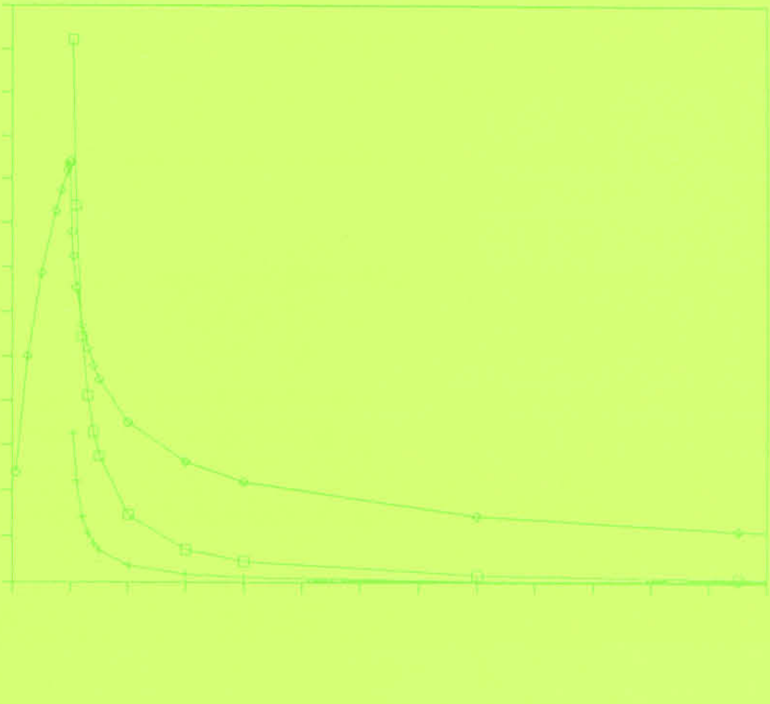
ASSOCIATION OF RIVER WATERWORKS

RIWA

March 2000

Biocides



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Biocides

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SUMMARY AND CONCLUSIONS

The group “Biocides” is one of a series of substance groups for which RIWA has had drafted a survey document within the framework of the project “Studies on substances”.
This document addresses the issue whether using certain biocides is inconsistent with or will cause problems to using surface water for the production of drinking water.

Two criteria were used:

- a situation, in which conventional techniques for the production of drinking water are inadequate, is undesirable
- a situation in which the good health of the ecosystem is affected, will in general affect the suitability of surface water as a source for the drinking water supply.

From the substantial group of “Biocides” (non-agricultural pesticides) three important applications have been selected that seem to be important with regard to the production of drinking water: wood preservatives, biocides for cooling water and anti-fouling coatings. These three applications make up a substantial group of various substances, ranging from simple inorganic compounds to complex organic molecules.
First a selection has been made from the large group of known biocides, based on the legal registration for these three applications, excluding substances that are mainly applied in agriculture and horticulture. Furthermore, from a practical point of view, the number of substances has been reduced by excluding the readily degradable substances: after all, these will disappear from surface water after a short residence time.
For the remaining substances the following issues have been described: the use and emission to surface water, analytical methods and concentrations in surface water (if available), the toxicity, an environmental risk assessment based on concentrations in surface water and toxicity, the behaviour in a simple water purification process and the policy plans for these three applications.

Wood preservatives

Twenty two substances have been selected. The emission of arsenic, when applied as a wood preservative, into surface water is considerable. This may cause local and temporary exceeding of the ecological standards. During the production of drinking water arsenic is eliminated sufficiently. The sludge, containing arsenic up to 150 mg/kg d.s. As, must be treated as a waste material which has to be eliminated at a controlled landfill site because of possible leaching. Although plans for a useful application of sludge containing iron and manganese, as raw material for bricks, offer a positive perspective, leaching of arsenic remains a possibility and additional policy in order to reduce the arsenic emission is needed.

The emissions of chromium and copper, when applied as a wood preservative, may lead to an exceeding of the ecotoxicological standards both locally and temporarily. Copper and chromium are, like arsenic, sufficiently eliminated during the production of drinking water and lead to increased concentrations of Cu and Cr in the sludge of drinking water production (approx. 60 mg/kg d.s. Cr and 90 mg/kg d.s. Cu).
The reduction of the total environmental pollution with Cr and Cu is desired for ecological reasons and a governmental policy for heavy metals is expected shortly. The contribution to the environmental pollution with Cr and Cu from wood preservation, however, is relatively small.

The emissions of boron and fluorine from wood preservatives are not known. Boron is probably not eliminated during production of drinking water, whereas fluorine salts are eliminated. In view of the relatively low toxicity and the relatively large contribution to the environmental pollution with boron and fluorine from other sources, a specific policy for the application as wood preservatives does not seem to be urgent.
The emission of various organic (-azolic) compounds and of quaternary ammonium compounds has not been quantified. Hence, a simple risk assessment cannot be made. It is expected that leaching is low and elimination by adhesion to sludge is effective. Consequently, the drinking water quality will probably not be affected adversely.

In future the application of creosote oil and tar, containing PAH, will no longer be admitted in The Netherlands. However, the present PAH contents in surface water constitute no direct danger to the production of drinking water, since the adhesion of these substances to sludge causes either a drastic disposal or biodegradation of these substances.
Accumulation of PAHs from a large number of diffuse sources does, however, cause problems to the water quality.

Policies for wood preservatives have been developed to a large extent. Until now these policies have mainly been directed to the application of wood preservatives in industry.
In industry the emissions have been reduced considerably. In particular for PAHs (creosote) policy has been developed to a large extent. These substances, however, are still not prohibited completely. In this study these substances have not been selected because of their prohibition in the near future.
Policy attention was also paid to CCA-salts (chromium, copper, arsenic). At the moment the application of these salts is restricted to the most environmentally friendly type (C) having the lowest leaching potential. A national policy for arsenic no longer exists, although at a local level the standards may still be exceeded. The future policy is directed towards a further reduction of the application of CCA-salts and other substances by searching for alternatives and certification of more environmentally friendly preserved wood.

Generally, the development of environmentally friendly alternatives for wood preservation could be stimulated more, especially on a European level. With regard to this, methods that will reduce the use of tropical hardwood, such as the PLATO process, are especially interesting.

Biocides for cooling water

Chlorine compounds are by far the most widely applied anti-fouling agent. The application of the remaining agents is insignificant. Probably isothazolines and quats do not lead to problems for the aquatic organisms in surface water. They will probably be eliminated in the production of drinking water and thus constitute no hazard to man.

The presently applied chlorine compounds constitute a negligible hazard to aquatic organisms and humans. The toxicity of sodium bromide can be compared to that of bromochloro dimethylhydantoin and is not eliminated during water purification.
During ozonization in the production of drinking water sodium bromide might give rise to problems because of the formation of bromate.
Probably bromochlorine dimethylhydantoin is also poorly eliminated through a water purification process. It is expected that neither of these substances constitutes a hazard to aquatic organisms or humans, through the consumption of drinking water.

The reaction products of halogenated degradation products are not completely eliminated during a simple water purification process. Since these reaction products include mutagenic and carcinogenic products, the hazard to the public health has to be investigated further. At present the chlorous micro-contaminants are being investigated by i.a. the Institute for Inland Water Management and Wastewater Treatment (RIZA) and the University of Amsterdam.

The use of β-bromo-β-nitrostyrene might cause problems to aquatic organisms in surface water and to humans through the production of drinking water because of its degradation products (particularly bromonitromethane). It is not sufficiently known how to eliminate this degradation product during water purification and further investigations are needed.

Because of its metabolites dibromonitrilopropionamide may constitute a hazard to aquatic organisms and humans. Moreover, the substance is poorly eliminated by water purification. Further investigations are needed.

Insufficient information is available concerning dazomet and 5-oxo-3,4-dichloro-1,2-dithiol in order to assess the hazards to humans and aquatic organisms. Moreover, dazomet is probably poorly eliminated by means of water purification. For these substances further investigations are needed.

The policy concerning biocides for cooling water has not made much progress yet. The objective is optimising and reducing the use of biocides for cooling water by means of consultations between industry and government, and applying the most environmentally friendly adaptations and alternatives.

Anti-fouling coatings

Seven out of the nine selected substances probably do not constitute a hazard to humans and the environment when applied as an anti-fouling agent. Insufficient data are available about the remaining two substances.
For none of the selected substances concentrations in surface water are available caused by the application as anti-fouling agents.

Zinc compounds and the widely used copper compounds might constitute a hazard to the aquatic environment at a local level. During the production of drinking water these substances are sufficiently eliminated.
Bitumen probably constitutes no hazard to aquatic organisms or humans and moreover, it is effectively eliminated by water purification.
Insufficient reliable data are available about barium metaborate and 2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine for a risk assessment by the application as an anti-fouling agent. For these substances further investigations are needed.

In 1994 the Ministry of Housing, Spatial Planning and the Environment (VROM) started an action plan for anti-fouling nautical coatings. This was the basis for the policy plan "Anti-fouling Nautical Coatings".
The necessity to reduce the emission from anti-fouling nautical coatings is universally endorsed. For The Netherlands a 100% emission reduction in 2010 is pursued. There are no new national regulations yet. Every 3-4 years a report is issued regarding the action plan. Two areas for special attention are: the tributyltin issue and the copper contamination of inland waterways. For both issues an action plan was drafted [Second Chamber, 1997]:

1. With regard to tributyltin (TBT) the Marine Environment Protection Committee (VN-IMO-MEPC) has passed a recommendation to limit the maximum leaching of TBT-coatings. This resulted in terminating the application of the so-called "free-association" type of coatings causing a high TBT emission. Presently mainly "self-polishing" copolymers are being applied; they cause lower TBT emission and have a longer life span.

   The North Sea countries wish to reduce the TBT emission even more and are considering to prohibit this substance. The use of TBT coatings has been prohibited since 1990 for ships < 25 meters [EU guideline 89/677 EEC]. The objective is an international stop of the application of TBT in approx. 5 years.
   For the coasting trade and the ocean shipping TBT has a priority over copper, since copper is less problematic in the nautical environment and is no subject for international discussion. Furthermore, measures have been taken on a national level at shipyards and marinas. For the long term a more structural solution is being prepared for the anti-fouling issue.

   The objective is to stop the application, in approx. 15 years, of methods or agents which release pesticides. This may be reached, for instance, by the application of non-stick coatings and/or a periodic mechanical cleaning procedure.

   The action plan for TBT includes:
   a) optimising the possibilities for emission reduction;
   b) developing alternatives (replace tin with copper and organic biocides, and cleaning techniques;
   c) influencing international frameworks.

2. For copper a policy has been made within the scope of the Rhine and North Sea Action Plan (RAP/NAP) for a copper reduction of 50% between 1985 and 1995. On a national level measures are mainly taken for ship yards and marinas.
   The objective is a reduction of the copper pollution of surface water by anti-fouling coatings. This requires harmonisation with the approach of other sources of copper pollution, such as copper water pipes. The approach is phased. In the first phase an inventory is drawn up of the problems, alternatives are explored and information is given. Then a decision is taken about a further reduction of the copper pollution from coatings and a possible prohibition for anti-fouling coatings, containing copper, for inland waterways [Second Chamber, 1997].

1. INTRODUCTION

At the request of RIWA the available information concerning biocides which may be important to the quality of drinking water has been surveyed. It concerns a concise study into sources, usage, emissions and concentrations, Analysis and detection methods, the toxicological properties and possible treatment of these substances during the production of drinking water. In this report reference will be made to other, more extensive, sources. The main objective of this study is to give information on possible important substances with regard to the production of drinking water.

