Cooling water management in European power stations

Biology and control of fouling

Biologie et contrôle des salissures dans les circuits de refroidissement des centrales thermiques européennes

Henk A. Jenner, John W. Whitehouse, Colin J.L. Taylor and Michel Khalanski

AUTHORS

Henk A. Jenner, Ph.D., Biology, is a Senior Consultant at KEMA Power Generation in the Netherlands and is working in the fields of industrial cooling water use, biofouling research and ecotoxicology.

John W. Whitehouse is a graduate in biology, geology and ecology; he joined the Central Electricity Generating Board's research department in the UK, and worked on ecological problems associated to cooling water discharges, cooling towers and water intake screens. Presently he is a private consultant.

Colin Taylor is a Senior Environmental Officer in British Energy PLC's Health, Safety and Environment Division. Working in applied aquatic ecology, he is also responsible for dealing with the environmental regulatory authorities. He is a graduate in marine biology and estuarine ecology.

Michel Khalanski is a Senior Research Engineer at Electricité de France, R&D Division, Département Environnement. Working in applied aquatic ecology, he is presently in charge of the EDF biofouling research programme.

CONTRIBUTORS

Many colleagues have contributed to the writing of the book but in particular :

— Dr. J. Mattice of New-York Sea Grant (USA);

— Dr. J.H. l'Abeé-Lund of Norwegian Water Resources and Energy Administration (Norway);

— Dr. R. Ambrogi of ENEL (Italy);

— Dr. R.N. Bamber of Fawley Aquatic Research Laboratory (UK);

— Mr. J. Coughlan of Fawley Aquatic Research Laboratory (UK);

— Dr. L. Duvivier of LABORELEC (Belgium);

— Mr. T.H. Humphris (UK);

— Prof. J.-C. Moreteau and V. Bachmann of Université de Metz (France);

— Dr. S. Rajagopal of University of Nijmegen (The Netherlands);

— Dr. A.W.H. Turnpenny of Fawley Aquatic Research Laboratory (UK);

— Prof. Dr. G. van der Velde of University of Nijmegen (The Netherlands);

— our other colleagues from the various (power) companies who have helped us in this task, especially in completing the questionnaire which

formed the basis of review of problems faced by power stations in Europe.

ACKNOWLEDGEMENTS

We wish to thank Electricité de France, British Energy PLC, Akzo Nobel and KEMA Nederland B.V. for the finance which enabled us to write this book. We also wish to thank EDF for undertaking the unenviable task of printing and publishing it.

We also wish to thank Bangor Univ. for the photographs of mussel and Cypris larvae and Elsevier and Dr. Elisabeth Gosling for their courtesy of using their figures.

Preface

Electric power plants use huge amounts of water to complete the steam cycle and keep the electric turbines turning. Such volumes make it uneconomical to use treated water, so the sources are streams, lakes and the sea. But these waters contain bacteria and algae that can cause slime build-up on condenser tubes, and may as well contain the planktonic young of barnacles, mussels, etc. that attach and form mats on conduits and other plant structures. Uninhibited colonization by either these micro- or macro-fouling organisms will cause reduced efficiency and, finally, shut down the plant. In the current global economy there is increasing pressure for higher efficiency and lower cost of electricity. Because fouling organisms are more difficult to control the longer they remain undisturbed after gaining a foothold, maintenance of both society's supply and the price of electricity depend, to a certain degree, on prevention or control of biofouling.

It is difficult to think about biofouling control at power plants without focusing on chlorine. Historically, chlorine application to the intake water stream has been the universal method of choice to combat biofouling. Intermittent application has always been the most common, because slime formation or microfouling was observed to be the primary problem. However, where macrofouling threatened power plant operation (mostly at marine sites), continuous

application of chlorine at substantially lower concentrations was found to be effective. In addition, the cost of chlorine was small compared to the value of the electricity. The advantages of chlorine were overwhelming. However, in the early 1970's, organo-chlorine by-products were identified in power plant effluents during chlorination, and early toxicity tests suggested that these organo-chlorine by-products might be toxic at low parts per billion concentrations. Although it has not been possible to confirm the toxicity results, these potential environmental and public health implications sparked the first interest in a search for alternatives to chlorine for biofouling control.

During the middle 1970's, efforts were made to develop both physical and chemical alternatives that would avoid the byproducts of surface water chlorination. Physical methods for fouling control in the condenser tubes included the MAN brush system and the AMERTAP/TAPROGGE system's abrasive sponge balls. Both of these systems were found lacking for a number of reasons, the most important of them being increased erosion of the condenser and the need for supplemental chlorine application to control fouling of the service water system and other areas of the condenser cooling system. Other biocides, including ozone, bromine, bromine chloride, and hydrogen peroxide were also examined as poten-

tial biofouling control agents, but the search for alternatives faded away around 1980. The fact that in sea water all of these oxidants yielded the same active ingredient – bromine – probably played a role in abandoning the search, because similar unwanted, halogenated by-products could be expected. In addition, fresh water by-products of these alternatives appeared problematical. For example, it was predicted that the products of ozonation of natural waters could include ozonides, peroxides and epoxides. Although the likelihood of formation and identification of these products is uncertain, these classes of chemicals are of known environmental and public health concern. Whatever the reasons, the pressure to consider alternatives diminished, and the industry dependence on chlorine for biofouling control continued.

In the last few years, the response to the invasion of the US by the Zebra Mussel (*Dreissena polymorpha*) again focused attention on biofouling control alternatives. Further, over the past couple of decades, the water quality of lakes, rivers and estuaries in both Europe and the US has improved. This has raised expectations over the release of chemicals into natural ecosystems. One early example of this trend specifically related to biofouling was the State of Michigan's Chlorine Minimization Campaign: Utilities were required to reduce chlorine application until biofouling (microfouling) got out of control, then raise it to the minimum level required to establish control again. This resulted in a two-

thirds reduction in the amount of chlorine used, and discharged, by utilities in the state. On a general basis, the International Joint Commission (Canada and the US) recently recommended that all chlorine manufacture and use be prohibited in the Great Lakes Basin. Regardless of the validity of this recommendation (at least one state in the region has argued strongly against it), this is further indication of the regulatory and resource agency trend toward reduction of discharges of chemical products and by-products into natural waters. The Zebra Mussel invasion is occurring during this trend towards reducing chemical discharges, and other regulatory agencies in the US are threatening utilities with the spectre of abolition of all chlorine and/or chemical biofouling control agents once the Zebra Mussel crisis has been met. It is clear that non-chemical alternatives will be viewed as having advantages over chemical control agents and it appears that non-chlorine alternatives will be considered better than chlorine. However, as voiced by one regulator who had been asked to compare chlorine control with that by a proprietary chemical for which (he said) insufficient fate and non-target effects data were available, 'Better the devil you know than the devil you don't know'. In other words, lack of knowledge is not a good reason to choose an alternative. Without solid comparable information it will be difficult, perhaps impossible, to choose amongst alternatives.

This book will compare the advantages and disadvantages amongst the

biofouling control options or alternatives that are already in use in Europe. The objective is to provide a practical guidebook for selecting alternatives for use at a specific facility. Based on analogy with the Zebra Mussel, results will be useful, but may not be strictly predictive for North America. For example, Zebra Mussel growth and life cycle appear somewhat different in Europe and North America, suggesting that fine tuning of control strategies developed in Europe will be required on the other side of the Atlantic. This is not surprising given the complexity of biofouling and its dependence on the plant design and operational characteristics, and the organisms and conditions at the specific site. As indicated above, social and regulatory pressures can also influence choices. Conversely, the general principles developed over the long experience with the mussel in Europe were transferable and did save a lot of effort. In addition, the conclusions in the book will provide research direction for those who want to improve the tool chest of alternatives that can be used for biofouling control in the future.

The authors represent most of the groups involved in designing, operating and conducting research on power plant biofouling in Europe. They are privy to the sources of information, both in the grey and published literature. They have therefore been able to include information from studies that are difficult to locate and obtain because communication must usually occur not only across company, but national and language barriers as well.

The book is organized into five chapters plus references and annexes. Chapter 1 introduces the topics to be covered and reviews the problems. Chapter 2 presents synopses of pertinent life history information of the responsible fouling organisms. Methods that have proved useful to control or prevent biofouling in Europe are presented in Chapter 3. In Chapter 4 is dealing with the environmental impact of proven methods and the link with regulatory situation. Finally in Chapter 5 discussion and recommendations are presented, including future antifouling strategies.

Jack Mattice
New-York Sea Grant (USA)

CONTENT

1. INTRODUCTION	1
2. THE ECOLOGY OF FOULING	
2.1. The nature of biological fouling.....	15
2.2. The marine fouling species and their operational ecology.....	20
2.3. Estuarine fouling.....	32
2.4. Freshwater fouling.....	37
3. BIOFOULING CONTROL METHODS	
3.1. An overview of the antifouling methods	64
3.2. Water filtration	72
3.3. Cleaning.....	73
3.4. Water velocity.....	74
3.5. Heat treatment	79
3.6. Paints and coatings	83
3.7. Chemical treatments with oxidizing compounds.....	89
3.8. Chemical treatments with non-oxidizing compounds	145
3.9. Other physical methods.....	155
3.10. Biological control.....	160
3.11. Biological monitoring.....	161
4. REGULATORY CONTEXT	
4.1. Introduction.....	169
4.2. Basic principles of the European Union Legislation.....	169
4.3. Existing EU Legislation.....	171
4.4. Forthcoming EU Legislation	175
4.5. Other International Commitments.....	177
5. CONCLUSION AND RECOMMENDATIONS	179
6. REFERENCES	183
ANNEXES	
1. Heat treatment	205
2. Legislation and policy in North america and selected EU member states	207
3. European power stations quoted in the text.....	221
ALPHABETICAL INDEX ON KEY WORDS	223

Introduction

1.1 GENERAL

In 1985 a collaborative working group of three major European power companies (CEGB-EDF-ENEL) plus the KEMA Research Institute in the Netherlands produced what became known as the 'Blue Book' (Whitehouse *et al.* 1985). This document summarised the methods used to control biofouling in power stations using saline water for cooling. It was also intended that the 'Blue Book' should be used by designers, to reduce the need for biocidal control. Problems requiring control throughout the operational life of the plant might be reduced in severity, if not eliminated, thereby reducing any impact of the discharge on the receiving waters.

Since 1985 many things have changed. Firstly, there has been the enacting of subsidiary national interpretations of the primary European environment legislation and international conventions. This development in the regulatory regime is continuing with the forthcoming EC Directive on Integrated Pollution Prevention and

Control, the Framework Directive on Water Policy and moves to introduce ecotoxicological appraisal of discharges. Secondly, there has been the privatisation and rationalisation of the electricity industry in the UK and Netherlands and the increasing possibility of this taking place elsewhere. Thirdly, there are a number of technical changes. New types of plant, using new materials, are coming into use; a number of new alternative biofouling control methods have been suggested or trialed; and the biogeographic distribution of species has evolved – partially naturally – but partially too because of anthropogenic influences. Improving water quality has led to greater diversity and new invasive species have been introduced via ship hulls and ballast water.

We are observing the unfortunate contraposition of increasing technical problems, the risk of loss of expertise, and an increasingly prescriptive regulatory regime. These various changes have led the successors of the original working group to believe that an update to the "blue book" is timely.

In seeking to counter biological fouling, for all the reasons given above, we are currently in an extremely fluid situation.

As a consequence, the authors of this book do not consider it to be either exhaustive nor the final solution to these problems. Our objective is to describe the methods used to control micro- and macro-fouling in relation to the research and industrial applications undertaken in Europe over the past decades. In this book, we describe the methods used to combat the more usual forms of fouling known as micro- and macrofouling, based on many years of research and application of the methods in power stations in Europe. We also describe methods currently under investigation whose unproven efficacy and environmental impact do not, as yet, permit them to be included as standard methods.

1.2 COOLING WATER CIRCUITS

1.2.1 Water intake systems

The term 'intake system' is used here to mean those parts of the power station cooling water (CWS) system extending from the primary intake headworks at which water is withdrawn from the environment to the fine screens, of whatever kind employed (Fig. 1.1).

No matter the scale of the cooling water need, roughly the same collection of civil and mechanical systems

are necessary to provide the cooling water to the station itself. A convenient distinction can be made between "offshore" intake systems and "onshore" intake systems.

Offshore intake systems can be used at marine and estuarine sites to minimize the water recirculation. Such a system typically comprises a bored tunnel or buried culvert which runs out from land, below the seabed, to open in relatively deep water some distance offshore. The openings of the intake are usually close to the seabed to avoid drawing in the warmer surface layers, and, in order to do this, may be equipped with some kind of concrete capping arrangement, sometimes known as a "velocity cap". Such an arrangement is believed also to reduce fish ingress, by eliminating vertical water currents which fish are ill-equipped to avoid (Schuler & Larson 1974). Some form of coarse screening is always provided at the initial point of intake to prevent the entry of large items such as tree branches and fishing nets which might otherwise obstruct the CW tunnels.

Some offshore intakes have elaborate superstructures whilst others are entirely subsurface and their presence only evident from the necessary navigation marks. The former may provide access and support for cranes or other lifting gear designed for the insertion and removal of stop-logs and trash racks during maintenance. As such mechanical equipment is remote from normal power station operations and therefore difficult and costly to maintain in a hostile salt-water envi-

(a) Offshore Intake

(b) Onshore Intake

Fig. 1.1. – Comparison of the main features of offshore and onshore intake systems (sectional views).

ronment, it is commoner nowadays to dispense with such elaborations. The penalty of this evolution, however, is that it is now less practicable to dry down intake systems wholly to effect cleaning, forcing an increased reliance on pre-emptive antifouling controls.

The CW tunnel or culvert which conveys the water back to the main operational site is normally designed to do so with a velocity of 1.5-3.0 m/s, to prevent sedimentation. Typically, a descending shaft below the intake-headworks on the seabed leads to the near-horizontal tunnel to prevent air retention. At the onshore end, the tunnel opens into a forebay or “intake surge shaft”. This arrangement func-

tions like a manometer: flow into the forebay chamber occurs by gravity as water is withdrawn from it by the CW pumps. The benefits are twofold: mechanical pressure stresses on civil structures, potentially caused by starting and stopping CW pumps are avoided, and an area is left accessible for potential isolation and maintenance.

Onshore intakes become practicable where deep water is found immediately close to shore. A dredged channel, often based on a pre-existing tidal creek or associated with a harbour, can provide this opportunity.

From the intake entrance, water passes to a forebay guarded by coarse screen and with provision in-

serting stoplogs. From this point on, the CW system associated with both intake types become virtually identical: water drawn from the forebay passes through a series of parallel culverts. Across these culverts trash racks (vertical bar screens with 10 cm wide apertures) prevent drifting materials from being entrained further into the system. In some instances, for example where large quantities of loose seaweed occur, the trash rack can be equipped with automated rakes. These parallel culverts typically lead in turn to screen bays where fine materials are removed by moving screening systems. Here, two types of screening systems can be distinguished: band screens and drum screens.

Band screens are most common on older power stations, but are still used on new power stations having a CW flow of 5 m³/s or less. The screen comprises a continuously revolving belt of linked mesh panels (Fig. 1.2). Such a screen may be up to 4 m wide and the screens may descend into sumps up to 30 m deep, thus making them suitable for sites experiencing a large tidal range. Mesh sizes range from around 3.5 mm to 10 mm, depending on location. The travelling screen is backwashed continuously by spray jets and all the impinged material is carried via sluices to a trash collecting system for subsequent disposal.

A fairly common screening system for sewerage and industrial use, including the dewatering of sewage sludge, the drum screen was introduced

to power stations in order to avoid the maintenance difficulties associated with the large number of moving parts of bandscreens. In the 1960's drum screens were widely introduced they saw widespread use, especially where there was a need to cope with high debris loadings.

As the name suggests, such a screen is in the form of a large rotating drum, which may be anything up to 25 m in diameter and ranging from 1 to 5 m in width. The required diameter is determined by the CW flow and the tidal range. The largest diameter drum screens are those for once-through cooling nuclear units which require more than 40 m³/s of cooling water, or at sites where tidal range is extreme. Mesh sizes are as for band screens, but the common usage in France is for 3.5 mm meshes, whereas in the UK 15 mm and in The Netherlands 10 mm is used (Fig. 1.3). The smallest screen mesh used in power stations is approximately 1 mm.

1.2.2 Cooling Systems

Once water is obtained and screened via the intake system, it passes through the CW pumps and into the cooling system itself. One common component of all thermal power stations, whether nuclear or fossil fired, is a parallel series of heat exchangers of various sizes. These heat exchangers satisfy a diversity of needs, ranging from the very large condensers which cool the residual steam exhaled from the turbines, to auxiliary systems which cool ancillary plant such as die-

Fig. 1.2. – Conventional vertical travelling screen or "Band screen".

Fig. 1.3. – Drum screen arrangements.

sel generators, and standby plant which exists to provide additional cooling during outages or emergencies.

The bulk of the unwanted heat that such a power station has to deal with arises in the need to condense the residual steam exhaled from the turbines, in generating electricity. The steam is formed by heating water in a closed recirculating system as it passes through fossil fired boilers or analogous boilers or 'steam gener-

ators' in nuclear plant. It is the physical process of condensing the steam back to water that drives the cycle. The efficiency of the steam cycle is a fundamental constraint upon the operational effectiveness of all thermal power plant and thus considerable effort at the design stage goes towards the optimisation of the CW plant itself. This is one good reason for the considerable diversity of detailed design between stations.

Table 1.1. – Cooling water requirements and maximum temperature increase ($\Delta T_{\max}$) in French fossil fuel and nuclear power stations (Khalanski & Gras, 1996).

Cooling system	Type of power stations	Unit Power (MWe)	Cooling water required (m^3/s)	Heated water returned (m^3/s)	$\Delta T_{\max}$ ($^{\circ}\text{C}$)
Once-Through	Fossil fuel	125	5.5	5.5	7.5
		250	8 to 10	8 to 10	8
		600	22	22	9
		700	25	25	12
	Nuclear (PWR)	900	42	42	11
		1300	46 to 60	46 to 60	11 to 15*
Tower Assisted	Fossil fuel	250	0.2	0.1	
	Nuclear (PWR)	900	2 to 4.5	1.3 to 3.8	5 to 10
		1300	2	1.2	

* $\Delta T_{\max} = 11^{\circ}\text{C}$ on rivers, 15°C on the sea shore.

There are two types of heat exchanger : tube heat exchangers, where the coolant passes through the medium to be cooled via a bundle of narrow bore parallel tubes ; and plate heat exchangers where the coolant and the medium to be cooled pass each other whilst divided by a parallel series of closely adjoined plates. Tube heat exchangers have the merit of being mechanically simple, but because they encourage laminar flow they are relatively inefficient heat transfer engines and thus tend to be large. In contrast, the plates in plate heat exchangers can be pressed to each other giving complex shapes, in turn giving a highly turbulent internal flow which increases the efficiency of the heat transfer process. Unfortunately this same factor increases both the likelihood and actual cost of fouling. In practice, large volumes tend to be dealt with by tube heat exchangers

whilst ancillary plant often uses plate coolers.

There are two basic types of cooling system: direct and indirect.

In a direct system (sometimes called 'once-through') the water passes from the pumps through a parallel series of large and small heat exchangers before being passed straight back to sea or to river (Fig. 1.4). Unwanted heat is thus lost through dispersion of that effluent and its subsequent heat loss to the atmosphere. Very large quantities of fresh cooling water are necessary to satisfy such systems : typically $40\text{--}60 \text{ m}^3/\text{sec}$ per 1,300 MWe unit, with the coolant's temperature being raised by $11\text{--}15^{\circ}\text{C}$ (Table 1.1).

The primary driver for using an indirect cooling system is a fundamental shortage of water supply. In an indirect system (sometimes called 're-

Fig. 1.4. – Schematic view of a direct cooling water circuit for a nuclear power station.

circulating') the cooling water passes to a recirculating circuit which then cycles it between the power station's heat exchangers and a means of transferring the waste heat acquired direct to the atmosphere. The water then passes back to the heat exchangers. The typical means of transferring this waste heat to atmosphere is to use 'cooling towers' – large civil structures that optimise convective flows so as to maximise the efficiency

of the heat transfer process. Cooling towers can be divided into two types : dry and wet.

In a wet cooling tower (see Fig. 1.5 and Lecœuvre *et al.*, 1986) the warmed water is sprayed into the tower's void, descending against the incoming cooling air rising from its open base before being collected in a pond at the bottom. Such cooling towers normally have an internal cryptic structure (called 'packing') to maximise the surface

Table 1.2. – Variation in size of cooling towers in relation to heat dispersal. EDF Stations.

Station	Power per unit (MWe)	Base diameter (m)	Height (m)
Fossil fuel			
Pont-sur-Sambre			
unit 1	125	67	93
units 2/3	250	82	110
Nuclear Power stations			
Dampierre-en-Burly	900	131	163
Golfech	1300	144	178
Chooz	1400	142	172

area of cooling water exposed to the air. Evaporative heat loss plays a significant part in the cooling process but also results in a loss of volume which has to be made up by the cooling water system ('make-up water'). A degree of continuous purging of the system ('blow-down'), which also has to be made up with fresh water, limits the concentration of dissolved salts by evaporation and avoids the precipitation of scale.

A variant to these 'natural draught' cooling towers is to employ fans to increase their efficiency. More recently designs have been introduced which use "counter current" or "crossflow" systems. In the former film fill design, the heated water is sprayed by nozzles above a PVC honeycomb-shaped packing. The cooling air passes up through the honeycomb channels, whilst the water forms a film which streams down the cell walls in the opposite direction before being collected. In the latter, PVC slats occur in a ring round the inside of the tower. Heated water is driven up to a warm

basin above the ring and thence, through nozzles, is sprayed over the slats below. This splash fill arrangement allows water droplets to fall vertically through a horizontal air stream.

The increase in the scale of power plants in the decades to 1990 resulted in a tremendous increase in tower size (Table 1.2). For large nuclear units operated by EdF some 30,000 m³ of cooling water may typically be circulated, with a cooling water flow rate of 35 m³/sec and a 40,000 m³/sec air flow (Lecœuvre *et al.* 1986). Whether 'natural draught', 'forced draught', 'countercurrent' or 'crossflow', such 'wet' systems use only about 5% of the cooling water required by a direct cooled station of the same size (Table 1.1).

Where concerns may arise over the potential environmental and health impacts of an aerosol, the water supply is very poor, or a low power system is involved, 'dry' cooling towers have been introduced. In a 'dry' cooling tower the cooling water passes through sealed radiators, themselves cooled by the passage of air.

Fig. 1.5. – Schematic view of a closed cooling water circuit equipped with a natural draft wet cooling tower.

This 'dry pack' can be associated with fans, and such structures are known as 'forced draft' cooling towers. Although such a system does not suffer (and in thermal efficiency terms, benefit) from significant evaporative loss, the chemical additives necessary to prevent corrosion and microbial fouling need to be purged to some degree, again requiring make-up from the cooling water intake system. Cooling systems employing this particular type of tower are subject to quite different fouling problems than those using 'wet' towers and fall outside the scope of this book. Some information can be found in the report of the Pisa Symposium (EPRI, 1988).

Some stations have hybrid cooling water systems, where a direct system is used in some circumstances and an indirect in others, or the two are used in combination. The common driver for employing such a hybrid is variable cooling water supply (such as when ambient water temperatures rise or actual river levels fall).

1.3. Review of problems

The main fouling problems encountered by power station operators across Europe are summarized in Table 1.3, as indicated by a variety of

different companies and power stations through a questionnaire. It is obvious that various macroscopic organisms are responsible for problems in power station operation depending upon location and the source of the cooling water supply. Intractable and operationally difficult fouling is mainly caused by organisms with a shell of hard exoskeleton, such as mussels or barnacles. Special problems are found in cooling towers where bluegreen algae (Cyanobacteria) grow as thin sheets over the internal surfaces of the tower shell and the pack, causing blockage of the packing as well as the screens at the exits to the tower ponds.

Table 1.3. also shows that clogging at water intakes, caused by drifting plants, seaweeds, gelatinous organisms and entrained shoals of fish, is a major issue for the plant operators. Chemical fouling is also reported as a problem in circuits equipped with cooling towers.

As all internal surfaces of cooling systems can foul with biota, the complexity and variety of the systems in common use across Europe has resulted in a great diversity of fouling-related operational problems. The next chapter deals with the species involved whilst chapter 3 deals with the means of preventing and containing the problems they provide.

Table 1.3. – Survey of fouling and clogging organisms, and degree of fouling in marine, brackish and fresh water. In the last column, mitigation techniques and appropriate analytical methods are presented. (The degree of fouling is indicated as : + some; ++ fair; +++ heavy).

Country	Type of cooling water, associated fouling, clogging and scaling			Main antifouling mitigation techniques
	Marine	Brackish	Freshwater	
Belgium		Hydrozoa+ Slime++	Slime++ Zebra mussels+ Asiatic clams+ Bryozoans++ Gastropods++ In cooling towers : scaling++	Freshwater : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Discontinuous Chlorination with hypochlorite.
Denmark	Mussels+ Slime+	see marine	not used	Marine water : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Non-toxic antifouling paints.
France	Mussels+++ Barnacles++ Clogging by : seagooseberries (jellyfish)+++ seaweeds+++	Fouling : no special problems due to wide variations in salinity in large estuaries. Clogging by driftings macrophytes+	Zebra mussels++ Bryozoans++ Algae++ Gastropods++ Asiatic clams+ In cooling towers : scaling++	Marine water : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls (some units). Continuous chlorination at low dosing (0.5-1.0 mg/L), with electrochlorination Freshwater : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Shock chlorination once or twice a year.
Germany			Zebra mussels+ Slime++ In cooling towers : scaling++	Freshwater : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Discontinuous chlorination with hypochlorite. H ₂ O ₂ .
Ireland	Mussels+ Slime+ Clogging by : fish+++	see marine	Zebra mussels	Marine water : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Continuous chlorination with hypochlorite.

Table 1.3. – (suite)

Country	Type of cooling water, associated fouling, clogging and scaling			Main antifouling mitigation techniques
	Marine	Brackish	Freshwater	
Italy	Mussels+++ Hydroids++ Tubeworms++ Barnacles++ Slime++ Clogging by : seaweeds+ <i>Posidonia</i> +	(only one station) Clogging by : seaweeds+ debris+	Slime++ Clogging by : drifting plants, leaves+ Zebra mussels	Marine water : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Continuous or intermittent chlorination by hypochlorite or electrochlorination. Freshwater : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Intermittent chlorination (very few cases).
The Netherlands	Mussels+++ Slime++ Clogging by : jellyfish+++ fish++	Mussels++ Slime+ Clogging by : fish+	Zebra mussels+ Slime++ Clogging by : fish++	Marine & Freshwaters : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Heat treatment. Chlorination with hypochlorite: continuous or discontinuous, pulse chlorination.
Norway			Hydro-power : only problems with migrating fish.	
Portugal	Mussels++ Slime+		Asiatic clams+	Marine water : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls (some units). Continuous chlorination at low dosing (0.5-1.0 mg/L), with electrochlorination Freshwater : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls.
Spain	Slime+ Tubeworms+ Mussels++ Oysters+		Slime++ In cooling towers : scaling++	Marine & Freshwater : water filtration, debris filters. On-line condenser cleaning by abrasive sponge balls. Discontinuous chlorination, low and shock dosing, with hypochlorite and electrochlorination.
United Kingdom	Barnacles+ Mussels++ Slime++ Clogging by : fish+++ seaweeds++ jellyfish+	see marine	Slime++ In cooling towers : scaling++	Marine & Freshwaters : water filtration, debris filters. On-line condenser cleaning by sponge balls. Continuous chlorination (intermittent in winter) with hypochlorite and electrochlorination.

2.

The ecology of fouling

2.1 THE NATURE OF BIOLOGICAL FOULING

2.1.1 Introduction

Any surface exposed to natural fresh or saline waters provides an opportunity for the settlement and subsequent growth of organisms, as a very great diversity of aquatic species whose adults live attached to solid surfaces employ planktonic larvae for dispersal. The internal surfaces of the various engineering systems described in the previous chapter can provide an ideal habitat for such species. As the majority of these species are sessile and live by filtering suspended matter out of the overlying water, the internal CW systems are virtually ideal : the steady flow conditions guarantee a continuous supply of food and dissolved oxygen, and the velocity sheer and physical screening mean that predators are few. Given such perfect conditions, settlement occurs readily and growth can be rapid. Without constraint this growth can begin to interfere with the operational

systems, and will lead to their failure. The phenomenon is known as biological fouling, or 'biofouling', and is an entirely natural process. From the perspective of a power station operator the development of such fouling within the CW system is entirely undesirable and needs to be kept in check.

The fouling of power station CW plant is recognised as taking five different forms : 'trash', biological 'microfouling', biological 'macrofouling', siltation, and scaling.

2.1.2 Trash

'Trash' is the commonly used term (derived from American parlance) for the unwanted material swept into a power station which, unless intersected by screens, would lead to the immediate physical blockage of internal plant such as the condensers and heat exchangers. This material typically consists of inert debris such as plastic bags and bottles, driftwood, steel drums, drifting seaweed, hy-

Photo 2.1. – Trash rack, lifted out of the intake, showing severe fouling with plastics (Gravelines Nuclear Power Station).

droids, reeds and leaves, and sometimes sewage solids. It also includes the larger organisms, naturally occurring in the water column, casually entrained by the cooling water flow: jellyfish (including the sea gooseberry *Pleurobrachia pileus*) and fish. Given that this 'trash' can thus include very significant quantities of fish, otherwise of intrinsic or potential commercial value, the use of the word itself and its inference that the material is simply waste to be disposed of is singularly unfortunate.

The trash racks frequently placed downstream of the intake forebay (Photo 2.1) provide the first line of defence against this material, with the rotating screens removing much of the rest. Any material which passes through the screens and penetrates the main and secondary cooling systems is called 'debris'. This can include fragments of fishing nets, reed fibres, and hydroid or barnacle fragments. Such debris causes problems with screens and endplates in small sized heat exchangers.

The fish species entrained and subsequently impinged upon the screens can include those migrating along rivers or through estuaries, such as eels, lampreys, salmonids and shads (*Alosa* spp.). They can also include species such as sprat (*Sprattus sprattus*) and herring (*Clupea harengus*), which may occur in dense shoals. If such a shoal is entrained the volume of fish can begin to overload the capacity of the rotating screens, impeding the flow of cooling water to the condensers and endan-

gering sustained electricity generation. Similar impacts can occur with jellyfish, leaves and drifting seaweed.

As ameliorating fouling problems caused by 'trash' and 'debris' requires separate solutions to those employed in controlling the biofouling of surfaces, this topic will be the subject of a subsequent publication.

2.1.3 Microfouling

When a surface is first placed in seawater or riverwater it is immediately coated with a film consisting of proteins, polypeptides, polysaccharides and lipids produced by aquatic organisms or derived from their degradation products. Bacteria common to these waters settle on the film, especially those which have a pellicle and produce slime as a part of their metabolic functioning (Characklis, 1981), and within six hours will have consolidated their presence, as polymeric fibrils are exuded from them within the film.

The establishment of a microbial film can have a significant effect on heat exchange performance in the main condensers and auxiliary coolers, made worse by the fact that such fouling of untreated warm condenser tube surfaces will occur all year round. Within seven days at temperatures of 10 to 20 °C, a layer of bacteria some 50-100 µm or more thick will have developed on a freshly exposed surface. Waste products from these microorganisms contribute to the film itself. After fourteen days such a slime film

will reach its maximum thickness, which rarely exceeds a few hundred μm even in nutrient-rich waters. The biofilm so formed can act as an anchor for any silt or mud in the water and such deposits further impair heat transfer.

The speed of biofilm formation depends to a large extent upon the metals involved: titanium condenser tubes are very rapidly colonised, whereas the surface dissolution of cupronickel and brass condenser tubes has a toxic influence on bacteria, retarding settlement and growth.

Once a biofilm has become established, a succession then occurs where the original colonisers are progressively replaced, or supplemented, by others. This is a complex process made all the more so by the highly variable geographic distribution of species and the fact that some organisms are only present in the water column at certain times of year, with their relative abundance sometimes varying considerably from one year to another. The final 'climax' assemblage of species on a surface will thus depend upon geographic variables and the environmental conditions offered, such as substrate type, the presence or absence of light, flow conditions, salinity, and water quality. Some of the organisms that may settle are not microbial, but the larvae of macroscopic species. If these larvae survive to grow on towards maturity this will lead to macrofouling of the systems involved.

It is frequently quoted in the literature that a microbial film is a necessary precursor for macrofouling and

that the maintenance of a robust microfouling control tends to go a long way to controlling macrofouling too. Observations made with artificial collectors of larvae made up of PVC plates or glass slides, show that when larvae are ready to settle, they do not necessarily wait for the development of the microbiological layer. Larvae of zebra mussels, marine blue mussel and barnacles are capable of settling rapidly on surfaces free of a microbial film. This strongly implies that elimination of microfouling by a given treatment cannot be the only criteria of success in preventing macrofouling, as the toxic process responsible for bacterial control may have no effect on the macrofouling itself.

2.1.4 Macrofouling

Macrofouling organisms readily colonise man-made surfaces, including those of power station cooling water intake tunnels and culverts, the screen forebays and rotary screen wells, condenser tube plates and heat exchangers. One of the most troublesome of these organisms in coastal waters is the common blue or edible mussel, *Mytilus edulis*, and it is the problems caused by this species that first led to the development of fouling control strategies at power stations. Although blue mussels are a notorious example of a fouling species, there are many others. In non-tidal low salinity waters such as the Noordzeekanaal in the Netherlands the brackish water mussel, *Mytilopsis leu-*

cophaeata, is found; in freshwater the equivalent is the Zebra mussel, *Dreissena polymorpha*. Another bivalve mollusc, the Asiatic Clams *Corbicula fluminea* and *Corbicula fluminalis* are known for causing severe problems in North America but in recent years has been found in the Rhine, the Moselle (Bachmann *et al.*, 1995) the Rhone, (Khalanski, 1997a, b), and the Garonne basin (Dubois, 1995).

Each macrofouling species has its own characteristics in terms of settlement behaviour, and the effects and the occurrence of each species varies with site, season, and between years. The biology and ecology of the most significant species are described in Section 2.2 below.

2.1.5 Siltation

On a direct cooled power station silt can be deposited from suspension in the entrained water anywhere the water velocities drop below a critical value. Generally speaking, power station cooling water systems are designed to maintain laminar and constant flow within the pipeworks and culverts, and turbulent flow at intersections such as forebays and surge shafts. This design approach prevents the significant accumulation of silt, as the suspended material is simply flushed through. Slack areas do occur in wide forebay systems, but these are generally designed in such a way that any silt accumulations can readily be removed by occasional limited dredging.

When siltation is found to be occurring within cooling water culverts and auxiliary cooling systems it will very often stem from biological fouling, even though the evidence of that biological activity may have become obscured with the passage of time. There are two mechanisms for this. Firstly, when macrofaunal organisms settle onto surfaces and grow, the depth of the low flow boundary layer lying over the settled surface is increased. This increases the slack volume within a culvert or pipework and increases the likelihood that silt will settle. Secondly, both microfouling organisms and macrofouling organisms add waste organic matter to their surroundings. Silt can readily be incorporated into a biofilm, but it is the particular feeding habits of mussels that can provide the worst problems. As will be described in more detail later, mussels filter out suspended material from the passing water very efficiently. In conveying this material across their feeding gills, sorting favoured material, a mucus film is added. The unwanted material, bound by this mucus, is ejected as 'pseudofaeces'. A considerable volume of suspended material can be processed in this way, and the resultant pseudofaeces are more likely to adhere and settle to surfaces. This can result in very considerable drifts of accumulation within the cooling water systems, and can lead to great amounts of deposits in heat exchangers, especially plate heat exchangers. As a result, a problem that has a biological origin can readily be mistaken for a purely physical process,

and this can lead to an inadequate response being taken by the operator.

Within an indirect cooled power station, silt can be deposited if the make-up water has a high suspended solids load. This can lead to difficulties if the silt is deposited in low flow zones, especially cooling tower ponds. Silt may enhance the impact of biofilms by becoming entrained within them, greatly increasing the deposits in condenser tubes and on cooling tower packing. It is not unknown for silt to accumulate so quickly that the cooling tower ponds become filled to the brim, greatly reducing the carrying capacity of the closed circuit. Similar problems have overcome newly installed plastic packing systems.

2.1.6 Scale

This is a problem largely specific to power stations using cooling towers. Scale is the precipitation of dissolved salts, mainly calcium carbonate, which then form a layer on the cooling water side of heat exchangers, with a not dissimilar effect upon heat transfer efficiency to that caused by a biofilm. Scale deposit on plastic packing, especially on "honeycomb" film fill, can severely increase the fill weight, threaten the stability of the fill structure and reduce the thermal exchange capacity of the cooling tower. The quantity and quality of the make-up water entering the system, the flow rates of the circulating water, the inlet and outlet temperatures of the condensers, and the nature of any che-

mical additives, all influence the rate of scale formation.

As with trash, and siltation except in so far as it occurs as a consequence of biological fouling, the amelioration of potential scaling problems falls outwith the context of this publication.

2.2 THE MARINE FOULING SPECIES AND THEIR OPERATIONAL ECOLOGY

For the sake of consistency, the various species are described here in the context of their known ability to foul direct cooled systems, as described in Section 1.2. In practice, all power stations which use saline water for cooling are directly cooled. Further, on such stations the bulk of any fouling is found on the intake side of the cooling system. On the discharge side of cooling systems the water temperature is generally high enough during the summer months to eliminate most of the marine fouling species.

2.2.1 Mussels

Taxonomy and distribution

The best known of all the macro-fouling organisms and the one causing the most widespread and serious problems for coastal and estuarine power stations, is the Common or Blue Mussel, *Mytilus edulis* (Photo

2.2). Mussels of the genus *Mytilus* are bivalves belonging to the family Mytilidae, which are members of the Order Anisomyaria, bivalves with unequal muscles for shell closure.

M. edulis has a wide distribution in both the northern and southern hemispheres. Around Europe there are other closely related species which have a more restricted geographical distribution:

- Horse mussel (*Modiolus modiolus*) Bay of Biscay to North British Isles;

- Bearded horse mussel (*Modiolus barbatus*) Mediterranean, Biscay, English Channel and North Sea;

- Mediterranean mussel (*Mytilus galloprovincialis*) Mediterranean, Atlantic Coast, Biscay up to the English Channel and round the Irish coast.

All of these may colonise cooling water systems. A clear understanding of the distribution of the various *Mytilus* species and the implications of this for fouling control are unlikely to be forthcoming soon. *M. galloprovincialis* was only recently confirmed as a separate species from *M. edulis* over the northern part of its range. The two are difficult to tell apart, and frequently coexist in the same region.

Previously, (Whitehouse *et al.* 1985) it was suggested that *M. edulis* was the more widespread species, with a restricted distribution of *M. galloprovincialis*. It was also understood that more sites in France have *M. galloprovincialis* than those in Great Britain. This view has had to be revised in the light of recent genetic and mor-

Photo 2.2. – The common mussel *Mytilus edulis*, showing the characteristic clump formation normally found in cooling water intakes. Note also the byssus threads which anchor the mussel to the substrate.

phological analysis (see Gosling (ed.) 1992). It would now appear that there are six species, of which only three are relevant to the problems of power station macrofouling in European Waters: *M. edulis*, *M. galloprovincialis* and *M. trossulus* (Fig. 2.1).

What is known of the distribution of *M. galloprovincialis* in the British Isles and Northern France shows it is no longer a simple matter of identifying all mussels from northern power stations as *M. edulis*. This has never been a question for specimens from Mediterranean power stations, which were clearly *M. galloprovincialis*. Thus,

Fig. 2.1. – European distribution of the three species of *Mytilus* detected using morphological and electrophoretic markers (After Gosling, (ed.) 1992).

a problem has developed as there are clear zones of hybridisation between *M. edulis* and *M. galloprovincialis*. The physiology of these hybrids may differ from data determined on specimens

assumed to be uniformly *M. edulis* or *M. galloprovincialis*, and thus may differ in their relative success as fouling organisms and the relative success of the means of combatting them.

Fig. 2.2. – Growth curves of *M. edulis* in the North Sea and English Channel. Whitehouse *et al.* (1985b).

Biology and reproduction

The two shell valves of *Mytilus* spp. vary in colour from black to brown. The shells are often overgrown with barnacles, hydroids and other encrusting organisms. *Mytilus* is found throughout the intertidal zone and in the near subtidal region. Growth of the shell occurs through deposition of calcareous material by the mantle to the free edge of the shells. The mantle is the thin layer of tissue which lines the inside of the shells.

Food is acquired by filtering particles and by the use of dissolved organic matter from the sea water. So to a large extent the rate of growth is dependent on the nutritional status of the water and on water temperature. This accounts for large differences in growth between some sites from the English Channel, and the North Sea, for example, between Dungeness and Dunkerque (Fig. 2.2).

There is a wide range of salinity limits to the distribution or the survival of *Mytilus* spp. except their ability to cope with marked fluctuations between saline and fresh water conditions over twenty four hour periods as found in estuaries. Such mussels are usually stunted specimens which are very slow growing (see Seed & Suchanek, 1992).

Reproduction is highly temperature dependent, with the production of eggs (oogenesis) and sperm (spermatogenesis) taking place in specialised pockets over the whole of the mantle. Experimental studies have shown that gametogenesis is accelerated by water temperatures between 4 °C and 11 °C but slows down at about 11 °C. At 17 °C, gametogenesis and egg laying are partially inhibited and some cytolysis of oocytes is to be seen. Following sexual development in the winter, reproduction continues through spring and summer (Lubet, 1983). Prior to release of the eggs and sperm, the mantle is swollen by reproductive tissue. Fertilisation takes place in the sea when water temperatures have reached about 10 °C, that is after mid-March up to the end of September, with the main period in April to June. After fertilisation, the eggs develop into free-swimming larvae called veligers (Photo 2.3). Depending on water temperature and food, the larvae develop within 2-4 weeks into the final larval stage, the pediveliger. During reduced food conditions and/or low water temperatures, the planktonic stage can be prolonged by several weeks.

Photo 2.3. – Veliger larvae of *M. edulis*.

Settlement and growth

The pediveliger is the settlement stage of the mussel. It sinks to the sea bottom and starts crawling with its foot, searching for some filamentous structure such as algae or hydroids. The pediveliger prefers to attach to filaments in the first stage of settlement (e.g. upon the byssus threads of already settled mussels). Pediveligers then metamorphose to plantigrades. Later in the year, the plantigrades may leave the primary settlement sites and, again in the plankton, search for permanent sites, which are usually firm or hard surfaces. These late stage plantigrades (Photo 2.4) are called spat when they have completed their second larval

settlement, at which point they are considered to have metamorphosed into miniature adults (Fig. 2.3). At this stage they are between 0.9-1.5 mm in length, so there is hardly any possibility of removing them by filtering the incoming cooling water.

Natural spat densities of the order of $6 \times 10^5/\text{m}^2$ have been found but more usually they are in the range $1-2 \times 10^5/\text{m}^2$ (Dare, 1973). In power stations few data have been collected, but at Maasvlakte power station near Rotterdam numbers ranging from 50 to $2 \times 10^5/\text{m}^2$ were recorded between May and August 1981. Population density is normally limited by the availability of solid substrate for spat settlement: cooling water systems with their concrete walls are an ideal subs-

Photo 2.4. – *Mytilus edulis* larvae with late stage plantigrades or 'spat'.

trate for mussels. This artificial habitat is also ideal due to continuous flow, food, oxygen, the absence of predators and emersion. The important issue for operators is knowing when settlement occurs in cooling systems. At some sites, this may be over a distinct period of a few weeks in Spring, but it may elsewhere take place at any time of the year. The period of spatfall is generally geographically determined.

Unless settlement is quickly identified, it is possible for the spat to grow unnoticed to a size where they may interfere with functioning of particular parts of the station. For example, very little growth is required before the mussels reach a size equal to the interplate gap of plate heat exchangers,

at which point blockage may occur. When mussel fouling is known to pose a significant risk, it is essential to have some rigorous form of monitoring for spat settlement throughout the period in which the sea water temperature is at or above 12 °C. Spat settlement monitors have been used by EDF, KEMA and British Energy to detect settlement and also to verify the efficacy of the treatment regime.

Settling periods at Gravelines have been determined with a spat settlement monitor (Travade & Khalanski, 1986). In 1983, the main settlement period was at the beginning of June with secondary peaks at the end of July and the beginning of September. In 1984 the main settlement was at the end of May with secondary peaks

Fig. 2.3. - Biological cycle of *M. edulis* in the English Channel.

at the end of June and mid-October. The main settlement periods were seen to vary by several weeks from one year to the next. In the UK settlements have been recorded for most months in the year.

Mussel growth depends on water temperature. According to Bayne (ed.) (1976), growth does not start until the seawater temperature is above 12 °C. The same author reports that growth is seasonal, there being little in winter when the water temperature is below 10 °C. However, in practice, in some eutrophic coastal waters such as

those at Le Havre or Dunkerque, growth is not negligible. The winter growth is greater for continuously immersed mussels than for natural populations located on the tidal shore that are submitted to daily emergence. The shell growth of mussel populations located below the tidal level (as in the CW systems) is rapid, and the shells of these populations are thinner than shells of nearby intertidal populations.

In these populations, below 10 °C, a significant growth takes place (Fig. 2.4). The effect of water tempe-

Fig. 2.4. – Growth of *Mytilus* spat in the intake canal of the Gravelines Nuclear Power Station according to shell length measurements made from 1980 to 1998.

ature, as distinct from season, on the growth rate of mussels have been observed by comparing growth in the intake and discharge channels at Gravelines over 1983-1984 :

— In winter, mussels placed in the outfall channel, where the water is heated to about 10 °C, the growth was 20-25% greater than that in the intake channel.

— When the water reached a temperature of 18-20 °C in the outfall channel the growth was strongly reduced by comparison with that in the intake channel.

It is evident that growth in the unheated parts of cooling systems of po-

wer stations is as good as the best recorded in natural populations. Because of this ability to grow very rapidly, spat can reach a size where they can lodge in condenser tubes within one year of settlement. In the intake channel at Gravelines Power Station the average shell length was recorded in the range of 20-30 mm in November 1983, six months after settlement. Heavy settlement densities had been followed by rapid shell growth, with a maximum of 10 mm in 30 days. One year later in November 1984 the average length was 55 mm (Travade & Khalanski, 1986).

Growth also depends on food availability (see Gosling (ed.), 1992). The

high plankton production on the North Sea Coast is responsible for that very high growth rate during the summer months.

In general it may be said that the most favourable conditions for the settlement and growth of *Mytilus* spp. are :

- A water velocity between 0.2-1.6 m/s;
- An annual thermal regime in which the temperature is between 10-18 °C for long periods;
- water rich in plankton, dissolved organic and particulate matter;
- Permanent immersion in water, no low tide exposure;
- Rough substrates, either from barnacle settlement or the natural surface of concrete;
- The presence of other mussels making the intake suitable for the settlement of mussel larvae;
- The lack of the main predators, shore crabs (*Carcinus* sp.) and wading birds.

These various conditions, where food, oxygen supply and substrate availability are essentially non-limiting, are typical of most culverted cooling water system.

This ecological profile explains the presence of mussels in all cooling circuits using sea water, especially in the intake channels, tunnels and culverts, on steel bar screens, concrete culverts and the walls of rotating screen chambers. They are absent from channels and tunnels with high water velocities or heated discharges.

Photo 2.5. – Barnacle species *Balanus crenatus* from the intake canal of the Gravelines nuclear power station on the French North Sea coast.

The biology of marine mussels is comprehensively reviewed by Bayne (ed.) (1976) and Gosling (ed.) (1992). They present much of interest, particularly the information on the evolutionary flexibility of these species.

2.2.2 Barnacles

Taxonomy and distribution

Barnacles are members of the Sub-class Cirripedia, a highly modified group of the Class Crustacea. Thus they are related to Crabs, Lobsters and Shrimps. The main species found in cooling water circuits are *Balanus crenatus*, *Balanus improvisus*, *Chthamalus stellatus*, *Semibalanus balanoides* and *Elminius modestus*, (Photo 2.5). Less commonly, The exotic *Balanus amphitrite* occurs in Zeeland, The Netherlands and estuaries as in Shoreham Harbour Canal and

Swansea Docks in the UK (Rainbow, 1984), where heated effluents are discharged from power stations. Most European species are small, of the order of 10-25 mm across the base and rarely more than 25-30 mm high; a contrast with some tropical species (e.g. *B. tintinnabulum*), which are ten times this size and cause serious operational problems for power stations.

Barnacles have a distinct zonation pattern on European rocky shores: *Semibalanus balanoides* is found mid-shore, with *Balanus perforatus* being found lower down. *Balanus crenatus*, is always found below the low water level, thus constantly immersed.

Reflecting this tidally driven distribution, *Balanus crenatus* is the most common species found in underwater circuits.

Most barnacles are stenohaline but *B. improvisus* is only found in estuaries including ports and brackish water.

Biology and reproduction

In adult life, barnacles are sessile organisms, fixed head-down on firm substrates. They look like truncated cones, the walls of which consist of overlapping calcareous plates. They are cemented to the substrate by the whole of the base plate, a modified head. Feeding is by means of the four to six pairs of legs, found inside the plated cone. The legs extend rhythmically to beat outside, creating a current of water flowing through the legs allowing planktonic particles to be filtered off as food.

Barnacles are hermaphrodite, having both male and female sex or-

gans. Fertilisation is internal. Eggs are laid inside the external plates and hatch to give a free swimming shrimp-like larva, the nauplius. These develop through several moults to become bivalved cypris larvae (Photo 2.6). Each cypris moves onto a firm surface, fixing itself by its head and antennae. The larva then develops the various adult characteristics.

Settlement and growth

In the English Channel, off the coast of Normandy, the release of larvae of the barnacle *Semibalanus balanoides* continues throughout the year with maximum abundance of the cypris larvae from March to May. The main settlement period is in March-April (Plessis-Fraissard, 1961).

The range of monthly mean temperatures at the time of the peak settlement of barnacles at Flammanville (1986-93) was 9 °C in March and 10 °C in April (Dreves *et al.*, 1994).

At Penly power station, there are two naupliar peaks, one in spring, the other from July to September (CNEXO 1983). The first peak is of *S. balanoides* the second of *B. crenatus*. In 1996, the first settlement of barnacles occurred between April 5 and April 11 at a water temperature of 8 °C. The first settlement peak was recorded at the end of April at 10 °C. Settlements have been observed up to 1st of October. The population at end of August is dominated by *Balanus crenatus* with a maximum height of 11 mm and a basis diameter of 4 mm. The biomass of settled organisms, mainly bar-

Photo 2.6. – Cypris larva, the planktonic settlement stage of barnacles.

nacles, on the PVC collector reached 27 kg/m^2 on August 27.

Monitoring of fouling organisms at Gravelines on the North Sea in 1983-84 showed massive settlement of *B. crenatus* in the first two weeks in May at a water temperature of 11°C . One month later, in June, the PVC collecting plates were covered with a layer of *Balanus crenatus* several cms thick. The wet weight was estimated at 7.5 kg/m^2 .

Barnacles may settle and develop on any surface exposed to seawater from culvert walls to rotating drum screens. As mussels, they tend to be very much less successful in colonising surfaces exposed to high rates of flow or particularly high temperatures. Dead individuals, or rather their

calcareous plates, fall to the bottom of culverts and these debris can be washed downstream and cause significant problems to filters and heat exchangers.

2.2.3 Other Organisms

Oysters

Oysters: (*Ostrea edulis* and *Crassostrea virginica* (Portuguese), *C. gigas* (Japanese)), like mussels, are members of the Anisomyaria. However, the foot is smaller and the sexes are not separated. The shells are asymmetrical with one valve normally more concave than the other. The concave valve is firmly cemented to its substrate while the other valve provides a lid.

The shell is externally ridged and shows a greyish-green colour. Its surface texture is stratified, noticeable more pronounced in adults, which gives the impressions that they are formed of sheets or layers of calcareous material. It measures between 7-10 cm and the inside is smooth and has a pearly, whitish, shiny colour with a violet mark. Inside the mantle, which lines the shell, are the four circular membraneous gills. These have many cilia which generate a current which enables water to pass through them carrying oxygen for respiration and micro-organisms for their food supply. Like other bivalves, oysters can close their shells tightly for long periods which enables them to resist the effects of toxic substances in the water.

Oysters are hermaphrodite but their sex does not develop at the same time. Individuals first become male, later female. In summer the male sexual products are shed into the water and fertilize the ovum of the females. About one to two million eggs are fertilized and deposited in the gills of the female. The development stage in the gills lasts between one to two weeks after which the larvae are released. This planktonic stage lasts for two to three weeks, when they metamorphose and sink to the bottom seeking a suitable substrate to settle. This part of the life stage happens at water temperatures of at least 18 °C.

The oysters, which arrive by swimming as veliger larvae in July and August, attach themselves to the walls of cooling conduits especially in areas

Photo 2.7. – Calcareous tubes of marine worms *Pomatoceros triqueter* (left) and *Protula tubularia* (right). Photo Studio Yves (Chatou). Main div. = 1 cm.

with lower water velocities. With continuous chlorination most of the oysters will die and the upper valve will detach and may block condenser tubes and/or sieves. In general oysters require higher chlorine (hypochlorite) doses to kill them than mussels, but in the case of chlorine dioxide the dose is equal. The only serious case of fouling by oysters is known from a chemical plant in the Western Scheldt, the Netherlands.

Tubeworms

This include a variety of species of polychaete Annelids living in tubes, forming encrusting colonies which reduce water flow in culverts and can only be removed by mechanical means. Several fouling species, with calcareous tubes are found in power

Photo 2.8. – The brackish water mussel : *Mytilopsis leucophaeata*.

station cooling systems, including *Serpula vermicularis* (about 7 cm long) *Protula tubularia* (to 5 cm long), *Pomatoceros triqueter* with a triangular tube (photo 2.7), *Hydroides norvegica*, *Salmacina tribranchiata* (*Filograna implexa*) are smaller (maximum length of 2.5 to 3.0 mm), but also form encrusting colonies which are difficult to remove. They are distributed in the Mediterranean, the Atlantic, The English Channel, the North Sea, and the west coast of the Baltic sea.

Tubeworms are less significant than barnacles in terms of their contribution to the debris which accumulates at the bottom of culverts and water chambers.

2.3 Estuarine fouling

Estuarine fouling is something of a special case. Firstly, the species di-

versity found in estuaries is more limited than in nearby coastal waters. The species present are those tolerant of high turbidity and variable water quality, making them particularly robust fouling species. Secondly, estuaries provide a potential habitat for opportunistic alien species.

2.3.1 Brackish water mussels

Taxonomy and distribution

The Brackish water mussel, *Mytilopsis leucophaeata* (Photo 2.8), is a bivalve in the Family Dreissenidae. The Brackish water mussel and the Zebra mussel are thus taxonomically closely related. Previously, *Mytilopsis leucophaeata* was known as *Congerina cochleata*, and was introduced into Belgium from the subtropical Caribbean in the early part of the 19th Century (Marelli and Gray, 1983). Currently it is found along the coast of the North Sea from Germany through The Netherlands and Belgium into France and recently in Great-Britain (Oliver *et al.*, 1998). The only recorded cases of fouling are in The Netherlands, where it causes problems in the Velsen and Hemweg power stations which draw cooling water from the Noordzeekanaal (Jenner & Janssen-Mommen, 1993; Rajagopal *et al.*, 1994).

Biology and reproduction

This species is reported to be able to live in a wide range of intermediate salinities but not full sea water (Siddall 1980). Mussels of a length of 2.4 mm

Fig. 2.5. – Seasonal variations in the spat settlement of *M. leucophaeata* on experimental PVC – panels and water temperature in the Noordzeekanaal during the years 1989–1994 (Rajagopal *et al.*, 1994).

are occasionally found to be sexually mature but generally the mean size of sexually mature specimens is > 7.0 mm when the mussels are about two months old. Spawning in the Noordzeekanaal has been observed between June and September when the water temperature is at or above 20°C , and salinity is at its highest. This mussel has a planktonic veliger as its larval stage and the settled stages become attached by byssus threads. Densities of veligers in the Noordzeekanaal has been observed in the order of $15\,000/\text{m}^3$.

Settlement and growth

Spat settlement densities on panels located in the intake of the Velsen power station have been up to $6.5 \times 10^6/\text{m}^2$ whereas spat settlement densities on panels in the canal (Fig. 2.5) showed maximal values of $0.5 \times 10^6/\text{m}^2$. Spat settlement in the

canal is related to water depth, with a maximum at 2 m and lower densities at 1 m and 3 m depths. There was no depth variation in settlement density in the power station intake. One month after settlement, these mussels are 3 mm in length; they can reach 14 mm at the end of their first year.

