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CONFEDERACIÓN
HIDROGRÁFICA
DEL EBRO

Consultancy services to assist and advise Confederación Hidrográfica del Ebro for control and mitigation of the Zebra mussel within the EU regulations

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EXECUTIVE SUMMARY

The Zebra mussel was detected for the first time in the waters of the Ebro Basin in July 2001, at the Flix bend and the Ribarroja reservoir. Since 2001, the Ebro Hydrographic Confederation (CHE) has been developing measures of control against the invasion and disclosure of this pest species and to prevent its spread to the rest of river basins in Spain. KEMA has been contracted to provide the Confederación Hidrográfica del Ebro with consultancy services and assistance for the control and mitigation of the Zebra mussel in the Ebro river basin. For this, information on the biocides which can be applied by the companies according to the European legislation will be provided.

This report describes the first two phases of this project which consists of:

Phase 1:

- analysis of the previous works made by the CHE: critical review of the work performed by the CHE in this area
- international analysis: an international research and analysis (‘*desk study’)* in order to identify all the current techniques that are used to control the mussel as well as the regulatory requirements that are applicable in other countries, with a focus on the EU countries
- preparation of a handbook/document presenting the international best practices in mitigation of the Zebra mussel, including advantages and disadvantages of each technique
- evaluation of the possible coming innovative technologies that can be applicable to control the mussel in the near future.

Phase 2:

- definition of groups of companies along the Ebro River ('clusters') and identification of the different techniques that are applicable per group of companies
- Best Available Techniques (BAT) per cluster of companies and technology
- a definition of the limits of the emissions to the water per BAT and cluster of companies and technology. These limits will be according international regulations and will confirm the IPPC BREF document
- identification of the potential threat for invasion of new macro fouling species in the near future
- identification of some key initiatives (‘*road map*’) to be done by the CHE afterwards.

From the study carried out for CHE the following conclusions and remarks can be made:

- no technique is BAT for all cooling water intake systems. The intake flow, system design and water quality determine which type of fouling control method is BAT for each type of company. Therefore the BAT as determined during this research study should be used as a guideline and for each different company the BAT should be determined when more information is available from this specific location
- in general it can be concluded that chlorine is the most cost effective method to prevent fouling of Zebra mussels in cooling water systems. Chlorine is relatively cheap, easy to dose and when applied correctly there are no negative long term effects on the receiving environment
- heat treatment to control fouling in a cooling water system is an accepted method in The Netherlands. Thermoshock can be used only if the cooling water system is equipped with a proper recirculation system and can withstand a temperature increase to about 45°C. The thermoshock method involves a certain level of production penalty for the power plant due to recirculation of heated water
- the use of coatings can be very beneficial since they do not produce byproducts which can be discharged in the river system. Also coatings can be very helpful to prevent fouling of intake structures like bar screens. Coatings could be used also in combination with chlorine. A coating could protect the intake structure until the dosing point of chlorine
- Pulse-Chlorination could also further reduce the amount of chlorine that needs to be dosed to mitigate zebra mussels that settled. However, due to the CAPEX costs to install this dosing technology it will be only cost beneficial for CWS with an intake flow > 5 m^3/second
- the period to mitigate zebra mussels should be adjusted to the cooling water system capability to flush a certain size of shells through their system. This is only applicable in once through cooling water systems and could reduce the chlorine dosing period to only 4 to 6 weeks per year
- dosing period needs to be adjusted to fouling season, this means that the period of using a biocide can be reduced in time and tailor made for specific species and location
- further optimisation using tailor made dosing structure to optimize dosing and dispersion and minimise use of product
- monitoring both chemical and biological is advised to have a reliable check on the dosing and discharge concentrations and the efficacy of the treatment
- discharge limits can be implemented according to EU regulations however it is mandatory to apply BAT. Within the BAT the permit must contain the emission limit values
- the discharge limits for the biocides used can be adjusted by CHE if required.

1 INTRODUCTION

1.1 Background

Zebra mussel

The Zebra mussel was detected for the first time in the waters of the Ebro Basin in July 2001, at the Flix bend and the Ribarroja reservoir. Since 2001, the Ebro Hydrographic Confederation (CHE) has been developing measures of control against the invasion and disclosure of this pest species and to prevent its spread to the rest of river basins in Spain. The Ebro Hydrographic Confederation is concerned about the toxicity of effluents in the environment. In 2004, the presence of adult zebra mussels was confirmed in the Mequinenza reservoir and, in 2006, in the Sobron reservoir.

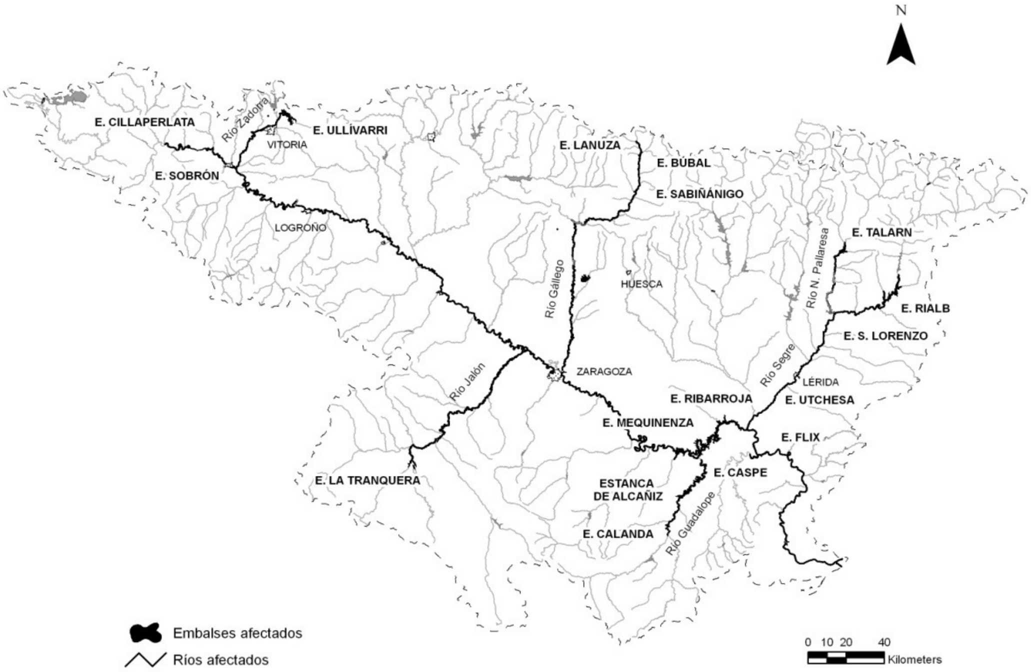

Figure 1 Distribution of the Zebra mussel in the Ebro River

Control of fouling

Both micro fouling (biofilms) and macro fouling (mussels, hydroids, etcetera) have to be mitigated in order to ensure the continuous operation of the cooling system in all kinds industrial production processes. Too much fouling in the cooling system can impair its

performance and lead to physical damage in the construction. Colonization of cooling water systems by mussels and other fouling organisms is a major concern for power plants and industrial companies, all over the world in any water type.
The affected companies apply biocides as the principal method to control the settlement and growth by Zebra mussels in their cooling and process water systems. However, in many cases, due to the lack of knowledge, the proper dose is not applied in accordance to the volume of water to be treated. This can cause effluents with high residual biocide concentrations (overshooting) with potential impact in the environment, or too low concentrations (no-effect) with potential effects in the cooling water system.

In this project, KEMA has been contracted to provide the Confederación Hidrográfica del Ebro with consultancy services and assistance for the control and mitigation of the Zebra mussel in the Ebro river basin. For this, information on the biocides which can be applied by the companies according to the European legislation will be provided.

1.2 **Objective**

The project is divided in three phases:

- phase 1; performance of a comprehensive analysis of both CHE’s specific situation and needs (‘internal’) and the international best practices ("external")
- phase 2; assistance of the Confederación Hidrográfica del Ebro in setting up a dedicated handbook for all industrial (cooling) water users
- phase 3; assistance of Confederación Hidrográfica del Ebro during the implementation.

This report covers phase 1 and 2 of the project.

2 PROJECT SETUP

Phase 1 of the project includes the following tasks:

- analysis of the previous works made by the CHE: critical review of the work performed by the CHE in this area (and provide recommendations)
- international analysis: an international research and analysis (‘*desk study’)* in order to identify all the current techniques that are used to control the mussel as well as the regulatory requirements that are applicable in other countries, with a focus on the EU countries
- preparation of a handbook/document presenting the international best practices in mitigation of the Zebra mussel, including advantages and disadvantages of each technique
- evaluation of the possible coming innovative technologies that can be applicable to control the mussel in the near future.

In the second phase of the project, a dedicated handbook for all industrial (cooling) water users is set up. The following tasks are involved:

- definition of groups of companies along the Ebro River ('clusters') and identification of the different techniques that are applicable per group of companies
- Best Available Techniques (BAT) per cluster of companies and technology
- a definition of the limits of the emissions to the water per BAT and cluster of companies and technology. These limits will be according international regulations and will confirm the IPPC BREF document
- identification of the potential threat for invasion of new macro fouling species in the near future
- identification of some key initiatives (‘*road map*’) to be done by the CHE afterwards.

3 PREVIOUS WORK CARRIED OUT BY CHE

The first population of the zebra mussel (*Dreissena polymorpha*) in Spain was discovered in 2001 in a reservoir called Ribarroja. The two main ways in which the zebra mussels spread to other areas are by external fouling on exposed hulls and by bait buckets of fishing vessels. For these reasons, the CHE drew up a new navigation code according to Environmental and Wild Life Services of local governments which was passed in the Government's Session on 16/09/2002 and was published in the Official Bulletin of the Spanish State (BOE, 2002). The new code established a new set of rules for the zebra mussel infected area, as for example, a special license for this area, the obligation to disinfect vessels which go in and out of these areas, etc. In 2003 a Technical Working Group was established to define Actions Plans.

Considering the experience of other countries and our knowledge of the new environmental conditions of Lower Ebro (previously described), which allows for quicker growth and a higher reproductive rate of the zebra mussel, it is expected that mussels in the Ebro basin waters would show a very high adaptability to the new environmental conditions, which could result in quick proliferation and spread. Years of monitoring have confirmed this prediction. An eradication of the species will be impossible and therefore different actions are taken with the main objective of slowing down or preventing its expansion and to make people aware of the serious situation of the invasion, the damage it causes and the need to act responsibly to prevent the spread.

The results of larval studies show a maximum population of larvae in the Ribarroja-Flix reservoir in the month of July, coinciding with the maximum temperature. Besides this reservoir the Mequinenza reservoir is also a major source. These results support the suspicion that the reservoir is, at this moment, the main source of zebra mussel larvae and this information is vital for proper control. The data, obtained from the fixed test units, provides information about the development and colonization of zebra mussels and its spread to other areas of the river. These test units have been shown to be efficient for early zebra detection in the whole region, both in reservoirs and in rivers sections. It has been decided by CHE to install this methodology in other reservoirs and rivers that are not colonized, but which are at risk due to the fishing, canoeing, etc. Manual cleaning is mentioned in other reports from CHE, however this was not possible due to the size of the infected area (more than 10,000 ha). The experience with manual removal, has demonstrated that huge resources in terms of time and manpower are necessary to remove zebra mussels. Mechanical extraction such as vacuum suction seemed promising for small places or local structures, although it would be necessary to improve its design. The changes in the navigation rules to stop the invasion of zebra mussel has been not sufficient to avoid the spread but is needed to slow down the invasion of zebra mussels of other areas within the basin or of other basins. National Legislation would be needed to manage any future invasion. The inventory of jetties was essential, especially for the control of navigation in the affected area. Although, in spite of the measures taken to regulate the access, the size of the Ribarroja reservoir (2,000 ha) has limited its success. Also, sufficient staff has not been available to control the whole area. There are two problems related to the disinfecting stations: 1) it is not possible to ensure the efficiency of the wash and 2) it is impossible to ensure that all navigators use them.

According to CHE, the establishment of a Working Group has been one of the best measures, because part of the success controlling the invasive species is the rapid response of all involved parties. The contribution of the technicians of the different places allows a general vision of the problem and the implication of all the affected agents. The eradication of *D. polymorpha* from the low basin of the river Ebro was considered in the initial phase of working. The application of chemical treatment in Ribarroja reservoir was not possible because it is a water body with multiple functions. It cannot be isolated from the river per se, which itself has many functions too, and the presence, downstream of the reservoir of Threatened Species (*Margaritifera auricularia*) and Sites of Communitarian Importance limit these plans. Another possibility presented was the drying of the reservoir. The success of this measure is highly unlikely and this possibility was ruled out. The efforts of the Working Group are directed to control the zebra mussel population and prevent the spread of zebra mussel into new areas. Nowadays, the discussion is centered around taking advantage of the knowledge of the natural dynamics of the river.

An “Environmental and Socio-Economics Study” has been carried out to establish the impacts of any measure. Nowadays a National Plan against Exotic Species has been set up, and the National Commission of Nature Protection has created an internal Zebra Mussel Taskforce. In the affected areas, television, newspapers and radio gave daily information about the beginning of the pest. Today most people in these regions know the problems derived from zebra mussel invasion, but in the rest of Spain only ecologist groups are conscious of the problem. The efforts do not show the desired results –prevent the pest spread-: few people in the affected regions are conscious and participate to prevent the spread. Meetings with affected parties (local governments, anglers, businessmen, farmers, etc.) were necessary to improve the situation. Figure 2 shows the spread of the zebra mussel in 2008.

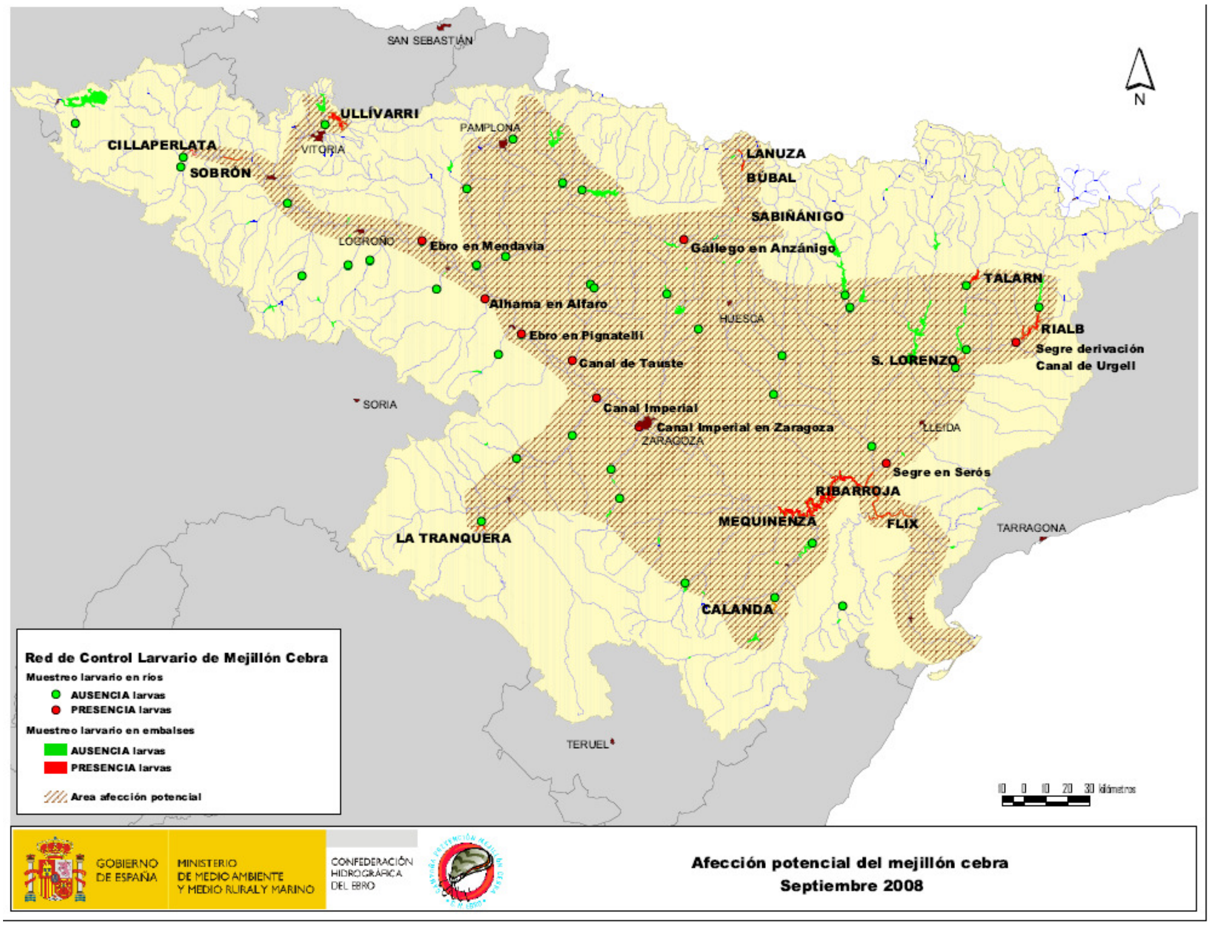

Figure 2 Spread of the Zebra mussel in 2008 (source CHE)

The works of CHE are described in several reports and publications (CHE 2002, 2004a, 2004b, 2005a, 2005b, 2006, 2007a, 2007b, 2007c, 2008, Environment Ministry of Spain 2007, Duran *et. al.*, 2008, 2010).

4 FOULING PROBLEMS IN INDUSTRIAL INSTALLATIONS

Growth conditions in the CWS often are ideal for sessile organisms: the steady water flow assures abundance of nutrients and oxygenated water, while access for predators is limited. The consequence of this is that substantial “biofouling” - defined as undesired biological growth - may take place inside the CWS. Biofouling may cause restriction of the cooling water flow, blockage of heat exchangers, increased rates of corrosion and loss of heat transfer, as well as increased costs for control and maintenance. All these have negative environmental and economical consequences. Biofouling is generally of two main types: macrofouling, involving organisms such as mussels, and hydroids; and microfouling or bio-slime, consisting of a sessile microbial population, comprising slime producing bacteria and anaerobic sulphate reducing bacteria.

Macrofouling may cause gross blockages of pipe work and culverts, and may cause so-called erosion corrosion, when shells get caught at the entrance or inside heat exchanger tubes. Biological growth in the cooling water system is therefore a constant threat to the operation efficiency. The fouling of heat transfer tubes is a never ending problem for almost every industry requiring heating or cooling. This demands for adequate anti fouling methods to prevent these problems. Macrofouling is very much location and water quality specific, both in terms of quantity and species variety.

The choice of using a specific biocide in CWS to control micro- and macro-fouling depends on several factors. These factors are:

- *legislation*: in many cases regulatory limitations are a driving force for the techniques and programs chosen by industries to control fouling in CWS
- *effectiveness*: a biocide has to be effective in the specific situation. However, it is important to realise that a biocide - or a cooling water treatment program - that is effective in one system, may not be so in another system, even if these systems are apparently identical
- *system type*: the system type determines the residence time of the cooling water in the CWS, and thus the contact time between the biocide and the cooling water. In once-through CWS, where residence times are short, fast reacting - oxidising - biocides are generally used. Slower reacting non-oxidising biocides, are presently only used in recirculating CWS. The majority of the recirculating cooling water systems in Europe are still being treated with sodium hypochlorite
- *water quality*: chemical and biological water quality affects the choice of a cooling water treatment program, and thus the choice of a biocide. Occurrence of macrofouling organisms is very much water quality related. Generally speaking, improved surface

water quality in the Netherlands has resulted in increased occurrence of macrofouling in CWS. For micro-organisms, water type does not play a major role in defining the types of organisms encountered. In theory, a pH value of approximately 7 is optimal for microbial growth. Acid conditions will favour growth of fungi and pH values higher than 8 will reduce microbiological growth. However, in practice micro-organisms prove to be highly adaptable and can colonise a variety of systems

- *interactions with other water treatment chemicals*: the choice of a suitable biocide can also be affected by other additives such as corrosion and scaling inhibitors. QACs for example are known to be partially neutralised by oxidative biocides and anionic dispersing agents. Isothiazolones on the other hand are stabilised by sodium hypochlorite. Ozone is such a strong oxidant that it will oxidise almost any other cooling water additive, which is specifically a problem for corrosion inhibitors. Interactions between cooling water additives are multiple and are not described in further detail in this report
- *economical aspects*: as any other part in industrial processes - cooling water systems - are to be operated at the lowest possible costs. In terms of volume, cooling water is an important process flow, making up for more than 95% of total process flows on-site, if a once-through system is used. In practice however, attention to design, layout and maintenance of the CWS has a relatively low priority compared to the environmental consequences of a poorly designed and/or operated CWS. Since little attention is paid to design factors, treatments often have to make up for bad design, and therefore need to be chosen in such a way that they minimise risks of fouling. Few changes of this attitude are to be expected as long as there is a low level of awareness of the long-term costs of operating and maintaining poorly designed CWS.

To get some more insight in the potential effect of macro fouling in a cooling water system, the different type of systems are described in the next paragraphs.

4.1 Types of cooling water systems

The two main types of cooling water systems are once-through and open/closed recirculating CWS.

4.1.1 Once-through systems

In "once-through" systems water is pumped from a source (e.g. a river, lake, sea or estuary), and passes through the heat exchangers. In most cases the heated water thereupon is discharged directly into surface water. 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 volumes of surface water. Generally speaking, water quality and chemistry in a once-through system are less restrictive than in recirculating systems. Typical flows for large power stations amount to 30 – 45 m^3/s per 1000 MWe and residence times inside the CWS typically vary between 2 and 15 minutes. In figure 3 a schematic view is presented of a once-through cooling water system.

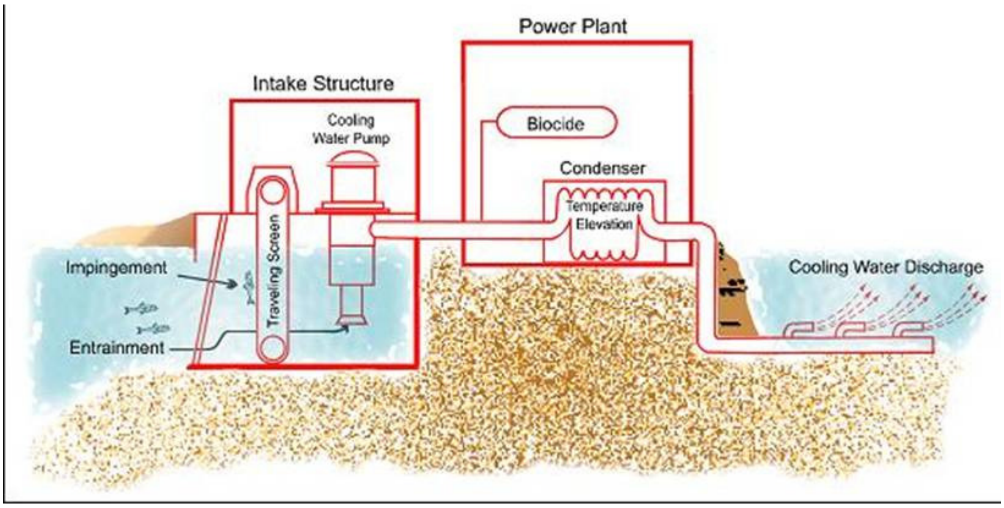

Figure 3 Schematic view of a once-through cooling water system

The temperature of the cooling water at the point of discharge will generally not exceed 30 °C, as this is the regulatory maximum in the Netherlands en other EU countries. In the biofilm on the heat exchanger temperatures will be higher than in the bulk water, up to approximately 5 °C, depending on the thickness of the biofilm and the type of material used for the heat exchanger.