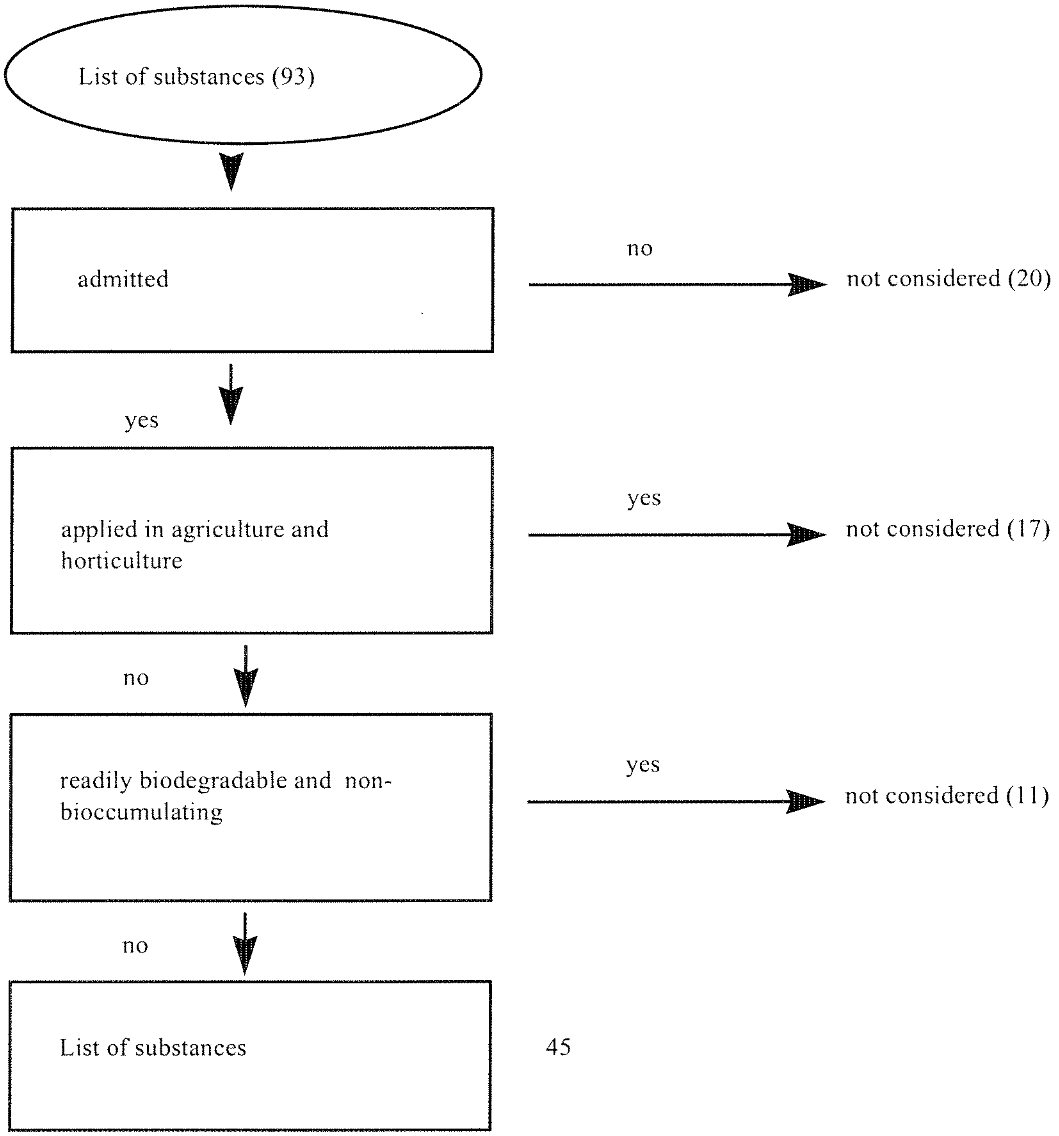
In preparation to the policy for non-agricultural pesticides (hereafter: biocides) of the Ministry of Housing, Spatial Planning and the Environment (VROM) a Multi-year Environmental Material Protection Plan was drafted, which has not been passed (yet). Anticipating the completion of this policy, a "leading-edge" letter was issued for the 5 main groups of biocides: swimming water disinfectants, wood preservatives, biocides for cooling water, methyl bromide in supply protection of feed stocks and anti-fouling nautical coatings. Consequently, these groups are the basis for this study.

2. THE SELECTION OF BIOCIDES

In consultation with RIWA three biocides were selected from the aforementioned groups of non-agricultural pesticides, viz.: wood preservatives, cooling water disinfectants and anti-fouling nautical coatings.
Swimming water disinfectants, methyl bromide and e.g. disinfectants in fish farms were regarded to be of little importance to the production of drinking water and these groups have not been considered in this report.

First of all a list of admitted (in 1994) biocides was drafted for the three applications mentioned (see Appendix 1). To this end the report by the National Institute of Public Health and Environmental Protection (RIVM) containing an environmental risk assessment of non-agricultural pesticides [Tas et al., 1996] was consulted and information was obtained from various contact persons. Although one of the original selection criteria for substances was the production and the quantity of the applied substances, it soon turned out that this information was not readily obtainable. Consequently, a selection of substances was made in a different way.

Table 1. Selection scheme



From a practical point of view de following selections have been made.
The substances which are no longer admitted in one of the three applications, have not been selected since these substances will be less important in the future.
Through Internet CTB was consulted in order find out whether the selected agents are still admitted for the applications mentioned. Substances which are also and mainly applied in agriculture and horticulture, are left out of consideration as well, since they were investigated earlier.
To this end e.g. WSV substance investigations of RIZA [Teunissen-Ordelman and Schrap, 1996] were consulted.

Next, a selection was made based on ready biodegradability and low bio-accumulation potential of the substances. These substances are not likely to occur in surface water after discharging, so problems with the production of drinking water are not expected. Table 1 shows the results of these steps.
The tendency of a substance to dissolve in fat is indicative for its bio-accumulation ability, expressed as log Kow. In order to predict biodegradation and log Kow, the Syracuse program EPIWIN [Boethling, 1993] was used. According to this program methylene bisthiocyanate and ethyl hexanoate (wood preservatives) are readily degradable and have a log Kow <3 (non-bioaccumulative), so that these substances do not lead to problems in the production of drinking water. Copper(I)oxide, copper(II)oxide and boric acid contain elements which persist in the environment.
According to the Syracuse program the following biocides for cooling water are readily degradable and have a log Kow <3: 2-methyl-4-isothiazoline-3-one, glutaric aldehyde, 2,2-dithio bisbenzamide, methylene bisthiocyanate, isopropanol and sodium dichloro isocyanurate. Sodium hydroxide and hydrogen peroxide are unstable substances that decompose rapidly. The anti-fouling agents copper(I)oxide and zinc oxide contain heavy metals which persist in the environment.
The biodegradation assessments and log Kow values are listed in Appendices 4 and 5.

The tables in Appendix I indicate why some substances were not selected. The remaining substances are included in Appendix 2, grouping chemically related substances. For these groups an investigation was carried out into application, emissions and concentrations, Analysis and detection methods, toxicological properties and the possible treatment for the production of drinking water. The behaviour of these substances in the environment and in a simple water purification process (aeration tank without presedimentation; oxidation ditch) has been examined as well.

3. SURVEY AND EVALUATION OF DATA FOR SELECTED SUBSTANCES

3.1 Wood preservation

3.1.1 Introduction

Wood preservatives are chemical products that have to be able to penetrate easily into the wood for a prolonged protection against fungi, insects and bacteria. Wood preservatives can be classified in various ways. A widely used classification according to physical and chemical properties is:

1. *water soluble agents (salts and oxides)*
2. *agents dissolved in organic liquids*
3. *agents of the coal tar group*

Prior to use, wood can be treated by impregnation (vacuum and pressure; vacuum method) or saturation/immersion in a preservative, if necessary followed by diffusion. Curatively it can be treated by e.g. brushing, spraying, atomising, wiping the preservative [Tas et al., 1996; Jonge, 1991].

Immersion will protect wood for a shorter period than the actual preservation method will. Immersion and subsequent diffusion may be considered to be as effective as preservation under pressure. In The Netherlands there are 36 companies that impregnate wood under vacuum and 50 companies that apply immersion [Second Chamber, 1997].

The first group of wood preservatives is mainly applied in the preventive treatment of wood. Fixation means physical or chemical binding of the active substance to the wood fibre in such a way that washing away by water no longer occurs. Agents are either highly, moderately and non-fixing or poorly-fixing.
The highly fixing mixtures are compounds of salts of copper-chromium and copper-chromium-arsenic products (the so-called Wolman salts) and agents based on alkyldimethylbenzylammonium chloride. These mixtures are often brought into the wood using the vacuum/pressure method.
The salt mixtures usually consist of combinations of copper, chromium and arsenic or simply copper and chromium compounds. Sometimes they are combined with other active substances, such as boron and fluorine compounds. The chromium compounds mainly serve as a fixing agent for copper and arsenic salts. The copper compounds mainly act as an anti-fungi agent, whereas the arsenic compounds mainly act as an insecticide [Anon., 1985a]. In 1991 the admission of Wolman salts was restricted to the least leaching type [Second Chamber, 1997].
Moderately fixing salt mixtures contain boron, fluorine, dinitrophenol, chromium and arsenic. Boron and fluorine almost always leach out to a certain extent. Besides fluorine-chromium-arsenic, fluorine-chromium-boron, copper-chromium-boron, fluorine-chromium and copper-chromium-fluorine, azaconazole and propiconazole belong to this group.

The non-fixing or poorly fixing agents include agents with boron or fluorine as active agent and simple metal salts such as mercury chloride, zinc chloride, copper sulphate and mixtures of bifluoride, silicon fluorides, borax and boric acid. The three first mentioned are hardly used at present since they are liable to leaching under wet conditions.

The salt mixtures are applied to wood by saturation, immersion, spraying and brushing. In case of permanent contact of preserved wood with soil and/or water, part of the agent is liable to leaching. Poorly fixing agents should not be used for these applications [Jonge, 1991].

The second group of wood preservatives is dissolved in an organic solvent. These are: pentachlorophenol, chloronaphthalene, lindane and organo metallic compounds of copper, zinc, tin and mercury, e.g. copper naphthanate.
Copper naphthanate is a wood preservative used to prevent the adverse effects of fungi, because of the toxicity of both the naphthenic acids and copper to fungi [Anon., 1985a]. This group includes the active agents azaconazole, tributyltin phosphate, tributyltinoxide (TBTO), copper naphthanate and zinc naphthanate. All of these agents are applied to prevent the attack by fungi. Moreover, the insecticides cyfluthrin, cypermethrin, deltamethrin and permethrin, dissolved in weak oily products, are applied as wood preservative.
The third group of wood preservatives contains creosote oil and carbolineum (coal tar distillate), that belong to the tar oil group. The intention to prohibit these substances as from July 1, 1997, because of their emission of many hazardous PAHs, has been postponed for approx. 3 years.It is stated in the notification procedure for issuing new rules, laid down in the European Union, that national measures can only be implemented after completion of the notification procedure [Knippenberg and Wermeskerken, 1986; Jonge, 1991; Meijer, 1997; Second Chamber, 1997].
Since these substances will eventually be prohibited, they have not been included in this study.
Still much creosoted wood is in use (3,613,750 m^3 in 1992) liable to leaching [Second Chamber, 1997].
The substances that will be investigated further are listed in Table 2.1 of Appendix 2.

3.1.2 Sources, use and emission

In 1992 creosote was the most widely used wood preservative (83%), followed by metal salts (10%). The other preservatives make up for the remaining 7%. More recent data show that the application of metal salts is increasing, whereas the application of creosote is decreasing [Tas et al., 1996]. In Table 2 a survey is given of the use and emissions of wood preservatives.

Wood preservatives can enter the environment in three stages:

- wood treatment: impregnation, fixation , etc.;
- wood processing/usage;
- waste.

Berbee [1989] assumes a use of impregnated wood of 260,000 m^3/yr in The Netherlands in 1985 (not including the use by Dutch Railways of 35,000 m^3/year). In hydraulic engineering 15,500 m^3 of spruce was used for sheet pilings and 10,000 m3 for pilefacing. Next to that 15,000 m3 of azobe wood was used. It is estimated that 2,000 m^3 of the spruce was applied unimpregnated. Of the remaining amount half was creosoted and half was wolmanised. In 1986 2,925 m^3/year of wolmanised spruce was used and 8,825 m^3 of wolmanised pinewood (75%) [Berbee, 1989].

In The Netherlands 120 tonnes of chromium was applied in impregnating salts in 1986 [Slooff et al., 1989]. According to Knippenberg and Wermeskerken [1986] 325 tonnes/year of Cu/Cr and Cu/Cr/As salts were used in 1980. The emissions from the phase of wood treatment (impregnation and fixing) are negligible. The storage of wood caused in 1986 an emission to water of 0,2 tonnes/year.
Leaching caused an emission of chromium to surface water of 36 kg/year. Most of the chromium remains in the wood and is not released until the waste phase [Slooff et al., 1989b]. The main emission sources of chromium are industry, fertilisers and traffic.