2.3.2 Barnacles

Taxonomy and distribution

The taxonomic status of barnacles has been described in section 2.23.2. The only estuarine species, *Balanus improvisus* (see Photo 2.5) has a wide distribution, being found in Europe (Furman & Yule, 1991) including the Baltic and the Eastern USA.

Biology and reproduction

This species is euryhaline and is found in a range of salinity from 5 ‰ to 15 ‰, and occasionally lower. Ge-

nerally, it is not found where salinity is above 25 ‰ (Rainbow, 1984); although Barnes (1994) suggests a salinity up to 35 ‰. As with all barnacles, *B. improvisus* is hermaphrodite but usually reproduces by cross fertilisation. However, when adult density is such that the individuals are more than 3-5 cm apart then self fertilisation takes place. Several broods are produced per year at intervals of six weeks. The release of nauplii starts when the water temperature reaches 10 °C and stops when the temperature falls below that threshold.

Settlement and growth

B. improvisus can settle on both concrete and steel structures. They are reported as preferring rough surfaces (Barnes, 1971). At the time of settlement, the presence of one or more settled cyprids leads to settlement of large numbers of the same species (Clare *et al.*, 1994). This behaviour is also stimulated by the presence of adults of the same species (Marchand & Denayer, 1991).

Settlement has been found to start in the Noordzeekanaal (The Netherlands) during June/July, with maximum densities in the region of the intake at Velsen power station of 37,200/m² in July 1994. The effect of the water intake was to promote a heavier settlement at 2 m depth, in mid water. A second spawning started during September/October and ended in November. The maximum settlement density was of the same order as that found by De Wolf (1973).

Growth of *B. improvisus* at Velsen power station was monitored on settlement panels and showed a basal diameter of 10-11 mm after 45 days.

2.3.3 Other organisms

Tube Worms

The tube worm *Ficopomatus enigmaticus* (syn. *Mercierella enigmatica*), is one of two others currently recorded as causing problems for power station cooling systems. This is an immigrant species which originally was found in subtropical regions; it probably derived from Australia or the subtropical Australian region (Allen, 1953; Dixon, 1981). It was first recorded in Europe by Fauvel in Normandy in 1921, and then found in the London docks in 1922. It is now found in the Mediterranean, the harbour at Vlissingen (Flushing, SW Netherlands), the Noordzeekanaal (near Amsterdam and Velsen) in Cavendish Dock, Barrow-in-Furness (UK), Roath Basin, Cardiff docks, South Wales together with *Mytilopsis leucophaeata* (Oliver *et al.*, 1998). The interesting point about Cavendish Dock is that *F. enigmaticus* and *B. improvisus* both colonized the dock in the same year, 1959, after a period of two years in which the salinity was, on average, below 10 ‰. (Markowski, 1962). The tube worm formed a thick lining in the intake cooling water pipes, which had to be cleaned manually from time to time.

F. enigmaticus is a euryhaline species living in salinities from 1-35 ‰; larval development is best at salinities

between 10-30 ‰ and inhibited below 6 ‰ (Hartmann-Schroeder, 1967). Below 2.0-3.0 ‰ chlorinity, no reproduction takes place and there is high mortality after a long time at such chlorinity levels (Wolff 1969a). Low salinities reduce growth of the calcareous tubes because of the lowered calcium concentrations in fresh water (Straughan, 1971). Settlement takes place on most substrates, but preferably in waters without low current speeds, as this species is unable to withstand deposition of mud. The larvae settle and metamorphose and may reach a tube length of 30 mm within 16 days (Ten Hove & Van den Hurk, 1993).

In the Noordzeekanaal, the first settlement of *F. enigmaticus* was observed in the summer of 1991, followed by an increasing intensity of settlements after 1992. Settlement occurred from July to August, when temperatures > 15 °C and salinity > 5 ‰. The resulting settlement densities were $64 \times 10^3/\text{m}^2$, recorded on PVC panels in October 1993 after 160 days of exposure. There was intense competition for settlement space with both *M. leucophaeata* and *Cordylophora caspia* the result of which appeared to be a reduction in overall growth. The newly settled tube worms grew at a rate of 10 mm/week for the first 4-6 weeks but only reached a size of 60-70 mm by the end of the first year (pers. obs.).

Fouling by tube worms is strongly dependent on water velocities, high settlement is to be expected at velocities below 1 m/s. Old encrustations

of dead tube worms will serve as substrate for new ones, which can lead to a firm crust up to 30 cm of thickness in six years. It is obvious that these encrustations serve also as a perfect substrate for mussels and other hydroids (Photo 2.9).

Hydroids

Cordylophora caspia is the main hydroid species causing fouling problems. It is a colonial hydroid found in brackish or estuarine waters and in fresh waters with often changing salinity or modified ionic conditions (Arndt, 1973; Kinne, 1956). This is an animal belonging to the same part of the animal kingdom as Sea Anemones, Jellyfish and Corals. It has a wide but discontinuous distribution throughout Europe, Asia, North and South America and Australasia.

Reproduction is by asexual budding of small colonies or from pieces of the basal attachment mesh or hydrorhiza called menonts. Growth is also by budding so the production of new colonies and increase of the size of the colonies is by the same process. As colonies usually die back in the winter, regrowth in the spring is from hydrorhizal pieces.

Colonies develop in brackish water with a salinity of 0.2-10 ‰, but there is a wide variation in the temperature and salinity conditions for optimal growth (Vervoort, 1946, Arndt, 1965; 1973; 1984; and Kinne, 1956). In the Noordzeekanaal, since 1986 it has been observed that these hydroids are the first colonisers of the fouling panels and attachment starts in May

Photo 2.9. – *Ficopomatus enigmaticus*, showing the individual worms and the natural aggregations of worms (with *M. leucophaeata*) as found in cooling systems.

and finishes in October. These primary settlers are subsequently covered to various degrees by the brackish water barnacles and mussels. However there is a strong interaction between *F. enigmaticus* and the colonial-hydroid, *Cordylophora caspia*, as the latter prevents the settlement of the former by causing great accumulations of mud.

Similar observations have been made at Cattenom Power Station on the river Moselle, where *Cordylophora* is amongst the first organisms to settle in April. As this species grows it covers all the walls of the intake culverts and chambers and is in turn a suitable substrate for settlement by

the Zebra mussel (*Dreissena polymorpha*) (Moreteau & Khalanski, 1994).

2.3.4 Microbial fouling

The development of microbial fouling on surfaces in cooling systems depends on two features, the materials of the cooling system and the quality of the water. The materials affect the speed at which organic molecules and bacteria colonise the surfaces. Water quality controls the rate of growth, the 3-D architecture of the microbial community and thus the ultimate thickness of the slime layer. It is the rate of growth of this layer

which determines the type and frequency of the treatment needed to control growth or to eliminate the slimes from condenser tubes.

In all environmental and power plant conditions, biofouling by micro-organisms proceeds in a standard sequence: conditioning of the surface by attraction, adsorption and followed by adhesion of micro-organisms. The common species are those whose metabolism causes the release of extracellular metabolites called mucopolysaccharides. Recently, it has been a commonplace to replace copper alloy condenser tubes, with titanium steel tubes. These latter have a higher heat transfer coefficient but are colonized much more rapidly by slime-forming bacteria than the copper alloy tubes. The principles of bacterial effects in power stations are the same in marine, brackish and fresh waters.

2.4 FRESHWATER FOULING

Power stations sited on rivers, lakes or reservoirs may be directly-cooled where there is an adequate supply of water, as for example the River Rhine, in Germany and The Netherlands, the river Rhône in France, or they may need to be tower assisted where the water flows are lower, as on the River Trent, in England. Tower assisted cooling is also needed to avoid excessive temperatures in the receiving water, as with inland nuclear stations in France and all inland river-

ine stations in England. Should the discharge cause the water temperature to exceed the limits defined in the Freshwater Fisheries Directive (EEC 1978), then obviously the choice would be that of a tower assisted circuit. The impact of fouling on the performance of the power station differs greatly between the direct and indirect cooling systems. A wide variety of organisms are found and a useful description of them has been given by Callow (1993).

2.4.1 Directly cooled circuits

Zebra mussels

Taxonomy and distribution

The Zebra Mussel (*Dreissena polymorpha*), (Photo 2.10) is a freshwater bivalve mollusc, member of the Family Dreissenidae. It is widely distributed, where its current status has been aided by attachment to the hulls of boats and rafts used in the transportation of goods since 1760 (Kinzelbach 1992). Zebra mussels are now widely distributed throughout Europe, from the original area of the Ponto-Caspian to Britain and Ireland (recently), and from Sweden to the south of France and the Po river in Italy.

After the introduction of the Zebra Mussel in North America via ballast water since 1985-1986, two species have been identified: *Dreissena polymorpha* and *Dreissena bugensis* called the 'Quagga mussel' in the US and Canada.

Photo 2.10. – *D. polymorpha*, adults. Main div. = 1 cm.

Biology and reproduction

There is a vast European literature on all aspects of the biology of *D. polymorpha*. Much of the work is in Russian and references are listed in Schloesser *et al.* (1994), which also includes references to much published western European work. There have been many recent papers, conference proceedings and books covering the effects of this species on cooling water circuits, municipal water treatment plants and also the ecolo-

gical impact of the excessive spread of zebra mussels in North America. Most useful in this respect are the following: Proceedings of the International Zebra Mussel Conference (1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998); EPRI (1992), Neumann & Jenner (eds) (1992), Nalepa & Schloesser (eds) (1993), Claudi & Mackie (1994) D'Itri (ed), (1997), and Khalanski (1997a, b).

The most important features of the biology of this species with regard to

fouling of power station cooling systems are the presence of a planktonic larval phase, the veliger, and the retention of the byssus thread system into the adult stage, enabling the adults to adhere in large numbers to hard surfaces.

The life cycle is divided into two phases, the larval and the adult. The adults, of separate sexes, release eggs and sperm into the surrounding water; after fertilisation and completion of the embryological stages, the eggs hatch to release a free swimming larva, the veliger. Reproduction is continuous throughout that part of the year in which the water temperature is above 13-15 °C but settlement appears to be confined to distinct phases, of which there are a maximum of three in a good year (Neumann & Jenner (eds), 1992). Ion concentration required for fertilization and early stage development has been investigated by Lynn *et al.*, 1997; there is no development at $\text{Ca}^{++} < 8.0 \text{ mg/L}$, and development is reduced at $\text{K}^+ < 0.39 \text{ mg/L}$. This veliger grows to give rise to the pediveliger, the settlement stage, which attaches itself to firm surfaces by the secretion of byssus threads. The newly settled juveniles grow to become the adult.

Veliger larvae are found during the summer months when there are higher water temperatures and the food supply is much increased. In the River Moselle at Cattenom veligers are found from April up to August with two peaks occurring round Mid-June and the end of August (Moreteau &

Khalanski, 1994). The time of first occurrence of veligers in the River Seine near Paris was strongly associated with a water temperature greater than 13 °C (Testard, 1990). Similar data have been reported from the River Meuse (Gillet & Micha, 1985) and the River Rhine (Jantz & Neumann, 1992). Data from the Moselle show the highest veliger densities in any one year to be associated with water temperatures of 21 °C to 24.7 °C (Moreteau & Khalanski, 1994).

The plankton larval stages duration also depends on the water temperature (Table 2.1). In spite of significant differences in the estimated time, all the data show that during the summer period, it requires at least two to three weeks between the spawning and the settlement. This biological feature implies that, in rivers, the settled mussels are generated by parental populations located upstream far from the location of settlement (Neuman and Jenner (eds), 1992).

Settlement and growth

The densities of newly settled mussels can be as high as $7 \times 10^5 \text{ m}^2$ during one breeding season, but because of competition for space and food the maximum adult densities are 2×10^5 per m^2 , more than enough to cause serious impairment of cooling system functioning. There is some variation in settlement density of the spat with geographical location. In the River Waal (1984/5), a branch of the Rhine in The Netherlands, 400-600 / m^2 were recorded but in the Hollandsch Diep, another branch of the

Table 2.1. – Duration of the plankton stages in Zebra mussels depending on the water temperature.

Species	Location	Water Temperature	Time between spawning and settlement	References
<i>Dreissena polymorpha</i>	Two lakes near Köln (Germany)	15 °C – 20 °C 16 °C – 24 °C	28 days 18 days	Sprung 1987, 1989
<i>Dreissena polymorpha</i> and <i>D. bugensis</i>	Experimental data	24 °C	15 to 20 days	Baldwin 1995
<i>Dreissena polymorpha</i>	Experimental data	20 °C	18 days	Vanderpoeg <i>et al.</i> , 1995
<i>Dreissena polymorpha</i>	Experimental data	22 °C	21 days	Seltzer-Hamilton <i>et al.</i> , 1995

Rhine, $16 \times 10^3 - 60 \times 10^3/\text{m}^2$ the range was similar to that in the Ysselmeer ($16 \times 10^3 - 45 \times 10^3/\text{m}^2$) (Jenner & Janssen-Mommen, 1993).

The biological cycle of this species is summarized on Figure 2.6. and data on settlement and growth of the zebra mussel in European rivers and lakes are reported in Table 2.2.

Growth varies with temperature, food supply and flow water (Jantz & Neumann, 1992; Jenner & Janssen-Mommen, 1993) and shows an increment rate which decreases exponentially with increasing length (Jantz & Neumann, 1992; Moreteau & Khalanski, 1994). In the first growth season after settlement (0+) *D. polymorpha* shells may be expected to reach 15-16 mm, a length equal to approximately 50% of the total growth over three years. Growth of mussels at Cattenom has been modelled showing that cohort growth depends on time of settlement (Moreteau & Khalanski, 1994). The first cohort, corresponding to the first settlement

peak in the year, gives growth of approximately 15 mm whereas the last cohort in that year gives a maximum length of 10 mm (Fig. 2.7).

The important point here is that mussels of 15 mm in length are likely to block plate heat exchangers and even condenser tubes if they are dislodged in clumps.

Asiatic clam

Taxonomy and distribution

The Asiatic Clam *Corbicula fluminea* is a fresh water bivalve mollusc of the Family Corbiculidae, recorded for the first time in 1924 (McMahon (1983) or 1938 in North America near the mouth of the Columbia River (Burch, 1944), and probably introduced in Europe in the second part of the 20th century. First observations in The Netherlands were made in 1988 in the western part of the River Rhine, but in the south of France and Portugal *Corbicula fluminea* was already

Table 2.2. – Biological data on larval stages, settlement and growth of *Dreissena polymorpha* in European rivers and lakes (adapted from Khalanski 1997b).

Rivers and lakes	Plankton stages		Settlement	Growth: Shell length (mm) at the end of			References
	Year	Record period Peaks, density		1st summer	2nd summer	3rd summer	
Most of European rivers and lakes				4.0 - 5.0	10.0	20.0 - 22.0	Testard, 1990
Meuse at Tihange (Belgium)	1984	May to October 1st record at 13°C	August to October		7.0		Gillet & Micha, 1985
Meuse at Chooz (France)	1994	May to October 2 peaks in June and July 570-400 /L	August to end of November No settlement if T > 25 °C	15.0			Duvivier & Vanmaele 1995
Mosel at Cattenom (France)	1991	1st record at 13.8 °C April 10.	1st record 04 June 1 peak end of June				Moreteau & Khalanski 1994
	1992	2 peaks: June, July 190-220 /L	1st record 24 June 2 peaks: end of June and mid-August				
	1993	2 peaks: July and August. 100-450/L	1st record 17 June 2 peaks: July and August				
	1991-1993	Peaks at 21.1 °C to 24.7 °C	Peaks at 17.9 °C to 24.9 °C	9.5 - 15.5	22.1 - 24.4	29.8	
Rhône (France)	1982	1st record 20 April at 12 °C	1st record 01 June at 21 °C Peaks in July - August	8.0 - 10.0	15.0		Garric & Migeon 1983
Seine (France)	1986 - 1987	May to September 5 peaks					Testard, 1990
Oise (France)	1984 - 1987	May to September 5 peaks. 1st records at 14.5 °C to 21.0 °C		5.0 - 7.0	16.0 - 17.0		
Rhine (Germany)	1989 - 1991	1st record mid April at T > 13.0 °C					Janitz & Neumann 1992
Upper Rhine				13.3 3.0	24.0 14.0		
Lower Rhine				2.3 13.0			Sprung 1992
Two German lakes							
Lake Esrom	1969	Post veligers from mid July to the beginning of September		2.1 2.9	7.5 11.0	17	Dall & Hamburger 1996
Denmark	1979					> 22	

present before 1988 (Mouthon 1981). In France the present distribution is : Garonne and tributaries (Lot and Tarn), Dordogne, Adour river basin, Aude and the canal du midi and the canal lateral à la Garonne, lower Loire, upper Rhône and the Moselle. This covers the south, the west and the north east. In addition *Corbicula* is found in the Rio Minho in Spain and the Rio Tejo in Portugal. The river

Rhine has populations of this species from The Netherlands as far upstream as half way along the German part of the river. The Asiatic clam is found in Belgium, in the river Meuse and in the canal Bocholt – Herentals; it has also invaded rivers in the UK. A second species is also found in some European rivers : *C. fluminalis* in the Rhine, the Weser and the French part of the Moselle.

Fig. 2.6. – Biological cycle of *Dreissena polymorpha*, adapted from Ackerman (1995).

Fig. 2.7. – Shell growth modelling of 5 cohorts of *Dreissena polymorpha* recorded into the Cattenom cooling circuits from 1991 to 1993.

The two species may be distinguished with the aid of the table 2.3 and photo 2.11.

Biology and reproduction

The clam *Corbicula fluminea* is a free-living species found crawling around in the top layer of the river substrate, which in the Moselle is gravel and small pebbles on a clay base (Bachmann *et al.*, 1995). Locomotion is accomplished by means of an extrusible foot (Photo 2.12). According to Morton (1983) a part of the population is hermaphrodite (30% hermaphrodite; 40% female; 30% male). The percentage differs with the flow rate of the river. At higher currents,

more females should occur. Reproduction can start at a length of between 6 and 13 mm (Mattice, 1983; Dubois, 1995). Depending on water temperatures, two to three peaks in reproductive activity can occur annually. The eggs are fertilized in the female and brooded on the two inner gills, till the larvae attain a length of about 220 μm . The non-planktonic larvae are then released and settle nearby. Up to a length of 14 mm, they are capable of active transportation by water currents, by producing slime threads, and simultaneously opening the shells widely (Prezant & Chalmers, 1984). Often, there is large-scale migration which results in distinct populations of clams all of

Table 2.3. – Distinction of the two species of *Corbicula* by the shell shape and biological features.

Species	Criteria	Reference
<i>C. fluminalis</i>	Shell triangular, pointed with a rounded base, thicker than in <i>C. fluminea</i> . Concentric ridges thinner and less spaced than in <i>C. fluminea</i> . Maximum length 25 mm. Separate sexes, larvae probably incubated on the gills. Life span > 10 years.	Zadhin 1965 (in Dubois 1995); Morton 1979; 1986
<i>C. fluminea</i>	Shell an oval triangle. Concentric ridges widely spaced. Maximum length > 30 mm. Hermaphrodite. Larvae incubated on inner gills. Life span approx. 3 years.	Zadhin 1965 (in Dubois 1995); Morton 1979; 1986 Dubois 1995

about the same size. The number of larvae per female clam under optimal conditions can be 400 to 900 per day in a population of 20-90 clams/m² (Aldridge & McMahon, 1978). Dubois (1995) showed that larval numbers were proportional to the shell length : $N_m = 691 \cdot L - 8568$ (L = shell length in mm), giving a rate of larval production in the canal-lateral of the Garonne of 571-1372 for populations of 80-360 clams/m². Compared to *Dreissena* with numbers up to 10⁶, these numbers seem low, but as *Dreissena* eggs are fertilized in the water outside the female there will be high initial mortality. The maximum age of *Corbicula*, depending on the species, is thought to be 3-10 years.

Settlement and growth

Only the juveniles can form byssus threads, and these may be used temporarily for attachment. However, as this is only a transitory capability the

juveniles and the adults can not attach to vertical walls of intake systems. According to Belanger & Farris (1985) the clam prefers the more coarse aerobic sediment fraction with a particle size of 0.25-0.7 mm. It is a species from subtropical regions and would die in winter if water temperatures stay near to 0 °C longer than one week (Graney *et al.*, 1980). However, in the muddy substrates in the Dutch river system, combined with the low water temperatures, the clams survive rather well. Presumably, the outlet regions of power stations serve as 'stepping stones' for this species.

Juveniles and adults, up to 14 mm in length, have been observed to drift in flowing water with the aid of mucous threads (Preznant & Chalermwat 1984). Live specimens have a variable response to flow depending on the nature of the substrate. On rough sandy bottoms, part of the population drifts at velocities of 10-17 cm/s whilst the other part only drifts at 40-45 cm/s

Photo 2.11. – The shell morphology of *Corbicula fluminalis* (on the left) and *Corbicula fluminea* (on the right). (Photo V. Bachmann).

(Table 2.4). Dead animals are entrained by water velocities of 15-30 cm/s (Dubois, 1995).

The maximum shell size measured in the US is 60 mm; in the Garonne it was 41 mm in 1995 (Dubois, 1995).

Table 2.4. – Experimental determination of water velocity required to entrain *Corbicula fluminea* on rough sandy substrata (Dubois, 1995).

Categories	Shell length (mm)	Water velocity (cm/s) inducing entrainment
Dead animals	4.5-15.5	15-30
Active drifting animals	5.5-14.5	10-17
Non drifting animals	6.5-16.5	40-45

Optimum water temperatures are about 25 °C and a growth rate of 1 mm per week is possible (Welch & Joy, 1984).

In specimens from the Garonne the growth, which is temperature dependent, is very low when the temperature is below 15 °C with an optimum very close to 25 °C (Dubois, 1995) as in

the USA. Dubois used one year's measurements to simulate the growth of the shell of the *Corbicula fluminea* population of a canal of the Garonne Basin. Dubois developed a shell growth model (Fig. 2.8) on three years, based with the thermal regime of 1993-1994. It shows that for the first cohort, the maximum size at the

Photo 2.12. – *Corbicula fluminea*, note the extruded foot used for locomotion but not for byssus thread production.

Fig. 2.8. – Shell growth modelling of *Corbicula fluminea* in the "Canal latéral à la Garonne" for 4 cohorts starting in June, July, August and September. Su : summer, A : autumn, S : spring, W : winter. The black rectangles indicate the reproduction periods. From Dubois (1995 b).

end of the first summer is about 13 mm, and it reaches 21 mm at the end of the second year.

Amphipods – *Corophium curvispinum*

Taxonomy and distribution

The Order Amphipoda are relatives of the Crabs and Lobsters and belong to the Class Crustacea (photo 13). They are commonly known as Sandhoppers or Scuds. The particular species *Corophium curvispinum* is a recent invader of the Rhine, originating from Eastern Europe (Behning 1914). Although it has a brackish origin, the var. *devium* is adapted to fresh water. This species was first recorded in the middle and lower Rhine in Germany and The Netherlands in 1987, since when it has also invaded the northern parts of the Rhine delta

(Van den Brink *et al.* 1989, 1993). It was earlier recorded since about 1935 (Lincoln, 1979; Harris, 1991) in rivers in the UK. In France the species has been recorded at only two sites in north east rivers : the river Meuse at Chooz (Duvivier & Vanmaele, 1995) and in the river Moselle on a boulder and cobble bottom (Bachmann *et al.*, 1995).

Biology and reproduction

C. curvispinum is a small tube-living animal : maximum length is 7.0 mm. The tubes are formed from mud particles cemented together with mucus. Because of the density of the individuals on hard substrates and the tube dwelling habit, they form mud banks up to 4 cm thick (on stones).

Reproduction of *Corophium curvispinum* occurs in the lower Rhine from April to October when water temperature is in the range of 12 °C to 20 °C. Oviparous females (carrying eggs) appear in April and reach a peak in May-June corresponding to 50% of the population. In July, the overwintering stock of gravid females decreases and reproduction ends in October.

The females carry their eggs in a brood pouch formed by plates on either side of the laterally flattened body. Egg numbers may be as large as 39 per female at the new sites in the lower Rhine, much higher than recorded previously at eastern European sites, and there is a strong positive relation between body length and egg number (Van den Brink *et al.*, 1993, Rajagopal *et al.*, 1999b).

Growth

As a filter-feeder, *C. curvispinum* growth is maximum in rivers rich in plankton or organically polluted. The density of individuals on the stones is positively correlated with current velocity (Van der Velde *et al.*, 1994).

The maximum density recorded from the River Rhine at Tiel in The Netherlands (River Waal) in the years 1986-1994 was 7.5×10^5 per m^2 at a depth of 2-3 m (Fig. 2.9). As already stated, density increased with current velocity. As biomass, ash free dry weight (AFDW), at the maximum den-

Photo 2.13. – *Corophium curvispinum*. Photo V. Bachmann.

Fig. 2.9. – Density of *C. curvispinum* on stones in the Rhine (Rajagopal *et al.*, 1999a).

sity was found to be equivalent to 73.0 g (Van der Velde 1995, pers. comm.). In the Moselle, the maximum density recorded in September 1994 was 97.500/m² (Bachmann *et al.*, 1995).

This species can accumulate and consolidate a large volume of mud in building its tubes.

Microbial fouling

Development of microbial slimes will occur on all the heat exchange surfaces. As with all slimes the rate of growth depends on the water quality and the ultimate thickness of the

slime coatings will depend on the species, and how much silt is entrapped in the slimes. This problem is also exacerbated by the development of chemical scale within the slimes. Details are given in section 2.4.2.

Chemical fouling

Scale may develop on heat-exchanger surfaces of direct-cooled power stations when water which has a high natural alkalinity is used as cooling water. However, this problem is not as prevalent as that which occurs in recirculating cooling systems, details will be given in section 2.4.2.

2.4.2 Tower assisted cooling

Introduction

Circuits equipped with cooling towers are large structures comprising ponds, pipes, culverts, dispersing devices and packing. Compared with once-through cooling circuits, the critical design aspects of the cooling water circuits with regard to the bio-fouling are the greater surface offered to settlement for fouling organisms and the greater extent of low water velocity areas. Such complex circuits have consequently more problems with bio-fouling, they have specific problems with chemical fouling in the form of "scaling".

The cold water pond of such a circuit is especially susceptible to fouling, as flows and temperature are non-limiting. Conduits or water chambers in which the water velocity stays at low level also favour the settlement of bio-fouling and sediment deposits. The shell of the cooling tower and the packing supply extremely large surfaces suitable for the settlement of various species.

The diversity of fouling problems is thus very much greater in such a closed circuit cooling water system than for directly-cooled (open) plant.

Bivalve molluscs

Significant infestations of Zebra Mussels and Asiatic clams have been reported in cooling tower assisted power stations. Large accumulations of *Dreissena polymorpha* are found in

make-up water pipes and basins at the Cattenom station (Moreteau & Khalanski, 1994) and *Corbicula fluminea* is abundant in the Golfech station cold-water pond (Khalanski, 1997 a,b). The data and general comments on these species are given in section 2.4.1.

Unionids. These large bivalves, members of the family Unionidae live in muddy sediments covering the bottom of the water ponds, travelling screens chambers and parts of the cooling circuits where the water velocity is low enough to favour sedimentation. Two genera are commonly found in the circuits: *Unio* and *Anodonta* (photo 2) The length of the shell can reach up to 20 cm. *Anodonta* can be recognised by its thin shell on which teeth are absent.

In muddy sediments, small size bivalves are very common, they generally belong to two genera of the family Sphaeriidae: *Sphaerium* and *Pisidium* (photo 2.15).

The shell length does not exceed 12 mm for *Sphaerium* and the maximum shell length is usually less than 10 mm for *Pisidium*. Sphaeriidae are characterized by a larval development on the gills inside of the pallial cavity.

In cooling circuits, their shells are frequently found in plate heat exchangers in association with muddy deposits.

Bryozoans

Taxonomy and biology

The Moss Animalcules are represented in the freshwater fouling com-

Photo 2.14. – Shells of *Anodonta* sp. (one valve) from the Seine river and *Unio* sp. (two valves from the Loire river. Main div. = 1 cm.

munity by several species : *Plumatella fungosa*; *Plumatella emarginata*; *Plumatella repens*; *Fredericella sultana*; *Paludicella* sp.

These are members of the Phylum Ectoprocta, one of the minor phyla of the animal kingdom, and are characterized by their colonial habit. The colonies are formed of individuals which are about 1-2 mm in length, and have tentacles surrounding the mouth, the lophophore. The colonies are formed and grow by asexual budding of the animals located within an external chitinous branching sheath. There are both male and female adult members of the colony but reproduction is nor-

mally limited to the production of specialised buds with a resistant external cover, known as statoblasts. These are the overwintering and dispersal stage and the means by which the animal recolonises new substrates each spring. Bryozoa feed on planktonic algae and are especially abundant in eutrophic rivers where algal biomass is of the order of several tens of mg/l of chlorophyll-a.

Some species produce big colonies; for example, *Plumatella fungosa* colonies are rounded masses which can reach a diameter of 50 cm. Others are thin rampant or arborescent filaments as *Paludicella* sp.

Photo 2.15. – Sphaeriidae bivalves from the Seine river. Main div. = 1 cm.

Photo 2.16. – *Plumatella* colonies on a screen at the exit of a cooling tower pond.

Distribution and growth

In rivers such as the Trent (UK) where there is a high suspended solids load, colonies are small, no bigger than a few centimetres in height. However, in water which is low in suspended solids and at the appropriate temperature, as in the ponds under cooling towers of power stations on the River Loire, the colonies of *P. fungosa* grow to a diameter of 50 cm (Photo 2.16). This size difference is related to the efficiency of filter feeding between clear and turbid water. The rate of growth of these large colonies is between 5–8 mm/d and they can interfere with water outflow from the cooling ponds within one year following settlement of the statoblasts (Thome *et al.*, 1989; Aprosi *et al.*, 1986).

Statoblast settlement is optimal at 25–30 °C (Aprosi & Nepveu de Villemarceau, 1988), but the growth of the colonies by budding is found to be between 15–30 °C. Below 15 °C, growth stops (Duvivier & Vanmaele, 1995).

Water flow also affects the settlement of statoblasts and has been found to be optimal at 0.2 m/s. Colonies stop growing at 0.6 m/s and are detached by flows of 0.9 m/s (Aprosi & Nepveu de Villemarceau, 1988).

Light has no significant effect on settlement and growth: Bryozoa can settle and grow rapidly in dark pipes but it seems that the optimum for settlement and growth is semi-darkness.

At the Tihange nuclear power station, on the river Meuse in Belgium, the colonies of *Plumatella fungosa* and *Plumatella emarginata* are to be

found growing in a band at levels of between 10-90 cm above the bottom of the cooling tower ponds (Thome *et al.*, 1989). At this level the flow rate of the pond water is 0.2-0.3 m/s. Two generations of colonies develop in the ponds during the course of a year:

— The spring generation from April-June, with growth in April/May and die back in June;

— The summer/autumn generation with growth at the end of August to the end of September followed by die back in October.

In the Tihange cold water ponds, the maximum biomass (dry weight) recorded during the year 1988 was 1,218 kg for *P. fungosa* and 456 kg for *P. emarginata*.

Gastropoda

Taxonomy and distribution

Gastropods (snails) are very abundant on the muddy bottoms of slow flowing channels, and also in the intake canals and ponds of French nuclear power stations. Four genera are commonly found, *Bithynia*, *Viviparus*, *Lymnaea* and *Physa* (Photo 2.17).

Small *Lymnaea* are very abundant in the cooling tower honeycomb packing at Golfech Power Station on the river Garonne and *Bithynia* are also abundant in the intake structure at power stations on the river Loire. The main problem caused by *Bithynia* is the clogging of the plate heat exchangers in the auxiliary cooling circuits. The same genus has also caused problems at stations on the river Trent

(UK) where they lodged in the water distribution spray jets of the cooling towers, thus interfering with tower efficiency.

Cyanobacteria (Blue green algae)

These photosynthesizing microorganisms are found on the inner surfaces of cooling tower shells, and are consequently known as 'shell algae' or 'algues de coque'. They grow as sheets over the inner surface of the towers and interfere with plant operations when the sheets or parts of the sheets fall off the tower shell. This happens when the tower is out of commission during the summer refueling and maintenance period. The algal debris (photo 2.18) collects on the drift eliminators and the top of the plastic honeycomb packing, and end up blocking the grids at the tower ponds exits. This problem is of great concern where a single large tower is used to cool one unit. Much work has been carried out to define the problem (Aprosi & Nepveu de Villemarceau 1988; Aprosi & Mossé, 1989; Aprosi & Costaz, 1989; Aprosi & Chauvel, 1990; Siclet, 1991).

Taxonomy and distribution

Shell algae, identified by the Museum National d'Histoire Naturelle (Paris), were collected from six EDF sites: Bugey and Cruas on the Rhône; Chinon, Saint-Laurent and Dampierre on the Loire and Cattenom on the Moselle, (Aprosi & Mossé, 1989; Aprosi & Costaz, 1989; Siclet, 1991).

Photo 2.17 A. – *Bithynia tentaculata*.

Photo 2.17 C. – *Radix ovata* = *Lymnaea ovata*.

Photo 2.17 B. – *Viviparus* sp.

Photo 2.17. – Gastropods commonly found in cooling circuits of power stations on the rivers Seine, Loire and Garonne (main div. = 1 cm).

Photo 2.18. – Typical shape of "shell algae". Fragment found at the Saint-Laurent-des-Eaux power station on the river Loire (25 cm length).

Three stages are recognised in the colonisation of the concrete shell :

1. Pioneering infestation by small filamentous species (*Lyngbya* sp., syn. *Phormidium*).

2. On the primary colonising layer larger species grow (*Scytonema multiramosum*) with a filament diameter of 15-20 μm . This second layer completely covers and kills the pioneer species.

3. *S. multiramosum* still dominates the algal population but additional species of colonial Cyanobacteria (*Chroococcus*, *Nostoc*, *Gloeotheca*), some diatoms and green algae make for a more diverse flora.

Shell algae form a more or less continuous layer over the inner surface of the tower. Nutrients, carbon

and nitrogen, are supplied by the air current whilst others, phosphorus, potassium, calcium, magnesium etc., come from the water flowing over the surface of the tower.

As Cyanobacteria and algae require light to function, it is evident that light is the main factor limiting growth in towers (Table 2.5).

The quantity of algae formed on the inner surface of a tower was estimated at Cruas (France). This showed that 394 kg of dry weight algal material was detached from a surface area of 9,650 m^2 of the shell, equal to half the total internal surface area. In addition to the dried algae falling off the tower shell the sheet also contained small quantities of the inner surface concrete of the tower. This amounted to 252 kg from the same

Table 2.5. – Stratification of algae on the Cruas unit 2 tower with solar light measurements. The green colour is caused by loss of pigments from *S. multiramosum* filaments.

Vertical areas	Height (m)	Algal layer colour	Light (% incident sunlight)
Top level (neck to summit)	120-155	brown layer	25 % at 140 m
Neck level	100-120	brown layer	
Below the neck	70-100	green layer	6 % at 90 m
lower level	70	no algae	3 % at 70 m

detached surface area. The total annual dry weight of shell algae detached from the cooling tower in Cruas unit 2, was thus 646 kg (Aprosi & Chauvel, 1990; Siclet, 1991).

The distribution of the detached algae was estimated to be :

— 18% (100 kg) is entrained outside the tower by the air current,

— 82% (530 kg) fall on the drift eliminators and pass through the packing to go to the cold water pond (57% or 371 kg) or stay into the packing (25% or 159 kg).

The algal sheets staying in the packing are presumably more or less rapidly decomposed by bacteria but they also agglomerate suspended matters and can form organo-mineral plugs clogging the canals as observed in Cruas power station.

The second nuisance is the risk of clogging grids located in the cold water basin where water goes back to the condenser. However, shell algae contribution to the matters removed from the grids at the Cruas power station is very low compared to Zebra mussel shells.

This loss of concrete could pose a threat to the engineering integrity of the tower, so the weight data were recalculated as a thickness measurement, showing the loss to the surface was 20 mm per annum. Over a 40 year life this corresponds to an average loss of 2 mm with local maxima of 3 mm (Siclet, 1991). This does not pose a serious risk for the lifetime of the tower.

Filamentous green algae

Taxonomy and biology

The green alga *Cladophora glomerata*, belongs to the Thallophyta, Division Chlorophyceae, Order Siphonocladiales. These algae have a branched thallus, in which each branch consists of several multinucleate cells or coenocytes. The individual branches are called filaments. It is present in all rivers, especially those receiving sewage effluent. This alga is well known as 'Blanket Weed' in garden ponds. In power stations, it may cause reductions in efficiency by interfering with the flow of water over the packing in cooling towers. According to Sladeckova (1969), a wide variety of other algal species

and genera are found fouling freshwater cooling systems, but these systems were of old design with wooden water distribution troughs.

Reproduction and growth

The alga reproduces both sexually and asexually. Asexual production of zoospores occurs throughout the year whilst gamete production is only found in spring.

Growth takes place at the free ends of the branches, by an apical segment and the filaments may grow to several metres in length. In power stations, they grow on the support legs of cooling towers, on packing exposed below the base of the tower shell (especially when the pack is of wooden slats) and on the walls of the open channels which distribute the warmed cooling water to the cooling tower spray jets and which return the water to the pump suction docks. The filaments may impair water distribution at the outer regions of the pack, causing an insufficient reduction of return water temperature and a consequent lowering of thermal efficiency.

Monitoring for the presence of growth of green algae can be done by eye or by settlement plates of glass or other suitable material placed in the cooling circuit. Serious problems have been reported only where the packing in the tower is exposed below the base of the tower shell, when the filaments grow to a length of several metres and interfere with the water flow on the packing (Whitehouse & Blank, 1985). In France, *Cladophora* are found growing on the walls of the tower ponds at sta-

tions on the rivers Loire, Rhône and Garonne.

Microbial Slimes

Development of layers of slime form as a result of the colonization of surfaces by bacteria of the genera *Pseudomonas*, *Flavobacterium* and *Bacillus*. These bacteria are found on all surfaces throughout the cooling water system, but have most effect on the heat exchange surfaces of the condensers and auxiliary heat exchangers. They are also found on the surface of the plastic fill which is now standard in cooling towers. The conversion of the surface of the plastic sheets from the hydrophobic to the hydrophilic condition, known (to the engineers) as conditioning, is a direct function of the colonization of the surfaces by slime forming bacteria of the *Pseudomonas* group (Puckorius, 1997). This is only a problem in cooling towers if the slime acts as a base into which either scale or silt or both become entrapped. However, this expression of the slime problem is serious only if the deposits become so thick that the weight of the pack approaches or exceeds the load-bearing capacity of the pack support structure.

Details of the development of slimes has been described by Characklis (1981), who has shown that their growth follows standard bacterial kinetics and is thus dependent on temperature, nutrition and in this case, the surface area available for colonization. Growth also depends on

the flow of the circulating water relative to the surface which is being colonized. In cooling towers, the flow is below the rate at which shear stress would operate to cause biofilm detachment (Characklis & Cooksey, 1983), whereas in condensers, it is feasible to have flow rates which maintain the film at a minimum thickness. Growth usually follows the typical sinusoidal curve, showing a lag phase, when colonization is taking place, followed by accelerated growth up to a stationary phase, when diffusion of oxygen and nutrients are limited by the thickness of the biofilm. The rate of colonization is influenced by the choice of materials for the components of the cooling system, for example copper alloys leach copper ions which retard colonization (Chamberlain 1988). Titanium steel condenser tubes have no natural toxicity to bacteria and are therefore colonized very rapidly. The final phase in the development of a bacterial film is dying off, when the thickness of the film may decrease if the reattachment of new cells or the reproductive rates of surface living cells are lower than the death rates of existing cells (Fig. 2.10). A detailed description of microbial fouling and its effects on condensers in power stations is given by EPRI (1993).

Nutrition in cooling tower circuits is proportional to the quantity of make-up water entering the system. The make-up rate is a function of the cycles of concentration used in the system and decreases as the concentration factor (C.F.) increases. Thus, the higher the C.F., the lower the total organic load, and the smaller the bac-

terial growth (Whitehouse 1990a; 1990b). Not only is the bacterial nutrient load smaller with a high C.F. but so is the import of all dissolved and suspended materials. The entraining of silt in the slime is also reduced as the C.F. increases.

Other problems are associated with microbial slimes, when thermophilic pathogens such as the bacterium *Legionella pneumophila* and the protistan amoeba *Naegleria fowleri* develop in the heat exchangers. Thus *N. fowleri* has been detected in the warm water discharge from power plants in France (Delattre & Oger, 1981), where it was also present in the discharges from steel works, and in the USA (Tyndal *et al.*, 1989). When a public health risk is identified, either for personnel working on the cooling water circuits or for the public when swimming in designated waters, then specific measures must be taken. These have assessed by Bard

Fig. 2.10. – General growth pattern of slime built-up on surfaces.

& Siclet (1995), Cabanes *et al.* (1997).

Chemical scaling

Since chemicals, such as carbonates and phosphates are concentrated in the cooling circuit due to evaporation, a dilution with make-up water is required to avoid deposition of scale. The most usual type of scale is calcium carbonate, the input flux of carbonate in large nuclear power stations can vary between 10-60 tonnes per day. Precipitation of carbonate takes place when the solubility product is reached giving rise to scaling of the cooling circuits.

In general, three factors contribute to scaling in cooling circuits at power stations (Whitehouse, 1990a, 1990b; Combaz, 1994) :

- heating of the water up to 30 °C in direct cooling and 45 °C in tower assisted circuits,

- evaporation of water to effect cooling in passage through the cooling towers, giving rise to concentration of the dissolved salt up to a factor of 1.6,

- the loss of free carbon dioxide during passage of water through the towers causing a rise in the pH which varies with the flow rate and the type of packing. With older timber latted packs, the pH was generally 7.5-7.8, with plastic film flow pack, this increases to 8.2-8.4 in small towers (250 Mwe) and to 8.5-9.0 in large towers (900 Mwe or greater).

It is evident that power stations using cooling towers are more susceptible to scaling if the source of make-up water is rich in calcium. Also the materials of construction used in the cooling circuit have an effect on scaling; copper alloys scaling less than stainless steel and PVC (Dedieu *et al.*, 1994). In addition, in experimental test loops (Bolsee *et al.*, 1995), it has been shown that the form of various types of packing influences the rate of scaling (Table 2.6), and also the rate of development and growth of biodeposits (Whitehouse & Coughlan, 1990; Whitehouse *et al.*, 1987).

These experimental studies show what has been found in practice where massive scaling continued in spite of acid treatment. Thus, at the Golfech power station on the Garonne, 200 tonnes of scale were deposited on 17 months following start-up of the first unitised circuit. Weighings, taken at fortnightly intervals, showed the scaling rate in 1994 was 1 tonne per day (Combaz, 1994). Scaling came from the type of packing, over optimisation of temperature fall giving rise to zones of excessive evaporation, resulting in a heavy well fixed scale. The general view is that towers with plastic packings are more susceptible to scaling than the tubular or plate heat exchangers. Occasionally, excessive scaling has knock on effects; following a break down in the acid treatment, unit 1 at Nogent-sur-Seine power station developed a 10 tonnes per day deposition rate which necessitated the replacement of the packing (Combaz, 1994).

Table 2.6. – Comparison of the susceptibility of different packing to scaling; from Bolsee *et al.*, 1995.

Material	PVC	PVC	PVC	Polypropylene	PVC
Specific surface (m^2/m^3)	60	180	130	45	120
Thermal efficiency	Satisfactory	High	Very High	Satisfactory	High
Scaling rate at 40 °C (g $\text{CaCO}_3/\text{m}^2/\text{month}$)	Non significant	4000	200	Non significant	400

Film fill packs deposits are a combination of mineral and organic components. In absence of scaling process, dust and silt transported with air and make-up water contribute to the inorganic deposits. The organic layer on film fill packs is mainly produced by the slime forming bacteria of the *Pseudomonas* group (Puckorius, 1997). Different cooling water treatments can be made to control the deposits :

- use of biocides, such as chlorine, glutaraldehyde, to eliminate the bacterial development,

- use of dispersants to remove the muddy deposits from the fills.

In closed cooling circuits equipped with cooling towers, severe corrosion problem of copper alloy condensers can be avoided by addition of corrosion inhibitors, mainly aromatic triazoles, to the circulating water. Some research is in progress in the US to reduce the toxicity associated with this type of compounds by using more degradable substances (Rao *et al.*, 1997).

Silt/suspended solids

Suspended solids are brought into the cooling system with the make-up water. Suspended solids in quantities greater than 100 mg/L give rise to two problems, accumulation in cooling tower ponds and entrapment in slimes found in condensers and on plastics packing in cooling towers. However, it appears that these problems only become serious when the load of solids in the make-up water is greater than 250 mg/L, equivalent to a mass of 50 t/d for a daily make-up volume of $2 \times 10^5 \text{ m}^3$, the water replacement for a 2,000 MW plant operating at a concentration factor of 1.5. Evidently power stations with cooling towers utilising water with high suspended solids loadings are at risk from loss of system volume and therefore from thermal efficiency losses associated with running the plant at incorrect concentration cycles, caused by lack of observation of the loss of system volume.

Single towers of 1,300 MWe nuclear units have a mass air flow of

35,000 to 40,000 m³/s which contains dust and various sorts of debris (leaves, feathers, insects, papers etc.). These airborne imports contribute si-

gnificantly to the mineral and organic load in the cooling circuit and interfere with the mechanical and thermal functioning of these circuits.

3.

Bio-fouling control methods

The search for the most efficient methods for the control of fouling in fresh and salt water circuits has been 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). This was followed by the publication of two books, 'Marine Fouling and its Prevention' (Woods Hole 1952) and 'Marine Boring and Fouling Organisms' (Ray 1959). The two works summarize the state of knowledge up to that time, but do not offer useful data upon which to base a marine fouling control protocol at power stations where very large volumes of sea water are continuously passed through the cooling system. However, the value of these two books is in the background information given on the wide variety of compounds investigated in the search for suitable chemicals, and in the details of the life history, colonization and growth rates of the various fouling organisms. Many papers reporting the efficacy of chlorine for the control of mussels have been published since that period (Whitehouse 1975).

It is clear that, to date, the major emphasis for work on fouling control has been in the marine field (White-

house *et al.*, 1985). The reasons for this have been well summarized (Mat-tice 1983), but it is also clear from experience in Europe and the USA in the last half century that freshwater fouling has been seen to pose an equally serious problem, especially as species are transported around the globe and colonize new geographical zones. Good examples of this problem are the Zebra Mussel and the Asiatic Clam. They are also good examples of the need to undertake new research to develop control procedures, as it has been found that previous work on fouling control has been based on american fauna species only and is thus inappropriate. Many studies conducted in Canada and the United States to control the impact of invasion of inland waters by the Zebra mussel at the end of the 80's have given rise to publications of great interest (EPRI 1992; Claudi & Mackie 1994). Such on going research has been presented yearly since 1991 at the International Zebra Mussel and Aquatic Nuisance Conferences. At the same time, in Europe, continuing effort has been made in the optimization of conventional anti-fouling treatments. New methods have also been investigated.

3.1 AN OVERVIEW OF ANTI-FOULING METHODS

Direct experience of cooling systems and their operational functioning is a prerequisite to the design and monitoring of fouling control in power stations.

Several types of anti-fouling processes have been used on large cooling water circuits, falling into two main categories: physical methods, in which there is no addition of chemical substances to the cooling water, and chemical treatments. Their development status is very variable: some are in widespread or moderate industrial use, others are being tested on site, and many remain for the moment at the level of laboratory research.

It is important to remember that the central focus of this book is biofouling in large cooling water systems (CWS) fed with natural raw waters with flow rates exceeding $1 \text{ m}^3/\text{s}$. Effective processes developed for other types of circuits, or to protect ship hulls, are not suitable for industrial applications such as power stations.

In order to achieve economically practicable solutions, it is also important to note that methods must be appropriate to each type of fouling (bacterial slime, settled animals or plants) and to the specific design of the cooling circuits.

While there do exist generic solutions applicable to major categories of organisms, optimizing the procedures requires a minimum of biological knowledge. The objective of an eco-

nomically and environmentally optimised anti-fouling regime is not total elimination of settled organisms; in most cases, the goal is to control species which settle in the circuits and to prevent their development from becoming excessive. Thus for the period between two scheduled physical cleaning procedures, a chemical treatment must limit fouling of circuits and heat exchangers below the threshold at which plant operation begins to be affected. In many cases, anti-fouling methods on a given site are concerned with only one or two invasive species, for which generic procedures must be adapted in light of their ecological demands which determine the most sensitive parts of the circuit, as well as their periods of larval settlement and their growth rate. This implies acquiring biological knowledge and carrying out long-term bio-monitoring on each site so as to follow the evolution in populations and note the appearance of new species as they are introduced (Khalanski, 1997a, b).

Other important elements to be considered are the configuration of the circuits and feedpump operation. These determine the hydraulic regime, most particularly variations in discharge and water velocity, as well as the areas most favorable to settlement and growth of biofouling organisms.

A list of the methods generally used on the cooling circuits of European power stations is given in Table 3.1. As is clear there, many different methods are currently used in European power stations. The phy-

Table 3.1. – Physical anti-fouling methods and chemical treatments commonly used on cooling circuits of European power stations.

N.B. : Macro-biofouling is that biological fouling of CWS typically caused by : Algae, Sponges, Hydroids, Annelids, Bryozoans, Barnacles, Bivalve shellfish and Gastropod molluscs.

Processes and treatments	Methods	Biofouling Target	Uses in European power stations
Water filtration	Gross filtration (> 1 to 10 cm)	To remove natural or artificial drifting debris at water intakes.	Used everywhere
	Fine mesh filtration (1 to 10 mm)	To remove natural or artificial drifting debris at water intakes. Stops biological debris arising from the fouled walls of the intake culverts (shells).	Used everywhere
Mechanical cleaning	Manual cleaning	To remove settled macro-biofouling. To eliminate bacterial slime on condensers or plate-type heat exchangers.	Used everywhere
	High-pressure water cleaning of rotating screens.	To remove drifting debris from the screen.	Used everywhere
	Automated cleaning systems	To remove bacterial slime (and some scale).	Widely used
	Self-cleaning debris filters	To remove biological debris produced by macro-biofouling.	Widely used
Other physical methods	Cleaning plate-type heat exchangers by vacuum suction processes.	To remove biological debris and mineral deposits.	Some uses
	High water velocity	To avoid settlement of macro-biofouling.	Used everywhere
	Heat	To avoid settlement of macro-biofouling on parts of the circuits with lower water velocities.	Some marine and freshwater power stations

Table 3.1. – *Contd.*

Processes and treatments		Methods	Biofouling Target	Uses in European power stations
Chemical treatments	Low-toxicity paints and coatings	Applied on parts of the circuits with lower water velocities	To avoid settlement of macro-biofouling	Some parts of cooling circuits. Increasingly used
	Chlorination with sodium hypochlorite or chloramine	Continuous treatment at a low dosage (generally < 1 mg/L). Possibility of semi-continuous injection.	To control marine macro-biofouling and bacterial slime. To eliminate Bryozoans in cooling tower basins	Widely used at marine power stations; some use in cooling towers.
		Shock chlorination of cooling tower basins : 8 to 40 mg/L for 4 to 6 hours.	To eliminate green and blue-green algae.	Some cooling towers in France & Belgium

Table 3.2. – Methods used in 1996 in EDF power stations on rivers to control biofouling (Khalanski, 1997a).

Main Fouling Organisms						New invasive species
Anti-fouling methods	Bacterial slime	Zebra mussels	Bryozoa	Algae on cooling tower walls	Green algae on cold-water basins	<i>Corbicula</i> sp. <i>Corophium curvispinum</i>
Water filtration		Travelling screens Debris filters	Small mesh grids Travelling screens	Small mesh grids Travelling screens	Small mesh grids Travelling screens	Travelling screens Debris filters
Cleaning	Continuous cleaning by sponge balls	High pressure water Mechanical cleaning	High pressure water Mechanical cleaning	High pressure water Mechanical cleaning	High pressure water Mechanical cleaning	High pressure water Mechanical cleaning
Increasing water velocity		Water velocity > 1 m/s	Water velocity > 0.6 m/s			
Shock chlorination					NaOCl 8 to 40 ppm 4 to 6 hours	

sical methods comprise water filtration, mechanical cleaning, high water velocity, heat shocks and the use of toxic or non-toxic paints. Among the chemical treatments, chlorination is the most common biocidal approach. This table is in no way exhaustive; the data presented comes essentially from experience acquired by power station operators in France, the United Kingdom, the Netherlands and Italy. For the purposes of illustration, the methods now used in France to control bacterial slime and settled organisms in power stations operated by EDF are summarized in Table 3.2.

New methods have developed from the zebra mussel research projects conducted in North America since the introduction of this species at the end of the 80s. Ontario Hydro and EPRI programs have played a major role in testing these new methods. Some have been tested on-site and have proven to be efficient against this particular invasive species.

Trials have been conducted or are now in progress to test the efficiency of physical methods or selected oxidizing compounds and organic compounds (Table 3.3). These include micro-filtration, non-toxic coatings, UV light, electrolytic currents, cathodic protection, sound energy and organic compounds. In European countries, alternatives to chlorination (chlorine dioxide or ozone) and some organics have been investigated.

All have proven efficient in controlling at least one type of biofouling; however, their field of application, their cost or environmental impacts will li-

mit their uses on cooling water systems.

Zebra mussel control programs have shown that some methods such as magnetic fields are not effective or suitable for large cooling water systems. It is also known that bromination and ozonation of sea water generate the same oxidants and by-products as does chlorination but are more expensive.

Finally, some methods can be useful for very specific applications, such as addition of potassium chloride in fire circuits to eliminate zebra mussels.

Table 3.4 presents a list of potential methods not currently used to control biofouling in large cooling water circuits. These primarily include natural repelling agents, natural biocides, toxins and biological control methods. For these methods, no data is yet available to allow assessment of their efficiency, cost and environmental acceptability on the basis of actual industrial feedback. Some are currently used on completely closed circuits or those with low discharge, or are still in the research phase. Of these, some appear promising and may, in coming years, find applications in large cooling water systems; others will not be applicable to these circuits or will not go beyond the laboratory stage.

It is clear that in this field, we cannot be exhaustive; we shall therefore base our discussion here on recent developments in Canada and the United States as they have been presented in "Zebra Mussel and Aquatic Nuisance International Conferences".

Table 3.3. – Physical anti-fouling methods and chemical treatments tested on-site on large cooling circuits.

N.B. : Macro-biofouling : Especially Algae, Sponges, Hydroids, Annelids, Bryozoans, Barnacles, Bivalve shellfish and Gastropod molluscs.

(1) KEMA BV listed 13 different organic compounds used as anti-fouling agents in the Netherlands in 1996.

Processes and treatments	Methods	Function	Biofouling Target	Uses on large cooling water circuits
Water filtration	Microfiltration (< 0.1 mm)	Filters to protect the entire circuit.	Stops plankton larvae (zebra mussels, marine mussels, barnacles...) to prevent settlement on the walls of the circuit.	Tested at the Bergam power station and in Canada at an Ontario Hydro power station against Zebra Mussels.
	Ultra-Violet light	Kill macro-fouling plankton larvae at the water intake.	To prevent settlement of macro-biofouling on the walls of the circuit.	Tested in Canada at an Ontario Hydro power station against Zebra Mussels.
Other physical methods	Sound blasts	Remove macro-fouling from the walls of some parts of the circuits.	To prevent development of macro-biofouling on the walls of the circuit.	Tested in the US on power stations against Zebra Mussels.
	Non-toxic paints and coatings	Especially efficient on the parts of circuits where the water velocity is high enough to produce a synergistic effect.	To reduce settlement of macro-biofouling. To facilitate cleaning of fouled walls.	Some parts of cooling circuits. Increasingly used in the US and Japan.
Chemical treatments	Chlorine dioxide		To eliminate macro-biofouling and bacterial slime.	Tested on power stations in Italy and Spain; used on large cooling circuits in Italy and France.
	Oxidizing compounds	Ozone : continuous treatment of cooling water.	To eliminate macro-biofouling and bacterial slime.	Tested on a cooling tower circuit in Belgium. Applied at RoCa power station (tower assisted) in Rotterdam, Netherlands.