4.1.2 **Open recirculating systems**

In an open recirculating CWS 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 cooled water is collected in a basin, generally located under the cooling tower, from where it is pumped to the heat exchangers.

The tower design can be based on natural air draft or induced draft. 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. The water that is purged from the system is referred to as “blow down”. In order to compensate for water losses due to blow down, evaporation, drift and leakages, water is added: the so-called “make-up”. The make-up water flow used by an open recirculating system is 1 – 3% of the flow of a once-through system with the same cooling capacity. Blow down flows generally range from 0,5 - 3 m^3/hr/MWt, with concentration factors ranging from 4 – 1,5 . Residence times vary between one hour and four days. In Figure 4 a schematic view of an open recirculation power station is presented.

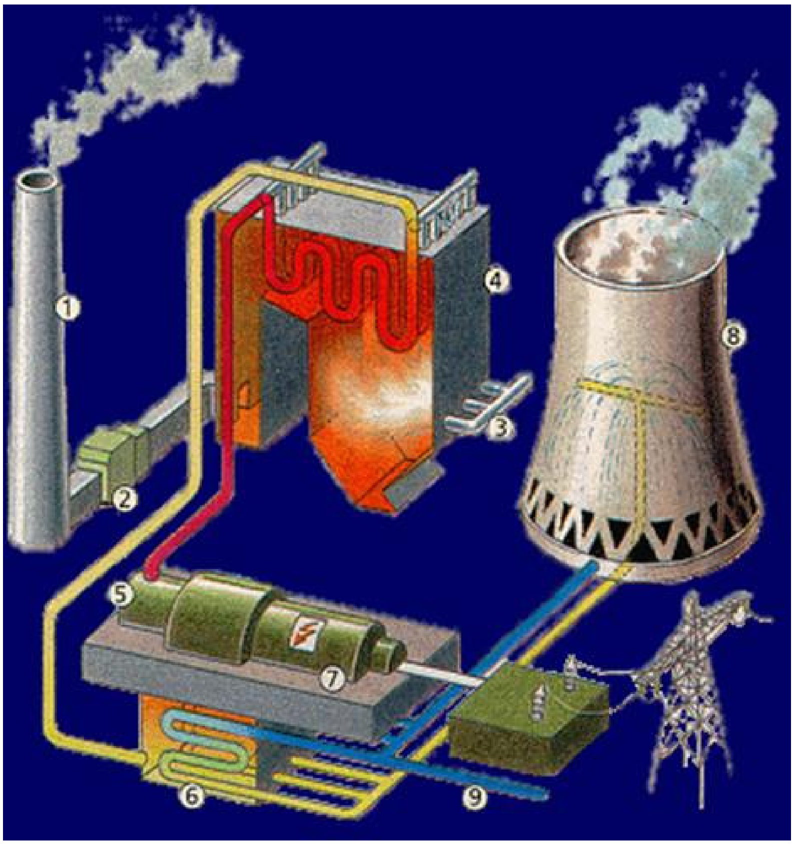

Figure 4 Schematic view of an open recirculation station

The water in a recirculating CWS 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 and, sometimes, 3) process fluids leaking from heat exchangers. The first source is unique to open recirculating systems, the other two also occur in once-through CWS. From an environmental viewpoint, leakages of process fluids are more problematic in once-through systems, since the cooling water here is discharged directly into the receiving water while in a recirculating system contaminants will be temporarily retained. In a recirculating CWS both the cooling tower and the heat exchangers are subject to fouling processes. Fouling of the heat exchanger is generally more critical than fouling of the cooling tower, although cases of operational problems due to severely fouled cooling towers are known.

Open recirculating systems are mainly used for industrial applications with a heat capacity ranging from 1 – 100 MWth, 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 flows in warm summer months. For industrial sites the heat capacity is normally lower than for power stations.

There are three processes causing a biocide to disappear from a recirculating CWS:

- reactions with suspended matter, debris and organisms in the CWS, *e.g.* due to adsorption, hydrolyses, conversion into other compounds; all these render the biocide ineffective in the CWS, the total consumption of biocide by these processes is called “biocide demand”
- the blowdown stream carries off a percentage
- the air flux through the cooling tower scrubs biocide from the water.

In practice in Dutch recirculating CWS, sodium hypochlorite is used as a biocide in > 90% of the recirculating cooling water systems treated. In other cases - mostly smaller systems, and systems with high organic loads where oxidizing biocides would require very high doses - non-oxidizing biocides are used.

4.1.2.1 Closed recirculating cooling water system

There are a number of Closed Cooling Water (CCW) system designs. Some systems cool plant components that contain radioactive fluids and serve as barriers between radioactive fluids and the service water system. Other CCW systems are on the evaporator side of a refrigeration chiller (chiller systems) and some cool the jackets of emergency diesel generators. Some of the CCW systems cool safety-related components while others cool non-safety-related components. Low temperature (< 82 ºC) closed hot water systems (often for building heat) are often included, based on system design. A closed system is defined as “a heating or refrigerating piping system in which circulating water or brine is completely enclosed, under pressure above atmospheric, and shut off from the atmosphere, except that the expansion tank could be open to the atmosphere”. A closed system has also been defined as “one in which the water is circulated in a closed loop with negligible evaporation or exposure to the atmosphere”.

In table 1 some key data on water characteristics, together with fouling related data per CWS type are presented.

Table 1 Characteristics of industrial cooling water systems

Cooling water characteristics							**Fouling related data**			
Type	**Residence Time**	**Water type**	**Intake flow (m^3/s)**	**Temp. of Bulk (°C)**	**pH value**	**Concentration factor**	**Fouling problems**	**Biofouling organisms**	**Cooling water additives**	**Biocides used**
Once-through	2-15 min	fresh, brackish, marine	2-60	max. 30	7-9	1	Biofouling Corrosion Scaling[1]	- Macrofouling: mussels, oysters, barnacles, hydroids, amphipods, tubeworms - Microfouling	Biocides	- oxidizing (NaOCl most frequently used, > 90% of biocide using systems)
Open recirculating	1 hour - 4 days	fresh	0.1-0.2	20-30, sometimes higher	7-9	3-5[2]	Biofouling Corrosion Scaling Pathogenety	- Macrofouling[3]: algae, bryozoa, snails - Microfouling	Biocides, corrosion inhibitors, scaling inhibitors, dispersants[4], pH adjustment (acid)	- oxidizing (NaOCl most frequently used > 90% of the cooling water systems) - non-oxidizing
Closed Recirculating	up to 6 months	fresh	0	30-50 and higher	7-9	n.r.	Biofouling Corrosion	- Microfouling: (of minor importance)	Biocides, corrosion inhibitors, dispersants, pH adjustment (acid)	- non-oxidizing

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[1] Scaling does not frequently occur in once-through CWS, it is a more relevant problem in recirculating CWS

[2] these are typical values as low as 2 (power stations) up to 9 are found in practice

[3] macrofouling can be a problem in intake conduits, but not in the recirculating CWS itself

[4] typical conc are: biocide 1 – 50 mg/L (as active compound); corrosion inhibitors 2 – 20 mg/L; scale control agents 2 – 20 mg/L dispersants 1 mg/L

5 BIOFOULING PROBLEMS

Macrofouling is generally confined to once-through CWS, although it may occur in the intake conduits of recirculating CWS. Inside recirculating CWS, the high temperatures and the concentration of salts inhibit macrofouling growth. In once-through systems the fouling potential is directly associated with the source of the 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. The cooling water treatment program is mostly limited to dosing of a single biocide.

In open recirculating systems, additional contamination of the cooling water may occur in the tower from contact with atmospheric air. In recirculating CWS 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, as active ingredient, depending on the nature of the fouling problem and its magnitude. Whereas in once-through CWS pretreatment of the cooling water is limited to the use of macrofilter (to keep out trash), in open recirculating systems, microfiltering, flocculation, and/or precipitation are sometimes used to improve water quality.

Together with the cooling water, a wide range of living organisms is entrained into the CWS, which can readily colonize the available concrete, metal, wood and plastic surfaces in the heat exchangers, the cooling water conduits, and the cooling tower. Growth conditions in the CWS often are ideal for sessile organisms: the steady water flow assures abundance of nutrients and oxygen, while access for predators is limited. The consequence of this is that substantial “biofouling” - defined as undesired biological growth - may take place inside the CWS. Biofouling may cause restriction of the cooling water flow, blockage of heat exchangers, increased rates of corrosion and loss of heat transfer. All these have negative environmental and economical consequences.

Macrofouling may cause gross blockages of pipe work and culverts, and may cause so-called erosion corrosion, when shells get caught at the entrance or inside heat exchanger tubes. Macrofouling is very much location and water quality specific, both in terms of quantity and species variety. Huge costs can be involved due to problems with macro fouling and therefore a sufficient treatment to prevent settlement and growth in a cooling water system is advised (Connelly, 2007).

When chemicals are used to prevent macrofouling problems in the cooling water systems it needs to be taken into account that side effects could occur like corrosion or scaling (recirculation system). The choice of the chemical needs to take these possible side effects into account.

6 CURRENT TECHNIQUES TO CONTROL THE ZEBRA MUSSEL

The search for the most efficient methods for the control of fouling in fresh and sea water cooling water systems (CWS) is going on for a very long time. The first major paper on the subject, with particular reference to power stations, was that of Ritchie (1927). Considerable efforts have been put into developing new technologies or assessing the applicability of known methodologies in order to eliminate or eradicate organisms in CWS. Most technologies proposed or presented as a transfer prevention measure are often adopted from other applications than that of treatment of seawater.

As mentioned, much work has been undertaken to find suitable chemical treatments and to save time in describing them, the existing compounds separated into oxidising and non-oxidising compounds are presented in the table below (table 2 and 3). Oxidising biocides include chlorine, bromine, and iodine. These chemicals act by destroying cell membranes or their extra cellular enzymes which leads to cell death. Non-oxidising biocides include numerous chemicals that act by interfering with a necessary life function such as metabolism or reproduction. The net result of all known chemical applications is that the most often used chemical is still sodium hypochlorite.

One of the principal reasons for the length of time taken in developing a suitable regime for mussel control was the lack of good analytical methods for estimation of chlorine residuals. Following the methods of Palin (1975) and the development of an universally acceptable standard for calibration of methods for on-line continuous measurement in freshwater (see Standard Methods, 14th edition, 1992) finally comparisons between determinations in different regions of the world was possible. This led to a clear understanding of the mode of action of chlorine on the mussel, which gave rise to the standard control regimes in use today.

6.1 Oxidising biocides

Historically, the application of chlorine to treat intake water streams has been the universal method to combat micro- and macrofouling. The dosing of sodium hypochlorite for the control of fouling species in the cooling water systems of power stations and chemical plants is well known. More specific, chlorination is still the best known and widely applied antifouling method, and up to now the pros are outshining the cons. However, in the early 1970's, organo-halogen by-products have been identified in power plant effluents during chlorination procedures. Early toxicity tests suggested that these organo-halogen by-products might be toxic at microgram level. Although it has not been possible to confirm the toxicity results, *i.e.*

bromoform toxicity ranges in milligrams per litre (Jenner *et al.*, 1997; Taylor, 2006), these potential environmental and public health implications sparked the first interest in a search for alternatives to chlorination for micro- and macrofouling control. Table 2 presents a summary of the most applied oxidising biocides.

Table 2 Oxidising biocides

Group	**Biocide**	**Chemical formula**	**Reaction**	**Target organisms**
Chlorine Based	Sodium hypochlorite	NaOCl	fast	all
	Sodium dichloroisocyanurate	$C_3HCl_2N_3Na$	fast	all
	Chlorine Dioxide	ClO_2	very fast	all
	Trichloroisocyanuric	$C_3O_3N_3Cl_3$	slow	all
Bromine-Based	Sodium hypochlorite + NaBr	NaOCl + NaBr	fast	all
	1-bromo-3-chloro-5,5,dimethylhydanthoide (BCDMH)	$C_5N_2O_2H_6ClBr$ NaOCl	fast	all
Other	Ozone	O_3	very fast	all
	Hydrogen Peroxide	H_2O_2	fast, unless stabilized	all
	Peracetic acid	$C_2H_4O_3$	fast	all
	Ultraviolet (UV) light		fast	larvae

In the last decades efforts were made to develop both physical and chemical alternatives that would avoid the production of by-products during surface water chlorination. One of the physical methods is heat treatment, which is now an accepted method to control biofouling in large cooling water circuits of power stations. Other oxidising chemical biocides, including ozone, bromine, bromine chloride, per-acetic and hydrogen peroxide were also examined as potential biofouling control agents, but the search for alternatives faded away around 1980. Peracetic acid is a very powerful oxidant; the oxidation potential outranges that of chlorine and chlorine dioxide. The fact that in sea water all of these oxidants yielded finally the same active ingredient - bromine – due to oxidising the existing 60 – 65 mg/L bromide in seawater probably played a role in abandoning the search, because similar unwanted, halogenated by-products are to be expected.

Regarding chemical corrosion experience show that initial chlorine dosing concentrations of > 5 mg/L FO the metal parts of the CWS are vulnerable for chemical corrosion. In general this concentration will not be obtained during standard operational conditions.

6.1.1 **Chlorine based biocides**

6.1.1.1 Hypochlorite and hypobromite

Sodium hypochlorite (NaOCl) is either purchased in bulk or generated as Cl_2 gas on-site by an electro chlorination station (ECP) by electrolysis of brine or seawater. Hypochlorite stored on-site is subject to decay, which is temperature dependent (Harfst, 1993). The recommended storage time is maximum one month. Commercially available sodium hypochlorite has an active chlorine concentration (ACC) of 10 - 15%, which means 10 to approximately seven weight units of sodium hypochlorite yield the same oxidative power as one weight unit of gaseous chlorine. Dosed concentrations should always be expressed as mg/l Cl_2. The commercial hypochlorite solution may be used as such, but more often it is diluted prior to dosing to about 500 - 2000 mg/l Cl_2 of TRO to improve mixing with the cooling water.

6.1.1.2 Sodium dichloroisocyanurate

Sodium dichloroisocyanurate is the sodium salt of a chlorinated hydroxytriazine and is used as a source of free available chlorine (in the form of hypochlorous acid, HOCl) for the disinfection of drinking-water. Sodium dichloroisocyanurate can be manufactured either as the anhydrous salt or as the dihydrate. It has not been evaluated previously by the Committee. At its present meeting, the Committee considered the safety of sodium dichloroisocyanurate in relation to its possible use as a disinfectant for drinking-water in emergency situations, and for routine use in some water supplies.

When sodium dichloroisocyanurate is added to water, it is rapidly hydrolysed to release free available chlorine, establishing a complex series of equilibria involving six chlorinated and four non-chlorinated isocyanurates. As free available chlorine is consumed by reaction with organic material in the water, chloroisocyanurates will rapidly dissociate and continue to release free chlorine. Conventional chlorination of drinking-water with elemental chlorine gives rise to a number of by-products as a result of the reaction of free available chlorine with natural organic matter. The safety of these by-products has been addressed by WHO, with the development of guidelines for drinking-water quality. The use of sodium dichloroisocyanurate as a source of free available chlorine is not expected to lead to greater production of such by-products than does the use of elemental chlorine.

In contact with saliva of about pH 7.0, chlorinated isocyanurates react extremely rapidly such that, at the concentrations required to deliver free available chlorine at the levels typically used in drinking-water, no detectable chlorinated isocyanurate remains

6.1.1.3 Chlorine dioxide

Chlorine dioxide is receiving an increased interest recently due to, firstly its effectiveness as a disinfectant for freshwater biofouling control, and secondly for a reduction in the formation of some by-products (Lykins *et.al.*, 1986). Additionally, chlorine dioxide does not react with nitrogen compounds to form halogenated amines, as in the case of sodium hypochlorite. This can be advantageous in freshwater systems having high loadings of certain compounds (e.g. ammonia or glycol).

The concentrated gas is sensitive to pressure and temperature, and has therefore to be generated on-site. Unlike gaseous chlorine, chlorine dioxide does not dissolve in water to form hypochlorous acid or hypochlorite ion, but exists in solution as the chlorine dioxide molecule, ClO_2. As such the disinfection rate of chlorine dioxide in once-through CWS is not affected by pH. Operation and maintenance of the on-site generator is sometimes mentioned as a disadvantage.

International practical applications are both found in recirculating and once-through CWS. Information about its use for seawater treatment is still limited. The toxicological effects of chlorine dioxide used as a disinfectant for potable water are relatively well known, but so far few studies have been focused on the effects of ClO_2 on freshwater and marine macrofouling organisms (Hose *et al.*, 1989).

Practical experience in once-through CWS in Europe has been obtained at a coastal power station in Italy. Here experimental work was done on the treatment with ClO_2 in seawater, in order to assess the feasibility, effectiveness and environmental acceptability in comparison with the traditional chlorination. However, the application of ClO_2 at power stations is stopped (info CESI). Also in Spain chlorine dioxide treatment has been applied at a coastal nuclear power station. Results showed a good control of both microbial and mussel fouling. A significant reduction in the formation of chlorination by-products was found compared with hypochlorite, which is difficult to explain seen in the light of rapid oxidation of bromide to bromine followed by CBP formation.

Limited practical experience with ClO_2 in CWS is available in the Netherlands, although chlorine dioxide is frequently applied in drinking water systems. In an experimental case in a recirculating CWS in the chemical industry, the antifouling action was found to be satisfactory. However, high doses were required and maintenance and safety of the generator appeared to be a disadvantage.

6.1.1.4 Trichloroisocyanuric

Trichloroisocyanuric acid is a stabilised chlorine product in tablet or granule form, which for this reason is less (instantaneous) reactive than liquid sodium hypochlorite. It is used in some smaller systems (paper industry) in the Netherlands. It is a very effective chlorine compound but expensive compared to Na-hypochlorite and its affectivity is on the longer term instead of the instantaneous reactivity needed in a once through CW system.

6.1.2 **Bromine based biocides**

In some freshwater CWS, when concentration NH_4 are very high, sodium hypochlorite is dosed in combination with NaBr. From an antifouling efficacy point of view hypochlorite dosing in combination with NaBr - in freshwater - may indeed lead to a reduction of the required dose, since bromamines have proven to be far more toxic than chloramines. In seawater, with natural Br- concentrations of 65 mg/l, additional dosing of NaBr makes no sense.

BCDMH (bromochlorodimethylhydantoin) is a broad spectrum biocide used to control microbial growth in a wide range of smaller CWS. BCDMH hydrolyses instantly on contact with water to liberate HOBr, the primary biocide, HOCl, and the carrier molecule DMH. Because of the limited solubility of BCDMH it must be fed into the cooling water using a by-pass chemical feeder, which makes it more suitable for open recirculating systems instead of large once through CW systems.

6.1.3 **Other oxidizing biocides**

6.1.3.1 Ozone

Ozone is a strong oxidant, more so than chlorine dioxide, which in turn is a stronger oxidant than sodium hypochlorite. As a consequence ozone will react with all organic material present in the cooling water. For this reason ozone is difficult to use in other than very clean recirculating CWS, and it makes ozone unsuitable for application in once-through CWS.

It must be mentioned that ozone will also produce byproducts as bromate (BrO_3) and aldehydes. The acceptable level of bromate in drinking water is 25 µg/l (WHO, 1993). It is proposed to reduce this level even further to 10 µg/l. Dissolved in water ozone is very toxic for juvenile fish in fresh water (LC50 48 hr, circa 0,04 mg/l).

6.1.3.2 Hydrogen peroxide and peracetic acid

Hydrogen peroxide is sometimes applied as algaecide or biocide in small open and closed recirculating CWS. Hydrogen peroxide disintegrates easily and reacts with some materials. One practical application in a CWS is known in the Netherlands, in the food sector. This is a recirculating system, fed with demineralised water, with hydrogen peroxide dosed continuously at a concentration of 15 ppm. The concentration is maintained at a high level, because bacterial counts in this system need to be low. A motive to choose for peroxide in this CWS is that it does not add salts (Cl^-) to the cooling water.

6.1.3.3 Peracetic acid

Peracetic acid is very corrosive and its application in recirculating CWS to prevent micro fouling. Special attention has to be taken in relation to the choice of dosing pump, since one of the decomposition products is methane which can become explosive in an optimal mixture with oxigen. In the food sector mixtures of peracetic acid, acetic acid and hydrogen peroxide are applied on a small scale for disinfection, but only little applications in CWS are known and the results look promising. A dosage of 1 to 10 mg/L is required with a contact time of 1 to 3 hours; however this is based on micro fouling mitigation. For the mitigation of macro fouling contact times of several days will be required to sort any effect.

6.1.3.4 Ultraviolet (UV) light

UV light is capable of killing bacteria in the bulk water of circulating water systems (Gilpin *et al.*, 1985) and is now commonly applied by hospitals and food industries for water sterilisation purposes. It has become a popular disinfecting agent for small volumes of drinking water and recreational pools on a small scale. More recently, the ability of some of the equipment to treat large volumes of water has led to the promotion of UV disinfection in CWS. Small scale tests at Ontario Hydro, Canada, suggest that UV light may be effective in preventing the settlement of macrofouling spat, but is unable to prevent settlement of older stages entering in the CWS.

UV light can not be a complete alternative for biocides since the technique does not serve the basic goal of biofouling treatment (*i.e.* controlling fouling at surfaces of heat exchange surfaces). The antifouling action of UV light can be preventive, it may kill organisms in the bulk water, but it can not exert a direct effect on the sessile populations present on the heat exchanger surfaces and other relevant surfaces in the CWS. Additionally, a certain minimum clarity of the water is needed for sufficient penetration of the UV light. In recirculating CWS this problem can be partially resolved by filtration. In spite of these drawbacks, UV light may be used as a supplemental method in biofouling control in recirculating CWS.

6.2 **Non-oxidising biocides**

Non-oxidizing biocides in the Netherlands are only applied in recirculating CWS. While oxidizing biocides exert a non-specific biocidal action on the target organism, non-oxidizing biocides have more specific modes of action, on the cell surface (e.g. QAC's), or inside the cell, affecting metabolic processes. From the non-oxidizing biocides isothiazolones and QAC's are the most frequently used in the Netherlands. The biocide glutaraldehyde is specifically encountered in the food industry.

The application of non-oxidizing biocides is only recommended in cases where oxidizing biocides are not able to give sufficient protection, such as in systems with high organic loads, or in recirculating CWS systems where daily control is not a practice. In large recirculating CWS, where mostly sodium hypochlorite is used, sometimes constant monitoring is applied to ensure that the correct level of free oxidants is available in the circuit. For many smaller recirculating CWS however, and for those operated by water service companies who do not have personnel permanently on-site, application of non-oxidizing biocides that are less influenced by the water quality are preferred over the oxidizing biocides.

Another reason to use non-oxidizing biocides instead of oxidizing biocides is illustrated by a case from the chemical industry. Here in an open recirculating CWS, fed with demineralised water, nitrite is used as a corrosion inhibitor of carbon steel. The application of oxidizing biocides would convert nitrite into nitrate, thus rendering the corrosion inhibitor ineffective, and giving rise to the risk of nitrate stress corrosion cracking. For this reason non-oxidizing biocides, such as QACs, isothiazolones, and glutaraldehyde are used. Table 3 gives an overview of the most applied non oxidising biocides.