Table 2 Survey on use, emissions and concentrations in the environment of substances used as wood preservatives

Groups of substances	Substances	Used as wood preservative (tonnes/year)	Emissions to surface water (kg/year)	Concentrations in surface water (µg/l)
Chromium	ammonium-bichromate	325 Cu/Cr and Cu/Cr/As (1980)[c] 450 Cu/Cr/As (1993)[g] 671 Cu/Cr (1993)[g]	200 (wood storage)[e] 36 (leaching)[d]	67-0 (leaching 20d-120d)[d]
	potassium bichromate			
	sodium bichromate			
	chromium trioxide			
Boron	boric acid	8 boric acid comp.. (1980)[c]		
	borax			
	sodium octaborate	4 Cu/Cr/B (1980)[c]		
Arsenic	Arsenic pentoxide	40-45 As[f]	949 (leaching)[d]	185-20 (leaching 20d-240d)[d]
Copper		290 Cu (1993)[g]		
	Copper naphthanate	40 (1980)[c]	173 (leaching)[d]	245-0 (leaching 20d-240d)[d]
	copper(I)oxide			
	copper(II)carbonate-hydroxide			
	copper(II)oxide			
	copper sulphate			
Metalfree salt		60 (1993)[g]		

Groups of substances	Substances	Used as wood preservative (tonnes/year)	Emissions to surface water (kg/year)	Concentrations in surface water (µg/l)
Fluorides	copper silicofluoride	11 biF-salt (1980)[c] 6 (1993, immersion)[g]		
	potassium bifluoride			
	zinc silicofluoride			
	ammonium-bifluoride			
Organic compounds	propiconazole			0,004[a] 6,6[b]
	tebuconazole			0,002[a] 0,704[b]
	azaconazole			11,34[b]
Quats	didecyldimethyl-ammoniumchloride	34 (1993; quat wood for buildings, and gardening, immersion)[g] 113,5 (1993, quat, antistain)[g]		
Creosote oil		3350 (1993)[g]		
		30 F/B/Cr (1993, immersion)[g]		

a calculated concentration in surface water by saturation/immersion; [Tas et al., 1996]
b calculated concentration in surface water by impregnation, [Tas et al., 1996]
c information volume wood preservation, [Knippenberg en Wermeskerken, 1986]
d [Baltus en Berbee, 1989]
e integrated criteria document Chromium; [Slooff et al., 1989]
f integrated criteria document Arsenic; [Cleven et al., 1992]
g based on import data [Second Chamber, 1997]

In The Netherlands arsenic is mainly applied in wood preservation. In 1987 this took place in approx. 35 companies. The emissions during the preservation process are negligible. Also storage causes only little emission. The impregnated wood is mainly applied in the building industry, the ship-building industry, the packing industry and bank improvement. Approximately 40-50 tonnes of arsenic is applied annually in wood preservation. This, however, mainly remains in the product and is released only in the waste phase [Slooff et al., 1990a]. Only a limited amount of the impregnated wood comes into contact with surface water. According to Berbee [1989] 949 kg of As is annually emitted from impregnated wood to surface water.
In 1980 40 tonnes/year of copper naphthanate were used as wood preservative [Knippenberg and Wermeskerken, 1986]. According to Berbee [1989] 173 kg of Cu is annually emitted from impregnated wood to surface water.
Compared to the emission from other anthropogenic sources the copper and chromium emission from impregnated wood is not relevant. The arsenic emission as a result of wood preservation amounts to approx. 10% of the total arsenic emission [Berbee 1989].

In 1980 8 tonnes of boric acid compounds were used as wood preservatives and 4 tonnes of Cu/Cr/B salts [Knippenberg and Wermeskerken, 1986]. No data are

available on the emissions to water.
In the same year 11 tonnes of bifluoride salt were used as wood preservatives [Knippenberg and Wermeskerken, 1986]. No data are available on the emissions to water caused by wood preservation.

Zinc is applied as a wood preservative in zinc naphthanate. Zinc silicon fluoride is not mentioned [Cleven et al., 1992]. The total emission of zinc to surface water amounted to 1965 tonnes/year in 1989 and was mainly caused by corrosion of galvanised steel in building steel and crash-barriers [Cleven et al., 1992]. The emission of zinc caused by wood preservation is negligible in relation to the total emission.
No data are available on the applications and emissions of organic compounds and quats as wood preservatives.

Leaching (leaching amounts)
0.69 kg/m^3 of Cr, 0.59 kg/m^3 of Cu and 1.1 kg/m^3 of As are absorbed into the wood. From these amounts 2.3-2.7% of Cr; 2-2.9% of Cu and 5.3-14.8% of As, respectively, leaches out of pinewood and 0.3% of Cr; 9.6-11.4% of Cu and 2.7-9.5% of As, respectively, leaches out of spruce .
The flux of Cr, Cu and As after 50 days is 0.3 mg/m^2, 1.1 mg/m^2 and 4.2 mg/m^2, respectively, for spruce and 0.2 mg/m^2, 2.5 mgm^2 and 14.8 mg/m^2, respectively for pinewood [Berbee, 1989]. For the other sources no data on leaching are available. In Appendix 8 the amounts of Cu, Cr and As leached from pine and spruceare modelled in two figures.
In 1991 the admission of Wolman salts has been restricted to the least leaching type (type C).
Recent investigations into leaching of womanised wood during utilisation in hydraulic engineering were carried out by SHP in 1995. It is probably that the MPR-values for copper and - to a lesser extent - for arsenic are exceeded especially just after placing the wood in the water. However, this investigation only included Dutch wood and not imported wood. The environmental impact of imported wood is unknown [Second Chamber, 1997].

3.1.3 Analysis and detection methods

Arsenic
A widely used technique to determine the total concentration of arsenic in liquid samples is atomic absorption spectrometry (AAS). Both the AAS technique using the flame type and in the graphite furnace (NEN 6457)) and the hydride generation technique (NEN 6432) are in use. The detection limits are 20 µg/l, 1 µg/l and 0.2 µg/l, respectively. Voltametry determines the total arsenic content after reduction to As(III) with a detection limit of 0.2 µg/l. Using spectrophotometry arsenic can be determined in solutions with an absolute detection limit of 0.15 µg/l [Slooff et al. 1990 a]. Neutron activation analysis is one of the more sensitive methods, with detection limits of approx. 1 ng. The method, however, is susceptible to interference, particularly from sodium. Pulse polarography, anodic stripping voltametry, atomic emission spectroscopy (AES), X-ray fluorescence (XRF) and isotope dilution mass spectrometry are used as well for the determination of trace elements of arsenic [WHO, 1981].

For the determination of specific arsenic compounds the following analysis methods are available:

- selective hydride generation, followed by AAS-detection;
- hydride generation, followed by selective evaporation and AAS detection;
- hydride generation, followed by evaporation and separation by GC and detection by AAS, FID, or MS;
- separation of the arsenic compounds by ion exchange chromatography, followed by hydride generation and AAS detection;
- voltametric techniques [Slooff et al., 1990a].

The method using hydride generation and AAS is preferred. This method converts the arsenic components into their hydrides, which are subsequently decomposed in an argon hydrogen flame.
If interferences are absent, the electrothermic AAS method (detection limit 1 µg/l) can more easily be applied. The silver diethyl dithiocarbamate method, generating arsenic by sodium boron hydride in an acidic solution, can be applied in the determination of the total concentration of inorganic arsenic if interferences are absent and if the sample does not contain methyl arsenic compounds. The minimum detectable arsenic concentration amounts to 1 µg. The induction coupled plasma (ICP) method is useful for concentrations >50 µg/l [Eaton et al., 1995].

Boron compounds

Residues of borax can be determined by colorimetry, titration and AAS [Worthing, 1987]. Analyses in surface water can be carried out by ICP-AES (inductive coupled plasma - atomic emission spectrometry; NEN 6426) (detection limit 11 µg/l) [BKH, 1996]. According to Eaton [1995] the detection limit amounts to 5 µg/l.
To boron the curcumin method is applied in the range of 0.1 – 1 mg/l, whereas the carmin method is suited for the analysis of boron in the range of 1 - 10 mg/l. The range of these methods can be extended by dilution or concentration of the sample. Boron can also be determined with the ICP method (detection limit 0.2 µg B) [Eaton et al., 1995].

Chromium

For the analysis of toxic amounts of chromium an analysis method is necessary at the level of 1 µg/l. The most sensitive methods, such as NAA (Neutron activating analysis) and flameless AAS have detection limits of around the biological active concentrations. For AAS the detection limit is 2 µg/l.
This method measures all of the extracted chromium, although without oxidative pre-treatment only hexavalent chromium is extracted.
The other methods to measure the concentrations of chromium in water are:

- spectrophotometry (detection limit 3 µg/l); the disadvantage of this method is that after chelation only the hexavalent chromium in the solution is determined;
- NAA (detection limit 10 ng. This method determines the total content of chromium;
- gas chromatography (electron capture detection) (detection limit 0.03 pg);
- chemi-luminescence (detection limit 30 ng/l for trivalent chromium and 300 ng/l for hexavalent chromium);
- X-ray fluorescence;
- PIXE (particle induced X-ray emissions);
- DPP (differential pulse polarography) (detection limit 2 µg/l) [Slooff et al., 1989b; WHO, 1988].

According to BKH [1996] the detection limit of the electrothermic GF (graphite furnace)-AAS method (NEN 6444) amounts to 0.15 µg/l.
The colorimetric method is useful for the determination of hexavalent chromium in surface water meant for the production of drinking water. Ion chromatography is suitable for the determination of dissolved hexavalent chromium in drinking water, groundwater and effluents (detection limit 0.3 - 0.4 µg/l). The GF-AAS method is suitable for the determination of low concentrations of total chromium (< 50 µg/l) in water and wastewater. The flame AAS method or the ICP method are used for measurements up to the level of mg/l [Eaton et al., 1995].

Fluorides

Insoluble fluorides in water have to be decomposed using sodium hydroxide followed by steam distillation. Fluoride ions can be analysed using the fluoride ion selective electrode. The electrode potential is related to the F concentration according to the law of Nernst. With this electrode the total amount of free and bound fluoride dissolved in water can be determined. Addition of TISAB reagent ensures that the variations in ion concentration between the various samples become negligible, the pH is optimum, and that other metal ions are hidden.
This method is applicable to all water samples containing at least 20 µg/l F [Slooff et al., 1989].

The electrode method is suitable for fluoride concentrations ranging from 0.1 to > 10 mg/l. Addition of a buffer may prevent interference. This is important for the SPADNS method having an analysis range of 0 - 1.4 mg/l F. Absorption is determined by means of a filter photometer or a spectrophotometer [Eaton et al., 1995].

Copper

The total amount of copper is determined by means of electrolysis or iodometry. Residues can be determined by reaction with concentrated sulphuric acid and colorimetric determination of derivatives or by AAS [Worthing, 1987].
Copper naphthanate is analysed by an electrolytic estimation of copper or by iodometric titration [Worthing, 1987].
The usual analysis techniques for copper in surface water are spectrometry (ICP-AES, AAS) and Sequential Pulse Anodic Stripping Voltametry (SPASV). Also neutron activating analysis (NAA) may be used. De lowest detection limits for these techniques are in the range of 1-100 ng/g and 0.1 - 10 µg/l [Slooff et al., 1990b].

The AAS, ICP and the neocuproin methods (detection limit 3 µg of Cu up to 6 µg of Cu) are recommended because of their independence of interferences. The bathocuproin method may be used for drinking water (detection limit 20 µg/l) [Eaton et al., 1995].

Organic compounds

Residue analysis of propiconazole is carried out by means of GLC with FID [Worthing, 1987].

Quats

In Germany a standard method is used for quats to analyse the cationic surfactants in water [Stockhausen-Standard; STN 6.037/92; GWF Wasser/Abwasser 111, 1970, S.282].

After the formation of an ion pair from the cationic surfactant with disulphide blue flotation is applied and the product is extracted, followed by colorimetric determination. However, this method is not specific and does not discriminate between the different types of cationic surfactants. A separation technique is needed if a specific cationic surfactant has to be determined, for instance High Performance Liquid Chromatography (HPLC)
Many quaternary compounds are non-UV absorbing, which makes a direct photometric method unsuitable. For ion pair HPLC this can be avoided by using a light absorbing or fluorescent anion.
A different technique is the application of a conductivity measurement based on the ionogenic properties of the surfactant. With this technique detection limits of 0.2 µg/l can be reached [Nitschke et al., 1992].
Another analysis method uses a high performance liquid chromatograph with a conductive detector, which enables separation and quantification of the long alkyl chain of the quaternary ammonium compound up to the level of µg/l. This can also be applied to non-UV absorbing quaternary ammonium compounds with long alkyl chains [Wee et al., 1982].
Mass spectrometry can be used as well for the characterisation of non-volatile surfactants. Be means of field desorption (FD) and a specially designed tandem mass spectrometry the various surfactants can be analysed up to the level of 5 pg/l [Simms et al., 1988].

3.1.4 Concentrations in the environment

Copper, chromium and arsenic salts
Based on data regarding leaching, Berbee [1989] calculated which concentrations of chromium, arsenic and copper will end up in surface water (see Appendix 8). This calculation is based on leach experiments and a modelled approach in model ditches. The basis was a leachable wood surface per meter length of the ditch, a cross surface of the ditch of 7.5 m^2 and a hydraulic retention time of 20 days [Berbee, 1989].
Leaching resulted in a chromium concentration of 67 µg/l after 20 d and after 250 d no chromium was detected in surface water anymore. The arsenic concentration after 20 d of leaching amounted to 185 µg/l and after 250 d 20 µg/l of arsenic was still found in surface water.
The copper concentration after 20 d of leaching amounted to 245 µg/l and after 250 d no copper was found in surface water anymore (see Table 2).