Organic compounds	Organic tin in coatings or added in solution.	To eliminate macro-biofouling and bacterial slime.	Tested at some marine stations over 10 years ago. Abandoned for environmental reason
	Fatty amines : short- term (24 h) or long-term intermittent treatment (2 times 20 mn a day)	To control macro-biofouling and bacterial slime.	Tested at some marine power stations in the Netherlands, France and Belgium.
	Quaternary amines for short-term (24 h) or long-term intermittent treatment (2 times 20 min a day) Glutaraldehyde Isothiazolones	To control macro-biofouling and bacterial slime. Glutaraldehyde does not eliminate fungi and algae.	Widely used in the US. Some use in European countries.

Chemical treatment strategies

Claudi & Evans, 1993, defined four basic chemical treatments strategies to eliminate zebra mussels (fig. 3.1), which can be more generally applied to all the macrofouling :

1. End-of-season, consisting in killing the adults and juveniles established in the system at the end of the settlement period of the fouling species. It is only convenient when the operation is not threatened by the excessive development of fouling during the breeding and settling season. Depending on the chemical and the dosage, the required time can be shorter than a day or can cover some weeks.

2. Periodic treatments can be applied if the critical density of fouling is reached in the system before the

"end-of-season", it is a variant of the end-of-season treatment.

3. Intermittent treatments are made at frequent dosing (every day or every three days for example) for short period of time (some minutes to one hour). This procedure generally kills or remove the settled fouling organisms on a long-term basis, it must be applied over all the settling season of the target organisms.

4. Continuous dosing at low level of chemical biocide was initially designed to stop the settlement of larvae, but in fact it was observed that this treatment stops or reduces drastically the growth of fouling and kills or removes the biofouling in the long-term more effectively than it is achieved with intermittent dosage.

A fifth category, intermediate between intermittent and continuous, can

Table 3.4. – Physical anti-fouling methods and chemical treatments not presently used on large cooling water systems or still under investigation (laboratory studies).
Macro-biofouling : Especially Algae, Sponges, Hydroids, Annelids, Bryozoans, Barnacles, Bivalve shellfish and Gastropod molluscs.

Types of methods	Methods and Treatments	Biofouling Target	Major current uses
Toxic metals	Electrolytic generation of copper and aluminium ions	Micro-fouling and macro-fouling.	In small cooling water systems (ships, offshore oil and gas industry)
Ultra sonics			
Microwaves			
Settlement inhibitors	Artificial or natural compounds	To prevent settlement of mussel and barnacle larvae.	Research in progress in the US and European countries.
	Toxic paints with no toxic releases : Quaternary ammonium grafted on the paint	To eliminate the bacterial film and possibly to prevent settlement of macro-biofouling.	Research in progress
Oxidizing compounds	Hydrogen peroxide	To eliminate bacterial slime and algae; probably efficient against macro-biofouling (known to be involved in some natural antifouling processes, by Echinoderms).	Disinfection of swimming pools and in the food industry.
	Paracetic acid	To eliminate bacterial slime and algae; probably efficient against macro-biofouling.	Disinfection in the food industry.
	Brominated compounds such as BCDMH (bromochlorodimethyl-dantoin)	Bacterial slime.	Used in small cooling water systems.
Pathogen agents	Bacterial toxins	To kill macro-biofouling such as Zebra mussels.	Research in progress in the US.
Natural biocides	Produced by plants or animals	To kill macro-biofouling such as Zebra mussels.	Research in progress in the US.

Fig. 3.1. – Chemical treatment strategies. After Claudi & Mackie, (1994).

be added; semi-continuous dosing. A low dose of the chemical applied for a short period (15-60 minutes) then stopped for an equally brief period. This long-term, high-frequency treatment, (for instance 30 minutes on / 45 minutes off), can have the same effect as continuous dosing at the same low level.

Regarding efficacy, four selection criteria of chemicals have to be considered :

- the biology of the target biofouling, in particular the location and duration of the settlement period;
- the growth rate of the target species depending mainly of the trophic resource level;
- the mode of action and the toxicity of the chemical (acute or chronic biocidal strategy);
- the maximum fouling density acceptable in the cooling system to be protected (operational tolerance).

For various ecological and economic reasons, continuous or semi-continuous dosing at subacute (chronic) toxicity levels most often is found to be the most pragmatic option.

Cooling towers microfouling

Film fill packs deposits are a combination of mineral and organic components. In absence of scaling process, dust and silt transported with air and makeup water contribute to the inorganic deposits. The organic layer on film fill packs is mainly produced by the slime forming bacteria of the *Pseudomonas* group (Puckorius, 1997). Different cooling water

treatments can be made to control the deposits :

- use of biocides, such as chlorine, glutaraldehyde, to eliminate the bacterial development,
- use of dispersants to remove the muddy deposits from the fills.

In closed cooling circuits equipped with cooling towers, severe corrosion problem of copper alloy condensers can be avoided by addition of corrosion inhibitors, mainly aromatic triazoles, to the circulating water. Some research is in progress in the US to reduce the toxicity of this type of compounds by using more degradable substances (Rao *et al.*, 1997).

3.2 WATER FILTRATION

Water filtration devices of various types are always installed on cooling water systems fed by natural waters. Such devices have specific purposes.

The **coarse grid** (about 10 cm spacing) is the first protection; it is located at the opening of the water intake and is frequently equipped with trash racks for removing the largest natural and artificial drifting debris entrained with the water.

The design of this grid and the dimensions of the trash rack system depend on the drifting debris most common in the area in question : kelp at marine sites, aquatic plants on rivers, anthropogenic debris everywhere.

The debris removed is most often accumulated in a special tank and processed as solid wastes.

Travelling screens represent the second filtration level. These generally consist of a band screen when the flow rate is lower than $10 \text{ m}^3/\text{s}$, or drums for higher flow rates. The screen mesh is in the range of 1 mm to about 1 cm, depending on the type of heat exchangers to be protected: 1 cm corresponds to circuits with tubular exchangers, 1 to 3 mm corresponds to plate-type heat exchangers in which the distance between two plates is a few mm.

Such rotating screens are equipped with automated cleaning systems which use pressurized water sprays. The debris removed is sometimes driven with the washing water to the outlet system and mixed with the cooling water; in other instances, it is again accumulated in skips for latter disposal. A great variety of debris is removed by these rotating screens such as seaweed, aquatic plants, mussel mats from the intake canal, shells of organisms settled on the walls of the cooling circuit, etc.

Rotating screens or removable grids with small-mesh screens (1 to 3 mm) are installed on the outlet of the cold water basin in cooling towers in order to protect the condenser tubes and the plate exchangers against biological debris coming from the tower: algae, bryozoans, bivalves, gastropods.

Specific **debris filters** are also sometimes to protect heat exchangers. This type of filter is installed just before the exchanger; the mesh size is generally 1 mm and the debris is removed by backwashing or intermit-

tent maintenance. Equipping plate-type heat exchangers with debris filters generally reduces the frequency of cleaning heat exchanges and the investment cost of the filters is thus economically justified.

Microfiltration backwashed systems have recently been developed to remove very small particles (50 to $100 \text{ }\mu\text{m}$) and theoretically eliminate the plankton larvae of barnacles or mussels from the cooling water. These new filters are claimed to work in high flows, up to $4 \text{ m}^3/\text{s}$. Trials have been conducted in Canada by Ontario Hydro to eliminate zebra mussels from an auxiliary circuit of a power station on a lake. In this very pure water, the system succeeded. In practice, this type of system has two major drawbacks in most large European rivers: its low availability in waters heavily loaded with suspended matter, and the limited water flow which can be filtered before clogging occurs. As a result, filtration costs for the high flow rates found in the main cooling system of power stations (8 to $240 \text{ m}^3/\text{s}$) are prohibitive.

3.3 MAINTENANCE OF FILTRATION SYSTEMS AND CLEANING

It is difficult to keep a rotating screen fully efficient on a long-term basis; degradation of rubber seals or holes in the screening panels can easily cause entrance of raw water into the circuit, entraining debris such as shells or aquatic plants. One means

of overcoming this difficulty is to allow in-line maintenance using removable grids, such a system comprises two successive grids, each of which is periodically removed and washed with high-pressure water sprays.

Maintaining trash racks, rotating screens and removable grids in good operating condition requires considerable effort. This induces significant maintenance costs.

Tubular heat exchangers, like condensers in power stations, are frequently cleaned by an **on-line cleaning system**. The technique consists in recirculation of sponge rubber balls released in the inlet water box of the condenser, then extracted by a strainer at the outlet water box and pumped back to the inlet. This system is convenient for large heat exchangers and commonly used in European power stations supplied by freshwater. Several types of balls covered with specific coatings are used to eliminate more or less hard deposits. With this system, additional chemical treatment is generally not required, but on some sites, such as the Gravelines nuclear power station in France and Hartlepool power station in the UK, continuous water chlorination is combined with sponge rubber balls to control bacterial slime. On-line cleaning systems are costly in terms of investment and operation.

Off-line cleaning can take place at the time of scheduled unit shutdowns for maintenance, inspection, and refueling in nuclear power stations, or during periods of reduced output. Heat exchangers are cleaned with

high-pressure water jets or by shooting hard objects into the tubes. Plate-type exchangers must be dismantled for cleaning and then remounted, requiring several hours' work on each. Sometimes, they can also be rapidly cleaned by a physical process: vacuum suction or back-flushing which removes any clogging debris and muddy deposits.

Dry manual cleaning of filter chambers, galleries, culverts, pipes and basins, is periodically performed by scraping the macro-biofouling from the walls during maintenance operations. On some sites, in the parts of the circuit which cannot be dried, underwater cleaning is also carried out by divers. The debris covering the bottom of the circuits is removed by suction pumps.

3.4 WATER VELOCITY

Water velocity and the potentially complex hydrodynamics of circuit design are important factors in the "fouling potential" of a given cooling 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 waters, while others require strong speedy currents.

Water velocity varies considerably in cooling circuits from the water intake structure to the outlet. It is low near filtering devices like traveling screens and in basins, especially coo-

ling tower basins. It is higher in pipes leading to heat exchangers and in tube 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 system is an extremely favourable factor as it provides a source of particulate nourishment and dissolved oxygen. For this reason, when water velocity is not excessive, organisms show optimum growth, generally more rapid than among populations in a natural environment. When the velocity exceeds a critical threshold, larvae no longer settle and adults can no longer feed well; they are even detached from the substrate. In the absence of water circulation, dissolved oxygen becomes the limiting factor and causes death by asphyxia in one to three weeks, depending on the temperature.

These considerations lead to three recommendations :

1. maintain a sufficient water velocity to prevent settlement and growth of macro-biofouling, threshold values are discussed below.

2. avoid a regime with long periods of velocities favourable to the development of biofouling, followed by periods with unfavorable higher velocities, as the larvae can settle and begin growth which will then be temporarily halted. When pumps operate alternately on several circuits, frequent rotation is desirable so as not to leave one circuit at a low velocity

for more than one to two consecutive days.

3. avoid temporarily suspending all circulation in a circuit invaded by macro-biofouling for a period of more than three days. During the summer thermal peak, organisms die in about five days. Upon startup of the pumps, they are massively detached and filters at the inlet to heat exchangers are plugged, and often damaged, by the arrival of tons of shells.

Freshwater biofouling and water velocities

Bryozoans are extremely abundant in the cold water basins of cooling towers on the Loire in France and the Meuse in Belgium. Experimental and field data on the influence of water velocity on the development of bryozoans are summarized in Table 3.5.

In cooling tower cold basins where the water velocity is less than 0.5 m/s, gastropod molluscs (*Bithynia*, *Physa*, *Lymnaea*) and Asiatic clams (*Corbicula*) develop well. Small individuals of these species are also found on the packing.

In pipes and galleries or basins, at maximum water velocities of 0.6-0.7 m/s, mud deposits favour the development of large Unionid bivalves (*Unio*, *Anodonta*) and Asiatic clams.

In natural running waters, Zebra mussels *Dreissena polymorpha* tolerate a wide water velocity range from 0.05 cm/s to 1.0 m/s (Leglizé & Ollivier, 1981). Post veligers (< 1 mm) are more sensitive to current than adults :

Table 3.5. – Water velocity and growth of freshwater Bryozoans. Data from Aprosi *et al.*, 1988, Thome *et al.*, 1989.

Species	Site	Optimum for growth	Water velocity	
			Growth inhibition	Detachment of colonies
<i>Plumatella fungosa</i>	Chinon on the Loire	≤ 20 cm/s	≥ 60 cm/s	> 90 cm/s
<i>Plumatella fungosa</i> , <i>P. emarginata</i> <i>P. repens</i>	Tihange on the Meuse	20 cm/s to 30 cm/s		

attachment strength is two order of magnitude less than adults (Ackerman *et al.*, 1995). This species is not found at 2 m/s although some isolated settled mussels can resist 2 m/s. At the Mery-sur-Oise drinking water plant near Paris, it was observed that a water velocity of 1.5 m/s detaches clusters of mussels. In cooling water circuits of some EDF power stations, zebra mussels are very abundant in all areas where the water velocity is in the range of 10 cm/s to 50 cm/s but the species is not observed on the parts of the circuit with water velocities exceeding 1 m/s.

Marine biofouling and water velocities

The effect of water velocity on concrete walls is clearly visible in the data in Table 3.6, collected at the Le Havre plant on the English Channel, operated by EDF.

In a conduit with a large circular section (3 to 5 m²), colonization of the walls by mussels (*Mytilus edulis*), barnacles (*Balanus crenatus*) and hy-

droids (*Tubularia*) is considerably reduced when the mean velocity in the section is in the range of 1.8 m/s to 2.2 m/s; organisms settle in depressions in the walls (anfractuosités, seals). Hydroids trap suspended matter and deposit mud and organic debris. In practice, it appears that settlement and growth of macro-biofouling is halted at 1.8 m/s except in specific zones very limited in area. The organic film of bacterial origin, including some hydroids, develops up to 2.2 m/s on very rough concrete and is rich in mud. Deposits are completely eliminated at 2.9 m/s.

In a conduit with a large rectangular section (5 to 11 m²), colonization of walls by mussels, barnacles and hydroids is significant at mean velocities of 1.4 m/s, but seems to be limited at 2.0 m/s. In galleries with elbows, one wall is less colonized than the other, due to the heterogeneity in velocities.

At the Esbjerg power station (Denmark), the walls of a square section intake conduit (6.25 m²) are totally covered by mussels, the mean water velocity is 1.4 m/s.

Table 3.6. – Biofouling development in two intake conduits at Le Havre power station units 1 and 2, as a function of mean water velocity.

	Water chamber rotating screen	Rectangular section 5.5 m ² to 11.0 m ²		Circular section Diameter : 3.0 m ² to 4.9 m ²		
		1.4 m/s	2.0 m/s	1.8 m/s	2.2 m/s	2.9 m/s
<i>Ascidians</i> <i>Ascidella</i> <i>aspera</i>	Important coverage	Absence	Absence	Absence	Absence	
Mussels <i>Mytilus</i> <i>edulis</i>	Important coverage	Total coverage of one wall ; 14,400/m ²	Total coverage of one wall ; the other is less colonized than at 1.4 m/s	Presence on seals only	Presence on seals and some small mats.	
Barnacles <i>Balanus</i> <i>improvisus</i>	Important coverage	Total coverage of one wall ; the other is less colonized (mussels are settled on this surface).	Infrequent living barnacles	Presence on seals only	Infrequent living barnacles	Total absence of settled organisms and organic debris
Hydroids <i>Tubularia</i>	Important coverage	Total coverage of one wall ; the other is less colonized	Some mats of hydroids in decomposition	Presence on seals only	Some mats of hydroids in decomposition	
Mud and organic debris	Abundant deposits	Abundant deposits	Abundant deposits	Very little organic deposit		

New observations made at the Vado Ligure power station, operated by ENEL in Italy, show that in the intake pipe where the water velocity is near 3.0 m/s, there are barnacles everywhere, and mussels located mainly on the seals of the pipe, but this "residual fouling" does not pose any problem for the plant operation.

From Japanese experimental data, Kawabe (pers. com.) concluded that the appropriate velocity value must be taken very close to the walls, at 1 mm from the surface, rather than the mean water velocity. As a consequence, the critical water velocity to avoid macro-fouling growth depends on the size of the conduits. In large

Fig. 3.2. – Average water velocity required to eliminate marine biofouling and erosion-corrosion on metal pipes. Redrawn from Kawabe *et al.*, 1985.

pipes, the velocity must be higher than in small condenser tubes. A second factor has to be taken into account: the surface roughness which can favour the settlement of larvae. According to this approach, A. Kawabe recommends to maintain in intake conduits a velocity of 1.4 m/s at 1 mm from the walls. In conduits of a 2 m diameter, the mean water velocity must be ≥ 3.3 m/s to prevent the macro-fouling development.

Whatever the discrepancy of these observations and experimental data, it can be concluded that, in pipes maintained without the presence of dead legs or low flow areas, marine mussels generally do not settle in water where the velocity is near 3.0 m/s, and that macro-biofouling is already reduced at 2.0 m/s.

The worst case is represented by a square section conduit with water velocities lower than 2.0 m/s, and rough concrete walls.

On metal walls, Kawabe *et al.* (1985) tested settlement of mussels and barnacles in circular conduits of three types: a copper-nickel alloy, an aluminum alloy and an acrylic coating. The nomogram obtained from this study (Figure 3.3) gives the mean velocity needed to prevent biofouling and erosion-corrosion of the wall in a pipe with a diameter between 20 cm and 1 m. On a non-toxic surface (acrylic coating), a velocity of 2 m/s must be reached in a large conduit to eliminate mussel settlement totally. This velocity is markedly less than that which determines erosion-corrosion on metal structures (> 4 m/s).

One important point highlighted by this study is the important influence of the composition of the wall; the efficient velocity in copper or aluminum alloy conduits is considerably lower than that found for the acrylic coating. We can assume that a toxic reaction of the metal ions on the wall makes mussels, and barnacles to an even greater degree, more sensitive to water velocity.

3.5 HEAT TREATMENT

Thermal treatment is a highly efficient way to eliminate all macro-bio-fouling from cooling circuits and is adopted on some European power stations. In the Netherlands, four stations use heating as the only anti-fouling method (Jenner, 1983a).

The cooling water is progressively heated by means of recirculation (see Annex 1) to a maximum temperature of about 40 °C. This maximum temperature is maintained in the circuit for a short time (30 minutes to two hours). All macro-biofouling organisms are killed by the heat shock. It is necessary to optimize this type of treatment in order to kill very small organisms to avoid clogging of exchangers or filters, which requires that one know precisely the settlement periods and growth rate of the major fouling species.

Thermal treatment is not effective against bacterial slime, as the temperature level required to control the bio-

film on the heat exchangers is much higher (70 to 80 °C).

This type of treatment requires a special design of the cooling water system and this needs to be adopted at an early stage of plant construction. Subsequent adaptations are often technically difficult and expensive.

Problems of the expansion and contraction of the concrete walls of the tunnels and conduits as they warm and cool in the cycle of treatment must be solved. Probably even more important are the effect on the turbine and the loss of generation during the treatment period.

Experimental data on freshwater biofouling

Many experiments have been performed to determine the lethal temperature for the zebra mussel, *Dreissena polymorpha*, in European countries (Hoestland and Lassablière, 1959; Fejgina, 1959; Kirpichenko *et al.*, 1962; Gillet & Micha, 1985; Jenner & Jenssen-Mommen, 1993; Khalanski, 1993; Rajagopal *et al.*, 1997) and in North America (Griffiths, 1992; Iwanyzki & McCauley, 1993; McMahon *et al.*, 1993). The thermal resistance of the zebra mussel depends on the acclimation temperature and the biological stage; it would appear that it also depends on mortality criteria (Iwanyzki & McCauley, 1993).

Table 3.7. shows selected data corresponding to the acclimation temperature of 25 °C, which is close to

Table 3.7. – Time to kill 100% zebra mussels exposed to upper lethal temperatures. All data refer to mussels acclimated to 25 °C.

Upper lethal temperature (°C)	Exposure time (min)	Reference
40	15	Hoestland & Lassablière, 1959
36	60	
37	40	Khalanski, 1993
37	20	
40	5	
40	20	
34	687	Griffiths 1990 in Claudi & Mackie, 1993
35	271	
36	202	
37	126	
38	66	
35	525	
36	261	
37	153	
38	78	
30	5702	Iwanyzki & McCauley, 1993
31	3157	
32	2812	
33	1848	
34	253	
35	41	
36	39

Fig. 3.3. – Time-temperature treatment to kill 100% of adult zebra mussels acclimated to 25 °C. From experimental data of Table.

the maximum water temperature in European rivers. A regression line has been fitted on the maximum values (Fig. 3.3), having the formula :

$$\text{Log Time (min)} = -0.251 * \text{Temperature (}^{\circ}\text{C)} + 11.38 \quad r^2 = 0.95.$$

According to this relationship, at 40 °C or 39 °C, the exposure time is only 20 to 40 minutes; 1 hour is required at 38 °C and 2 hours at 37 °C, but more than 11 hours at 34 °C.

In fact, the optimum temperature for this treatment is in the range of 35 to 40 °C and the exposure time will consequently be in the range of 30 minutes to 10 hours.

In practice, the temperature rise which can be achieved is relatively slow (a 1 °C to 2 °C increase per hour), and it generally takes several hours to reach the maximum temperature.

Experimental data on brackish water biofouling

Laboratory studies have shown that at 37 °C, a 100 % kill of the brackish water mussel *Mytilopsis leucophaeata* can be achieved by maintaining this temperature for a period of 2 hours. At given target temperatures, *M. leucophaeata* appears to need a longer exposure to ensure 100 % kill than the time needed by *M. edulis*, (Jenner, 1982) and *D. polymorpha* (Jenner & Janssen-Mommen, 1993). The greater environmental stress imposed by brackish

waters compared with fresh and marine waters presupposes a higher temperature tolerance in estuarine species (Wright *et al.*, 1983) and this would conform to expectations for an animal originating in the Caribbean (Marelli & Gray, 1983).

Experimental data on seawater biofouling

Information on thermal death point for marine organisms can be found in the scientific literature. Marine mussels have been extremely studied and a recent study has been made on the mussels in several parts of the northern hemisphere (Gosling, (ed.), 1992).

In principle, it is best to determine the lethal thermal dose curve for the population of mussels in the area from which the cooling water is to be extracted. Because it is not always possible to do this, an envelope curve can be drawn based on the lethal thermal data for fouling species. Using the equation of the envelope curve :

$$T(^{\circ}\text{C}) = 50 - 2.46 \ln t \quad (T \text{ in } ^{\circ}\text{C}, t \text{ in minutes}) \quad [\text{see Fig. 3.4}].$$

It has been found that 40 °C for a period of one hour will kill *M. edulis* and *M. californianus*, and coincidentally all other macrofouling organisms such as barnacles, hydroids, sea anemones etc. (Jenner, 1983a; Rajagopal *et al.*, 1994).

Where heat has been used as the method for the control of mussels, as at Eems power station in the Netherlands, it has been found that barna-

Fig. 3.4. – Lethal thermal dose curves for marine mussels (Jenner, 1982), brackish water mussels (Rajagopal *et al.*, 1994) and the theoretical curve for thermal data lethal for all fouling species found in the northern hemisphere.

cles, *Balanus crenatus*, are killed by the application of a temperature of 38 °C for 30 minutes. The time-temperature mortality curve shows that the mussels are killed in only 30 minutes, but prudence in use of this method of control, due to the narrow band separating survival and mortality, would suggest the use of 60-minute treatments rather than repeated treatments. This approach is consistent with the observation that barnacles have a lower lethal temperature than mussels (Foster, 1969).

Implementation at industrial sites

In the Netherlands, practical application of thermal treatment at the pre-

sent time is restricted to a limited number of locations operating with seawater CWS (Hoogovens, IJmuiden; Eems power station, Delfzijl). In the future it will be used at freshwater-cooled locations as well (Diemen power station; Moerdijk power station). In Dutch marine power stations, blue mussels and barnacles are eliminated by heat treatments 4 to 5 times a year, while treatment can be limited to once or twice a year on cooling circuits using freshwater.

In Italy, thermal treatment is used at La Spezia power station on the Mediterranean coast.

The crucial factor for the determination of treatment frequency is that

Table 3.8. – Examples of heat treatment at power stations.

Power station	Location	Heat treatment procedure	Reference
Eems	Eems-Dollard estuary in the Netherlands	3 to 4 treatments a year. Maximum temperature : 38 °C for 60 min	Whitehouse <i>et al.</i> , 1985
La Spezia	Mediterranean coast in Italy	20 treatments per year. Maximum temperature : 35 °C for 10 hours	
SCEC plant	Pacific coast in the USA	Maximum temperature : 51.7 °C	Graham <i>et al.</i> , 1977
Commonwealth Edison plant	Power stations cooled by fresh water.	Maximum temperature : 37.2 °C for 6 hours.	Claudi & Mackie, 1994

mussels detached from the walls be small enough to pass through heat exchangers or not be abundant enough to clog the filters.

Typical heat treatments used at power stations are summarized in Table 3.8, and details regarding the Eems and La Spezia power stations are given in Annex 1.

Environmental assessment

There are advantages to this approach, the greatest being that there is no addition of chemicals, but heat does not function as a method for the control of slime in the condenser and special terms would have to be agreed with the local and national Environment Control Agencies to permit the discharge of water at temperatures well in excess of 30 °C. In practice, if the physical methods adopted are not sufficient to control bacterial slime, or if some critical parts of the circuit cannot be treated by heat, it

becomes necessary to complement heat treatment by some use of chemical antifouling products.

3.6. PAINTS AND COATINGS

Rather than adding toxic substances into the rapid flow of cooling water circuits, it is possible to treat the surfaces on which biofouling develops so as to prevent settlement of larvae and halt the growth of settled organisms. Paints or complex multi-layer coatings may be applied at different locations in the cooling water systems : intake conduits, screens, pipes, condenser waterboxes and condenser tube plates.

Two major classes of paints and coatings have been developed : those containing one or several toxic substances, and those which contain none and whose action is due rather to their physical surface properties.

Table 3.9. – Antifouling efficiency of Cu_2O paints depending on the leaching rate of the copper. Adapted from Kawabe, 1997.

Copper leaching rate	Antifouling action
> 20 $\mu\text{g} / \text{cm}^2 / \text{day}$	No fouling
20 $\mu\text{g} / \text{cm}^2 / \text{day}$	First weed settlement
15 $\mu\text{g} / \text{cm}^2 / \text{day}$	Settlement of Hydroids
10 $\mu\text{g} / \text{cm}^2 / \text{day}$	Settlement of Barnacles
< 10 $\mu\text{g} / \text{cm}^2 / \text{day}$	Settlement of all macro-biofouling

These products have mainly been developed for treating boat hulls. For use on cooling water circuits, such paints must be selected in the light of four criteria (Ewans *et al.*, 1992) :

- ability to resist fouling or to provide an "easy-clean" surface,
- absence of toxic releases, or release of toxic substances at an acceptable level,
- long lifetime,
- applicability to concrete and/or steel.

Two other criteria must also be considered : the cost of the product and of product application, and the way in which the coating degrades. To be applicable to cooling water systems, coatings must not detach from the surface at the end of their lifetime, producing fragments which might plug up heat exchangers. The points also have to be applied in the brief opportunities allowed by maintenance programmes and outages.

3.6.1 Toxic paints and coatings

Selected toxic substances are introduced in these paints and are progressively released to the surface by

a leaching process and by surface erosion. Very low amounts of such substances can generate a sufficient concentration in the immediate surface water layer to have adverse effects on settled organisms. In some new paints, the toxic substance (quaternary ammonium) is fixed on the polymer matrix.

Amongst those surface treatments incorporating toxic organic compounds, those paints and coatings containing tributyl tin oxide (TBTO) are very efficient against all types of marine organisms. Because of its extreme toxicity to marine molluscs, TBTO was rapidly abandoned for power stations antifouling treatments in Europe (Whitehouse *et al.*, 1985) and in Japan (Kawabe, 1997). The toxicity of organic tin is now well documented and severe biological effects have been reported for tin concentrations below 1 $\mu\text{g/L}$ (His, 1995). However, some organic biocides, such as 4,5 dichloro-2-n-octyl-4-isothiazolin-3 in Rohm & Haas paints, are apparently degradable and generate non-toxic metabolites.

Commercially-available toxic coatings generally contain inorganic zinc

and copper. They are marketed as slow-release, self-polishing and ablativ coatings for protection against micro- and macrofouling. In self-polishing paints, the leaching rate of the biocide is constant, whereas it decreases rapidly in traditional paints.

Zinc silicate paint was found to be efficient against zebra mussels, while a copper paint lost its efficacy after 7 months of tests conducted by Ontario Hydro at a power station on Lake Erie (Ewans *et al.*, 1992).

In 1992, 77 % of the marine power stations in Japan used toxic antifouling paints. The more commonly used (39 %) are copper oxide paints (Cu_2O) and 8 % are paints containing copper powder. In units painted with Cu_2O paints, the repainting time interval is generally one to two years (77 %), but 23 % of the units can withstand a 4-year rhythm (Kawabe, 1997). Tests performed with paints containing Cu_2O (Yokouchi *et al.*, 1996), have nonetheless demonstrated that they are efficient for only 9 months. The efficacy of such paints depends on the leaching rate of copper ions : the paint is totally ineffective when the rate is less than $10 \mu\text{g Cu} / \text{cm}^2 / \text{day}$ (Table 3.9). Thus in about 9 months, the leaching rate can decrease from $60 \mu\text{g Cu} / \text{cm}^2 / \text{day}$ to $10 \mu\text{g Cu} / \text{cm}^2 / \text{day}$.

Several types of toxic and non-toxic coatings were tested by Electricité de France on PVC and concrete panels at the Cattenom on the Moselle, from 1991 to 1993. Copper panels were also tested. The reference panels were totally colonized by Hydroids

(*Cordylophora caspia*) and by zebra mussels. After four months of tests, the copper panel had no settled organisms and four of the coated panels were less colonized than the controls. A new 12-month series of tests demonstrated the total efficacy of copper against zebra mussels, and the partial efficacy of certain chlorinated vinyl resins containing quaternary ammonium.

The possibility of surface antifouling protection by means of localized production of chlorine at an anode was reported by Lovegrove & Robinson (1968). Electro-conductive coatings have been developed in Japan for applications in seawater. A current passes through the paint film, generating hypochlorous ions by electrolysis of seawater. The power consumption is very low : a few w per 100 m^2 . Field tests have proved the antifouling efficiency of such coatings applied with favourable results on the hulls of boats (Usami & Ueda, 1993), and four marine power station units have experimented with this type of paint. This process generates very small amounts of chlorine, and could be a good solution in environmental terms. However, experiments performed on model canals at the Anan power station showed that cracks appeared in the paint after 6 months and that thereafter biofouling spreads rapidly even on previously treated areas (Yokouchi *et al.*, 1996).

3.6.2 Non-toxic coatings

Non-toxic foul-release coatings reduce biofouling by weakening the

adhesive bond between the organism, film or deposit and the coating. The most promising products available for CWS at this moment are silicone-based paints.

Although silicone-based coatings are fouled by biogrowth, the rate of fouling is lower and it can be wiped off more easily by the cooling water flow.

Silicone-based coatings need generally be applied to a perfectly clean and dry surface, or to clean and almost dry (5 % or less moisture) concrete. For this reason, the technique is more difficult to apply in existing systems, where dry conditions are hard to obtain, than in newly-built CWS. The coatings are usually applied in layers, although experiments with a single layer have also shown good results. The silicones are physically soft and therefore susceptible to impact damage and abrasion. Attempts to toughen silicone paints have always resulted in diminished antifouling performance. The development of a paint with both properties remains a challenge to the paint industry (Leitch 1994). The estimated lifetime of commercially-available silicone coatings is claimed by manufacturers to be 4-5 years, but experimental data generally indicate a shorter period of efficacy.

Results in the U.S. have shown that silicone-based coatings applied to intake pipes accumulate less fouling than those applied to intake walls and other areas exposed to lower flow velocities (EPRI, 1989; Gross, 1991).

In 1990-1991, Ontario Hydro tested different antifouling paints on panels placed at a forebay of the Nanticoke power station on Lake Erie (Ewans *et al.*, 1992). The water velocity was relatively low : 7 to 8 cm/s. Some silicone paints gave good results : zebra mussel coverage was ≤ 1 % compared to the 100 % coverage on the control, and the settled mussels were only weakly attached to the painted panel. Unfortunately, it was observed that the topcoat of the best silicone paints is easily damaged during handling and preparation of the panels.

Similar findings were obtained by Electricité de France in 1991-1993 in tests at the Cattenom plant on the Moselle, using a silicone epoxy resin which proved efficient against zebra mussels, but which showed poor adherence on a PVC panel.

According to Kawabe (1997), 30 % of Japanese marine power stations used silicone-based paints in 1992. Areas painted with this type of paint are generally retreated every 2 years, but 22 % of the units are repainted on a 4-year rhythm. This does not mean that they are efficient for this long, since tests conducted with these paints on experimental canals in the Anan plant, with a velocity of 20 cm/s, showed that organisms can settle after 3 to 9 months (Yokouchi *et al.*, 1996).

Practical experience has been acquired in the Netherlands through a number of pilot trials with exposure panels, inlet culverts and heat exchanger inlet boxes at Dow Benelux, Terneuzen, Dodewaard power station

(freshwater) and Maasvlakte power station. Two commercially-available silicone-based coatings have been tested on exposure panels by KEMA for two seasons in fresh, brackish and sea water. In freshwater, the panels were still clean after two seasons. In brackish water and seawater, fouling developed, although less than on reference (PVC) panels, although the biofouling that had developed was easily removed by hand. The coatings proved to be effective in cooling water intakes, conduits and the inlet chambers of heat exchangers.

At Dow Benelux, experiments with a coated plate in the "KEMA Biofouling Monitor", showed that young stages of mussels settled on the coating, and detached when having reached a length of approximately 1 mm. On the uncoated PVC plates in the same device, mussel spat settled and grew up to 2 cm within one fouling season.

In a recent study subsidized by the German Federal Environmental Agency, some non-toxic coatings were tested in seawater at four sites on the North Sea and the Baltic coast (Watermann *et al.*, 1997). The marine fouling organisms on the control panels were barnacles, Bryozoa, mussels, annelids, hydroids and ascidians. Nine silicone coatings were selected as being the most representative of "non-stick" coatings and were tested in "static conditions" with water velocities in the range of 0.22 m/s to 0.45 m/s generated by tidal currents or with a short-term increase to 2.2-2.7 m/s for one hour a month when panels were placed on board a catamaran. Four sili-

cone polydimethylsiloxanes (PDMS) were very effective in the prevention of macrofouling over the 6-month period. The four coatings showed no significant variation in surface free energy over the 6-month test period. The adhesion force of adult barnacles *Balanus amphitrite* was considerably reduced compared with the control (Table 3.10). In this study, some discrepancies appeared between laboratory experiments and field trials: Intersleek and Everclean did not inhibit cyprid settlement in the laboratory whereas they do in the field.

Prospects for antifouling paints in cooling water systems

At the moment, the most promising paints and coatings are :

- self-polishing paints containing Cu_2O and possibly some organic biocide with no adverse ecological effects,
- silicone-based "foul-release" coatings, whose efficacy depends to a large extent on the water velocity : they are more effective at high water velocities.

It remains necessary to perform on-site tests with rigorous measurement procedures to verify the conditions of applicability on treated surfaces, the antifouling effects and the lifetime. Only on-site experiments can provide the quantitative data required for an economic estimation, by indicating the reduction in the cost of cleaning processes and of loss of power generation.

Table 3.10. – Adhesion force of barnacles on different coatings and areas free of macrofouling in % of the test area after 6 months of trials. Data from Watermann *et al.* (1997).

Tested coatings	Laboratory experiments	Field trials	
	Adhesion force of barnacles (10^5 N/m ² per basal plate)	Stationary exposure trial : water velocity 0.22 m/s to 0.45 m/s	Changes in water velocity 0.22 to 0.45 m/s and one hour a month at 2.2 to 2.7 m/s
Control Epoxy resin	1.59 to 3.49	0%	0%
PDMS containing a hydrophobic liquid (Bioclean)	0.01 to 0.52	93.9%	99.6%
PDMS containing a hydrophobic liquid (Biox)	0.01 to 0.80	98.2%	95.0%
PDMS polymer (Everclean)	0.02 to 0.27	88.8%	98.0%
PDMS-based elastomer (Intersleek)	0.01 to 0.52	64.1%	97.4%
PDMS with surface methyl groups (Kiss Cote)	—	0%	0%
Silicone resin with silicone fluid (TMP1 and TMP3)	—	0%	0%
Silicone oil mixed with polyurethane paint (TMP2 and TMP4)	—	0%	0%

Despite the uncertainties, it is clear that antifouling paints are of particular interest in the control of macro-biofouling and will probably see great development and use by European operators in the future.

Some U.S. utilities operating marine power stations which have problems with barnacles, oysters and mussels developing in intake conduits, have collaborated with EPRI in testing silicone-based foul-release coatings with some success (Tsou 1996, Gross 1996). At a LILCO power station, such a coating was still found to provide excellent macrofouling protection in the fourth year after application. The use of non-toxic coatings is encouraged by the U.S. EPA

and generates financial benefits due to savings on cleaning, disposal and fuel costs.

In Denmark at the Esbjerg power station, a marine site with severe mussel fouling, a full-scale experiment with a three-layer silicone coating from a Danish manufacturer was found to be successful during 3 years of operation. Inspection of the culverts during maintenance showed that the top-layer of the coating was still intact; which expects a lifetime of at least 4 years.

In Spain, toxic and non-toxic coatings were applied in 1997 to intake conduits at the Vandellos B nuclear power station, operated by UNESA.

3.7 CHEMICAL TREATMENTS WITH OXIDIZING COMPOUNDS

3.7.1 Chlorine

Chlorine was first used in Europe and North America in the early 1900s for the disinfection of drinking water, and resulted in a dramatic decline in typhoid and cholera cases. At the present time, it is largely used as a powerful oxidizing agent for water treatment, such as taste and odour control, disinfection of drinking water and waste water, in the food industry and for biofouling control. Of all the disinfectants, it is certainly the most extensively studied with regard to chemistry, toxicity and ecotoxicity. Due to its well-tried technology, its long-term worldwide industrial uses and its acceptable cost, chlorine remains the most common antifouling treatment to date.

The ideal biocide is highly toxic to one particular organism or group of organisms but has no side effects on 'non-target' organisms. It is not consumed by reactions with materials in the water (i.e. there is no 'demand') and as soon as it enters the environment, it breaks down into non-toxic forms. Chlorine is a long way from this ideal: 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 effects of non-longer term oxidants. This situation is changing and the time has now come to consider the complex mixture of halogenated by-products produced by water chlorination.

3.7.1.1 Chlorine storage and on-site production

Chlorination in natural waters is possible in one of three ways: dissolution of chlorine gas, mixture with a sodium hypochlorite solution which, like the gas, may be stored on site, or production of a sodium hypochlorite solution *in situ* by electrolysis of seawater.

Chlorine gas (Cl_2), can be kept under pressure in tanks, which presents the advantage of storing large amounts of chlorine in a small volume and of allowing for treatment of water at high flow rates. Chlorine gas is the least expensive of chlorine products. A few accidents during transport or storage have led industry to prefer sodium hypochlorite. Great progress has recently been made, however, in ensuring safe storage of chlorine gas.

Sodium hypochlorite (NaOCl) in concentrated solutions is stored on-site in tanks with no metal walls, to prevent decomposition. In the dark, decay is temperature-dependent. The recommended maximum storage time is one month. Commercially available sodium hypochlorite has an active chlorine concentration of 10% to 15%. To improve mixing with cooling

Fig. 3.5. – Electrochlorination cells at the Paluel Nuclear power station, operated by EDF.

water, the concentrated solution can be diluted prior to dosing to about 0.5 g/L to 2.0 g/L.

At marine sites, when large amounts of chlorine are required to treat cooling water, electrochlorination enables on-site production of the sodium hypochlorite required by the demand, by means of the following global chemical reaction :

This process is somewhat more costly than purchasing sodium hypochlorite due to the investment cost of the electrolysis cells, energy consumption, and maintenance costs.

Electrochlorination is largely used to treat the cooling water of large marine power stations in the UK, France, Italy and Spain. Recently, problems with mal function have led some power station operators to shift over to sodium hypochlorite or chlorine dioxide.

3.7.1.2 Chlorine chemistry

Terminology

When dissolved in natural waters, chlorine gas or a sodium hypochlorite solution produce different oxidizing compounds depending on the reaction of hydrolysis and oxidation of ammonia, leading to chloramines or bromamines. The oxidants also react with organic matter to produce chlorinated or brominated organics. As a result, water chlorination chemistry involves many molecular and ionic species or groups, whether oxidants or non-oxidants, whose terminology must be precisely defined.

Chlorine is described in the literature as 'free', 'active', 'available', 'combined' or 'residual' – or by a combination of these adjectives.

(a) **Free chlorine/Free available chlorine (FAC)** is present as an equilibrium mixture of hypochlorous acid (HOCl) and hypochlorite ions (OCl^-). Both are oxidants, but OCl^- is far less effective than HOCl. Fugitive elemental chlorine can be ignored.

(b) **Combined chlorine/Combined available chlorine** is available in chloramines or other compounds having a N-Cl link; these are also oxidants.

(c) **Total available chlorine (TAC)** is the sum of (a) and (b).

(d) **Residual** is analogous to Available, but serves to emphasize the concept of a pool of oxy-disinfectant capacity that persists after the initial demand (below) has been met. Hence: free residual chlorine, combined residual chlorine and total residual chlorine (TRC/TRO).

(e) **Chlorine demand** is defined as the difference between the amount of chlorine added (dosage) and the useful (residual) chlorine remaining at the end of a specified contact period. Demand is best considered as a once-off reaction that "mops up" a finite quantity of oxidizable substrate.

(f) **Chlorine decay** is a continuing series of reactions that will in time lead to the complete disappearance of all measurable chlorine. Decay, unlike demand, is not substrate-limited.

The toxicity of chlorinated water, and particularly its acute toxicity, is correlated with its oxidizing potential. It is suggested that for a chlorine species to have any significant efficacy as a biocide, it must have an oxidation-reduction or redox potential (ORP) sufficient to oxidize iodide to iodine at pH 7. It is becoming more common and is, in many instances (e.g. seawater) is more correct, to refer to "oxidants" rather than to chlorine.

(g) **Total Residual Oxidant (TRO)**. Most methods for determining "chlorine" actually measure oxidant capacity via the stoichiometric iodide/iodine route. For this reason

alone, it is preferable to refer to total, free and combined residual oxidant rather than to total, free and combined residual chlorine in seawater where brominated oxidants are the dominant species. TRO is numerically and operationally equivalent to TRC and TAC as defined above.

(h) **Chlorine Produced Oxidants (CPO)** is a self-explanatory term, reminding us that oxidants occur naturally in many waters and that some will be measured as though they were CPOs. These will appear as 'background' in blank determinations but for most practical purposes their concentrations are so low that they can be ignored.

When using oxidant terminology, it is important to remember that the instrument or method used for measurement was almost certainly developed and calibrated for chlorine and that (strictly) the result should be expressed as "mg/L TRO as Cl_2 ". Generally, the calibration curve is drawn for free chlorine in HOCl-dominant solutions, which means that chloramines, bromamines and brominated oxidants are measured as free chlorine equivalents.

The concept of **Available chlorine** (as distinct from 'free available' and 'total available') is confusing and should be avoided wherever possible. It originated as a way of comparing bleaching agents, much as water hardness may be measured 'as CaCO_3 '. The concept can be applied equally well to oxidants containing no chlorine at all (e.g. ozone) and to those whose chlorine does not hydro-

lyze to produce hypochlorous acid (e.g. chlorine dioxide), but the calculations are heavily dependent upon knowledge of valence state during reaction conditions. Neither ozone nor chlorine dioxide are **Available chlorine compounds** – specifically chlorine compounds that hydrolyze to hypochlorous acid. This is therefore another term to be avoided. A similar source of error is the expression of biocide concentrations as, for example, mg/L bromine. Such values must be reduced by the atomic weight ratio 33.5 : 80 to be directly comparable with chlorine oxidants.

To summarize, it is more precise and thus preferable in most situations to use the term **residual oxidant** prefaced by **free, combined** or **total** as appropriate, with “as Cl_2 ” implicitly understood.

Among the non-oxidizing **chlorine by-products (CBPs)** generated by reactions with organic matter, several categories have been defined.

a) **Organohalogens (OX)** designates organochlorinated or organobrominated compounds; altogether, these compounds constitute **Total Organohalogens (TOX)**.

b) **Purgeable Organohalogens (POX)** designates volatile organohalogenes. The **trihalomethanes (THMs)** represent a significant proportion of POX.

c) **Adsorbable Organohalogens (AOX)** designates organohalogenes adsorbable on activated carbon. These are all the heavy (non-volatile) compounds as well as some volatile com-

pounds not eliminated before dosage. If the AOX measurement is performed after elimination of the volatile compounds, AOX represents the non-volatile compounds, such that $\text{TOX} = \text{AOX} + \text{POX}$.

d) **Extractable Organohalogenes (EOX)** designates organohalogenes extracted in an organic solvent. As for the AOX, some of the volatile compounds may persist in the extract, so that EOX represents the sum of non-volatile compounds and some volatile compounds.

POX, AOX and EOX are global measurements obtained by microcoulometry of halogens. EOX was especially developed for measurements in solutions rich in chloride ions (≥ 1 g/L) and is used on chlorinated seawater.

CBPs also contain polar compounds (haloacetic acids) which are not measured by such methods.

Part of these CBPs can be identified and measured by gas or liquid or ion chromatography when calibration standards are available.

Chemistry of chlorine in freshwater

Free oxidant chemistry

The addition of chlorine (or sodium hypochlorite) to water can be viewed as an instantaneous reaction resulting in an equilibrium mixture of hypochlorous acid – HOCl and hypochlorite ions OCl^- :

Both are oxidants and comprise the **free residual**, but OCI^- is far less effective as a biocide than HOCl .

Decreasing the concentration of H^+ ions (increasing the pH) shifts the equilibrium towards OCI^- , which is substantially less effective as a biocide than HOCl .

The ionization constant also varies with temperature; the percentage of undissociated HOCl at temperatures between 0°C and 30°C over the pH range 5.0 to 11.7, is summarized in Table 3.11.

Comparison of the percentage of undissociated HOCl as a function of pH is given in Figure 3.8.

The effect of ionic strength (or TDS concentration) on the dissociation of HOCl over the pH range 6.0 to 8.5 at 25°C is shown in Table 3.12; it should be noted that fully saline seawater contains around 32,000 mg/L TDS.

The influence of Ammonia : combined chlorine

Chlorination would follow the simple and predictable chemistry outlined above were it not for the presence in the water of nitrogenous compounds. Chlorine reacting with any amines (compounds containing the N atom with one or more hydrogen atoms attached) will form a molecule broadly classified as a chloramine or N-chloro compound. The terms "combined (residual) chlorine" or "combined (residual) oxidant" generally refer to such halogenated nitrogen compounds of which the most significant are the inorganic chloramines, formed by reac-

tion with free ammonia. Relatively little is known about the formation or biocidal potential of organic chloramines, since organic amino nitrogen is generally far more abundant than ammonia.

The reaction with ammonia proceeds by sequential substitution of each of its hydrogen atoms. As such, the reactions are competitive and, for practical purposes, may be considered as irreversible :

(1)(monochloramine)

(2) (dichloramine)

(3) (trichloramine/nitrogen trichloride)

The reactions are dominated by 5 factors: pH, temperature, contact time, the initial ratio of chlorine : ammonia and, most importantly, by the initial chlorine and ammonia concentrations. The first reaction is almost instantaneous at pH 8.3 and will convert all the free chlorine to monochloramine when the initial ratio is equimolar (5 : 1 by weight) or less. The other reactions are slower (several minutes), consistent with the decreased basicity of the chloramines. At higher chlorine : ammonia ratios, chloramines disappear and the TRC decreases to a minimum so-called "breakpoint" value theoretically located at the molar ratio of 1.5 (7.6 by weight) as shown in Figure 3.6.

These reactions, and the breakpoint phenomenon, are of fundamen-

Table 3.11. – Variation in percentage of undissociated hypochlorous acid (HOCl) with changing pH and temperature.

Temp pH	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C
5.0	99.85	99.82	99.80	99.79	99.74	99.71	99.68
6.0	98.53	98.28	98.00	97.73	97.45	97.18	96.92
6.5	95.50	94.75	93.96	93.16	92.37	91.60	90.87
7.0	87.04	85.08	83.10	81.16	79.29	77.53	75.90
7.2	80.91	78.25	75.64	73.11	70.73	68.52	66.52
7.4	72.78	69.42	66.20	63.18	60.39	57.87	55.63
7.6	62.79	58.89	52.27	51.98	49.03	46.43	44.17
7.8	51.57	47.48	43.81	40.58	37.77	35.35	33.30
8.0	40.18	35.32	32.98	30.12	27.69	25.65	23.95
8.2	29.77	26.46	23.69	21.38	19.46	17.88	16.58
8.4	21.10	18.50	16.38	14.64	13.23	12.07	11.14
8.6	14.44	12.53	11.00	9.77	8.77	7.97	7.33
8.8	9.62	8.29	7.23	6.39	5.72	5.18	4.75
9.0	6.29	5.39	4.69	4.13	3.69	3.33	3.05

Table 3.12. – Effect of the total dissolved solids (TDS) concentration on the percentage of undissociated HOCl.

25 °C TDS mg/L	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0	pH 8.5
0	97	92	78	52	26	10
400	96	89	73	45	22	9
4,000	95	88	67	37	17	7
40,000	94	84	60	30	13	5

tal importance when treating natural freshwaters because the combined forms are less toxic (efficacious), but are more persistent than free chlorine. Chlorination by-products

Since the discovery of the halogenation of organic matter by Rook (1974), a wide range of compounds

have been associated with the chlorination of freshwater for the production of drinking water and for the primary sterilization of effluents in sewage treatment (see Jolley *et al.*, 1983 and other Chlorination conferences Jolley *et al.*, 1976, 1978, 1980, 1983, 1986, 1990).

Fig. 3.6. – Example of a chlorination curve in freshwater containing ammonia.

The formation of organohalogenated compounds depends mainly on the organic matters present in all river and lake waters; the role of humic acids as precursors of THMs is well documented (Doré, 1989; Duvivier, 1993). On the other hand, chloramines produce less THMs, POX and AOX than free chlorine (Fig. 3.7). The major volatile compound is chloroform, but among the organics, many chlorinated compounds can be detected: chlorophenols, cyanogen chloride, chlororesorcinol, etc.

The U.S. EPA has proposed monitoring of selected CBPs when chlorine is used as a disinfecting agent for drinking water (Richardson 1997):

THMs.

Haloacetic acids, six HAAs (chloro-, dichloro-, trichloro-, bromo-, dibromo-

and bromochloro- acetic acids).

Haloacetonitriles (dichloroacetonitrile and trichloroacetonitrile, bromochloroacetonitrile, dibromoacetonitrile).

Haloketones (1,1-Dichloropropanone, 1,1,1-trichloropropanone).

Chloral Hydrate.

Chloropicrine.

Finally, traces of bromates are found in sodium hypochlorite solutions; 2 to 5 mg BrO_3^- per g of chlorine.

Chemistry of chlorine in seawaters

Free oxidant chemistry

When added to seawater, chlorine oxidizes the bromide ions (68 mg/L bromide at full salinity), yielding hypobromous acid (HOBr). This reaction is rapid, with 99% conversion within 10

Fig. 3.8. – Comparison of the dissociation of hypochlorous acid and hypobromous acid with changing pH at 20 °C.

seconds at full salinity and within 15 seconds even at half salinity (Hergott *et al.*, 1978).

Thus in seawater, the free oxidants are predominantly composed of HOBr and the hypobromite ions OBr⁻

The dissociation of hypobromous acid depends on the same factors as the dissociation of hypochlorous acid, however the HOBr acid remains undissociated at higher pH values than for HOCl (Fig. 3.8). This implies that, at the pH of seawater (8.0 to 8.2), the free oxidant (HOBr) is essentially undissociated and consequently more efficient as a biocide than the dissociated OCl⁻ in the same range of pH in freshwater.

Where ammonia levels are high with respect to the chlorine dose, a competitive reaction of HOCl to ammonia leads to the formation of monochloramine (NH₂Cl). Moreover, HOBr reacts rapidly with any NH₂Cl that has been formed, yielding dibromamine NHBr₂ and a bromine-based chemistry. In coastal seawater, the brominated compounds largely dominate but a mixed chlorine/bromine system can prevail at estuarine sites with varying salinity and ammonia levels.

In seawater containing ammonia, the combined oxidants formed by chlorination are monobromamine NH₂Br, dibromamine NHBr₂ and tribromamine, and a breakpoint curve similar to that of freshwater is found in chlorinated seawater (Fig. 3.9). In this case however, the combined oxi-

Fig. 3.9. – Experimental chlorination of seawater from the Gravelines power station intake canal. N- ammonia = 0.21 mg/L, contact time 20 min. (Allonier & Khalanski 1997).

dants are brominated compounds but the chlorine : ammonia ratio is the same : 5.0 at the maximum of combined TRO and 7.6 at the breakpoint.

A second feature of bromine chemistry is that bromamines, unlike chloramines, interconvert rapidly and reversibly. NHBr_2 decays rapidly, as does NHCl_2 , but unlike NHCl_2 it does not form a persistent monohalamine at seawater pH. This high oxidative reactivity leads to claims that bromo-compounds are more potent biocides than their chlorine analogues.

Formation of by-products

In seawater, global analysis of EOX and POX gives poor results in the range of low concentrations ($\leq 40 \mu\text{g/L}$), probably due to interference with chlorides (Allonier 1996). Chromatography is therefore needed to measure organohalogenated compounds in low concentrations.

The chemistry of oxidant species in seawater is dominated by brominated compounds and, consequently, the major organohalogenated compounds produced by chlorination of seawater are also brominated. Experimental data (Abarnou, 1979) have shown that the major THM is bromoform CHBr_3 , with a molar formation yield of a few % of added chlorine.

A long-term survey of the THM level at the Gravelines power station, operated by EDF on the North Sea coast, confirms this yield but shows consistent variations due to water quality changes and, more importantly, the ammonia content of the coastal water (Fig. 3.10).

The linear regression fitted on the data from Penly and Gravelines corresponds to a bromoform formation yield of $28.6 \mu\text{g/L}$ for a 1 mg/L injection of chlorine. The formation yield of bromoform, based on weight, is thus

Data from PENLY 1993-1996 and GRAVELINES 1995-1996.

Fig. 3.10. – Bromoform in chlorinated seawater with changing chlorine dosage at the Penly and Gravelines power stations. Data from measurements taken by Institut Pasteur de Lille and the EDF Environment Department.

Fig. 3.11. – Average distribution of organohalogenes measured by gas chromatography in seawater chlorinated at 0.8 mg/L at the Gravelines power station. EDF DER data (Allonier & Khalanski, 1997).

Table 3.13. – Bromoform and dibromoacetonitrile at the outfall of selected marine European power stations, mean $\pm$ 95 %. Chlorine dosage in the range of 0.3 to 1.5 mg/L. (Jenner *et al.*, 1997).

Power station	Period	Bromoform ($\mu\text{g/L}$)	DBAN ($\mu\text{g/L}$)
Heysham (UK)	11/08/92-15/12/92	29.20 $\pm$ 24.25	3.15 $\pm$ 3.59
	12/01/93-07/09/93	23.00 $\pm$ 8.24	2.12 $\pm$ 1.08
Dungeness (UK)	03/08/93	5.75	0.20
Wylfa (UK)	21/09/93	27.00-27.50	0.79-0.87
Bradwell (UK)	19/10/93	25.00	0.87
Hartlepool (UK)	17/08/93	3.50	< 0.10
Sizewell (UK)	23/08/93	14.50	< 0.10
Penly (France)	27/05/93-18/08/93	13.37 $\pm$ 4.17	NA
	21/06/94-27/07/94	15.01 $\pm$ 3.22	NA
Paluel (France)	14/10/92	3.10 – 9.65	0.10 – 1.05
Gravelines (France)	03/05/93-25/10/93	18.63 $\pm$ 3.70	NA
Maasvlakte (NL)	02/07/92-22/10/92	11.54 $\pm$ 5.40	0.83 $\pm$ 0.56
	16/05/93-10/08/93	8.35 $\pm$ 12.35	0.94 $\pm$ 1.22

about 3% of chlorine dosage. The kinetics of THM formation in seawater is a more rapid process than in freshwater. About 80% of the final bromoform concentration is formed in three hours (Allonier & Khalanski, 1997).

Using gas chromatography, only THMs, dibromoacetonitrile and tribromophenol were detected in seawater samples from the Gravelines power station, chlorinated at 0.8 mg/L (Allonier & Khalanski 1997), giving the following average concentrations :

- bromoform : 24 $\mu\text{g/L}$,
- dibromoacetonitrile (DBAN) : 3 $\mu\text{g/L}$,
- tribromophenol : 0.3 $\mu\text{g/L}$.