Table 3 Non-oxidising biocides

Group	**Name of Biocide**	**Chemical formula**	**Reaction**	**Half-life, 1)**	**Target organisms**
Isothiazolones	2-methyl-4-isothiazolin-3-one	$C_4H_4NO_5$	slow	long	all
	5-chloro-2-methyl-4-isothiazolin-3-one	$C_4H_4ClCNO_5$	slow	long, 2)	all
	1,2-benzoisothiazolin-3-one	$C_9H_6N_2S_3$	slow	long	all
QACs	alkyl-dimethyl-ethyl-benzyl-ammoniumchloride	$R(CH_3)2(CH_3$-$CH_6H_4)$-NCl-R-$(CH_3)2(C_8H_9)$-N.Cl	average	average	all
	didecyl-dimetyl-ammonium-chloride	$C_{22}NH_{48}.Cl$	average	average	all
	alkyl-dimethyl-benzyl-ammoniumchloride	R-$CH_3CH_3CH_2C_6H_5$ NCl	average	average	all
	poly[oxyethylene(dimethyliminio)ethylene -(dimethyl-iminio)- ethylene-dichloride]	$C10H_{24}N_2O.Cl_2$	average	average	all, mostly used as algicide
Mexel	aliphatic amines		average	average	mostly micro organisms
Other	b-bromo-b-nitrostyrene	$C_8H_6NO_2Br$	fast	short	all
	2,2,-dithiobisbenzamide	$C1_4S_2NH_{10}$	3)	-	-
	methylenebisthiocyanate	$CH_2(SCN)2$	fast	short	all, except algae

Group	Name of Biocide	Chemical formula	Reaction	Half-life, [1]	Target organisms
	2-bromo-2-nitropropane-1,3,-diol (BNPD)	$C_3H_6NO_4Br$	average	long	all, except algae
	2,2,-dibromo-3-nitrilo-propionamide (DBNPA)	$C_4N_2H_2OBr_2$	fast	short	all
	glutaraldehyde	CHO-(CH_2)3-CHO	average	average	all, except fungi and algae

[1] Based on hydrolysis. The half-life of non-oxidizing biocides varies significantly with pH value and temperature. This variation can be as much as x100. In this table a short half-life is defined as 0 to 10 hours, average as 10 hours to 7 days and long as 7 days, and longer.

[2] The half-life of 5-chloro-2methyl isothiazolone is claimed to be less than the non-chlorinated isothiazolones cited.

[3] Information was not available.

In general, water service companies advise to use relatively high shock doses of non-oxidizing biocides, instead of continuous dosing of low levels. Continuous dosage of non-oxidizing biocides at lower levels is more likely to create tolerance. Amoebae, for example, have been shown to adapt in a short time to alternating biocide dosing in open recirculating systems. Since amoebae may harbor *Legionella* sp., and others are pathogenic in itself and may cause human diseases, these results may be important in designing effective strategies for controlling pathogens in cooling towers.

6.2.1 **Isothiazolones**

Isothiazolone biocides are currently used for microbial control in a wide range of industrial applications, including cooling water and paper. These biocides are effective at low concentrations, stable in use applications, fast-acting to inhibit growth and metabolism, and provide control over biofilm development. The initial studies on the fate and dissipation of isothiazolones in the environment were published by Krzeminski *et al.* (1975). Since this early work, regulatory requirements have changed and new methods and protocols have been specified for conducting environmental studies.

6.2.2 **QAC's**

Some quaternary ammonium compounds are used as biocides in cooling water systems. Initially these compounds were only applied in recirculating systems, but since the invasion of the Zebra mussel in the US, QACs are also used in once-through cooling water systems as an alternative for sodium hypochlorite (Diamond *et al.*, 1993). Quaternary ammonium compounds are organic salts. The cation is composed of a central nitrogen atom linked to four organic groups. The anion is mostly a chloride ion. QACs are cationic surface-active agents, visually seen as clear, slightly viscous liquids. The positive charge of the nitrogen atom allows the QAC to adsorb rapidly and strongly via ion-exchange to sediments, suspended solids, clay minerals, organic matter, micro-organisms and other negatively charged surfaces. Reported soil adsorption coefficients ($_{KD}$) for QACs, used in detergents, range from 10.000 to 200.000. QACs are highly water soluble and have relatively low octanol-water partition coefficients (Boethling, 1984). The biocidal activity of QACs is related to their surface activity. QACs readily attach to cell walls and membranes and interfere with metabolism (Reck, 1982). Commercial biocidal products used as cooling water biocides, that comprise QACs as active ingredient are presented in table 4 (Diamond *et al.*, 1993).

Table 4 Commercial formulations containing quaternary ammonium compounds

Product [1)]	**Bulab 6002**	**Calgon H-130**	**Calgon DM-DACC**	**Clam-Trol CT-1**	**Macro-Trol 7326**
DDMBAC				X	X
DDEBAC					X
TDMBAC				X	X
TDEBAC					X
HDMBAC				X	X
ODMBAC					X
$DD_{10}DMAC$		X			
DMDACC			X		
WSCP	X				
DGH[2)]				X	

DDMBAC = n-dodecyl-n,n-dimethyl benzyl ammonium chloride
DDEBAC = n-dodecyl-n,n-dimethyl ethylbenzyl ammonium chloride
TDMBAC = n-tetradecyl-n,n-dimethyl benzyl ammonium chloride
TDEBAC = n-tetradecyl-n,n-dimethyl ethylbenzyl ammonium chloride
HDMBAC = n-hexadecyl-n,n-dimethyl benzyl ammonium chloride
ODMBAC = n-octadecyl-n,n-dimethyl benzyl ammonium chloride
DDDMAC = didecyl-dimethyl ammonium chloride
DMDACC = poly(dimethyl diallyl ammonium chloride)
WSCP = poly[oxyethylene(dimethylimino)-ethylene(dimethylimino)ethylene dichloride
DGH = dodecylguanidine hydrochloride

6.2.3 **Mexel**

The product Mexel was developed by the French company MEXEL Industries in 1990. The Mexel 432/0 emulsion is composed of aliphatic amines. Aliphatic amines are characterized by a hydrophilic part composed by amine or alcohol functions, and by a hydrophobic part composed of carbonaceous chains. Due to this hydrophilic/hydrophobic composition, aliphatic amines are at the same time attracted and pushed back by water. That is why, they are called "amphiphiles" or more generally "surfactants".

The commercial product Mexel 432/0 is a yellowish non-homogenous liquid comprising of amines. Mexel 432/0 is an alkaline product (pH 11.3), which does not contain quaternary ammonium compounds, aromatic derivatives, heavy metals, or halides. The product has a density of 0.998 and can be stored at ambient temperature for several months. Due to the physical and chemical properties of Mexel 432/0, the product moves to the surface when dispersed in water.

The product Mexel 432/0 is suggested to have anti-fouling and anti-corrosion (IfAM; Ifremer) properties. And therefore could provide an alternative to common anti-fouling techniques using oxidative biocides as hypochlorite. The anti-fouling activity of the product is based on its film-forming properties, as presented in Figure 5. The product is suggested to impede settlement and growth and forces mussels to move out of a cooling water system.

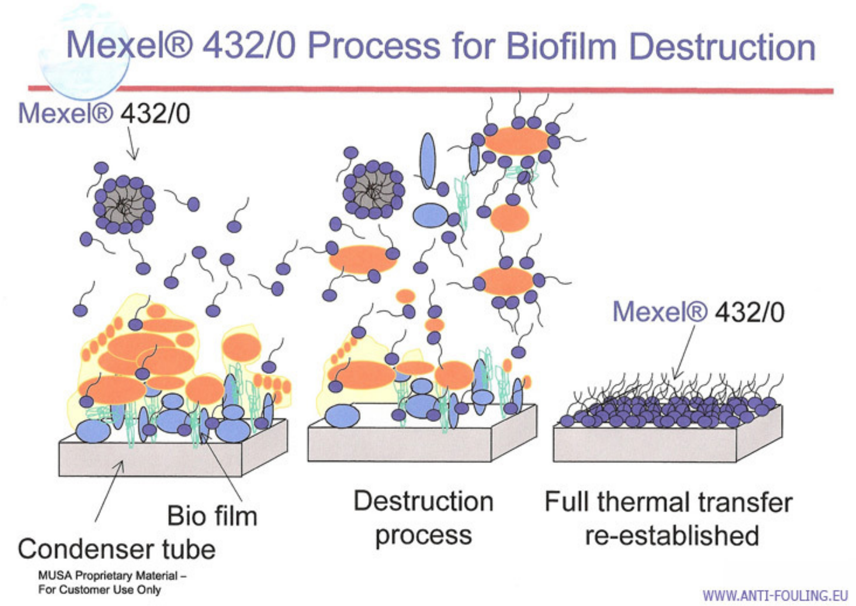

Figure 5 Anti-fouling activity of Mexel 432/0 (*Source: Mexel Industries*)

The anti-fouling activity of Mexel 432/0 is tested in both freshwater and seawater. Anti-fouling tests in France, carried out by EdF (Khalanski 1993a; 1993b) at the Le Havre power plant showed an additional fouling protection of the product Mexel 432/0 to blue mussels (*Mytilus edulis*), barnacles (*Balanus sp.*), and hydroids. In this plant, the Mexel 432/0 product is injected daily at the nominal concentration of 6 mg/l during 30 minutes. In these conditions, the residual Mexel 432/0 concentration at the inlet of the condenser is around 3 mg/l and at the discharge around 0.2 to 2.5 mg/l depending on the treated unit and the number of units in operation. This power plant, is successfully using Mexel 432/0 since 1996 in unit 1 (9 m^3/s), since 1997 in unit 2 (22 m^3/s) and since 2006 in unit 4 (22 m^3/s).

KEMA did several studies and tests during the mid-nineteen's at its own laboratory and at power stations. The test at Maasvlakte Power Stations (540MW) was carried out in 1997. At the power station full scale tests were carried out in one of the two units (CW flow 18 m^3/sec). From these tests it could be concluded that Mexel 432 had a reducing effect on the formation of biofouling in a cooling water system and results in an anti fouling effect. Mexel has to be dosed several times a day to build up a film and at least once a day to maintain this film. However, the effect was much less than using hypochlorite and did not result in a complete anti fouling strategy, the application of Mexel 432 was not a (cost) effective additive to mitigate severe biofouling settlement at this location.

When dosed in a cooling water system were already biofouling (mussels, oysters, barnacles or other macro fouling organisms) is present it is very difficult to establish an effective Mexel film. This is because the activity of the product at the used dosage is mostly on the velligers stage. If the concentration of suspended solids and humic compounds is changing each day, then it is very difficult to stabilize the residual Mexel concentration and to obtain an effective treatment.

Also it has to be mentioned that there is no accurate information in the degradability of the product in fresh- and sea water in the discharged water. Biodegradation tests on the Mexel product have been performed only in freshwater. The results obtained in these test shown that the biodegradation rate is depending on the condition of the test itself: in some cases the biodegradation is higher than 60% and in some cases the biodegradation is less than 60 %. These differences seemed to be linked to the bacterio-static activity of the product at high concentration.

6.2.3.1 Toxicity Mexel

The product Mexel 432/336/0 is according to the 'Algemene Beoordelings Methodiek (ABM)' (General Assessment Methodology (GAM) as described in the paper 'Assessment of substances and preparations within the context of the implementation of the water discharge policy' of May 2000 by the Integrated-water Management Committee), classified as 'toxic to aquatic organisms' with decontamination effort 'B' similar to 7B. Taking into account the toxicity of the product itself towards aquatic species (<1 mg/L), it is proposed to classify the product Mexel 432/336/0 with 'very toxic to aquatic organisms' with decontamination effort 'B' similar to 5B (TNO, 2009).

According to MEXEL Industries the Mexel 432/336/0 and Mexel 432/0 product have the same physicochemical and toxicological properties. The formulation of Mexel 432/336/0 is similar to the Mexel 432/0 product. It is a reformulation of this last product, in order to be in conformity with the directive 98/8/EC of the European Parliament concerning the introduction of biocidal products on the market (BPD). This reformulation is based on 1.7% of the Mexel 432/0 product and corresponds to the replacement by one alkylamine not notified in the BPD by another one, having the same alkyl chain, notified on the BPD.

The action mechanism of the Mexel 432/0 product is that the product acts quickly, by the alteration of the gill epitheliums (Arehmouch, 1998; Giamberini *et al.*, 1993, 1996). According to this mechanism the toxicity level to mammals or to aquatic organisms having gills protected is low, but relatively high to aquatic organisms whose gills are protected only by the mucus layer. Toxicity tests performed on the product Mexel 432/0 showed the following results:

- to the freshwater algae, *Pseudokirchneriella subcapitata*, the effective concentrations which involve a reduction of 50% (EC50) of the biomass or the growth rate after 72 hours are respectively 170 µg/l and 230 µg/l (SGS, 2006a)
- to the sea water algae *Phaeodactylum tricornutum*, these values are respectively 250 µg/l and 100 µg/l (SGS, 2007)
- to *Photobacterium phosphoreum*, by using the Microtox test®, the concentrations inhibiting 50% of the bacterial bioluminescence (IC50) after 5 and 15 minutes of exposure are respectively 6.2 and 5.4 mg/l (Coulon, 1993)
- to freshwater crustacean and notably to *Daphnia magna* the concentration inhibiting 50% of the mobility (IC50) after 48 hrs of exposure is 630 µg/l (SGS, 2006b)
- to the marine copepod *Acartia tonsa* the LC50 48-hrs is 960 µg/l (SGS, 2007)
- to the freshwater fish *Brachydanio rerio* and toward the marine water fish *Scophthalmus maximus*, the LC50 96-hrs are respectively 850 µg/l (SGS, 2006c) and 3.7 mg/l (SGS, 2007)
- to the marine water fish *Dicentrarchus labrax* direct exposure to 5-6 mg/l Mexel 432 during a daily period of 30 minutes, does not lead to mortality or acute toxic effects (KEMA, 1997a).

6.2.3.2 Biodegradability

According to the substances producers, the active substances used in the Mexel 432/0 product are classified as biodegradable. For the soluble alkylamine, an ultimate degradability of 96% in 12 days was measured (NICNAS, 1992). Moreover, for low soluble substance, according to the data of Toxicology/Regulatory Services, Inc. (2002), the used model predicts a rapid photo degradation ($t_{½}$ was 0.7 hour). Stability in water was not calculable by the model. The estimated transport and distribution of these chemicals was 11% to water and 89% to sediment. Based on data from the other chemicals in the FND Amines Category, biodegradation of these chemicals would be expected if procedures adequate to ensure bioavailability were employed.

Literature shows that the principal strategy used by the micro-organisms to degrade the alkyl chains of surfactants consists in separating the hydrophilic head from the hydrophobic tail by an O or N-oxidase. The hydrophobic carbonaceous chain is transformed into alkanal as first intermediate by an alkylamine dehydrogenase (Kravetz, 1981; White, 1993; White & Russel, 1994; Yoshimura, 1980; Yoshimura *et al.*, 1980). Then, this intermediate is immediately transformed into fatty acids. These lasts are further degraded via the β-oxidation to carbon dioxide, water and biomass. In both cases, the loss of the surfactant nature of the compound is quickly obtained (White, 1993; White & Russel, 1994), leading to more hydrophilic product and then less soluble in fatty tissues.

Many tests were carried out on Mexel 432/0, under varied physico-chemical conditions, to study its disappearance from the aqueous phase:

- in dematerialized water and in absence of agitation, the Mexel 432/0 solutions are stable over a long period of time. After 21-28 days of incubation, approximately 68.3% to 92.1% of the nominal concentration of Mexel 432/0 is found in solution (Allonier, *et al.,* 1997)
- in reconstituted water of varied physico-chemical characteristics (suspended solids, dissolved organic matter etc.) between 9.1% and 68.6% of the Mexel 432/0 concentration disappeared from the aqueous phase in few seconds (Allonier, *et al.*, 1997). This ‘immediate demand’ is also observed in natural water and can reach 81%. That is why, during the use of Mexel 432/0, it is necessary to evaluate the nominal concentration required. After this immediate demand, a reduction in the Mexel 432/0 concentrations is observed during time
- in fresh river water 97.4% to 99.8% of Mexel 432/0 cannot be found after 21 days of incubation and agitation of river water by a magnetic stir bar but especially air injection will increase the reduction of Mexel 432/0 (Allonier, *et al.*, 1997)
- chemical oxygen demand (COD) of Mexel 432/0 is 453 gr O_2/kg (Bourdon, 2001)
- bacteria strains of *Pseudomonas aeruginosa* could growth, in a Simmons liquid medium without carbon, using the Mexel 432/0 at concentrations ranged between 10 and 100 mg/L as the only carbon source (Allonier & Khalanski, 1996).

6.3 Coatings

From the first known patent in 1625, by 1870 there were more than 300 antifouling paints registered. Most of the formulations used biocides to kill organisms through a leaching process using heavy metals or organo-metallic compounds. Various heavy metals have been added for providing antifouling and anticorrosive properties.

Copper has been the traditional compound used as a biocide in antifouling paints. The concentration of copper in antifouling paints is reported to be 10-30%, but as much as 50% has been used. Normally Cu_2O is used as the biocide, but also CuSCN and copper metal are in use.

Mercury was added to antifouling paints as a biocide in the past. Both inorganic mercury and organo-mercury were used. The concentration of mercury in paints is somewhat uncertain but about 5% could have been added to the paint. Arsenic was also used in the past as a biocide in antifouling paints. Lead has been added to antifouling paints as a stabilizer, a pigment and a biocide. Both inorganic and organo-lead compounds are used in marine paints. The concentration of lead in antifouling paints is typically 1-5%. Lead was previously widely used in anticorrosive paints, but has now to a great extent been replaced by zinc and aluminium. Cadmium and Chromium were also in the past added to give the paint anticorrosive properties and colour.

In the late 1960s, a particular breakthrough in anti-fouling paints came with the development of so-called self-polishing paints, in which the organo-tin compounds are chemically bonded to the polymer base. This organo-tin compound replaced the traditional copper-containing antifouling paints, because of its excellent antifouling properties. The leaching rate of these paints is controlled because the biocide is released when seawater reacts with the surface layer of the paint. Once the surface layer is worn off, the reaction to release the biocide begins again with the next layer. In this way, the leaching rate is the same throughout the life of the paint - and it became possible for ships to go up to 60 months without repainting. Tributyl-tin oxide (TBTO) was the most used organo-tin compound but also triphenyl-tin (TPT) was used. The amount of organo-tin compounds in paints is normally about 10-15%.

In the 1970s-1980s, it became clear there was a price to pay for the efficient self-polishing anti-fouling paints containing TBTO. Environmental studies began to provide evidence that organo-tin compounds persist in the water and in sediments, killing sealife other than that attached to the hulls of ships and possibly entering the food chain. Specifically, TBT was shown to cause shell deformations in oysters; sex changes (imposex) in whelks; and immune response, neurotoxic and genetic affects in other marine species.

In 1990, as a result of this persistence, the Marine Environment Protection Committee of the International Maritime Organization (IMO) adopted a resolution in 1990, recommending governments to adopt measures to eliminate antifouling paints containing TBT. It has proposed a ban on the application of TBT based antifouling paints from January 2003 and the ban of the presence of such paints on the surface of vessels from January 2008 (Yebra *et al.*, 2004).

Alternatives to organo-tin-based systems include, copper-based coatings (include copper (I) oxide/cuprous oxide/-dicopper oxide), zinc pyrithione, SeaNine 211, Irgarol 1051 and vinyl or chlorinated paint (include dichlofluanid, chlorothalonil), filled with copper and biocides or biocidal silicon-based systems. Several pesticides were used as a biocide in antifoulants. Examples of pesticides in use were Diuron and Zineb. DDT was also used as a biocide in antifoulants in the past and it is possible that other persistent chlorinated pesticides have been used in antifoulants. Lot of these toxic compounds were persistent, prone to bioaccumulation and harmful to the marine environment. In the last decade, environmental concerns about the long term effect of leachable antifouling biocide have led to increased interest in the development of environmental friendly alternatives. Several products have reached the commercial market, and claimed their effectiveness as regards the prevention of marine biofouling in an environmentally friendly manner. Lots of research activities are centered on biodegradable toxic compounds and non-toxic adhesion inhibitors. However, based on the information from the "IMO Anti-Fouling Convention: TBT Alternatives", lots of companies are active in the production of biocide free antifouling products, but still the most antifouling products are biocidal products. Alternatives to organo-tin-based antifouling coatings are roughly divided into the following two-classes:

- Biocidal Coatings:
  - biocide releasing coatings & booster biocides
  - self-polishing copolymer coatings(SPC)
  - coatings with natural resistance (natural biocides) and enzymatic antifouling coatings
  - copper/nickel epoxy coatings
  - nanosized copper based coatings
  - electro conductive coatings
- Fouling Release Coatings (coatings with a very low surface energy and lower surface roughness than traditional biocidal coatings. Consequently, the adhesion strength of settled marine biota is less:
  - biocide-free SPC coatings
  - non-stick coatings
  - stenoprohiluric coatings
  - non-toxic fiber coatings.

However, while nearly all coatings are formulated to possess at least some level of abrasion resistance, one technology segment, based on sol-gel chemistry, focuses primarily on that one performance attribute.

The application of coatings in power plant cooling water conduits and other surfaces is well documented and there are a number of coatings specifically developed for this. In the Netherlands, coatings are not widely used in cooling water intakes of power plants, while antifouling coatings and paints are able to play an important role in the reduction of fouling settlement and growth. They can indirectly reduce the amount of biocide needed for adequate control.

Generally, toxic and non-toxic coatings and paints are distinguished between. Non-toxic foul release coatings weaken the adhesive bond between the organism, film or deposit and the coating. The most promising product available for cooling water systems at this moment are the non-toxic, fouling release, silicone-based and fluoropolymer-based coatings. Although foul release coatings can be fouled by biological growth, the rate of fouling is significantly less and is normally removed by the cooling water flow.

The silicone-based and fluoropolymer-based coatings should be applied to perfectly clean and dry surfaces, or to clean and almost dry (5% or less moisture) concrete over the appropriate epoxy primers. For this reason the technique is more difficult to apply in existing situations, where dry conditions are more difficult to obtain than in newly built cooling water systems. In cooling water systems foul release coatings can be durable up to 10 years (including a re-coat of finish only after 5 years). Fluoropolymer-based coatings are more hard wearing than the silicones-based ones.

Test programs have shown that silicone based coatings performed better than other surfaces due to a slower rate of fouling accumulation, a tendency to slough, and ease of cleaning (Musalli, 1989; Meyer & Baier, 1992; Watermann *et al.*, 1997). It was initially considered that the poor abrasion resistance and tear strength of the silicone elastomers would inhibit their general use as marine antifoulings, but that they had potential for use in coastal power stations, offshore and in aquaculture (Milne & Callow, 1984). However, silicone paints have since shown potential in ship trials (Brady *et al.*, 1987; Matsushita & Ogawi, 1993), as well as in controlling fouling on salmon-cage netting and for resisting the invasive zebra mussel in power station cooling water conduits in the Great Lakes (Leitch & Puzzuoli, 1992). Some practical results are:

- the Electric Power Research Institute (EPRI) in the U.S. evaluated 30 non-toxic fouling release coatings for control of fouling on steel and concrete surfaces and found silicone coatings performed best with predicted field lives of two to four years (Musalli, 1989)
- two-year exposure tests were undertaken in Italy on sets of panels coated with silicone-based coatings, with and without additives, and results compared both to sets of panels coated with ablative copper and non-toxic epoxy paints (Terlizzi *et al.*, 2000). The best performing coatings were silicone foul release coatings without additives, and these substantially influenced community composition, shifting it to the earliest stages of colonisation and proving to be unsuitable for colonisation typical of mature communities due to their low surface energy. The study led to the conclusion that silicone coating technology represented an alternative to the use of biocidal antifouling paints. However, the need for improvements in aspects such as delamination and abrasion were noted
- reduced macrofouling abundance on silicone fouling release coatings may be due, at least in part, to biotic factors. Caging experiments have demonstrated that fouling development on caged panels was much higher than on uncaged and partially caged panels, suggesting that grazing and predation influences community development (Swain *et al.*, 1998). The implications of these findings were that silicone coatings exposed in environments with high biotic disturbance would perform well but, in environments where predators were absent, heavy fouling may occur
- nonfouling silicone rubber coatings that have proved worthy of large scale testing include Bioclean BC and Bioclean DX (CMP Chugoku), Biox (Kansai Paint Co.), and Exsil 2200 (GE Silicones). Two additional silicone rubbers that look promising, at least after short term exposures, are Intersleek and CSL 560 (CSL Silicones, Inc., previously Serrnatech). Of these five silicone rubbers, the first to be found acceptable, from its very first panel tests, was Bioclean DX. The other brands had to go through one or more iterations before acceptable performance was achieved. The Bioclean is still providing “fair” protection after six years but, while the coating is still intact its non-fouling characteristics are waning (Gross, 1994).