The standards for copper are exceeded in 90% of the sampling sites, however, only 0.2% of the copper pollution of surface water is caused by preserved wood. The contribution to the pollution of surface water with chromium through use as a wood preservative amounts to 0.1%.

Boron compounds
In 1991 and 1992 the average boron content amounted to 0.17 mg/l in the river Rhine and to <0.2 mg/l in the river Meuse in the period 1989-1992. These values are below the IAWR-limit value (International Association of Waterworks in the Rhine Catchment area), the RIWA limit value and the Dutch quality objective "Surface water for the production of drinking water" of 1 mg/l (RIWA, 1993]. No data are available on the concentrations ending up in water as a result of the application of boron compounds as wood preservatives. Detergents are an important source for

boron in surface water.

Fluorides

No data are available on the fluoride concentrations in water caused by wood preservation. Industrial decomposition of phosphates is an important source for the emission of fluorides to surface water.
In 1985 the average concentration for drinking water pumping stations per province ranged between 0.08 mg/l and 0.23 mg/l [Slooff et al., 1989].
In 1990 and 1991 the fluoride concentration in the river Rhine amounted to approx. 0.2 mg/l and in 1989-1992 in the river Meuse this amounted to 0.4 mg/l near Keizersveer and 1.1-2.0 mg/l at Eijsden [RIWA, 1993].

Organic substances

Tas et al. [1996] calculated the concentrations in surface water during the process of impregnation, by means of USES. The estimated azaconazole concentration in water amounts to 0.01 mg/l for impregnation, a factor 10,000 lower for saturation/immersion. For propiconazole the concentration in water amounted to 7 µg/l for impregnation and lower by a factor of 2,000 for saturation/immersion. For impregnation with tebuconazole the concentration was very low. The concentrations of these substances in water caused by wood storage and leaching from preserved wood will probably be higher. However, they are not known.

Quats

No data on concentrations in water are available for these substances.

3.1.5 Behaviour in the environment

Copper, chromium and arsenic salts

The organic copper, chromium and arsenic salts are degraded in water, however, the heavy metal ions remain in surface water. All selected chromium salts are Cr^{6+}, but Cr^{6+} is in surface water rapidly reduced to Cr^{3+}.
Copper and chromium adsorb to suspended solids in water. A small part of the substances is present in water as free metal ion. This adsorption is i.a. dependent of pH, redox potential and the presence of suspended solids. Copper strongly accumulates, mainly in shellfish (BCF >1000). Chromium accumulates to a limited extent (BCF 20-300). Neither copper nor chromium accumulate through the food chain (biomagnification) [Slooff et al., 1989b and 1990b].

Arsenic

Due to its high water solubility arsenic pentoxide does not form a precipitate in surface water. Arsenic strongly adsorbs to iron hydroxide, aluminium hydroxide and aluminium groups of clay minerals. This adsorption strongly depends on pH, redox potential and the amount of suspended matter.

Maximum adsorption takes place at a pH between 5 and 7. A higher pH causes a high concentration of dissolved arsenic in water. Bioaccumulation of inorganic arsenic ranges from slight to moderate (BCF 150-700), whereas organic arsenic does accumulate [Slooff et al., 1990a]. In aquatic organisms of lower trophic levels higher bioconcentration levels are detected than in organisms of higher trophic levels (BCF for algae, invertebrate and fish are 700, 400 and 150, respectively). Biomagnification does not seem to occur [Slooff et al., 1990a].

Boron compounds

The persistence of borax in soil is less than 2 years, however, the protection by borax depends on rainfall and soil structure [Worthing, 1987]. The boron ion will persist in the environment after decomposition. No information is available on bioaccumulation of boron compounds.

Fluorides

In water with pH >5 dissolved fluor is mainly present as free fluoride ion. At higher fluoride concentrations somewhat more bioaccumulation occurs than at background concentrations of fluor. At concentrations up to 50 mg/l F bioconcentration factors of <10 have been calculated [Slooff et al., 1989a].

Organic substances

According to a calculation carried out by means of the Syracuse program [Boethling, 1993], propiconazole, azaconazole and tebuconazole are poorly degradable (see Table 4.1 in Appendix 4). This increases their residence time in water. Propiconazole is degraded in aquatic systems by hydroxylation of the propyl side of the chain and the dioxylane ring, followed by the formation of 1,2,4-triazole. The half life in aquatic systems amounts to 25 to 85 days at 25°C [Anonymous, 1991a]. Less than 20% of tebuconazole vaporises [Anonymous, 1991]. Propiconazole is will probably bioaccumulate since the calculated log Kow amounts to 4.13. Bioaccumulation of azaconazole is expected to be absent or low (log Kow 2.72). The measured log Kow of tebuconazole is 3.7, hence this will probably bioaccumulate [Boethling, 1993].

Quats

Quaternary ammonium compounds rapidly adsorb to suspended matter, anions and organic particles. A large part of these substances is bound to these particles [STOWA, 1995]. These substances are probably poorly degradable. Biodegradability increases with decreasing length of the chains.
Because of the size of their molecules (mol.weight >700), bioaccumulation does not take place, since the large molecules cannot pass the cell membranes.

3.1.6 Toxicity

Data on the aquatic toxicity and acute mammal toxicity are included in Appendix 3, Table 3.1. For an assessment of the toxicity data, use was made of the classification described in Appendix 7.

Exposure of humans to wood preservatives

The main risks for humans occur during treatment of the wood in the preserving process. In general only a very small amount of wood preservative remains present on the wood after drying, so consumers of preserved wood run little risk during the use of wood. However, at this low level the naphthanates still form a risk by inhalation of the active substance. Therefore the indoor application of these wood preservatives is only allowed to a limited extent [Jonge, 1991]. Indirect hazards by exposure through drinking water may occur when leaching of the wood preservatives cause higher concentrations in water than the drinking water criteria for this specific substance.

Arsenic

Acute oral LD50 values range from 10 to 300 mg/kg body weight (b.w.) of As for inorganic arsenic. For arsenic pentoxide the LD50-values range from 8 mg/kg to 55 mg/kg b.w. for rodents (see Table 3.1 in Appendix 3). In general trivalent arsenic is more toxic than pentavalent arsenic. The lethal dose for humans is 70-180 mg of arsenic trioxide (0.8-2.3 mg/kg b.w. As). Subacute effects are fever, anorexia and insommia. The effects on infants may be more serious. Accidental exposure of infants to pentavalent arsenic in powder milk for two to three weeks caused deaths, deteriorated hearing abilities, deviations of the electrocardiogram, liver enlargement and eye aberrations. The estimated intake in these cases was 1.3-3.6 mg of arsenic per day [Slooff et al., 1990a].

The acute toxicity of arsenic to crustaceans ranges from very high to moderate with an LC50 ranging from 0.8 to 12 mg/l. The acute toxicity to fish ranges from moderate to little (LC50 1-80 mg/l).
The chronic toxicity of arsenic to algae (NOEC 0.01-10) is moderate to very low; to fish (NOEC 0.09-1 mg/l) low to very low and to crustaceans (NOEC approx. 1 mg/l) very low (see Table 3.1 in Appendix 3).

Boron compounds

Boric acid and borates are toxic to all cells. After resorption the highest concentration is reached in kidneys, so the damage of these organs is strongest. Excretion by the kidneys often takes one week. The biological half life in blood is 12-24 hours. The lethal doses of boric acid and borates for an adult are estimated to be 5-20 g, for children 5-6 g and for infants 2-3 g. Poisoning can also take place through damaged skin [Anonymous, 1986].
The average lethal dose for humans is estimated to be 200 mg/kg b.w. [Anonymous, 1985a]. The acute oral LD50 for rodents ranges from 2,000 to 5,100 mg/kg for all boron compounds (see Table 3.1 in Appendix 3), which means that the acute toxicity of boron compounds to mammals is low.

Both the acute and chronic toxicity of boron compounds to aquatic organisms are low (see Table 3.1 in Appendix 3).

Chromium

Compounds of chromium are corrosive to skin and mucous membranes by precipitation and oxidation of proteins. After intake of 100 mg, toxic effects may occur. The lethal dose is 1-8 g, however, a recovery after 15 g has been described [Anonymous, 1985].
Hexavalent chromium is more toxic than trivalent chromium. Intake of animal feed, containing 2,000 and 330 mg/kg Cr^{3+} , did not cause toxic effects in cattle/sheep and chickens, respectively. Intake of animal feed, containing 30 mg/kg Cr^{6+} , did not cause any adverse effects in chickens. Trivalent chromium is an essential trace element for mammals, whereas hexavalent chromium is regarded to be a genotoxic carcinogen to mammals. The acute oral LD50 for rodents ranges from 50 to 350 mg/kg for all compounds of chromium, indicating an (acute) toxicity of chromium to mammals ranges from high to moderate. However, another study mentions an acute oral LD50 of sodium bichromate to rats of 14 to 21 mg/kg (see Table 3.1 in Appendix 3) [Slooff et al., 1989b].

No difference exists in the toxicity of trivalent chromium and hexavalent chromium to aquatic organisms in freshwater. The acute toxicity of chromium to crustaceans is

very high and to fish it ranges from moderate to low.
The acute toxicity of chromium to algae and bacteria is low. The chronic toxicity of chromium to aquatic organisms is low (see Table 3.1 in Appendix 3).

Fluorides

Fluorides inhibit the activity of a number of enzymes and interfere in the calcium metabolism. Fluorides have a strong corrosive effect on skin and mucous membranes. Severe corrosion of skin and mucous membranes occur at concentrations of 1-2%.
All fluorides are highly toxic to humans. Serious symptoms of toxic effects have been described after intake of 10-15 mg. Lethal toxic effects have occurred after intake of 5-10 g. Calcium silico fluoride is less toxic because of its lesser solubility. Solutions of 10% have corrosive effects in the oesophagus [Anonymous, 1985a, 1986].

Fluoride has a protective effect on teeth at concentrations in the drinking water of 0.5-2 mg/l F. At concentrations of 1.5-2 mg/l F teeth fluorosis starts to occur. High concentration of fluoride may also result in osteofluorosis, with development of an abnormal bone structure. Prolonged exposure to concentrations up to 5 mg/l F does not lead to osteofluorosis.
At high oral doses in animal experiments (22-100 mg/l F in drinking water) effects to the kidneys of the test animals are observed [Slooff et al., 1989a]. The acute oral LD50 value to rats amounts to 180 mg/kg for NaF. The LD50 value of zinc silico fluoride to rats amounts to 100 mg/kg (see Table 3.1 in Appendix 3), indicating a high toxicity of these substances to mammals.

The acute toxicity of fluoride to fish is moderate, and to bacteria, algae and crustaceans it is absent or very low. Fluoride is not chronically toxic to aquatic organisms (see Table 3.1 in Appendix 3).
At fluoride concentrations of 150 to 800 mg/l a synergistic reaction was found at rather low concentrations of both arsenic and chromium on the nitrification inhibition. Higher arsenic and chromium concentrates caused an antagonistic reaction with fluoride. No effect was observed on bacterial degradation of wastewater and bacterial survival at concentrations of 0.5-5 mg/l F to 360 mg/l F [Slooff et al., 1989].

Copper

Copper compounds are highly irritating to the skin and the mucous membranes. Internal intake may cause liver and kidney damage and changes in the haemogramme. 1 g of copper sulphate is toxic, whereas 8-15 g is lethal, however, recovery has been described after a dose of 150 g. Solutions of 10% have a corrosive effect in the oesophagus [Anonymous, 1986].
The various copper-chromium-arsenic salts have been classified as being (highly) toxic to harmful. Prolonged (occupational) exposure to these salts causes an increased risk of cancer [Anonymous, 1986].
The acute oral LD50 of copper naphthanate ranges from 450 to >6,000 mg/kg, of copper(I)oxide this is 470 mg/kg and of copper(II)oxide 700 mg/kg. For copper carbonate hydroxide the acute oral LD50 ranges from 159 to 900 mg/kg and for copper sulphate it ranges from 300 to 960 mg/kg (see Table 3.1 in Appendix 3), indicating a moderate toxicity of copper to mammals.

The copper oxides are poorly soluble, resulting in a low availability of these copper compounds in water. Copper sulphate is readily soluble in water. These salts are highly toxic to water organisms [Anonymous, 1986]. The acute toxicity of copper to crustaceans and fish ranges from very high to moderate. The chronic toxicity of copper to crustaceans and fish ranges from low to moderate and is high to algae (see Table 3.1 in Appendix 3).