The average distribution is given in Figure 3.11.

This evaluation does not take into account the haloacetic acids (HAA). Preliminary results indicate that the main HAA formed by sea water chlorination is dibromoacetic acid, at a level higher than DBAN. Nevertheless, bromoform remains the major organohalogenated compound formed by low-level chlorination of sea water ($\text{Cl}_2 \leq 1 \text{ mg/L}$).

In an effort to compare the range of compounds produced under conditions of on-load chlorination at power stations, a large-scale survey was undertaken in France, the Netherlands and the UK. The study was conducted between 1992 and 1994 with the express purpose of examining as wide as possible a range of water qualities used for cooling by power stations (Jenner *et al.*, 1997). The data collected in this survey confirmed that the organohalogen produced in the lar-

gest quantity was bromoform (Table 3.13).

The results from this survey show that point-of-discharge bromoform concentrations varied from 53.45 $\mu\text{g/L}$ (Heysham) to 3.1 $\mu\text{g/L}$ (Paluel) and dibromoacetonitrile concentrations from 11.39 $\mu\text{g/L}$ (Heysham) to 0.1 $\mu\text{g/L}$ (Paluel). Other compounds detected in the surveys at discharge were bromodichloromethane and dibromochloromethane, with concentrations of 0.8 and 0.7 $\mu\text{g/L}$ respectively at Maasvlakte and Heysham; 2,4,6-tribromophenol at 0.25 $\mu\text{g/L}$ (Heysham) and 0.29 $\mu\text{g/L}$ (Maasvlakte) and 2,4-dibromophenol at 0.055 $\mu\text{g/L}$ (Dungeness). These large discrepancies can primarily be explained by differences in chlorine dosage or dilution with non-chlorinated cooling water, and secondly by differences in water quality.

3.7.1.3 Measurement of residual oxidants

Chlorine residuals may be measured in the laboratory using several techniques, including amperometric and potentiometric titration, colorimetric titration using the FAS-DPD (Ferrous ammonium sulfate/DPD) method and colorimetry. Field determinations are usually colorimetric since most titration equipment is insufficiently robust for field use; indeed, it can be argued that since titrimetric methods offer little if any improvement in precision and accuracy over colorimetric methods, there is not much of a case to be made for them. Brief descrip-

tions of the principal methods and their limitations are given in White (1986) and in APHA-AWWA-WPCF (1992).

The methods were developed for potable water where quality (colour, odour and taste) is almost as important as microbial purity. Consequently, great emphasis is attached to the ability of the various methods to discriminate between the products of chlorination, particularly between free and combined forms. These distinctions are largely irrelevant to cooling water chlorination – and even to environmental monitoring – where the merits of the various methods may be judged on the more basic criteria of practicability and reliability. Information on a probe designed for combined measurements of biofilm growth and chlorine dosage is given on section 3.11.

DPD is the only colorimetric method capable of differentiating chlorine residuals; Syringaldazine is responsive only to free residuals. In the absence of iodide ions, free available chlorine reacts instantly with DPD to produce a red colour. Subsequent addition of a small amount of iodide causes monochloramine to produce colour, while addition of excess iodide activates dichloramine as well. Since iodide is already present in seawater, it follows that free 'chlorine' cannot be estimated without some breakthrough from halomines.

All small portable water test kits now on the market will handle chlorine by colorimetric DPD. The great advantage of portable kits is that the

samples can be tested without delay, which is of crucial importance in view of the loss of chlorine from seawater samples through decay reactions. DPD reagents are available as compressed tablets in foil or as sachets of powder. The tablets are stable for a year or more, depending on conditions of storage, but should be discarded if the white tablet shows brown or greasy mottling. Liquid reagents are no longer available commercially prepacked in dropper bottles but can be made up from stock. The shelf life of the DPD component is comparable with that of tablets.

Small photometers using a standard 10-15 mm cell can theoretically read down to 0.01 mg/L TRO (10 mg/L). Visual comparison, using 113 mm path length Nessler cells, also reads down to 0.01 mg/L TRO but it is possible to extrapolate a value 0.01 mg/L TRO (i.e. TRO between zero and 0.01). The FAS-DPD titration has a lower limit of 18 mg/L. Potentiometric titration limits depend very much on the type of electrode employed but are around 10 mg/L. Amperometric titration can be improved from 30 mg/L (manual titration) to 10 mg/L with a recorder and to 2 mg/L with a polarograph.

In practice, several factors complicate measurement of residual oxidants in natural waters :

— interferences : most methods for determining TRO are sensitive to other compounds present in the water such as metals or oxidants that have neither antifouling value nor potential for environmental harm; in the Loire,

the interferences measured by colorimetric DPD reach 0.15 mg/L TR;

— turbidity and water colour are of particular importance for the use of colorimetric methods;

— water temperature : the response of electrochemical methods depends on the water temperature and, to a certain extent, on the conductivity of the water.

As a result, laboratory calibrations are generally much better than field measurements due to the respective sensitivity and accuracy of the methods. In practice, the quantitative measurement threshold for colorimetric DPD can generally not be lower than 0.02 mg/L in FRC; it frequently happens that the variability of the blank gives a threshold of 0.05 mg/L. While electrochemical methods always produce a signal related to the oxidants present in the sample to be analyzed, they also have limitations in natural waters, and the theoretical threshold of 0.01 mg/L (10 µg/L) is rarely reached.

Due to these limitations, it is recommended to perform a series of field measurements in order determine the quantitative threshold corresponding to natural waters of a given quality.

Continuous monitoring

Regulatory authorities are in favour of continuous records for discharges – particularly as an adjunct to self-monitoring. At present, there would appear to be no really satisfactory instrument for use with raw freshwater,

let alone seawater. Some instruments are totally unsuited to seawater use, either by virtue of materials or process. The instrument must be capable of accommodating variations in salinity, temperature and suspended solids and, at the lower TRC levels, must be able to withstand bacterial slimes growing on their internals or be self cleaning. Nearly all the instruments currently available can be made to work; there is, however, a world of difference between this labour-intensive situation and continuous monitoring. The lower limits of detection are effectively 0.05-0.10 mg/L (50-100 µg/L). The concept of using monitoring not merely for simple recording but actually for reliable feedback control of chlorine injection is therefore not realistic.

There do, however, exist analyzers based on semi-continuous colorimetric DPD measurement of free and total oxidants which give satisfactory results. The devices must nonetheless be regularly checked, the tanks cleaned and the measurement systems recalibrated.

3.7.1.4 Experimental data on the efficacy of chlorine

Freshwater biofouling

Bacterial slime

Continuous low-level chlorination was found effective in tests carried out from July to November with Lake Erie water at concentrations as low as TRC = 0.1 mg/L (Ewans *et al.*, 1992). In this experiment, discontinuous chlorination treatments for 30

minutes every 12 hours was not effective: substantial biofilm growth was seen at all dosages from 0.5 mg/L to 1.5 mg/L.

Zebra mussels

Much experimental data is available on the effect of different protocols in treatment of zebra mussels: continuous, intermittent and shock chlorination.

Table 3.14 gives the data on continuous low-level chlorination. These data, presented graphically in Figure 3.12, clearly show an influence of water temperature on the exposure time needed to kill from 90% to 100% of the Zebra mussels. It must nonetheless be noted that, even at very low temperatures (0-4 °C), chlorination causes partial mortality in the long term.

Age has little influence on the lethal dose: juveniles (1 to 5 mm) respond like adults (> 10 mm). Considerable differences are observed in the experimental results, particularly at the lowest concentrations.

Furthermore, the minimum exposure time reaches a plateau at 5 to 7 days at the highest concentrations and temperatures. For water temperatures ≥ 15 °C, a continuous exposure time of 3 weeks kills all the exposed mussels.

Data from Van Benschoten *et al.* (1993) on mortality of zebra mussels exposed to a TRC level of 0.5 mg/L indicate that the 95% mortality level is reached in about 42 days at 10 °C, but in only 7 days at 25 °C. The following equation has been fitted for

Table 3.14. – Mortality of adult and juvenile zebra mussels exposed to continuous low-level chlorination.

Experimental conditions: TRC (mg/L)		Exposure time t (days) Mortality rate M (%)		Reference	
Thames River. Adults					
T = 10 °C	0.5	t = 7 d	M = 5 %	Greenshield & Riedley, 1957	
T = 10 °C	2.0	t = 7 d	M = 20 %		
T = 10 °C	5.0	t = 7 d	M = 40 %		
T = 21 °C	0.25	t = 7 d	M = 40 %		
T = 21 °C	0.5	t = 7 d	M = 70 %		
T = 21 °C	2.0	t = 7 d	M = 100 %		
Seine river					
Shell length : 28-30 mm	0.2	t = 19 d	M = 99 %	Garric & Migeon, 1983	
	0.5	t = 15 d	M = 99 %		
	1.0	t = 12 d	M = 99 %		
T = 22 °C	0.1 to 10.0	M = 99 % $t = (-9.69 \cdot \text{Log TRC}) + 11.92$			
Meuse river. Adults					
T = 14.5 °C	0.3	t = 44 d	M = 0 %	Gillet & Micha, 1985	
	1.1	t = 41 d	M = 65 %		
	1.5	t = 35 d	M = 83 %		
The Netherlands.					
Adults	0.25	t = 21 d	M > 90 %	Jenner, 1985	
	0.5	t = 16 d	M 93 %		
T = 12 to 15 °C	1.0	t = 14 d	M 95 %		
Niagara river. Adults					
T = 9.0 to 15.0 °C	0.2	t = 27 d	M = 50 %	De Girolamo <i>et al.</i> , 1991 in Van Benschoten <i>et al.</i> , 1993	
T = 9.0 to 15.0 °C	0.5	t = 27 d	M = 50-70 %		
T = 9.0 to 15.0 °C	1.0	t = 27 d	M = 100 %		
T = 18.0 to 21 °C	0.5	t = 9 d	M = 100 %		
Shell length : 10-15 mm					
T = 12 to 15 °C	0.5	t = 17 d	M = 93 %	Klerks & Fraleigh, 1991	
T = 12 to 15 °C	1.0	t = 15 d	M = 95 %		
T = 17 to 27 °C	0.5	t = 9 d	M = 100 %		
T = 17 to 27 °C	0.9	t = 5 d	M = 100 %		
T = 17 to 27 °C	3.0	t = 6 d	M = 100 %		
Shell length : 14-16 mm					
T = 7.2 to 17.5 °C	0.32	t = 54 d	M = 50 %		
T = 7.2 to 17.5 °C	0.62	t = 32 d	M = 50 %		
T = 4.8 to 9.5 °C	1.74	t = 17 d	M = 50 %		
T = 4.8 to 9.5 °C	4.3	t = 25 d	M = 50 %		
T = 4.8 to 9.5 °C	9.02	t = 20 d	M = 50 %		
Shell length : 2-6 mm					
T = 20 to 22 °C	0.5	t = 20 d	M = 7 %	Martin <i>et al.</i> , 1990	
T = 20 to 22 °C	1.0	t = 13 d	M = 100 %		
T = 20 to 22 °C	2.5	t = 9 d	M = 100 %		
T = 20 to 22 °C	5.0	t = 7 d	M = 100 %		
Shell length : 2-5 mm					
T = 8 to 12 °C	1.0	t = 28 d	M = 70 %	Van Benschoten <i>et al.</i> , 1993	
T = 10 to 11.5 °C	0.6 ± 0.2	t = 15 d	M = 40 %		
T = 21.5 to 24.0 °C	0.6 ± 0.2	t = 8 d	M = 100 %		
Shell length : 0.75-2.0 mm					
T = 8 to 12 °C	1.0	t = 25 d	M = 100 %		
Lake Erie. Adults					
T = 0 to 4 °C	0.3 to 0.5	t = 27 d	M = 30 %	Barton, 1990

Fig. 3.12. – Exposure time required to kill 90 to 100% of Zebra mussels exposed to continuous chlorination from data in Table 3.14.

temperatures of 0 °C to 25 °C (Fig. 3.13) :

$$\text{LOG}(\text{LT}_{95}) = 3.458 - 0.0486 \cdot T$$

LT_{95} : exposure time to achieve 95% mortality in days, T = water temperature in °C.

The effectiveness of the **combined use of heat and oxidants** – chlorine and ozone – to control adult Zebra mussels has been investigated by Harrington *et al.* (1997). It is possible to reduce the exposure time by heating the water to higher temperatures. At 30 °C, the time required to reach 95% mortality at a chlorine concentration of 0.5 mg/L is one day; at 34 °C, it is only one hour (Fig. 3.13).

At the Ontario Hydro experimental facility located on Lake Erie at Nanticoke, experiments were conducted at different intermittent chlorination regimes (Ewans *et al.*, 1992). This study produced extremely interesting results, later applied to Ontario Hydro installations.

Continuous treatments at $\text{TRC} \geq 0.3$ mg/L was efficacious : no attachment of mussels was observed in the experimental flow-through cells.

Discontinuous treatment (half an hour every 12 hours) was not effective even at higher chlorine dosages : TRC of 0.5 mg/L to 1.5 mg/L. This type of discontinuous chlorine regime also failed to kill the mussels at a Cleveland Electric Illuminating Company installation on Lake Erie with a TRC of 0.3 mg/L for 28 days (Barton, 1990).

Experiments with semi-continuous treatments have shown good results at $\text{TRC} = 0.5$ mg/L with “high-frequency treatments” : 15 minutes on/15 minutes off and 15 minutes on/30 minutes off. On the other hand, as soon as the “off” time reaches 60 minutes, efficacy drops (Wiancko & Claudi, 1994).

Some physiological responses of juvenile and adult zebra mussels to

Fig. 3.13. – Exposure times to reach 95% mortality of adult zebra mussels depending on the water temperature. Triangles : chlorination at 0.5 mg/L on mussels acclimated to the test temperature, according to data of Van Beschoten *et al.* (1993). Circles : combined effects of 0.5 mg/L chlorination and heat shocks in the range of 30 to 36 $^{\circ}\text{C}$ on mussels acclimated from 5 to 25 $^{\circ}\text{C}$, according to data of Harrington *et al.* (1997).

low-level chlorination (0.1 to 1.0 mg/L) have been investigated by Van der Velde *et al.* (1997), who measured the filtration rate, the foot activity, the byssus thread production and the strength of byssus threads at 20 $^{\circ}\text{C}$. All physiological activities are affected by continuous exposure to chlorine with a dose-dependent relationship in the range of 0.1 to 0.5 mg/L TRC. The filtration rate is reduced by 50% at 0.3 mg/L and up to 90% at 0.5 mg/L (Fig. 3.14). Juvenile mussels are slightly more affected than the adults. The filtration rate remains very low at 1.0 mg/L TRC : 5% to 9% of the control.

Shock chlorination has been tested by Khalanski (1993) on adult zebra mussels (17-22 mm). In this static ex-

periment, it was necessary to apply two successive shocks of 24 hours each, at 200 mg/L chlorine dosage, to kill 100% of the tested mussels over 9 days. In 24 hours, the chlorine concentration decreased from 200 mg/L to 30 mg/L.

Asiatic clam

According to Doherty *et al.* (1986) and Ramsey *et al.* (1988), *C. fluminea* could be killed by continuous chlorination for two to three weeks at concentrations of 0.5 mg/L total residual chlorine (TRC). It must be noted that water temperatures were relatively high (20-25 $^{\circ}\text{C}$).

Table 3.15. – Data on zebra mussel attachment on flow-through cells after exposure to intermittent chlorination regimes. (Evans *et al.*, 1992, Wiancko & Claudi, 1994). The values in parentheses correspond to percentages of attached mussels after 10 weeks compared to the control.

TRC (mg/L)	Exposure time	Efficacy	
		On zebra mussels	On biofilm
0.1	Continuous	Inefficacious ($\geq 50\%$)	Inhibition
0.2	Continuous	Some efficacy (10%)	Inhibition
0.3	Continuous	Efficacious (0%)	Inhibition
0.4	Continuous	Efficacious (0%)	Inhibition
0.5	Continuous	Efficacious (0%)	Inhibition
0.5	30 min. every 12 hours	Inefficacious ($\geq 50\%$)	Substantial biofilm
1.0	30 min. every 12 hours	Inefficacious ($\geq 50\%$)	growth
1.5	30 min. every 12 hours	Inefficacious ($\geq 50\%$)	
0.5	15 min. on/15 min. off	Efficacious	Inhibition
0.5	15 min. on/30 min. off	Efficacious	Inhibition
0.5	15 min. on/45 min. off	Some efficacy	Inhibition
0.5	30 min. on/60 min. off	Some efficacy	Inhibition

Brackish waters

On the brackish mussel *Mytilopsis*, exposure times for 100% mortality with chlorination show a size-dependent effect; 2-mm mussels require 29 days and 10-mm mussels, 36 days using 1.0 mg/L TRO (Table 3.16). Filtration rate, foot activity and byssus thread production were reduced in proportion to the increase of the applied chlorine dose below 1.0 mg/L TRC (Rajagopal *et al.*, 1994). This species is significantly more resistant to chlorination than the mussel, *Brachidontes striatulus*; tests in Madras (India) also showed a high resistance to chlorine (Table 3.16).

Marine mussels *Mytilus edulis* and *Mytilus galloprovincialis*

Trials using continuous chlorination in the range of 0.2-1.0 mg/L total residual oxidant (TRO) showed that total mortality requires periods of treatment between 15 and 135 days, according to Lewis (1983 a and b). (Fig. 3.16).

Temperature was the driving parameter in this toxicity model when TRO fell below 1.0 mg/L. Data based on this model show an almost tenfold decrease in the time required to kill when comparing mortality at 10 and 25 °C (Table 3.17).

Table 3.16. – Data on lethal chlorine doses for two species of brackish water bivalves.

Species	Temperature	TRC (mg/L)	Exposure time (days)	Mortality rate M (%)	Reference
<i>Mytilopsis leucophaeata</i> 10 mm The Netherlands	T = 20 °C	1.0	t = 36 d	M = 100 %	Rajagopal <i>et al.</i> , 1994
	T = 20 °C	2.5	t = 23 d	M = 100 %	
	T = 20 °C	5.0	t = 15 d	M = 100 %	
	T = 20 °C	10.0	t = 7 d	M = 100 %	
<i>Modiolus modiolus</i>	T = 29-30 °C	1.0	t = 11 d	M = 100 %	Rajagopal <i>et al.</i> , 1997b
<i>Brachidontes</i> (<i>Modiolus</i>) <i>striatulus</i> India	T = 29-30 °C	1.0	t = 24 d	M = 100 %	
	T = 29-30 °C	2.0	t = 15 d	M = 100 %	
	T = 29-30 °C	3.0	t = 10 d	M = 100 %

Fig. 3.14. – Effect of water chlorination on the filtration rate of *Dreissena polymorpha* juveniles (5.6 mm) and adults (10.3 to 20.1 mm) at 20 °C. Redrawn from data of Van der Velde *et al.*, (1997).

A comparative study of the efficacy of two chlorination levels was conducted at the Gravelines plant from May to November in 1983 and 1984 (Tra-

vade & Khalanski, 1986). During this field experiment, settlement, growth and mortality of larvae were monitored in spat monitors supplied with wa-

Table 3.17. – Data for the time (in days) required for 100% mortality at various temperatures and two TRO levels, from Lewis (1983a).

Temperature (°C)	10	15	20	25
TRC				
0.2 mg/L	788	369	172	81
0.4 mg/L	451	211	99	46

Fig. 3.16. – Plot of TRO against time for continuous chlorination regimes (injection level) with zone of 100% mortality indicated by lines of temperature for residual and exposure (after Lewis, 1983 a,b).

ter taken from two circuits chlorinated at 0.8 mg/L and 0.4 mg/L with mean TRO concentrations of respectively 0.49 mg/L and 0.29 mg/L. The results summarized in Table 3.18 confirm Lewis's model of adult mussels: they

survive in the long term (5 months) when exposed to relatively high TRO levels, even though growth is stopped.

On the other hand, observations using spat monitors show clearly that recently settled mussels are far more

Table 3.18. – Comparison of the efficacy of two continuous low-level dosages over a 150-day period on *Mytilus edulis* spat and adults at Gravelines (Travade & Khalanski, 1986).

Chlorine dosage mg/L	TRO mg/L	Spat (< 5 mm)			Adults (> 10 mm)	
		Settlement	Growth	Detachment and mortality	Growth	Mortality
0.8	0.49	none	none	90 to 95 % in 20 days. 100 % in 30 days.	none	≤ 25 % in 150 days.
0.4	0.29	less than in the control	none	50 to 71 % in 15 days. ≤ 30 % remain settled in 150 days.	no data	no significant mortality in 150 days.

sensitive to residual oxidants : spat do not grow and a large proportion detach or die in 20 to 30 days at 0.49 mg/L TRO ; at 0.29 mg/L TRO, growth is also inhibited and half the spat detach in 15 days, though up to 30 % still remain in 150 days. In conclusion, continuous chlorination in low concentrations is more effective on recently settled juveniles than on adults ; it should be performed as soon as they begin to attach. Continuous treatment with a TRO of 0.1 mg/L for one week in the spring, during the period of mussel (*M. edulis*) larva settlement, is sufficient to reduce the density of spat fifteenfold, according to experiments conducted at the Astoria power station (NY, U.S.A.). In these tests, barnacles (*Balanus eburneus*) proved more resistant to chlorination than mussels (Sarunac *et al.*, 1994).

Continuous low-level chlorination (dosage ≤ 1.0 mg/L) has the effect of eliminating mussels due to two processes (Khalanski & Bordet, 1981) :

— a major decrease in the water filtration rate, which deprives the mussels of food,

— progressive intoxication by oxidant compounds absorbed with the small amounts of seawater necessary to survival of the mussels.

Measurements performed on adults show that the filtration rate is reduced by 60 % at TRC = 0.2 mg/L. In 35 to 45 days at this dosage, we find a 70 % decrease in the growth rate of juveniles, according to Bucaille (1981) (Fig. 3.17).

In continuous low-level chlorination, the effect is to reduce filtration and thus food intake and cause the mussels to use up their food reserves and tissues until their body weight is so reduced that they are unable to continue filtration and die.

The availability of food for mussels, and for filter-feeding organisms in general, determines to a large degree their resistance to chlorination. In a

Fig. 3.17. – Reduction of the filtration rate for adults and growth reduction for juvenile blue mussels (*Mytilus edulis*) exposed for 35 to 45 days to continuous chlorination. Redrawn from previous data by Khalanski (1995).

food-rich environment, the mussels can withstand a substantial reduction of their filtration rate while maintaining rapid growth, and this is the case in certain coastal areas. In water with scant food supply, any reduction in filtration activity will affect growth.

The most favourable conditions for the development of mussel populations are eutrophicated waters, as found in some parts of the English Channel and the North Sea coasts. The Mediterranean coasts are normally very poor in food for filter-feeding organisms but some harbour areas, such as La Spezia, Naples and Brindisi in Italy, are very rich and suitable for mussel growth.

Intermittent chlorination

In waters rich in food particles, discontinuous treatments of a few hours per day or a few days per month at high concentrations (3 to 5 mg/L) do

not kill mussels, which merely close their shells during the treatment.

On the other hand, semi-continuous treatments can kill mussels in nourishment-poor waters due to trophic limitation: an 8-hour treatment each day can be sufficient to halt mussel growth.

Finally brief, frequently repeated chlorine shocks are extremely disturbing for mussels, as they do not recover their filtration capacity immediately following the shock (Khalanski & Bordet, 1981). To optimize the effect of reduced filtration, it is advisable to suspend treatment for less than one hour, which corresponds to experimental findings for zebra mussels (Wiancko & Claudi, 1994).

In 1997-1998, KEMA developed a new system to optimize a chlorination regime called Pulse-chlorination®. This system is based on the exact

measurement of the valve movement behaviour of mussels with the Moselmonitor[®]. Pulse-chlorination[®] uses the recovery period of the mussel species to be mitigated. By short chlorination periods, alternating with periods without chlorine (i.e. recovery periods), the mussels will experience the total period as continuous chlorination. Reduction in hypochlorite is possible of 50 %, and even 75 % reduction is expected, compared with continuous chlorination.

Barnacles

As there are several species of barnacles which colonize surfaces in cooling systems, those for which treatment data are available will be mentioned on a species-by-species basis. First, unnamed adults tolerated residuals of 1.0 mg/L for up to 15 days, though 75% of them survived only 5 days (Turner *et al.*, 1948). *Elminius modestus*, showed growth inhibition at chlorine residuals of 1.0 mg/L and above, with partial growth limitation at 0.5 mg/L, leading to the deduction that free chlorine in excess of 0.5 mg/L causes heavy mortalities and a marked reduction in growth of survivors (Waugh 1964). This agrees with other data showing 80% average mortalities using *Balanus improvisus* with 5-minute exposures to 2.5 mg/L total chlorine (McLean 1973). In general, it has been found throughout Europe that when mussels are controlled by chlorination, no operational problems are caused by barnacles.

3.7.1.5 Chlorine use at industrial sites

Bacterial slime in cooling water systems

Cooling water circuits of power stations on rivers are generally equipped with on-line sponge ball cleaning systems which control bacterial slime perfectly.

At marine sites, bacterial slime in heat exchangers is controlled using different types of treatments depending on the potential growth of bacteria.

In France, continuous low-level chlorination at ≥ 0.2 TRC at the inlet of the heat exchangers is efficient during the spring and summer months (May to November) at the EDF power stations located on the English Channel. Using this procedure to eliminate macro-biofouling, no additional cleaning system is required at these sites. However, in areas where the bacterial slime is very high, as in some harbours or at Gravelines on the French North Sea coast, it is necessary to combine continuous low-level chlorination with an on-line sponge ball cleaning system.

Discontinuous treatments are efficient in waters with low amounts of organic matter, as at the EDF Martigues-Ponteau power station on the Mediterranean coast, where a chlorine dosage at 3.0 mg/L for one hour every eight hours was successfully applied. At the Maasvlakte power station, Rotterdam, a semi-continuous treatment (4 hours on/4 hours off) at 0.2 to 0.3 mg/L TRC is used to control

both macro- and micro-biofouling. According to the experience of KEMA in the Netherlands, micro-biofouling can be generally controlled by dosing hypochlorite at 0.5 mg/L TRC for 30 minutes a day. A specific condenser biofouling treatment has been designed by EPRI, so-called "targeted chlorination", consisting in injecting a relatively high chlorine dose (1 mg/L TRC) at the inlet of the condenser for a few minutes each day (Mussali *et al.*, 1985). The water box of the condenser is divided into zones; injection nozzles are placed in each zone to treat the tubes in that zone selectively. The zones are chlorinated alternately and the chlorine consumption can be reduced by more than 80% compared to conventional mass chlorination (Thompson *et al.*, 1994). This system is perfectly suited to protection of condensers, but has the disadvantage of not protecting other parts of the cooling circuit, especially against macro-biofouling.

Shock chlorination of recirculating circuits

In large natural cooling towers, algae tend particularly to develop in three areas:

- on the inner surface of the shell, all the wet parts exposed to some light are covered with a layer of Cyanobacteria (Blue-green algae) whose detachment during the shutdowns leads to a great input of organic matter in the packing,

- on the parts of the honeycomb packing structure exposed to light, essentially at the base; here again, they

are Cyanobacteria in addition to filamentous green algae and a great deal of microalgae,

- in cold-water basins, on all concrete walls and pillars, Cyanobacteria and filamentous green algae can be very abundant.

In the 1980s at inland power stations operated by the CEGB in the UK, periodic changes of the packing elements within the tower shell were carried out to reduce the exposure time of packing to light. Discontinuous chlorination is the second control method used by CEGB. For this type of treatment, it is necessary to raise the water level in the tower ponds so there is no need to add make-up water or to purge the system during the course of treatment. When the water is at its highest operational level, hypochlorite is added to give a residual of 2.5 mg/l TRC to be maintained over a period of 24 hours or until the residual level has fallen to the permitted discharge level (Blank 1984). This method kills the outer layers of the encrusting algae, turning the filaments white, but does not kill the deepest layers of horizontal filaments adhering to the timber slats. When the dead filaments have been washed off, the horizontal filament system is once again exposed to the flow of cooling water and growth begins again.

A discontinuous mass chlorination process was implemented by EDF to prevent or eliminate algae in the cold-water basins. To avoid the discharge of residual chlorine and to ensure more efficient cleaning, the blowdown is shut down for a few hours and

Table 3.19. – EDF mass chlorination procedure used in some cooling towers to eliminate algae (Lutz & Merle, 1983).

TREATMENT STEPS	TIMING
Set-up — Make-up flow stopped — blowdown suppressed — water level lowered in the basin	2 to 3 hours
Hypochlorite injection Dosage 20 to 40 mg/L as chlorine	10 to 30 minutes
Oxidant decay Down to 0.1 mg/L as free residual chlorine Duration dependent on fouling and operating temperature Water level regulation through intermittent makeup	From 6 hours in hot water to 10 hours in cold water
Analytical control Using DPD colorimetric method	Semi-continuous measurements
Return to normal service Continuous make-up flow	< 1 hour

make-up flow is regulated to balance the loss through evaporation and maintain a constant level in the basin (Lutz & Merle, 1983). The typical process of this type of mass chlorination treatment is described in Table 3.19.

Mass chlorination is used to control algae as required at EDF-operated power stations: once a year on average, one or two treatments are performed at three sites. The chlorine concentration can be decreased at some sites, where 8 mg/L is sufficient. This type of mass chlorination was also performed in Belgium to clean the packing of a cooling tower fouled by organic deposits.

Continuous and semi-continuous treatments on freshwater

Experimental data have shown that, depending on water temperature

and condition of the mussels, *Dreissena polymorpha*, the Zebra mussel, can be killed in a few weeks with continuous low-level chlorination (Fig. 3.12). As Jenner & Janssen-Mommen (1993) explain, it is recommended to chlorinate at water temperatures – 15 °C to keep the duration of treatment as short as possible, but the threshold temperature can be lowered to 12 °C according to some industrial experience in the Netherlands. If we assume that "low-level" means TRC from 0.2 to 0.5 mg/L, the following envelope for the duration of continuous chlorination treatment can be proposed:

For water temperatures ≥ 12 °C
— at TRC of 0.2 to 0.3 mg/L, the treatment time is 28 days,
— at TRC of 0.4 to 0.5 mg/L, the treatment time is 21 days.

The chlorination period should be scheduled at the end or after the re-production period to ensure that no 'new' spat will enter the system.

In the Netherlands, continuous low-level chlorination is used to treat large cooling water systems in petrochemical plants and power stations for two to four weeks after the mussel settlement period; this treatment, called "autumn chlorination", begins in mid-September (Jenner 1985, Jenner & Janssen-Mommen, 1993).

At the Monroe drinking water plant and the Monroe power station on Lake Erie, continuous chlorination at 0.5-0.6 mg/L TRC has been applied from June to November to eliminate Zebra mussels (Lepage 1993, Kovalak *et al.*, 1993).

Hydro Quebec implemented periodic chlorination at the Beauharnois Hydropower plant, with two 30-day treatment periods, in spring and autumn, at a dosage of 2 mg/L TRC.

All dead mussels are small enough to pass through the cooling system without blocking the condenser tubes. Care should be taken in situations when the mussels are clustered and, after death, fall from the wall in small clumps and block the tubes. Even after death, the mussel shells are clustered because the byssus is not degraded. If settlements are dense and successional, there is a danger that one treatment will not be sufficient to protect the cooling system, so additional chlorination treatments may be necessary.

At the Dampierre-en-Burly power station on the Loire, equipped with cooling towers, a two-month (July-August 1996) continuous chlorination with a TRC of 0.3 mg/L resulted in total elimination of bryozoans, Zebra mussels and gastropod molluscs (*Physa* and *Bithynia*) from the cold water basins.

The treatment can be optimized and adapted to a given site by means of biomonitoring. A spat monitor can detect settlement peaks in the intake water and the chlorination time can be reduced by monitoring the survival of samples of mussels in test cells.

Since 1994, **semi-continuous chlorination** has been implemented at Ontario Hydro plants to eliminate Zebra mussels using the following procedure developed on the basis of experimental findings :

- chlorine dosage : TRC = 0.5 mg/L,
- chlorine addition regime : 30 minutes on, 45 minutes off,
- treatment throughout the Zebra mussel growing season.

Control of macro-biofouling in marine cooling water systems

As is clear from experimental data, the treatment procedure must be designed in light of two major criteria :

- the reproduction period, which determines larval settlement for a more or less long period in the year,
- the growth rate, which determines the size reached by the organisms by a given time after settlement.

These two biological processes are dependent on the thermal regime; in the English Channel, for example, barnacles settle in early spring, sooner than the mussels which begin to settle at the end of spring. It has been shown that growth of natural mussel populations does not start until the seawater temperature is above 12 °C (Bayne (ed.), 1976). This winter growth halt is mainly due to immersion of the mussels at low tide. Populations settled in cooling water circuits which are constantly underwater may have strong winter growth rates.

Continuous low-level chlorination

Water temperature is often adopted as the criterion for starting and stopping continuous low-level chlorination in the Channel and the North Sea. Continuous chlorination is performed in EDF-operated plants for as long as the temperature of the seawater exceeds 10 °C or 12 °C, with a chlorine dosage of 0.5 to 1.0 mg/L depending on the site. The objective is to keep a TRC level of 0.2 to 0.4 mg/L at the inlet to the condensers and auxiliary exchangers. This represents a long period of treatment: 7 to 8 months per year in the Channel and North Sea.

The use of low-level dosing has important consequences for the operational staff in power stations. It is evident that the dosing equipment must be well-maintained in order for the supply of chlorine, from whatever source, to be sustained for periods of at least 200 days per year. As breakdowns are inevitable but usually

unforeseen, guidance is required on the outage times permitted for completing maintenance of the dosing equipment. This is not a problem, provided the total time without chlorine in any annual dosing period does not exceed 30 days. Within this annual outage total, no single outage exceeding 15 consecutive days without chlorination is allowed. This maximum allowance is related to the growth of newly-settled mussels, which will not reach a length greater than 10 mm in 15 days and therefore will not block condenser tubes (19.0-mm diam.).

Auxiliary circuits are generally protected by means of chlorinated water derived from the main cooling system. It is recommended to ascertain that the residual chlorine level remains below the minimum required concentration. If this is not the case, the best solution is to have separate chlorine injection systems for the auxiliary circuits (Whitehouse *et al.*, 1987).

These are of two main types, offshore and onshore intakes. In the case of offshore intakes, there are one or more tunnels of varying length and the chlorine distribution pipework is usually located as close to the point of ingress of the water as possible; the water transit time to the condenser generally exceeds 20 minutes. Where onshore intakes are used, the water transit time from the distribution point to the condenser inlet is about 5 to 10 minutes. This means that the dose needed at the onshore intakes will be lower than that used for offshore intakes.

Engineering design recommendations for implementation of chlorination at marine power stations may be found in Whitehouse *et al.*, 1985. Among these, the following should be noted :

- the distribution device must be placed at the water intake far enough upstream of the fixed bar screens to give adequate protection,

- all injectors must distribute the same quantity at all dosing points,

- at the dosing point, the best achievable mixing of the hypochlorite solution in the cooling water is required to avoid zones with low chlorine concentrations,

- the injection rate must be adjustable, requiring in turn that the flow and the concentration be measured with good precision.

Semi-continuous chlorination

The DOW Chemicals plant at Terneuzen (the Netherlands), located on the Escaut estuary north of Antwerp, uses three types of antifouling treatments on cooling circuits : semi-continuous low-level chlorination of circuits with constantly flowing water, targeted chlorination of the tubular heat exchangers and intermittent chlorination of still water zones. The regime for semi-continuous chlorination is 30 minutes on / 30 minutes off with a TRC of 0.2 to 0.3 mg/L.

The fact that high-frequency semi-continuous chlorination reduces the amount of chlorine needed prompted EDF in 1997 to change the conti-

nuous chlorination regime at Flamanville to the following semi-continuous regime : 30 minutes on / 30 minutes off at 0.5 mg/L. The limited growth of mussels on this site is a positive element in favour of this regime, which was found to be effective, saving 50 % of chlorine from May to November.

At the Maasvlakte power station in Rotterdam, semi-continuous hypochlorite dosing, 4 hours on / 4 hours off, is applied when the water temperature is above 12 °C, with a TRC of 0.25 to 0.35 mg/L at the condenser inlet. Continuous dosing is applied when mussel spat are detected, using a spat collector. The mussel settlement period is usually June-July on the Dutch coast. After the mussel spat period, chlorination returns to a semi-continuous regime (4 hours on / 4 hours off). Chlorination is stopped when the water temperature falls below 12 °C.

Discontinuous chlorination

At the Martigues-Ponteau plant on the French Mediterranean coast, a discontinuous chlorination protocol has been implemented with success on both *Mytilus galloprovincialis* and bacterial slime :

- from November to April, sodium hypochlorite injection for one hour per day at 2.5 to 3.0 mg/L,

- from May to October, sodium hypochlorite injection for one hour every eight hours at 2.5 to 3.0 mg/L.

Fig. 3.18. – Toxicity thresholds for aquatic organisms exposed to residual chlorine (Mattice & Zittel, 1976).

The success of this treatment is due to the low growth rate of macro-biofouling species, and especially of mussels, on this site with scanty nourishment for bivalves.

At other sites, however, discontinuous treatments have failed (Anderson & Richards, 1966) due to the rapid growth rate of local mussel populations. At the Dunkerque plant on the French North Sea coast, for example, chlorination was performed from 1969 to 1971 according to the following protocol (Lagouche & Guillon, 1976):

- two periods of continuous chlorination at 1.0 mg/L at the injection point, from May 15 to June 20 and from September 1 to October 15,

- the rest of the year, two 20-minute injections per day at 5.0 mg/L.

In 1971 at this plant, 360 m³ of mussels (*Mytilus edulis*) had to be removed from the pumping station and

the water intake tunnel. Since then, continuous low-level chlorination has been performed from May to November.

3.7.1.6 Environmental assessment of chlorination

The complex chemistry of chlorine in natural waters was discussed earlier (paragraph 3.7.1.2) and two major categories of compounds were distinguished: oxidants and non-oxidants. The distinction between these two chemical categories is important to the evaluation of ecotoxicological risk. They have neither the same lifetime, nor the same capacity for bioaccumulation, nor the same toxicity for aquatic organisms.

Oxidants disappear more rapidly than non-oxidants; they are not bioaccumulated, but are nonetheless toxic in low concentrations. Chlorine

Table 3.20. – Some bromoform bioaccumulation factors in freshwater fish.

Species	Bioaccumulation factor	References
<i>Lepomis macrochirus</i>	0.8	Barrow <i>et al.</i> , 1980
<i>Lepomis macrochirus</i>	0.2 – 0.4	
<i>Micropterus salmoides</i>	0.5	Anderson & Lusty, 1980
Cat fish	0.5 – 0.6	
Common trout	0.5 – 1.0	

by-products – CBPs – are, in the main, more persistent; some are accumulated in animal fats; they are not toxic in the short term, but some are mutagens and carcinogenic.

Freshwater chlorination

Chlorination of freshwaters leads to the formation of essentially chlorinated compounds.

Chlorine consumption in river water due to reactions with ammonia and dissolved organic matters is high, and a rapid decay of the TRC is observed in chlorinated waters. In once-through cooling circuits treated by low-level chlorination, at a TRC ≤ 0.5 mg/L at the heat exchanger inlet, the residual at the circuit outlet does not generally exceed 0.1 mg/L. In the mass chlorination procedure used for cooling towers, recirculation for 3 to 6 hours also reduces the TRC to 0.1 mg/L, which is the regulation limit. Dilution in the river water causes a rapid decrease of TRC and residual chlorine is not measurable by conventional methods in the discharge plume.

Mattice & Zittel (1976) reviewed the toxicity data of residual chlorine to aquatic organisms and proposed

acute and chronic toxicity thresholds (Fig. 3.18). Although the chronic toxicity threshold is very low (2 $\mu\text{g/L}$) and non-realistic in terms of measurement, dilution and chemical consumption of residual chlorine is normally high enough to eliminate risks of toxicity.

The main organohalogenated compounds identified in natural waters are chlorinated trihalomethanes, chloroacetic acids and chlorophenols; they represent, however, only a part of the total organohalogenes found with the AOX method. We shall therefore take a succinct look at the question of the environmental impact of these different categories of organohalogenated compounds.

Chloroform CHCl_3 , the main THM formed by chlorination of natural freshwaters, disappears rapidly from the water, passing into the atmosphere. Its half-life – the time needed to halve its concentration in the water – has been estimated at 36 hours in a large river, 40 hours in a relatively shallow body of water, and from 9 to 10 days in a lake. Chloroform is degraded by photolysis in the atmosphere, whereas the processes causing disappearance of chloroform

Table 3.21. – Some aquatic toxicity data on bromoform.

Species	Toxicity parameter	Concentration (mg/L)	Reference
Bacteria			
<i>Pseudomonas putida</i>	Toxicity threshold	125	
Cyanobacteria			
<i>Microcystis aeruginosa</i>	Toxicity threshold	185	
Green algae			
<i>Scenedesmus quadricauda</i>	Toxicity threshold	1100	Verschueren, 1983
Protozoa			
<i>Entosiphon sulcatum</i>	Toxicity threshold	> 6590	
<i>Uronema parduczi</i>	Toxicity threshold	> 6590	
Fish			
<i>Poecilia reticulata</i>	LC ₅₀ , 14 days	102	
Carp embryo	LC ₅₀ , 96 hours	161	
Oyster larvae			Trabalka <i>et al.</i> , 1980
<i>Crassostrea virginica</i>	LC ₅₀ , 48 hours	1	

Table 3.22. – Selected toxicity data for monochloroacetic acid to freshwater organisms (Verschueren, 1983).

Species	Toxicity parameter	Concentration (mg/L)
Oligochaete worms		
<i>Tubitex tubifex</i>	Toxicity threshold	150
Protozoa		
<i>Vorticella campanula</i>	Toxicity threshold	9
Crustacea		
<i>Gammarus pulex</i>	Toxicity threshold	30
Insects		
<i>Chironomus plumosus</i>	Toxicity threshold	140
Fish		
Trout		
<i>Salmo trutta iridea</i>	Toxicity threshold	20
Carp		
<i>Cyprinus carpio</i>	Toxicity threshold	14

in the water (hydrolysis, photodegradation, biodegradation) are negligible. Very little bromoform is adsorbed on suspended matter and sediments; bioaccumulation is also very limited (Table 3.20).

Toxicity bioassays show that bromoform has very low toxicity for bacteria, algae and freshwater fish. Only the oyster larva, an extremely sensitive bioindicator, shows a response to a one mg/L concentration (Table 3.21).

Monochloroacetic acid

This haloacetic acid (CH_2ClCOOH) is completely ionized at the pH of natural waters; it is not very volatile but is biodegradable: 73 % is converted into CO_2 in 8 to 10 days at 29 °C (Boetling & Alexander, 1979). Its toxicity for freshwater organisms is comparable to that of chloroform; toxic effects can be observed at concentrations over one mg/L (Table 3.22).

The octanol/water partition coefficient of monoacetic acid is very low ($\log K_{ow} = 0.22$); the lipophilic and bioaccumulation factors of this compound are therefore also very low. Application of the Isnard & Lambert (1988) relation ($\log \text{BCF} = 0.80 \log (\text{Kow}) - 0.52$) gives a bioaccumulation factor of 0.45, indicating that the compound is not bioaccumulated by aquatic organisms.

2,4,6 Trichlorophenol ($\text{C}_6\text{H}_3\text{Cl}_3\text{O}$)

This chlorophenol, taken as an example, is slightly volatile; it is photodegradable and biodegradable: 100 % biodegradation in 7 days in do-

mestic wastewater, according to Takbak (1981).

In view of the data available (Verschuere 1983), its toxicity can be qualified as moderate:

Goldfish (*Carassius auratus*), CL50, 24 hours: 10.0 mg/L

Fathead minnow (*Pimephales promelas*), CL50, 96 hours: 0.1 to 1.0 mg/L.

It is moderately bioaccumulated, according to available data. Its bioaccumulation factor can reach 32-63 for the sea mussel, 50 for the green alga *Chlorella* (Freitag *et al.*, 1982) and 250-316 for freshwater fish (Geyer *et al.*, 1982).

Case study: mass and continuous chlorination of a large recirculating cooling circuit

Since 1996, two 900-MW units of the Dampierre-en-Burly nuclear power station, located on the Loire River in France, have been chlorinated in summer from mid-June to mid-September to eliminate some pathogenic amoebae from the blowdown of the cooling towers. A two-step treatment has been implemented with success.

The first is mass chlorination, by adding sodium hypochlorite as rapidly as possible at 20 mg/L FRC in the cooling circuit and recirculating for a few hours. This procedure is applied at the beginning of cleaning of the cooling tower and the condensers.

The second step is the maintenance treatment, consisting in the continuous addition of sodium hypochlorite downstream the condensers at a concentration equivalent to 0.27

Table 3.23. – Levels of oxidants and AOX in the cooling system and at the outlet of the discharge canal at Dampierre power station during the summer 1996 continuous chlorination treatment (Cabanès *et al.*, 1997). FRC : Free residual chlorine.

	Chlorine addition (mg/L in 34 m ³ /s)	FRC (mg/L)	AOX (µg/L)
July	0.38	0.49	390
Unit 1 cooling water	0.36	0.48	422
Unit 3 cooling water		0.06	186
Power station outlet			
August			
Unit 1 cooling water	Off-line		
Unit 3 cooling water	0.36	0.48	387
	0.27	0.30	470
Power station outlet		0.01-0.02	110-113
September			
Unit 1 cooling water	0.27	0.35	393
Unit 3 cooling water	0.27	0.30	543
Power station outlet		0.02	220

to 0.38 mg/L into the 34 m³/s cooling water closed loop, in order to maintain a FRC concentration of 0.5 or 0.3 mg/L (Table 3.23). Due to the high pH in the cooling water in summer, the non-dissociated fraction of hypochlorous acid was in the range of 3% (pH 9) to 24% (pH 8) of the FRC. The Dampierre power station comprises 4 units with a common discharge canal, so that the blowdown of the chlorinated units is diluted with the blowdown of the other units in operation.

Very low levels of FRC have been found in the discharge canal during continuous chlorination. The maximum FRC value was measured at the end of the mass chlorination of unit 1, but the regulation limit was always respected : 0.1 mg/L FRC at the outlet of the discharge canal.

Ammonia was at a low level in the cooling water circuit, but the Loire is very rich in phytoplankton during the summer months (> 100 µg/L of chlo-

rophyll a), and experimental chlorination curves have shown the formation of combined chlorine, most probably corresponding to organic chloramines. Combined residual chlorine measured by colorimetric DPD was in the range of 0.58 to 0.90 mg/L in the cooling water and 0.13 to 0.21 mg/L at the outlet of the discharge canal.

The mass chlorination process generates large amounts of AOX at the outlet of the discharge canal (193 µg/L for unit 3 to 690 µg/L for unit 1), but chloroform remains at 20 µg/L due to volatilization in the cooling tower.

During continuous chlorination, chloroform stays at a low level : 5.1 to 9.6 µg/L for FRC = 0.5 mg/L and 2.4 to 3.8 µg/L for FRC = 0.3 mg/L. Bromodichloromethane varied between 0.2 and 0.6 mg/L, and dibromochloromethane remained below 0.2 µg/L. Thus, THMs represent no more than 5% of the AOX in the discharge canal, where concentrations ranged from 110 to 220 µg/L.

Table 3.24. – EOX concentrations measured in fish flesh upstream and downstream of the Dampierre en Burly power station, after one month of continuous chlorination in July 1996. Measurements made by F. Hayer at Université de Metz.

Sampling site	Species	EOX (µg/g of dry weight)	EOX (µg/g of fat)
Upstream	Chub (<i>Leuciscus cephalus</i>)	11.72	250.9
	Roach (<i>Rutilus rutilus</i>)	9.28	92.36
	Pumpkinseed (<i>Lepomis gibbosus</i>)	8.15	192.4
Downstream	Barbel (<i>Barbus barbus</i>)	15.65	208.2
	Chub (<i>Leuciscus cephalus</i>)	6.37	148.4
	Dace (<i>Leuciscus leuciscus</i>)	14.8	200.3

Toxicity of the discharge water was monitored by using *Daphnia* and Microtox standardized bioassays; there was no acute toxicity throughout the chlorination treatment. In the ecological monitoring program at the Dampierre power station, samples of plankton, periphyton and macroinvertebrates are collected and fish are sampled by electrofishing up- and downstream the power station. No modification in these ecological compartments can be attributed to the continuous chlorination.

A temporary drop in periphyton algal diversity was observed following mass chlorination; it is most probably due to the addition of organic matters from cleaning of the cooling tower.

EOX dosages were performed on the flesh of fish caught up- and downstream of the plant after one month of continuous chlorination. The two zones of the river are separated by a sill which prevents caught fish

from returning upstream. The same EOX levels were measured upstream and downstream (Table 3.24).

CBPs and drinking water

When organohalogenated compounds are added to freshwater used to produce drinking water, a sanitation risk must be considered. WHO (1993b) guidelines and regulation limits exist on the main CBPs identified in chlorinated natural waters (Table 3.25). To be able to continue to use surface water for drinking purposes, it is advisable to reduce CBP loads as much as possible; production of drinking water therefore limits the potential for use of chlorination as an antifouling treatment in rivers.

Chlorination at marine sites

In seawater, chlorination produces primarily oxidizing and non-oxidizing brominated compounds.

Table 3.25. – Guideline values and regulation limits for the principal disinfectants used to produce drinking water.

Source	Chlorine and derived oxidants (mg/L)	Chlorine dioxide µg/L	Chlorites µg/L	Organohalogens µg/L	Bromate µg/L
WHO guidelines 1993b	Free chlorine : 5 Chloramines : 3	Absence	200	CHCl ₃ : 200 CHCl ₂ Br : 60 CHClBr ₂ : 100 CHBr ₃ : 100 DCAN : 90 DBAN : 100 TCAN : 1 BCAN : Absence DCAA : 50 TCAA : 100 MAA : Absence 246TCP : 200	25
European Directive EEC 1998				CHCl ₃ : 40 CHCl ₂ Br : 15 THMs : 100	10
US EPA (1)	Free Chlorine : 4 Chloramines : 4	800	1000	THMs : 80 5 HAA : 60	10

(1) Richardson, 1997. Maximum Residual Disinfectant Level.

DCAN : dichloroacetonitrile – DBAN : dibromoacetonitrile – TCAN : trichloroacetonitrile BCAN : bromochloroacetonitrile – HAA : haloacetic acids – MAA : monochloroacetic acid – DCAA : Dichloroacetic acid – TCAA : Trichloroacetic acid.

No chlorate limit in the WHO guidelines.

There is a considerable decrease in residual oxidants in thermal plant cooling systems, as seen from the example in Figure 3.19 : an hypochlorite injection at 0.8 mg/L gives a TRO of 0.3 mg/L at the condenser; the decrease along the outlet pipe is then sufficient to bring TRO to 0.1 mg/L at the point of discharge into the sea.

On-site measurements at power station sites in Gravelines, Penly and Heysham, (Khalanski, 1985, Jenner *et al.*, 1997) have shown that the residual chlorine concentration decreases very rapidly in the discharge

plumes due to dilution and chemical consumption of oxidants. Davis & Coughlan (1983) proposed a simple model to predict the residual oxidant concentration in the cooling circuits and in the plume.

Extensive field studies have been conducted at coastal power stations in the UK and in France (Davis & Coughlan, 1983; Khalanski, 1993) to assess the impact of seawater chlorination on the marine littoral system. The major changes concern the plankton passing through the cooling circuit during chlorination : oxidants

Fig. 3.19. – Decay of TRO at the Penly nuclear power station for a chlorine dosage of 0.8 mg/L.

Fig. 3.20. – Maximum extent of the discharge plume at Gravelines over one tidal cycle showing the effect on phytoplankton biomass. Cooling water flow 160 m³/s, chlorination 1.0 mg/L injected.

are responsible for decreases in the bacteria and phytoplankton biomass and production, but the disappearance of residual oxidants leads to recovery of plankton productivity. A return to normal conditions is observed as soon as one moves away from

the near vicinity of the release (Fig. 3.20).

Plume studies conducted at the same time showed that the bromoform concentration decreased along the plume with a non-linear reduction in concentration from 14 mg/L at the

Fig. 3.19. – Decay of TRO at the Penly nuclear power station for a chlorine dosage of 0.8 mg/L.

Fig. 3.20. – Maximum extent of the discharge plume at Gravelines over one tidal cycle showing the effect on phytoplankton biomass. Cooling water flow 160 m³/s, chlorination 1.0 mg/L injected.

are responsible for decreases in the bacteria and phytoplankton biomass and production, but the disappearance of residual oxidants leads to recovery of plankton productivity. A return to normal conditions is observed as soon as one moves away from

the near vicinity of the release (Fig. 3.20).

Plume studies conducted at the same time showed that the bromoform concentration decreased along the plume with a non-linear reduction in concentration from 14 mg/L at the

Fig. 3.21. - Dilution of bromoform in the discharge plume of the Penly nuclear power station, located on the English Channel. (Marcos & Gailhard, 1994).

discharge to approximately 1.0 mg/L 2 km from the discharge at Heysham and Sizewell (Jenner *et al.*, 1997).

Measurements of THMs have been taken at the Gravelines power station with a flow of 160 m³/s, chlorinated to 1 mg/L (Khalanski & Lutz, 1987). The bromoform concentration falls rapidly to about 1 µg/L in the plume. Similar measurements at Penly showed three zones in the vicinity of the offshore outlet:

100-200 m from the discharge

1.66 ± 0.40 µg/L

200-1500 m from the discharge

0.44 ± 0.13 µg/L

1500-15 km from the discharge

0.26 ± 0.10 µg/L

The dilution of bromoform in the discharge plume of the Penly power station was modeled using the TELEMAC 3D code (Marcos & Gailhard, 1994) (Fig. 3.21) showing that the concentration level is less than 1 µg/L at that site.

These results may be compared with published data on the toxicity of chlorination by-products in a marine environment (Table 3.26). The evidence available up to 1995 suggests that the concentrations of THM in the discharges from a wide variety of power stations in Europe are on the order of 10⁻³ times the EC50 and LC50 data from published results. This implies that in the marine environment, there is no expected acute toxic effect from these compounds.

Until recently, it was considered that natural sources of halocarbons were extremely rare and the presence

of halocarbons in the environment indicated anthropogenic contamination. It is now recognized that many organisms, particularly in the sea, produce halocarbons which closely resemble those found in chlorinated water (e.g. THMs, halophenols and halo-aromatic acids) (Gribble, 1994). Natural production of AOX in the Rhine is approximately 50% of the total (Hoekstra & De Leer, 1994) and Harper (1994) estimates the natural global air-ocean flux of bromoform at 1 to 2 × 10⁶ tons annually. This indicates not only that some organisms are capable of thriving in the presence of these compounds but also that if there are natural sources, there must also be natural sinks.

3.7.2 Chloramine

A number of power stations in Belgium (Drogenbos, Seraing and Ti-hange) suffer from fouling by bryozoans, *Plumatella* sp, very abundant in the cold basins of the towers or in some water chambers. To eliminate Molluscs and small colonies of Bryozoans, the procedure used in Belgian power stations is a periodic treatment to kill the bio-fouling from the main settlement peak to the end of the developing period in autumn. The chloramine dosage at a concentration ≥ 5 mg/L is applied twice a weeks (about 10 times a month), for 3 to 4 hours. Monochloramine kills bryozoans for 3 hours at 6.0 mg/L (Duvivier & Vanmaele, 1995), but it is also effective against zebra mussels.

Table 3.26. – Summary of selected data on THM toxicity to marine organisms.

Compound	Marine groups	Toxicity index	Concentration mg/L	Reference
Bromoform	Diatoms, Flagellates	EC ₅₀ , 7 days	> 32	Erikson & Freeman, 1978
	Molluscs	LC ₅₀ , 96 hours	40-140	Gibson <i>et al.</i> , 1980
	Crustaceans	LC ₅₀ , 96 hours	26	
	Fish	LC ₅₀ , 96 hours	12	
Bromodichloromethane	Ciliate	EC ₅₀ , 24 hours	240	Yoshioka <i>et al.</i> , 1985
Chloroform	Diatoms, Flagellates	EC ₅₀ , 7 days	> 32	Erikson & Freeman, 1978
	Molluscs	LC ₅₀ , 48 hours	0.15-1	Stewart <i>et al.</i> , 1979
	Crustaceans	LC ₁₀₀ , 24 hours	464-800	Okubo & Okubo, 1962
	Fish	LC ₅₀ , 96 hours	28	Madeley, 1973

At Drogenbos and Seraing (450 MW each) the method currently used to control and kill this organism is chloramination. Monochloramine is produced on-site by means of mixing solutions of sodium hypochlorite and ammonia chloride (NH₄Cl). The optimum mass ratio chlorine/nitrogen must be 5/1 to produce monochloramine (Duvivier, 1993).