Disadvantages of silicone systems were that they are expensive, more difficult to apply than biocidal antifouling paints mechanical frailty and persistence. The latter aspect is important with respect to silicone peeling off into the sea and the exudation of silicone oils. An additional problem is that these systems cannot be applied on single component products and therefore cannot be used on top of existing antifouling systems. Griffith & Bultman (1997) warn that, if there is a defect in a silicone coating that can allow an immature barnacle to achieve a solid attachment, the coating will be undermined at that spot. Widespread research has continued in attempts to improve both the durability and the fouling release properties of fouling release coatings. The fouling release life of silicone elastomers varies according to the formulation from a few, to up to 12 years (Callow, 1996).

In the pictures below an impression is given from the use of different types of coatings, left a picture of a non coated trash rack and right a coated trash rack with different products. The trash racks were placed in sea water from April until October.

Figure 6 Test with different coatings, left non coated and right coated trash rack

6.4 Osmotic shock

In principle it is possible to apply osmotic shock to either fresh- or seawater systems, by subjecting them to seawater and freshwater respectively. As a result, cells of organism may come under the effects of internal pressure followed by cell lysis or alternatively to become water deficient, which may result in death. The technique is difficult to apply when using seawater to combat biofouling in freshwater CWS, due to likely problems of corrosion and the environmental aspects of a saltwater discharge.

Zebra mussels have a requirement for minimal or threshold amounts of Na, K, Mg and Cl for survival. It cannot tolerate de-ionised water for any appreciable length of time. The lethal time for 50% mortality (LT_{50}) is < 4. Other fresh water bivalves will tolerate de-ionised water for months with no mortality (Dietz *et al.*, 1994; Krogh, 1939; McCorkle & Dietz, 1980; Murphy & Dietz, 1976; Scheide & Dietz, 1982).

The salinity threshold for zebra mussels' existence varies. In "native" areas, a zebra mussel occurs from 0.5 to 3.5 gr/L in the Black Sea basin (Liakhnovich *et al.,* 1994), and from 0.2 to

2 gr/L in the Northern Caspian Sea and the Volga River delta (Karpevich, 1953). In the Netherlands delta region zebra mussels are present in ponds with stable salinities up to 4 gr/L (Wolff, 1969). There are numerous reports of Dreissenids being present in salinities ranging to 4 to 5 gr/L in the brackish waters of Europe and Russia (Klimowicz, 1958; Jarvekiilg, 1984; Lamanova, 1970; Schloesser *et al*, 1994). In the Baltic Sea region, *D. polymorpha* usually inhabits waters from entirely fresh to 6.0 gr/L (Jarvekulg, 1979), in the Gulf of Finland, it occurs from the Neva River estuary (usually fresh) to Luga Bay (6 – 7 gr/L) (Antzulevich *et al.,* 1992) and in the Kiel Canal at 3.8 and 6.2 gr/L (Strayer & Smith, 1993). They are abundant in the northern Caspian Sea at salinities of 6 - 9 gr/L, but are not present in the main body of the sea at 13 gr/L (Strayer & Smith, 1993). They were abundant throughout the Aral Sea at salinities of 10 gr/L; as water diversions raised the salinity of the sea, mussel populations began to decline at around 12 gr/L and had virtually disappeared when salinities reached 14 gr/L (Stayer & Smith, 1993). Dreissenids have also been identified in tidal reaches of the St. Lawrence River and in estuarine areas of North America (Mellina & Rasmussen, 1994; Strayer & Smith, 1993). These mussels tend to be smaller in higher salinities suggesting either they do not survive for much longer than a year or that they grow slower. These brackish water are continually be resupplied with *D. polymorpha* larvae from river populations.

From information gained in the literature it can be concluded that:

- *D. polymorphas'* salinity limits depend not only on salinity levels, but also on the rate of change of salinity and on the composition of the salt. They show more tolerance to higher salinity levels when the increase in salinity is gradual rather than abrupt
- veliger larvae appear to be the most tolerant stage for salinity. The post-veligers are more sensitive to nonoxidizing compounds than other life stages of mussels including veliger larvae. Changes in physical characteristics of the post-veligers may be responsible for greater sensitivity
- if veligers move into a system during periods when salinities are lower than 4 gr/L, the population may survive if the postveligers can develop to adult stages before salinities increase above 4 gr/L
- the *D. polymorpha* exhibits tolerance to moderate salinity when it is constant (8 - 12 gr/L), but to lower salinities (0.5 gr/L) if the salinity undergoes frequent changes, as in tidal estuaries
- by increasing potassium concentration *D. polymorpha* can survive for months following an acute transfer from pound water to ~ 3.5 gr/L NaCl
- the first successful eradication of zebra mussels using KCl (100 mg/L) was carried out in the USA by a three-week dosing period
- *D. polymorpha* has a pH tolerance ranging from 9.0 to 9.5.

6.5 Physical methods

Besides chemical methods also physical methods can be used to prevent settlement and/or to mitigate the individuals settles. A number of techniques are available for reducing the effects of potential fouling in tube heat exchangers or other parts of the CWS, without the need of taking it off-stream. Some of the methods are only applicable for certain CWS or heat exchangers, while others are more universal in application.

6.5.1 Filtration

6.5.1.1 Microfiltration

Micro-filtration is a method to reduce the zoo- and phytoplankton load (including larvae) of the cooling water, which also reduces the organic load. This reduces the biocide demand. Existing methods are rotating drumfilters and sandfilters. Because of the large water volumes involved, microfiltration up to now is not a feasible option for large once-through CWS.

Recently, continuously backwashed microfilters have been developed with mesh sizes of 50-100 µm, which claim to give effective protection against macrofouling. These filters are claimed to be able to deal with relatively high water flows (up to 4 m^3/s). The youngest stages of mussels and barnacles have lengths of above 150 µm, so a microfilter with 75 µm mesh width is likely to give effective protection against entrance of larvae of mussels and barnacles. These filters require a back flush flow and cause a pressure loss in the CWS.

The effectiveness of a “Taprogge” dynamic 75µm was tested by KEMA at the auxiliary CWS of the Dutch power station ‘Bergum’, unit 10 (320 MWe). The cooling water was taken from the Bergum Lake and flows through the filter by circa 190 m^3/h. The test results showed that due to the high amount of (zoo)plankton in lake Bergum the filter was in cleaning operation every 2 minutes, which is undesirable for continuous operation (KEMA,1998). Still this type of application is promising for the future. Purchase costs of a ‘Taprogge’ micro-filtration unit (75 µm) which is capable to filter 648 m^3 of water per hour is estimated by Taprogge (1996) at EURO 58.700, --.

6.5.1.2 Side-stream filtration

Side-stream filtration techniques - that filter part (2 - 3%) of the recirculating cooling water flow - are an effective technique to minimise the total suspended solids in a recirculating

CWS. Frequently encountered techniques are rapid sand filters and continuously backwashes filters, which filter out a minimum particle size of 20 µm. Side-stream filtration in recirculating CWS is becoming more frequently employed.

Rapid sand filtration is the first step in treating potable water in drinking water preparation in the Netherlands. A study by KEMA at the drinking water company in Nieuwegein, into what extent mussel spat could be filtered out in these sand filters, showed that more then 99% of the spat was retained in the sand bed. The result led to a considerable decrease (> 50%) in the use of hypochlorite for antifouling purposes in the long distance transport conduit.
Experience in the chemical industry has demonstrated that side-stream filtration with sand filters considerably reduces biocide use (90%) in recirculating CWS, by exerting a combined mechanical and biological filtering action. If incorrectly operated there is a risk that the sand filter can become an added source of anaerobic sulphur reducing bacteria, adding to the corrosion control problems. More information on the mode of operation of these filters can be obtained from Capdeville and Rols, 1992.

It appears to be advisable to have the side-stream sand filter switched off during periods of shock dosing of sodium hypochlorite. This prevents the destruction of the biofilm present in the sand filter, which would lead to unnecessary release of nutrients back into the recirculating water, where it may feed micro-organisms. A second reason for shutting of the side-stream filter temporarily is that it causes a direct - extra - biocide demand, which does not serve the prime goal of biocide dosing: keeping heat exchangers surfaces clean.

In summary a side-stream filter removes nutrients from the recirculating water, and thus reduces risk for microbiological growth on the heat exchanger surfaces. It should be avoided that biocides are used to kill the microbial population on the sand filter. It is advisable to further optimise the application of side-stream filtration in recirculating CWS since their application may lead to considerable reduction of biocide use. For example, research into carrier materials other than sand may result in increased effectiveness.

The above standing comments apply to all biocides, however some non-oxidising biocides (*e.g.* QACs) are more likely to be neutralised by organic matter than others (*e.g.* isothiazolones).

6.5.1.3 Alfa Laval filters

To prevent settlement and growth of mussels in a cooling water system filter systems can be used. To prevent blockage of this filter a self-cleaning filter can be used. A filter that can be applied is the Alfa Laval filter (ALF) system. This filter can filter out the solid particles of > 1mm, as these may have detrimental consequences for the integrity of the cooling water system surfaces and heat exchangers. The ALF is a pressure filter, specifically designed for the filtration of large particles (mm-range) from raw water streams, such as cooling water intakes from rivers, lakes, or the sea. The raw water is filtered by means of a filter basket with a mesh size of 1 mm. At certain time intervals the filter is automatically backflushed. The filter capacity determines the necessary model needed.

The costs for engineering and implementation of such a filter are high. Also, there is an effort needed to operate the filters, controlling the cleanliness and filtration flow to keep optimal filtration rate and prevent clogging. Also, the residual filtered material must be removed, probably as waste and possibly treated before it can be dumped.

It also has to be stated that these filter systems do filter larvae smaller than 1 mm, these individuals can pass the filter and settle downstream. These settled mussels can give huge problems if no other anti fouling method is applied than only this type of filter system.

6.5.1.4 Zebra Mussel Filter Systems, Inc.

This company delivers filter systems with a mesh size of 20 microns which should be capable to prevent ingress of larvae in the veliger stadium. However, the maximum capacity is about 10 Liters per second which is too small for industrial installations. Also due to the small mesh size these systems are very susceptible for blockage.

6.5.2 **Water velocity in cooling water system**

Water velocity and the potentially complex hydrodynamics of circuit design are important factors in the 'fouling potential' of a given cooling water system. Settlement of larvae and the ability of settled organisms to remain on a given surface depend greatly on water velocity. Some species are well adapted to slow-running or even stagnant water, while others require strong water currents.

Water velocity varies considerably in cooling water circuits from the water intake structure to the outlet. It is low near filtering devices like traveling screens and in basins, especially cooling tower basins. It is high in pipes leading to heat exchangers and in heat exchangers. The operating regime of pumps in any given circuit must also be considered as this can cause both variations in flow rate locally and even periods of stagnation.

For organisms which settle on circuit walls, the routine renewal of water in a cooling water system is an extremely favorable factor as it provides a source of nutrients and dissolved oxygen. For this reason, when water velocity is not excessive, organisms show optimum growth, generally more rapid than that of the corresponding population in the natural environment. When the velocity exceeds a critical threshold, larvae are no longer able to settle and adults are not able to feed well. They may even become detached from the substratum. In the absence of water circulation, dissolved oxygen becomes the limiting factor and can cause mortality by asphyxia in one to three weeks, depending on the temperature and the organisms present.

6.5.2.1 Water velocities in conduits

When designing a CWS, stagnant zones and sharp curves in conduits and heat exchangers (*e.g.* man holes and dead end lines) should be kept to a minimum. In the stagnant zones biological growth thrives, because water velocities are low which favours settlement of biofouling organisms. Additionally, the mass transfer of biocides to the biofilm will be reduced if the water velocity is too low. This is especially important in once-through CWS at locations where macrofouling is an issue. Water velocities, therefore, are a very important factor in the design of cooling water conduits and heat exchangers. Low water velocities favour precipitation of debris in general, and allow settlement of macrofouling. A general rule of thumb for the cooling water conduits is to keep water velocities above 2.5 m/s, to prevent settlement of macrofouling as much as possible.

6.5.2.2 Water velocities in fresh water CWS

For fresh water fed once-through cooling water systems, the zebra mussel (*Dreissena polymorpha*) is the most important hard shell fouling species. In natural waters, zebra mussels tolerate a wide water velocity range from 0.05 – 1.0 m/s (Leglize and Ollivier 1981). Post veligers (<1 mm) are more sensitive to current than adults, as their attachment strength is two order of magnitude less than that of adults (Ackerman et al., 1995). This species is not found at 2 m/s, although some isolated specimens can resist 2 m/s. In several cooling water systems, zebra mussels are found in high numbers at velocities of 10 – 50 cm/s, but not in parts of the circuit where water velocity exceeds 1 m/s.

6.5.3 Heat treatment

Heat treatment or “Thermoshock” is a well-known control method (Jenner 1982; Jenner and Janssen-Mommen, 1992; Rajagopal et al., 2005), see also figure 4. Thermal treatment consists of heating the cooling water to a temperature of 35-40 ℃ by means of (partial) recirculation, and maintaining this for 2½ hours. Thermal treatment is accomplished by recirculating the heated condenser discharge back to the circulating water intake. With each pass of the recirculated water through the condenser, additional heat is provided, thereby raising the temperature of the cooling water. The time needed to raise the temperature to ~40 ºC depends on the starting temperature of the cooling water, the amount of thermal losses, and the volume of water to be heated. In general it takes 1 to 3 hours to reach the target temperature. These factors vary with station arrangement and environmental conditions, such as lake temperature, at the time of treatment. This type of treatment, however, is restricted to a few plants. This is due to the fact that a special design is required for the cooling water system at an early stage of plant building. Adaptations afterwards are often expensive or technically difficult.

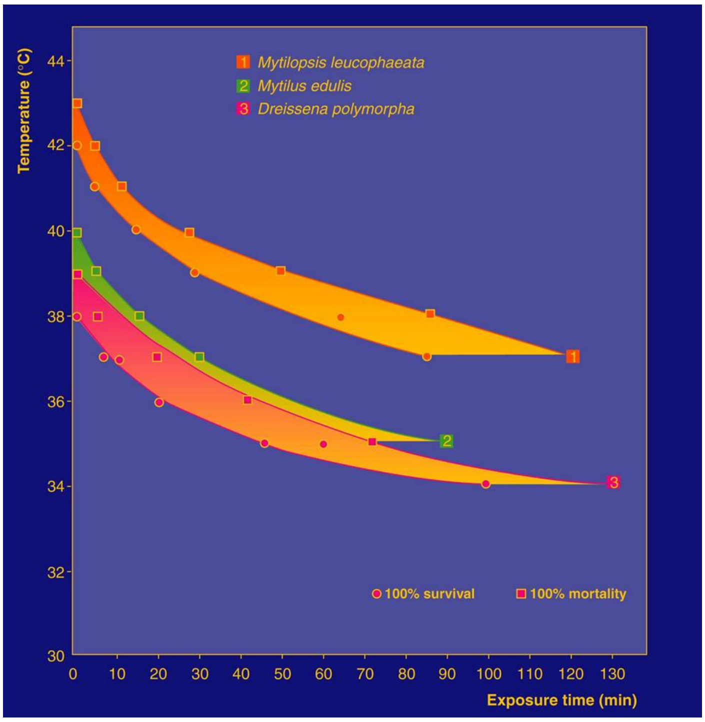

Figure 7 Comparison time mortality (100%). Source van der Velde et al., 1997

In The Netherlands “Thermoshock” is applied at two fresh water cooled stations (units) and two seawater cooled units at the moment. The mortality curve of *D. polymorpha* is about 4 °C lower than that of *Mytilus edulis* and *Mytilopsis leucophaeata* in The Netherlands. It has to be noted that the results are valid for the climatic conditions as found in the inland and seashore waters of The Netherlands. Mussel populations from different geographical locations, with different water temperatures can have higher or lower lethal temperatures during heat treatment as was shown by Graham et al. (1975) in California. Lethal temperatures were found to be 2 to 3 degrees higher for mussels acclimated at higher water temperatures. Recently, the effectiveness of the ‘thermo-shock’ treatment to control the quagga mussel (*D. rostriformis bugensis*) in comparison to the effectiveness to the zebra mussel, has been investigated by KEMA in the Netherlands. Hundred percent mortality of the quagga mussel was achieved after treatment 35 ºC for a period of two hours. The zebra mussels, however, showed a lower mortality rate and the quagga mussel is more sensitive to heat treatment than the zebra mussel. Advantages of heat treatment include minimal environmental impact and relatively low operating and maintenance costs. Disadvantages are the high capital cost in design and construction and production loss even at treatment in the weekends during low load.

6.5.4 **Sonic technology**

The principle underlying the application of sound is that the vibration created by the energy associated with the transmission of sound will remove deposits on surfaces, by “shaking” the deposit free. Cavitation produced by the propagation of sonic waves in the continuous phase near the deposit surface, can also assist the removal process. Claudi and Mackie, (1994) describe how acoustic energy in the range of 39 to 41 kHz fragments early stages of mussels within a few seconds. It also killed attached adults within 19 to 24 hours. The main disadvantage of the technique is the high energy costs involved and the potential harm to the integrity of the CWS. To date there are no commercial devices available using this technique, making the practical value of this technique limited. In Europe no application is known.

6.5.5 **Electric magnetic fields**

An electro-physical treatment as substitute for conventional chemical treatment is the Hydroflow electronic fluid conditioning system of the company Hydropath (England). This system stops scale forming in pipes, boilers and process equipment by creating a nuclei in the water to which scale-forming salts become attached as a result of temperature and pressure changes. Instead of attaching to pipes and other surfaces, the suspended crystals wash out with the water flow. Experiments at Haifa power plant (Israel), using the Hydroflow-system in a marine fed heat exchanger showed anti-fouling activity for micro- and macrofouling, also.

6.6 **Design aspects CW system**

Many design and layout features directly, or indirectly affect the amount of biocide needed for adequate biofouling control in an operation CWS. In chapter 6.5.2. the velocity in the pipes is already mentioned and can have a beneficial impact on fouling control.

Many antifouling techniques require special provisions to be integrated in the design of the CWS. Examples of these are filtering devices, mechanical cleaning devices and facilities, backwash systems, provisions for recirculation of the cooling water (for thermal treatment) or special dosing racks and dosing points. Provisions can also be of a more simple nature, for example connection points for chemical and biological monitoring devices.

Intake structures should be designed in such a way that entrainment of fish, debris, organic and inorganic material, including suspended matter is kept at a minimum. Macro filters, such as rotating filter screens, in combination with automatically cleaning trash-racks are useful to prevent larger (> 5 mm) particles from entering into the CWS.

When designing a CWS, stagnant zones and sharp curves in conduits and heat exchangers (*e.g.* man holes and dead end lines) should be kept to a minimum. In the stagnant zones biological growth thrives, because water velocities are low which favours settlement of biofouling organisms. Additionally, the mass transfer of biocides to the biofilm will be reduced if the water velocity is too low. This is especially important in once-through CWS at locations where macrofouling is an issue. Water velocities therefore are a very important factor in the design of cooling water conduits and heat exchangers. Low water velocities favour precipitation of debris in general, and allow settlement of macrofouling. A general rule of thumb for the cooling water conduits is to keep water velocities above 2.5 m/s, to prevent settlement of macrofouling as good as possible. In the heat exchanger tubes velocities should be kept higher than 2.5 m/s, to ensure effective heat transfer and to prevent macrofouling settlement. Ti tubed condensers can withstand velocities up to 3 m/s without any problem. Too high water velocities however, introduce a risk of corrosion erosion. Critical water velocities depend very much on the type of material used (*e.g.* 7 m/s for carbon steel, 2 m/s for 90/10 Cu/Ni alloys).

Titanium heat exchangers have proven to be corrosion-proof, even at locations where seawater is used as a coolant, under severe fouling conditions. Micro-organisms colonise titanium tubes much more rapidly than copper alloy heat exchangers, making it necessary to install on-line sponge ball cleaning system.

Consider the following preventive measures in the design phase of the CWS:

- avoid low water velocity zones (e.g. excess piping, T-joints, man-holes)
- apply smoothed hydrodynamic outlines of surfaces, avoid sharp bends
- avoid over-sizing of intake structures, since these are subject to heavy fouling
- design intake, such that intake of debris is minimized
- avoid low water velocities in cooling water conduits (< 2,5 m/s)
- avoid low water velocities in heat exchanger tubes (< 2 m/s)
- apply non-toxic, foul-release coatings on fouling sensitive spots
- apply corrosion resistant materials for heat exchangers (e.g. titanium)
- for conduits, heat exchanger in- and outlet boxes, reinforced plastics can be used.

In the design phase of the CWS, the following provisions should be considered:

- cooling water intake designed according to BAT-guidance with respect to intake velocities, trash rack and filter screens, including fish return system
- dosing racks that ensure good mixing of the biocide with the cooling water
- the application of targeted dosing, or section dosing
- small tubing connections for monitoring devices at crucial points (e.g. heat exchanger).

7 INNOVATIVE TECHNIQUES TO CONTROL THE ZEBRA MUSSEL

New developments to control zebra mussels in cooling water systems are an ongoing process. Lower cost and environmental impact are the two main key factors to stimulate the search for new techniques. In this paragraph several new techniques are described.

7.1 BioBullets

The University of Cambridge developed a new innovative method to gain a very effective mitigation of fresh water mussel (e.g. *Dreissena sp. Aldridge et.al. 2006, Costa et.al. 2008*). With this method crystalline shapes of active compounds (biocide) are coated with a digestible layer, which are called BioBullets. Potassium chloride (KCl) and quaternary ammonium compounds (QAC's) have proven to be interesting and effective compounds to mitigate Zebra mussels. However, a dosing of KCl and QAC's in a cooling water system might have disadvantages like the amount necessary and the discharge of the excess dissolved particles of QAC's that have to be neutralized. By applying the dosed chemicals as BioBullets most of these disadvantages can be prevented. Mussels will ingest BioBullets in the same way as its food and will therefore not close it valves immediately as a reaction on a toxic compound. The closure of valves is the natural reaction of mussels when exposed to a toxic compound (e.g. chlorine). Closing of the valves will reduce the dosing effect strongly because the mussel will switch its metabolism into anaerobe metabolism and will live on its reserves. The hypothesis that mussel will not close their valves immediately when BioBullets are dosed will be proven in this study. This will lead to a very effective mitigation on mussels. There are already several successful tests carried out in the UK. Most tests were carried out using KCl BioBullets. The tests were carried out by the University of Cambridge (Aldridge *et al.*, 2006). Figure 8 present a schematic view of the principle of BioBullets

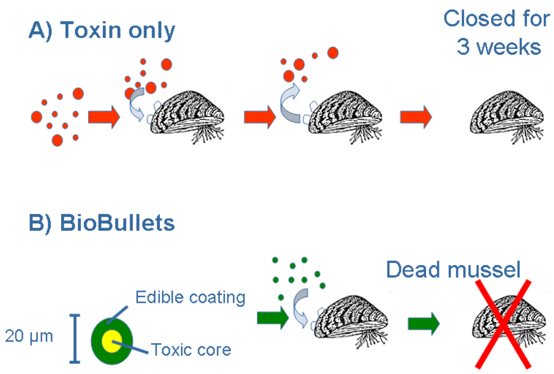

Figure 8 Principe of the BioBullets (source Aldridge)

KEMA also tested both types of BioBullets in 2008 using fresh water mussels (both zebra and quagga). From the results it is concluded that the principle of using BioBullets to mitigate mussel fouling has been proven. Especially the QAC BioBullets were very effective. However, to be able to dose at a power plant installation the dosing of the BioBullets has to be optimised. For smaller cooling water circuits this could in potential be a useful option. Also the necessity of a dosing of bentonite in the discharge area to bind the free available QAC compounds and make them harmless has to be studied.