Organic compounds

The acute oral LD50 for propiconazole is approx. 1,500 mg/kg and for azaconazole 310 mg/kg (see Table 3.1 in Appendix). These substances are moderately toxic to mammals.
Tebuconazole has an acute oral LD50 ranging from 625 mg/kg to 4,438 mg/kg. Owing to this, the toxicity of this substance to mammals and birds varies between moderate and low.

The acute toxicity of propiconazole and tebuconazole is high to algae, low to crustaceans and moderate to fish. The chronic toxicity of these substances to algae and crustaceans is low and to fish it is moderate. The acute toxicity of azaconazole to aquatic organisms is low (see Table 3.1 in appendix 3), whereas the chronic toxicity is very low (see Table 3.1 in Appendix 3).

Quats

Quats have a protein coagulating effect. The lethal dose for humans is estimated to be 3-7 ml. Solutions of more than 1% have an irritating effect on the skin and the mucous membranes. Solutions of 10% have a corrosive effect in the oesophagus [Anonymous, 1986],
Quats have a microbiocidal and surfactant effect. By absorption to the cell membrane of micro organisms they make the cell membrane permeable, to such an extent that certain cell elements disappear from the cell [Anonymous, 1985a]. The acute oral LD50 of didecyl-dimethyl ammonium chloride ranges from 84 to 268 mg/kg. Consequently, this substance is highly toxic to mammals. For quats (in general) the acute oral LD50 value amounts to 500 mg/kg (see Table 3.1, Appendix 3).

3.1.7 Environmental evaluation

Arsenic

The limit value for arsenic in water amounts to 10 µg/l for total arsenic and the drinking water standard value for arsenic amounts to 20 µg/l (see Table 3.4 in Appendix 3) [VROM, 1994]. After 20 days the calculated arsenic concentration as a result of leaching from impregnated wood amounts to 185 µg/l and after 250 days this amounts to 20 µg/l [Berbee, 1989]. Leaching of arsenic from impregnated wood causes a prolonged exceeding of the limit value for water, forming a hazard to the ecosystem. It also causes a prolonged exceeding of the drinking water standard value.
According to a more recent research by SHR (1995) the Maximum Tolerable Risk level (MTR) for arsenic is only exceeded for a short period of time (immediately after placing the wood) [Second Chamber, 1997].
However, wood preservation is one of the main sources of emission of arsenic to water (10%). In conclusion it can be stated that the use of arsenic in wood preservation may lead to risks for the production of drinking water.

Boron compounds

No data are available on emissions of boron compounds to water, nor on emissions by leaching from impregnated wood. The average boron concentration amounted to approx. 0.2 mg/l in the river Meuse in the period 1989-1992.
This value is below the Dutch quality objective "Surface water for the production of drinking water" of 1 mg/l [RIWA, 1993a and b]. The river Meuse, however, is one of the main rivers, whereas the main risks of wood preservation are expected in the smaller regional waters where the majority of preserved wood is applied and the residence time of the substances in the water is longer. The concentrations of boron in water as a result of leaching from impregnated wood are not available. A risk assessment for boron as a wood preservative is cannot be made because of the lack of data. At a local level the boron concentrations might be high.

Chromium

The limit value for chromium amounts to 20 µg/l for total chromium and the drinking water standard for chromium amounts to 50 µg/l (see Table 3.4 in Appendix 3) [VROM, 1994]. The estimated concentration after 20 days, caused by leaching from impregnated wood amounts to 67 µg/l Cr. It is not likely that chromium will be found in water after 120 days of leaching [Berbee, 1989]. During the first 20 days after placing impregnated wood the limit value and the drinking water standard are exceeded. In this period this will cause a hazard to the ecosystem and might be hazardous to man through the consumption of drinking water. The chromium emission by wood preservation, however, is low compared to other emission sources.

Fluorides

The limit value for fluor (total) amounts to 1,500 µg/l (see Table 3.4 in Appendix 3). In 1990 and 1991 the fluoride concentrations in the river Rhine amounted to approx. 0.2 mg/l and in 1989-1992 in the river Meuse this was 0.4 mg/l near Keizersveer and 1.1-2.0 mg/l near Eijsden. In the river Rhine these values are well below the IAWR-limit value (Rhine), the RIWA-limit value (Meuse) and the Dutch quality objective "Surface water for the production of drinking water" of 1 mg/l. However, near Eijsden these values are exceeded [RIWA, 1993a and b].
The river Meuse, however, is a governmental water, whereas the main risks of wood preservation are expected in regional waters.
No concentrations of fluorides in water, caused by leaching from preserved wood are available or calculated. The main emission sources of fluoride are various industries and the decomposition of phosphate ore. The amount of fluoride taken in with drinking water ranges from 0.03 to 0.68 mg per day at a water consumption of 1.65 l per day (excl. tea) [Slooff et al., 1989]. This causes no hazard for the public health. Moreover, fluor is also added to tooth paste.

Copper

The limit value for copper (total) amounts to 3 µg/l and the drinking water standard for copper amounts to 50 µg/l (see Table 3.4 in Appendix 3) [VROM, 1994]. The calculated copper concentration after 20 days of leaching from impregnated wood amounts to 245 µg/l and after 250 days no copper is found [Berbee, 1989]. A prolonged exceeding of the limit value is expected and during 30-40 days the drinking water standard will be exceeded. In this period this will cause a hazard to the ecosystem and it may cause hazard to man. According to a more recent investigation by SHR (1995) the Maximum Tolerable Risk level (MTR) for copper is only exceeded for a short time (right after placing the wood) [Second Chamber, 1997].

In conclusion it can be stated that the use of copper as a wood preservative may cause risks to the production of drinking water.

Organic compounds

In Tas et al. [1996] a environmental risk assessment is described of the wood treatment phase with regard to organic substances (impregnation, immersion, saturation). It is assumed that after impregnation and immersion/saturation 90-99% of the remaining wood preservatives are first discharged into a sewage treatment plant (STP). Subsequently a certain amount will end up in surface water, depending on the effect of the water purification process.

The risk assessment of leaching of these substances to surface water has not been carried out, since data are not available.

The risk during wood treatment, however, has been assessed [Tas et al., 1996]. The risk is expressed as the ratio between the Predicted Environmental Concentration (PEC) and the lowest concentration at which no effect occurs (No Effect Concentration (NEC)). A risk quotient of 1 means a hazard to the ecosystem. The risk quotients (PEC/NEC) for azaconazole and propiconazole, when saturation/immersion is applied, are negligible. When impregnation is applied, the risk quotients for tebuconazole and propiconazole are just below 1 and for azaconazole this is amply below 1 This indicates that no hazard to the ecosystem exist for the abovementioned substances when applied by immersion/saturation [Tas et al., 1996]. The Total Daily Intake (TDI) for propiconazole amounts to 0.04 mg/kg b.w. [Anonymous, 1991a]. Since the calculated concentration for propiconazole in water is very low (0.007 mg/l and 4 ng/l) and even decreases after dilution in surface water and the production of drinking water, the application of this substance by immersion/saturation will not cause any risk to man.

The emission to water by wood storage and leaching is probably higher. In these case there may be a risk to the ecosystem. However, in only 7% of the total use of wood preservatives organic substances and quats are used.

Quats

Expectations are that quats will only be applied as wood preservatives to a very small extent. In surface water these substances will readily bind to organic suspended matter and humic acids. Probably these substances will cause no risk to both aquatic organisms and man.

3.1.8 Behaviour during a simple water purification process

Arsenic, copper and chromium^{3+} are drastically eliminated by the combination of flocculation/sand filtration. Chromium^{6+} is poorly eliminated in the purification process, but it will probably hardly occur in surface water. Boron will probably be eliminated very poorly in a purification process.

Because of their log Kow >3.5, the organic substances propiconazole and tebuconazole are probably readily eliminated by adsorption to the organic substance of biomass in the sand filter.

For acazonazole the log Kow amounts to 2.3 and thus further investigation is needed.

The fluorides are likely to form a chemical compound into complex salts with calcium and phosphate, which are poorly water-soluble. Removal by means of sand filtration is likely.

The quaternary nitrogen compounds are drastically eliminated by means of adsorption during both flocculation and sand filtration.

3.1.9 Remediation measures

For wood preservation a considerable amount of policy has been developed and implemented. Within this scope also some alternative methods have already been investigated or are still under investigation. In the section Policy (3.1.11) these alternatives are described.

3.1.10 Conclusions

Using arsenic as a wood preservative may cause a risk for a prolonged period of time both to the aquatic ecosystem and for man (through the consumption of drinking water). Since this substance is readily eliminated by means of a water purification process, there is no hazard to public health.

For the boric salts no risk assessment can be made since data are not available.

Copper and chromium may cause a risk to the aquatic ecosystem for a short period of time. Copper and chromium^{3+} are readily eliminated by means of a purification process. Chromium^{6+} is poorly eliminated by means of a water purification process, however in surface water it is rapidly reduced to Cr^{3+}. Hence, no hazard to public health is expected through the consumption of drinking water.

Though no assessments of fluoride concentrations, caused by leaching from impregnated wood, are available, the application of this substance as a wood preservative probably does not cause any risk to the public health through the consumption of drinking water. These substances will probably be eliminated during a water purification process. Moreover, the substance is also added to tooth paste, so the contribution from wood preservation is of no relevance.

The treatment of wood with organic compounds does not cause any risk to the aquatic environment and the public health. The risk caused by leaching cannot be assessed. Concentrations in the environment are not available. Of one of the three model substances, azaconazole, it is also not known whether it can be eliminated in a simple water purification process. The quats are probably no risk to the aquatic environment and the public health.

3.1.11 Policy

Wood preservatives belong to the main groups of biocides, i.a. since 43% of the total volume of biocides is used in wood preservation. In the preceding years a policy has already been developed and implemented for sectors of wood preservation, mainly concerning emission reductions at production locations. Policy for wood preservatives can i.a. be found in e.g. in the National Environmental

Policy Plan (NEPP), MJP-H, KWS 2000, Policy Statement Environmental Objectives for the Building Trade (BMB '95), Policy Document on Wastewater Policy, Policy on PAH and Heavy Metals, Pesticides Act and EC-Guidelines.
Within the scope of the project KWS-2000 and the Policy Perspective PAH, the environmental policy was mainly directed to creosote oil and creosoted wood, causing a considerable reduction of the emission of PAH to air. As to CCA-salts, the industry voluntarily discontinued the use of CCA-type B, so that at the moment only CCA-type C (lowest leaching) is applied. Recently the Commission for the Authorization of Pesticides (CAP) has decided that creosote oil is only to be admitted for applications without contact with water or groundwater. The CAP has started a procedure in order to reach this restriction. Besides to creosote oil, political attention was paid to mainly copper, chromium and arsenic salts. For copper and chromium emission targets have been formulated in the National Environmental Policy Plan 2 within the scope of the priority substances policy and heavy metals policy. At the end of 1997 the Policy plan for heavy metals was presented which included a survey of measures taken and measures still to be taken. For arsenic there is no national policy anymore. At a local level the standards may still be exceeded.

Up to now the policy has been directed to storage, production and use of preserved wood. The number of companies preserving wood by saturation has decreased by 90% and the reduction of leaching during storage after 14 days has decreased by 81-99% (Cu 81%; Cr 95%, As 90%, PAH 99%). Moreover, the environmental load of the wastewater by preservation companies has decreased for salts by approx. 90% and for PAH by >99%.
The use of preservatives has decreased in the period 1985-1995 by approx. 60% (in volume) and the use has shifted from creosote oil to salt, particularly arsenic-free salts. Moreover, some alternative wood preservation methods have been developed or are still under development: PLATO-method (thermic preservation without chemicals), acetylation of wood en drying of wood by means of "high temperature drying". The latter as an alternative for the application of quats. Furthermore, various projects are going on in the waste phase and mid 1996 the dumping of wastewood was prohibited (except for building and demolition waste) [Second Chamber, 1997].

Ongoing policy is mainly still needed in the use phase and in the waste phase.
The objectives in the use phase, in the short run, are the improvement of the chemical wood preservation, while in the long run alternatives for the various application fields with a reduced environmental pollution are being investigated.

The procedure in the short run aims at:

- the European position regarding creosoted wood;
- reducing the release of substances that are harmful to the environment;
- certifying wood which is less harmful to the environment;
- stimulating the use of certified wood;
- investigating whether certified wood can meet the environmental quality demands.

In the waste phase research has to be directed to a solution, per branch of industry, for wood which is already in use. Furthermore, for storage and processing the application of Dutch guidelines on an European level will be an objective.
For older preservatives the admission will be re-judged. In the maintaining phase

the progress of this biocide policy will be monitored [Second Chamber, 1997].