3.7.3 Chlorine dioxide

Chlorine dioxide is a potential alternative to chlorination because of its effectiveness as a disinfectant (Bernarde *et al.*, 1965), for control of microbial slimes in condenser tubes of inland power stations (Rauh 1979, Mayack *et al.*, 1984) and because there is less production of organoha-

logenated by-products (Ben Amor *et al.*, 1988, Lykins & Griese, 1986). Although the main uses of chlorine dioxide are pulp and paper bleaching, food processing and drinking water and wastewater disinfection, the efficacy of chlorine dioxide has been tested on-site on large marine cooling water systems in Italy and Spain.

3.7.3.1 Production of chlorine dioxide

Chlorine dioxide gas cannot be condensed and liquefied as chlorine because of the risk of explosive disintegration. For this reason, it is produced on-site from sodium chlorite NaClO₂ in two principal ways (Schneider 1997) :

- chlorite oxidation by chlorine gas.

This reaction requires an excess of chlorine to optimize the chlorine dioxide production yield.

- acidification of chlorine.

This is the most common industrial process used for cooling water treatments. To maximize the production yield of chlorine dioxide, up to 95%, and to reduce resulting by-products, a large excess of HCl (> 250%) is required.

According to Schneider (1997): "There is no such thing as stabilized chlorine dioxide in a canister! These claims are simply unfounded. Our own experiments and those of external institutes have shown that these preparations are invariably diluted sodium chlorite solutions."

Safety. Chlorine dioxide solutions are explosive above a concentration of 30 g/L; this means that the concentration must be below 30 g/L at all points of the production system. It is also necessary to avoid any accidental mixing of the reagents (chlorite and acid), which can explode. In the gaseous state, they can explode at air concentrations above 10% in the presence of a flame (Masschelein, 1979). Chlorine dioxide generators are therefore especially designed to eliminate this risk. Acute exposure of workers results in irritation of eyes, nose, throat and lungs. For people working in chlorine dioxide production

areas, the short-term exposure limit is 0.9 mg/m³ (Gordon & Bubnis, 1997).

3.7.3.2 Chemistry of chlorine dioxide in aqueous solution

Chlorine dioxide is a gas at ambient temperature; its ebullition point is 11 °C. It is very soluble in water and is decomposed by light. As mentioned above, it is very unstable and explosion must be avoided. It is a powerful oxidant with the following global reduction reaction involving 5 electrons (Belluati *et al.*, 1997):

Contrary to free chlorine, the oxidizing power of chlorine dioxide does not depend on the pH in a wide pH range (5.0 to 9.5).

In aqueous solutions, chlorine dioxide does not react with bromide ions as do other oxidants: ozone, chlorine, hypochlorite. This means that it does not produce free bromine in seawater.

It does not react with ammonia to form chloramines and does not chlorinate organic compounds; as a consequence, it does not produce chlorophenols, THMs and, in general, AOX.

Chlorine dioxide oxidizes metals in reduced forms (Fe²⁺, Mn²⁺), nitrites (NO₂⁻) and sulfites (SO₃²⁻) and dissolved organic matter (Doré 1989). This process can cause a very high demand in polluted or eutrophicated natural waters. It can also produce deposits of Fe(OH)₃ and MnO₂ in heat exchangers.

Inorganic by-products – chlorite ions (ClO_2^-) and chlorate ions (ClO_3^-) are produced during the generation phase (Lefebvre & Deguin, 1997), but chlorite is also formed by the oxidation process itself :

The chlorite concentration in treated water depends on the demand of the water; it will be $> 1 \text{ mg/L}$ if the ClO_2 demand is higher than 1 mg/L (Gordon & Bubnis, 1997).

At pH 7, chlorine dioxide solutions are stable but hydrolysis occurs at basic pH to form chlorite and chlorate :

Photochemical reactions result in formation of chlorate ions.

Some organohalogenated compounds can also be formed by indirect chlorination due to the hypochlorous acid produced by chlorine dioxide reactions on different chemical structures such as phenolic compounds (Doré, 1989).

Finally, the U.S. E.P.A. has identified bromates and aldehydes as by-products which can be formed by chlorine dioxide. The aldehydes include the propanal to decanal series, glyoxal, methyl glyoxal, and benzaldehyde (Richardson, 1997).

Several analytical methods have been developed to measure chlorine dioxide and its inorganic by-products. The amperometric method (Standard methods 1992) determines concentrations of ClO_2 , ClO_2^- and ClO_3^- ; this

method by difference is, however, subject to major errors, in particular for chlorates (Gordon & Bubnis, 1997). On-line amperometric systems exist for continuous monitoring of the chlorine dioxide level with a detection threshold on seawater as low as $10 \text{ } \mu\text{g/L}$. ENEL has developed a continuous potentiometric method with the same detection threshold of $10 \text{ } \mu\text{g/L}$.

Among the colorimetric methods (lissamine green B, chlorophenol red, amaranth), amaranth has the best specificity and the lowest quantification limit, at $20 \text{ } \mu\text{g/L}$ (Mantisi *et al.*, 1997).

Ion chromatography is used to measure chlorites and chlorates at the $10 \text{ } \mu\text{g/L}$ level (Gordon & Bubnis, 1997).

3.7.3.3 Experimental data on efficacy of chlorine dioxide on biofouling

To eliminate the micro-biofouling and filamentous algae which develop on the packing of cooling towers, experiments performed at a pilot plant fed with Seine river water have shown that a residual dose of 1.5 mg/L chlorine dioxide for two hours is required. At the 0.3 mg/L concentration, the exposure time required is a few days (Merle & Montanat, 1980).

With respect to freshwater systems, laboratory tests have been conducted on zebra mussels *Dreissena polymorpha* (Montanat *et al.*, 1980; Van Benschoten *et al.*, 1993; Khalanski, 1993; Matissoff *et al.*, 1996).

An initial series of tests in Seine river water bore on the effect of single injections at high concentrations ranging from 10 to 40 mg/L (Montanat *et al.*, 1980). It was observed that brief exposure (13 minutes at 10 mg/L or 3.2 minutes at 40 mg/L) kills 50% of adult mussels. On the other hand, there is no significant mortality for 6

hours of exposure at 2 mg/L (Table 3.27).

On Lake Erie mussels (Matisoff *et al.*, 1996), intermittent injections of 1 mg/L for 30 minutes a day for 28 days are not effective; mortality is significant at 5 mg/L and it takes only 4 days of exposure at 40 mg/L to kill 95% of adult mussels (Table 3.28).

Table 3.27. – Mortality of adult zebra mussels exposed to single shocks of chlorine dioxide. Experiments on river Seine and Moselle water at temperature of 15 °C to 20 °C. ns : non significant data.

Concentration (mg/L)	Exposure time	Mortality rate	Location
2	4 to 6 hours	ns	Seine river (Montanat <i>et al.</i> , 1980)
10	12.9 minutes	50 %	
10	60.0 minutes	50 %	Moselle river
20	20.5 minutes	50 %	
20	60.0 minutes	60 %	
30	6.2 minutes	50 %	
30	60.0 minutes	80 %	
30	24 hours	70 %	
40	3.2 minutes	50 %	
40	3.2 minutes	50 %	

Table 3.28. – Mortality of adult zebra mussels exposed to intermittent chlorine dioxide doses in Lake Erie water at temperatures of 13 °C to 20 °C (Matisoff *et al.*, 1996).

Concentration (mg/L)	Frequency of treatment	Exposure time	Mortality rate (Standard error limits)
1	30 min/Day	28 Days	10 %
5	30 min/Day	28 Days	33 %
10	30 min/Day	7 Days	65 %
10	30 min/Day	7 Days	45 % (10-75)
13	30 min/Day	3 Days	50 %
20	30 min/Day	3 Days	70 % (45-98)
40	30 min/Day	3 Days	95 %

These findings show that chlorine dioxide shocks in relatively low concentrations, whether single or repeated over several days, kill between 50% and 90% of adult zebra mussels. Chlorine dioxide is therefore more effective than chlorine in intermittent treatments at high concentrations.

Continuous treatment with chlorine dioxide kills adult zebra mussels in 8 days at a residual of 0.2 mg/L (Table 3.29). The lethal time (LT_{100}), the time required to kill 100% of the exposed mussels, is given by the following relation (Fig. 3.22) :

$$LT_{100} = 4.47 + 3.79 \cdot \text{LOG}(\text{ClO}_2) \\ r^2 = 0.94$$

Table 3.29. – Mortality of adult zebra mussels exposed to continuous chlorine dioxide doses.

Concentration (mg/L)	Exposure time	Mortality rate	Water Temperature	Reference
0.15	7 days	100 %	15 °C	Montanat <i>et al.</i> , 1980
0.20	8 days	100 %	20-25 °C	Khalanski, 1993
0.25	6 days	45 ± 20 %		
0.50	6 days	70 ± 10 %		
1.00	2 days	60 ± 7 %	13 °C to 20 °C	Matissoff <i>et al.</i> , 1996
1.00	3 days	90 ± 10 %		
1.00	4 days	99 ± 10 %		
5.00	2 days	100 %

Fig. 3.22. – Lethal time for 100% of adult zebra mussels exposed to chlorine dioxide. Data from Table 3.29.

ENEL has tested the efficacy of chlorine dioxide on seawater in model culverts. No macro-biofouling development was found on concrete plates at residual concentrations of 0.1 to 0.2 mg/L and after a month of continuous treatment at 0.1 mg/L, there was no microfouling growth on condenser tubes (Ambrogio, 1997).

Experiments on the Mediterranean hydroid *Laomedea flexuosa* exposed to chlorine dioxide by ENEL (Geraci *et al.*, 1993) have given the following results :

- no significant reduction of hydroids at 0.05 mg/L for 96 hours' exposure,
- significant reduction at 0.1 to 0.2 mg/L for 48 hours' exposure,
- elimination of hydroids at 0.1 to 0.2 mg/L for 96 hours' exposure.

On the Mediterranean coast of Catalonia in Spain, experiments have been conducted on the marine mus-

sel *Mytilus galloprovincialis* at the Vandellos II nuclear power station (Bielza *et al.*, in Belluati *et al.*, 1997). A comparison between the efficacy of chlorine and chlorine dioxide treatments in killing the marine mussel has shown that chlorine dioxide at a residual of 0.2 mg/L kills the mussels more rapidly than chlorine at a residual of 1.1 mg/L (Table 3.30). Specific experiments shown that long-term semi-continuous additions of chlorine dioxide at a residual of 0.2 mg/L, 1 hour on, 2 hours off, is as efficient as continuous treatment. This semi-continuous procedure is also efficient with hypochlorite at a residual of 1.0 to 1.2 mg/L (Castellnou, pers. com).

As regards other macro-biofouling, intermittent treatment with chlorine dioxide can significantly reduce biological development when the oxidant is added for 8 hours per day (Table 3.31).

Table 3.30. – Exposure time to reach 50%, 80% and 95% mortality on three sets of adult Mediterranean mussels *Mytilus galloprovincialis*, having different shell size when exposed continuously to chlorine dioxide (0.2 mg/L residual) or to hypochlorite (1.1 mg/L residual). Data from a figure in Belluati *et al.*, 1997.

	Shell length	Chlorine dioxide 0.2 mg/L	Chlorine 1.1 mg/L
50 % mortality	Small	15 days	> 26 days
	Medium	10 days	15 days
	Large	8 days	13 days
80 % mortality	Small	20 days	> 28 days
	Medium	14 days	28 days
	Large	14 days	28 days
95 % mortality	Small	26 days	> 28 days
	Medium	20 days	> 28 days
	Large	20 days	> 28 days

Table 3.31. – Efficacy of intermittent chlorine dioxide treatments on macro-biofouling growth at Vandellos, Mediterranean coast of Catalonia in Spain. UNESA data.

Chlorine dioxide treatment	Marine fouling organisms	Magnitude of fouling
control (0)	Hydroids Algae Tubeworms	Large deposits
4 hours/day	Hydroids Algae Tubeworms	Moderate deposits
6 hours/day	Hydroids Algae Tubeworms	Moderate deposits
8 hours/day	Hydroids	Some deposits

3.7.3.4 Chlorine dioxide testing at industrial sites

An on-site experiment was conducted for 4 months on a recirculating cooling water system at a chemical plant located at Höcht on the Main river in Germany (Wasel-Nielen & Baresel, 1997). Chlorine dioxide was added to the circulating water (6,000 m³/h) twice a day for at least 2 hours to reach the concentration peak of 0.2 mg/L. This target concentration was difficult to achieve even after 8 hours of treatment because of the chlorine dioxide demand in the cooling water, which was high and variable. In this experiment, high levels of chlorine dioxide were measured: 1.5 to 5.0 mg/L. Nevertheless, this treatment reduced the AOX production in comparison to that produced by chlorination.

As for the cooling circuits of power stations fed with seawater, large-scale experiments have been conducted in recent years in Italy and in Spain.

Brindisi Nord power station, operated by ENEL on the Adriatic Sea

(4,320-MW units) (Ambroggi, 1997). The cooling water intake is located in a sheltered basin of the Brindisi harbour where municipal sewage discharges high amounts of organic matter. Biofouling is mainly composed of calcareous tube serpulids (*Spirorbis*, *Hydroides elegans*), hydroids, mussels and barnacles. The biomass, measured on 20 × 30 cm panels, reaches a maximum wet weight of 160 g for 3 months. The condenser tubes are not equipped with a sponge-ball cleaning system. Chlorine dioxide produced on-site by a chlorite/HCl generator was continuously added to the cooling water from 1989 to 1992. In 1989, the dosage was 0.22 mg/L; since 1990, it has been reduced to 0.18 mg/L during the summer season and 0.07 mg/L in winter from November to May. This variation of dosage allows for the seasonal variation in chlorine dioxide demand. Control panels placed inside the condenser box were invariably clean of both macrofouling and slime.

At the end of the outlet canal, amperometric measurements of chlorine

dioxide showed very low residuals (≤ 0.024 mg/L); outside the canal, residuals were below the quantification limit of 0.010 mg/L. Chlorite was always present in both the canal and the harbour water.

Leghorn – Livorno power station operated by ENEL on the Mediterranean (2,160-MW units). Short-term injection of chlorine dioxide at ≤ 0.2 mg/L was performed for 20 days in 1995 and 1996 to eliminate Serpulid growth in the circuit downstream of the point of injection of hypochlorite.

Vandellos II nuclear power station, operated by UNESA on the Mediterranean coast of Catalonia in Spain (1,000 MW). A program was conducted to compare the efficacy of chlorination and chlorine dioxide and the production of THMs with these two methods.

Half the cooling water flow (25 m³/s) was treated with chlorine dioxide produced by a chlorite/HCl generator; the remainder was treated by electrochlorination. At Vandellos, the water is treated 3 to 4 months a year, depending on biofouling monitoring data. The following dosages were adopted :

- continuous addition of ClO₂ at 0.16 mg/L to 0.20 mg/L; the residual at the outlet was around 0.04 mg/L;
- continuous addition of NaClO at 1.1 mg/L to 1.2 mg/L; the residual at the outlet was 0.3 to 0.4 mg/L.

Both procedures eliminate the macro-biofouling organisms. The cost of chlorine dioxide has been estimated

to be some 30% higher than electrochlorination.

Three *steel plants* in Italy and two *petrochemical plants* in Italy and France use chlorine dioxide as an anti-fouling agent on seawater.

The Taranto steel plant, located in the south of the Italian Peninsula, uses 35 m³/s seawater for cooling a power station and numerous circuits with heat exchangers. Macro-biofouling is composed of mussels, barnacles, hydroids and serpulids; the biomass reaches 60 kg/m²/year. At the beginning of the treatment, in 1980, the dosage was 0.5 mg/L continuously. Intermittent chlorine dioxide treatment was further applied :

- 0.5 mg/L for 9 hours per day in winter,
- 0.5 mg/L for 16 hours per day in summer.

The residual in the circuits of the power station remains in the range of 0.02 to 0.05 mg/L. Monitoring of fouling by visual inspection with cameras and installation of fouling collectors showed no macrofouling development; a few juvenile settlements can be observed during the reproduction periods. As the water demand is in the range of 1.3 to 1.8 mg/L, this indicates that all the ClO₂ disappears prior to the discharge (Belluati *et al.*, 1997).

At the petrochemical plant in Lavera (Mediterranean coast, south of France), the dosage is in the range of 0.15 mg/L to 0.20 mg/L depending on the seawater chlorine dioxide demand. This dosage is sufficient to maintain a 0.02 mg/L residual in all

Table 3.32. – By-products formed by river waters treated with chlorine dioxide (ClO_2) and sodium hypochlorite (Cl_2). All data on chlorine dioxide and chlorine correspond to dosages with the exception of data on the Main river, corresponding to residual concentrations.

By-products	Moselle river (1)				Mirgenbach lake fed with Moselle water (1)				Meuse river Recirculating water (2)		Main river Recirculating water (3)	
	ClO_2 dosage (mg/L)				ClO_2 dosage (mg/L)				Cl_2 (mg/L)	ClO_2 (mg/L)	Cl_2 (mg/L)	ClO_2 (mg/L)
	1.0	2.0	4.0	8.0	1.0	2.0	4.0	8.0	10	10	0.3	0.2
AOX production ($\mu\text{g/L}$)	21	63	76		4	14	82		200 to 700	100 to 300	150 to 350	10 to 20
THMs ($\mu\text{g/L}$)	1	2	3		1	2	3					
ClO_2 (mg/L)		1.31	2.39	3.31		1.05	1.78	2.79				1.5 to 5.0
ClO_2 (mg/L)		0.18	1.15	2.36		0.60	1.11	2.45				

(1) Khalanski, 1993 with complements, (2) Duvivier, 1993, (3) Wasel-Nielen & Baresel, 1997.

parts of the circuit needing protection against slime and macrofouling. The chlorine dioxide level is continuously monitored by amperometry with a detection threshold of 0.01 mg/L, and the addition of ClO_2 is determined by the residual target of 0.02 mg/L.

3.7.3.5 Environmental assessment

Treatments on freshwaters

Three types of by-products can be found in natural waters treated with chlorine dioxide :

- residual chlorine dioxide ClO_2 , but this powerful oxidant disappears rapidly in the cooling circuit itself or in the discharge plume,

- weak oxidant ions : chlorites (ClO_2^-) and chlorates (ClO_3^-), and possibly bromates (BrO_3^-),

- organics, including organohalogenated compounds (THMs, AOX) and aldehydes.

The formation yield of these products depends on the production yield of chlorine dioxide in the generator and on the chemical composition of the water, which determines the chlorine dioxide demand.

Table 3.32 gives data relative to the production of chlorite and chlorate ions and organohalogenated compounds in river water. Measurements in Moselle water show that, for an injection of between 1 and 8 mg/L, 40% to 60% of the chlorine dioxide is found again in the form of chlorites. Chlorine dioxide treatment of river water or of a solution of humic acids can produce from 60% to 80% of

Table 3.33. – Comparison of lethal concentrations (LC₅₀) of chlorine dioxide and chlorite ion for *Daphnia* and zebra fish (Montanat *et al.*, 1980).

Species	Compound	LC ₅₀ (mg/L)
Crustacean <i>Daphnia magna</i>	chlorine dioxide	24 h : 0.30-0.42
	sodium chlorite	24 h : 20.0
Fish <i>Brachydanio rerio</i>	chlorine dioxide	24 h : 0.34
	sodium chlorite	48 h : 450.0

chlorites (Doré, 1989). As for chlorates, the proportion in relation to the chlorine dioxide injected in Moselle water ranges between 10% and 30%.

Chlorite and chlorate ions are transformed by anaerobic bacteria into chlorides by the chlorite dismutase enzyme; this is one step in the reduction of perchlorates as follows (Rikken *et al.*, 1996) :

Chlorine dioxide produces very little THM (< 5 µg/L), and forms only 10% to 50% of AOX in comparison with equivalent treatments with sodium hypochlorite, according to data in the table. Here again, formation of AOX is dependent on the quality of the water treated.

The toxicity of chlorine dioxide is far greater than that of chlorites, as found in toxicity tests performed in Seine water (Montanat *et al.*, 1980) (Table 3.33). While chlorine dioxide is toxic in the short term in concentrations of 1/10 mg/L, chlorites are toxic in the tens to hundreds of mg/L range.

The toxicity of chlorite is very low when the concentration is below 10 mg/L (Couri *et al.*, 1982).

Chlorate toxicity is also very low for freshwater organisms, as found in a review of toxicity data by Van Wijk & Hutchinson (1995) (Table 3.34). NOECs range from several tens to several hundreds of mg/L for invertebrates and freshwater fish. Marine brown algae are the group of organisms most sensitive to chlorates, the long-term (6 months) NOEC is only 5 µg/L.

With respect to the *health risk* of chlorine dioxide by-products in drinking waters, WHO 1993b did not set any limit for the following reason : "A guideline value has not been established because of chlorine dioxide's rapid breakdown and because the chlorite guideline value is adequately protective for potential toxicity from chlorine dioxide". The new U.S. maximum concentration level will be 0.8 mg/L for chlorine dioxide (Richardson, 1997).

For chlorites, WHO 1993b recommends 0.2 mg/L as a provisional guideline and the new U.S. maximum concentration level is 1.0 mg/L (Table 3.25).

WHO 1993b established no guideline for chlorates, due to the present lack of data.

The new projected European Directive on drinking water set no limits

for chlorites and chlorates (Ottaviani, 1997).

Treatments on seawater

As observed on freshwaters, the formation of THM following chlorine dioxide treatment of seawater is lower than that resulting from chlorination. Laboratory findings on seawater enriched with humic acid (Table 3.35) confirm that, at the same dosage in the range of 0.5 mg/L to 2.0 mg/L, chlorine dioxide produces no more than 3% to 4% of the THM produced with hypochlorite treatments (Ambrogi, 1997).

At higher chlorine dioxide dosages (20 to 40 mg/L), THM formation increases up to 58% of the THM formed with chlorine.

With a chlorine dioxide dosage of 0.2 mg/L at the Vandellos II nuclear power station, operated by UNESA in Spain, the ClO_2 residual at the outlet was about 0.04 mg/L and the THM concentration was estimated at 3.5 $\mu\text{g/L}$, whereas hypochlorite treatment generates 30 $\mu\text{g/L}$ of THMs.

At the Taranto steel plant, intermittent chlorine dioxide treatment at a dosage of 0.5 mg/L for 9 to 16 hours

Table 3.34. – Comparative toxicity of the chlorate ion for aquatic organisms (Van Wijk & Hutchinson, 1995). EC50 : median effect (lethal) concentration, LOEC : lowest observed effect concentration, NOEC : no observed effect concentration.

Taxons	ClO_3 (mg/L) Geometric mean and range		
	EC50	LOEC	NOEC
Marine and freshwater bacteria	38.823 (34.510-43.137)	1.7 (0.1-1900)	
Marine and Freshwater Microalgae (phytoplankton)	563.1 (298-1350)	20.7 (0.1-3340)	118.2 (0.05-3137)
Marine Macroalgae (<i>Fucus vesiculosus</i> , <i>Fucus serratus</i>)	0.1 (0.08-0.13)	0.1 (0.015-0.58)	0.06 (0.005-0.58)
Marine algae in mesocosms (6 months)		0.015	0.005
Freshwater Invertebrates	2442.4 (880-12549)	3325	600
Freshwater Fish	3815.3 (< 31-10667)	8628	109.6 (35-784)

Table 3.35. – THM formation ($\mu\text{g/L}$) in seawater treated with chlorine dioxide and sodium hypochlorite after addition of standard humic acids (T.O.C = 5 mg/L), temperature : 35 °C, reaction time : one hour. (Ambrogi, 1997).

Oxidizing agent	0.50	Dosage of oxidizing agent (mg/L)			
		1.00	2.00	20.00	40.00
Chlorine dioxide	0.93 $\mu\text{g/L}$	1.63 $\mu\text{g/L}$	4.25 $\mu\text{g/L}$	452.02 $\mu\text{g/L}$	460.48 $\mu\text{g/L}$
Sodium hypochlorite	22.42 $\mu\text{g/L}$	48.52 $\mu\text{g/L}$	112.90 $\mu\text{g/L}$	788.28 $\mu\text{g/L}$	787.63 $\mu\text{g/L}$

a day generates no THMs and a mussel farm located close to the outlet is not affected by the discharges from the plant (Belluati *et al.*, 1997).

ENEL has conducted some studies on the toxicity of chlorine dioxide for non-target marine organisms. The first test was intended to evaluate sperm toxicity and embryotoxicity in the sea urchin *Sphaerechinus granularis*. The sperm inactivation test, with 10 minutes' contact before fertilization of the ovocyte, showed that a significant reduction in the percentage of fertilized eggs occurred at 0.74 mg/L. The development of embryos was blocked at the morula stage at concentrations higher than 2.0 mg/L, whereas there is no significant difference with the untreated control at concentrations of 0.74 mg/L and 0.22 mg/L (Geraci *et al.*, 1993).

Acute toxicity of chlorine dioxide for young sea bass (*Dicentrarchus labrax* of 7 g) showed a 96-h LC₅₀ of 20.8 µg/L while there was no significant toxicity after 96 h at 15 µg/L (Ambroggi *et al.*, 1994). Under the same experimental conditions on the same species with sodium hypochlorite, the TRO 96-h LC₅₀ was 78.6 µg/L (Sarglia & Scarano, 1974).

3.7.4 Ozone

Ozone is an allotropic species of oxygen obtained by means of the ionisation of oxygen by the action of an electric field.

Molar mass : 48 g/mole

Density vs air : 1.657

Volumetric mass at 0 °C, 760 mm Hg : 2.134 kg/m³.

Ozone is produced on-site from air or pure oxygen. Two types of ozone generators are available : plated and tubular generators ; the largest units, which can produce 5 to 10 kg/h, are tubular generators (Duvivier *et al.*, 1996). Recently, Mitsubishi Electric developed a storage system (MA-BOS), which makes it practical to apply intermittent ozonation to cooling water (Nakayama *et al.*, 1997). This system is tested since 1996 by Ontario Hydro.

Ozone is very volatile compared with other oxidizing biocides. McCoy *et al.* (1990), compared the volatility of various oxidants in cooling towers. From this study, the following order of volatility appeared :

ozone > chlorine > chlorine dioxide > chloramine > hypochlorous acid > hypobromous acid.

Compared to other oxidizing agents, ozone shows two major specificities.

Ozone is a stronger oxidant than chlorine, it can decompose high molecular organic substances like humic acids to produce low molecular compounds such as aldehydes and carboxylic acids. It is thus a very effective sterilisation agent whose main appliances are in disinfection of drinking water and bathing waters but also in food industry. The use of ozone decreases the organic carbon content of water and AOX formation (Duvivier, 1993).

On the contrary, this property is responsible for the generation of bro-

minated oxidants in sea water. Ozone oxidises the bromide ions almost instantaneously to form active bromine, producing the same oxidising products as those occurring after chlorination. This is why ozonation of sea water is not suitable as an anti-fouling treatment.

Ozone decomposes rapidly in water, its half-life time in pure water is a few hours but in raw waters used for cooling purpose, the half-life is reduced to minutes by consumption with organic matters. The rate of decomposition also depends on the pH, it increases with increasing pH. At acidic pH, the dominant species is molecular ozone (O_3), but at alkaline pH, ozone generates very short-lived (micro-seconds) hydroxy free radicals ($OH^\bullet$).

3.7.4.1 Experimental studies

In Switzerland, in a small closed cooling water system ($10\text{--}12\text{ m}^3/\text{s}$), a two years period continuous treatment with approximately $50\text{ }\mu\text{g/L}$ was found effective against bacterial slime and total bacteria counts decreased by a factor of about 100 times (Wellauer & Kyas, 1987; Wellauer and Oldani, 1990). Some corrosion was observed on C-steel materials; corrosion rate was 1.5 times higher when ozonising water was used but no corrosion was recorded in the presence or absence of ozone for stainless steel alloys, titanium and also copper alloys. A pilot plant ($1,000\text{ m}^3/\text{h}$) was set up at the EVS Heilbronn coal-fired power station in Germany where the

cooling water is conditioned river water.

In Canada, experimental data on Zebra mussels mortality in ozonised water (Claudi & Mackie, 1994) show that mortality rate for adult mussels depends on the water temperature. At the ozone concentration of 2 mg/L , the 90% to 100% mortality level is reached in 9 days at 4°C and in 5 days at 20°C (Table 3.36).

Experimental trials have been made on Zebra mussels and freshwater snails in Belgium (Duvivier *et al.*, 1996). It was observed that adult Zebra mussels (2 cm to 3 cm) exposed to dissolved ozone keep their shell open but stop to filter the water. At 21°C , the 100% mortality rate is observed at a concentration of 0.32 mg/L in 39 days (Table 1). Ozone is also very efficient in preventing the settlement of mussel's larvae and there is no production of byssal threads for ozone concentration in the range of $20\text{ }\mu\text{g/L}$ to $30\text{ }\mu\text{g/L}$.

The fresh water snail *Physa acuta* is more susceptible to ozone than adult Zebra mussels: at 21°C , 100% mortality is observed in 10 days for 0.32 mg/L (Table 3.36).

Lethal concentration for 100% (LC_{100}) of the tested adult Zebra mussels at temperatures of 20°C to 21°C are represented on the figure 3.23. A power function curve can be fitted to the data for exposure time ≥ 2 days:

$$LC_{100} (\text{mg/L}) = 17.73 \cdot t^{-1.1127}$$

$$r^2 = 0.91, \text{ with } t = \text{exposure time in days.}$$

Table 3.36. – Experimental data on the mortality of fresh water molluscs exposed to dissolved ozone.

Species and Experimental Conditions	Water Temperature	Concentration (mg/L)	Exposure time (Days) and Mortality rate (%)	Reference		
Zebra mussel	4 °C	1.0	9 Days, 55 %	Claudi & Mackie, 1994		
<i>Dreissena polymorpha</i>	4 °C	2.0	9 Days, 90 %			
Canada	15 °C	0.5	9 Days, 100 %			
Adults	5 °C	1.0	8 Days, 100 %			
	15 °C	2.0	4 Days, 100 %			
	20 °C	0.5	8 Days, 75 %			
	20 °C	1.0	7 Days, 90 %			
	20 °C	2.0	5 Days, 100 %			
	20 °C	5.0	4 Days, 100 %			
Larvae (veligers and post-veligers)	15 °C to 20 °C	0.5	≥ 5 Days, 100 %			
Zebra mussel	20 °C	0.28	> 6 Days, 40 %	Van Benschoten et al., 1993		
<i>Dreissena polymorpha</i>		0.54	> 5 Days, 50 %			
		1.1	14 Days, 100 %			
Adults (12.1 to 16.4 mm)		1.3	11 Days, 100 %			
		2.2	7 Days, 100 %			
		4.6	4 Days, 100 %			
Zebra mussel	21 °C	0.026	39 Days, 45 %	Duvivier et al., 1996		
<i>Dreissena polymorpha</i>		0.077	36 Days, 50 %			
		0.18	32 Days, 50 %			
Belgium		0.233	32 Days, 50 %			
Adults (2 cm-3 cm)		0.233	39 Days, 55 %			
		0.32	12.5 Days, 50 %	Duvivier et al., 1996		
		0.32	39 Days, 100 %			
Fresh water snail	21 °C	0.015	7.5 Days, 50 %	Leynen et al., 1997		
<i>Physa acuta</i>		0.015	11 Days, 65 %			
		0.048	7.5 Days, 50 %			
Belgium		0.048	11 Days, 80 %			
		0.18	7.5 Days, 50 %			
		0.18	11 Days, 85 %			
		0.23	4.5 Days, 50 %			
		0.23	11 Days, 90 %			
		0.32	3.5 Days, 50 %			
		0.32	11 Days, 100 %			
			4.00		4 Days, 50 %	
Fresh water bryozoans		21 °C	0.072		2 Days, 50 %	Leynen et al., 1997
<i>Plumatella emarginata</i>			0.080		4 Hours, 100 %	
Belgium

Fig. 3.23. – Ozone lethal concentration for adult zebra mussels depending on the exposure time.

The young colonies of the bryozoan *Plumatella emarginata* are very sensitive to ozone : $LC_{100} = 0.08$ mg/L with a 4 hour exposure. Statoblasts and large colonies are more resistant. Nevertheless, Leynen *et al.*, (1997), concluded that a continuous low level ozone treatment up to 0.1 mg/L is sufficient to eliminate Bryozoans and Zebra mussels ; however, at 20 μ g/L, there is no effect on zebra mussels, Duvivier *et al.*, 1996.

Intermittent application of ozone has been tested in Canada in a test rig at Lake Ontario Hydro (Nakayama *et al.*, 1997), Addition of about 10 mg/L of ozone leading to a residual of 2 to 8 mg/L for 6 minutes twice a day was found efficient on microfouling which was reduced by 94% to 99%. Zebra mussel mortality was very low (3%), but a 30% reduction in tissue weight was observed. In this experiment, the ozone storage system

developed by Mitsubishi Electric was used.

3.7.4.2 Ozone testing at industrial sites

On-site studies performed in the USA, at the Bergen power station on the Delaware river, have been clearly negative for ozone (Sugam, 1985). Ozone is an efficient biocide against the bacterial slime but it produces deposits of manganese dioxide and the cost of ozone treatment is much higher compared to chlorine.

Ozone was implemented in 1995 at the Mol power station, operated by Electrabel in Belgium : injection in the inlet canal at 0.3 mg/L, at pH 8 ozone half-life is 25 minutes. The ozone consumption was very rapid and the effect on Zebra mussel was limited in the canal to only the first 50 meters.

The use of ozone as a biocide still remains a very expensive method, estimated to 3.8 times the cost sodium hypochlorite (Duviol *et al.*, 1996).

At the Seraing power station, in Belgium on the river Meuse, ozone dosing is implemented at 1.0 mg/L in the auxiliary cooling system. This circuit is the make-up of the main semi-closed cooling system. In this system, the concentration factor reaches 1.8. In the cold water basin of the cooling tower, the ozone residual is as low as 5 µg/L. This treatment kills 100% of bivalves (*Corbicula* and *Dreissena*) in 18 days. Total bacteria decreases below 100/ml and DOC was reduced by 30%.

In Germany, the recirculating cooling system of the air separation plant at Höchst is continuously treated by ozone since 1985. This circuit, fed with river Main water, comprises four cooling towers, the recirculating rate is 4,800 m³/h (Wasel-Nielen and Baresel, 1997). Ozone is added at 0.10 to 0.15 mg/L and the ozone is measured in the water supply at 0.05 to 0.08 mg/L. The water is clear and colourless "like a mountain stream". A slight reduction of the AOX was measured in the cooling system compared to river Main levels (5 to 30 µg/L). Corrosion of copper alloy was stopped by addition of a nonferrous corrosion inhibitor. New systems are ozonised since 1992 with a mean recirculating rate of 12,000 m³/h to 22,500 m³/h. The ozone level must be at least 0.1 mg/L in the supply water, it is sufficient to eliminate all biological deposits in the heat exchangers.

In the Netherlands, ozonation is applied at a cooling tower assisted power station (RoCa) in Rotterdam. Make-up water is filtered over sand filters, improving the water quality which enables the use of ozone. A recirculating cooling water system at a chemical plant is also treated with ozone in the Netherlands. This system is completely made out of stainless steel and fed with demineralised water. The system was put in operation in 1995 and the results have so far been excellent.

Safety of workers

The high volatility of ozone causes enrichment of ozone gas in the vicinity of treated waters. The air concentration limit to protect the workers is 0.2 mg/m³. Ozone generators are presently equipped with removing systems destroying the excess ozone in the air using different processes: thermal destruction, activated carbon, catalytic systems.

3.7.4.3 Ozone environmental assessment

Although the formation energy of ozone is high, the application of ozone is often referred to as more environmentally acceptable than hypochlorite, since it leads to less formation of trihalomethanes (THMs) and extractable organic halides (EOX).

Compared chlorination by-product formation, relatively little attention has been paid to by-product formation re-

sulting from ozonation. Ozonation may however lead to formation of bromate (BrO_3) and aldehydes (Cavanagh *et al.*, 1992). The new WHO guidelines for drinking water (WHO, 1993b; Table 3.25), recommends a limit of 25 $\mu\text{g/L}$ for bromate and a new proposed regulation in the European Union countries (Ottaviani, 1997) and in the USA (Richardson, 1997), require a lower limit at 10 $\mu\text{g/L}$.

The formation of bromates by ozonation can be reduced at $\text{pH} < 7$, but the pH of most of the large European waters suitable for cooling purposes is frequently higher. At the Höcht plant on the river Main, in Germany, no bromate was detected in the recirculating cooling system treated with ozone at 0.10 to 0.15 mg/L , but the detection level for bromate was 100 $\mu\text{g/L}$ (Wassel-Nielen & Baresel, 1997).

By-product formed by ozonation at a dosage of 6 to 12 mg/L of effluent from a wastewater treatment plant in La Roche-sur-Yon (France) was investigated by Langlais *et al.* (1992). Ozo-

nisation led to complete or partial elimination of aromatics (allyltoluene, dichlorobenzene, dimethoxybenzene...) and non saturated fatty acids, whereas no significant change on the concentration of long-chain saturated fatty acids was observed. Aldehydes (heptanal, nonanal) and short-chain saturated fatty acids appeared or increased in concentration.

Short-term toxicity tests carried out on the ozonised effluent showed no mortality on fish (*Brachydanio rerio*) and crustacean (*Artemia salina*), but some growth inhibition on the green algae *Scenedesmus subspicatus*. These tests were made with no residual dissolved ozone and the conclusion was that ozonation of wastewater does not generate acute toxicity.

Dissolved ozone is very toxic for fish, as shown on juveniles of fresh water fishes (Table 3.37). However, the high ozone consumption in river waters can be used to eliminate the residuals by diluting the ozonised water.

Table 3.37. – Toxicity data on ozone for juveniles of fresh water fish.

Species	LC ₅₀ , 48 h	Reference
Carp <i>Cyprinus carpio</i> 1.1 cm	0.043 mg/L	Duvivier, 1993
Chub <i>Leuciscus cephalus</i> 1.7 cm	0.036 mg/L	
Sharptooth Catfish <i>Clarias gariepinus</i> 1.1 cm	0.037 mg/L	

3.7.5 Other oxidizing compounds

Bromine

In some freshwater CWS, sodium hypochlorite is dosed in combination with NaBr. Some practical experiments are presently being carried out in the Netherlands. 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 free bromine is not totally dissociated at basic pH and bromamines have proven to be more toxic than chloramines. In seawater, with natural Br – concentrations of 65 mg/L, additional dosing of NaBr makes no sense.

Hydrogen peroxide and peracetic acid

Hydrogen peroxide is sometimes applied as algicide or biocide in small 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.

Hydrogen peroxide does not produce organohalogenated compounds and there are no known harmful decomposition products. Its use for CWS treatments is mainly limited by

a poor anti-fouling activity at low concentrations and at low temperatures and by the inactivation by bacterial enzymes (catalases and peroxidases).

Peracetic acid, or peroxyacetic acid ($\text{CH}_3\text{CO}_3\text{H}$), is a weak acid, which does not exist as a pure compound. The peracetic acid solutions are equilibrium mixtures of acetic acid and hydrogen peroxide:

Commercial solutions for water treatment applications are available at concentrations of 1% to 15%. Peracetic acid is very corrosive at higher concentrations.

The final decomposition products are methane, carbon dioxide, oxygen and water, but acetic acid is the major intermediate compound. According to Fraser (1986) the disinfection activity is based on the production of oxygen free radicals breaking the chemical bounds SH and S-S in cell membrane's enzymes.

In the food sector industry, peracetic acid is applied on a small scale for disinfection, (Swinnen, 1995), but no applications in large CWS are known. However, peracetic acid seems to have a greater efficacy than glutaraldehyde and isothiazolones for elimination of *Pseudomonas aeruginosa*, common slime forming bacteria, and could be used to control biofilms in cooling towers (Kramer, 1997). The dosage in cooling water should be in the range of 1 to 10 mg/L for a contact time of 1 to 3 hours.

3.8 CHEMICAL TREATMENTS WITH NON-OXIDIZING COMPOUNDS

This category groups mineral or organic components with biocidal effects on the main species responsible for biofouling of cooling systems. The composition of the commercial products, particularly in the case of organic products, is generally more complex than that of the "active substance"; in this case, the chemical and ecotoxicological properties of the product may differ from those of the active substance. For this reason, it appears to us to be necessary in certain cases to identify the products by their commercial brand name.

While oxidising biocides exercise non-specific biocidal action on the target organisms, from bacteria to mussels, organics have more specific action, for example on weeds (algicides), or molluscs (molluscicides). Their greater or lesser toxicological specificity is an important characteristic of these anti-fouling agents.

3.8.1 Organic agents

Toxics for molluscs were produced in the Sixties to combat parasitic diseases, such as bilharziosis, in which aquatic snails are intermediate hosts of the parasitic agent. Some of these products are also very toxic for Zebra mussels (Hoestland, 1972). In a review of toxicity data on molluscicides used in African continental waters, Dejoux (1988) concluded that they cause mortality of non-target organisms. For water treatment against

macro-biofouling in industrial systems, specific products have been developed.

Three major groups of organics currently used in industry to control fouling in cooling water systems can be identified :

- products containing isothiazolones as the toxic substance,
- products containing quaternary amines as the toxic substance,
- other organics, such as glutaraldehyde, 2,2-dibromo-3-nitrilo-propionamide (DBNPA), 2-bromo-2-nitropropane-1,3-diol (BNPD), methylene-bisithiocyanate, 2-dithiobisbenzamide, b-bromo-b-nitrostyrene, etc.

This is probably the situation in most European Countries, but it should be added that use of products containing filming agents, composed of fatty amines, is developing for anti-fouling applications.

Figure 3.24. shows the chemical structure of QACs, isothiazolones and fatty amines.

All have the common property of not being detected as toxic (at least for short-term applications) by the target organisms. Thus, bivalve molluscs continue to filter the water when the product is added at a non-excessive dosage, and they are exposed to the toxic until the first detrimental effects cause a behavioural response : valve closure, reduction of the water filtration rate.

As a consequence, most of these organic agents are effective for short-term applications : 12 to 48 hours, while others require a few days' exposure (Table 3.38). They are generally used in recirculating cooling water systems.

Table 1. Commercial application of some organic products to eliminate Zebra mussels and Asiatic clams (mortality rate $\geq 95\%$).

Commercial Brand Active substance	Target organism	Concentration		Exposure time (hours)	Temperature ($^{\circ}\text{C}$)	Reference
Clam-Trol (Betz) ADBAC (QUAC) + dodecylguanidine	Asiatic clam	15.0 mg/L	1.95 mg/L	24	20.0	Mowery <i>et al.</i> , 1989
		25.0 mg/L	3.25 mg/L	24	5.0-7.0	
		25.0 mg/L	3.25 mg/L	12	24.0-29.5	
	Zebra mussel	15.0 mg/L	1.95 mg/L	24	11.0	Lyons <i>et al.</i> , 1990
		10.0 mg/L	1.30 mg/L	24	15.0-20.0	
		14.3 mg/L	1.90 mg/L	12	19.0	
		14.3 mg/L	1.90 mg/L	12	14.5	Petrille & Werner, 1993
			1.30 mg/L	24	20.0	
			1.30 mg/L	48	15.0	
		15.0 mg/L	1.95 mg/L	12	20.0	
		15.0 mg/L	1.95 mg/L	24	15.0	
		15.0 mg/L	1.95 mg/L	48	10.0	
			2.60 mg/L	24	15.0	
			2.60 mg/L	72	10.0	
			2.60 mg/L	72	5.0	
H-130 M (Calgon) DDAC (QUAC)	Zebra mussel	2.0 mg/L		24	22.0	Muia <i>et al.</i> , 1993
		2.0 mg/L		72	18.0	
		2.0 mg/L		120	14.0	
		1.0 mg/L		24	$\geq 12^{\circ}\text{C}$	Command & Matthews, 1994
Bulab 6002 (Buckman) Polyquat	Zebra mussel	0.5 mg/L	0.3 mg/L	826	22.0-25.0	McMahon <i>et al.</i> , 1990
		1.0 mg/L	0.6 mg/L	680		
		2.0 mg/L	1.2 mg/L	313		
		4.0 mg/L	2.4 mg/L	244		
		8.0 mg/L	4.8 mg/L	197		
TCMTB Isothiazole Bulab 6009 (Buckman)	Zebra mussel	0.25 mg/L	0.07 mg/L	> 825	22.0-25.0	McMahon <i>et al.</i> , 1990
		0.50 mg/L	0.15 mg/L	758		
		1.0 mg/L	0.30 mg/L	485		
		2.0 mg/L	0.60 mg/L	313		
		5.0 mg/L	1.20 mg/L	260		
TD 2335 (Atochem) Pesticide + alkylamine Filming agent	Zebra mussel	3.0 mg/L (1.27-3.52)		8	20.0	Piccirillo <i>et al.</i> , 1994
		5.1 mg/L		8		Piccirillo <i>et al.</i> , 1995
		2.0 mg/L		48		
		2.0 mg/L		8		
Mexel 432 Fatty amines Filming agent	Zebra mussel	3.5 mg/L (residual)	0.7 mg/L	19	20.0	Khalanski, 1993
		6.0 mg/L	1.2 mg/L	3h/day for 30 days	18 $^{\circ}\text{C}$	Giamberini <i>et al.</i> , 1994
		10 mg/L	2.0 mg/L	3h/day for 15 days	18 $^{\circ}\text{C}$	
Dichloro-2' nitro-4' salicylanilide (Baylucide)	Zebra mussel	0.1 mg/L		24		Hoestland, 1972
Niclosamide		0.5 mg/L		2		Sheide, 1997
N-triphenyl methylformoline (Frescon)	Zebra mussel	0.9 mg/L		24		Hoestland, 1972

QUATERNARY AMMONIUM

ADBAC

DDAC

ISOTHIAZOLONES

BENZOTHIAZOLES

FATTY AMINES

Fig. 3.24. – Chemical structure of some organic anti-fouling agents.

3.8.1.1 Quaternary ammonium compounds (QAC)

This chemical category has long been known to have strong bactericidal properties. Some products in particular are used as molluscicides in industrial systems :

- Clam Trol from Betz, whose active substance is an ADBAC (Alkyl dimethyl benzyl ammonium chloride), associated with dodecylguanidine ;

- H-130 M, from Calgon, whose active substance is a DDAC (didecyl dimethyl ammonium chloride) ;

- Bulab 6002, from Buckman, whose active substance is a poly [oxyethylene(dimethyliminio)ethylene (dimethyliminio)ethylene dichloride].

Their spectrum of action is wide, ranging from micro-organisms to molluscs. The toxic effect is due to destruction of the cellular membrane of bacteria or the destruction of branchiae of molluscs. Some of these products act rapidly ; others require longer exposure. Their effectiveness is heavily dependent on water temperature, which is to say the physiological activity of the organisms (Petrille & Werner, 1993).

Treatments are of the "periodic" type (see 3.1), and are applied 1 to 6 times a year depending on the site and the system, with exposure times of 6 to 24 hours. One example is given by Command & Matthews (1994) who treated a cooling water system supplied by water from Lac Saint-Clair (Canada) with DDAC in two injections at 1 mg/L for 24 hours in mid-July and late September. These periods were

chosen due to the water temperature, as the product is less effective below 12 °C.

QACs are surfactants which are adsorbed on suspended matter in water or on colloids such as humic acids. To reduce the concentration of active compounds in the treated water before discharge, clay is added, resulting in immediate detoxification. The bentonite concentration required to detoxify the discharged water is in the range of 5 mg/L to 40 mg/L.

Degradation of ADBAC has been measured by carbon dioxide production tests ; 66% is degraded in 29 days in aerobic conditions with an initial concentration of 10 mg/L (Dobbs *et al.*, 1995).

QACs are not metabolized by aquatic organisms ; they are but little accumulated in the consumable parts of fish (factor 40 to 50) ; they are immobilized in the ground and do not pass into underground waters (Schroenig *et al.*, 1995).

3.8.1.2 Isothiazolones, benzothiazoles

3-isothiazolone compounds exhibit high toxicity toward micro-organisms, and are used to control bacterial slime in recirculating cooling water systems.

Krzeminski *et al.*, 1975a, have investigated the degradation process of 3-isothiazolone. They found that these compounds are rapidly degraded in aqueous systems by hydrolysis (at basic pH) and by biological processes. Degradation products have no

special toxicity toward aquatic organisms (Krzeminski *et al.*, 1975b).

Benzothiazoles are mainly used as vulcanization accelerators for rubber, but they also have uses as slimicides, fungicides and herbicides. TCMTB (2-(thiocyano-methylthio)-benzotiazole) is effective against Zebra mussels in low concentrations, but requires exposure times of at least 10 days (Table 3.38).

TCMTB also hydrolyzes in alkaline waters and is partially adsorbed on suspended matters. According to Buckman Laboratories, TCMBT is rapidly degraded in aerobic conditions (half-life of 3.7 days). However, the degradation pathway of benzothiazoles is relatively complex, comprising hydrolysis in anaerobic and aerobic conditions, biomethylation and photolysis. The recent isolation of bacteria (*Rhodococcus*) capable of growth on first-stage degradation by-products is an important finding for elucidating the degradation pathway (De Wever & Verachter, 1997).

3.8.1.3 Filming agents

Some long-chain alkylamines (fatty amines) destroy the gill tissues of aquatic organisms by acting directly on the cell membrane, and/or by combination with the mucous layer produced by the gills.

TD 2335 (Elf Atochem) contains, as active agent, a dimethylalkylamine salt of an algicide and herbicide compound: endothall. Extensive studies

have been made on the degradation and aquatic toxicity of endothall. Endothall disappears rapidly in natural waters, with a half-life of less than 1 day.

Thus, TD 2335 offers the dual efficacy of a pesticide and of a filming agent. On-site trials at the Toledo power station (Ohio) showed that 8 hours of application at 3.0 mg/L is enough to kill Zebra mussels. The decrease in concentration over long stretches including a fly ash pond resulted in low residual concentrations of the active agent, and the absence of toxicity on non-target organisms (Piccirillo *et al.*, 1994).

Mexel 432 is a commercially available compound primarily constituted of long-chain aliphatic amines. In aqueous emulsions, this product forms a film on the cell membranes causing destruction of tissues in a varying proportion depending on the dosage. It can be effective against bivalves on a periodic treatment basis: at residual concentrations of 3.5 mg/L, the product rapidly causes major damage to the gills of Zebra mussels and causes death after 19 hours of exposure (Khalanski, 1993). The efficacy of long-term intermittent treatments on zebra mussels has also been shown in experiments: a dosage of 3 hours per day at 6 mg/L kills 100% of zebra mussels; the effective concentration corresponding to the residual was probably close to 3 mg/L (Giamberini *et al.*, 1994). In this experiment, it was also observed that byssus thread formation was reduced or inhibited by intermittent Mexel 432

injections. It has a broad spectrum of action on microfouling and macrofouling in both seawater and freshwater. An example of control of slime deposits on condenser tubes at a marine power station is presented in Figure 3.25. As this product also has anti-corrosion and anti-scaling properties, the treatment procedure is generally intermittent, intended to renew the film on the surfaces to be protected, but periodic treatments can be more effective on macrofouling.

Three processes are involved in the disappearance of Mexel 432 in solution: an immediate demand wherein clays and humic acids play an important role, the effect of stirring the water and injecting air bubbles, and bacterial degradation in aerobic conditions. Isolated bacterial strains in the Seine degrade Mexel 432; one of these degrades 98% of the product in 10 days. A first-order kinetics equation fitted to the experimental results frequently shows disappearance of 60% of the product in one day in river water, independent of the immediate demand. This kinetics is close to that of bacterial biodegradation with the most efficient strain. (Allonier *et al.*, 1997).

Information acquired regarding the toxic effects of the product on freshwater organisms shows rapid disappearance in natural waters of the product in its toxic form, and absence of detectable toxicity during its degradation (Arehmouch *et al.*, 1998).

On the basis of the data now available, acceptable residual concentration thresholds are proposed to protect freshwater organisms exposed continuously to the product: be-

tween 1 and 3 mg/L for brief releases (less than 1 hour) and 0.25 mg/L for continuous treatments lasting over 36 hours (Khalanski, 1997c).

3.8.1.4 Some General conclusions on treatment of industrial cooling water systems with organics

Organics present certain favourable characteristics for controlling fouling in industrial cooling systems.

They are easy to use. The minimum equipment required is an injection pump operated with a timer and an injection device which also mixes the product; this can sometimes be done by the pump used for circulating water in the system.

Generally, they have a wide spectrum of action on microfouling and macrofouling, depending on the selected procedure: periodic or intermittent treatments. Some, as can be demonstrated with a filming product, have also anti-corrosion and anti-scaling properties.

The cost of treatments with organic compounds depends on the protocol adopted, as well as on other factors such as the quality of the water to be treated and the characteristics of the target system. The most unfavourable conditions are found when the target species have a lengthy period of larval settlement and a high growth rate, and when particulate matter and colloids consume a large proportion of the product.

Fig. 3.25. – Evolution of the cleanliness of condenser tubes treated by a filming agent (Mixel 432) at a marine power station. Procedure : First injection at 4 mg/L then 4 mg/L once a day for 15 minutes. (Garey & Gross, 1997).

With respect to environmental acceptability for the products most commonly used in cooling systems, they disappear more or less rapidly in waters due to adsorption on suspended solids and colloids and by degradation involving no production of toxic by-products. Toxicity data on aquatic organisms exist which are consistent with this. For some QACs and filming agents, it is possible to eliminate toxic residuals at the outlet of the cooling systems by adding clay, which adsorbs the toxic agents. On the other hand, dilution of treated water with non-treated water inside the cooling system can eliminate any residual toxicity at the outlet of the system.

In the United States, the EPA authorizes use of QACs in continental waters under two conditions (Schroening *et al.*, 1995) :

- mixing : discharge in the river in which the release is made must be sufficiently high, which can preclude use of this kind of treatment in open circuit hydroelectric plants;

- detoxification of the effluent by the addition of clay prior to release, for products adsorbed on suspended matter.

Even despite this, environmental regulatory agencies are often opposed to the use of organics as an alternative to chlorination; they tend to prefer physical methods which are thought to eliminate the risk of chemical inputs in the aquatic environment. More and more, it will be necessary to prove that the choice of a given method can be justified by a "BATNEC Approach". In this sense,

when physical methods are not applicable or ineffective, certain organic products can provide the best available solution.

3.8.2 Metals

The efficacy of coatings containing leachable copper and zinc was discussed earlier (3.6.). There is no doubt that these metals have a toxic effect in their immediate vicinity. Devices have been developed to treat water circuits by producing metals in soluble form. These metals must remain in the water in a concentration which is toxic for the target organisms.

Most of the commercially available devices are electrolysis systems; the metals are generated by dissolving copper anodes with which, in certain cases, aluminum anodes have been associated. Aluminum is claimed to produce a floc of aluminum hydroxide, forming a complex with copper ($\text{Cu}(\text{OH})_3\text{Cu}_2\text{O}$) which has a coating effect. Davenport *et al.* (1986) have shown that this floc only inhibits larval settlement in low flow areas where it forms a physical choking barrier, but it is not toxic for biofouling organisms.

This technique has been used in seawater since the Sixties, essentially in boat cooling systems, but also in cooling systems in factories on land. A copper ion concentration of several dozen mg/L is required to eliminate marine biofouling : the long-term toxic concentration for the marine mussel is between 10 mg/L and 20 mg/L (Davenport *et al.*, 1986).

To treat high flows, the electrodes must be dimensioned accordingly; it is poor dimensioning which is responsible for the failure of these processes (Mussali, 1988). In one device proven effective in circuits with flow up to 3.3 m³/s, the electrodes are composed of a cathode with copper and aluminum anodes which deliver copper in a concentration of 25 mg/L in the circuit. The current varies between 10 A and 250 A in the largest installations. Other systems, also effective against marine biofouling, maintain a copper concentration which varies between 13 mg/L and 54 mg/L (Roch *et al.*, 1986).

In addition to the investment cost, the cathodes must be periodically changed: consumption of copper can be up to 65 kg per month, for a treated flow of 1 m³/s. The use of this type of process for direct cooling systems (a few dozen m³/s to a few hundred m³/s) would add several dozen tons of metal per year to the coastal environment. Unlike paints, for which leaching generates but little additional copper, electrolysis processes are not environmentally acceptable for direct cooling systems.