During tests in the UK Environment Agency accepted a discharge limit for QAC compounds in drinking water of 10 mg/l.

BioBullets look to be an attractive alternative for mussel fouling mitigation in terms of effectivity and dosing time. However, the effect on other fouling organisms (e.g. hydroids) is unknown and has to be studied in another study.

Pros:

- targeted dosing for mussels
- no excessive dosing / discharge of ‘unused’ chemicals
- will not affect other non-target organisms in the receiving water.

Cons:

- only larger specimens take up sufficient amounts of BioBullets
- amount of material needed to treat a full cooling water volume
- relatively costly compared with Chlorine.

7.2 Zequanox™

Zequanox™ is a microbial pesticide comprised of *Pseudomonas fluorescens* CL145A (Pf CL145A) discovered in North American soil. It represents the first selective, environmentally friendly product to control invasive zebra and quagga mussels (*Dreissena polymorpha* and *Dreissena rostriformis bugensis*). In earlier work, the New York State Museum found that Pf CL145A was highly selective and efficacious for killing Dreissenid mussels. Extensive nontarget ecotoxicity testing shows that it does not harm other species. Recently, Marrone Bio Innovations (MBI) has been working to realize the commercial potential of Pf CL145A. MBI isolated, identified, and quantified some of the novel chemicals in Pf CL145A responsible for its selective activity against invasive mussels. These novel chemicals have potential as a new family of specific molluscicides. MBI optimized its fermentation process to produce high concentrations of active compounds within Pf CL145A. Now, they are developing stable formulations of killed Pf CL145A cells that are cost-effective and user-friendly.

In 2009, MBI began manufacturing Zequanox™ for field trials at hydropower facilities. MBI is working with its customers to guide product development. Zequanox™ meets EPA's criteria for registration as a reduced risk pesticide; MBI expects EPA registration in June 2010. Although product development is continuing, MBI is prepared to provide Zequanox™ to initial customers after EPA registration to replace current, less-selective molluscicides. In early 2010, MBI will provide Zequanox™ to the U.S. Bureau of Reclamation to treat its facilities along the Colorado River under an EPA FIFRA Section 18 Emergency Use Exemption registration.

Pros:
- all zebra mussels, regardless of size, are susceptible to this bacterium
- probably also effective against other filter-feeding bivalves.

Cons:
- affect other non-target organisms in the receiving waters
- bacterial mass production not available
- lack of knowledge on bacterial cell formulation for long-term storage
- trials were conducted and not practically tested in power plants sites
- additional details on its effect on other non-target species.

7.3 Clean anti fouling coatings

As part of an effort to discover antifoulants with a reduced environmental footprint, the endocannabinoid, anandamide and nine other compounds sharing structural or functional features were tested for their ability to inhibit zebra mussel byssal attachment. The compounds were used as part of a coating to prevent byssal attachment. Some of these new compounds had no negative impact on mussels at concentrations maximally inhibiting byssal attachment and three of some had no significant cumulative toxicity towards a non-target organism, Daphnia magna. This discovery demonstrates that both naturally occurring and synthetic cannabinoids can serve as non-toxic efficacious zebra mussel antifoulants. Applications with this technology may lead to a new genre of cleaner antifoulants, because the strategy is to prevent attachment rather than to poison mussels. This method is still under development and no major field tests are applied yet.

Pros:

- promising new technique
- non toxic.

Cons:

- no proven technology at this moment.

7.4 **Carbon dioxide**

Laboratory studies on fouling control to mitigate Zebra Mussels have demonstrated narcotizing effects of carbon dioxide at concentrations of 100 mg/1 and toxic effects at concentrations of 500 mg/L (KEMA, 2003, Elzinga 1994). The narcotizing effect also resulted in releasing of the settled mussels due to the release of the byssus threats. In addition the use of carbon dioxide proved to be very effective as a pre-treatment for chemical dosing, e.g. chlorination. Since the mussels open up completely once narcotized they are not capable to close up and protect themselves for a chlorine dosage. This resulted in a very short effect with 100% mortality within several days. In addition it was observed that mussel were not capable to produce byssus threads during increased concentrations of carbon dioxide in the water. Also attached mussels came loose when the carbon dioxide concentrations increased. This means that even with a dosing of carbon dioxide only mussels can be mitigated an removed from a water system although are not killed. Once the concentration of carbon dioxide is back to background levels the mussels recover and attach themselves again.

However this technique looks very promising there are some disadvantages like the reduction of pH of the intake water due to the carbon dioxide concentration increase. Also the method of dosing carbon dioxide into the intake water to result in the necessary concentrations is a big challenge, especially for large water intake systems. To be able to apply this technology in practice it needs some additional research and upgrading before it is applicable. Tests up to water flows up to 0,01 m^3/second have been proven effective.

Pros:

- proven to be very effective to mitigate Zebra mussel fouling
- usable as pre-treatment, reduces the of other oxidant strongly
- applicable in flow up to 0.01 m^3/second
- Hazop study before use.

Cons:

- not proven technology at full scale
- dosing of carbon dioxide still difficult
- reduction of pH intake water could result in increased corrosion risks.

8 EUROPEAN REGULATIONS FOR APPLYING BIOCIDAL CONTROL TECHNIQUES

Chemical control of biofouling is generally applied as an economically viable option for the smooth operation and integrity of the cooling water system and its components. However, it imposes an environmental risk due to the discharge of water treatment chemicals. Antifouling treatment by chemicals (biocides) must therefore be effective in controlling biofouling and remain within environmental limits.

The ideal biocide is effective to one particular organism (or group of organisms) in the cooling water system, but has no side effects on non-target organisms. It is also not consumed by reactions with other chemicals and materials in the water (*i.e.* there is no ‘demand’) and as soon as it enters the environment, it breaks down into non-toxic compounds.

Sodium hypochlorite is world wide still the most applied antifouling chemical in cooling water systems and numerous other applications were sanitation is needed. However, chlorine is in principle not as ideal as described above: it is non-specific and reacts with virtually all constituents of natural waters – including man-made pollutants – to yield products having varying degrees of persistence and toxicity. Traditionally, the main environmental concern has been with the acutely toxic, but easily measured oxidants, rather than with possible chronic long-term effects of non-oxidants. In addition, the chemistry and even the terminology of water chlorination is complex.

Although a variety of alternative compounds are available, sodium hypochlorite is considered one of the best available technologies for the control of micro- and macro-fouling organisms, especially in once through cooling water systems. This statement is also described in the IPPC BREF Industrial Cooling System document, which is due to its proven effectiveness, large industrial experience, moderate costs and by the fact that low-level chlorination has proven not to have major ecological impact. However, sodium hypochlorite reacts with organic compounds present in the surface water (*i.e.* oxidation and substitution reactions between chlorine and organic matter). These reactions take place in seconds and form a largely, undefined mixture of halogenated organic chemicals, so-called chlorination by-products (CBPs). The formation and degradation of these CBPs in cooling water systems and in the receiving water body is complex due to the complexity of reaction involved and high number of compounds involved, which also depend on the local water quality (presence of precursors such as humic and fulvine acids). Due to this complexity and the lack of satisfying data on the long term toxicity of the discharged CBP levels and their environmental effects to different groups of organisms, chlorination is still regarded as an (eco)toxicological concern.

The driving factor for permitting the application of chlorination as biofouling method in cooling water system is the precaution principle employed by the water authorities, *i.e.* when there is reasonable suspicion that the discharge of FO/TRO and/or CBPs could form a problem, action must be taken. At this moment, many water authorities world wide exert pressure to industries to diminish their chlorine use, driven by the acute toxicity of free and total chlorine/bromine and the formation of chlorination by-products (CBPs). European chemical legislation affecting the application of cooling water additives in particular can be found in:

- the Biocidal Products Directive 98/8 (EU, 1998)
- the Integrated Pollution Prevention and Control (IPPC) Reference Document on the application of Best Available Techniques to Industrial Cooling Systems December 2001 (IPPC, 2001)
- the Water Framework Directive (EU, 2000), which however does not mention implicit chlorine, but does contain some of the CBPs in the Priority (Hazardous) Substances list.

Next to these European directives, member states of the EU have their own particular regulations for permitting and controlling the application of chlorine.

8.1 Europe

8.1.1 Biocidal Product Directive

The Biocidal Product Directive (BPD) of the European Union describes biocides as: ‘products used to control the growth and settlement of biofouling organisms (microbes and higher forms of plant or animal species) on vessels, aquaculture equipment or other structures used in water’ (EU, 1998). The scope of the Directive is very wide, covering 23 different product types. These include disinfectants used in different areas, chemicals used for preservation of products and materials, non-agricultural pesticides and anti-fouling products used on hulls of vessels. The Directive does not apply to certain product types already covered by other Community legislation, such as plant protection products, medicines, and cosmetics.

The basic principles of the Directive are:

- active substances have to be assessed and the decision on their inclusion into Annex I of the Directive shall be taken at Community level

- comparative assessment will be made at the Community level when an active substance, although in principle acceptable, still causes concern. Inclusion to Annex I may be denied if there are less harmful, suitable substitutes available for the same purpose
- Member States shall authorise the biocidal products in accordance with the rules and procedures set in Annex VI of the Directive. They can only authorise products which contain active substances included in Annex I
- the producers and formulators responsible for the placing of the market of the biocidal products and their active substances must apply for authorisation and submit all necessary studies and other information needed for the assessments and the decision making
- a biocidal product authorised in one Member State shall be authorised upon application also in other Member State unless there are specific grounds to derogate from this principle of mutual recognition.

The biocides work area provides Technical and Scientific support to Member States' Competent Authorities and the Commission with respect to the implementation of the Biocidal Products Directive (BPD) 98/8/EC on the placing on the market of biocidal products, which entered into force on 14 May 2000.

The Directive defines biocidal products and sets out a frame for their evaluation in a two step procedure where the first step is the entry of the active substances onto Annex I (or IA or IB) and the second step is the authorisation of the products in which the active substances are used. Active substances are divided into:

- new active substances that cannot be placed on the market for biocidal purposes unless they are included onto Annex I
- existing active substances evaluated in the Review Programme, according to Article 16 of the BPD. The Review Program was established via several Regulations. The latest Regulation is Regulation (EC) No 1451/2007, which repeals Regulation (EC) No 2032/2003, and entered into force on 31 December 2007.

8.1.1.1 European Commission: RAR

The Scientific Committee on Health and Environmental Risks (abbreviated SCHER) is one of the independent scientific committees managed by the Directorate-General for Health and Consumer Protection of the European Commission, which provide scientific advice to the Commission on issues related to consumer products.

Council Regulation 793/93 provides the framework for the evaluation and control of the risk of existing substances. Member States prepare Risk Assessment Reports on priority substances. The reports are then examined by the Technical Committee under the Regulation and, when appropriate, the Commission invites the Scientific Committee on Health and Environmental Risks (SCHER) to give its opinion.

The draft risk assessment report (RAR) was published in November 2007. In 2008, the SCHER concluded that the Risk Assessment Report (RAR) was of good quality, but on some points needs more information and details of the procedures applied for reaching the conclusions (see Annex A).

From the RAR, since it is a valuable source, relevant information related to cooling water systems is described in this report.

8.1.1.2 Integrated Pollution Prevention and Control Guideline (IPPC)

The IPPC reference document on the application of best available techniques (BAT) to Industrial Cooling Systems (IPPC, 2001) draws the conclusion that ‘industrial cooling processes are very site- and process-specific’. So site-specific conditions determine the actual practices applied. Both chlorine and hypochlorite are included as recommended techniques in the BAT document.

The IPPC will be replaced by the Industrial Emissions Directive (IED). The IED states that the BREFs are applied as reference for setting permit conditions and those competent authorities may set stricter permit conditions than those achievable by the use of BAT.

8.1.1.3 Water Framework Directive (WFD)

The Water Framework Directive was voted by the European Parliament and the European Council in October 2000 and entered into force in December 2000. It aims to establish a legal framework for the protection of water quality in European countries (for river water, sea water, groundwater and coastal water). The directive recognizes that specific measures have to be adopted at a European level against water pollution by individual pollutants, or groups of pollutants, presenting a significant risk to the aquatic environment and water used for the production of drink water.

These measures aim to progressively reduce the level of pollution for 33 priority substances, which could threaten human health or ecosystems. The goal is to decrease naturally occurring pollutants to the background value and man-made synthetic pollutants to values close to zero. The complete removal of emissions from all potential sources is obviously impossible for substances produced through natural processes, but the legal framework should prevent all emissions and discharges of those priority substances which derive from human activities.

The list of 33 priority substances was composed by the European Commission with a panel of experts in the field of chemistry and maritime pollution, delegates of the member states and European firms and the European Environment Agency. The framework states that the emissions of priority substances need to be reduced progressively. The priority substances include 13 priority hazardous substances. These are substances which are toxic, persistent and likely to bioaccumulate and other substances which give rise to equal concern. The emissions, discharges and losses of these substances need to be ceased or phased out.

The Directive on Priority Substances of 2008 (a daughter directive of the Water Framework Directive) also made a list of substances for which it should be investigated whether they should be included in the list of priority substances or priority hazardous substances. [1]

List of 33 priority substances

The following 33 substances and chemical compounds are included in the list of priority substances established by the European Union. Some of these priority substances are also priority hazardous substances.

List of 20 priority substances

The following 20 substances are priority substances, but not priority hazardous substances:

- Alachlor
- Atrazine
- Benzene
- Chlorfenvinphos
- Chlorpyrifos
- 1,2-Dichloroethane
- Dichloromethane
- Di(2-ethylhexyl)phthalate (DEHP)
- Diuron
- Fluoranthene
- Isoproturon

- Lead and its compounds
- Naphthalene
- Nickel and its compounds
- Octylphenols
- Pentachlorophenol
- Simazine
- Trichlorobenzenes
- Trichloromethane
- Trifluralin.

List of 13 priority hazardous substances

The following 13 substances are priority substances and priority hazardous substances:

- Anthracene
- Anthracene
- Pentabromodiphenylether
- Cadmium and its compounds
- C_{10-13}-chloroalkanes
- Endosulphan
- Hexachlorobenzene
- Hexachlorobutadiene
- Hexachlorocyclohexane
- Mercury and its compounds
- Nonylphenols
- Pentachlorobenzene
- Polyaromatic hydrocarbons
- Tributyltin compounds.

Substances subject to review for possible identification as priority substances or priority hazardous substances

The following substances and chemical compounds are included in the list of substances, established by the European Union, for which it should be reviewed whether they should be included in the list of priority substances or priority hazardous substances:

- AMPA
- Bentazon
- Bisphenol-A
- Dicofol
- EDTA

- Free cyanide
- Glyphosate
- Mecoprop
- Musk xylene
- Perfluorooctane sulphonic acid (PFOS)
- Quinoxyfen, Dioxins, PCB.

With the adaptation of permits to the IPPC-guideline, based on article 22 paragraph 6 of the WFD, the priority (hazardous) substances (PS/PHS) from the WFD must be taken into account. Annex III of the IPPC-guideline contains an indicative list of substances that are to be address during permitting. Article 22 paragraph 6 of the WFD determines that the priority (hazardous) substances that are not on the indicative list, must be added. Based on article 9 of the IPPC-guideline a permit must contain emission limit values for all these substances, when these substances are released from the IPPC-installation in significant quantities. Also, where possible these substances must be tested against the applying water quality standards. For this, an integrated approach, as determined in the '*immission-evaluation*', must be applied.

Priority substances are subject to reduction. Priority hazardous substances are subject to cessation or phasing out of discharges, emissions and losses within an appropriate timetable. For practical all these substances environmental quality standards are available, on which further measures can be demanded. Important questions are the extent of reduction of emissions of priority substances, within which time frame priority hazardous substances must be phased-out and whether this can be attained. On the priority substances list several chlorination by-products are listed:

- 1,2 dichlorethane
- dichloromethane
- hexachlorobenzene
- pentachlorophenol
- trichlorobenzene
- trichloromethane
- C10-C13 alkanes.

Not all these substances are necessarily formed during chlorination and present in the discharged cooling water, this depends on the dosed hypochlorite concentration and the presence of necessary precursors.

8.1.1.4 Directive 2000/60/EC

Decision No 2455/2001/EC of the European Parliament and the of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC.

Under Directive 2000/60/EC specific measures must be adopted at Community level against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, including such risks to waters used for the abstraction of drinking water. Such measures are aimed at the progressive reduction and, for priority hazardous substances, as defined in the second sentence of point 30 of Article 2 of Directive 2000/60/EC, at the cessation or phasing out of discharges, emissions and losses within 20 years after their adoption at Community level, with the ultimate aim, as recognised in the context of achieving the objectives of relevant international agreements, of achieving concentrations in the marine environment approaching background values for naturally occurring substances and close to zero for man-made synthetic substances. With a view to the adoption of these measures, it is necessary to establish, as Annex X to Directive 2000/60/EC, the list of priority substances, including the priority hazardous substances. The list has been prepared taking into account the recommendations referred to in Article 16(5) of Directive 2000/60/EC.

8.2 National regulations in Europe

8.2.1 Netherlands

In the Netherlands cooling water biocides belong to the groups of non agricultural biocides which are applied on the largest scale. In order to minimize adverse effects on the receiving environment industrial and governmental officials agreed on a plan for the reduction of the use of non agricultural biocides. This is described in the Dutch Policy Plan on non-agricultural biocides. Optimization of the use of biocides (see also annex B) in cooling water is one of the key elements in this plan. To realize the reduction of hypochlorite use in cooling water systems, a stepwise approach is followed. The first step for companies is to develop reference on hypochlorite usage, based on experience over recent years. Various factors such as composition of cooling water and climatic effects should be taken into account. The next step is to frame a quantified reduction plan how the company will reduce the usage of hypochlorite, including a time table. Also, completely alternative fouling control methods can be considered in this stage, for instance ozone and air cooling.

For once through cooling water systems[5], within a period of three to five years, the reduction plan in step 2 should result in realization of discharge limits of 0.1-0.2 mg free chlorine/L as a maximum value in periods that chlorine is applied. In specific cases with regard to the discharge limits, more specific tailor made solutions can be applied. Also in this step the primary goal still remains the reduction of hypochlorite usage. For open circulating cooling systems a plan for the reduction of the hypochlorite use should be developed as well.

In order to evaluate the effectiveness of the biocide reduction program companies should report periodically the used amounts of hypochlorite and the analytical data of the free chlorine measurements to the authorities. If necessary the reduction program can be readjusted in debate between company and authorities.

8.2.2 **UK**

UK Legal Framework

Reviewing the standards for discharge of chlorine and chlorine derivatives is complicated by the different control regimes in different parts of the United Kingdom. In England and Wales the Environment Agency (EA) is the competent authority, but Scotland and Northern Ireland have their own regulatory organizations (Scottish Environment Protection Agency (SEPA) and Environment Agency of Northern Ireland (EANI) respectively) and can set their own standards within the framework of European Law. Certain offshore Islands (including Guernsey, Jersey and the Isle of Man) are not subject to European directives (though they tend to comply with them voluntarily) and, strictly, are not even part of the UK.

Free Chlorine

The complexity of ‘free chlorine’ chemistry in saline waters is well understood by the Environment Agency. Nevertheless the only formal guidance issued by the Agency is as part of a series of standards for Non-Statutory (Operational) Environmental Quality Standards (EQS) and specifies chlorine (which it won’t be!).

Chlorine/TRO: Under the WFD “River Basin Districts Typology Standards and Groundwater threshold values (Water Framework Directive) "England and Wales Directions 2009”, chlorine/TRO is a ‘specific pollutant’ with a statutory saline waters EQS of 10ug/l (Annual Average)

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[5] For power plants and industrial cooling systems that already discharge less than the limits indicated this should not result in higher dosage and discharge of hypochlorite.

In practice ‘chlorine’, ‘free chlorine’, ‘chlorine produce oxidant (CPO)’, ‘total residual oxidant (TRO)’ and et cetera are not distinguished as there is no available method for distinguishing between them in environmental samples. The DPD colorimetric method is the only one in use. This is considered unreliable at concentrations as low as 10µg/L and consequently considerable use is made of modelling with the uncertainties this introduces.

Exceeding of the MAC is acceptable within a mixing zone around the discharge. Recommendations for assessing the extent of a mixing zone are given in an internal guidance Environment Agency guidance document *Water Quality Consenting Guidance Dangerous Substances in Discharges to Surface Waters* (EA, 2005), but no specific guidance is currently provided on how to define the acceptable extent of a mixing zone in Transitional and Coastal (TraC) waters. A practical consideration often applied is that a mixing zone should avoid any inter-tidal areas.

SEPA has published specific guidance for assessing marine mixing zones in Scottish Waters (SEPA, 2009).

The UK is contributing to current discussions for a consistent ‘tiered approach’ under the Common Implementation Strategy of the Water Framework Directive for the identification of mixing zones under Article 4(4) of the EQS Directive 2008/105/EC to support Working Group E on Priority Substances.

Future developments

In 2007 the Environment Agency and the Scotland & Northern Ireland Forum for Environmental Research (SNIFFER) published on behalf of the Water Framework Directive UK Technical Advisory Group a report on proposed Environmental Quality Standards for chlorine (free and available) (SNIFFER, 2007).

For saltwater the following standards were proposed for free and available chlorine:

Table 5

Receiving medium/exposure scenario	**Proposed PNEC (µg/L)**	**Existing EQS (µg/L)**
saltwater - long-term	0.04	-
saltwater - short-term	0.05	10 (TRO)

* *PNEC = predicted no effect concentration*

These proposal received much criticism, the major ones being:

a the standards were derived on chlorine toxicity which is inappropriate in saline waters

b there is no practical method of measuring concentrations at this level.

No action has been taken on this report.

The Scottish Environment Protection Agency recently (December 2009) published a methodology for prioritization and ranking chemicals of concern to Scotland's environment (Clarke *et al.*, 2009). It will be used to identify and prioritize chemicals under Annex VIII of the Water Framework Directive. Chemicals are ranked on the basis of hazard and exposure risk from 1 (least risk) to 6 (greatest risk) Chlorine (free) is given an exposure score of 2 and a hazard score of 4 giving an overall risk of 3. The Environment Agency is currently undertaking a similar exercise. In summary the UK has identified 'chlorine' as a possible priority pollutant, but currently there are no current active moves to introduce new standards. It is reasonable to assume that improved methods of detection and speciation at low levels (<<10µg/L TRO) will be required for any new standards to be credible.

Chlorine Derivatives

Brominated compounds are invariably found in chlorinated marine cooling waters. Bromoform dominates, with dibromoacetonitrile and 2,4,6,-tribromophenol frequently also detected. Whilst there is no standard for bromoform, chloroform is a 'list 1' substance under the Dangerous Substances directive and has a statutory Environmental Quality Standard.