3.2 Cooling water

3.2.1 Introduction

Cooling water systems serve to discharge the superfluous heat that is generated by industrial processes. In the cooling water system heat exchange takes place from the process stream to be cooled to the cooling water. The heated cooling water is discharged or re-used. In the cooling water systems problems may arise through growth of micro and macro organisms, because of the good conditions for biological growth and development of algae, fungi, yeast and bacteria. Growth of these organisms causes slime layers and biofilms. This may reduce the effectivity of the heat transfer and increase the costs of energy for pumping cooling water through the system. In order to reduce/control this growth, biocides for cooling water are used.
There are two types of cooling water systems: open, flow-through systems and recirculation systems. The greater part (99%) of the cooling water used in The Netherlands is applied in flow-through systems. To prevent growth in these flow-through systems, biocides are used. The water is discharged immediately after use. These systems are particularly used along the main rivers.

In recirculation systems water is cooled down after use in cooling towers and re-used. Part of the water in the recirculation systems is discharged for technical reasons. To prevent growth in these systems both oxidative and non-oxidative biocides are used or a combination of both [Baltus and Berbee, 1996]. The biocides for cooling water end up in surface water through the effluent of a water purification plant or by means of a direct discharge.

In flow-through systems the hydraulic retention time is short. In these cases a oxidative fast-acting biocide will often be selected. In recirculation systems the hydraulic retention time is longer, which also enables the application of more specific non-oxidative biocides [Baltus and Berbee, 1996]. Recirculation systems are mainly used by industry and at places where there is shortage of surface water or where the increase in surface water temperature is too high if flow-through systems are used [Second Chamber, 1997].

The emission of biocides for cooling water mainly occurs at power plants (75%) and larger industries (chemical plants, refineries, primary metals industry, etc.) In most cases the main discharges take place to surface water which is under the control of the Directorate General for Public Works and Water Management [Tas et al., 1996; Second Chamber, 1997].
In Table 2.2 in Appendix 2 the selected biocides for cooling water are given. These biocides have been taken into consideration further.

3.2.2 Sources and use

For the greater part biocides for cooling water consist of chlorine and chlorine forming compounds (93%), whereas the organic compounds make up for only 7% of the biocides for cooling water. (figures 1992) [Tas et al., 1996].
In cooling systems mainly oxidative biocides are applied. In 90% of the cooling

systems hypochlorite is applied. The estimated total use of active chlorine (an oxidative biocide) in cooling systems in 1994 is 1,800 tonnes/year [Baltus and Berbee, 1996]. The greater part of this was used in industry (75%) and the remainder in power plants (25%) [Second Chamber, 1997].

Non-oxidative biocides

Isothiazolines are the most applied biocides of the non-oxidative biocides. In recirculation systems 330 up to 1,500 kg/year of isothiazolines are used in 28% of the companies.

β-bromo-β-nitro styrene is used in 3% of the companies using recirculation systems in amounts of 540 up to 1,950 kg/year.
370-800 kg/year of 2,2-dibromo-3-nitrilopropionamide is used in recirculation systems in 3% of the companies [Baltus and Berbee, 1996]. The branch organisation Aqua Nederland the total use of non-oxidative biocides is estimated to be approx. 360 tonnes/year, having active substance contents ranging from 1-50% [Second Chamber, 1997].

Oxidative biocides

Sodium bromide is applied in 7% of the companies in amounts varying from 22.5 to 31.4 tonnes/year. Sodium hypochlorite is used most: 478 tonnes/year in 41% of the companies having recirculation systems. Of these companies 9% used 1-bromo-3-chloro-5,5-dimethyldantoin with a total amount of 270 to 1,000 kg/year

Table 3 Survey of factual information on the use of biocides for cooling water [Balthus and Berbee, 1996]

Guidance substances	Substances	Application in % at 56 companies having recircul. cooling syst.	Applic. in active substance (kg/yr) based on inquiry consumers	Appl. in active substance (kg/yr) based on suppliers
Non-oxidative	**Isothiazolines**			
	5-chloro-2-methyl-4-isothiazoline-3-on	28% isothiazolines	330 isothiazolines	1.500
	Quats			
	didecyldimethylammoniumchloride	-	-	-
	alkyldimethylbenzyl ammoniumchloride	-	-	-
	alkyldimethylethylbenzyl ammoniumchloride	-	-	-
	poly[oxyethylene(dimethyl imino)ethylene-(dimethyl imino)ethylene dichloride]	-	-	-
	Bromine compounds			
	β-bromo-β nitrostyrene	3%	540	1.950
	2-bromo-2-nitropropane-1,3-diol	-	-	-
	2,2,-dibromo-3-nitrilopropionamide	3%	370	800
Oxidative	**Bromine compounds**			
	sodium bromide	7%	31400 (active Br)	22500 (active Br)
	Chlorine compounds			
	sodium hypochlorite	41%	478.000 (1800000)[a]	no data
	chlorine dioxide	-	-	-
	sodium chlorite	-	-	-
	Remaining organic compounds			
	1-bromo-3-chloro-5,5-dimethyldantoin	9%	270	1.000
	5-oxo-3,4-dichloro-1,2-dithiol	-	-	-
	dazomet	-	-	-

[a] The total application of active chlorine in cooling systems in The Netherlands is estimated to be 1800 tonnes/yr

3.2.3 Emissions

Baltus and Berbee [1996] estimated the emission of biocides from cooling water from recirculation systems, based on a simple model description with nine assumptions. The loss of non-oxidative biocides is mainly determined by discharging water from the system. Other losses such as evaporation, biological degradation, adsorption and activity of biocides are negligible. However, many non-oxidative biocides do hydrolyse, depending on the pH, which results in a rather low emission. Isothiazolines and bromonitro propanediol, however, may be emitted in rather large quantities because of their slow hydrolysis.

Depending on the temperature 80 to 99.8% of the applied amount of these substances is discharged, [Baltus and Berbee, 1996]. The emission of β-bromo-β-nitrostyrene amounts to only 8% of the dosage. This is i.a. caused by its fast hydrolysis [Balthus and Berbee, 1996]. It should be noted that the main emissions of bromide to water are caused by horticulture (methyl bromide), the printing industry and the chemical industry [CCRX, 1987].

The wastewater is discharged either to a wastewater purification plant or directly to surface water. The companies using non-oxidative biocides discharge 65% of the cooling water effluents directly to surface water (for isothiazolines this is even 75%). The companies using oxidative biocides discharge 63% of the cooling water effluents directly to surface water [Baltus and Berbee, 1996].

3.2.4 Analysis and detection methods

Non-oxidative biocides

Bromine compounds
The analysis of bromide in water can be carried out by means of gas chromatography or photometric methods. Bromide reacts in an acid environment with ethene oxide to 2-bromo ethanol, which is analysed by gas chromatography using an ECD (Electron Capture Detection). The detection limit for this method is 10 µg/l and the recovery is 95%. The bromide content of surface water can also be determined by an automated photometric analysis method (reagent fuchsin) (detection limit 800 µg/l).
The EOX can be determined as well. This is a group variable indicating the amount of halogenated organic compounds (i.a. pesticides) in the water. The water sample is extracted with acetone or petroleum ether. The extract is injected into an oven and the halogenated hydrogen is determined micro colometrically. The detection limit amounts to 0.2µg/l [CCRX, 1987]. The colorimetric method is suitable for the determination of bromide in most of the drinking waters.
Bromide can also be determined by means of ion chromatography. The detection limit is 0.1 mg/l Br [Eaton et al., 1995].

Isothiazolines
No methods have been found for the analysis of isothiazolines.

Quats

The analysis of quats has been described in section 3.1.3.

Oxidative biocides

Bromine compounds
For bromine compounds see the preceding section.

Chlorine compounds
The chloride content of a solution is determined by the addition of an o-toluidine solution followed by measuring of the resulting yellow colour by means of a spectrophotometer. Although this is the most sensitive analysis method, it is not often used because o-toluidine is suspected to be carcinogenic. In another method a methyl orange indicator colour is used to absorb the chloride. Subsequently the colour is measured by means of a spectrophotometer. The detection limit is 5-10 mg free chlorine/10 ml of solution. The instrumental methods comprise gas chromatography, colorimetry, amperometry and mass spectrometry [WHO, 1982]

By means of the iodometric method an exact determination can be obtained of the total concentration of a solution with respect to the possibility to liberate iodine from

iodide (detection limit 20 µg/l ClO_2). However, it is not easy to discriminate between ClO_2, chlorine, chlorite and hypochlorite. The amperometric method is suitable when a distinction is needed between the various chlorine components.
The N,N-diethyl-p-phenylene diamine (DPD) method has the advantage of a relatively easy colorimetric test and the possibility to distinguish between the various forms of chlorine [Eaton et al., 1995].

Hydantoin
No data were found on the Analysis and detection methods for this substance.

Organic substances
No information was found on 2-oxo-3,4-dichloro-1,2-dithiol.
A product analysis of dazomet is performed by an acid hydrolysis, absorption of the produced carbon disulphide and iodometric titration [Worthing, 1987].

3.2.5 Concentrations in the environment

Non-oxidative and oxidative biocides
According to Baltus and Berbee [1996] little is known about the concentrations of biocides for cooling water in surface water. Occasionally concentrations of 0.01 µg/l of isothiazolines were found.

In the Decree on Drinking Water [1983] no standard has been included for bromide. In general the bromide content of the drinking water is low. According to an investigation by RIVM the bromide content in 1977 ranged between 10 and 580 µg/l (average 90 µg/l). No major changes were found in these contents since. The quality of drinking water from littoral groundwater is extensively described by the KIWA.
This report shows that approximately 10% of the drinking water is prepared from littoral groundwater, pumped up along the rivers Rhine, Lek and IJssel, having a bromide content ranging from 10 to 670 µg/l. The bromide from littoral groundwater originates for the greater part from dispersed sea water and mixed with brackish of salt ground water, which is proved by the bromine/chlorine ratio. The bromide in water of the river Rhine originates for the greater part from salt waste of the Elzas [CCRX, 1987]. Only a small part of the bromide concentrations in water originates from biocides for cooling water.

3.2.6 Behaviour in the environment

Biocides for cooling water are readily soluble in water, indicating that, in general, these substances will not accumulate in organisms [Baltus and Berbee, 1996].

Non-oxidative biocides
Non-oxidative biocides can disappear by pH-dependent hydrolysis and to a lesser extent by evaporation, photolysis and biodegradation.

Isothiazolines
Biodegradation is the main degradation route for isothiazolines ending up in the environment. Micro cosmos experiments showed that the biodegradation half life for isothiazolines under aerobic and anaerobic conditions is less than 1 day. The

biodegradation velocity of 5-chloro-2-methyl-4-isothiazoline-3-on (t½ = 0.93 d) is lower than that of 2-methyl-4-isothiazoline-3-on (t½ = 0.48 d).
Furthermore, the biodegradation assessment by means of the Syracuse program [Boething, 1993] indicates a reasonably fast degradation of both substances (see Table 4.2 in Appendix 4).
Another degradation route for isothiazolines is hydrolysis, which is pH- and temperature dependent. The hydrolysis half life in The Netherlands will be longer than 100 days. Also degradation of isothiazolines takes place under the influence of sunlight. The photolysis half life is 5 days for 5-chloro-2-methyl-4-isothiazoline-3-on and 11 days for 2-methyl-4-isothiazoline-3-on.
According to QSAR estimations by Baltus and Berbee [1996] the degradation products of isothiazolines: N-methyl amino malonic acid, malonic acid, acetic acid and formic acid are twice to four times less toxic than the substances themselves.

Isothiazolines are very mobile in the environment, unlike their degradation products. Adsorption of isothiazolines to sediment and suspended matter is poor. However, the substances are readily absorbed by plants, followed by a fast metabolization to CO_2. Isothiazolines are highly hydrophilic and non- lipophilic which makes bioaccumulation unlikely. The metabolites, however, can accumulate in organisms [Baltus and Berbee, 1996].

Bromine compounds

Bromo nitro propanediol (BNPD)
No experimental data are available on the biodegradation velocity of bromo nitro propanediol (BNPD). According to the Syracuse program [Boethling, 1993] bromo nitro propanediol is probably not readily degradable (see Table 4.2 in Appendix 4). The hydrolysis half life of BNPD at 5°C and pH=6 is longer than 6 years. However, BNDP is subject to photolysis.
At 25°C and pH = 4, 5 mg/l of BNDP is degraded within 7 days [Baltus and Berbee, 1996].

Dibromo nitrilopropionamide (DBNPA)
The two degradation routes for DBNPA are:

- hydrolysis to dibromo acetonitrile, subsequently this degrades into dibromo acetamide. The hydrolysis of DBNPA takes approx. 2 hours at pH = 8 and 24°C. The degradation product of this process exceeds the toxicity of the substance itself by a factor of three. Also, the half life of the degradation product is longer;
- the degradation to monobromo nitrilopropionamide. This may take place in the presence of organic material. This degradation is more rapid than hydrolysis and the degradation product is twice less toxic than the substance itself [Baltus and Berbee, 1996].