In recirculating cooling systems, with lower flow rates (3 to 8 m³/s), metal releases are lower but nonetheless represent an important occasional source in the river. The toxicity of copper in freshwater depends to a large degree on the hardness of the water. The European Union Directive regarding water quality requirements to protect the fish populations sets concentrations as a function of water hardness (Table 3.39).

Table 3.39. — Guideline soluble copper concentrations to protect freshwater fish populations depending on the hardness of the water (EEC 78/659).

Total Hardness (mg/L CaCO ₃)	Soluble Copper (µg/L)
10	5
50	22
100	40
300	112

In water with a low mineral content, copper is toxic in low concentrations for certain invertebrates and for salmonids. It is thus clear that water quality determines the amount of copper needed to eliminate invertebrates in freshwater: a few mg/L in soft water at 25 mg/L CaCO₃, as opposed to hundreds of mg/L in hard waters, with 300 mg/L CaCO₃ (Kelly, 1988).

The use of copper to combat freshwater biofouling in cooling systems with high flows therefore poses a problem, though tests are being conducted to eliminate the Zebra mussel with a concentration of around 10 mg/L (Blume *et al.*, 1994).

A biocide combining hydrogen peroxide and silver is used in closed systems for sterilization in the food industry, and poses no particular problems for this type of application. On the other hand, treatment of direct cooling systems and even of recirculating cooling systems, with releases into the environment, is environmentally questionable due to the addition of non-negligible amounts of metal.

Lastly, in this succinct overview, we should list the products which are probably, among those commercially

Table 3.40. – Effects of tributyltin acetate on embryogenesis and larval development of the oyster *Crassostrea gigas* (His, 1995).

TBT acetate (µg/L)	Biological effects
100	Inhibition of fertilization
50	Inhibition of cleavage of eggs
10	No development of trochophore larvae
3 to 5	No D larvae, all trochophores abnormal
1	Abnormal D larvae, no survival beyond day 6
0.5	No survival beyond day 8
0.2	No survival by day 12
0.1	Sub-total mortality on day 12
0.05	High mortality on day 10
0.02	No significant effect observed

available, the most effective against all types of biofouling: the organotins. Twenty years ago, Tributyl tin oxide (TBTO) was successfully tested on marine power stations in Italy, in the Netherlands, and probably in other European countries. It was found effective against bacterial slime and all kinds of macro-biofouling organisms in very low concentrations (7.5 mg/L in TBTO or 50 mg/L in commercial products).

However, the release of small amounts of organotin from the anti-fouling paints on pleasure boats was found responsible for a drastic reduction of oyster reproduction in the Bassin d'Arcachon on the southwest coast of France from 1976 to 1981. The extreme toxicity of TBT has been demonstrated on oyster larvae (Table 3.40) and adults (Alzieu *et al.*, 1980, His, 1995), on plankton crustaceans, and on various invertebrates. Sexual disturbances (imposex) are found in marine molluscs with concentrations

as low as 0.5 mg/L (Hall, 1988). Because of their toxicity, organotins are no longer used in cooling water circuits in European Union countries and their use in anti-fouling paints has been restricted by regulations.

3.8.3 Oxygen deprivation

Tolerance of the Asian clam *Corbicula fluminea* and the Zebra mussel *Dreissena polymorpha* to chronic hypoxia has been investigated by Johnson & McMahon (1997) and shown to be dependent on water temperature. On the zebra mussel, at the 5% dissolved-oxygen saturation level, the time required to kill 50% of the tested animals (LT50) is 44 days at 5 °C, 25 days at 15 °C and only 5 days at 25 °C. On the Asian clam, the LT50 is 20 days at 5 °C and 6 days at 25 °C (Table 3.41).

Oxygen deprivation was tested in France on an intake pipe at the Méry-

Table 3.41. – Lethal time (LT₅₀) for *Corbicula fluminea* and *Dreissena polymorpha* depending on dissolved oxygen saturation (DO%) and water temperature (Johnson & McMahon, 1997).

DO saturation (%)	<i>Corbicula fluminea</i>			<i>Dreissena polymorpha</i>		
	25 °C LT ₅₀	15 °C LT ₅₀	5 °C LT ₅₀	25 °C LT ₅₀	15 °C LT ₅₀	25 °C LT ₅₀
5.0	6 days	20 days	20 days	5 days	25 days	44 days
7.5	9 days	16 days		9 days	> 30 days	
10.0	9 days			9 days		
15.0				> 30 days		

sur-Oise drinking water processing plant. The test consisted in isolating the pipe and injecting sodium bisulfite to consume dissolved oxygen. The procedure was not effective: it took two weeks to consume the oxygen in the long pipe, where mixing of the reductive solution was difficult, and some of the mussels survived the treatment.

Hypoxia-based control methods require very low oxygen concentrations and sustained application at water temperatures lower than 20 °C. They are only potentially applicable to stagnant or semi-stagnant waters.

3.8.4 Potassium ions toxicity to Zebra mussels

Since the experimental work of Fisher *et al.* (1991) potassium ion is known to be a specific toxic agent for Zebra mussels: LC₅₀, 24 h is 138 mg/L at 20 °C.

Total mortality for 7-11 mm *Dreissena polymorpha* in the Moselle river

was achieved for 48 hours at 600 mg/L of KCl (K = 314 mg/L) (Khalanski, 1993). These high concentrations are not compatible with treatment of large cooling water systems but can be a convenient solution for circuits containing stagnant or semi-stagnant waters, such as fire protection systems. At Bruce B nuclear power station, operated by Ontario Hydro, treatment with commercial potash, at potassium concentration of 100 mg/L for some days was successfully applied to a fire protection system (Lewis *et al.*, 1997b).

3.9 OTHER PHYSICAL METHODS

3.9.1 Ultraviolet (UV) light

UV light ($\lambda \leq 253.7$ nm) is capable of killing bacteria in the bulk water of circulating water systems (Gilpin *et al.*, 1985) and is now commonly used by hospitals and food industries for

water sterilization 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 equipment to treat large volumes of water has led to the promotion of UV disinfection of different types of water and some applications have appeared in the field of antifouling treatments.

One important limiting factor for the use of UV light on natural raw waters is the adverse effect of turbidity, suspended solids and dissolved organic substances on UV absorbance. It is recommended to filter the wastewaters prior to treatment with UV light to eliminate coliform bacteria (Darby *et al.*, 1993).

3.9.1.1 Antifouling treatments on fresh water

Experiments were performed by Ontario Hydro on freshwater exposed for 40 seconds to a UV light (flux of 24 W/cm^2 at the lamp surface) produced by a germicidal system to test the effect on Zebra mussel settlements. No larval settlement was observed, but mussels of 2 mm to 5 mm in length were occasionally observed; these translocators are protected by their shell against UV light (Ewans *et al.*, 1992).

Ontario Hydro has tested a UV device at the Bruce B nuclear power station. Two banks of UV lights were installed on the cooling water inlet gallery for a service water circuit. This power station is located on the shore of Lake Huron, whose water is very

clear. The racks of lamps were located downstream of the traveling screen. Initial results are promising: the UV treatment killed about 85% of the Zebra mussel veligers. Trials were in progress in 1997 to verify the effect of UV light on bacterial slime and Zebra mussel development in the treated circuit.

Ontario Hydro tests suggest that UV light may be effective in preventing the settlement of macrofouling spat, but that it cannot prevent settlement of older stages entering the CWS.

3.9.1.2 Antifouling treatments on seawater

In Japan, UV irradiation is considered as a potential alternative to seawater chlorination (Hori *et al.*, 1993). Laboratory experiments on nauplii larvae of the barnacle *Chthamalus* spp. (Hori *et al.*, 1990), led to four important conclusions:

1°) The larval mortality depends on the UV dosage: energy density (mW/cm^2) $\times$ exposure time (s). All irradiated larvae are killed within 71 to 75 hours at a UV intensity of 5.6 mW/cm^2 for a minimum exposure of 2 minutes; 4 minutes of exposure are needed at 3.0 mW/cm^2 . The effective dosage is thus 672 mW.s/cm^2 .

2°) The lethal effect of UV irradiation is felt in around 3 days.

3°) Irradiated nauplii lose their swimming capacity at sub-lethal dosages: 93% of larvae exposed to 85 mW.s/cm^2 are unable to swim after 72 hours.

Fig. 3.26. – Intake conduit of the Isogo power station (Japan), equipped with an UV irradiation system. Redrawn from Hori *et al.* (1993).

4°) Exuvia production is inhibited at a dosage of 45 mW.s/cm^2 and there is no production of exuvia at 246 mW.s/cm^2 .

On cypris larvae, the only barnacle larval stage which can settle, settlement is reduced by 40% at 17 mW.s/cm^2 and by 96.8% at 30 mW.s/cm^2 (Hori *et al.*, 1993).

Based on these promising experimental results, a UV treatment system was designed and installed at the Isogo power station. This is a 530-Mw marine power station operated by Electric Power Development Co. Ltd. It is located near the mouth of Tokyo Bay (Hori *et al.*, 1993). The irradiation system consists in a panel of low-pressure UV lamps (160 W) attached to the side wall at one of the four intake conduits of the power station, in the area between the bar screen and the traveling screen (Fig. 3.26); the water flow in this conduit is $4.6 \text{ m}^3/\text{s}$. Lamps are positioned 75 mm from the

wall and the UV dosage is 17 W.s/cm^2 at a distance of 150 mm from the wall. Severe problems occurred with water leakages into the UV lamps due to imperfect sealing, and the initial design was changed to prevent leakage. The target efficiency for the system was some 50% reduction in settlement. The results of the field test showed a global reduction of 59% of macro-biofouling in wet weight, mainly due to the decreased mussel and tube worm settlement (Kawabe, 1997).

3.9.1.3 Benefits and drawbacks of UV antifouling technology

The great benefit of UV light is the absence of chemical discharge and the relatively low energy consumption.

The antifouling action of UV light is preventive; it may kill plankton organisms in the bulk water (bacteria,

larvae), 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. Furthermore, a certain minimum clarity of the water is needed for sufficient penetration of the UV light.

In spite of these drawbacks, UV light may be used as a supplemental method in biofouling control.

Feedback must nonetheless be acquired on industrial site tests in order to define the fields of application of the technique and provide needed information on the investment and maintenance costs of the treatment systems.

3.9.2 Electric fields

The use of electric fields as an antifouling method involves preventing the settlement of larvae due to the effect of high-energy electric shocks or low-level currents. Theoretically, the biological effect, and consequently the efficiency, is proportional to the square of the electric field intensity in V/cm. This requires that the water pass between plate electrodes close enough to each other to achieve the optimum intensity.

The energy consumption also depends on the salt content of the water: it is inversely proportional to the water resistivity. In order to minimize the energy consumption of this type of system, experiments have been conducted on pulsed fields: shocks of 0.77 microseconds (μ s) with an inten-

sity in the range of 1 to 10 kV/cm can halt larval settlement. In seawater, the barnacle larva does not settle with 0.77 μ s shocks at 7 kV/cm, and a more than 90% reduction in settlement was observed at an intensity of 3 kV/cm. A field study performed in river water at Norfolk, Va, USA, showed that pulses of 0.77 μ s at 6.5 kV/cm can protect pipes against biofouling. The energy consumption in this trial was about 1 MW to treat a flow of 2 m³/s, but better efficiencies are expected in the future (Schoenbach *et al.*, 1997).

Aside from the question of electricity consumption, use of this method on large volumes of relatively fast-flowing raw waters can not be envisaged until industrial experience is acquired. Among other things, the long-term resistance of a device containing electrodes must be determined.

Low-level electric fields could also be effective against settlement of Zebra mussels, as shown by promising experiments conducted at the Nanticoke thermal power station operated by Ontario Hydro. Panels with electrodes were placed 5 cm apart and electrified with currents of 16 to 20 V, 1.0 to 1.9 A, generating a field intensity of 3 to 10 V/cm (Fears & Mackie, 1997).

Cathodic protection

In the former Soviet Union, cathodic protection systems were used to prevent Zebra mussel settlement, with higher current densities than required for the anti-corrosion effect: 50 to 75

mA/ft^2 . Studies were carried out in the 90s in the U.S. and Canada in order to test the effectiveness of cathodic protection with currents in the range of 2 to 10 mA/ft^2 (Lewis & Pawson, 1993). Larval settlement was greatly reduced at current densities of 6 to 9 mA/ft^2 (Table 3.42).

Hydro Quebec equipped a large sluice gate with special anodes (Cu, Ni, Pt) electrified at current densities of approximately 13 mA/ft^2 . After 5 months, 70% of the Zebra mussels settled on steel and concrete walls were removed and probably killed (Serli *et al.*, 1994).

Ontario Hydro tested cathodic protection to control Zebra mussels on the concrete walls of a pump well at the Bruce B power station (Lewis *et al.*, 1997a). Anode mesh panels were fixed on the walls of the well between trash racks at the inlet and the traveling screens. After two years, a reduction of 90% of the older age classes (0.5 cm to 2.0 cm) was observed in comparison with the control wells. The

Table 3.42. – Results of two experiments on cathodic protection against zebra mussel settlement, at various current densities (Lewis & Pawson, 1993).

Current density	Larval settlement	Corrosion
Control (0)	137/ m^2	Yes
2 mA/ft^2	156/ m^2	some
4 mA/ft^2	80/ m^2	No
5 mA/ft^2	32/ m^2	No
Control (0)	29/ m^2	Yes
6 mA/ft^2	2.6/ m^2	No
9 mA/ft^2	2.6/ m^2	No

dry weight of the remaining mussels was also less than that of the control. This experiment led to the following conclusion: current densities of less than 10 mA/ft^2 and voltage < 40 V are effective in controlling the development of Zebra mussels on steel and concrete walls. A cathodic protection system has also been installed in some basins of the intake structure at the Darlington nuclear power station operated by Ontario Hydro.

3.9.3 Magnetic fields

Magnetic systems are known to control scaling in pipes; this would suggest a biological effect on calcium metabolism, which could disturb and even stop shell growth in molluscs. To date, there is no evidence of such an effect. Experimental trials on river water passing through cells with magnets have been conducted at a Rochester Gas & Electric Corporation testing station. After 99 days, the Zebra mussels on the control and test bioboxes showed no significant differences in terms of mortality, shell length or calcium-magnesium content in soft tissues (Smythe *et al.*, 1997).

3.9.4 Acoustic energy

Ontario Hydro conducted experiments on high acoustic energy (173 to 199 dB), using juvenile mussels to test their attachment on the wall of an aluminum pipe (Ewans *et al.*, 1992). During the 4-hour treatment,

the most effective frequency was in the range of 8 to 16 kHz (100% mussels not attached).

Pulses with a high acoustic energy can remove the biofouling cover from concrete walls and avoid mechanical cleaning in pipes, basins and wells fed with raw water. A submersible unit has been specifically designed for this purpose (Bryden, 1997). It is equipped with a sparker unit delivering 5-kilojoule pulses every 45 seconds. This device generates a sound intensity of 200 plus dB. It was tested successfully for 6 months against Zebra mussels and biofilm at municipal water treatment facilities.

3.10 BIOLOGICAL CONTROL

The principle of biological control is to combat a targeted species by favouring the development of its natural enemies. This involves a wide variety of biological and ecological processes: pathogens, parasites, predators and competitors can reduce populations of biofouling species. The recent introduction of Zebra mussels in North America has prompted numerous studies in this field.

Natural aquatic bacteria capable of killing Zebra mussels have been selected from stressed mussels; some lead to 100% mortality in 5 days. Toxins (polysaccharides and proteins) have been extracted from these strains and have been tested with success in organic coatings (Gu & Mitchell, 1997).

The association between a parasite and a host is the result of a co-evolution process, thus parasitic species are frequently strictly host-specific. Preliminary research has shown that some ciliates parasiting the digestive gland of *Dreissena polymorpha* could have deleterious effects (Molloy *et al.*, 1997).

Coatings based on naturally-produced anti-foulants and enzymes have been reviewed by Berger *et al.*, 1994. To date, no commercial products have resulted from this.

Chemicals are capable of repelling settled organisms; thus xanthatin, isolated from leaves of *Xanthium strumarium*, has a repellent activity against the blue mussel – *Mytilus edulis* – (Harada *et al.*, 1985) and diphenylamine was found to be an excellent repelling agent for zebra mussels, and phenols extracted from wood are also efficient as repellents (Gu & Mitchell, 1997).

Competition for space is important for settled organisms, and it has been observed that Zebra mussels populations have declined in some parts of the Rhine where an amphipod crustacean (*Corophium curvispinum*) has recently massively developed, though according to observations in 1996-1997, the two species co-exist in the Moselle. Zebra mussels are not found on the sponge *Spongilla*, but the latter has a low rate of coverage of hard substrates. Bryozoan *Lophopodella carteri* reduces the settlement of zebra mussels in the Great Lakes, according to Lauer *et al.* (1997).

It is unlikely that one species can be efficiently controlled by occupation of all available space by another species. The replacing species would then be at least as undesirable as the species replaced. It is, on the contrary, extremely frequent to find several species co-existing on the walls of cooling water systems :

- in seawater, hydroids and barnacles, on which marine mussels settle (*Mytilus edulis*),

- in freshwater, a layer of hydroids (*Cordylophora caspia*) on which Zebra mussels settle.

Competition for food is equally decisive in development of biofouling species. Most consume particles in suspension, but any excessive development is merely due to better use of food resources than that of their competitors. The same is true of predators : if one species has developed extensively, this implies that it is but little consumed by predators.

Finally, it is necessary to take the specificities of the circuits themselves into account; they are extremely favourable to biofouling and the basic ecological factors (water velocity, availability of food, absence of predators) are equally favourable to biofouling development. For all these reasons, ecological factors involving competition and predation do not apply to cooling water systems, though they often play an important role in natural systems. In northeast France, the Zebra mussel is controlled in many lakes and reservoirs by diving ducks which limit mussel development, whereas thermal power

plant circuits are overrun by this species.

Some biological control methods, mainly those involving pathogens and parasites, offer interesting prospects for the future but are still in the experimental phase and cannot yet be used for industrial applications. If effective methods were available, they would still need to be proven harmless to aquatic fauna. The conclusion proposed by Claudi & Mackie (1993) remains true today : "This type of research requires a long-term commitment and usable products are probably years away".

3.11 BIOLOGICAL MONITORING

3.11.1 Macrobiofouling

Long-term monitoring of biofouling at industrial sites provides information on the composition and abundance of populations settled in the circuits. Sometimes major fluctuations are found with invasive species over the years. These changes are revealed by sampling at selected points in the cooling system (water intake structure, screens, pipes, galleries, basins, heat exchangers) during scheduled shutdowns, particularly for cleaning (Khalanski, 1997a, b).

Long-term monitoring enables detection of the appearance of new invasive species, and can be performed outside the cooling system, in the river or on the sea coast. In France,

Fig. 3.27. - Abundance of the Asiatic clam (*Corbicula* sp.) in the river Rhône from 1990 to 1994 in the vicinity of the Le Bugey nuclear power station (CEMAGREF Data, Khalanski, 1997a).

ecological monitoring of the aquatic environment around nuclear power plants began in the early 80s. This program revealed the appearance of invasive species like the Asian clam in the Rhône (Fig. 3.27) and that of the amphipod crustacean *Corophium curvispinum* in the Moselle.

Schedules for treatment are defined on the basis of the periods of settlement of the main fouling larvae and the growth rate of organisms in the circuits to be protected. For this, it is indispensable to collect data inside the circuits, given that the water velocity and temperature conditions are highly specific to location in the circuit. In particular, it should be remembered that the growth rate of organisms in

the natural environment is generally slower than for populations settled in plant circuits. If the necessary data is available, a growth model applicable to the circuits can be developed (Moreteau & Khalanski, 1994).

During the critical period in the year, corresponding to settlement and optimum growth of biofouling species, biomonitoring can be installed to provide the data needed for optimization of the treatment in light of the specificities of any given year. This type of monitoring is especially helpful in the case of periodic treatments and "end of season" treatments.

In the Netherlands, KEMA has developed a "mussel monitor" consisting in a closed cylindrical PVC container

in which the water flows from top to bottom (Jenner, 1983b). This monitor can be used to detect spat settlement of bivalves such as *Mytilus edulis*, *Dreissena polymorpha* and *Mytilopsis leucophaeata*. It is installed at power stations during chlorination, and is used to follow the course of treatment and evaluate its success (Jenner & Janssen-Mommen, 1993).

In 1998, a new design of a biofouling monitor was tested at several power stations. This design was the collaborative result of Fawley ARL and KEMA. Main feature is the choice for flow direction which is now bottom-top. The design allows operators to sample the monitor during operation. Silting-up of the monitor is solved by building in a sediment trap. The monitor can be equipped with extra analysers for pH, dissolved oxygen, turbidity and temperature. For mussel spat detection a non-woven 3M mat is used which is the absolute favourite settling material for mussels.

ENEL uses a simple monitoring procedure to provide power station operators with an indication of the periods when chlorination can be avoided in once-through cooling seawater systems. Plates are immersed monthly near the intake and observed under a dissecting microscope in order to count the surface units (1 cm^2) colonized by fouling organisms. This value is converted into conventional percentage of total cover. During spring, plates are also observed fortnightly, for more precise determination of the start of settlement. Figure 3.28 gives the monitoring results

from a two-year survey in a Northern Adriatic power station, with an indication for suspension of chlorination for 5 months.

Biofouling has also been monitored at the Vandellos nuclear power station (operated by UNESA on the Mediterranean coast of Spain) to determine the periods of chlorination.

ENEL has produced a manual for monitoring macrofouling settlement periods and optimizing chlorination in thermoelectric power plants (ENEL-CRAM, 1996).

A bibliographic survey on Mediterranean fouling has been published by Relini (1993) with references on earlier papers about fouling studies in power stations (Relini & Romaiore, 1976; Relini & Bianchi, 1979; Relini *et al.*, 1980; Relini, 1984; Gitay & Glazer, 1979; Glazer & Gitay, 1988/89; Ambrogi, 1993.)

3.11.2 Microbiofouling on line monitors

Some monitoring devices which are able to detect biofilm growth through induced physical effects (changes in thermal conductivity or in the friction factor) are already available, but their sensitivity proved to be low during the crucial first phase of the biofilm build-up (Characklis, 1990). Such devices are generally able to signal the presence of biofilm when its thickness is more than $\approx 30\text{--}40 \text{ }\mu\text{m}$. Furthermore, their use for driving the

A - Percentage of cover of the main fouling groups of organism and monthly mean temperature

B - Percentage of total cover, monthly mean temperature and period of possible suspension of chlorination (December 20, 1995 - May 15, 1996).

Fig. 3.28. – Monthly monitoring of fouling settlement at a power stations on Northern Adriatic, operated by ENEL, from M1 (Jan. 18-Feb. 15, 1995) to M25 (Dec. 11-Jan. 8, 1997).

A: Percentage of total cover on plates at the intake,

B: monthly mean temperature and period of possible suspension of chlorination (December 20, 1995 – May 15, 1996).

biocide programs, often, was not effective to keep satisfactory cleaning conditions in time. The experiments conducted by Lewis (1982) to monitor chlorination treatments employing sensors based on change in thermal conductivity : for example, pointed out that, at the end of a chlorination, if residual biofilm stays on the surfaces, the bacterial populations undergo a selection and the biofilm quickly grows and becomes more resistant to chlorine.

In order to produce biofilm sensors with higher sensitivity, during the last few years some innovative systems were set up. They are now available on the market (BIOX, BIO-George, Bioguard). These systems utilise electrochemical probes, inserted in an appropriate way into the cooling circuits. They permit the evaluation of the changes in kinetics of electrochemical processes occurring on metal surfaces and induced by bacterial settlement : through the continuous measurement of one or more electrochemical parameters (current density, potential difference, impedance, potential noise, polarisation resistance). It has been recently proven that the variation of some of these parameters is directly associated to the growth of the biofilm at the metal-sea water interface on an active-passive alloy (Chandrasekaram & Dexter, 1993; Mollica *et al.*, 1988).

Furthermore, it was shown (Mollica *et al.*, 1996) that the galvanic current due to the coupling of a stainless steel electrode with a sacrificial anode is associated with the biofilm deve-

lopment on the surface of the stainless steel electrode. Because the galvanic current reveals the changes of the cathodic properties on the stainless steel surface, i.e. the change in the oxygen reduction rate, the electrochemical effect of the biofilm growth is usually named "the oxygen reduction depolarisation" (Mollica *et al.*, 1990). It was proven that the electrochemical sensors of biofilm growth are able to detect, in real time, the effect of antifouling procedures and are able to drive their application (Mollica & Ventura, 1993a, b).

The main advantage of these devices, is that their use does not require personnel skilled in the biological or chemical field.

The lack in the control of sea water chlorine concentration can be the cause of ineffectiveness of the biocide treatments (Cristiani & Bianchi, 1997). To control and optimise the dosage time and the concentration of sodium hypochlorite during the biocide treatments, ENEL has recently set up an innovative electrochemical system BIOX (available on the market by STELAR, italian factory) which allows the monitoring both of the biofilm growth and the evaluation of the changes in water TRO (total residual oxidant).

ENEL system (Cristiani *et al.*, 1997) employs a new simplified version of electrochemical biofilm sensors. The response of the sensor permits to have a direct index of biofilm growth and the effective TRO on the sensor surface. The signal increases from V_0 to V_b as a consequence of the highest cathodic efficiency in-

Fig. 3.29. – Lay-out of the biofilm and TRO electrochemical monitoring performed at Vado Ligure power plant during May 1996.

duced by biofilm growth on sensor and, of course, reverts to its initial value when the biofilm is completely destroyed by a suitable biocide addition to sea water. The cathodic efficiency induced by TRO on sensor has the same effect as the biofilm growth, but it is possible to discriminate the contribution of the two parameters.

At present, BIOX is used in some Italian power stations.

At the Vado Ligure power station, the chlorination program was performed in this way : 4 treatments per day, each lasting about half an hour, with "1 ppm (as TRO) of sodium hypochlorite. The graphs (Fig. 3.29) show that the chlorination has been regularly

carried out for one day only, after that TRO concentration decreased to very low values and, consequently, the biofilm started to grow.

The advantages expected from the introduction of such devices in all the plants that suffer from biofouling problems may be summarised as follows :

1. on-line information about biofouling growth on the water-side surface of the condenser tubes;
2. possibility of defining in real time the amount of sodium hypochlorite (or other oxidising agents) needed to obtain an effective concentration of TRO in the cooling water, thereby avoiding the need for carrying out continuous laboratory analyses for chlorine demand and concentration, and avoiding the use of other instruments which require careful and frequent maintenance;

3. optimisation of the consumption of sodium hypochlorite (or other oxidising agents), with respect to the treatment duration and concentration which are strictly necessary to inhibit the microbiological (the first stage of the biofouling) growth.

At KEMA, good results have been obtained with the BioGeorge™. The BioGeorge™ online monitoring system measures the electrochemical effect caused by the biofilm on metal surfaces. The probe of the system consists of two identical electrode systems. Increase of the «applied» or «generated» current indicates an increase of biofilm activity. Treatment of an existing biofilm shows a rapid return to the initial level. Summarised : the here presented systems are valuable tools for improvement of heat exchanger performance.

Regulatory context

4.1 INTRODUCTION

Any fouling control procedure, involving the chemical treatment of cooling water, can result in a residual discharge of toxins to the environment. The costs of such procedures are generally sufficient to provoke a common interest with the environmental protection need of minimizing these residuals, their presence being both wasteful and inefficient.

An antifouling agent which acts by inhibiting the normal development of aquatic organisms, as most in common use do, will inevitably pose some degree of risk of environmental impact if discharged. To use such agents, it has become necessary to operators to delimit that risk, support the development of an informed understanding of the degree of tolerability of that risk, and minimize that risk where both practicable and needfull. Where the risk of any particular procedure has been found to be intolerable, that procedure has had to change.

The antifouling procedures in use today are those which present a ba-

lance between operational practicability and the requirements of the environmental regulators, either stated or anticipated. Given that operational practicability tends (on the basis of accumulated and shared experience) towards an innate conservatism of practices, and that there is currently a rapid development in environmental regulation, the balance is probably altering. One function of this publication is to document the operator's understanding of current best practice in such a way that it can be considered in this context, in an informed manner, by both the operators themselves and the environmental regulators.

4.2 BASIC PRINCIPLES OF THE EUROPEAN UNION (EU) LEGISLATION

The reduction and control of water pollution and contamination have always been important priorities in the European Union's environment pro-

gramme. EU controls on water pollution apply at several levels :

- at the level of the market, where specific products are controlled,
- at the level of industrial sector, where practices within a specific industry or type of industries are controlled,
- at the level of end-of-pipe discharges, where the release of specific dangerous substances is controlled; and
- at the level of environmental quality, where quality objectives are defined.

A variety of principles have become established in European law: perhaps the most fundamental are those of "sustainability", "polluter pays" and "subsidiarity".

There is now an increasing acknowledgement of the need to reconcile the needs for continued development with the long term goal of protecting the environment. A common working definition of sustainable development is "development which meets the needs of the present without compromising the ability of future generations to meet their their own needs" (Brundtland, 1987). Sustainable development was the central theme of the UN Conference on Environment and Development in Rio in June 1992 which resulted in Agenda 21, a programme to work towards a more sustainable future. The European Union's Fifth Action Programme "Towards Sustainability (1993-2000)" builds on earlier EU policies aimed at, amongst other things, maintaining and improving water quality by the prevention

of pollution of groundwater and fresh and marine surface waters.

The sustainable development approach is contributing to pressure for a move away from the use of chemicals which are persistent or give rise to persistent by-products. This may lead in some instances to a switch to using non-oxidising biocides, although some of them are themselves persistent. The pressure to use chemicals which are less persistent, and for which ecotoxicological data are available in order to conduct risk assessment, may lead to a reduction of the variety used.

"Polluter pays" is implicit to much European legislation and is a recognition that there is a need to internalise environmental costs, making industry itself accountable for its emissions and liabilities, rather than the public purse. This accountability is seen to extend to the cost of regulation. In practice, the various mechanisms which enforce this principle exist at national rather than at European Union level.

The principle of subsidiarity means that it is for member states within the EU to implement Directives through national legislation and regulation, establishing standards of compliance no less strict than the Directive themselves stipulate. In practice, the diversity of pre-existing legislation and national regulatory policy tends to result in somewhat different arrangements locally.

The EU has thus introduced a variety of regulatory controls that have both a direct and indirect effect on the

use of oxidising biocides in cooling waters. These controls are summarised below.

4.3 EXISTING EU LEGISLATION

4.3.1 Market controls

There is a considerable body of legislation (e.g. 76/769/EEC and amendments) relating to the marketing, use and disposal of dangerous substances, including organochlorine compounds. Whilst not directly impacting on the use of chlorine as a biocide, this contributes to a general pressure from a variety of sources to reduce the overall utilisation of chlorine. More recently, legislation has been proposed that may result in the imposition of controls on chlorine as a biocide: this may have a significant impact on current antifouling practices in the power generation sector (see 4.4).

4.3.2 Discharge controls

The use of chlorine based biocides results in the formation of organohalogen, as chlorination by-products, or the release of free oxidants that may combine with substances in the receiving waters to form halogenated organics. The EU has introduced a number of measures to prevent or limit the discharge of organochlorines to the aquatic environment, but to

date the formation of organochlorine due to the use of chlorine as a biocide has not been considered as meriting control at Community level; the possibility remains.

One specific Directive is relevant.

The Dangerous substances Directive (76/464/EEC)

This 'Framework' Directive (76/464/EEC) was adopted with the intention of reducing the input of a number of the most dangerous substances to the aquatic environment. The directive was based on two lists: pollution due to the discharge of List 1 substances was to be eliminated by the use of either uniform emission standards (UESs or end of pipe limits) or environmental quality standards (EQSs), whilst pollution by List II substances was to be reduced solely by the use of EQSs.

List I covers eight families of substances, considered dangerous by virtue of their toxicity, persistence and tendency to bioaccumulate, including 'organohalogen compounds and substances which may form such compounds in the aquatic environment'. The European Commission drew up a priority candidate list of substances to be considered for List I status. A significant number of the 132 substances on this list were chlorine based. To date daughter Directives have now been adopted for discharges of mercury, cadmium, hexachlorocyclohexane (HCH), DDT, pentachlorophenol (PCP), carbon tetrachloride, the 'drins' group of pesticides (aldrin, endrin, dieldrin and

isodrin), hexachlorobenzene (HCB), hexachlorobutadiene, chloroform, and most recently (in 1990), 1,2-dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene. In all cases, the Directives provide for emission limits and quality objectives, and they encourage the use of best available technology in new plant.

Only the trichlorophenols can be regarded as chlorination byproducts, and only chloroform, for which an EQS of 12 µg/L has been set for all waters, could be considered to have implications for the use of chlorine based biocides in cooling waters.

List II includes substances known to have a deleterious effect on the aquatic environment having a somewhat lesser significance than those of list I. This list includes metals such as zinc, nickel, chrome, lead, arsenic and copper, "biocides and their derivatives not appearing on list I", and substances such as cyanide and ammonia. The Directive required member states to provide environmental quality objectives and standards for list II substances.

This legislation is in the process of being replaced, and new lists of priority substances are being considered. This review will probably result in point source discharge controls from the most polluting industries, including the power generation sector, being covered by the Directive on Integrated Pollution Prevention and Control (IPPC), whilst the discharge of hazardous substances from other point sources as well as diffuse sources, agriculture etc., will be covered within

the new "Ecology of Natural Waters Directive".

4.3.3 Water Quality Controls

The EU has adopted a number of measures stipulating concentrations, usually known as "environmental quality standards" (EQSs), that should not to be exceeded in designated use-related receiving waters. Because limits tend only to apply in nationally designated waters they have had fairly limited impact on cooling water discharges to date; this may change with the introduction of the developing Ecology of Natural Waters Directive (see 4.4).

Existing use-related Directives are summarised below.

The Quality of Surface Water for Abstraction Directive(75/440/EEC)

This Directive was adopted with the intention of setting minimum standards for surface waters intended for abstraction for drinking water purposes. Over 40 parameters are listed in an Annex, most of which are assigned environmental quality standards that should not be breached if an abstraction for drinking water purposes is to be made. One of the few listed parameters for which an EQS is not set is total extractable organic chlorine. It was expected at the time that standards for this parameter would be developed in the future, although this has not occurred.

*The Directive on Water Intended
for Human Consumption
(80/778/EEC)*

This Directive (usually known as the Drinking Water Directive) was adopted with the intention of protecting human health by setting quality standards for drinking water to be met at the consumer's tap. Although, in effect, the Directive relates to the quality of a 'product', it has resulted in the introduction of measures to improve the quality of water abstracted from the aquatic environment in order to minimise treatment costs and ensure that certain onerous standards, for example that relating to the pesticide parameter, can be met.

Amongst the parameters listed in the Directive is one relating to residual chlorine. No standard is set for this parameter but member states are required to ensure that no substance used in the treatment of drinking water supplies should constitute a threat to human health. Because tainting of tap water may occur as a result of water treatment, the authorities may place additional pressures on dischargers who contribute to the presence of CBPs in the raw water prior to its abstraction for treatment and subsequent supply to the consumer. There are proposals to review this Directive (see 4.4).

*The Freshwater Fisheries Directive
(78/659/EEC)*

This Directive was adopted with the intention of protecting freshwater fish by setting environmental quality

standards (EQSs) for certain substances in designated freshwater fisheries. The Directive sets standards for 14 parameters, including one of $< 5 \mu\text{g/L}$ for hypochlorous acid.

*The Shell Fisheries Directive
(79/923/EEC)*

The Directive lays down the standards required to ensure a suitable environment for shellfish growth in specifically designated brackish and coastal waters. The Directive does not stipulate an EQS for chlorine but does require that no organohalogenated substance should be present that may be harmful to shellfish growth or use.

*The Biocidal Products Directive
(98/8/EC)*

This Directive "On the placing of Biocidal Products on the Market" is intended to complement the existing Plant Protection Products ("Pesticides") Directive (91/414/EEC). It requires that biocides have prior authorisation before being marketed and used. All biocides presently purchased by the power industry will eventually require authorisation in this manner.

The Directive is provoking a system for authorising the use of biocides throughout the EU. Application for authorisation for a biocidal product will be the responsibility of the person placing the biocide on the market, and any submission will require :

1. Prior recognition on a positive list of active ingredients

Only active ingredients listed in a subsequent Annex to the Directive will be permitted for use in authorised biocides. Inclusion of an active ingredient on the "positive list" will be dependent on it satisfying a number of human health and environment-related criteria. These are outlined in detail in Annex II of the Directive and can be summarised as :

- description of the applicant,
 - identity of the active substance,
 - physical and chemical properties of the active substance,
 - analytical methods of detection and identification,
 - effectiveness against target organisms,
 - toxicological profile for man and animals including metabolic effects,
 - ecotoxicological profile including environmental fate and behaviour,
 - measures necessary to protect man, animals and the environment,
 - classification and labelling ; and
- a summary and evaluation of the information gathered above.

2. Submission of dossiers on the biocidal products

In addition to the dossiers submitted to support the inclusion of active ingredients on the positive list, dossiers must also be submitted to support an application for authorisation to use each biocidal product. The data requirements are the same as those outlined above for active ingredients.

The competent authorities in each member state will only authorise a biocide if it satisfies the following criteria :

a) Its constituent active ingredients are on the positive list.

b) On the basis of the supporting dossier, the biocide :

- is sufficiently effective,
- has no unacceptable effect on the target organisms,
- has no harmful effects itself or as a result of its residues, on human or animal health, directly or indirectly (e.g. through drinking water, food or feed) or on ground water,
- has no unacceptable effects on the environment, having particular regard to the following considerations :
 - its fate and distribution in the environment (particularly contamination of water including drinking water and ground water and its impact on non-target organisms),
 - it does not cause unnecessary suffering and pain to vertebrates to be controlled.

c) The nature and quantity of its active ingredients and, where appropriate, any toxicological or ecotoxicological significant impurities and co-formulants, and its residues of toxicological or environmental significance, which may result from authorised uses, can be determined according to the information submitted in the appropriate dossiers.

d) Its physical and chemical properties have been determined and deemed acceptable for purposes of the appropriate use, storage and transport of the product.

A biocide authorised in one member state shall be automatically authorised in any other member state within 120 days of a use application being made, unless the behaviour of the biocide or target organism differs markedly from one country to another. As a minimum, authorisations must be reviewed after 10 years, with a review being initiated immediately whenever new evidence arises that the existing authorisation may no longer be appropriate.

The Directive on Integrated Pollution Prevention and Control (IPPC) (96/61/EEC)

This Directive was adopted in 1996, and forms the framework for the control of discharges from the most polluting industrial sectors in the EU, including most fossil-fuelled power plants. The intention is to more readily integrate the control of releases to different media: discharges to air and water, waste to landfill. The model for this initiative already exists in a number of member states, for example with Integrated Pollution Control in the UK. IPPC however establishes a wider definition of "installations" and prescribes a wider list of processes. The primary control mechanism will be the introduction and enforcement of Best Available Techniques (BAT).

EURELECTRIC, representing the electricity generation sector across Europe, have produced a technical report on BAT for cooling water systems (EURELECTRIC, 1998).

The Directive on Drinking Water (98/83/EC)

The residual chlorine parameter of the original directive (80/778/EEC) has been removed but new standards for bromate (10 µg/L) and total THM's (100 µg/L) may have implications for discharges of chlorinated cooling waters in the vicinity of drinking water abstraction points. An additional factor in such instances may be the requirements that taste and odour be acceptable to the consumer.

4.4 FORTHCOMING EU LEGISLATION

The natural development of earlier initiatives, together with a wide ranging review of European legislation, means that a number of potentially highly significant revised and completely new Directives will appear over the next few years. The outlines given here will inevitably become dated as the final versions of the text evolve.

The Proposed Ecological of Natural Waters Directive

This proposal was drafted following concerns that Member States were only seeking to protect surface waters with well defined uses, for example, abstraction for drinking water purposes and bathing, whilst little or no attempt was made to protect the general ecological quality of the aquatic environment as a whole.

The Directive will require that a high or good level of ecological quality, be achieved in all waters, and not just those that have been designated for a particular use. When adopted, the proposed Directive will replace the Dangerous Substances, Surface Water Abstraction, and Freshwater Fisheries Directives.

This goal will be achieved by :

- defining operational targets for ecological quality in all EU surface waters,

- setting up a comprehensive monitoring system for water quality,

- preparing an inventory of all point source discharges and sources of diffuse pollution,

- drawing up a series of integrated programmes to improve surface water quality.

Annexes to the proposed Directive outline the elements upon which a definition of good ecological water quality should be based. These include :

- dissolved oxygen,

- concentrations of toxic and other harmful substances in water, sediment and biota,

- diseases in aquatic life forms,

- diversity of invertebrate, aquatic plant, fish, and higher vertebrate communities,

- sediment structure and quality,

- aesthetics of the site.

Although not yet finalised, implementation groups have already been formed by the member states.

Directive on the Control of Major Accident Hazards involving Dangerous Substances (COMAH) (96/82/EC)

In 1982 the EC adopted the 'Seveso' Directive on major accident hazards of certain industrial activities. The Directive required certain defined industrial installations at which dangerous substances were stored in greater than threshold quantities to introduce accident prevention programmes. It applied mainly to chemical, petrochemical and metal production facilities. The new COMAH Directive extends the provisions to cover many more industrial sites.

The basic requirements of COMAH now apply to any industrial site at which more than 10 tonnes of chlorine and/or 40 tonnes of bromine are stored. More stringent requirements relating to the identification of potential hazards and the preparation of a Major Accident Plan apply to sites at which more than 25 tonnes of chlorine and/or 100 tonnes of bromine are stored.

4.5 OTHER INTERNATIONAL COMMITMENTS

4.5.1 Oslo and Paris Conventions, North Sea Ministerial Conferences (OSPAR, NSC)

A number of international conventions bear upon members of the EU, either directly or indirectly. Amongst

these, historically, were the "dumping at sea" and "discharge to sea" agreements embodied in the separate Oslo and Paris Conventions – subsequently revised and consolidated within the renewed Paris Convention. At the heart of this is an agreed need to protect the seas of the Northeast Atlantic from unsustainable industrial practice, from both diffuse and point sources. All the relevant member states have ratified this convention with the EU itself, are members of the allied commission. Both the workings of this commission and the associated North Sea Ministerial Conference process have a significant effect on environmental regulatory policy within Europe, with signatories also being obliged to regard their detailed recommendations with a high level of commitment. As far as cooling water biocides are concerned, and as with current EU legislation, these initiatives have encouraged a reduction in the input of organochlorines to the aquatic environment.

The final declaration of the 1992 Ministerial meeting of the Oslo and Paris Commissions stated :

"as a matter of principle for the Convention area, discharges and emissions of substances which are toxic, persistent and liable to bioaccumulate, in particular organohalogen substances, and which could reach the marine environment should, regardless of their anthropogenic source, be reduced, by the year 2000, to levels that are not harmful to man or nature with the aim of their elimination : to this end signatories of the

Convention are to implement substantial reductions in these discharges and emissions and where appropriate, to supplement reduction measures with programmes to phase out the use of such substances, and instruct the Commissions to keep under review what timetables this would require." More recently, in 1998, in what is now known as the "Sintra Declaration", all signatories agreed "to move toward the target of cessation of discharges... of hazardous... of hazardous substances by 2020". Whilst doing this they emphasized the importance of the Precautionary Principle. Procedures are now engaged for revising the list of priority hazardous substances.

4.5.2 World Health Organization (WHO) Drinking Water Guidelines

Although the WHO Drinking Water Guidelines (WHO 1993b) do not have any statutory (legal) basis, they have proved to be very influential in shaping EC legislation in this area. For example, the proposed revisions to the Drinking Water Directive have been based on the WHO Guidelines, (see section 4.4.).

A brief summary of the guidelines is provided (Table 4.1) with respect to the power industry's operations. It must be emphasised that these guidelines only apply to the presence of these substances in drinking water.

The use of chlorine as a disinfectant in drinking water supply is causing a number of worries for

regulatory authorities due to the formation of halogenated by-products. At present, the established view is that the presence of low concentrations of these chemicals in drinking water is an acceptable trade-off ensuring the microbiological safety of water. However, this view is changing and there will be inevitable pressure placed on water supply companies to reduce their use of chlorine. Because of the broadly accepted need for a disinfection stage in drinking water treatment, pressure may be diverted to on other sources of disinfection by-products discharges e.g. from the use of chlorine and bromine as a biocide in cooling waters which discharge to waters also used for drinking water supply.

Table 4.1. – WHO Drinking Water Guidelines for Disinfectants and Disinfectant By-products.

Compound	Guideline value
Free Chlorine	5 mg/L
Chloramines	3 mg/L
2,4,6-Trichlorophenol	200 µg/L
Bromoform	100 µg/L
Dibromochloromethane	100 µg/L
Bromodichloromethane	60 µg/L
Chloroform	200 µg/L
Trichloroacetic acid	100 µg/L
Dichloroacetonitrile	90 µg/L
Dibromoacetonitrile	100 µg/L
Bromate	25 µg/L

CONCLUSIONS AND RECOMMENDATIONS

The design and optimization of antifouling methods involves technological, biological, toxicological and ecotoxicological considerations. Selection of the best method is always based on three criteria :

- technical feasibility,
- cost,
- environmental acceptability.

Across Europe, there is a need to maintain and build an understanding of :

- a. The presence of new "invasive" species which may present a fouling risk;
- b. Likely settlement periods and growth rates of fouling species, and the means of monitoring;
- c. Worked examples optimising controls applied to fouling.

There is an express need to build up the appropriate databases in common ownership.

5.1 WATER FILTRATION SYSTEMS AND CLEANING UP ARE THE MOST COMMON ANTI-FOULING PROCESSES

a. These are practices common to all power stations and industrial cooling water circuits; to a greater or lesser degree, such systems reduce the need for chemical treatment.

b. Water filtration is necessary to remove drifting organisms entrained at the water intake and, further downstream, to protect heat exchangers from detachment of fouling organisms. There are several types of filtration systems now in use, including rough grids equipped with trash racks, rotating filters and microfiltration, well suited for various drifting and settling organisms.

c. Cleaning procedures include continuous on-line mechanical cleaning of condenser tubes with sponge balls, as well as cleaning during scheduled shutdowns, maintenance periods or in the event of incidents. A

number of cleaning processes are possible :

- manual removal of organisms settled on the concrete walls of basins, pipes, culverts, etc. This is done underwater by divers, or after draining the area to be cleaned,

- cleaning of biofilm and mineral deposits on heat exchangers with high pressure jets,

- suction and pumping of mud and deposits.

d. Filtration and cleaning can be costly, especially since sophisticated systems and regular maintenance are required.

5.2. DESIGN OF CIRCUITS.

It is generally advised that :

- a. For water intake pipes, avoid square sections and bends.

- b. If possible, maintain the water velocity above the critical thresholds for the target organisms :

- > 1 m/s to eliminate bryozoa and Zebra mussels

- > 2 m/s to minimize, and around 3m/s to completely eliminate marine biofouling.

- c. Keep all concrete walls in good condition; settlement of biofouling organisms is facilitated by irregularities on surfaces.

5.3. PHYSICAL TREATMENT

Some alternatives to chemical dosing are possible :

- a. Heat treatment, applied by recirculation, is an effective method for the control of macrofouling in fresh water, estuarine and sea water, but it requires specific design of circuits. It is very difficult to back-fit, in particular in complex cooling systems such as large nuclear power stations with cooling towers. Heat treatment by direct water heating is technically possible in some cases (temporarily closed galleries with special filling systems), but is costly.

- b. Heat controls neither bacterial slime nor certain thermophilic pathogens.

- c. Heat treatment requires a permit for the discharge of water above normal regulatory thermal limits.

- d. New non-toxic coatings can, to a large extent, reduce macrofouling settlement and facilitate the clean-up of fouled walls. They do, however, pose certain problems :

- They generally require specific conditions for application (dry, clean surfaces) and top coatings have to be applied every 4 to 5 years;

- they are costly;

- they are not suitable for protecting heat exchangers, wherever there is a need to maintain high thermal efficiency.

5.4. CHEMICAL TREATMENT.

The principal means of managing the residual risk of biological fouling on operational power stations is chemical treatment, but there is increasing regulatory pressure on such practices :

a. Chemical treatments can be tightly optimized only if one has access to precise biological data (monitoring of biofouling, reproduction and larval settling periods, growth rates of juveniles), but they cannot be completely eliminated in many cases :

- in areas where macrofouling growth is very rapid,

- in protecting plate heat exchangers,

- in disinfecting circuits containing thermophilic pathogens.

b. Chlorine is currently the basis of the most commonly-used treatments, as :

- Chlorine can be generated on site at marine power stations by electrochlorination at an acceptable cost;

- There is long-term data available on industrial experience with low-level chlorination (0.5-1.0 mg/L) in the UK, France Italy, and the Netherlands;

- Chlorine is efficient against all fouling categories from bacteria to molluscs;

- The acute toxicity generated by oxidizing compounds disappears rapidly.

The environmental risk of chlorine by-products (CBPs) such as THMs,

haloacetic acids, AOX, remains a concern in the production of drinking water. One means of addressing this is through the use of monochloramine, which reduces the formation of THM and AOX in fresh water.

Low level chlorination of sea water produces low amounts of CBPs which have no acute or effective chronic toxicity on the marine littoral ecosystem.

c. Other oxidizing agents :

Ozone and chlorine dioxide are thought to have less environmental impact due to the reduction of CBPs, mainly THMs.

Ozone is efficient against macrofouling and bacterial slime in fresh water. Some experiments using ozone on closed circuits are promising but ozonation is costly compared with chlorine. In sea water, ozonation generates free bromine and related CBPs; it is therefore not a suitable substitute for chlorine.

Chlorine dioxide in low doses (0.2 mg/L) has been used in Italy and Spain in power stations using sea water. The consumption of chlorine dioxide by sea water is generally very low, but in fresh water the demand can reach 2 mg/L due to the presence of nitrite ions and other reducing agents.

Chlorine dioxide is more costly than chlorine but it is easily applied with specially designed on-site production systems. There are, however, significant safety measures required (risk of explosion).

Peroxides such as hydrogen peroxide or peracetic acid produce no

known by-products, but have not yet seen application in large cooling water systems.

d. Organic compounds :

To be used in large cooling systems, an organic compound must not be persistent or toxic, nor be bioaccumulated after release into the aquatic environment. The worst historical example is TBTO.

Several organic antifouling compounds are efficient against molluscs and can control the major macrofouling organisms in river waters.

Some compounds containing neither aromatics nor quaternary amines, and which are degradable by common bacteria such as fatty amine polymers, may yet provide good alternatives to oxidizing agents, but they remain relatively unknown as far as either their effectiveness and environmental acceptability are concerned.

5.5. THE FUTURE OF ANTIFOULING METHODS

The great bulk of power generation plant in Europe operates efficiently only by using the basic tools of physical screening, physical cleaning, and chemical dosing. These tools are well known by the industry, but the regulatory environment is changing and any casual use of chemical dosing, which might cause environmental

harm, is challenged. There are a number of avenues where further investigation may well be profitable :

a. First of all, improvements must be made in existing methods.

(i) Water filtration covers a wide range of systems, from rough filtration using grid-trash racks to fine mesh screens and microfiltration. Better solutions for washing the fine mesh screens and microfilters need to be found in the near future. New systems for the removal of large amounts of algae and gelatinous organisms at water intakes are also needed.

(ii) Cleaning processes can be improved by standardizing procedures. Underwater cleaning techniques are needed which can be applied to large cooling water systems.

(iii) Design options for applying heat treatments to specific parts of cooling systems should be considered.

(iv) Chlorine treatment can be optimized by on-site biological monitoring; high-frequency intermittent injection (pulse chlorination) is one possible solution.

(v) The interaction of chemical fouling (scaling) and biological fouling in cooling towers continues to need to be taken into account.

b. New methods such as UV, electrical fields, natural toxins or pathogens, remain far from industrial application, but it will be necessary to monitor developments in this field worldwide; the possibility of a "pleasant surprise" cannot be excluded.

References

- Abarnou A., 1979. Trihalométhanes formés par chloration de l'eau de mer. 2^e Journées de la Thermoécologie. Institut Scientifique et Technique des Pêches Maritimes. 14-15 Novembre 1979.
- Ackerman J.D., Cottrell C.M., Ethier C.R., Allen D.G. & Spelt J.K., 1995. A wall jet to measure the attachment strength of zebra mussels. *Can J. Fish. Aquat. Sci.* 52, pp. 126-135.
- Alabaster J.S. & Lloyd R., 1980. Water quality criteria for freshwater fish. Butterworth & Co. London. ISBN 0-408-10673-5, 297 pp.
- Aldridge D.W. & McMahon R.F., 1978. Growth, fecundity and bioenergetics in a natural population of the Asiatic Freshwater Clam, *Corbicula manilensis* Philippi, from north central Texas. *J Molluscan Studies* 44, pp. 49-70.
- Alexander H.C., Bodner K.M. & Mayes M.A., 1983. Evaluation of the OECD "fish prolonged toxicity study at least 14 days". *Chemosphere* 12, pp. 415-423.
- Allen F.E., 1953. Distribution of marine invertebrates by ships. *Aust. J. Mar. Fresh. Res.* 7, pp. 307-316.
- Allonier A.S., 1996. Evaluation of the performance of an organohalogenated compound measurement device using microcoulometry and comparison with gas chromatography. *Hydroecol. Appl.* 8 (1,2), pp. 193-210.
- Allonier A.S., Khalanski M. & Arehmouch L., 1997. Colorimetric measurement of Mexel 432. Application to the study of evolution of the product in river waters. EDF/DER Report HE/31/97/010.
- Allonier A.S. & Khalanski M., 1997. Chlorination by-products in sea water. EDF DER Report HE-31/97/027, 12 p.
- Alzieu C., Héral M., Thibaud M.J. & BOUTIER B., 1980. Evaluation des risques dus à l'emploi de peintures antisalisures dans les zones conchylicoles. *Rev. Trav. Inst. Pêches Marit.*, 44, pp. 301-348.
- Ambrogi R., Festa V. & Toscano A., 1994. Acute toxicity of chlorine dioxide on juvenile *Dicentrarchus labrax*. Relaz. ENEL-DSR-CRAM E4/94/11 presented at VI Congress of S.I.T.H. Venezia 26-29 September 1994.
- Ambrogi R., 1992. Fouling control systems for water treatment. Paper presented at the 8th International congress on marine corrosion and fouling. Sept. 21-25, Taranto (Italy).
- Ambrogi R., 1993. Fouling control system for water treatment. *Oebalia*, 19, suppl., pp. 355-373.
- Ambrogi R., 1997. Environmental impact of biocidal antifouling alternative treatments on seawater once-through cooling systems. In Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection". Rome 1996, November 7-8. Collana Ambiente, vol. 17, pp. 119-132.