Chloroform (total): The previous Dangerous Substances Directive value of 12 ug/l (annual average) has been superseded by one of 2.5 ug/l AA under the Environmental Quality Standards Directive (2008/105/EC). Both are statutory limits.

Bromine compounds typically exhibit a lower eco-toxicity than their chlorine analogue, so the chloroform standard is usually applied by the EA as a precautionary approach, though there is no formal policy to underpin this.

Where fresh/waste water is used for cooling (albeit with a final discharge to saline waters) the presence of ammonia will lead to the formation of chloramines (monochloramine, dichloramine & etc.) These are not normally characterized but included in a TRO concentration.

8.2.3 France

In France, the current limits of chlorination concentration are ≤ 1 mg/L at the discharge. The specific site authorization and discharge limits for bromoform discharge in marine environment are shown in Table 6.

Table 6 Site authorization and discharge limits for marine field in France

	Annual flow (kg)	**24 hr flux (kg)**	**2 hr flux (kg)**	**Maximum concentration in the effluent (mg/L)**	**Daily average concentration added before discharging (mg/L)**
Ramanville May 11th 2000	11,000	120	10	0.05	0.01
Gravelines November 7th 2003	230,000	950	85	0.05	-
Penly February 15th 2008	-	230	-	0.03	-
Paluel May 11th 2000	175,000	715	65	0.05	0.01

Concerning fresh waters, continuous chlorination of nuclear power plant cooling towers is currently forbidden because of CBP's in the discharge. Some shock chlorinations are nevertheless autorised in certain cases.

8.2.4 Italy

In Italy the general limit of chlorine at the discharge is 0.2 mg Cl_2/L in freshwater as well as in sea water. Some specific restrictive local regulation banded completely the use of hypochlorite and chlorine gas, as in the cases of the discharge in the Venice lagoons and in some other special protected areas the limit is 0.1 mg Cl_2/L.

Non-oxidizing biocides

The product Mexel 432/336/0 is according to the ‘Algemene Beoordelings Methodiek (ABM)’ (General Assessment Methodology (GAM) as described in the paper ‘Assessment of substances and preparations within the context of the implementation of the water discharge policy’ of May 2000 by the Integrated-water Management Committee), classified as ‘toxic to aquatic organisms’ with decontamination effort ‘B’ similar to 7B. Taking into account the toxicity of the product itself towards aquatic species (< 1 mg/L), it is proposed to classify the product Mexel 432/336/0 with ‘very toxic to aquatic organisms’ with decontamination effort ‘B’ similar to 5B (TNO, 2009)

According to MEXEL Industries the Mexel 432/336/0 and Mexel 432/0 product have the same physicochemical and toxicological properties. The formulation of Mexel 432/336/0 is similar to the Mexel 432/0 product. It is a reformulation of this last product, in order to be in conformity with the directive 98/8/EC of the European Parliament concerning the introduction of biocidal products on the market (BPD). This reformulation is based on 1.7% of the Mexel 432/0 product and corresponds to the replacement by one alkylamine not notified in the BPD by another one, having the same alkyl chain, notified on the BPD.

8.3 Overview regulations for applying biocidal control techniques

An overview of the regulations for applying biocidal control techniques is given in Table 7.

Table 7 Discharge regulations/guidelines

IPPC - Europe

	MCL (mg l^{-1})
Chlorine 24h-average	0.2 mg/L FO max
Chlorine max. conc.	0.5 mg/L FO max
AOX	0.15 mg/L AOX

U.S. EPA Regulations

DBP	MCL (mg l^{-1})
Total THMs	0.080
5 Haloacetic acids	0.060
Bromate	0.010
Chlorite	1.0

World Health Organization (WHO) Guidelines

DBP	Guideline value (mg l^{-1})
Chloroform	0.2
Bromodichloromethane	0.06
Dibromochloromethane	0.1
Bromoform	0.1
Dichloroacetic acid	0.05
Trichloroacetic acid	0.2
Bromate	0.01
Chlorite	0.7b
Chloral hydrate (trichloroacetaldehyde)	0.01
Dichloroacetonitrile	0.02
Dibromoacetonitrile	0.07
Cyanogen chloride	0.07
2,4,6-Trichlorophenol	0.2
Formaldehyde	0.9

European Union Standards

DBP	Standard value (µg l^{-1})
Total THMs	100
Bromate	10

Total THMs: sum of the concentrations of chloroform, bromoform, bromodichloromethane, and dibromochloromethane.

WHO guidelines: the five haloacetic acids represent the sum of monochloro-, dichloro-, trichloro-, monobromo-, and dibromoacetic acid.

9 COST OF FOULING CONTROL

For the indication of costs, this is always very site specific. The amount of water flow and the system specifications determine largely the cost benefits of each method. Basically it can be said that chlorination is the most cost beneficial method, however if the cooling water system is designed to apply heat treatment (by recirculation) this could also be very cost beneficial. It is suggested to carry out a cost benefit analysis per different company to get a clear indication of the most cost beneficial option for this specific company.

10 DETERMINATION OF BAT

The BAT is in general a local matter taken into account the specific requirements of process, environment and economics. To determine the general BAT for cooling systems the IPPC BREF document prepared an “approach” described below.

In numerous industrial processes, heat has to be removed by what is called a waste heat removal system or cooling system. Operating these cooling systems has certain environmental consequences. The level and character of the environmental impact varies depending on the cooling principle and the way these systems are operated. To minimise this impact an “approach” can be followed which aims at prevention of emissions by proper design and selection of techniques. Within the framework of IPPC, cooling should be considered as an integrated part of the overall energy management of an industrial process.

The intention should be to reuse superfluous heat of one process in other parts of the same process or in different processes on site in order to minimise the need for discharge of waste heat into the environment. This will affect the overall energy efficiency of a process and reduce the demand for cooling, for the required capacity of the system and for its operational demands. The optimization of energy efficiency, however, is a complex exercise and regarded as highly process-specific and as such beyond the scope of this horizontal document. If there are no options for reuse on-site, this does not have to lead automatically to discharge of heat into the environment, but options for reuse off-site in industrial or civil applications may be considered. In the end, if options for reuse of heat cannot be exploited any further, discharge of superfluous heat into the environment is to be considered.

Once the level of heat to be removed has been assessed, a first selection of the appropriate system for cooling can be decided upon. Much of the environmental performance due to the operation of a cooling system can be influenced by proper design and by selection of the right material taking into account the process requirements and local aspects. It is reported that 80% of cooling system performance has already been determined at the design table and 20% by the way the cooling system is operated (so-called 80/20 rule). Many different factors need balancing in assessing what is BAT (best available techniques) for the reduction of the environmental impact of cooling. Right from the start it is important to realise that a cooling system is an auxiliary, but generally crucial and integrated system for an industrial process and that every change applied to the process of cooling may potentially affect the performance of the industrial or manufacturing process to be cooled.

Therefore, the integrated assessment of the consumption and emissions of cooling systems and the decision on the application of a cooling technique both should be made in the light of the total environmental performance of the plant and within the requirements of the process to be cooled, ultimately balanced with costs. The required level of cooling must be guaranteed, with minimal consequences for the environment. The required level of cooling is process-specific. Where some processes can tolerate a certain temporary rise in process temperature, other more temperature sensitive processes might not, as this will have a large impact on the environmental performance of the whole plant.

In the document BAT-cooling: European IPPC bureau Sevilla, (Document on the application of Best Available Techniques to Industrial Cooling Systems, Nov. 2000 (http://eippcb.jrc.es). BREF (11.00) Cooling systems) the approach for BAT is described by (van Donk and Jenner, 1996). This “approach” should lead to a balanced decision on the application of a system for cooling and on its optimization based on BAT for both new and existing situations. The Figure 9 shows all the steps to be considered in the selection of biocides. In an existing CWS it is important to characterize the biofouling population and the size of the biofouling risk. Adequate biological monitoring is a prerequisite for this. The cause of the biofouling problem should be analyzed and addressed. The quality of the cooling water can be improved by pre-treatment of the water (e.g. micro- and macro-filtration). This can remove a part of the biofouling risk by reducing the amount of incoming organisms and nutrients. If process leakages are the main cause of increased biological growth, they should be eliminated, for instance by application of corrosion resistant materials or by installation of spare heat exchangers, which allows more frequent mechanical cleaning. In order to improve system conditions, all options mentioned in scheme 1 should be considered.

In figure 10 this biocide selection scheme for BAT approach is presented.

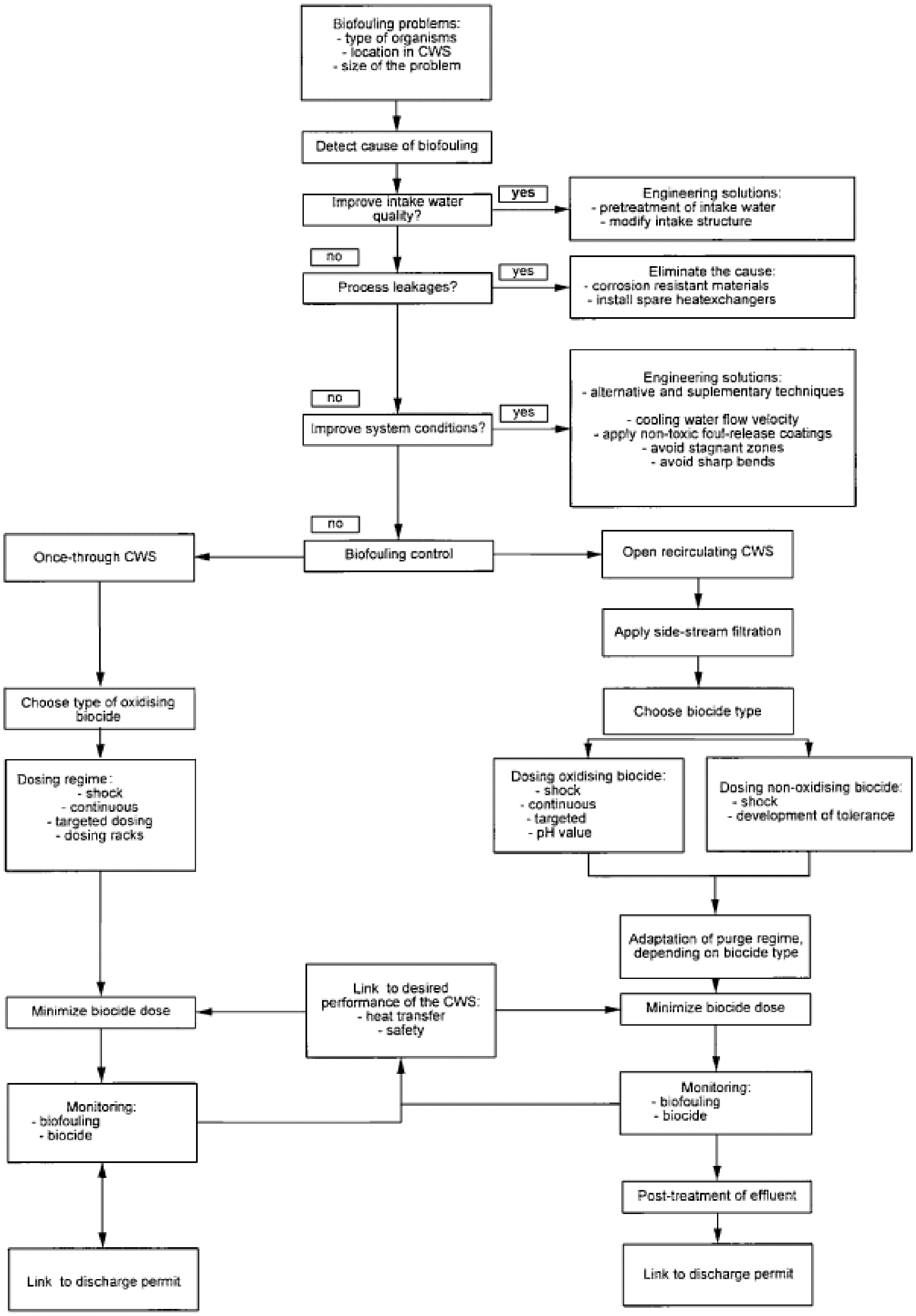

Figure 10 “Approach” for reduction of biocide use in industrial cooling water systems

For new cooling installations it is BAT to start identifying reduction measures in the design phase, applying equipment with low energy requiring requirement and by choosing the appropriate material for equipment in contact with the process substance and/or the cooling water.

For existing installations, technological measures can be BAT under certain circumstances. Generally, a change in technology is cost-intensive where overall efficiency must be maintained. Cost evaluation should then compare investment costs of the change versus the change in operational costs and validate the reduction effect versus other environmental consequences. For example, it would need a comparison between the environmental effects of recirculating the cooling water - requiring the application of biocidal water treatment - against a once-through system without biocides, but a large heat emission to the aquatic environment.

In this report we focus on the emissions to surface water from cooling systems. Emissions from cooling systems can be caused by:

- applied cooling water additives and their reactants
- airborne substances entering through a cooling tower
- corrosion products caused by corrosion of the cooling systems’ equipment, and
- leakage of process chemicals (product) and their reaction products.

10.1 BAT approach for CHE

In the evaluation made for CHE, we focused on the applied cooling water additives and their reactants. The technologies described in chapter 4 of this report are used to prepare the BAT for the companies on the Ebro River. For this evaluation only companies with an once-through or an open recirculation cooling water system are relevant. It must be noted that the company information received by CHE which retracted water from the Ebro River for cooling purpose, did not provide details on the cooling water specification (type of system). Therefore the BAT approach applied is general and needs to be specified more in detail depending on the type of cooling water system. Therefore it is advised to use this general approach and specify more in detail for each individual company.

10.2 **Ranking BAT techniques for the Ebro**

Table 9 Overview of BAT

Company (m3/s)	**Biocide**		**Other Oxidising**			**Non-oxidising**			**Coating**	**Osmotic shock**	**Physical methods**				
	Chlo rine	**Bro mine**	**Ozone**	**H2O2 Peracetic acid** [1]	**UV**[2]	**Isothio-zolone**	**QAC** [3]	**Mexel**[4]			**Filtra tion**	**Water velocity**	**Heat Treatment**[5]	**Sonic treatment**	**Elektr. Magn. Field**
> 5	++	+	-	-	-	-	-	+	+	-	-	+	++	-	-
1 – 5	++	+	-	+	-	-	-	+	+	+	+	+	++	-	-
0.1 – 1	++	+	+	+	-	-	+	+	+	+	+	+	++	-	-
0.01 - 0.1	++	+	+	+	+	-	+	+	+	+	+	+	+	-	-
< 0.01	+	+	+	+	+	-	+	+	+	+	+	+	+	-	-
Other intake types	+	-	+	+	+	-	+	+	+	+	+	+	+	-	-

[1] restricted due to safety and pH impact

[2] restricted for clear waters and recirculation systems

[3] excess needs to be neutralised before discharged

[4] usable for recirculation systems

[5] system needs to be designed to use this treatment

From table 9 it can be concluded that chlorine (as sodium hypochlorite) is for intake water systems at this moment still the BAT technology. It needs to be stressed that a proper tailor made dosing (with pre-dilution) is advised to prevent ineffective control and high discharge concentrations. The disadvantage of chlorine dosing is the risk of producing chlorination byproducts such as THM's. However, studies in the past (Taylor et. Al. 2006) showed that low level chlorination of seawater did not result in proven negative effects for the environment. Since chlorination has to be tailor made and adjusted to the local species that need to be controlled the effects of these byproducts are negligible. For large systems thermal treatment is even more preferred since nu byproducts are formed, however the systems design needs to allow this methodology.

Chlorine dioxide can also be applied, however this is a more costly option. The advantage would be that this product does not produce and THM's, however studies in the USA have proven that chlorine dioxide in fresh water can result in a rise of aldehydes, ketones, carboxylic acids, and brominated organics is given. Moreover, by chlorine dioxide some organics are produced (Richardson et al, 2005). Using spectral identification techniques, more than 40 different DBPs (at sub-ng/l levels) were identified including carboxylic acids and maleic anhydrides.

In reaction with natural organic matter ozone also forms aldehydes, such as formaldehyde, acetaldehyde, and heptanal (Jacangelo et al., 1989; Song et al., 1997) and many other compounds at low levels, e.g., carboxylic acids, aliphatic and alicyclic ketones, glyoxal, methyl glyoxal etc. (Glaze et al., 1989). Formaldehyde is suspicious of carcinogenity. According to the regulation No. 376/2000, its limit concentration is 0.9 mg/l.

The disadvantage of UV is that it is restricted to clean waters, this makes it not very applicable for surface waters. In smaller systems other products could be beneficial, Mexel, coatings, or filter systems. Depending on the systems specifics certain methods can be applied.

New products such as BioBullets or CO_2 seem promising for the future. However, field proven applications in cooling water systems need to be developed and therefore these methods are not defined as BAT at this moment in time.

11 EVALUATION OF INDUSTRIES RELATED BAT

11.1 Industries along the Ebro River

CHE has provided a list of companies that use water taken from the Ebro river or side rivers within the Ebro basin. The companies are ranked in different categories based on the volume of water withdrawn from the river and on the type of industry.

Based on this ranking, the Best Available Technique per group of companies will be determined and elucidated. In appendix I the total list of companies is presented. The methods determined as BAT can be further optimized if the mitigation strategy is adapted to the intake (cooling) water specifications and the breeding periods of Zebra mussels. This ways of optimization is described in chapter 11.2.

According to the table presented in paragraph 10.2 we can advise the following for the different companies that retract Ebro River water for cooling purposes.

11.1.1 Water intake for cooling purposes (> 5 m^3/second)

The companies in the basin which have a water intake capacity from the Ebro River of > 5 m^3/s are nuclear power stations with an once through cooling water system. For cooling water systems with this amount of water flow chlorination and thermal treatment are the BAT, also according to Integrated Pollution Prevention and Control (EU-IPPC) document as accepted within Europe. To be able to apply thermal treatment at an existing location the cooling water system has to be designed accordingly. If this is not the case then chlorination is BAT. It must be noted that this is applicable when only the specific required dosing concentration is applied to prevent the formation of large numbers of chlorination byproducts (CBP's). The required concentration depends on the water quality and species but for the Zebra mussel in general it can be noted that an effective concentration of 0,35 mg/L FO is sufficient to prevent fouling and to mitigate settled organisms. The dosing can be optimized in several ways to reduce the required concentration and related formation of CBP's. One of the methods of dosing so is to apply the dosing method Pulse-Chlorination®. This method is based on the behaviour of local species and requires the minimum amount of chlorine to prevent and mitigate zebra mussel growth in intake water systems. For this type of capacity it is the most efficient and cost beneficial option and therefore BAT.

11.1.1.1 Pulse-Chlorination®

Pulse-Chlorination®, a relative new method for chlorine dosing in once through cooling water systems developed by KEMA in 1998, is based on the principle that bivalve biofouling species like oysters, mussels and clams, in general have a recovery period after exposure to a chlorination period, before fully opening their valves and start filtering water. Pulse-Chlorination takes advantage of this recovery time by short successive pulses of chlorine, alternating with periods without chlorine. Using continuous chlorination, bivalves will close for longer periods and switch to an anaerobic metabolism. When dosing intermittently, i.e. for several hours a day, bivalves will only close during the dosing period. During Pulse-Chlorination, bivalves are forced to continuously switch their metabolic mode between aerobic and anaerobic, leading to a rather quick physiological exhaustion. This dosing procedure does not apply chlorine as biocide, but rather as a trigger to force mussels to switch between their metabolic modes, resulting in a rapid effect. Pulse-Chlorination is Best Available Technique under the European terms of the Integrated Pollution Prevention and Control (EU-IPPC) for macrofouling mitigation in once-through seawater systems and is successfully implemented through on-site field tests worldwide such as Europe, Middle East, Asia and Australia (Polman 2002, 2008, 2010). The method is universally applicable in all water types, but needs to be attuned to local conditions. In the Netherlands this method is successfully applied to mitigate Zebra mussels in fresh water cooling systems.

11.1.2 **Water intake for cooling purposes (5 > intake flow > 1 m^3/second)**

From the information from CHE, the company which has an water intake capacity from the Ebro River of 5 > m^3/s > 1 is a cogeneration plant. Cogeneration, also known as “combined heat and power” (CHP), Cogen, district energy, total energy, and combined cycle, is the simultaneous production of heat (usually in the form of hot water and/or steam) and power, utilizing one primary fuel. For this type of system chlorination is BAT. It must be noted that this is applicable when only the specific required dosing concentration is applied to prevent the formation of large numbers of chlorination byproducts (CBP’s). The required concentration depends on the water quality and species but for the Zebra mussel in general it can be noted that an effective concentration of 0,35 mg/L FO is sufficient to prevent fouling and to mitigate settled organisms. The dosing can be optimized in several ways to reduce the required concentration and related formation of CBP’s. Due to the relative low intake water flow an optimization according Pulse-Chlorination® is not cost beneficial since the CAPEX costs to implement this technology is relative high. Therefore the optimization should focus more on fouling season and acceptable size. In addition, a coating of the intake structure could result in prevention of fouling in parts of the intake system were chlorine is difficult to dose and disperse.

11.1.3 Water intake for cooling purposes (1 > intake flow > 0.1 m^3/second)

For this cooling water intake flow several options could be applied to prevent mussel fouling and ingress of larvae. A micro filtration system will result in prevention of larvae entering the system to settle and cause future problems. However, the filtration systems require clear waters without much debris or suspended solids. Because the concentration of sediment could be high in the Ebro (communication CHE), other methods had to be applied such as chlorine.

11.1.4 Water intake for cooling purposes (0.1 > intake flow > 0.01 m^3/second)

For this cooling water intake flow several options could be applied to prevent mussel fouling and ingress of larvae. A micro filtration system will result in prevention of larvae entering the system to settle and cause future problems. However, the filtration systems require clear waters, without much debris or suspended solids. If the intake water is not clear, other methods could be applied, such as chlorine or coatings. Other methods could be applicable but this depends mainly on the type of cooling water system. This needs to be studied for each individual case.

11.1.5 Water intake for cooling purposes less than 0.01 m^3/second

For this cooling water intake flow several options could be applied to prevent mussel fouling and ingress of larvae. A micro filtration system will result in prevention of larvae entering the system to settle and cause future problems. However, the filtration systems require clear waters without much debris or suspended solids. If the intake water is not clear other methods could be applied such as chlorine or coatings. However, the size of this type of system is very small and large investments on fouling control are not cost beneficial.

11.1.6 Water intake for other than cooling purposes

This group of companies retracts Ebro water for other purposes than cooling its processes. This could be for example for drinking water make-up or for process water.

To prevent fouling in intake systems which deliver water from a River for drinking water, make-up strict concentrations of chemicals acceptable in drinking water have to be taken into account. Therefore coatings could be a good alternative for this type of intake water system. Coatings will also make cleaning much more easy to apply.

11.1.7 Hydropower stations

The large majority of the River water flows through turbines of the hydropower stations to produce energy. The water flow along these turbines is normally > 3m/s which means that there is no risk of settlement of Zebra Mussel larvae in this part of the station. The risk of fouling on the trash racks can be reduced using a coating.

A small part of the River water is normally used to cool down generators or other equipment (auxiliary cooling water system). However, no information on the amount of water used by this auxiliary cooling water system was available. We therefore refer to the ranking made in paragraph 11.1 and apply the mentioned BAT methods to the applicable flows.