According to the Syracuse program [Boethling, 1993] the degradation of dibromo nitrilopropionamide is probably poor (see Table 4.2 in Appendix 4). The degradation product mono bromonitrilopropionamide is probably self-degradable.

β-bromo-β-nitrostyrene
Little is known about the behaviour of these substances in the environment. The hydrolysis half life is 1.5 hr at pH=8.5 and 4.8 hr at pH=7 and a temperature of 25°C. The substance is degraded into benzaldehyde and bromo nitromethane. Subsequently, benzaldehyde is oxidised to benzoic acid [Baltus and Berbee, 1996].

According to the Syracuse program [Boethling, 1993] the biological degradation of β-bromo-β-nitrostyrene is slow (weeks to months; see Table 4.2 in Appendix 4).

Quats
Only some of the more than 200 quats are admitted in The Netherlands as biocides for cooling water. Quats can adsorb rapidly to sediment and to suspended dissolved organic material because of their polar quaternary nitrogen group and apolar alkyl chain. Biodegradation is reciprocally proportional to the length of the alkyl group. Increase of the number of long alkyl groups will cause a decrease of the biodegradation. Also UV limits the biodegradation of quats.
The quats concentration is likely to decrease rapidly after discharging to surface water because of a combination of biodegradation and adsorption [Baltus and Berbee, 1996].
The size of the molecules (mol.wt >700) prevents bioaccumulation of these substances since these large molecules cannot pass the cell membranes.

Oxidative biocides
In wastewater both chloric ions and chlorated reaction products will occur. Free chlorine will react with organic and inorganic substances. Reaction with humic acid and fulvenic acid may result in the formation of trihalomethanes. Reaction with phenols may result in the formation of chlorophenols. Furthermore, chlorinated ketones and haloacetonitrilic compounds can be formed. Reaction of amines with chlorine may lead to chloramines. All of these reaction products have a different half life. The available free bromine can react identically. The reaction products formed in this process can be: bromoform, tribromophenol, bromamines [Baltus and Berbee, 1996].
Hypochlorite, sodium bromide and bromo chlorodimethyl hydantoin have a hydrolysis half life of some minutes and dissociate rapidly in water, releasing the active biocides HOCl and HOBr. The dissociation products HOCl, HOBr, bromamines and chloramines are more stable than the starting substances themselves.

For oxidative biocides evaporation may play a role: HOCl (hypochlorite) decreases by 10-15% every time the cooling tower is passed [Baltus and Berbee, 1996].
No information is available on dazomet and 5-oxo-3,4-dichloro-1,2-dithiol.

3.2.7 Toxicity

Data on the toxicity of the substances are included in Appendix 3, table 3.2. For a toxicity assessment use was made of the classification as described in Appendix 7.

Non-oxidative biocides
The mechanism of non-oxidative biocides is selective, which means the effect on one organism differs from the effect on another. Two mechanisms can be distinguished. Firstly the substances can attack the cell membranes of organisms, which disturbs the transport of substances from and to the cell and cell components may start leaking.

Secondly, de substances may damage the biochemical mechanism which regulates the energy production and energy consumption of organisms. The mechanism of non-oxidative biocides is more complex than that of oxidative biocides, resulting in

an often longer reaction time of non-oxidative biocides.
Non-oxidative biocides are often applied in formulations with several active substances. This enables the use of these biocides against a broader range of (micro)organisms. The disadvantage is the specific activity of these substances, by which the target organisms may become resistant [Baltus and Berbee, 1996].

Isothiazolines
Isothiazolines are often applied in mixture of related structures. The activity is based on a fast interaction of the substances with the cell proteins, inhibiting the ATP synthesis. The substances are effective at low concentrations and have a wide-range spectrum effect. They are effective against aerobic bacteria, fungi, yeasts and algae. The activity of these substances is inhibited by chlorine, amino-N, hardness, chlorides and dissolved particles in the cooling water [Baltus and Berbee, 1996].

Isothiazolines are highly toxic to aquatic organisms with LC50 values <1 mg/l (see Table 3.2 in Appendix 3). No data were found on the toxicity of isothiazolines to mammals.

Bromine compounds
β-Bromo-β-nitrostyrene: this biocide inhibits the transport and production of energy within the cell, which inhibits the glucose metabolism.
The substance is applied against bacteria, fungi, yeasts and algae. It is a fast-acting biocide and hydrolysis is fast at pH = >8 [Baltus and Berbee, 1996].

β-Bromo-β-nitrostyrene is moderately to highly toxic to aquatic organisms (see Table 3.2 in Appendix 3).

Bromonitropropanediol (bronopol): this substance catalyses the formation of disulphide bonds between sulfhydryl compounds (sulfide bridge), in this way blocking the enzyme activity. Since many enzymes contain sulfhydryl groups, this biocide can be used against a wide range of micro organisms [Baltus and Berbee, 1996]. Bronopol is widely used in cosmetics as well. The advantage of the substance is its good solubility in water. The disadvantage being its relatively rapid decomposition in a neutral or alkaline environment, causing toxic compounds (instability) [Doorne, 1985]. The acute oral LD50 for mice, rats and dogs ranges between 180 and 400 mg/kg (see Table 3.2 in Appendix 3), which makes bronopol moderately to highly toxic to mammals.
The acute toxicity of bronopol to algae is high, to crustaceans this is moderate and the acute toxicity to fish is low. Chronically bronopol is little to non-toxic to aquatic organisms.

Dibromonitrilopropionamide: this is a broad range active biocide which is effective at low concentrations, particularly against bacteria. At high concentrations it is active against algae and fungi as well. Hydrolysis is fast at pH = >8 [Baltus and Berbee, 1996].
The acute oral LD 50 for rats is 308 mg/kg (see Table 3.2 in appendix 3), which makes this substance moderately toxic to mammals.

Dibromonitrilopropionamide is highly toxic to algae and crustaceans and moderately toxic to fish. Chronically dibromonitrilopropionamide is non-toxic to aquatic organisms (see Table 3.2 in Appendix).

Quats
The cationic load of these substances forms an electrostatic bond with the negative load of the cell membrane of the micro organism. This changes the permeability of the cell membrane and denaturation of proteins occurs, causing the cell to die. These substances are effective against algae and bacteria at neutral and alkaline pH. The activity of most quats is restricted by high chloride contents, oil and other organic pollutants in water. Polymer quats are broad range active biocides which are effective against micro organisms. The reaction time is longer than that of alkyl quats and their effect is inhibited by (organic) particles in water [Baltus and Berbee, 1996]. Quats are disinfectants in formulations of 2-100% [Anonymous, 1986]. Alkyldimethylethylbenzyl ammonium chloride is highly to moderately toxic to rodents with an acute LD50 ranging from 84 to 300. Poly[oxyethylene(dimethylamino) ethylene-(dimethylimino) ethylene dichloride] is moderately toxic to rats with an acute oral LD 50 of 1,850 mg/kg (see Table 3.2 in Appendix 3).

Quats are highly toxic to algae and crustaceans and highly to moderately toxic to fish. The chronic toxicity of quats to fish is very low (see Table 3.2 in Appendix 3).

Oxidative biocides

The mechanism of oxidative biocides is non-specific. The substances oxidise chemical components on the cell membranes, penetrate into the cell and oxidise cell components. These substances have a rapid effect on a broad range of micro organisms [Baltus and Berbee, 1996].
Most of the used oxidative biocides are based on active chlorine.

Bromine compounds
Sodium bromide is often applied in combination with hypochlorite. This combination results in a quantitative conversion of HOCl into HOBr, turning HOBr into the effective biocide. HOBr is effective on a broad pH range against bacteria, fungi, yeasts and algae. When converted into bromamines, the biocidal effect is still present. Moreover, bromamines are less persistent than chloramines [Baltus and Berbee, 1996].
Bromide and chloride are absorbed to an considerably small extent by most of the tissue cells. In active transport the bromide passes the cell membranes more rapidly than chloride. The oral LD50 for bromide in rodents ranges from 3,500 to 7,000 mg/kg b.w. [CCRX bromine] (see Table 3.2 in Appendix 3), indicating a low toxicity of sodium bromide to mammals.

The toxicity of sodium bromide to aquatic organisms varies strongly and ranges from high to considerably low (see Table 3.2 in Appendix 3).

Chlorine compounds
Sodium hypochlorite is applied most. Addition of sodium hypochlorite or gaseous chlorine to water causes the formation of a mixture (equilibrium) of hypochlorous acid (HOCl) and hypochlorite ions (OCl^-). The biocidal effectiveness depends on the concentration of HOCl in water. The equilibrium between HOCl en OCl^- strongly depends on pH. With increasing pH de concentration of HOCl decreases and so will the biocidal effect. Ammonium compounds in cooling water inhibit the HOCl effect since HOCl reacts with these compounds to form chloramines [Baltus and Berbee, 1996].
Sodium hypochlorite, potassium hypochlorite and calcium hypochlorite form active

chlorine. By this the cell elements of the micro organisms are oxidised to such an extent that recovery is impossible [Anonymous, 1985a].
Hypochlorite is admitted ex officio and consequently it can only be used to a limited extent.
Organic chlorine compounds are more stable than inorganic chlorine compounds such as hypochlorite and less aggressive [Rohde, 1994].
In a concentrated form hypochlorite causes serious burns. The active chlorine which is released by the reaction with water, is toxic to aquatic organisms. However, it has a short-time activity and with that it looses its toxicity [Anonymous, 1985a].
The acute oral LD50 for rodents for sodium chlorite ranges from 165 to 375 mg/kg (see Table 3.2 in Appendix 3), indicating that it is highly to moderately toxic to mammals. Hypochlorite has an acute LD50 value of 880 to 6,000 mg/kg, consequently it is moderately to little toxic to mammals.

Hypochlorite is highly toxic to all aquatic organisms having acute LC50 values of <1 mg/l. The acute toxicity of sodium chlorite to crustaceans is extremely high and to activated sludge this is moderately to little toxic. The acute toxicity to fish varies from low to very low.

Chlorine dioxide: the use of this substance is less extensive than of the other inorganic chlorine compounds. The use of chlorine dioxide causes less halogenated by-products than the use of hypochlorite; its disadvantage, however, is its high volatility. Another disadvantage are the safety aspects [Baltus and Berbee, 1996].
Chlorine dioxide contaminates the water through the sewer and sewage purification plants [AMECO, 1996].
Chlorine producing agents have a corrosive effect on mucous membranes and skin because of their chlorine emission and their alkalinity. The toxic dose is 15-30 ml of a 4-6% solution or 2.5 ml of a 20% solution. Solutions of 12-15% are highly dangerous. Solutions up to 0,5% rarely cause intoxication. At oral intake the concentration is more important than the quantity [Anonymous, 1986].
The acute toxicity of chlorine dioxide to fish is extremely high, having an LC50 value of 0.02-0.17 mg/l (see Table 3.2 in Appendix 3).
Organic substances
Bromo chlorodimethylhydantoin is based on both active chlorine and active bromine. The substance is dissociated in water into the active substances HOCl, HOBr and the carrier molecule dimethylhydantoin. The sodium bromide then is the primary biocide. The moment bromide is released as a residue of the oxidation reactions HOCl is converted into HOBr. In this process pH is of less influence than it is in chlorine compounds. The effect of the substance is also not limited by the presence of organic contaminants.
The biocidal effect is based on the inhibition of certain steps in the oxidation reactions of glucose by the release of hypobromic acid (HOBr). Interaction with the cell membrane subsequently causes breaking of the cell membrane [Baltus and Berbee, 1996].
The substance is highly toxic to aquatic organisms such as crustaceans and fish (see Table 3.2 in Appendix 3).

Dazomet is poorly reabsorbed by the skin, but it may cause irritation of the skin and the mucous membranes. In soil dazomet may be converted into methylisothiocyanate and formaldehyde. Under certain circumstances this might also happen in the body [Anonymous, 1996].
The acute oral LD50 to rodents for dazomet ranges from 120 to 650 mg/kg (see

Table 3.2 in Appendix 3), indicating an acute toxicity ranging from high to moderate to mammals.
The acute toxicity of dazomet to bacteria and algae is moderate and to crustaceans this ranges from high to moderate. Toxicity to fish varies between high and low (see Table .2 in Appendix 3).

On 5-oxo-3,4-dichloro-1,2-dithiol no data were found.