- Anderson D.B. & Richards B.R., 1966. Chlorination of sea water. Effects on fouling and corrosion. *Journal of Engineering and Power*, Trans ASME. July, pp. 203-208.
- Anderson D.R. & Lusty E.B., 1980. NUREG/CR-089 Richland, Wa; Pacific NW Labs, pp. 8-26. Ref. from Howard P.H. (ed), (1990) Handbook of environmental fate and exposure data for organic chemicals. Lewis Publishers Inc., Chelsea, USA.
- APHA-AWWA-WPCF, 1976. Standard methods for the examination of water and wastewater. 14th edition Washington.
- APHA-AWWA-WPCF, 1992. Standard methods for the examination of water and wastewater. 17th edition Washington.
- Aprosi G., Bidard F. & Nepveu de Villemarceau C., 1986. Expérience d'exploitation des aéroréfrigérants des centrales nucléaires françaises : Hydrobiologie-chimie aquatique. *Revue Générale Nucléaire* n° 5, Septembre/Octobre 1986, pp. 425-429.
- Aprosi G. & Chauvel D., 1990. The quantity of algae settling on the inside shell of cooling towers and the consequence on the wear of the shell. 7th Congrès AIRH. Leningrad 1990. Rapport EDF/DER HE/31-90.05, 9 pp.
- Aprosi G. & Costaz J.L., 1989. La formation des algues sur les coques des réfrigérants. Rapport EFD/DER HE/31-89.14, 10 pp.
- Aprosi G. & Mossé J., 1989. Algues de coque d'aerorefrigerants. Composition et premiers éléments quantitatifs. Rapport EDF/DER HE/31-90.05, 9 pp.
- Aprosi G. & Nepveu de Villemarceau C., 1988. French operational experience on fouling problems (Algae, Bryozoa) in cooling towers. Paper presented to the 6th IAHR Cooling Tower Workshop, Pisa (Italy) Oct. 4-7, 1988, 24 p.
- Arehmouch L., Tfibel V., Chaillou C., Ghuillebaert F. & Roubaud P., 1998. Lethal effects of Mexel ® to common carp embryological stages in river water: influence of physicochemical parameters in synthetic iso water. *Environ. Toxicol. Chem.*, vol. 17, n° 9, pp. 1767-1776.
- Arndt E.A., 1965. Über das Vorkommen und die Morphologie von *Cordylophora caspia* (Pallas), (Hydrozoa), in der Umgebung der zoologischen Station Tvärminne, Finland. *Commentat Biol* 28, pp. 1-8.
- Arndt E.A., 1973. Ecophysiological and adaptational problems confronting animals living in brackish water. *Oikos* 15, pp. 239-245.
- Arndt E.A., 1984. The ecological niche of *Cordylophora caspia* (Pallas, 1771). *Limnologica* (Berlin) 15, pp. 469-477.
- Bachmann V., Cegiela E., Wagner P., Usseglio-Polatera P. & Moreteau J.-C., 1995. Installation de l'Amphipode *Corophium curvispinum* et de la palourde asiatique *Corbicula* sp dans le cours français de la Moselle. *Hydroécologie Appliquée*, pp. 185-190.
- Baldwin B.S., 1995. Settlement and metamorphosis of larvae Zebra and Quagga mussels : implications for their colonization and spread. In Fifth International Zebra mussel and Aquatic Nuisance Organisms Conference, Toronto, Ontario.
- Bamber R.N., 1990a. Environmental impact assessment, the example of marine biology and the UK power industry. *Mar Pollut Bull* 21, pp. 270-274.
- Bamber R.N., 1990b. Power station thermal effluents and marine crustaceans. *J Therm Biol* 15, pp. 91-97.
- Bamber R.N., 1994. A literature review of the response of migrating salmonids to raised water temperature, with particular reference to heated effluents. Fawley arl Ltd Report to KEMA, FCR 115/94, pp. 21 p.
- Bamber R.N., Seaby R.M.H., Fleming J.M. & Taylor C.J.L., 1994. The effects of entrainment passage on embryonic deve-

- lopment of the Pacific oyster *Crassostrea gigas*. Nuclear Energy 33, pp. 353-357.
- Bamber R.N. & Spencer J.F., 1984. The benthos of a coastal power station thermal discharge canal. J. mar. biol. Ass. UK 64, pp. 603-623.
- Bard D. & Siclet F., 1995. Amibes libres et santé publique. Editions ENSP, Électricité de France. ISBN 2 85952 751, 142 p.
- Barnes H., 1971. A review of some factors affecting settlement and adhesion in the cyprids of some common barnacles. In: Manly R.S. (ed.) Adhesion in biological systems. Academic Press, New York, pp. 89-111.
- Barnes R.S.K., 1994. The brackish water fauna of Northwestern Europe. Cambridge University Press.
- Barrow M.E. et al., 1980. Dynamic exposure hazard assesement. Toxic. Chem. Ann Arbor, MI: Ann Arbor Press, pp. 379-392.
- Barton L.K., 1990. Control of Zebra mussels at CEI facilities. Annual Meeting of the American Power Conference, April 23-25 1990, Chicago (USA), 5 pp.
- Bayne B.L. (ed.) 1976 Marine mussels: their ecology and physiology. Cambridge University Press.
- Behning A., 1914. *Corophium curvispinum* Sars und seine geographische Verbreitung. Zool Jahrb Zeitschr. Syst. Geogr. Biol. 37, pp. 385-400.
- Belanger S.E. & Farris J.L., 1985. Sediment preference of the freshwater Asiatic clam *Corbicula fluminea*. Nautilus 99, pp. 66-73.
- Belluati M., Bartole L. & Bressan G., 1997. In Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection". Rome 1996, November 7-8. Collana Ambiente, vol. 17.
- Ben Amor H., De Laat J., Dore M., 1988. Incidence de la préoxydation par ClO_2 sur le potentiel de formation des composés organohalogènes. Environ. Technol. Letters 9, pp. 1105-1114.
- Benarde A., Israel B.M., Oliveri V.P. Grandstrom M.L., 1965. Efficiency of ClO_2 as a bactericide. Appl Microbiol 13, pp. 776-780.
- Benefield L.D., Judkins J.F. & Weand B.L., 1982. Process chemistry for water and wastewater treatment Prentice-Hall Inc. Englewood Cliffs NJ, 510 pp.
- Berger H-D., Langner K., Watermann B., 1994. Natürliche Biozide und biozidfrei Mittel zur Bewuchshemmung, ihre Effektivität und Anwendung auf Schiffen im marine Bereich, Teilvorhaben 1 zum Forschungsvorhaben 'Möglichkeiten zur biozidfreien Konservierung technische Produkte und Verfahren'. Im Auftrag des Umweltbundesamtes. ISSN 0722-186X.
- Betz Laboratories Inc., 1991. Betz handbook of industrial water conditioning.
- Blank L.W., 1984. Control of algal biofouling at High Marnham; 1981-83. CERL Note No TPRD/L/2649/N84.
- Blum D.J.W. & Speece R.E., 1991. A database of chemical toxicity to environmental bacteria and its use in interspecies comparisons and correlations. Res J Water Pollut C 63, pp. 198-207.
- Blume W.J., Fraleigh P.C. & Van Cott W.R., 1994. Evaluation of copper ions and aluminium floc for preventing settlement of Zebra mussels. Fourth International Zebra Mussel Conference. Madison, Wisconsin. EPRI TR-104029, Proceedings, pp. 15-31.
- Boetting R.S. & Alexander M., 1979. Appl. Environ. Microbiol. 37, pp. 1211-1216.
- Bolsee F., Delanaye J.-N., Deleval J., Duvivier L., Roothoof R. & Van Damme A., 1995. Influence des types de packings utilisés dans les réfrigérants atmosphériques sur la précipitation du carbonate de calcium. Tribune de l'Eau, 5/95, Sept-Oct., pp. 43-49.
- Bordet F., 1983. Conception des ouvrages d'eau des centrales nucléaires littorales

- les. Note EDF E-SE.E.3011 20/09/83, 20 p.
- Bruntland G.H., 1987. Our common future. Report of the World Commission on Environment and Development. Oxford University Press.
- Bryden A.D. 1997. Pulsed acoustics and water supply, system benefits and assessment for the prevention of zebra mussel veliger settlement. Communication at Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans.
- Bucaille D., 1981. Etude expérimentale des effets de la chloration sur la biologie de la moule (*Mytilus edulis* L.) Mollusque Lamellibranche. Thèse 3^e Cycle. 26 mai 1981. Université de Caen. 129 pp.
- Burch J.Q., 1944. Checklist of West American mollusks, Family Corbiculidae. Minutes of the Conchological Club of Southern California 36, pp. 18.
- Cabanes P-A., Pringuez E., Siclet F., Khlanski M. & Pernin P., 1997. Continuous chlorination to control pathogenic amoebae in a closed-loop power plant. The Environmental Professional, Vol. 19, pp. 192-200.
- Callow M.E., 1993. A review of fouling in freshwaters. Biofouling 7, pp. 313-327.
- Cavanagh J.E. *et al.*, 1992. Ozonation By-products, Identification of Bromohydrins from the Ozonation of Natural Waters with Enhanced Bromide Levels. Environ. Sci. Technol. 26, pp. 1658-1662.
- CEC, 1976. Noxious effects of dangerous substances in the aquatic environment. Commission of the European Communities, ENV/588/76.
- CEC, 1982. Study of noxious effects of dangerous substances in list II. Final report of the Commission of European Communities, Brussels EUR 7970/11.
- CEMAGREF Suivi hydrobiologique du Rhône au Bugey. In EDF.CNPE du Bugey. Rapports annuels d'environnement, années 1989, 1990, 1991, 1992, 1993, 1994.
- Chamberlain A.H., 1988. In : CAS Sequiera and KA Tiller (eds) Microbial corrosion, Elsevier Applied Science.
- Chandrasekaram S. & Dexter C., 1993. Factor Contributing to Ennoblement of Passive Metals Due to Biofilm in Seawater, Corrosion Control for Low-Cost Reliability. Proceedings of "12th International Corrosion Congress", NACE, pp. 3696-3707.
- Characklis W.G., 1981. Fouling biofilm development. A process analysis. Bio-technol. Bioeng. 23, pp. 1923-1960.
- Characklis W.G. & Cooksey K.E., 1983. Biofilms and microbial fouling. Adv. Appl. Microbiol. 29, pp. 93-138.
- Characklis W.G., 1990. Kinetics of microbial formation in biofilm, W.G. Characklis & K.C. Marshall (eds), p. 233.
- Clare A.S., Freet R.K. & McClary M., 1994. On the antennular secretion of the cyprid of *Balanus amphitrite*, and its role as a settlement pheromone. J. Mar. Biol. Ass. UK 74, pp. 243-250.
- Claudi R. and Evans D.W., 1993. Chemical addition strategies for zebra mussel (*Dreissemia polymorpha*) control in one through Service water system, in Zebra Mussels Biology, Impacts and Control, Nalepa Y.F. and Schloesser D.W. (eds) Lewis Publishers, pp. 563-573.
- Claudi R. & Mackie G.L., 1994. Practical manual for zebra mussel monitoring and control. Lewis Publishers, London, 227 p.
- CNEXO, 1983. Etude écologique de projet. Site de Penly, deuxième cycle, rapport general.
- Combaz P., 1994. Entartrage des réfrigérants atmosphériques. Rapport EDF-DE-SEPTEN PX/97 046, 14 p.
- Command D.A. & Matthews R.C., 1994. The first-oxidizing molluscicide treatment in Canada. Fourth International Zebra Mussel Conference. Madison,

- Wisconsin. EPRI TR-104029, Proceedings, pp. 33-44.
- Couri D., Abdel-Rahman M.S. & Bull R.J., 1982. Toxicological effects of chlorine dioxide, chlorite and chlorate. *Environ. Health Perspect.* 46, pp. 13-17.
- Cox G.C. & Humphris T.H., 1976. The use and reuse of sewage effluent. *J. Inst. Wat. Pollut. Cont. No 4.*
- Cristiani, G. Bianchi, 1997 "Microbial Corrosion Prevention in ENEL Power Plants", Microbial induced Corrosion, n. 22, European Federation of Corrosion Publications, The Institute of Materials ISSN 1354-5116, London, 1997.
- Cristiani, A. Mollica & Ventura G., 1997. "On-line monitoring of biofilm and T.R.O. by a new ENELS system", "Understanding Heat Exchanger Fouling and Its Mitigation" conference, 11-16 maggio, Lucca, 1997.
- Dall P.C. & Hamburger K. 1996. Recruitment and growth of *Dreissena polymorpha* in Lake Esrom, Denmark. *Limnologia* 26 (1), pp. 27-37.
- Darby J.L. & Snider K.E., Tchobanoglous G., 1993. Ultraviolet disinfection for wastewater reclamation and reuse subject to restrictive standards. *Water Environmental Research*, vol 65; 2, pp. 169-180.
- Dare P.J., 1973. The stocks of young mussels in Morecambe Bay Lancashire shellfish. Info Leaflet No 28 MAFF UK, 14 p.
- Davenport J., Oxford P. & Awobamise A., 1986. A study on the effectiveness of antifouling electrodes in the marine environment. *Water Research*, vol. 20, n° 6, pp. 703-708.
- Davis M.H. & Coughlan J., 1983. A model for predicting chlorine concentration within marine cooling water circuits and its dissipation at outfalls. In *Water chlorination, pp. Environmental impact and health effects*, Jolley *et al.* (eds) Vol. 4, Ann Arbor Sci. Publs. 1983, pp. 347-357.
- De Wever H. & Verachter H., 1997. Biodegradation and toxicity of benzothiazoles. *Wat. Res.* vol. 31, 11, pp. 2673-2684.
- De Wolf P., 1973. Ecological observations on the mechanisms of dispersal of barnacle larvae during planktonic life and settling. *Neth. J. Sea. Res.* 6, pp. 1-129.
- Dedieu L., Hort C., Martinez-Dominguez A., Rola M. & Roques H., 1994. Contribution à l'étude des phénomènes d'entartrage. Première partie. *Tribune de l'Eau*, 571 (5., Sept-Oct.), pp. 3-19.
- Dejoux C., 1988. La pollution des eaux continentales africaines. Éditions de l'ORSTOM. Collection Travaux et Documents n° 213. Chapitre B II. Le contrôle des mollusques vecteurs de schistosomiasis, pp. 110-137.
- Delattre J.-M. & Oger C., 1981. *Naegleria* pathogènes et pollution thermique. *J. Fr. Hydrol.* 12 (35., asc. 2), pp. 239-244.
- D'Itri F. (ed.), 1997. Zebra mussels and Aquatic Nuisance Species. Ann Arbor Press inc. Chelsea, Mi 48118.
- Dixon D.R., 1981. Reproductive biology of the serpulid *Ficopomatus enigmaticus* in the Thames estuary, SE England. *J. Mar. Biol. Assoc. UK* 61, pp. 805-815.
- Dobbs M.G., Cherry D.S., Scott J.C. & Petrille J.C., 1995. Environmental assessment of an alkyl dimethyl benzyl ammonium chloride based molluscicide using laboratory tests. Fifth International Zebra Mussel and Aquatic Nuisance Organisms Conference. Toronto, Feb. 21-24.
- Dobson J.G., 1946. The control of fouling organisms in fresh and saltwater circuits *Trans ASME*, pp. 247-265.
- Doherty F.G., Farris J.L., Cherry D.S. & Cairns Jr J., 1986. Control of freshwater fouling bivalve *Corbicula fluminea* by halogenation. *Arch. Environ. Contam. Toxicol.* 15, pp. 535-542.
- Doré M., 1989. Chimie des oxydants et traitement des eaux. Lavoisier, Paris.

- Dow Chemicals, 1980. Bromine chloride newsletter, 101-165, September 1980.
- Dreves L., Erard Le Denn E., Lunven M., Martin J., Miossec D., Piriou J.-Y. & Quintin J.-Y., 1994. Surveillance écologique et halieutique du site de Flamanville. Année 1993. Rapport IFREMER DEL/BREST - 94.09 pour EDF, 105 pp.
- Dubois Ch., 1995. Biologie et démo-écologie d'une espèce invasive, *Corbicula fluminea* (Mollusca, Bivalvia) originaire d'Asie. Etude en milieu naturel (canal latéral à la Garonne) et en canal expérimental. Thèse de doctorat de l'Université Paul-Sabatier (Toulouse). 12 Novembre 1995, 147 p.
- Duvivier L., 1993. Formation et élimination des organo-halogénés lors de la désinfection des eaux. Thèse de doctorat es-sciences. Université catholique de Louvain-la-Neuve (Belgique).
- Duvivier L. & Vanmaele R., 1995. Centrale de Chooz B Biologie. Rapport de synthèse. Rapport LABORELEC C03-800-95-005/F/LDU/RVM, 18 p.
- Duvivier L., Leynen M., Olivier F. & Van Damme A., 1996. Fighting zebra mussel fouling with ozone. In Proceedings of the EPRI PSE Service water Systems Reliability Improvement Seminar. June 25-27, Daytona Beach, Florida, 14 p.
- EEC, 1975. Council directive concerning the quality required of surface water intended for the abstraction of drinking water in the Member States (75/83/EC). Official Journal L 194, 25/07/75.
- EEC, 1975. Council directive of 25 May 1975 on the quality of surface water for the abstraction of drinking water (75/460/EEC) Official Journal 194.
- EEC, 1976. Council directive of 6 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment (black and grey lists) (76/464/EEC) Official Journal L129, 18/5/76.
- EEC, 1976. Council directive of 8 December 1975 concerning the quality of bathing water (76/160/EEC) Official Journal L31, 5/2/76.
- EEC, 1978. Council directive of 18 July 1978 on the quality of waters needing protection or improvement in order to support fish life (78/659/EEC) Official Journal L22, 30/11/78.
- EEC, 1979. Council directive of 30 October 1979 on the quality required of shellfish (79/923/EEC) Official Journal L281, 10/11/79.
- EEC, 1980. Council directive of 15 July 1980 relating to the quality of water intended for human consumption (80/778/EEC) Official Journal L229, 30/8/1980.
- EEC, 1980. Council directive of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances (80/68/EEC) Official Journal L20, 26/1/80.
- EC, 1996. Council directive concerning integrated pollution prevention and control (IPPC Directive - 96/61/EC). Official Journal L 257, 10/10/96.
- EC, 1998. Council directive on the quality of water intended for human consumption (98/83/EC). Official Journal L 330, 05/12/98.
- EC, 1998. Directive of the European Parliament and the Council concerning the placing of biocidal products on the market, the establishment at Community level of a list of active substances which may be used in biocidal products (98/8/EC). Official Journal L 123, 24/4/1998.
- Efremov A.D., 1975. Treating the effluent after chemical cleaning in a recirculating cooling system. Teploenergetika Akad. Nauk. SSSR. Energ. Inst. 22, pp. 79-80.
- ENEL-CRAM, 1996. Manuale per il controllo dei periodi di insediamento del macrofouling e per l'ottimizzazione dei

- trattamenti di clorazione. Report n° 19960016, April 1996, 28 p.
- EPRI, 1983. Symposium on Condenser Macrofouling Control Technologies, pp. The State of the Art. Dias-Tous IA Miller MJ and Mussali YG (eds) Hyannis Mass. USA.
- EPRI, 1988. 6th IAHR Cooling Tower Workshop. Pisa, Italy. 4-6th Oct. 1988.
- EPRI, 1989. Non-toxic foul-release coatings. EPRI GS-6566. Final report, October 1989.
- EPRI, 1992. Zebra mussel monitoring and control guide EPRI-TR-101782 December 1992.
- EPRI, 1993. Condensor microfouling control handbook, Final Report, October 1993 TR-102507.
- Erickson S.J. & Freeman A.E., 1978. Toxicity screening of fifteen chlorinated and brominated compounds, using four species of marine phytoplankton. In, Water Chlorination, Environmental impact and health effects, R.L. Jolley *et al.* (eds), Ann Arbor Sci, Vol. 2, pp. 307-311.
- EURELECTRIC, 1998. BAT for cooling systems. 78 p.
- Ewans D.W., Griffiths J.S. & Koopmans R., 1992. Options for controlling zebra mussels. Ontario Hydro research review, n° 7, pp. 1-25.
- Fauvel P., 1923. Un nouveau serpulien d'eau saumâtre *Mercierella n.g. enigmatica* n. sp. Bull. Soc. Zool. Fr. 46, pp. 424-430.
- Fears C.D. & Mackie G.L., 1997. Effectiveness of low-level electric current (A-C) for preventing settlement of zebra-quagga mussels on concrete and steel panels after one year of exposure at Naticoke T.G.S. forebay. Poster presented at Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans.
- Fejgina Z.S., 1959. Utilisation d'eau chaude pour lutter contre la prolifération des *Dreissena* dans les centrales thermiques (in Russian). Elekticheskies Stantsii 10, pp. 38-40.
- Fisher S.W., Stromberg P.S., Bruner K.A. & Boulet L.D., 1991. Molluscicidal activity of potassium to the zebra mussel, *Dreissena polymorpha*: toxicity and mode of action. Aquatic Toxicology, 20, pp. 219-234.
- Foster B.A., 1969. Tolerance of high temperatures by some intertidal barnacles. Mar. Biol. 4, pp. 326-332.
- Fraser, 1986. Peroxygens in environmental protection. Effluent and Water Treatment Journal, pp. 186-199.
- Freitag D. *et al.*, 1982. Ecotox. Environ. Safety, 6, pp. 60-81. Ref. from Howard P.H. (ed.), (1990) Handbook of environmental fate and exposure data for organic chemicals. Lewis Publishers Inc., Chelsea, USA.
- Furman E.R., Yule A.B., 1991. *Balanus improvisus* Darwin in British Estuaries, gene flow and recolonization, pp. 273-276. In: Elliott M. and J.P. Ducrotoy (eds) Estuaries and Coasts: spatial and temporal intercomparisons. ESCA 19 Symp. University of Caen, France. Olsen and Olsen Internat. Symposium Series.
- Garey J. & Gross C., 1997. Long Island Lighting Company Mexel Trials, 3 p.
- Garric J. & Migeon B., 1983. Étude du cycle de reproduction de *Dreissena polymorpha* sur le Rhône en aval de Lyon. Rapport EDF-DER. HE/31-83.22. 42 p.
- Geiger D.L., Northcott C.E., Call D.J. & Brooke L.T. (eds), 1984/85. Acute toxicities of organic chemicals to fathead minnows Vols I and II. Centre for Lake Superior Environmental Studies Univ. Wisconsin-Superior Superior Wisconsin, pp. 326.
- Geraci S., Ambrogi R., Festa V. & Piraino S., 1993. Field and laboratory efficacy of chlorine dioxide as antifouling in cooling systems of power plants. Oebalia 19, pp. 383-393.

- GESAMP, 1984. Thermal discharges in the marine environment. IMO/FAO/UNESCO/WMO/WHO/IAEA/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution. Reports and Studies No. 24.
- Geyer *at al.*, 1982. *Chemosphere*, 11, pp. 1121-1134. Howard P.H. (ed.), (1990) Handbook of environmental fate and exposure data for organic chemicals. Lewis Publishers Inc., Chelsea, USA.
- Giamberini L., Czembor N. & Pihan J.-C., 1994. Effects of Mexel 432 on the settling, detachment and mortality of adult zebra mussels. Fourth International Zebra Mussel Conference. Madison, Wisconsin. EPRI TR-104029, Proceedings., pp. 73-81.
- Gibson C.I., Tone F.C., Schirmer R.E. & Blaylock J.W., 1980. Bioaccumulation and depuration of bromoform in five marine species. *Water Chlorination Environmental Impact and Health Effects*, Jolley et al. (eds) Ann Arbor Sci. Vol. 3, pp. 517-533.
- Gillet A. & Micha J.-C., 1985. Étude de la biologie d'un mollusque bivalve en vue de son élimination dans le circuit de la centrale nucléaire de Tihange. *La Tribune du CEBEDEAU* n° 504, 38, pp. 3-28.
- Gilpin R.W., Dillon S.B., Keyser P., Andro-kites A., Berube M., Carpendale N., Skorina J., Hurley J., 1985. Disinfection of circulating water systems by ultra-violet light and halogenation. *Wat. Res.* 19, pp. 839-848.
- Gitay A. & Glazer A., 1979. Biological fouling in Israel power station and in a proposed inter sea conduit. *Isr. J. Zool.* 28 (1), p. 61.
- Glazer A. & Gitay A., 1988/89. The fouling communities at the Haifa and Adera power station (Mediterranean coast of Israel). *Isr. J. Zool.*, 35 (1/2), p. 88.
- Gledhill T., Sutcliffe D.W. & Williams W.D., 1976. A revised key to the British species of Crustacea, Malacostraca occurring in fresh water. *Freshw. Biol. Assoc. Sci. Publ.* 32, pp. 1-71.
- Godet J.L. & Guillemot M.L., 1998. Conséquences de la nouvelle directive européenne relative à la qualité des eaux destinées à la consommation humaine. *Proceedings of International Ozone Regional Conference*. Poitiers France, 23-25 September 1998, pp. 1-1 – 1-13.
- Goldstein D., Wei I. & Casana J., 1987. Wastewater Reuse as Cooling-Tower Makeup, EPRI Research Project 1260-19, CS-5373.
- Gordon G., Kieffer R.G. & Rosenblatt D.R., 1972. The chemistry of chlorine dioxide. *Prog. Inorganic Chem.* 15, pp. 201-286.
- Gordon G. & Bubnis B., 1997. Chlorine dioxide, chemistry and technology. In *Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection"*. Rome 1996, November 7-8. *Collana Ambiente*, vol. 17, pp. 15-26.
- Gosling E. (ed.), 1992. The mussel *Mytilus*, Ecology, physiology, genetics and culture. *Developments in Aquaculture and Fisheries Science* 25, Elsevier, Amsterdam, 590 pp.
- Graham J.W., Stock J.N. & Benson P.H., 1977. Further studies on the use of heat treatment to control biofouling in seawater cooling systems. *IEEE Ocean'77*, pp. 23A1-23A6.
- Graney R.L., Cherry D.S., Rodgers J.H. & Cairns J., 1980. The influence of thermal discharges and substrate composition on the population structure and distribution of the Asiatic clam, *Corbicula fluminea*, in the New River, Virginia. *Nautilus* 94, pp. 130-135.
- Greenshield J.F. & Ridley J.E., 1957. Some research on the control of mussels in water pipes. *J. Inst. Wat. Engrs.* II, pp. 300-306.
- Gribble G.W., 1994. The natural production of chlorinated compounds. *Environ. Sci. Technol.* 7, pp. 310-318.
- Griffiths J.S., 1992. Control of zebra mussels by thermal shock. *Ontario Hydro*

- report 92-65 K. Quoted in Claudi and Mackie, 1994.
- Gross A.C., 1991. Evaluation of nonfouling coatings for power plant cooling water intake systems. In Proceedings of Condenser Technology Conference. EPRI. GS-7349, August 1991.
- Gross A.C., 1996. Non-toxic foul-release coatings help utilities reduce costs for cooling-water intake systems. Innovators with EPRI technology. IN-100297, 2 p.
- Gu Ji-Dong & Mitchell R., 1997. Use of metabolites and natural products for zebra mussel control. Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans, Jan. 28-31.
- Gunten U. von & Hoigné J., 1994. Bromate formate during ozonation of bromide-containing waters, interaction of ozone and hydroxyl radical reactions. Environ. Sci. Technol. 28, pp. 1234-1242.
- Hall L.W., 1988. Tributyltin environmental studies in Chesapeake Bay. Marine Pollution Bulletin, 19 (9), pp. 431-438.
- Harada A., Sakata K., Ina H. & Ina K., 1985. Isolation and identification of xanthatin as an anti-attaching repellent against blue mussel. Agric. Biol. Chem. 49 (6), pp. 1887-1888.
- Harper D.B., 1994. The contribution of natural halogenation processes to the atmospheric halomethane burden. In Int. Conf. on Naturally Produced Organohalogens 14-17 Sept. 1994 TNO Delft, pp. 3-4.
- Harris R.R., 1991. Amphipod also invades Britain. Nature 354, pp. 194.
- Hartmann-Schroeder, 1967. Zur Morphologie, Oekologie und Biologie von *Mercierella enigmatica* (Serpulidae, Polychaeta) und ihre Roehre. Zool. Anz. 179, pp. 421-456.
- Hasson D., 1979. Precipitation Fouling. In, Somerscales and Knudson (eds) Fouling and Heat Transfer Equipment. Proc Conf Rensselaer Polytechnic Institute Troy, N.Y. 13-17 Aug. 1979, pp. 527-568.
- Heinle D.R., 1976. Effects of passage through power plant cooling systems on estuarine copepods. Environ. Pollut. 11, pp. 39-58.
- Hergott S.J., Jenkins D. & Thomas J.F., 1978. Power plant cooling water chlorination in Northern California. J Water Pollut. Control. Fed. 50, pp. 2590-2601.
- His E., 1995. Embryogenesis and larval development in *Crassostrea gigas*, experimental data and field observations on the effect of tributyltin compounds, in "Organotin", Champ & Seligman (eds) Chapman & Hall.
- Hoekstra E.J. & De Leer E.W.B., 1994. AOX levels in the River Rhine, pp. fifty percent of natural origin? Water. Sci. Technol. 29, pp. 133-136.
- Hoestland H. & Lassablière J. 1959. Destruction thermique de la moule d'eau douce. L'eau, 46, 11, pp. 259-262.
- Hoestland H., 1972. Toxicité de deux molluscicides (Baylucide et Frescon) à l'égard de la moule d'eau douce (*Dreissena polymorpha*), Bulletin Français de Pisciculture, 244, pp. 104-110.
- Hori M., Lizawa M., Kawabe A., Wakisaka Y. & Ishiyama E., 1993. Application of a UV irradiation system for a power station intake. OEBalia, vol. XIX, suppl., pp. 395-403.
- Hori M., Nagayama S., Kawabe A. & Yamashita K., 1990. Influence of UV irradiation on the nauplius larvae of the barnacle *Chthamalus* sp., suppl. Denki Kagaku, vol. 58, n° 7, pp. 629-637.
- Hose J.H., Di Fiori D., Parker H.S. & Sciarrotta T., 1989. Toxicity of chlorine dioxide to early life stage of marine organisms. Bull Environ. Contam. Toxicol. 42, pp. 315-319.
- Humphris T.H., 1979. The control of phosphate scaling in power station condensers. In Somerscales and Knudson (eds) Fouling and Heat Transfer Equipment Proc. Conf. Rensselaer Polytech-

- nic Institute Troy, N.Y. 13-17 Aug 1979, pp. 603-616.
- Isnard P. & Lambert S., 1988. Estimating bioconcentration factors from octanol-water partition coefficient and aqueous solubility. *Chemosphere*, vol. 17, 1, pp. 21-34.
- Iwanyzki S. & McCauley R.W., 1993. Upper lethal temperatures of adult zebra mussels (*Dreissena polymorpha*). In : Nalepa T.F., Schloesser D.W. (eds) *Zebra mussels, biology, impacts and control*. Lewis Publishers, London, pp. 667-676.
- Jantz B. & Neumann D., 1992. Shell growth and aspects of the population dynamics of *Dreissena polymorpha* in the River Rhine. In : Neumann D and Jenner HA (eds) *The Zebra Mussel Dreissena polymorpha* Gustav Fischer Verlag, Limnologie aktuell 4. pp. 49-66.
- Jenner H.A., 1982. Physical methods in the control of mussel fouling in seawater cooling systems. *La Tribune du CEBEDEAU*, 33, pp. 13-19.
- Jenner H.A., 1985. Chlorine minimization in macrofouling control in the Netherlands. In : *Water Chlorination Environmental Impact and Health Effects*, Jolley *et al.* (eds) Ann Arbor Sci. Vol. 5, pp. 1425-1433.
- Jenner H.A., Taylor C.J.L., Van Donk M. & Khalanski M., 1997. Chlorination by-products in chlorinated cooling water of some European Coastal Power Stations. *Marine Environmental Research*, vol. 43, N° 4, pp. 279-293.
- Jenner H.A., 1983. A microcosm monitoring mussel fouling, 11 p. In I.A. Diaz-Tous, M.J. Miller, and Y.G. Mussalli [ed.] *EPRI Symposium on Condenser Macrofouling Control Technologies*, The State-of-the-Art, Hyannis, Massachusetts, June 1-3.
- Jenner H.A., Janssen-Mommen J.P.M., 1993. Monitoring and control of *Dreissena polymorpha* and other macrofouling bivalves in The Netherlands. In: Nalepa TF, Schloesser DW (eds) *Zebra mussels, biology, impacts and control*. Lewis Publishers, London, pp. 537-555.
- Johnson J.D. & Overby R., 1971. Bromine and bromamine disinfection chemistry. *Am. Soc. Civil Engineers Proc J. Sanitary Eng. Div.* 97, p. 617.
- Johnson J.D. & Sun W., 1975. Bromine disinfection of wastewater. In : JD Johnson (ed.) *Disinfection, Water and Wastewater*. Ann Arbor Science, Ann Arbor, Michigan, Chapter 9.
- Johnson P.D. & McMahon R.F., 1997. Oxygen deprivation as a control measure for zebra mussels and Asian clams, how should you go? *Seventh International Zebra Mussel and Aquatic Nuisance Species Conference*. New Orleans Jan. 28-31.
- Jolley R.J., Brungs W.A., Cotruvo J.A., Cumming R.B., Mattica J.S. & Jacobs V.A. (eds), 1983. *Water chlorination, environmental impact and health effects*. Vol. 4. Ann Arbor Science Publishers Michigan books, 1491 p.
- Jolley R.L. (ed.), 1976. *The environmental impact of water chlorination*. Oak Ridge National Laboratory Tennessee USA, 443 p.
- Jolley R.L., Brungs W.A., Cumming R.B., Jacobs V.A. (eds), 1980. *Water chlorination, environmental impact and health effects*. Vol. 3 Ann Arbor Science Publishers Michigan, 1171 p.
- Jolley R.L., Bull R.J., Davis W.P., Katz S., Roberts Jr M.H., Jacobs V.A. (eds), 1986. *Water chlorination, chemistry, environmental impact and health effects*. Vol. 5. Lewis Publishers Inc Michigan, 1575 p.
- Jolley R.L., Condie L.W., Johnson J.D., Katz S., Minear R.A., Mattice J.S., Jacobs V.A. (eds), 1990. *Water chlorination, chemistry, environmental impact and health effects*. Vol. 6. Lewis Publishers Inc Michigan, 1023 p.
- Jolley R.L., Gorchev H., Heyward Hamilton D. (eds), 1978. *Water chlorination, environmental impact and health effects*. Vol. 2. Ann Arbor Science Publishers Michigan, 909 p.

- Kawabe A. 1997. Non-toxic biofouling control technologies. Japanese review.
- Kawabe K., Yasui T., Ikeda N., Nishijima H. & Yamamoto A. 1985. Effects of flow dynamics on attachment of marine organisms for copper and copper alloy seawater pipes. *Denki Kagaku*, 53 n° 6, pp. 422-423.
- Kelly M., 1988. Mining and the freshwater environment. Elsevier Applied Science – British Petroleum. 231 p.
- Khalanski M. & Bordet F., 1981. Modalité d'action du chlore sur la moule marine. 2^e Journées de la Thermo-écologie. Institut Scientifique et Technique des Pêches Maritimes, 14-15 Novembre 1979, pp. 745-758.
- Khalanski M., 1985. Impact de la chloration sur la qualité de l'eau et le plancton. Bilan des études réalisées sur le site de Gravelines de 1979 à 1983. Report EDF DER HE/31-85.09, 70 pp.
- Khalanski M. & Lutz Ph., 1987. La chloration de l'eau de réfrigération. *Revue Générale Nucléaire*, n° 1, pp. 52-58.
- Khalanski M., 1993. Testing of five methods for the control of zebra mussels in cooling circuits of power plants located on the Moselle river. Proceedings, Third International Zebra Mussel Conference, Toronto 1993. EPRI Report TR-102077. June 1993, pp. 3.1-3.20.
- Khalanski M. & Delesmont R., 1994. Résiduels de chloration en mer à Penly. Report EDF DER HE/31-94.020, 52 pp.
- Khalanski M., 1995. La chloration discontinuée des circuits de réfrigération en eau de mer. Report EDF DER HE/31-95.05., 39 pp.
- Khalanski M. & Gras R., 1996. Rejets thermiques en rivières et hydrobiologie. Un aperçu sur l'expérience française. *La Houille Blanche*. N° 5, pp. 13-18.
- Khalanski M., 1997a. Zebra mussel and other invasive species in cooling water circuits of French Power stations on rivers. Seventh International Zebra Mussel & Aquatic Nuisance Species Conference. New-Orleans, Jan. 28-31.
- Khalanski M., 1997b. Conséquences industrielles et écologiques de l'introduction de nouvelles espèces dans les hydrosystèmes continentaux, la moule zébrée et autres espèces invasives. *Bull. Fr. Pêche Piscic.* 344/345, pp. 385-404.
- Khalanski M., 1997c. Data on the toxic effects of the anti-corrosion product Mexel 432 on fresh water organisms. EDF. DER. Report HE/31-97-016, 42 pp.
- Kinne O., 1956. Über den Einfluss des Salzgehaltes und der Temperatur auf Wachstum, Form und Vermehrung bei dem Hydroidpolypen *Cordylophora caspia* (Pallas), Thecata, Clavidae. *Zool. Jahrb. Abt. Allg. Zool. Physiol. Tiere* 66, pp. 565-638.
- Kinzelbach R., 1992. The main features of the phylogeny and dispersal of the Zebra mussel *Dreissena polymorpha*. In: *Limnologie aktuell* 4, Neumann D. and Jenner H.A. (eds). The Zebra Mussel *Dreissena polymorpha*, Gustav Fischer Verlag, pp. 5-18.
- Kirpichenko M.Y., Mikheev V.P. & Stren E.P., 1962. Lutte contre la prolifération des *Dreissena* dans les centrales hydroélectriques (in Russian). *Elekticheskies Stantsii*, 5, pp. 30-32.
- Klain S.J., Cobb G.P., Dickerson D.L., Dixon K.R., Kendall R.J., Smith E.E. & Solomon K., 1996. An ecological risk assessment for the use of the biocide, dibromonitropropionamide (DBNPA), in industrial cooling water systems. *Environmental Toxicology and Chemistry*, 15, pp. 21-30.
- Klerks P. & Fraleigh P., 1991. Control of adult Zebra mussels with sodium hypochlorite, potassium permanganate and hydrogen peroxide with iron. Abstract Zebra Mussels Mitigation Options for Industries. Toronto, Ontario.
- Kovalac W.P., Longton G.D. & Smithee R.D., 1993. Infestation of Power Plant water systems by the Zebra mussel.

- (*Dreissena polymorpha*). In : Zebra Mussels Biology, Impacts and Control. Nalepa T.F. & Schloesser D.W. (eds.) Lewis Publishers, London, pp. 359-380.
- Kramer J.F., 1997. Peracetic acid, a new biocide for industrial water applications. MP/August, pp. 42-50.
- Krzeminski S.F., Brackett C.K. & Fisher J.D., 1975a. Fate of microbicidal 3-isothiazolone compounds in the environment, modes and rates of dissipation. J. Agric. Food Chem., vol. 23, 6, pp. 1060-1067.
- Krzeminski S.F., Brackett C.K. & Fisher J.D., 1975b. Fate of microbicidal 3-isothiazolone compounds in the environment, products of degradation. J. Agric. Food Chem., vol. 23, 6, pp. 1068-1075.
- Lagouche A. & Guillon A., 1976. Protection des conduites d'eau de mer contre l'envahissement par la flore et la faune marine. TSM L'EAU, n° 5, pp. 197-210.
- Langford T.E., 1983. Electricity generation and the ecology of natural waters. Liverpool Univ. Press, 342 p.
- Langford T.E., 1990. Ecological effects of thermal discharges. Elsevier Appl. Sci., 468 p.
- Langlais B., Legube B., Beuffe H. & Doré M., 1992. Study on the nature of by-products formed and the risk toxicity when disinfecting a secondary effluent with ozone. Wat. Sci. Techn. vol. 25, N° 12, pp. 135-143.
- Lassus P., Maggi P., Le Baut C., Bardouil M., Bocquene G., Le Dean L. & Truquet, 1981. Influence de la chlorination sur les premiers stades larvaires de *Palaemon serratus* (Pennant). Unpublished report of the Institut Scientifique et Technique des Pêches Maritimes.
- Lauer T.E., Spacie A. & Barnes D.K., 1997. Competitive interactions between *Dreissena polymorpha* (Bivalvia) and *Lophodopodella carteri* (Bryozoa) in a southern Lake Michigan harbor. Communication at the Seventh International Zebra Mussel and aquatic Nuisance Species Conference., New-Orleans, Jan. 28-31.
- Lecœuvre J.-M., Caytan Y. & Granges J.-L., 1986. Des aéroréfrigérants performants. Epure. EDF DER publ. N° 9 Janvier 1986, pp. 43-57.
- Lefebvre E. & Deguin A., 1997. Chlorine dioxide, use in a drinking water process. In Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection". Rome 1996, November 7-8. Collana Ambiente, vol. 17, pp. 105-118.
- Legliz L. & Ollivier F., 1981. Mise au point bi-bibliographique sur la biologie et l'écologie de *Dreissena polymorpha* PAL-LAS (1771). répartition géographique en France et dans les pays limitrophes. EDF/DER Report HE/31-81.37.
- Leitch E.G., 1994. Evaluation of coatings to control zebra mussel colonization. Final report. Ontario Hydro Rept. 93/236/K.
- Lepage W.L., 1993. The impact of *Dreissena polymorpha* on waterworks operations at Monroe Michigan. A case history. In : Zebra Mussels Biology, Impacts and Control. Nalepa T.F. & Schloesser D.W. (eds) Lewis Publishers, London, pp. 333-358.
- Lewis B.G., 1961. Biological observations made during trials of chlorination for mussel control at East Yelland 1959 to 1960 CERL Report No RD/L/R 1052.
- Lewis B.G., 1983a. Development of a preliminary model to predict time in days for 100% kill of mussels subject to continuous chlorination CERL Note No TPRD/L/2469/N83.
- Lewis B.G., 1983b. Effects of continuous chlorination on mussels and validation of preliminary model CERL Note No TPRD/L/2594/N83.
- Lewis B.G., 1985. Mussel control and chlorination CERL Report No TPRD/L/2810/R83.

- Lewis R.O., 1982. The influence of biofouling counter-measures on corrosion of heat exchanger materials in seawater. Material performance, pp. 31-38.
- Lewis D. & Pawson R.L., 1993. Use of cathodic protection as a means of control and removal of zebra mussels. Communication at International Zebra Mussel Conference. Toronto.
- Lewis D., Pawson R. & Pickles S.B., 1997a. Electrolytic protection for zebra mussel control on concrete walls of an operating pump well, a pilot study. Communication at Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans.
- Lewis D.P., Butts D. & Cresswell R., 1997b. Control of zebra mussels in fire protection systems using commercially-available potash. Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans Jan. 28-31.
- Leynen M., Ollivier F., Duvivier L. & Van Damme A., 1997. Mitigation of macrofouling, pp. a comparative study of ozone and an organic filminducing polymer. Communication at the Seventh International Zebra Mussel and aquatic Nuisance Species Conference., New Orleans, Jan. 28-31.
- Lincoln R.J., 1979. British marine Amphipoda: Gammaridae. Brit. Mus. (Nat. Hist.) Lond., p. 658.
- Lovegrove T. & Robinson T.W. 1968. The prevention of fouling by localized chlorine generation. Biodeterioration, p. 617.
- Lubet L., 1983. Experimental studies on the action of temperature on reproductive activity of the mussel (*Mytilus edulis* L. Mollusca Lamellibranchia). J. Moll. Stud. suppl. 12A, pp. 100-105.
- Lutz P. & Merle G., 1983. Discontinuous mass chlorination of natural draft cooling towers. Wat. Sci. Tech. 15, pp. 197-213.
- Lykins B.W. & Griesse M.H., 1986. Using chlorine dioxide for trihalomethane control. Journ. AWWA 6, pp. 88-93.
- Lynn J.W., Barre A., Smith S., Misamore M., Dietz T.D. & Silverman H., 1997. Ion requirements for fertilization and early cleavage events in *Dreissena polymorpha*. Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans.
- Lyons L.A., Petrille J.C., Donner S.P., Forbes R.L., Lehmann F., Althouse P.W., Wall L.T., Post R.M. & Buerger W.F., 1990. New treatment employing a molluscicide for macrofouling control of zebra mussels in cooling systems. American Power Conference, Chicago, April 23-25.
- Lyons L.A., Petrille J.C., Werner M.W., Bidwell J.R. & Cherry D.S., 1991. An on-site evaluation of zebra mussel control, comparing chlorine, bromine and a non-oxidizing molluscicide. EPRI Zebra Mussel Control Technology Conference. Oct. 22-23.
- Madeley J.R., 1973. The acute toxicity of hydrocarbons to fish. A review of the work carried out at the Brixham Laboratory to June 1973 ICI-BL/B/1521.
- Mantisi F., Gautier J.P. & Dernas M., 1997. A simple robust method for the determination of chlorine dioxide in drinking water. In Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection". Rome 1996, November 7-8. Collana Ambiente, vol. 17, p. 39.
- Marchand J. & Denayer J.C., 1991. Spatio-temporal comparisons of the development of fouling communities in the Loire Estuary (France). In: Elliott M. and Ducroty J.P. (eds), Estuaries and Coasts, pp. Spatial and Temporal Inter-comparisons. Int Symp Series 1991 Univ. of Caen France, pp. 265-271.
- Marcos F. & Gailhard J., 1994. Centrale de Penly. Modélisation tridimensionnelle des rejets chlorés. Report EDF/DER. HE/42-94.055/A., 59 pp.

- Marelli D.C. & Gray S., 1983. Conchological redescrptions of *Mytilopsis sallei* and *Mytilopsis leucophaeta* of the brackish western Atlantic. *Veliger* 25, pp. 185-193.
- Markowski S., 1962. Faunistic and ecological investigations in Cavendish Dock, Barrow in Furness. *J. Anim. Ecol.* 31, pp. 43-52.
- Martin I.D., Baker M.A. & Mackie G.L., 1990. Comparative efficacies of sodium hypochlorite and registered biocides for controlling the Zebra mussel *Dreissena polymorpha* (Bivalve Heterodonta). Abstr. Zebra mussels: The Great Lakes experience, University of Guelph, Guelph Ontario. From Van Benschoten *et al.*, 1992.
- Masschelein W., 1979. Chlorine dioxide, Chemistry and impact of oxichloride compounds. Ann Arbor Science, Ann Arbor MI.
- Matisoff G., Brooks G. & Bourland I.B., 1996. Optimizing treatment processes of chlorine dioxide to adult mussels. *Journal AWWA*. August 1996, pp. 93-106.
- Mattice J.S. & Zittel H.E., 1976. Site-specific evaluation of power plant chlorination. *J. Water Pollut. Control Fed.* 48(10), pp. 2284-2308.
- Mattice J., 1983. Freshwater macrofouling and control with emphasis on *Corbicula*. In: *Condenser Macrofouling Control Technologies*, pp. The State of the Art. Tous I.A.D., Miller M.J., Mussali YG (eds) Hyannis, Mass. USA 1-3 June 1983 EPRI.
- Mayack L.A., Coracco R.J., Wilde E.W. & Pope D.H., 1984. Comparative effectiveness of chlorine and chlorine dioxide biocide regimes for biofouling control. *Wat Res.* 18, pp. 593-599.
- McCoy W.F., Blatchley III E.R. & Johnson R.W., 1990. Hapohalous acid and haloamine falsoff in industrial evaporative cooling systems. Cooling tower institute 1990 annual meeting. Technical paper number TP90-09.
- McLean R.I., 1973. Chlorine and temperature stress on selected estuarine invertebrates. *Am. Zool. J. Wat. Poll. Cont. Fed.* 45, pp. 837-841.
- McMahon R.F., 1983. Ecology of an invasive pest bivalve corbicula. In *The Molluscs*, Hunter W.D.R. (ed.), vol. 6. Ecology. Academic Press, New-York, pp. 501-561.
- McMahon R.F. & Tsou J.L., 1990. Impact of European Zebra Mussel infestation to the electric power industry. Annual Meeting of the American Power Conference, April 23-25 1990, Chicago (USA), 10 pp.
- McMahon R.F., Shipman B.N. & Erck D.E., 1990. Effects of two molluscicides on the freshwater macrofouling bivalve *Dreissena polymorpha*, the zebra mussel. Annual Meeting American Power Conference, Chicago, April 23-25, 6 p.
- McMahon R.F., Ussery T.A. & Miller A.C., 1993. Thermal tolerance in zebra mussels (*Dreissena polymorpha*) relative to temperature increase and acclimatation temperature. Third International Zebra Mussel Conference. Toronto, Canada, Feb. 1993.
- Merkens J.C., 1958. Studies on the toxicity of chlorine and chloramines to the rainbow trout. *Water and Waste Treat. Jour.* 7, pp. 150-151.
- Merle G. & Montanat M., 1980. Essai d'utilisation du dioxyde de chlore dans la boucle TERA installée à Montereau. Résultats des tests d'efficacité. EDF DER Report HE/31-80.045.
- Mollica A., Alabiso G., Scotto V., Traverso E. & Ventura G., 1988. "Influence of biofouling on active-passive alloys in sea water" (in Italian). Congress Corrosione Marina, Genova.
- Mollica A., Traverso E. & Ventura G., 1990. Electrochemical monitoring of the biofilm growth on active-passive alloy tubes of heat exchange using sea water as cooling medium, XI Proceedings of International Corrosion Congress, Firenze 2-6 April 1990, Italy, AIM Ed., vol. 4, pp. 333-340.

- Mollica A. & Ventura G., 1993a. Proceedings of 8th Int. Cong. on Marine Corrosion and Fouling, 1992, Taranto (Italy), "Oebalia", vol. 19, pp. 313, 322.
- Mollica A. & Ventura G., 1993b. Proceedings of 12th Int. Corr. Cong., Houston, TX, U.S.A., NACE Int., vol. 5B, pp. 3807-3812.
- Mollica A., Ventura G., Andrei E., Cristiani P. & Rocchini G., 1996. "Simple Electrochemical Devices for Biofilm Monitoring on Stainless Steels in Seawater", Proceedings of EUROCORR '96, September 24-26, 1996, Nice (France).
- Molloy D.P., Fokin S., Laruelle F.H. & Lynn D.H., 1997. Ophryoglenine Ciliates parasitizing zebra mussels. Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans, Jan. 28-31.
- Montanat M., Merle G., and Migeon B., 1980. Essai d'utilisation du dioxyde de chlore dans la boucle TERA installée à Montereau. Résultats des tests de toxicité. EDF DER Report HE/31-80.044.
- Moreteau J.C. & Khalanski M., 1994. Settling and growth of *D. polymorpha* in the raw water circuits of the Cattenom Nuclear power plant (Moselle, France) 4th Int Zebra Mussel Conf. Madison Wisconsin Mars 1994 (EDF/DER rapport HE 31/94/012).
- Morris J.C., 1978. Chemistry of aqueous chlorine in relation to water chlorination Chapter 2 In: R.L. Jolley (ed.) Water Chlorination, Environmental Impact and Health Effects. Volume 1, Ann Arbor Science, Ann Arbor, Michigan.
- Morton B., 1979. Freshwater fouling bivalves, pp. 1-14 In: Britton J.C. (ed.) Proc. First Int. Corbicula Symp. Texas Christian Univ., Fort Worth, Texas, USA 313 pp.
- Morton B., 1983. The sexuality of *Corbicula fluminea* (Muller) in lentic and lotic waters in Hong Kong. J. Moll. Stud. 49, pp. 81-83.
- Morton B., 1986. *Corbicula* in Asia-an updated synthesis. Am. Malacol. Bull. Spec. ed. No 2, 113-124.
- Mouthon J., 1981. Sur la presence en France et au Portugal de *Corbicula* (Bivalvia, Corbiculidae) originaire d'Asie. Basteria 45, pp. 109-116.
- Mowery D., McClellan E., Lyons L.A., Austin D.M. & Karlovich D.M., 1989. Asiatic clam control experience at Peach Bottom atomic power station. EPRI Service Water Systems Reliability Improvement. Charlotte, North Carolina, 6 p.
- Muia R.A., McGough C.M. & Gill P.H., 1993. Effects of temperature on a non-oxidizing biocide being applied for Mollusk control. Calgon Bulletin N° 11, p. 612.
- Mussali Y.G., Hecker G., Padmanabhan M., Kasper J. & Chow W., 1985. Targeted chlorination. Condenser Biofouling Control Symposium: The state of the art. June 1985. Lake Buena Vista, Florida. EPRI Report, 27 pp.
- Mussali Y.G., 1988. Biofouling control at water intake structures. Journal of Hydraulic Engineering, vol. 114 n° 6, pp. 616-625.
- Nakayama S., Shinio, Claudi R. & Evans D., 1997. Use of intermittent application of ozone for biofouling and zebra mussel control. Communication at the Seventh International Zebra Mussel and aquatic Nuisance Species Conference, New-Orleans, Jan. 28-31.
- Nalepa T.F. & Schloesser D.W. (eds), 1993. Zebra mussels, biology, impacts and control. Lewis Publishers, London, 810 pp.
- Nancollas G.H. & Reddy M.M., 1976. Crystal Growth Kinetics of Minerals Encountered in Water Treatment Processes. In: Aqueous-Environmental Chemistry of Metals Rubin A.J. (ed.). Ann Arbor Science Publishers, Ann Arbor.
- Neumann D. & Jenner H.A. (eds), 1992. The Zebra Mussel *Dreissena polymor-*

- pha*. *Limnologie aktuell* 4, Gustav Fischer Verlag, 262 pp.
- Nosetani T., Sato S., Onda K. & Kato Y., 1989. Biofouling control of titanium condenser tubes by new-type abrasive sponge balls. ASME, National Heat Transfer Conference, HTD Vol. 108, pp. 281-288.
- Okubo K. & Okubo T., 1962. Study on the bioassay method used for the evaluation of water pollution II Use of fertilized eggs of sea urchins and bivalves. *Bull Tokai Reg. Fish. Res. Lab.* 32, pp. 131-140.
- Oliver P.G., Holmes A.H. & Mettam C., 1998. *Mytilopsis leucophaeta*, (Conrad, 1831) [Bilvalvia : Dreissenoidea] species new to the British fauna. *J. Conch.* 36 (2) : pp. 13-18.
- Osborn D.W., 1970. Factors affecting the use of purified sewage effluent for cooling purposes. *Water Pollut. Contr.*, 69(4), pp. 456-464.
- Ottaviani M., 1997. Evolution of EC Directives and regulations for drinking water, disinfection issues. In *Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection"*. Rome 1996, November 7-8. Collana Ambiente, vol. 17, pp. 73-82.
- Palin A.T., 1957. The determination of free and combined chlorine in water by use of diethyl-p-phenylenediamine. *J. Amer. Water Works Assoc.* 49, pp. 873.
- Palin A.T., 1967. Methods for determination, in water, of free and combined available chlorine, chlorine dioxide and chlorite, bromine, iodine, and ozone using diethyl-p-phenylenediamine (DPD). *J. Inst. Water Eng.* 21, p. 537.
- Palin A.T., 1975. Current DPD methods for residual halogen compounds and ozone in water. *J. Amer. Water Works Assoc.* 67, pp. 32.
- PARCOM, 1995. Report on the workshop on products containing or generating organohalogen compounds. Oslo and Paris Conventions for the Prevention of Marine Pollution Working Group on Diffuse Sources (DIFF), Bremen, 10-13 October 1995.
- Parent J.-F., Monfort J., 1985. Seashore power stations and protection of the marine environment. EDF DER Report HE/42/82/85/18, 43 p.
- Petrille J.C. & Werner M.W., 1993. A combined treatment approach using a non-oxidizing molluscicide and heat to control zebra mussels. Third International Zebra Mussel Conference. Toronto, Ontario. Feb. 23-26.
- Piccirillo V.J., Malik N., Van Dresar W. & Flood T., 1994. TD 2335, Laboratory and field efficacy studies for control of zebra Mussels in electric power plants. Fourth International Zebra Mussel Conference. Madison, Wisconsin. EPRI TR-104029, Proceedings, pp. 111-118.
- Piccirillo V.J., Sandberg G., Fobell J. & McAllister D., 1995. TD 2335, Field efficacy studies for control of Zebra Mussels on electric power plants. Fifth International Zebra Mussel and Aquatic Nuisance Organisms Conference. Toronto, Feb. 21-24.
- Plessis-Fraissard Y., 1961. Écologie de l'estran rocheux du Calvados, pp. étude des biocénoses et recherches expérimentales. Thèse Université de Paris. 29 Juin 1961. A. N° 3698, 4549.
- Poje G.V., Riordan S.A., O'Connor J.M., 1981. Power plant entrainment simulation utilizing a condenser tube simulator. US Nuclear Regulatory Commission Report NUREG/CR-2091 RE, 25.
- Prezant R.S. & Chalermwat K., 1984. Floatation of the bivalve *Corbicula fluminea* as a mean of dispersal. *Science Proceedings* 225, pp. 1491-1493.
- Proceedings of the First International Zebra Mussel Conference. 1991.
- Proceedings of the Second International Zebra Mussel Conference. Toronto Ontario. 1992.
- Proceedings of the Third International Zebra Mussel Conference. Toronto Ontario. 1993. EPRI Report TR-102077.