11.2 Necessary mitigation period

Since Zebra mussels have a distinguished breeding season the period of the year when they need to be mitigated can be adjusted accordingly. However, the design and specifications of the intake water system and especially the condenser and heat exchanger specification define the amount (size) of fouling that is tolerable. In other words, the size of the fouling that is capable of passing the cooling water system (condenser/heat exchanger) without causing problems determines the maximum period fouling can be tolerated in the system. Of course prevention of settlement of larvae and mitigation of settled larvae is the preferred option to prevent fouling in the intake system. Some techniques (e.g. heat treatment) make it impossible to apply on a regular basis and can only take place every several weeks or months. To reduce the amount of biocide it can also be decided to allow macro fouling larvae to settle and grow until an allowable size. Once the mussels reach this size the fouling mitigation will be applied during a certain period to mitigate the settled mussels. This is a proven method in the Netherlands and applied for mitigation of Zebra mussels using sodium hypochlorite. In practice, this means the dosing period (Pulse-Chlorination) can be restricted to a maximum period of 6 weeks per year. This of course is very cost effective and results in a further minimization of the environmental impact. To be able to reduce the dosing period and allow a certain amount of mussel fouling it is important to install a reliable macro fouling monitoring system capable of detecting the settlement and growth of the mussels. Monitoring of larvae and growth of mussels can be carried out using different kind of objects such as ropes, tiers, fouling plates or monitoring systems.

In Figure 11 a schematic view of the breeding season of the Zebra Mussels in the Ebro Basin is presented.

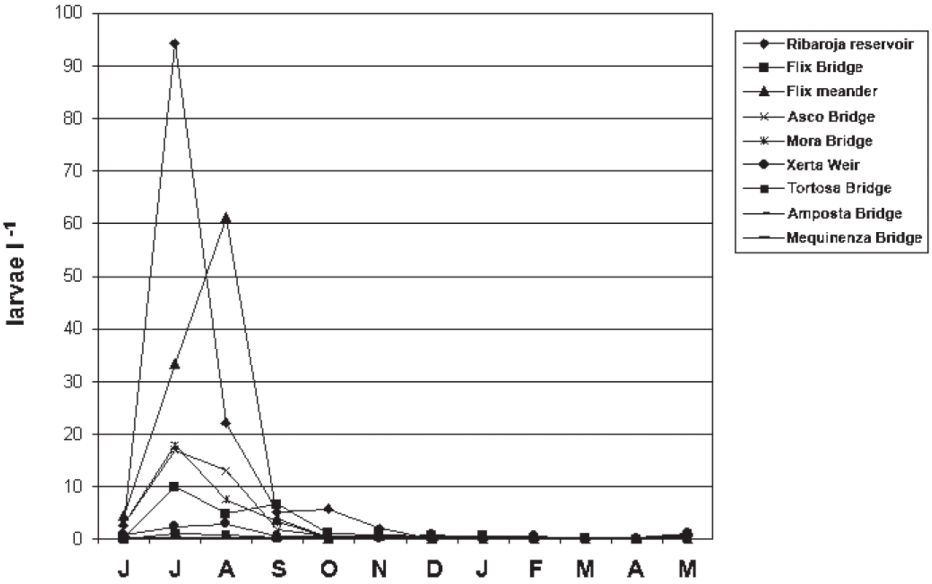

Figure 7. Monthly average of larvae per litre at all sample points in the period 2004/05.

Figure 11 Breeding season Zebra mussels in the Ebro basin

KEMA developed a monitoring system which mimics the conditions inside a cooling water system and presents therefore a realistic image of the fouling situation inside a cooling water system, KEMA Biofouling Monitor (KBM). This monitor is successfully applied at many industrial locations around the world.

11.2.1 KEMA Biofouling Monitor (KBM)

The KBM is an ideal device for detecting and monitoring fouling, determining both the settlement of spat (bivalve larvae) as the development of fouling organisms during the season (settlement, densities and growth). The fouling succession within the KBM is representative for the fouling within the cooling water system. By monitoring the KBM, the efficiency of the applied mitigation treatment can be not only determined, but also optimised. The application of the KBM provides:

- direct and continues insight in the development of fouling in the cooling water system
- direct insight in the efficiency of the mitigation method.

The monitor is connected in a by-pass loop of the cooling water system and duplicates the fouling patterns of mussels occurring in the system. The KBM is specially designed to create optimal conditions for settlement of fouling organisms. In order to increase the settlement of fouling organisms within the KBM, the flow in the monitor is strongly reduced compared to the flow in the seawater distribution system and condensers.

The application of the KBM in a cooling water system of an industrial plant is to gain accurate insight in the fouling period and to check the efficacy of the anti fouling dosing regime. Insight in the periods of this biological variable makes it possible to set a specific period during which the dosing regime is operated. If a distinct period for spawning and spat settlement is found, the dosing period can be shortened to dose only this period. In figure 12 the KBM is presented.

Figure 12 KBM, overview, top view and fouling plates which are placed in the monitor

12 BIOCIDE DOSING

The objective of a biocide treatment can be different. Depending on the target organisms and the extent into which biofouling has progressed, treatments are either preventive or curative. Also the dosing scheme that is employed can be different (continuous, semi continuous or shock dosing). This chapter describes aspects of dosing of oxidizing biocides and non-oxidizing biocides. It should be noted that a dosing scheme often is a site specific result of experience obtained over many years and not a general rule of thumb.

In once-through CWS, contact time between the biocide and the cooling water is short, dictating that fast reacting biocides should be used. In practice in the Netherlands this is almost always sodium hypochlorite. In the US, due to EPA regulations, a shift towards alternatives such as ClO_2, ozone and some surface active non-oxidizing biocides is seen.

When dosing hypochlorite into cooling water, instantaneous reactions with suspended and dissolved organic material - especially with N-containing compounds - will take place. This process is called “chlorine demand”. Reactions between N-containing compounds and chlorine produce halogenated amines are referred to as “bound oxidants”, which are toxic to fouling organisms. Brominated amines are as toxic as hypobromous acid, but chloramine is about 100-fold less effective than hypochlorous acid. The effective part of the hypochlorite dose is the total toxicity of free oxidants and bound oxidants. This is defined as total residual oxidants (TRO). In order to be effective, hypochlorite should be dosed in order to:

- to saturate chlorine demand, which is called breakpoint chlorination
- to leave a desired surplus of “free oxidants” (FO) in the bulk water.

12.1 Dosing in an once-through CWS

When hypochlorite is dosed into a once-through CWS it will function as a tube reactor, with a complex myriad of reactions taking place between hypochlorite and organic matter. The exact demand of the intake water determines the initial dosing concentration that needs to be dosed at the intake to achieve an effective concentration within the system (e.g. in front of the condenser or heat exchanger).

Killing adult mussels and other macrofouling organisms and completely preventing settlement requires very high chlorine doses on a continuous basis (> 1 mg/l as TRO). Hypochlorite, is an unspecific biocide, the toxicological working principle is based on oxidation of membranes leading to cell disintegration. Organisms like bivalves will close there valves and switch over from aerobic to anaerobic metabolism.

12.2 Dosing in open recirculating CWS

In open recirculating systems the dosing to prevent macro fouling in the intake system needs to be the same as in closed recirculation systems. However, in practice dosing of oxidizing biocides (mostly hypochlorite) is generally by daily shock dosing for a period of about an hour in order to prevent micro fouling.

12.3 Dosing techniques

In CWS, dosing of hypochlorite typically takes place at the intake only, although in more complex once-through CWS, various dosing points are installed to allow targeted treatment of microfouling in sections of the CWS. Dosing is aimed to maintain a defined level of FO or TRO at a fixed point, where often a continuous chemical analyser is installed, typically before the heat exchanger and/or at the point of discharge.

There are compounds or materials that neutralise the biocidal effect of a biocide, such as sodium thiosulphate and benthonic clay. These can be applied to cooling water, aiming to reduce the environmental impact of the discharge. To achieve an optimal fouling control from the dosing points onwards an optimal mixing from the dosing point onwards is required. Therefore a single dosing point is not optimal. It is advised to install a structure in the first part of in front of the cooling water system. This could be a dosing rack in front of coarse screens or a dosing ring in the first part of the cooling water system. This will result in a more optimal mixing from the beginning of the cooling water intake structure onwards which will improve the mitigation in the first part of the intake structure. This dosing rack or ring has to be designed for this specific intake structure, but dosing the hypochlorite at several points in the water column (1 per 50 cm, *i.e.* 4 per m^2) will improve the mixing through the complete water column. In figure 13 an example of a dosing rack is shown, this one is placed in front of the intake at Maasvlakte power station in the Netherlands.

Figure 13 Dosing rack at Maasvlakte power station

To get insight in the current dosing system and to optimise the chlorine dosing with an improved design of the hypochlorite dosing systems a computer model can be used. Injection points should be designed to be resistant to fouling and corrosion and to be as easily accessible as possible for examination. It is advised to perform Computational Fluid Dynamics (CFD) modelling of the dosing system to check adequate mixing of the dosed chlorine in the cooling water intake area. An example of the use of CFD modelling is provided in figure 14 wherein a dosing ring structure is modelled.

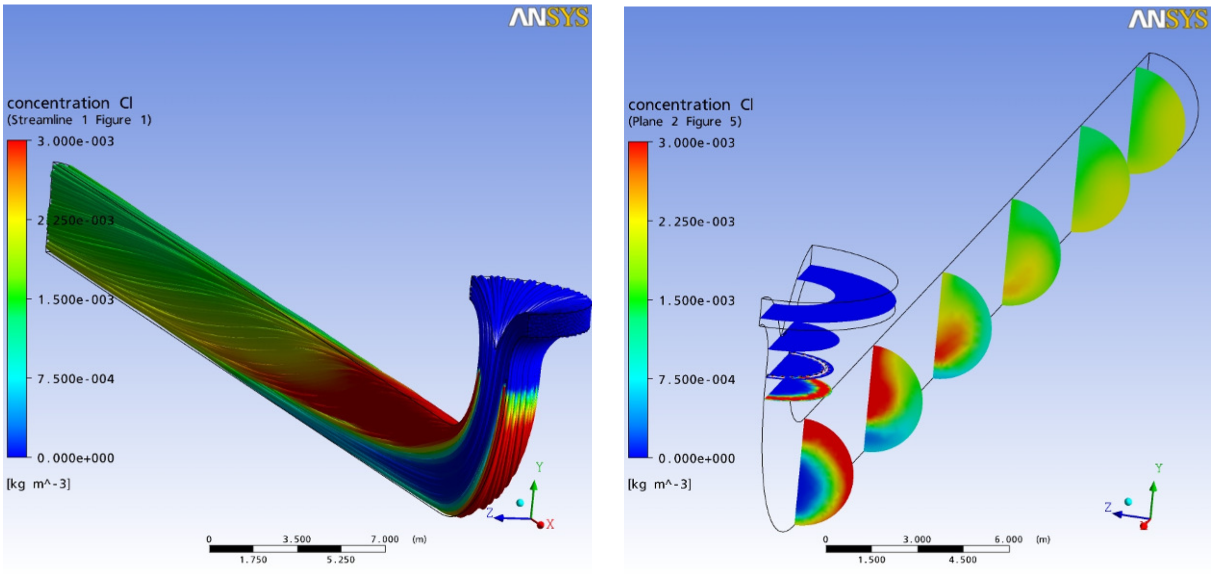

Figure 14 Example of CFD modeling. Chlorine concentration results are presented on scale 0 – 0.3 mg/l. Hypochlorite concentration ≥ 0.4 mg/l is presented as a red color

Using this model a guaranteed mixing of biocide will be achieved and results in an optimal (= minimum) amount of biocide.

13 BIOCIDE ANALYSIS AND MONITORING

Generally, analytical methods exist for all oxidizing biocides and non-oxidizing biocides mentioned in this report, but in practice only oxidizing biocides can - and in fact are - monitored adequately on-site. Adequate monitoring is a prerequisite for adjusting the biocide dose when biocide demands of the cooling water changes. To adjust the required biocide concentration monitoring should be done in front of the heat exchanger, since this is the most critical part in the CWS, at which the biocide treatment is targeted. Besides this a monitoring at the discharge should also be applied to monitor the maximum level of biocide that is permitted to be discharged in the river system.

13.1 FO and TRO measurement

Currently there are no “ideal” methods available for quantifying chlorine and chloramines in surface water. All common methods of chlorine analyses display some lack of specificity and are not adequately selective to be completely free of interferences. The selection of an analytical system for chlorine testing will depend on several factors and situations. For example, if chlorine testing is performed to meet regulatory compliance, the selected method must be acceptable to the regulatory agency. Under certain situations, the use of visual field test kits will provide acceptable results. Some situations or regulations require near continuous analyses using a online monitoring system applying one of the possible methodologies. In appendix III the different methods are described.

13.1.1 Comparison and selection of method

To compare the methods described above and to be able to select the best suitable method for the purpose needed, a ranking can be applied (Current Technology of Chlorine Analysis for Water and Wastewater. Technical Information Series — Booklet No.17. By Danial L. Harp). In the table below the results are presented. On the scale “10” means the method meets the quality concept of the “ideal” method completely and “1” means the method does not meet the concept at all.

Table 10 Ranking of chlorine analytical methods according to D.L. Harp

AWA quality concept		**DPD Color.**	**DPD titration**	**Iodometric titration**	**Amper. forward**	**Amper. back**	**FACTS**	**Electrode**
1	Specificity	7	5	2	6	2	8	2
2	Selectivity	7	7	4	5	6	7	6
3	1 ppb MDL	9	5	1	7	7	3	6
4	0.2% precision	7	5	3	7	1	2	2
5	1% accuracy	8	7	5	7	6	5	5
6	4 orders linear range	6	7	9	8	7	8	9
7	Any sample matrix	8	7	7	4	7	6	3
8	No dilution required	7	8	6	8	8	8	7
9	Can automate	9	3	3	2	2	4	6
10	Traditional instruments	9	9	9	4	4	9	5
11	No special skills	9	8	8	2	1	8	6
12	Stable reagents	9	5	4	5	4	3	4
13	Fast procedure	8	5	5	3	2	6	3
14	Cost effective	9	7	6	4	3	6	3
	Total score	**112**	**88**	**72**	**72**	**60**	**83**	**67**

"1" **does not meet quality concept**

"10" **meets quality concepts fully**

From the table it can be concluded that the DPD colorimetric method is closer to the conceptual “ideal” method than any of the other common chlorine analytical methods. Most of the limitations associated with the traditional DPD chemistry (e.g., calibration linearity, reagent stability, reaction product stability, etc.) have been addressed sufficiently in current procedures and reagent formulations.

In view of the relative instability of chlorine and chloramines in aqueous solutions and the availability of accurate digital titrators, colorimeters and portable spectrophotometers, on-site testing for chlorine is preferable. Considering these factors and the DPD chemistry, the DPD colorimetric method provides highly reliable, accurate and precise data available with on-site testing using portable instrumentation. Hence, the DPD method can be considered as the best available system for routine chlorine measurements.

13.1.2 **Method Interferences and Sources of Errors**

A common source of error in testing for chlorine in water is the failure to obtain a representative sample. Because free chlorine is a strong oxidizing agent, its stability in natural waters is very low. It readily reacts with various inorganic compounds and will slowly oxidize organic compounds. Various factors, including reactant concentrations, pH, temperature, salinity and sunlight, influence the decomposition of free chlorine in water. Monochloramine, on the other hand, is much more persistent in the environment. Typically, the decay rate of monochloramine is tenfold slower than the decay of free chlorine in natural waters (Jolley 1983). Ideally, samples should be analyzed for chlorine on site. If sampling from a tap, allow water to flow at least five minutes before sampling to ensure a representative sample. Sample containers should be pretreated to remove any chlorine demand. Plastic sample containers should be avoided because they might exert an appreciable chlorine demand. Clean glass sample containers should be pretreated by soaking in a dilute bleach solution (1 ml commercial bleach solution to 1 liter of water) for at least one hour. After soaking, they should be rinsed thoroughly with deionized or distilled water or the sample. Another treatment is required only occasionally if sample containers are rinsed with deionized or distilled water after use. Do not use the same sample containers for free and total chlorine analysis. If trace iodide (from the total chlorine reagent) is carried over into the free chlorine determination, monochloramine will interfere in the free chlorine test. Ideally, separate and dedicated sample containers would be used for free and total chlorine determinations.

All of the common analytical methods for chlorine or chloramines in water are based on chemical oxidation reduction reactions. It should be emphasized that each of the chlorine methods is based on the total oxidizing capacity of the sample being analyzed and is readily subject to interferences from other oxidizing agents. Generally, all the accepted methods for chlorine are subject to potential interferences from particles, color, inorganic and organic compounds, and buffer capacity in the sample. Unfortunately, there is no “ideal” method for chlorine analysis which is specific and selective for the free chlorine and chloramine species.

The most commen interferences are:
- other disinfectants
- manganese compounds
- bromide in chlorinated waters.

All of the common total chlorine methods are based on the oxidation of iodide to triiodide ion. There are several potential sources of errors related to the iodide/triiodide reaction. They include:
- air oxidation of the iodide reagent
- volatilization of produced iodine
- iodine or iodate contamination in the iodide reagent
- consumption of triiodide by sample components.

14 DISCHARGE REGULATION FOR EBRO RIVER

Discharge limits can be implemented according to EU regulations however it is mandatory to apply BAT. Within the BAT the permit must contain the emission limit values. For each type of company the discharge limits can be adjusted according to the IPPC regulations. The regulations for applying biocidal control techniques as presented in Table 7, chapter 8.3.

15 OTHER INVASIVE SPECIES

New fouling species could enter the Ebro river basin in the future. New species can cause new fouling problems and could need another approach due to the fact they might be less sensitive for biocides used to control Zebra mussels.

15.1 Quagga mussel

The quagga mussel *Dreissena rostriformis bugensis* (Andrusov, 1897) was until early twenty-first century a slower invader than the zebra mussel *Dreissena polymorpha* (Pallas, 1771). Both mussel species originate from the Ponto-Caspian area. The original native range of the quagga mussel is the Lower Dniepr River and Southern Bug River. Over the last few decades, however, the quagga mussel has considerably extended its range in Russia. Furthermore, it invaded the Great Lakes area of North America probably simultaneous with the zebra mussel (1987), most likely as larvae via ballast water discharge. The quagga mussel was recognized for the first time in the Great Lakes in 1991. *D. rostriformis bugensis* seems to have an ecology similar to *D. polymorpha*, but often colonizes deeper water. It has a better ability than *D. polymorpha* to cope with low food conditions and high temperatures. Recently, *D. rostriformis bugensis* was recorded in Romania and in The Netherlands, where it occurred in relatively low numbers between the zebra mussels (1% were quagga mussels).

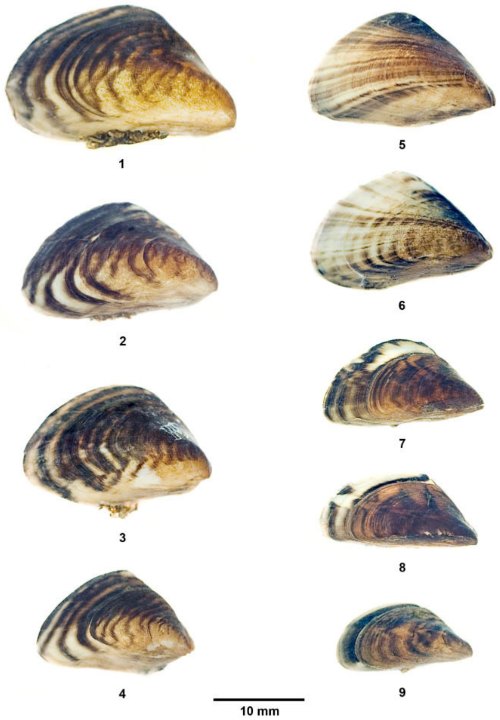

Figure 14 Quagga mussels (*Dreissena rostriformis bugensis*) (1-6) and Zebra mussels (*Dreissena polymorpha*) (7-9) collected at the same locality in the River Main (Germany). The shells of the Quagga mussels 5 and 6 show an atypical stripe pattern. The largest Quagga mussel on the figure has a length of 25 mm

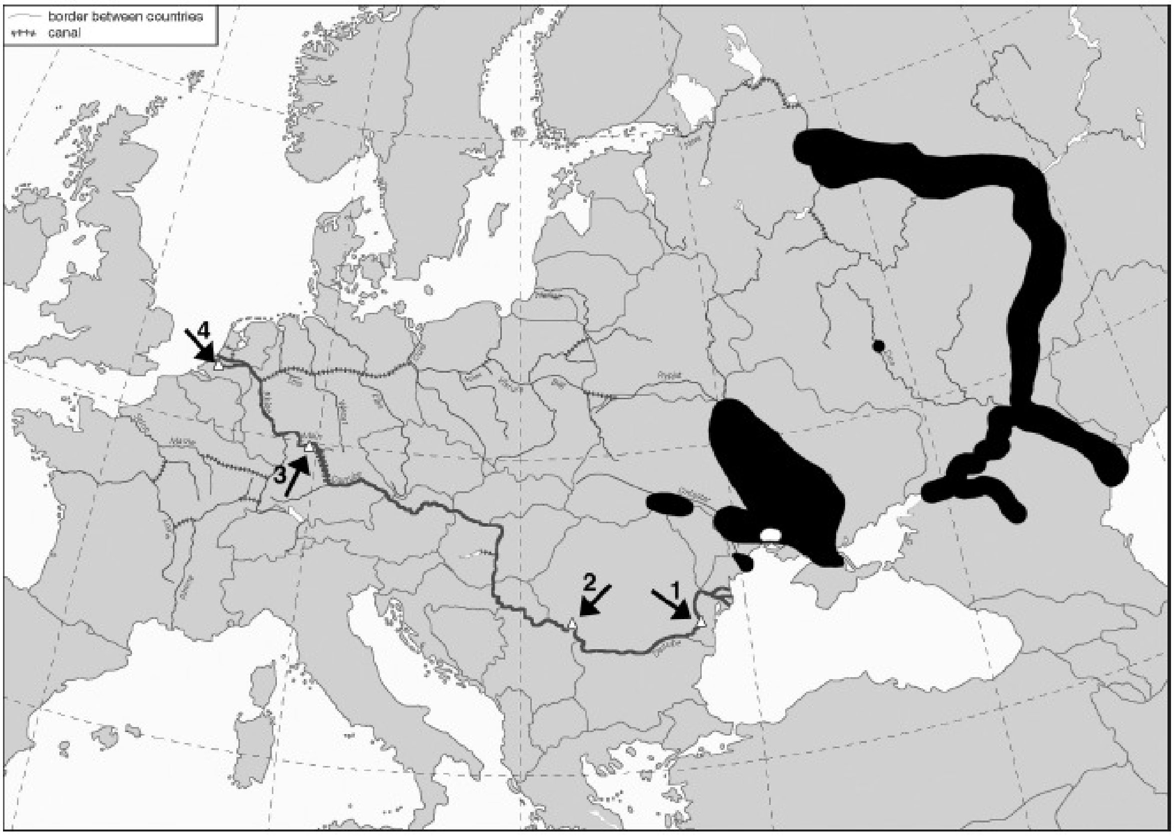

Figure 15 The distributional expansion of *Dreissena rostriformis bugensis* in Europe. Historical distribution indicated as white spot. Range extensions from 1941 till 2002 black (according to Orlova (2003) and Zhulidov et al. (2004, 2005)). Arrows indicate the most recent records (open triangles), Hollands Diep, The Netherlands (Molloy et al. 2007), Danube, Romania (Popa and Popa 2006) and Main, Germany

Dreissenid mussels are diverse, but also have some defined environmental limitations. Zebra mussels can live at water temperatures approaching freezing, but spawning stops below 10 ºC, and growth slows as temperatures decline. Cold temperatures can also reduce density. Zebra mussels die when the water temperature falls to levels that would cause ice to form within their bodies. On the opposite end of the temperature spectrum lethal high temperatures are reached at between 31 ºC and 35 ºC. Quagga mussels have a greater tolerance for cooler water temperatures than zebra mussels; thus, they have been found to colonize substrates at greater water depths. Observations and research suggest that the North American quagga mussel is a cold, deep-water form, contrasting with Ukraine populations where the quagga mussel thrives at higher temperatures. In North America, zebra mussels survive indefinitely at 30 °C, but the quagga mussel exhibits high mortality at this same temperature (Mills et al. 1996). Although there are indications that quagga die at lower temperatures than zebra mussels, there are a few exceptional quagga populations that are as tolerant of elevated temperatures as zebra mussels, so the potential thermal range of this species may be higher than recent experiments indicate (Mills et al. 1996).

