochlorite. Firstly because this is financially the most appealing option. In some situation sodium chlorite can not be applied. In case of heavy pollution of the cooling water with organic pollutants of with contaminants resulting from leakages from the production process, the use of chlorine will increase strongly and the active chlorine will be less effective. Other aspects that are important for the choice of a biocide are the costs, the handling and the safety aspects of the biocide. Furthermore the admissibility of the possible causes of the surface water in which the water is discharged is also important. (Baltus & Berbee, 1996).

In closed recirculating systems the remaining time in the system may be some months, by which reason great amounts of corrosion inhibitors are added to the system. Because only less make-up water is added to the system and because there is no contact with the atmosphere, the chance for microbiological pollution is limited and practically no or only some biocide is necessary. If they are necessary they will be applied together with corrosion inhibitors, they have to be fairly stable and will have to keep their biocide action for a long time (Baltus & Berbee, 1996).

The use of a broad spectrum biocide is part of a sound microbiological control programme used in process cooling water systems (prevention or routine maintenance). The greatest success of these broad spectrum biocides is achieved when broad-spectrum biocides are used in conjunction with consideration to:

- system design considerations
- selection of materials of construction
- physical and chemical maintenance cleaning
- water source considerations
- treatment during outages and wet layup
- treatment during hydrostatic testing
  (Lutey, 1995)

The same factors must be considered when facing an existing microbiological problem. In this more specifically algicide, fungicide or bactericide may be used. The application of a biocide is usually a second step following cleaning or in some cases s supplementary factor in conjunction with the chemical/physical cleaning (Lutey, 1995).
In actual operating systems the combined microbial population follow a typical biological growth curve. This consists of a lag phase where the reproduction rate and death rate of the micro-organisms are relatively equal at a low level. If the reproduction rates are stimulated by changes in the system, the population enters into the log phase. At this

point the critical level, at which problems begin to appear in the system, is exceeded. Once the limits of the environment for supporting an increasing population has been reached, the microflora enters into the stationary phase. In this phase most of the chronic or mature microbiological problems persist. Then a mitigation treatment programme is necessary.

It is obvious that maintaining the population in the lag phase is primary object. The understanding of the population dynamics and the conditions that control population growth curve, is important for the selection of the biocide and the conditions (when, where, how much, frequency, adjusting system parameters) under which this biocide is applied (Lutey, 1995).

When implementing a mitigation programme, the process cooling water system must be thoroughly cleaned (chemically and physically) after which the system should be drained and flushed with clean water. When the system is refilled it should be treated initially with a relatively high dosage of a biocide (3-5x the maintenance dosage). The use of a dispergant is recommended to assist removal of deposits and to help disperse plugging and fouling deposits (Lutey, 1995).

There are biocides wich kill the microorganisms and biostats that inhibit their growth or reproduction (Lutey, 1995). Both can be used to maintain the microbial population in the lag phase. Biostat concentration usually is maintained at a constant residual level, in contrary to a biocide. The biocide is used in such a way that the reproduction rate of the microorganisms never exceed the death rate. (Lutey, 1995)

For existing operating conditions usually broad spectrum biocides are used, except when certain specific troublesome microorganisms, such as Desulphovibrio sp., Gallionella sp, are present in the system (Lutey, 1995).

Once-through systems usually involve a more limited group of microorganisms with a fairly constant level of inoculum entering the system. Therefore a more selective biocide may be appropiate. In this case costs become a consideration because of the large amounts of water that go through the system (Lutey, 1995)

Closed loop systems have limited make-up water requirements and are not exposed to varied or continuous contamination. The water is typically circulated in a tightly closed loop. These conditions provide the situation where a specific biocide effective against a stable microflora with minimum recontamination can be selected (Lutey 1995)

Virtually all recirculation systems are treated with additional chemicals for the prevention of scale formation, minimizing sedimentary deposits, and inhibiting corrosion. The selected biocide should be compatible with the other treatments in the system.

The are several characteristics of the water being treated that affect the biocide effectiveness. The pH of water is perhaps the most significant factor that affects biocide efficacy. Above pH 8.3, many copper-based compounds precipitate into non-active salts. Methylene bisthiocyanate compounds hydrolyse at a rapid rate above pH 8.0. Phenate and chlorophenol-base biocides ionize to less active materials at above pH 8.5. Most oxidising biocides are significantly less active and have minimal oxidising capabilities above pH 8.0. On the other hand, some organo-sulphur and quarternary ammonium compounds have a higher level of effectiveness above pH 8.5 (Lutey, 1995).

Temperature may affect the activity of certain biocides. Quarternary ammonium compounds are sensitive to high temperatures (above 120 F). Organo-sulphur and thiocyanate compounds become less effective under most conditions when temperatures increases. Ozonation and peroxide materials are less effective as the temperatures increase. Excessive dissolved solids can effect biocide effectiveness. High levels of calcium (hardness ions) will inhibit the activity of certain cationic quaternary ammonium compounds, as will high levels of chlorides. Organo-sulphur and thiocyanates form complexes with dissolved iron and biocidal effectiveness is reduced. Most chlorine/bromine oxidising biocides are inactivated in the presence of hydrogen sulphide and ammonia. High levels of suspended solids can have a profound effect on the activity of certain biocides such as the cationic alkyl-quaternary and polymeric quaternary ammonium compounds. Cationic biocides will complex with the anionic charged suspended particles of silt, debris and other non-charged suspended materials in the water (Lutey, 1995).

Heavy metal biocides, phenolic-based compounds, formaldehyde donors and other persistent organic compounds have essentially been banned from use in many cooling water systems throughout the world.

The biocide chosen must be one that can easily be detoxicified, decomposed or biodegraded before discharged to water (Lutey 1995).