- Proceedings of the Fourth International Zebra Mussel Conference. Madison Wisconsin 1994, Wisconsin Sea Grant Institute.
- Proceedings of the Fifth International Zebra Mussel and Other Aquatic Nuisance Organisms Conference, 1995, Toronto Ontario.
- Proceedings of the Sixth International Zebra Mussel and Other Aquatic Nuisance Organisms Conference, 1996, Dearborn.
- Proceedings of the Seventh International Zebra Mussel and Other Aquatic Nuisance Organisms Conference, 1997, New-Orleans.
- Puckorius P.R. & Strauss S.D., 1995. Cooling water treatment. Power, May 1995.
- Puckorius P.R., 1997. Cooling tower fill water quality/operations guidelines to successful utilization. In Proceedings of Cooling Tower Technology Conference. EPRI TR-108483.2113. July 1997, pp. 3-1 - 3-13.
- Rainbow P.S., 1984. An introduction to the biology of British littoral barnacles. Field Studies 6, pp. 1-51.
- Rajagopal S., Van der Velde G. & Jenner H.A., 1997. Response of zebra mussel, *Dreissena polymorpha*, to elevated temperatures in the Netherlands. In: Zebra mussels and aquatic nuisance species (Frank d'Itri Ed.) Ann Arbor Press, Inc. Michigan, pp. 257-273.
- Rajagopal S., Van der Velde G., Jenner H.A., 1994. Biology and control of brackish water mussel, *Mytilopsis leucophaeta* in the Velsen and Hemweg power stations, The Netherlands. Part II. Control measures. Report No 163871-KES/WBR 94-3128, KEMA Environmental Research, 45 p.
- Rajagopal, S., Nair, K.V.K., Van der Velde, G. & Jenner H.A., 1997. Response of mussel *Brachidontes striatulus* to chlorination: an experimental study. Aquat. Toxicol. 39, pp. 135-149.
- Rajagopal S., Van der Velde G., Paffen B.G.P., 1999a. Growth and reproduction of *Corophium curvispinum* G.O. Sars, 1895 (Amphipoda), an invader in the Lower Rhine. Crustaceana. (in press).
- Rajagopal S., Van der Velde G., Paffen B.G.P., Van den Brink F.W.B. & Bij de Waate A., 1999b. Life history and reproductive biology of the invasive amphipod *Corophium curvispinum* (Crustacea: Amphipoda) in the Lower Rhine. Arch. Hydrobiol. 144(3), pp. 305-325.
- Ramsey, G.G., Tackett J.H. & Morris D.W., 1988. Effect of low-level continuous chlorination on *Corbicula fluminea*. Environ. Toxicol. Chem. 7, pp. 855-856.
- Rao N.M., Lu F.Y., Johnson D.A. & Nghiem J.P., 1997. Understanding aromatic triazole consumption in utility cooling towers and development of an environmentally friendly yellow metal corrosion inhibitor. In Proceedings of Cooling Tower Technology Conference. EPRI TR-108483.2113. July 1997, pp. 3-79 - 3-97.
- Rauh J.S., 1979. Disinfection and oxidation of waste water by chlorine dioxide. J. Envir. Sci 22, pp. 42-45.
- Ray D.L., 1959. Marine Boring and Fouling Organisms Friday Harbor Symposium. Univ Washington Press, 536 p.
- Relini G. & Bianchi C.N., 1979. Prime osservazioni sul fouling della centrale termoelettrica di Torvaldaliga (Civitavecchia). Atti XI Congr. S.I.B.M., Orbetello/Atti Soc. Tosc. Sci. Nat. Mem. ser. V, 86 suppl., pp. 308-311.
- Relini G. & Romaiore V., 1976. Cicli di insediamento del fouling in condotte di un impianto di raffreddamento con acqua di mare. Arho Oceanogr. Limnol., 18 (3), pp. 231-256.
- Relini G., 1984. Three years investigation on macrofouling of a Tyrrhenian power station. Proc. 6th Int. Congr. on Mar. Corr. and Fouling. Athens. Marine Biology, pp. 195-210.
- Relini G., 1993. Mediterranean macrofouling. Oebalia, vol. 19, pp. 103-154.

- Relini G., Bianchi C.N. & Pisano E., 1980. Macrofouling in the conduit of a middle Thyrrhenian power station. Proc. 5th Int. Congr. on Mar. Corr. and Fouling, Barcelona. Biologia Marine, pp. 279-292.
- Rice R.P. & Wilkes J.F., 1992. Fundamental aspects of ozone chemistry in recirculating cooling water systems - data evaluation needs. Ozone Sci & Engineer.
- Richardson S.D., 1997. Disinfection by-products, identification and future regulations. In: Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection". Rome 1996, November 7-8. Collana Ambiente, vol. 17, pp. 51-60.
- Rikken G.B. Kroon A.G.M. & Kengen S.W.M., 1996. Transformation of perchlorate into chlorite by a newly isolated bacterium, reduction and dismutation. Appl. Microbiol. Biotechnol. 45, pp. 420-426.
- Ritchie J., 1927. Report on prevention of growth of mussels in sub-marine shafts and tunnels at Westbank Electric Station. Portobello Trans. Roy. Scottish. Soc. of Arts.
- Roch M., Noonan P. & LcCarter J.A., 1986. Determination of no effect levels of heavy metals for rainbow trout using hepatic metallothionein. Water Research, vol. 20, n° 6, pp. 771-774.
- Rook J.J., 1974. Formation of haloforms during chlorination of natural waters. Water Treat. Exam. 23, pp. 234-243.
- Saroglia M.G., Scarano G., 1974. Risk from residual chlorine in cooling waters used for aquacultural purposes. Presented at the 4th Conference on Water Chlorination R. Jolley (ed.), Pacific Grove, oct. 1974, Risks, Issues and Answers, pp. 1437-1445.
- Sarunac N., Guida V., Weisman R. & Zhang Z., 1994. Integration of macrobiofouling control methods into an effective macrobiofouling control strategy. Proceedings Condenser Technology Conference. EPRI Report TR-103475, pp. 3.39 - 3.68.
- Schloesser D.W., Bij de Vaate A., Zimmerman A., 1994. A bibliography of *Dreissena polymorpha* in European and Russian Waters, 1964-1993. J. Shellfish Res. 13, pp. 243-267.
- Schneider R., 1997. Generation of chlorine dioxide. In Chlorine dioxide and disinfection. Proceedings of "First European Symposium on Chlorine Dioxide and Disinfection". Rome 1996, November 7-8. Collana Ambiente, vol. 17, pp. 27-37.
- Schoenbach K.H., Abou-Ghazala A., Alden R.W., Turner R. & Fox J.T., 1997. Biofouling prevention with pulsed electric fields. Communication at Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans.
- Schroenig G.P., Bisinger E.C., Laplante B.T. & Gill P.H., 1995. Environmental fate of a non-oxidizing molluscicide. Oral presentation at the Fifth International Zebra Mussel Conference. Toronto, Ontario.
- Schuler V.J. & Larson L.E., 1974. Experimental studies evaluating aspects of fish behaviour as parameters in the design of generating station systems. Amer. Soc. Civil Eng. Wat. Res. Eng. Prog, Los Angeles, CA, USA.
- Seed R. & Suchanek H., 1992. Population and Community Ecology of *Mytilus*, Chap 4, pp. 87-169. In Gosling E. (ed.) The mussel *Mytilus*: ecology, physiology, genetics and culture. Elsevier, 589 p.
- Seltzer-Hamilton E.M., Magee J.A., Wright D.A. & Kennedy V.S., 1995. Laboratory culture of *Dreissena polymorpha* and *Dreissena bugensis* from fertilization to F1 juveniles using estuarine algae. Fifth International Zebra Mussel and Aquatic Nuisance Organisms Conference. 21-24 Feb.1995. Toronto, Ontario, Canada.
- Serli N., Claudi R., Lewis D. & Pawson R., 1994. Use of cathodic protection for

- control of zebra mussel biofouling on steel and concrete surfaces. Communiqué at the Fourth International Zebra Mussel Conference. Madison, Wis, USA.
- SETAC (Society of Environmental Toxicology and Chemistry), 1994. Final Report, Aquatic risk assessment and mitigation dialogue group. Pensacola, FL, USA.
- Sheide J.I., 1997. Effect of niclosamide on adult zebra mussels (*Dreissena polymorpha*). Seventh International Conference Zebra Mussel and aquatic Nuisance Species. New-Orleans Jan. 28-31.
- Siclet F., 1991. Colonisation des réfrigérants atmosphériques par les algues. Effet sur la stabilité du réfrigérant et sur le colmatage du circuit de refroidissement. Rapport EDF/DER HE/31-91-14. 44 p.
- Siddall S.E., 1980. Early development of *Mytilopsis leucophaeata* (Bivalvia, Dreissenacea). Veliger 22, pp. 378-379.
- Sladeckova A., 1969. Control of slimes and algae in cooling systems. Verh. Int. Ver. Limnol. 17, pp. 532-538.
- Smythe G.A., Lange C.L. & Sawyko P.M., 1997. Evaluation of an On-line magnetic device as a control method for adults and settlement-stage mussels (*Dreissena* spp.). Communication at Seventh International Zebra Mussel and Aquatic Nuisance Species Conference. New Orleans.
- Sprung M., 1987. Ecological requirements of developing *Dreissena polymorpha* eggs. Arch. Hydrobiol., Suppl. 79, pp. 69-86.
- Sprung M., 1989. Field and laboratory observations of *Dreissena polymorpha* larvae: abundance, growth, mortality and food demands. Arch. Hydrobiol. 115, pp. 537-561.
- Sprung M., 1992. Observations on shell growth and mortality of *Dreissena polymorpha* in lakes. In The zebra mussel *Dreissena polymorpha*, Neuman D. & Jenner H.A. (eds), Limnologie Aktuell, 4, pp. 19-28.
- Srikanth S. & Berk S.G., 1994. Adaptation of Amoebae to Cooling Tower Biocides. Microb. Ecol. 27, pp. 293-301.
- Standard Methods for the Examination of Water and Wastewater., 1992. Greenberg A.E., Clesceri L.S., Eaton A.D. (eds).
- Stewart M.E., Blogoslawski W.J., Hsu R.Y. & Helz G.R., 1979. By-products of oxidative biocides, toxicity to oyster larvae. Mar. Pollut. Bull. 10, pp. 166-169.
- Straughan D., 1971. Establishment of non-breeding population of *Mercierella enigmatica* (Annelida, Polychaeta) upstream from a breeding population. Bull. South. Calif. Acad. Sci. 69, pp. 169-175.
- Sugam R., 1985. Chlorine minimization, dechlorination and ozonation. A case study. Proceedings of Condenser Biofouling Control Symposium, June 18-20. Lake Buena Vista, Florida. EPRI Report, Session III, 16 pp.
- Swinnen M., 1995. Milieu als drijfveer voor ontwikkelingen in koelwater technologieën. In « Watersymposium 1995 » organised by NACE Benelux.
- Tabak H.H., 1981. Biodegradability studies with organic priority pollutant compounds. J. Water Poll. Control Fed. 53, pp. 1503-1518.
- Ten Hove H.A. & Hurk van den P., 1993. A review of recent and fossil serpulid reefs; actuopalaontology and the Upper Malm serpulid limestones in NW Germany. Geol. Mijnbouw 72, pp. 23-67.
- Testard P., 1990. Eléments d'écologie du lamellibranche invasif *Dreissena polymorpha* Pallas. Étude de la dispersion des larves en région parisienne et de leur fixation. Réponse à la désoxygénation de l'eau. Thèse des Sciences Univ. Paris, 358 pp.
- Thome J.-P., Marneffe Y., Brene C. & Louvet M., 1989. Les Bryozoaires dans les centrales nucléaires de Tihange II et III,

- développement de techniques d'élimination. Rapport Université de Liège, non référencé, 44 pp.
- Thompson C., Carbonara J., Chow W. & Syrett B., 1994. Advanced targeted chlorination design. EPRI Report TR-103475, pp. 3.17 - 3.38
- Trabalka J.R., Tsai S.C., Mattice J.S. & Burch M.B., 1980. Effects on carp embryos and *Daphnia pulex* of chlorinated organic compounds produced during control of fouling organisms. Water Chlorination Environmental Impact and Health Effects, Jolley *et al.* (eds) Ann Arbor Sci. Vol. 3, pp. 599-606.
- Travade F. & Khalanski M., 1986. Contrôle de la salissure biologique des circuits de centrales thermiques côtières par les moules (*Mytilus edulis*). Étude d'optimisation de la chloration à Gravelines. *Haliotis* 15, pp. 265-273.
- Tsou J., 1996. Non-toxic foul-release coatings to reduce condenser macrofouling. Innovators with EPRI technology. IN-103476, 2 pp.
- Turner H.J., Reynolds D.M. & Redfield A.C., 1948. Chlorine and sodium pentachlorophenolate as fouling preventatives in sea water conduits. *Ind Eng Chem* 40, pp. 450-453.
- Tyndall R.L., Ironside K.S., Mettler P.L., Tan E.L., Haezn T.C. & Fliermans C.B., 1989. Effect of thermal addition on the density and distribution of *Naegleria fowleri* thermophilic amoebae and pathogenic in a newly created cooling lake. *Appl. Environ., Microbiol.* 55 (3), pp. 722-732.
- US EPA, 1992. Framework for ecological risk assessment. EPA/60/R-92/001. Washington DC.
- Usami M. & Ueda K., 1993. Antifouling system for ship hulls by electro-conductive coating. *CEbalia*, vol. XIX, Supplement, p. 641.
- Van Benschoten J.E., Jensen J.N., Lewis D. & Brady T.J., 1993. Chemical oxidants for controlling Zebra Mussels (*Dreissena polymorpha*): a synthesis of recent laboratory and field studies. In: Zebra Mussels Biology, Impacts and Control. Nalepa T.F. & Schloesser D.W. (eds) Lewis Publishers, London, pp. 599-619.
- Van den Brink F.W.B., Van der Velde G., Bij de Vaate A., 1989. A note on the immigration of *Corophium curvispinum* Sars, 1895 (Crustacea, Amphipoda) into the Netherlands via the River Rhine. *Bull. Zool. Mus. Amsterdam* 11, pp. 211-213.
- Van den Brink F.W.B., Van der Velde G., & Bij de Vaate A., 1993. Ecological aspects, explosive range extension and impact of a mass invader, *Corophium curvispinum* Sars, 1895 (Crustacea, Amphipoda), in the Lower Rhine (The Netherlands). *Oecologia* 93, pp. 224-232.
- Vanderpoeg H.A., Liebig J.R. & Gluk A.A., 1995. Development, survival and settling of *Dreissena polymorpha* the laboratory for different food concentrations, physical conditions and substrates. Fifth International Zebra Mussel and Aquatic Nuisance Organisms. Conference. 21-24 Feb. 1995. Toronto, Ontario, Canada.
- Van der Velde G., Paffen B.G.P., Van den Brink F.W.B., Bij de Vaate A., Jenner H.A., 1994. Decline of Zebra Mussel populations in the Rhine. Competition between two mass invaders (*Dreissena polymorpha* and *Corophium curvispinum*). *Naturwissen* 81, pp. 32-34.
- Van der Velde G., Rajagopal S. & Jenner H.A., 1997. Sublethal response of Zebra mussel, *Dreissena polymorpha* (Pallas) to low-level chlorination: a laboratory study. Conference proceedings Seventh International Zebra Mussel and Aquatic Nuisance Species. Conference. Jan. 28 to 31 1997. New-Orleans (USA), pp. 147-162.
- Van Wijk D.J. & Hutchinson T.H., 1995. The ecotoxicity of chlorate to aquatic organisms, a critical review. *Ecotoxicology and Environmental Safety*. 32, pp. 244-253.

- Vanmaele R., Leyneen M., Duvivier L., Girboux P., Delanaye J.N. & Ollivier F., 1998. Ozonization of an Auxiliary Circuit of a Cooling Water System from a Power Station. A Field Study. Proceedings of International Ozone Regional Conference. Poitiers France, 23-25 September 1998, pp. 33-1 – 33-7.
- Verschueren K. 1983. Handbook of environmental data on organic chemicals. Second edition. Van Nostrand Reinhold Company, New-York, 1310 pp.
- Vervoort W., 1946. Fauna van Nederland aflevering XIV Hydrozoa (C1. A Hydropoliepen AW. Sijthoff Leiden, 336 pp.
- Wasel-Nielen J. & Baresel M., 1997. The treatment of cooling water with ozone at Hoechst AG in comparison with other microbiocidal processes. VGB Kraftwerkstechnik 77, N° 2, pp. 124-128.
- Watermann B., Berger H.D., Sönnischen H. & Willemsen P., 1997. Performance and effectiveness of non-stick coatings in seawater. Biofouling. Vol. 11, pp. 1-18.
- Waugh G.D., 1964. Observations on the effects of chlorine on the larvae of oysters (*Ostrea edulis* (L)) and barnacles (*Elminius modestus* (Darwin)) Ann. appl. Biol. 54, pp. 423-440.
- Welch F.J. & Joy J.E., 1984. Growth rates of the Asiatic clam *Corbicula fluminea* in the Kanawha River, West Virginia. Freshw. Invertebr. Biol. 3, pp. 139-142.
- Wellauer R. & Kyas A., 1987. Ozone as a biocide for cooling water systems. Proc. 8th Ozone Congress (Zürich, Switzerland, Intl. Ozone Assoc.), pp. G12-G21.
- Wellauer R. & Oldani M., 1990. Cooling water treatment with ozone, Ozone: Sci. Eng., 12(3), pp. 243-253.
- White G.C., 1972. Handbook of chlorination for potable water, wastewater, cooling water, industrial Processes and swimming Pools. Van Nostrand Reinhold Company. New York, 744 pp.
- White G.C., 1986. The Handbook of Chlorination, Second Edition. Nostrand Reinhold Company, New York. ISBN 0-442-29285-6, 1069 p.
- Whitehouse J.W., 1975. Chlorination of cooling water, a review of literature on the effects of chlorine on aquatic organisms. Report No RD/L/M 496, Central Electricity Research Laboratories, Leatherhead, Surrey, 22 pp.
- Whitehouse J.W., 1990a. Commissioning of the biofouling control rig and the first experiment – July to November 1988 National Power Report No TEC/L/0316/R90.
- Whitehouse J.W., 1990b. The growth and control of biofouling deposits on cooling tower plastic packing, results from the biofouling rig. 1988-1990 National Power Report No TEC/L/0317/R90.
- Whitehouse J.W. & Blank L.W., 1985. Cooling tower design and operation and the incidence of algal biofouling – results of the 1983 survey CEGB Report No TPRD/L/2838/N85 CERL Leatherhead UK, 19 pp.
- Whitehouse J.W. & Coughlan J., 1990. Microbiofouling on plastic packing in cooling towers, a case for chlorine treatment? Proceedings 6th Conference on water Chlorination, Environmental Impact and Health Effects. Oak Ridge Tenn., May-3-8 1987, in Jolley *et al.*, 1990, pp. 555-563.
- Whitehouse J.W., Coughlan J. & Bamber R.N., 1987. An assessment of the requirements for chlorination for mussel fouling control at Wylfa power station CEGB Report No TPRD/L/3096/R86.
- Whitehouse J.W., Khalanski M., Saroglia M.G. & Jenner H.A., 1985. The control of biofouling in marine and estuarine power stations. Joint report of CEGB, EDF, ENEL and KEMA, 48 pp.
- WHO, 1993a. Environmental Health Criteria 93 – Chlorophenols other than pentachlorophenol. The World Health Organisation Geneva.
- WHO, 1993b. Guidelines for drinking-water quality. Vol. 1, Recommendations. WHO Geneva.

- Wiancko P.M. & Claudi R., 1994. The Ontario Hydro final strategy for Zebra mussel control. Fourth International Zebra Mussel Conference, Madison Wisconsin, USA.
- Wilde E.W., Soracco R.J., Mayack L.A., Shealy R.I., Broadwell T.L. & Steffen R.F., 1983. Comparison of chlorine and chlorine dioxide toxicity to fathead minnow and bluegill. *Wat. Res.* 17, pp. 1327-1331.
- Wolff W.J., 1969a. *Mercierella enigmatica* Fauvel, een borstelworm van het brakke water, voor het eerst in Nederland gevonden. *Levende Natuur* 72, pp. 85-92.
- Wolff W.J., 1969b. The Mollusca of the estuarine region of the rivers Rhine, Meuse and Scheldt in relation to the hydrography of the area. II. The Dreissenidae. *Basteria* 33, pp. 94-103.
- Woods Hole Oceanographic Institution, 1952. Marine fouling and its prevention. US Naval Institute, Annapolis, 388, pp.
- Wright D.A., Kennedy V.S., Roosenburg W.H., Castagna M. & Mihursky J.A., 1983. Temperature tolerance of embryos and larvae of five bivalve species under simulated power plant entrainment conditions, a synthesis. *Mar. Biol.* 77, pp. 271-278.
- Yamazaki M., 1965. Problems in using sea water for condenser cooling in thermal power stations. In *Proc Second Int Conf, Advances in Wat Poll Res.* Vol. 3 (Pearson E.A. Ed.), Pergamon Press Oxford England, pp. 117-132.
- Yokouchi H., Nonaka T. & Kawabe A., 1996. Comparative tests on non-toxic antifouling pipe treatment techniques using model canals. *Proceedings of 1996 Condenser Technology Conference*, EPRI TR-106781 2504, p. 17-14.
- Zibrowius H. & Bellan G., 1969. Sur un nouveau cas de salissures biologiques favorisé par le chlore. *Tethys* 1, pp. 375-382.

Annex 1

Heat treatment

In the Netherlands, the Eems power station, has been equipped with a recirculation system adapted for heat treatment. The plant (600 MWe) is located on the Eems-Dollard estuary and experiences serious mussel fouling. Heat treatment is being practised at the station on a trial basis (Jenner, 1982).

A schematic diagram is presented of the cooling system of the Eems power station (fig. 1). Normal operation is shown on the left side of the figure. The right side represents the situation during recirculation (heat treatment) of the A-culvert. Cooling water which has passed the condensers A and B is partly (about 50 %, $4\text{--}5 \text{ m}^3\text{s}^{-1}$) carried back via culvert A to the inlet of pump B. The recirculated water flows again through the condenser to pick up additional heat. In this way the cooling water temperature can be raised. Heat treatment of the B-culvert can be done similarly. The power station remains operational during heat treatment, but power production has to be reduced somewhat. The design of the circuits used by SCEC in order to treat the intake and discharge culverts is shown in fig. 2.

Fig. 1. – Schematic diagram of the cooling water flow at normal operation and during heat treatment of the Eems power station.

Fig. 2. – Diagram of heat treatment of the inlet and discharge canals used by SCEC (Graham *et al.*, 1977).

Annex 2

Legislation and Policy in North America and selected European Union Member States relating to the use of Biocides

In Europe, subsidiarity dictates that EU Directives are implemented through national regulations. However, local issues remain influential, and local initiatives in regulatory practice can be disseminated elsewhere. This annex summarises what is known of the local regulatory situation in North America and across Europe.

Current concerns over the use of chlorine as a biocide can be traced, in part, to the Great Lakes Area of North America. This area of the USA and Canada is highly industrialised and has a high population density. Chemical pollution of the Great Lakes has been of concern to various Government Agencies for over two decades and this has resulted in extensive research programmes examining the possible effect of chemical contaminants on the health of residents. These have particularly focused on chlorinated hydrocarbons such as PCBs and organochlorine pesticides (e.g. DDT and Lindane). These were of particular concern because of their persistence, toxicity, carcinogenicity

and a tendency towards bioaccumulation. These findings prompted programmes across the western world to eliminate their use where possible. More recently, research in Europe and in the USA has raised concerns that a number of industrial chemicals including chlorinated hydrocarbons may mimic natural oestrogens or anti-androgens and could potentially affect the reproductive success of animals or man.

This research is still on-going and is likely to continue to raise the public profile of chlorinated hydrocarbons and the release of chlorine to the environment in general.

1. NORTH AMERICA

1.1 USA

The United States Environmental Protection Agency (USEPA) has a pesticide programme which authorises all active ingredients for pesti-

des/biocides on a national basis. The Federal Insecticide, Fungicide, Rodenticide Act (FIFRA) requires that the ecosystem as well as humans, be protected from unreasonable risks associated with the production, distribution, storage and use of pesticides. Ecological risk assessments are undertaken to determine this for biocides. For example, DBNPA, a non-oxidising biocide, is registered under FIFRA for use in cooling waters and an ecological risk assessment of its use in once-through cooling systems is provided by Klaine *et al.* (1996). A tiered approach is adopted for ecological risk assessment, with those substances representing insignificant exposure to the environment being screened out at tier one to avoid the more detailed assessment required at tier two (USEPA 1992, SETAC 1994). All active ingredients, including chlorine, are currently being reassessed by the Pesticide Safety Division of the USEPA.

Whilst the use of chlorine as a biocide is controlled by FIFRA there has been a tendency to undertake less onerous risk assessments on its use in cooling waters. This is because, unlike most other pesticides/biocides, its primary release pathway to the environment is via point source discharges to the aquatic environment. These effluent discharges are controlled either by State Regulatory Authorities or, in a limited number of cases, the regional offices of the EPA. Thus unlike the highly centralised approach to the control of most agricultural pesti-

cides/biocides in the USA, under the Pesticides programme, the control of the use of biocides in cooling waters is very much a site specific issue. It would appear that in general the use of chlorine as a biocide for cooling waters does not appear to be of great concern in the USA, although there may be local instances where a higher priority is assigned to its control.

The USEPA has conducted a broader study into the use and release of biocides, including chlorine, into the environment. A draft report on this was produced earlier in 1996 but is not publicly available and this initiative appears to have stalled at present, possibly because of budgetary constraints (Inglow, pers. com. USEPA)

1.2 Canada

There is no national control on the use of biocides in cooling waters in Canada except where they are sold as pesticide control products, in which case they require registration.

The use of oxidising biocides in cooling waters is controlled at Provincial level through the use of permits. Environment Canada has produced environmental codes of practice for steam generation which are used as guidelines to support these permit granting activities. The majority of power generating systems are once-through systems using chlorine as a cooling water biocide. The Canadian Water Quality Guidelines (CCREM 1987) may also be used in framing permits and these suggest that for the

protection of freshwater aquatic life the concentration of Total Available Chlorine (as measured by the amperometric method) should not exceed 2 mg/L.

The environmental Codes of Practice for Steam Electric Power Generation (EPSI/PG/1 1985) have no legal status and were developed with a federal-provincial-industry task force. The codes encompass the siting, design, construction, operation and decommissioning phases of steam electric power projects, which includes all facilities which use a steam cycle to produce electrical energy (i.e. both fossil-fuelled [coal, oil and gas] and nuclear [CANDU] power station). The codes deal with multi-media considerations although the design phase primarily addresses water-related concerns.

The following recommendation relates to biofouling control in once-through condenser cooling systems (Recommendation R111):

1. chemicals should only be used when demonstrated as necessary;

2. when chlorine use has been demonstrated as necessary, then :

- Only the minimum amount necessary should be used;

- The maximum concentration of total residual chlorine at the outlet of the condenser undergoing chlorination should not exceed 0.5 mg/L;

- Chlorine should be applied intermittently and the injection point should be immediately upstream of the condensers and sets of auxiliary coolers, unless continuous chlorina-

tion or a different injection point has been demonstrated to be necessary to control biofouling; at no time, however, should chlorine be introduced upstream of the travelling screens;

- Chlorine application should be limited to no more than one condenser and set of auxiliary coolers at a time, and should occur in daylight hours.

The rationale presented for this is that chlorine is almost certain to cause mortality or sublethal effects to entrained organisms and has the potential for producing carcinogenic compounds in receiving waters subsequently used for drinking. The recommendation either eliminates or reduces the amount of chlorine used and injection in the most sensitive area is prohibited (i.e. the forebay). Because injection close to the condenser or heat exchangers will minimise the residual chlorine loss prior to contact with the most important biofouling organisms, less chlorine will be required.

The recommendation also identifies a number of opportunities to minimise biofouling control :

- The use of mechanical cleaning devices to clean condenser tubes during operation or shutdown, and

- The chemical or mechanical cleaning of condensers on heat exchangers during shutdown (with chemical wastes being collected and pre-treated before discharge).

Where the most common biocide, chlorine, is used, the recommendation goes on to say that :

— Its use can be minimised by an injection and control system designed so that injection is immediately upstream of the condenser with control being maintained by measuring total residual chlorine at each condenser outlet;

— A dechlorination system can be provided (e.g. sulphur dioxide or sodium sulphite injection) if, for process reasons, the individual condenser discharges have to exceed 0.5 mg/L TRC.

— Residual chlorine will be more readily chemically reduced in the receiving environment in the presence of ultra-violet light during the day.

Whilst the recommendation notes that intermittent chlorination is generally adequate for freshwater biofouling control it also states that continuous chlorination might be necessary for the control of mussels and barnacles in sea water.

Recommendations pertaining to the use of biocides, other than chlorine, were deferred.

Recommendation R 112 addresses the control of corrosion, scaling or silting in once-through or partially open cooling systems, and recommends the following :

— On-line application of chemicals should not be used unless they are demonstrated to be necessary and demonstrated not to cause environmental damage;

— If the use of on-line chemicals is demonstrated to be necessary but it cannot be demonstrated that such chemicals will not cause environmen-

tal damage, the dose rates and method of application should be such that only the minimum amount of chemical is used;

— Spent cleaning solutions generated from off-line chemical cleaning of condensers should be contained and treated before discharge.

Recommendation R 201 addresses contaminants arising from evaporative recirculating cooling systems for the purposes of controlling biofouling, corrosion and/or scaling in evaporative recirculating systems. It suggests that :

— Chemicals should not be used unless demonstrated to be necessary or to be environmentally innocuous;

— Asbestos based materials should not be used for cooling tower components;

— Chromium chemical additives should not be used for cooling pond recirculating systems;

— Chemical additive systems (if required) should be designed to minimise the use of chemicals while providing adequate biofouling, silting, corrosion, and/or scaling control.

The rationale behind this is stated as 'this recommendation eliminates, or at least discourages, the contamination of receiving waters with deleterious substances in blowdown from evaporative cooling systems, which are the largest wastewater volume in stations that use such systems. Asbestos-based materials used in cooling waters may become airborne (by drift) and may be carcinogenic if inhaled. Hexavalent chromium is highly

toxic and may form difficult to manage waste precipitate (sludge) in cooling ponds. Chlorine may form toxic and carcinogenic compounds, and other biofouling, silting, scaling and corrosion chemicals may be detrimental. Their use is discouraged but, if necessary for process reasons, their minimum usage is encouraged to minimise discharges.

2. EU Member States

2.1 The Netherlands

The Netherlands has a central Government with a large degree of functional decentralisation. The Ministry of Transport, Public Works and Water Management is responsible for the management of state waters (North & Wadden Seas, IJsselmeer, the major rivers, estuaries and deltas), including discharges to them. Its executive body, the Rijkswaterstaat, is helped by its Regional Directorates in the 12 Provinces and the Institute for Inland Water Management and Wastewater Treatment (RIZA) which advises on policy and technical matters.

Non-state waters (minor rivers, lakes and canals) are administered by the Provinces. However, all but three have delegated their responsibilities in this area to Water Boards. Power Stations, however, are likely to be sited on State Waters and thus discharges from them will tend to be controlled by the Rijkswaterstaat.

The approach adopted by the Rijkswaterstaat and RIZA to consenting cooling water discharges varies according to whether the system is once through, the main type of system operated in the country, or a recirculation system. In both cases the potential environmental impact on the relevant receiving waters will be assessed and the discharge permit will reflect this. The most commonly used oxidising biocide is chlorine, although RIZA generally tries to minimise its use. Where use is permitted, the regulator will generally stipulate a limit of 0.2-0.3 mg/L free chlorine at the end of the system (roughly equivalent to a dose of 2-3 mg/L).

The Netherlands has imposed abatement measurements on certain discharges for specific groups of organohalogenes which has resulted in an 88% reduction of AOX discharged to the aquatic environment over the last 15 years (PARCOM, 1995). Thus proportionally, the contribution of cooling water discharges to total AOX releases in the country is likely to be increasing. Further research is likely to be focussed on the oestrogenic potency of discharges and emissions from industry and reduction measures will be targeted on the largest discharges and emissions of AOX. The main sources in the Netherlands determined in 1990 included hypochlorite use in households, but did not include discharges from power stations. AOX may be used as a control parameter for industries such as the paper and pulp sector, but is not seen as applicable to more complex effluents.

2.2 Germany

Pollution control in Germany is the responsibility of the Lander (the 16 constituent States of the country). Therefore any national (Federal) pollution control legislation requires the collective agreement of the Lander and implementation of the legislation into the Laws of the individual Land.

The main law protecting the aquatic environment is the Federal Water Resources Act (Wasserhaushaltgesetz) last amended 1990. Article 7A of the Act requires that effluents containing dangerous substances must be treated by Best Available Technology (BAT) irrespective of whether they are discharged directly to surface water or to sewers. The Waste Water Origins Regulation (Verordnung über die Herkunftsbereiche von Abwasser, last amended 1991), defines those industrial branches which may contain dangerous substances in their effluents.

The standards to be achieved by applying BAT are laid down in Annexes to the Federal General Administrative Regulation which are applicable as a minimum throughout the country. More stringent standards may be laid down by the regulatory authorities on a site specific basis, if this is required to protect the receiving water. The need for more stringent standards than those based on BAT requires detailed justification as most of the Lander have not laid down Quality Objectives or Standards for the protection of the receiving waters. One exception is Nordrhein-Westphalia

which has stipulated minimum requirements for running waters for a number of parameters, which may be used as a guide to identify where more stringent controls need to be applied.

Cooling water has been defined as one of the 'effluents' potentially containing dangerous substances and which therefore requires the application of BAT. Minimum standards to be achieved before cooling water can be discharged are contained in annex 31 (water treatment, cooling systems, steam production) last amended 31 January 1994.

Continuous dosing of disinfectants (e.g. chlorine, chlorine dioxide) is generally not permitted. However, the regulation does allow shock dosing. In principle, provided dosing is discontinued during a short period every day this is classified as shock, rather than continuous. The regulators have indicated that this is seen as a loophole and will need to be dealt with in the future.

For each cooling water discharge produced, depending on the operation of the cooling system, some general requirements apply with more specific limit values being laid down.

The main control parameters for cooling water are the concentration of the residual oxidant (as chlorine), AOX (which can be considered as surrogate parameter for organic chlorinated and brominated substances formed when using chlorine, chlorine dioxide or bromine as disinfectants), and a luminescent bacteria test (a surrogate for acute toxicity).

The general requirements are :

a) With the exception of phosphates and polycarboxylates, all other organic complexing agents used must be easily biodegradable as defined in the German Chemical Act.

b) Chromium, mercury, nitrite and organometallic compounds and mercaptobenzthiozol may not be present in cooling water discharges.

The following specific minimum requirements apply, depending on the operation of the cooling system.

2.2.1 Requirement for cooling water in once through operation-shock dosing

	Qualified spot ⁽¹⁾ sample
Chlorine dioxide, chlorine(as free chlorine) ⁽²⁾	0.2 mg/L
AOX	0.15 mg/L

⁽¹⁾qualified spot sample requires that 5 individual samples are taken within 2 hours, which are mixed before analysis

⁽²⁾other biocides with the exception of ozone and H₂O₂ should not be present

2.2.2 Requirement for cooling water bleed effluent from main recycle power station cooling water

	spot sample
COD	30 mg/L
Phosphorus compounds (total P)	1.5 mg/L ⁽¹⁾

⁽¹⁾If only organic phosphorus compounds are used the limit value is 3 mg/L.

If shock dosing with a biocide is practised the following conditions apply :

	spot sample
AOX	0.15 mg/L
Chlorine dioxide, chlorine, bromine(as chlorine)	0.3 mg/L
Inhibition of bioluminescence (bacteria)	GL12 (see note)

The limit value for bioluminescence is also achieved if it can be shown from manufacturing information that the biocide has degraded sufficiently to a value below GL12 (GL12=dilution to non-toxic effect = 1 unit wastewater and 11 units dilution water) before the effluent bleed is released. Discussions are still going on in Germany how this can best be implemented (e.g. what data are required from the manufacturers). In addition the biocides should not contain any zinc compounds.

A PARCOM working Party has suggested that for cooling waters the biotest requirements are TL = 4 (i.e. GL = 4). This value does not, however, agree with the current legislative requirement.

2.2.3 Requirement for other cooling water bleed effluent

	spot sample
COD	40 mg/L
Phosphorus compounds (total P)	3 mg/L ⁽¹⁾
Zinc	4 mg/L
AOX	0.15 mg/L

⁽¹⁾ The limit is increased to 4 mg/L if no zinc compounds are used and to 5 mg/L if no zinc compounds and only inorganic phosphorus compounds are applied.

If shock dosing with a biocide is practised the following conditions apply :

	spot sample
After shock dosing with chlorine, chlorine dioxide, bromine (as chlorine)	0.3 mg/L
AOX	0.5 mg/L
Inhibition of bioluminescence :	GL12

In addition to these limits on the quality of the effluent they can discharge, dischargers have a powerful incentive for minimising their emission of biocides and associated by-products in the Federal Waste Water Charges Act. The charges levied on a discharger are based upon, amongst other things, AOX and acute effluent toxicity.

The standards outlined above are used as minimum requirements throughout the country but certain Land have derived stricter standards. The minimum quality requirements for running waters in Nordrhein-Westphalia give a value for AOX of 40 µg/L. Thus depending on the dilution available in the receiving waters, stricter standards than those given in Annex 31 of the Federal General Administrative Regulation may need to be met by the discharger.

2.3 France

Regulatory Framework :

France takes a dual approach to the protection of the aquatic environment based both on Integrated Pollu-

tion Control and the use of quality (EQOs) for the receiving waters.

2.3.1 Receiving Waters

French EQOs are almost entirely based on European Union Directives and /or WHO Guidelines (Pers. comm., F Bordet, EDF). The main French legislation relating to the quality of receiving waters are :

a) June 1975 (75/460/EEC), concerning the quality required of surface water intended for the abstraction for drinking water.

b) July 1978 (78.659/EEC), concerning the quality of fresh waters needing protection or improvement in order to support fish life.

c) October 1979 (79/923/EEC) on the quality required for shellfish waters.

These Directives have been incorporated into French law in two separate regulations :

— décret du 3 janvier 1989, relatif aux eaux destinées à la consommation à l'exclusion des eaux minérales naturelles (decree concerning water intended for human consumption, excluding natural mineral waters).

— décret du 19 décembre 1991, relatif aux objectifs de qualité assignés aux cours d'eau, sections de cours d'eau, canaux, lac ou étangs et aux eaux de mer dans les limites territoriales (decree concerning quality objectives for water courses, sections of water courses, canals, lakes or ponds and coastal waters within territorial limits).

The decree of 3 January 1989 (issued by circular dated 16 May 1989) imposes maximum values, for specific halogenated chemicals in water to be used for abstraction for drinking water supply. Those that have implications for the discharge of cooling waters containing biocides and their by-products are summarised below:

- carbon tetrachloride (tetrachloromethane) < 3 µg/L
- 1,2-dichloroethane < 10 µg/L
- trichloroethylene (trichloroethane) < 30 µg/L
- chloroform (trichloromethane) < 30 µg/L

The decree of 19 December 1991, requires that the concentration of each organohalogen substance (either in the surrounding water or in the tissue of the shellfish) must not exceed that which would provoke harmful effects on shellfish. No specific chemicals or limit values are provided. However, in an annex to this decree concerning the quality of surface waters needing protection or improvement in order to support fish life, a limit of 5 µg/L total residual chlorine (HOCl) is specified.

2.3.2 Effluents

There are also regulations on 'Installations Classées pour la Protection de l'Environnement (ICPE)' (classified installations) (Loi du 19 Juillet 1976, arrêté du 2 février 1998), which apply to the most polluting activities in France (with the exception of the nuclear industry, which is covered by separate legislation). This system sets

BAT based limits for point source discharges, including those of cooling waters. The conditions for power stations are summarised below.

The ICPE Regulations provide powers to set discharge consents for conventional power stations (coal and fuel oil) and, in particular, the order (arrêté) of 2 February 1998 specified a limit of 1 mg/L AOX (adsorbable organohalogens) or EOX (extractable organohalogens) where the discharge is greater than 30 g per day. The regulatory authorities acknowledge that this limit is probably more applicable to small industries and that in practice more stringent standards would be set for cooling water discharges from power stations. Before standards are set for cooling water discharges, the discharger would be expected to undertake toxicity testing and provide the regulator with the results.

The regulators approach to the control of the discharge is also dependent on the type of cooling system used. Two broad categories can be distinguished; power stations situated on coastal sites equipped with open-circuit once-through direct cooling and those inland, on rivers, using open-circuit recirculating tower assisted cooling.

(i) Coastal discharges

The conditions which are normally applied to installations on the English Channel or North Sea, allow continuous chlorination with an initial concentration of 1 mg/L (HOCl) at a water temperature of 10°C. No other condi-

tions are normally imposed on cooling water discharges of this type.

Conditions applying to two specific coastal power stations are :

- Flamanville : a requirement to reduce the level of chlorination to 0.5 mg/L within a 6 year period,
- Le Havre : the total concentration of free chlorine and chloramines in the discharge must be less than 0.1 mg/L.

(ii) River discharges

Conditions for chlorination normally specify intermittent treatment (once or twice per year) with a free chlorine residual in the discharge not exceeding 0.1 mg/L. For some sites, the Water Police can request that monitoring is carried out for trihalomethanes (chloroform).

As with Germany, French dischargers have an additional motivation to reduce the amounts of biocide and associated by-products that they discharge. This is from the pollution charge levied on the discharger by the Agences de l'Eau (public authorities responsible for water resource management).

The Agences use AOX as one of the parameters on which the discharge levy is based. The charge is calculated on the basis of the maximum quantity of 'pollution' discharged per day and, for AOX, this can vary from 0 FF per kg to 3000 FF per kg depending on the policy of the individual Agence de l'Eau involved. Since 1998, the Agence de l'Eau Seine-Normandie uses the bromoform concentration, instead of AOX, as the tax

parameter for cooling waters released by the nuclear power stations located on the English Channel coast.

Any future tightening of standards in France relating to the use of biocides by the power industry are likely to be stimulated by new European Directives, in particular, those relating to the Ecology of Natural Waters, the Drinking Water Directive and the Biocides Directive.

2.4 Belgium

Belgium has no legislation relating specifically to power stations (pers comm MM Deweyn and Malangreau, Electrabel). However, industrial discharges, including cooling waters, usually require a permit. The electricity generator, Electrabel, states that a discharge consent applies for cooling water, which specifies a limit for free chlorine of 1 mg/L at the discharge point for both fresh and brackish water. In addition, there are regulations on 'Etablissements Classes' (classified installations) which apply to the most polluting activities in Belgium which control the discharge of effluent via a permit system. Electricity generators do not at present appear to be classified under these regulations.

There is no move to use toxicity based consents in Belgium. An environmental tax system has been discussed by the regulators, however, such a system has not yet been implemented.

2.5 Sweden

The Swedish regulators have taken a series of measures to reduce the risk resulting from chlorine compounds e.g. reducing the exposure to man and the environment by limitations on marketing, discharge/emission restrictions and changes in the way chemicals are handled in the working environment (PARCOM, 1995).

An important area for risk reduction is seen to be the use of bleaches by the pulp and paper industry. The Swedish Chlorine Plan has been developed with the aims of increasing the actions taken against the use of chlorine compounds in Sweden and other countries. It recommends that the use of chlorine for disinfection should cease and also highlights the use of hypochlorite in cooling systems. The use of un-chlorinated disinfectants in addition to chlorinated disinfectants is recommended for use in swimming pools where the complete elimination of chlorine use would be difficult.

2.6 Denmark

Denmark has initiated a project to develop a model to estimate the industrial use of chlorine and organochlorine compounds. It will include net import, production and industrial use as well as an assessment of the final fate of selected hazardous compounds (PARCOM, 1995).

The use of chlorine in cooling water systems is not prohibited by law. However, in the Environmental Act, there is a clear intention to reduce the discharge of dangerous substances, including chlorine, and there is given a list of types of factories, including power stations, requiring authorisation from the local environmental authorities. This environmental authorisation is negotiated with the local authority every eight years, and under special circumstances, every four years. All power station units built the last 10 to 15 years are not allowed by local environmental authorities to use chlorine. Consequently, in Denmark, the use of chlorine in cooling water is not prohibited by law but, by regulation, it is made impossible to use.

2.7 Italy

The recently introduced Galli Law states that each region of the country has the right to set its own discharge limits. No Region has yet developed such standards and it has been recommended that in the interim the discharge limits stated in the old Merli Law of 1976 be used as guidelines.

The Merli discharge limits include free chlorine (0.2 mg/L), chloride (1200 mg/L) and chlorinated pesticides (0.05 mg/L) as parameters. The limits are stated as the maximum concentration which should be present in a single instantaneous sample, or a mean of samples taken within a time period specified by the regional body. Before 1979, the time period had to

be a minimum of 3 hours, but since 1979 it is left to the regional bodies to determine the time period. Italy is incorporating the standards specified in EC Directives e.g. Drinking Water and Dangerous Substances Directives, into Italian legislation by the adoption of decree laws.

2.8 Spain

When Spain entered as a member of the EC, it was necessary to incorporate community decrees to Spanish Legal Ordinance with regard to contamination on account of dangerous substances discharged to seawater. Thus, the general norms published in 74/464/EEC and 86/280/EEC have been incorporated into the Spanish Legal Ordinance by means of Decree Real 258/1989, which establishes the General Regulation of dangerous substances discharged to seawater which proclaims that emissions norms, quality points, reference measurement method and control procedures will have to dictate with regard to those substances included in black list substances or grey list substances. Subsequently, modifications have been produced in accordance with EC marks. These modifications are published in B.O.E. (State Official Bulletin): BOE 241 of 89-11-11; BOE 116 of 91-05-15; BOE 267 of 92-11-06.

2.9 United Kingdom

The UK has implemented all the EU water related legislation and has in addition implemented its own legislation to provide the basis for a comprehensive policy on the protection of the aquatic environment. This legislation assigns roles and responsibilities, but leaves the regulatory authorities to adopt their own approach for protecting the aquatic environment.

In addition, with the introduction of Integrated Pollution Control (IPC) in the UK a new emphasis has been placed on the control of discharges of the most dangerous substances (Red List) by the use of best available techniques (BAT).

2.9.1 Control of Pollution Act 1974 and Water Resources Act 1991

These two acts gave the UK environment agencies powers to protect the aquatic environment, including the power to consent and monitor effluent discharges. For most discharges the Scottish Environmental Protection Agency and the (English and Wales) Environmental Agency set site specific conditions, e.g. an EQS for Chlorine has been proposed (NRA 1994) and EQSs for Bromine and Chlorine Dioxide are in preparation. These will be applied to cooling water discharges as well as to other industrial discharges.

The Chlorine EQSs proposed for freshwater are 5 mg/L TAC as a maxi-

mum allowable concentration (MAC) and 2 mg/L TAC (Total Available Chlorine – free and combined chlorine) as an annual average (AA) in the receiving water, whilst the EQS proposed for the protection of solely marine environment is a MAC of 10 mg/L TRO (Total Residual Oxidant – free and combined chlorine and bromine).

The UK Government has also instigated setting legally binding (statutory) EQSs for the protection of certain uses of the aquatic environment for general physical and chemical parameters (e.g. BOD, COD, ammonia etc.) rather than dangerous substances. The first set of regulations – The Surface Waters (River Ecosystem) (Classification) Regulations 1994 (SI 1057) – define five classes of water in terms of their ability to support aquatic life. The classes are based on EQSs for nine parameters. These parameters do not include residual chlorine.

2.9.2 The Environmental Protection Act 1990

Part 1 of the Environmental Protection Act 1990 introduced a system of integrated pollution control (IPC) in the UK as a framework for controlling releases from certain prescribed in-

dustrial processes and ensuring compliance with relevant EC Directives on pollution control.

Power Generation using fossil fuels comes under IPC (Chief Inspectors Guidance note for Combustion Processes S2 1.01, HMSO, November 1995) and, as such, is subject to authorisation by HMIP. Nuclear Power Stations themselves do not come under IPC but are still subject to discharge consents issued by the environment agencies for their cooling water releases.

2.9.3 The Environment Act 1995

This act gave a responsibility to the UK environment agencies “to protect and enhance environment as a whole, so as to contribute to sustainable development”.

2.9.4 The Planning (Hazardous Substances) Regulations 1992.

The use of chlorine and bromine is also covered by legislation relating to the storage of dangerous substances above threshold amounts. Sites storing greater than 1 tonne of bromine and/or 10 tonnes of chlorine are required to obtain a storage consent.

Annex 3

List of European power stations quoted in the text

European Country	Power station
Belgium	Drogenbos Mol Seraing Tihange
Denmark	Esjberg
France	Bugey Cattenom Chinon Chooz Cruas Dampierre-en-Burly Flamanville Golfech Gravelines Le Havre Paluel Penly
Italy	Saint-Laurent-des-Eaux Brindisi La Spezia Leghorn – Livorno Vado Ligure
The Netherlands	Bergum Rota Delfzijl Diemen Dodewaard Eems Hoogovens Ijmuiden Maasvlakte Moerdijk Velsen
Spain	Vandellos
UK	Bradwell Dungeness Hartlepool Heysham Sizewell Wylfa

Alphabetical Index on Key Words

- A** Acoustic energy, 159-160
Adsorbable Organohalogens (AOX), 92, 95, 118, 121, 126, 128, 133, 135, 138, 152-153, 181, 211-216
Aluminium anode, 152-153
Anodonta, 50-51, 75
Anti-fouling methods (review), 64-70
Artemia salina, 143
Ascidians, 77
Ascidella aspersa, 77
Asiatic clam, 19, 40, 75, 105, 142, 162
- B** *Balanus amphitrite*, 28
Balanus crenatus, 28-29
Balanus eburneus, 109
Balanus improvisus, 28, 33-34, 111
Balanus perforatus, 29
Balanus tintinnabulum, 29
Band screen, 4-5
Barbus barbus, 122
Barnacles, 28-30
Benzothiazoles, 147-149
Biocide Authorisation Directive, 173-175
Biofilm, 58-59, 102, 106, 163-167
Biological control, 160-161
Biological monitoring, 161-164
Bithynia, 54-55, 75, 114
Brachidontes striatulus, 106-107
Brachydanio rerio, 136
Break point, 93, 95-97
Bromamines, 90, 91, 96, 97
Bromate, 95, 123, 175
Bromoform, 97, 100, 118-119, 124-127, 178
Bromophenols, 99, 100
Bryozoans, 50, 52-54, 75-76, 126
- Chironomus plumosus*, 119
Chloramines, 126-127, 178
Chlorate, 129, 135-137
Chlorella, 120
Chlorination Environmental Assessment, 117-126
Chlorination at industrial sites, 111-117
Chlorine chemistry, 90-100
Chlorine continuous monitoring, 101
Chlorine dioxide chemistry, 128-129
Chlorine dioxide efficacy on biofouling, 129-133
Chlorine dioxide Environmental Assessment, 135-138
Chlorine dioxide at industrial sites, 133-135
Chlorine dioxide production, 127
Chlorine efficacy on biofouling, 102-111
Chlorine storage, production, 89-90
Chlorite, 123, 127, 129, 135, 136
Chloroform, 118, 127, 172, 178, 215
Chthamalus, 28, 156
Chroococcus, 56
Cladophora glomerata, 58
Clarias gariepinus, 143
Cleaning, 73-74
Closed cooling systems, 7-11
COMAH proposed Directive, 176
Conger conchleata, 32
Continuous chlorination, 113-116
Cooling water requirements, 7
Copper, 152-153
Corbicula fluminalis, 19, 42, 44
Corbicula fluminea, 19, 40-47, 50, 105, 154-155, 162
Cordylophora caspia, 35, 161
Corophium curvispinum, 47-48, 160, 162
Crassostrea gigas, 30, 154
Crassostrea virginica, 119
- C** *Carassius auratus*, 120
Carcinus sp., 28
Cathodic protection, 158-159

- Cyanobacteria, 54, 55-58, 112
Cyprinus carpio, 119, 143
 Cypris larvae, 29-30, 156
- D** Dangerous Substances Directive, 171-172
Daphnia magna, 136
 Debris filters, 73
 Detoxification, 148
Dicentrarchus labrax, 138
 Direct cooling systems, 7-8
 Discontinuous chlorination, 116-117
 Dissociation (HOCl, HOBr), 96
 DPD method, 100-101
Dreissena bugensis, 37
Dreissena polymorpha, 75, 101-107, 113-114, 129-131-140, 154-156, 158-160
 Drinking Water Directive, 175
 Drinking water Guidelines (WHO), 177-178
 Drum screen, 6
- E** Ecological Quality of Water Framework Directive, 175-176
 Electric fields, 158-159
 Electrochlorination, 90
Elminius modestus, 111
Entosiphon sulcatum, 119
 European Legislation, 169-176
 Extractable Organohalogens (EOX), 92, 97, 122
- F** Fatty Amines, 145-151
Ficopotamus enigmaticus, 34
 Filtration of water (as anti-fouling method), 4-6, 12-13, 72-74
 Fouling (survey in European countries), 11-13
Fredericella sultana, 52
 Freshwater Fisheries Directive, 37
 Freshwater fouling, 37
Fucus serratus, 137
Fucus vesiculosus, 137
- G** *Gammarus pulex*, 119
 Gloeotheca, 56
 Green algae, 57-58
- H** Haloacetic acids (HAA), 95, 99, 120
 Haloacetonitriles (HAN), 95, 99
 Heat treatment, 79-83, 205-206
- Hydrogen Peroxide, 144
Hydroides elegans, 133
Hydroides norvegicus, 32
- I** Intermittent chlorination, 110-111
 IPPC Directive, 175
 Isothiazolones, 146-149
- L** *Laomedea flexuosa*, 132
Legionella pneumophila, 59
Lepomis macrochirus, 118
Leuciscus cephalus, 122, 143
Lophopodella carteri, 160
Lymnaea, 54-55
Lyngbia (Phormidium), 56
- M** Macrofouling, 18-19
 Magnetic fields, 159
Mercierella enigmatica, 34
Microcystis aeruginosa
 Microfouling, 17-18, 36-37, 72, 163
Micropterus salmoides, 118
Modiolus barbartus, 21
Modiolus modiolus, 21
 Molluscicides, 145
 Monochloroacetic acid, 120
 Mosselmonitor, 111, 162-163
 Mussels (marine), 20-28, 115
Mytilopsis leucophaeta, 18, 32, 35, 105, 107, 163
Mytilus edulis, 18, 20-22, 25-26, 161, 163
Mytilus galloprovincialis, 21-22, 132
Mytilus trossulus, 21-22
- N** *Naegleria fowleri*, 59
Nostoc, 56
- O** Oslo and Paris Convention, 177
Ostrea edulis, 30
 Oxidizing compounds, 144
 Oxygen deprivation efficacy on biofouling, 154-155
 Oysters, 30
 Ozone efficacy on biofouling, 139-141
 Ozone at industrial sites, 141-142
 Ozone Environmental Assessment, 142-143
 Ozone production. chemistry, 138
 Ozone safety of workers, 143
- P** Paints (anti-fouling), 83-86, 181

- Palucidella* sp., 52
 Pathogens, 59-60, 120-121
 Pediveligers, 24, 42
 Peracetic Acid, 144
Physa acuta, 75, 114, 140
Pimaphyes promelas, 120
Pisidium, 50
Pleurobrachia pileus, 17
Plumatella emarginata, 52-54, 76, 140-141
Plumatella fungosa, 52-54, 76
Plumatella repens, 82, 76
Poecilia reticulata, 119
Pomatoceros triqueter, 31
 Potassium toxicity to Zebra mussels, 155
Protula tubularia, 31
Pseudomonas putida, 119
Pseudomonas aeruginosa, 58, 144
 Pulse chlorination, 110-111
 Purgeable Organohalogenes (POX), 92
- Q** Quality of Surface water for Abstraction Directive, 172-173
 Quaternary Amines, 145-148
- R** *Radix ovata*, 55
Rutilus rutilus, 122
- S** *Salmacina tribranchiata*, 32
Salmo trutta iridea, 119
 Scale, scaling, 12-13, 20, 60-61
Scenedesmus quadricauda, 119
Scenedesmus subspicatus, 143
Scytonema multiramosum, 56
Semibalanus balanoides, 28
 Semi-continuous chlorination, 114-116
Serpula vermicularis, 31
 Settlement (larval), 24-26, 29-30, 33-34, 39-40, 44-45, 158
 Shell fisheries Directive, 173
 Shock chlorination, 112-113
 Silicone based coatings, 86-88
 Siltation, 19-20
 Silver, 153
 Slime, 58-59, 150-151
Sphaerechinus granularis, 138
Sphaerium, 50, 52
Spirorbis, 133
Spongilla, 160
 Statoblasts, 141
 Strategies (treatments), 69-72
- T** TBTO, 154, 181
 Total Organohalogenes (TOX), 92
 Trash, 15-16
 Trash racks, 17
Travelling screens, 4-6, 73
 Trichlorophenol, 120
 Trihalomethanes (THMs), 181
 TRO decay, 91, 123-124
 Tubeworms, 31-32
Tubifex tubifex, 119
Tubularia, 76-77
- U** *Unio*, 50-51, 75
 UV light, 155-158, 182
- V** Veliger larvae, 23, 39,
Viviparus sp., 54-55
Vorticella campanula, 119
- W** Water filtration (as anti-fouling method), 72-74
 Water intakes, 2-4
 Water Intended for Human Consumption Directive, 173
 Water velocity (as anti-fouling method), 74-79
- X** *Xanthium strumarium*
- Z** Zebra mussels 75, 101-107, 113-114, 129-131-140, 154-156, 158-160