Temperature is also a key factor in spawning and fertilization of *Dreissenid* mussels. A minimum spawning temperature of 12 °C has been reported for zebra mussels compared to a 9 °C spawning temperature for quagga mussels, which suggests the zebra mussel cannot successfully colonize hypolimnial waters. Although, zebra mussels have been reported to survive in the hypolimnion, they cannot reproduce there (Claxton and Mackie 1998). In contrast, a female quagga mussel with mature gonads was found in Lake Erie at a temperature of 4.8 °C, so areas that were thought to be immune to quagga mussel colonization may be at risk (Claxton and Mackie 1998).

The Quagga mussel is more sensitive to higher temperatures than the Zebra mussel. The Quagga mussel is a species that occurs at deeper, cooler locations. However, it is also found that some individuals have a better tolerance to higher temperatures. If these specimens are not effectively mitigated, it could be possible that the development of a Quagga mussel population with increased tolerance to higher temperatures is enhanced. It is therefore important to operate a proper monitoring of fouling development within the cooling water system as well as monitoring of the thermal treatment effectiveness.

The Quaggamussel is more sensitive for the ‘thermo-shock’ treatment than the Zebra mussel (KEMA, 2008). It is known that the applied thermal treatment procedure at the Power Station Moerdijk is sufficient to mitigate the Zebra mussel. It could be concluded that the thermal treatment is also effective for the Quagga mussel.

15.2 **Corbicula (Asian Clam)**

Two morphotypes of Asian clams occurred in investigated waters: *C. fluminea* and *C. fluminalis* (Figure 16). The taxonomic status of those taxa is still unclear, so we consider them as morphotypes, rather than as individual species.

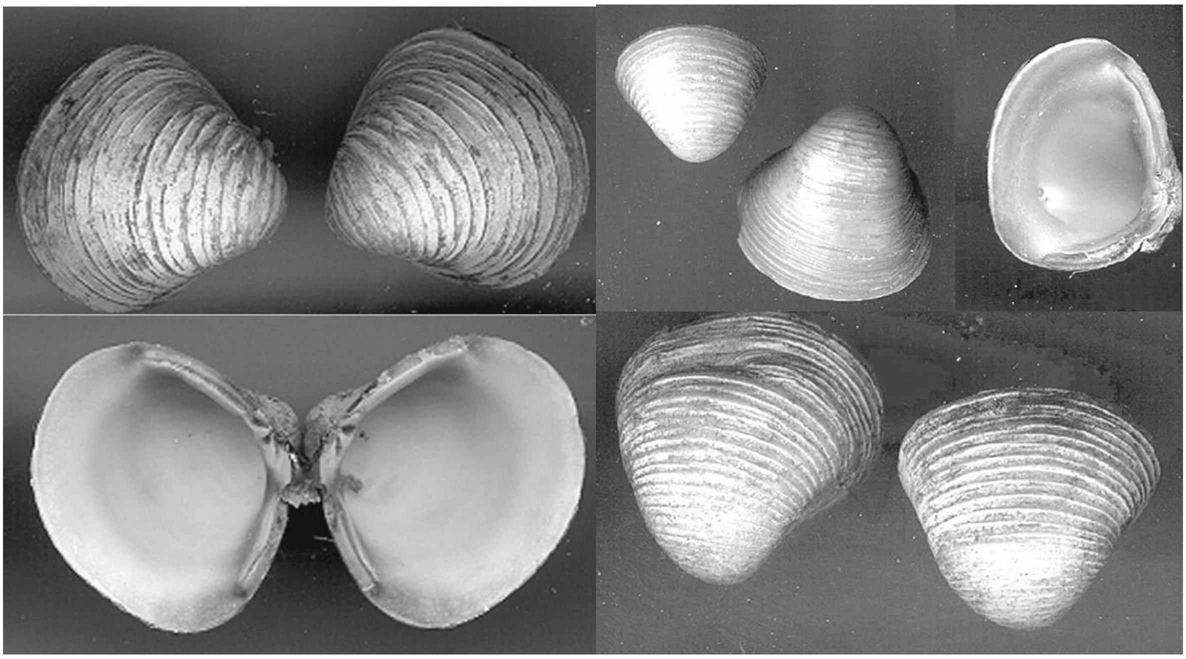

Figure 16 *Corbicula fluminea* and *Corbicula fluminalis* (Momir Paunović et. al., 2007)

The Asiatic clam prefers a lake or stream that has a sandy or gravel substrate. However, they are also located underneath large boulders and in soft silts of deepwater lakes. The clam thrives better in fast flowing waters because the currents supply a constant source of the particulate food that the clam consumes.

The Asiatic clam is hermaphroditic, with single genopores on each sides of the body. Reproduction and larval release occurs biannually in the spring and in the late summer. The clam is believed to practice self-fertilization, enabling rapid colony regeneration when colony populations are low. A typical settlement of the Asiatic clam occurs with a population density ranging from 100 to 200 clams per square meter. However, populations can grow as large as 3000 clams per square meter. There appears to be no competition for food among individuals within the species, however within high density populations, space competition is often important. The Asiatic clam is a filter-feeding bivalve. It filters microscopic organisms, such as plankton, from the water.

The Asiatic clam is found throughout Asia, North and South America, Europe and parts of Africa (Figure 17). The clam occurs primarily in streams south of 40 degrees latitude in the northern hemisphere.

Figure 17 European distribution *Corbicula fluminea* (O. F. Müller, 1774) in 2008

The first record of *Corbicula fluminea* (Müller, 1774) in the Guadiana River Basin (Iberian Peninsula) was present by Pérez-Bote and Fernández (2008). This exotic bivalve was found in June 2006 on the Lacarón and Guadiana rivers with mean density is between 3.3 and 16.9 individuals per squared meter. Population structure and the dates of the first records suggest that the introductions may have occurred between 2003 and 2004. The potential impact of the invasion on native freshwater bivalves is discussed along with the need for monitoring and prevention of further introductions of non-indigenous bivalves in the Iberian Peninsula.

Recently two exotic species of freshwater bivalves, both from Southeast Asia, have been introduced into Iberian inland waters. The zebra mussel *Dreissena polymorpha* (Pallas, 1771) was first reported in Spain from the Ebro River basin, in the early 1980´s (Altaba, 1992). *Corbicula fluminea* (Müller, 1774) was found for the first time in Iberian waters in 1980 in the Tagus River estuary (Mouthon, 1981). Later, the species was reported from the Douro River, Oporto, Portugal (Nagel 1989) as well as the Miño and the Douro rivers, Spain (Araujo et al. 1993). Both species are considered potential invasives because, they are characterized by early sexual maturity, high reproductive potential and a remarkable ability to adapt to the environments they colonize. Such characteristics allow exotic bivalves to disperse quickly in great numbers. Their entry in the Iberian Peninsula most probably occurred via trading ships from Southeast Asia. Casual observations of the presence of C.fluminea were made in June 2006 at several locations on rivers of the middle Guadiana basin see Figure 18.

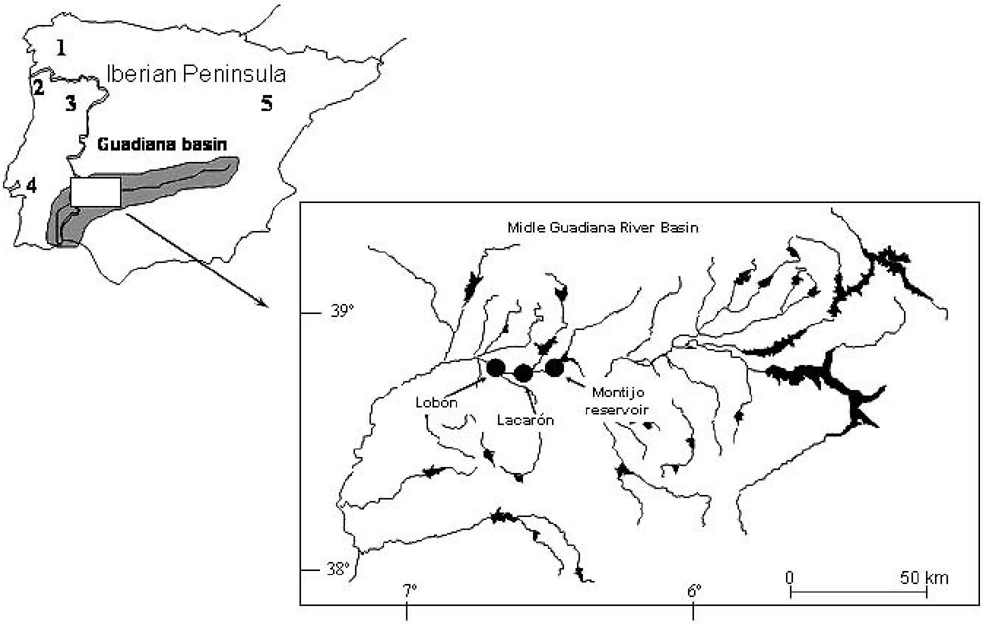

Figure 18 Map of the Guadiana River basin with localties where the Asian clam *Corbicula fluminea* was detected.

The Asian clam size frequency distributions at Lacarón site is shown (Figure 19). The population (n= 432) is composed of shells ranging from 12.53 to 25.72 mm in length with a modal size class of 18.1-19 mm. The approximate age distribution of each sample shows that the most of the individuals from the Lacarón sample (85.18%) are less than one year of age whereas the remainder (14.82%) is made up of one-year old individuals. Based on these age estimates and the dates of first records, the introduction of *C.fluminea* in the Guadiana River Basin may have taken place as recently as 2003 or 2004. The recent introductions of exotic bivalves to Iberian Peninsula should give rise to concern. There is an urgent need to monitor freshwater bivalves in order to determine the status of native species and possible impact of non-indigenous taxa.

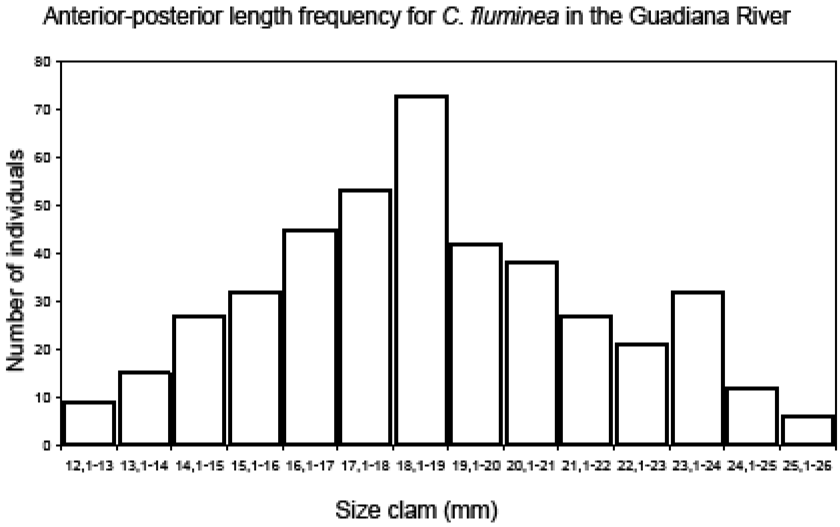

Figure 19 Asian clam size frequency distribution at Lacarón site

If we consider the negative impacts concerning the appearance of Asian clams in inland waters, it has been documented that the most prominent effect of the introduction of the Asian clams is bio-fouling of power plant and industrial water systems (Isom 1986, Williams and McMahon 1986). The mass occurrence of Corbicula could also cause problems in irrigation canals and pipes (Prokopovich and Hebert 1965, Devick 1991), as well as in drinking water supply facilities (Ingram 1959, Smith et al. 1979, Clarke 1981).

The clam creates a problem for power plants by blocking the ventalation systems and the water intake valves. Combined costs of outages, reductions in efficiency, capital investment in equipment, labor and chemical control, exceed 1 billion annually.

16 DISCUSSION AND CONCLUSIONS

From the study carried out for CHE the following conclusions and remarks can be made:

- no technique is BAT for all cooling water intake systems. The intake flow, system design and water quality determine which type of fouling control method is BAT for each type of company. Therefore the BAT as determined during this research study should be used as a guideline and for each different company the BAT should be determined when more information is available from this specific location
- in general it can be concluded that chlorine is the most cost effective method to prevent fouling of Zebra mussels in cooling water systems. Chlorine is relatively cheap, easy to dose and when applied correctly there are no negative long term effects on the receiving environment
- heat treatment to control fouling in a cooling water system is an accepted method in The Netherlands. Thermoshock can be used only if the cooling water system is equipped with a proper recirculation system and can withstand a temperature increase to about 45°C. The thermoshock method involves a certain level of production penalty for the power plant due to recirculation of heated water
- the use of coatings can be very beneficial since they do not produce byproducts which can be discharged in the river system. Also coatings can be very helpful to prevent fouling of intake structures like bar screens. Coatings could be used also in combination with chlorine. A coating could protect the intake structure until the dosing point of chlorine
- Pulse-Chlorination could also further reduce the amount of chlorine that needs to be dosed to mitigate zebra mussels that settled. However, due to the CAPEX costs to install this dosing technology it will be only cost beneficial for CWS with an intake flow > 5 m^3/second
- for hydro power stations the large majority of the River water flows through turbines of the hydropower stations and the water flow along these turbines is normally > 3 m/s which means that there is no risk of settlement of Zebra Mussel larvae in this part of the station. The risk of fouling on the trash racks can be reduced using a coating. A small part of the River water is normally used to cool down generators or other equipment (auxiliary cooling water system). The BAT method for this type of system is comparable with a once-through cooling water system
- the period to mitigate zebra mussels should be adjusted to the cooling water system capability to flush a certain size of shells through their system. This is only applicable in once through cooling water systems and could reduce the chlorine dosing period to only 4 to 6 weeks per year
- dosing period needs to be adjusted to fouling season, this means that the period of using a biocide can be reduced in time and tailor made for specific species and location

- further optimisation using tailor made dosing structure to optimize dosing and dispersion and minimise use of product
- monitoring both chemical and biological is advised to have a reliable check on the dosing and discharge concentrations and the efficacy of the treatment
- discharge limits can be implemented according to EU regulations however it is mandatory to apply BAT. Within the BAT the permit must contain the emission limit values
- the discharge limits for the biocides used can be adjusted by CHE if required.

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CHLORINE MEASUREMENT METHODS

In the following paragraphs the most frequent applied methods are discussed and compared.

DPD Colorimetric Method

The DPD (N, N-diethyl-p-phenylenediamine) method for residual chlorine was first introduced in 1957. Over the years it has become the most widely used method for determining free and total chlorine in water and wastewater. The DPD amine is oxidized by chlorine to two oxidation products. At a near neutral pH, the primary oxidation product is a semi-quinoid cationic compound known as a Würster dye. This relatively stable free radical species accounts for the magenta color in the DPD colorimetric test. DPD can be further oxidized to a relatively unstable, colorless imine compound. When DPD reacts with small amounts of chlorine at a near neutral pH, the Würster dye is the principal oxidation product. At higher oxidant levels, the formation of the unstable colorless imine is favored, resulting in apparent “fading” of the colored solution. The DPD Würster dye color has been measured photometrically at wavelengths ranging from 490 to 555 nanometers (nm). The measurement takes place at 530 nm as the measuring wavelength for most of the DPD systems. This “saddle” between the peaks minimizes any variation in wavelength accuracy between instruments and extends the working range of the test on some instruments.

Monochloramine and dichloramine are slow to react directly with DPD at a near neutral pH. To quantify these species, the test is performed under slightly acidic conditions in the presence of iodide ion. The iodide reacts with the chloramines to form iodine as the triiodide ion:

$NH_2Cl + 3I^+ H2O + H^+ \rightarrow NH_4OH + Cl^- + I_3^-$
$NHCl_2 + 3I^- + H2O + 2H^+ \rightarrow NH_4OH + 2Cl^- + I_3^-$

The triiodide, in turn, reacts with DPD, forming the Würster oxidation product. Two “standard” DPD colorimetric methods generally are recognized in the international community. These are the Standard Methods 4500-Cl G and International Organization for Standardization (ISO) Method 7393/2 (Ref. 2.4). The ISO method has been adopted by most of the members of the European Union. Germany's DIN Standard 38 408 G4 for free and total chlorine is modeled after ISO 7393/2.

Standard Methods and ISO procedures both use phosphate buffers to adjust the sample pH to between 6.2 and 6.5. The slightly acidic pH is preferred to quantitatively resolve the chloramine species and to minimize interferences. Phosphate buffers, however, do not work in hard or brackish waters. Calcium and magnesium ions in the sample will precipitate the phosphate and destroy the buffering capacity. Because aqueous phosphate solutions are excellent growth media for biological growth, highly toxic mercuric chloride is added to preserve the reagent. One company (Hach) overcomes the disadvantage using DPD liquid by modifying the DPD powder formulations. The DPD indicator and buffer are combined in powder form, minimizing degradation by oxidation and microbial action. Because Hach's DPD powder indicator does not exist in an ionized state, it is not subject to air oxidation as is the liquid DPD reagent. Hach's combined DPD reagents also incorporate EDTA to prevent metal catalyzed oxidation. Hach's buffer component makes use of a carboxylatephosphate system which works extremely well in high hardness and brackish water samples. Up to 1000 mg/l $CaCO_3$ hardness can be tolerated with either the free or total chlorine powder formulations.

DPD Titration Method

The DPD titration method is based on the same chemistry as the DPD colorimetric method, in that DPD is oxidized by chlorine (or iodine in the case of chloramines) to the magenta-color species. The red color then is titrated with a ferrous reducing agent to the colorless end point. Standard Methods and ISO DPD titration procedures both use the same buffer and indicator reagent formulations as those specified in the referenced DPD colorimetric methods. Hence, the inherent problems of reagent instability and buffering of hard water samples cited above also are applicable to the reference titration procedures. For most samples, there is no clear advantage to using the DPD titration method over DPD colorimetric method. In fact, there may be several disadvantages. First, the titration procedure requires additional time to perform. In the case of possible monochloramine intrusion into free chlorine, the additional time required for a free chlorine titration may lead to errors. Accurate measurement of sample volume for the titration is essential. To achieve accuracy, a pipette must be used – a procedure which can lead to loss of volatile chlorine species. The visual estimation of the titration end point is imprecise compared to the measurement of color obtained by using a colorimeter or spectrophotometer.

Iodometric Titration

The starch-iodide titration method, one of the oldest methods for determining chlorine, is very non-specific for oxidants and generally is used for total chlorine testing at levels above 1 mg/l Cl_2. The method is based on reaction with thiosulfate solution:

$Cl_2 + 3KI \rightarrow I_3^- + 3K^+ + 2Cl^-$
$I_3^- + 2Na_2S2O_3 \rightarrow 3I^- + 4Na^+ + S_4O_6^{2-}$

The end point of the titration is indicated by the disappearance of the blue-colored, starch-iodide complex. The titration usually is performed at a sample pH between 3 – 4. Research by Hatch and Yang (1983) has shown sample temperatures above 20 °C can produce significant errors if starch is used as the titration end-point indicator. Their studies indicate the release of triiodide from the starch helix is temperature-dependent. For maximum accuracy, iodometric titrations using starch indicator should be performed at sample temperatures less than 20 °C. A “back titration” is recommended for waters containing potential chemical interferences. In this case, a known amount of thiosulfate is added in excess of the chlorine in the sample. The amount of unreacted thiosulfate is titrated with a standard iodine solution. Then, the total chlorine is calculated, based on the thiosulfate equivalency in the sample. The chemical reactions are:

$Cl_2 + 2S_2O_3^{2-} \rightarrow 2Cl^- + S_4O_6^{2-}$
$I3^- + 2S_2O_3^{2-}$ (excess) $\rightarrow 3I^- + S_4O_6^{2-}$

Amperometric Titration Methods

Amperometry is an electrochemical technique that applies a small electrical voltage across two electrodes and measures the change in current resulting from chemical reactions taking place. Amperometric titration measures the current change as a function of titrant added. In the amperometric determination of free chlorine, chlorine is titrated with a standard reducing agent such as thiosulfate or phenylarsine oxide (PAO) at pH 7. A small potential is applied across the electrodes before the titration begins. Current cannot flow between the electrodes unless two substances are present, one that can be oxidized at the anode and another that can be reduced at the cathode. During the course of the titration, chlorine is reduced at the cathode to chloride (Cl^-) from the reaction with PAO. PAO is oxidized from the +3 to the +5 oxidation state at the anode:

$PhAsO\ (PAO) + Cl_2 + 2H_2O \rightarrow PhAsO(OH)_2 + 2Cl^- + 2H^+$
(Ph = phenyl)

The amperometric method is no longer accepted by ISO for the determination of chlorine species. This due to the considerable conflicting information about interferences with amperometric methods for chlorine in treated wastewater and effluents.

Standard Methods states the amperometric method “is the method of choice because it is not subject to interference from color, turbidity, iron, manganese or nitrite nitrogen”. In reality, several of these factors do affect the determination of chlorine species when using amperometric methods.

Orthotolidine Method

The orthotolidine (OT) method was dropped from the 14th edition of Standard Methods after the results of two round-robin studies (UEPA 1969, 1971) were released. Both studies indicated the OT method gave poor accuracy and precision and a high overall error in comparison with the other chlorine methods. Two aquatic toxicity studies (Tompkins, 1976 and Fava, 1976) compared the DPD colorimetric, amperometric titration and orthotolidine methods for determining chlorine residuals. In both studies, the OT method gave lower values at all concentrations of total chlorine relative to the other two methods. Because of relatively poor accuracy and precision and a lack of specificity, the orthotolidine method generally is not accepted in the United States and most developed countries. Usage of this method is mainly confined to low-cost pool testing applications.

Syringaldazine (FACTS) Method

This method is based on the reaction of 3,5- dimethyl-4-hydroxybenzaldazine (syringaldazine) with free chlorine on a 1:1 basis: The product is a red-purple compound with a absorption maximum at 530 nm. The published method generally is known as the FACTS method (free available chlorine testing with syringaldazine). A Standard Method procedure (18th ed.; op. cit., Method 4500-Cl H., p. 4-47.) for free chlorine determinations, it is not recognized by the ISO. Major disadvantages of the FACTS method are the insolubility of the indicator and its product, storage of the indicator solution and a variable sensitivity to chlorine.

Potentiometric Electrode Method

The electrode method is based on the potentiometric measurement of free iodine produced when iodide is added to an acidic sample containing an oxidant. The method is analogous to the iodometric titration method in that total oxidant is measured and speciation of disinfectants residuals is not possible.

Considering the volatility of chlorine and iodine in natural waters, a practical level of detection using the electrode method is closer to 50 µg/l. Wilde (1991) compared the electrode method to the forward amperometric method and the DPD colorimetric method on standards and cooling water samples for total residual chlorine at the Savannah River Site (SRS). Standard testing with high purity water dosed with chlorine showed no statistical difference among the three methods. However, measurements made with the electrode on cooling water samples were significantly lower than those obtained with the other two methods. Wilde concluded the DPD method is the recommended method for future monitoring at SRS due to its simplicity and suitability for both field and laboratory measurements.