3.2.8 Environmental evaluation

Non-oxidative biocides

Isothiazolines
Isothiazolines are the most widely applied non-oxidative biocides. These substances are most toxic to algae: growth inhibition occurs at 30 µg/l. Toxicity to crustaceans and fish is lower: LC50 values are 0.15 mg/l and > 0.1 mg/l, respectively.
The indicative MTR for isothiazolines amounts to 0.1 µg/l active substance. At this level 95% of the species are protected. No standard exists for isothiazolines as such in the production of drinking water, however, there is a standard for pesticides (individual) of 0.1 µg/l. Isothiazolines are used in cooling water systems at concentrations of 1-5 mg/l active substance [Baltus and Berbee, 1996].
In a worst-case approach, assuming the applied substance is completely discharged into surface water and degradation does not take place, the indicative MTR would be exceeded in stagnant waters, in small rivers, canals and in large rivers (dilution factor: 3 for stagnant waters, 10 for small rivers and canals and 100 for large rivers having a discharge flow of >10 m^3/s). Moreover, in that case the drinking water standard for individual pesticides will be exceeded as well. Isothiazolines, however, are readily biodegradable [Baltus and Berbee, 1996], which means the indicative MTR will probably be exceeded for only a short period of time. On account of the facts mentioned above, it is unlikely that the use of isothiazolines in cooling systems will yield problems to aquatic organisms in surface water and, through the consumption of drinking water, to man.

Quats
There is no evidence that quats are used in recirculation systems. Moreover, quats adsorb easily to organic substances in water. Since quats can also adhere to the gills of fish, this could result in a mechanical toxicity to fish [Baltus and Berbee, 1996]. Quats will probably not yield any problems to both aquatic organisms and man, since they are hardly used as biocides and they adsorb easily to organic substances.

Bromine compounds
β-bromo-β-nitrostyrene is highly toxic to crustaceans and fish with LC50 values of 24 µg/l and 17-57 µg/l, respectively. No data are available on algae.
The indicative MTR for the substance is 0.02 µg/l. As a standard in drinking water, the standard of 0.1 µg/l for individual pesticides can be used. The dosage in cooling systems amounts 1-5 mg/l.
Again, in a worst-case approach, assuming the applied substance is completely discharged into the water and degradation does not take place, the MTR and the drinking water standard will be exceeded in all waters.

However, β-bromo-β-nitrostyrene quickly hydrolyses to benzaldehyde, benzoic acid and bromonitromethane [Baltus and Berbee, 1996].
Possibly, the use of β-bromo-β-nitrostyrene in cooling systems will, through the degradation product, yield problems to aquatic organisms in surface water and to man through the consumption of drinking water.

Little data is available on bromonitropropane diol.
Although bromonitropropane diol is admitted in The Netherlands, there is no evidence of the use. Hydrolysis is poor and the substance is poorly degradable [Boethling, 1993]. Toxicity to fish ranges from 35.7 to 57.6 mg/l (LC50), to crustaceans from 1.4 to 5.9 mg/l (LC50) and to algae it amounts to 0.02 mg/l (EC50). The indicative MTR is 0.2 µg/l [Baltus and Berbee, 1996]. For drinking water the standard of 0.1 µg/l for individual pesticides can be used. The used dosage of bromonitropropane diol is not known, which means that no indication can be given of the risk to aquatic organisms and man. Tas et al. [1996] performed a risk assessment for a group of biocides for cooling water, see Table 4. For bromonitropropane diol a risk quotient was found to the aquatic environment (far) above 1.

Table 4. Risk assessment for some biocides for cooling water [by Tas et al., 1996]

Substance	Applied dosage in mg/l	Estimated concentration in surface water in mg/l *	PEC/LC50 acute	PEC/NOEC chronic	PEC/NEC (ecosystem-approach)
2-bromo-2-nitro-propane-1,3-diol	100	33,8	2,6-41	100 (algae.)	4.100
2,2-dibromo-3-nitrilo propionamide	2-4	0,03	0,03-0,08	-	8
poly(oxyethylene(dimethyl -amino)-ethylene......)	10	3,3	7-33	-	3.300

* derived from other values in Tas et al. [1996]

The toxicity of dibromonitriolopropionamide to crustaceans ranges from 0.7 to 0.86 mg/l, to fish from 1.8 to 10.1 mg/l and algae growth is inhibited from a concentration of 2 mg/l and up. The indicative MTR amounts to 7 µg/l. For drinking water the standard of 0.1 µg/l for individual pesticides can be used. The recommended dosage amounts to 4-10 mg/l.

Again, in a worst-case approach, assuming the applied substance is completely discharged into the water and degradation does not take place, the MTR and the drinking water standard in all waters will be exceeded. In water the substance is degraded into dibromoacetonitrile. This metabolite is more toxic than the original substance. In the presence of organic material mainly degradation into monobromonitrilopropionamide will occur. This metabolite is less toxic than the substance itself [Baltus and Berbee, 1996] and will probably degrade rapidly [biodegradation, Boethling, 1993].
The use of dibromonitrilopropionamide in cooling systems may cause problems to aquatic organisms in surface water through its metabolites. Exposure of humans is not expected.

In the risk assessment for biocides for cooling water (Table 4) the risk quotient for dibromonitrilopropionamide is above 1 [Tas et al., 1996]. Since this was based on the usual conservative assumptions (no degradation, very slight dilution in surface water) it is not clear whether dibromonitrilopropionamide actually constitutes a hazard to the environment.

Oxidative biocides

Bromine compounds
The chronic toxicity of sodium bromide to crustaceans amounts to 30 mg/l. However, sodium bromide is always applied in combination with hypochlorite, resulting in a toxicity comparable to that of bromochlorodimethylhydantoin. [Baltus and Berbee, 1996].

Chlorine compounds
Hypochlorite: in waste water (sluice) both HOCl and OCl^- will occur. The concentration of total chlorine (both chlorine and the chlorinated products), at which no effects in fishare expected, is estimated to be <0.001 mg/l. Algae growth is inhibited at a concentration of 0.001 mg/l total chlorine.
LC50 for crustaceans amount to 0.005 and 0.006 mg/l for HOCl and OCl^-, respectively. Chloramines are somewhat less toxic with LC50 values for crustaceans of 0.016 and 0.017 mg/l for monochloramine and dichloramine, respectively.

In surface water mainly less toxic chloramines will occur since free chlorine will react rapidly. The half life of free chlorine or hypochlorite in water amounts to some minutes. Residence time of residus is up to 24 hrs.
Generally, the concentrations of other by-products will also be in the range of 1-100 µg/l. However, these substances can be carcinogenic (trihalomethanes, chlorophenols) or mutagenic (haloacetonitrile, chlorinated ketones). The recommended dosage amounts to 0.1-0.2 mg/l. The indicative MTR for free available chlorine is 0.3 µg/l [Baltus and Berbee, 1996].
In a worst-case situation, assuming the applied substance is completely discharged into the water and degradation does not take place, the indicative MTR will be exceeded for a short period of time. On account of the reactive character of the chlorinated products only a fraction of the initial concentration will remain after a very short time, resulting in a negligible risk to aquatic organisms and man. Furthermore, in flow-through systems the dosage is chosen to assure only a minimum loss of active chlorine through drain water.
Hypochlorite is also applied in disinfecting swimming pools and to this end a policy is being developed.
A risk assessment of the mutagenic and carcinogenic reaction products cannot be made.

Organic substances
Bromochlorodimethylhydantoin readily decomposes in water into HOBr, HOCl and dimethylhydantoin. Also bromamines are formed as by-product. HOBr is the primary biocide.
The toxicity of total bromine to fish (LC 50) ranges from 0.4 to 2.25 mg/l and to crustaceans (LC50) this amounts to 0.75 mg/l.
At an LC50 value of >6,100 mg/l for fish and >1,300 mg./l for crustaceans, dimethylhydantoin is not acutely toxic to these organisms.
Chlorine oxidants turn out to be more toxic than bromine oxidants, when expressed

in mg/l. When expressed in equivalents/l bromine oxidants turn out to be 2-5 times more toxic than chlorine oxidants. Degradation of bromine oxidants is faster than that of chlorine oxidants.

According to field investigations, the area influenced by effluent water is eight times higher for chlorine oxidants than for bromine oxidants. Since bromamines have a biocidal effect as well, in all less biocide is needed compared to chlorine-based biocides. The dosage of bromochlorodimethylhydantoin amounts to 2-7 mg/l.

No indicative MTR is derived for bromochlorodimethylhydantoin, nor for bromide. However, use can be made of the pesticide standard. The target value for surface water and the drinking water standard for individual pesticides amounts to 0.1 µg/l (see Table 3.5 in Appendix 3).

In a worst-case situation, assuming the applied substance is completely discharged into the water and degradation does not take place, the Br^- concentration in all waters would exceed the target value and the drinking water standard for pesticides. However, on account of the reactive character of the substance and its metabolites only a fraction of the initial concentration will remain after a very short time, limiting the risk to aquatic organisms and man. A risk assessment of possible carcinogenic and mutagenic by-products cannot be made.

Dazomet is moderately to highly toxic to mammals. Toxicity to bacteria and algae is moderate and to crustaceans it is moderate to high. To fish toxicity is low to high. No indicative MTR for this substance is available. For drinking water the standard of 0.1 µg/l for individual pesticides can be used. The applied dosage is unknown, therefore an indication of the risk to aquatic organisms and man cannot be given.

On 5-oxo-3,4-dichloro-1,2-dithiol no information was available, neither regarding toxicity to aquatic organisms and man nor the applied dosage.
On dazomet and 5-oxo-3,4-dichloro-1,2-dithiol insufficient information is available for a risk assessment to man and aquatic organisms.

3.2.9 Behaviour during a simple water purification process

The quaternary nitrogen compounds are drastically eliminated by adsorption, both during flocculation and sand filtration.
Isothiazolines will rapidly biodegrade and consequently they will be eliminated during sand filtration.

Hypochlorite reduces to chloride and as such it passes the water purification plant. Sodium bromide passes through the water purification step in a practically unchanged state.
Complete elimination of the reaction products of halogenated biocides, such as halogenated alkanes, phenols and amines during a conventional water purification process is not guaranteed.

β-bromo-β-nitrostyrene has a low log Kow of 2.3, however hydrolysis takes place. Further investigations are needed regarding the elimination of the hydrolysis product (bromonitromethane).
Dibromonitriloprionamide, bromochloro dimethylhydantoin and dazomet all have a

low log Kow and are slowly biodegraded, consequently these substances might be poorly eliminated by a water purification process.

3.2.10 Remediation measures

Reduction of emissions
Emissions can be reduced by:

- closing sluice ways for a certain period of time directly after dosing the biocide. This will cause the biocide concentration to decrease by means of hydrolysis and biodegradation. This method is only effective for β-bromo-β-nitrostyrene and dibromonitrilopropionamide since hydrolysis and biodegradation of these substances is rather fast;
- reducing peak concentrations by building a buffer basin [Baltus and Berbee, 1996], in which waste water can remain for a short period of time, enabling degradation and hydrolysis. For the greater part of biocides for cooling water this would be a good solution;
- treating effluent by biological water purification. A number of quats are eliminated up to 90% by sewage water purification [Baltus and Berbee, 1996];
- de-toxifying biocides by addition of de-toxification substances. Toxicity of β-bromo-β-nitrostyrene and isothiazolines, for example, decreases by the addition of sodium bisulphite [Baltus and Berbee, 1996].

3.2.11 Conclusions

Isothiazolines and quats probably constitute no hazard to aquatic organisms in surface water. The substances are likely to be eliminated during water purification and subsequently a risk to man will be absent.
The risk of chlorine compounds to aquatic organisms and man is negligible. As for toxicity, sodium bromide is comparable to bromochloromethylhydantoin and is not eliminated during water purification. Sodium bromide may cause problems at the ozonization step during the production of drinking water because of the formation of bromate. Also bromochlorodimethylhydantoin is probably poorly eliminated during water purification.
Sodium bromide and bromochlorodimethylhydantoin are not likely to constitute a risk to aquatic organisms or man through the consumption of drinking water.

Halogenated reaction products are not completely eliminated during a simple water purification process. Since these reaction product include mutagenic and carcinogenic substances, the risk to the public health has to be investigated further. RIZA and the University of Amsterdam are performing an investigation into micro pollutants, containing chlorine.

The use of β-bromo-β-nitrostyrene may possibly cause a risk to aquatic organisms in surface water and to man through the consumption of drinking water by its degradation products (particularly bromonitromethane). Insufficient knowledge exists on the elimination of this degradation product during water purification and further investigations are needed.

Dibromonitrilopropionamide might cause a risk to aquatic organisms and man through its metabolites. Moreover, the substance is poorly eliminated during water purification. Further investigations are needed.

On dazomet and 5-oxo-3,4-dichloro-1,2-dithiol insufficient data are available to assess the risk for man and aquatic organisms. Moreover, dazomet is probably poorly eliminated by a water purification process. Further investigations regarding these substances is needed.

3.2.12 Policy

In the policy regarding biocides for cooling water, three essential points can be distinguished:

1. the approach of cooling water will receive more attention on the environmental agenda during consultations between industry and government;
2. in existing situations the objective will be optimisation of the use of biocides and emission reduction;
3. preventive approach: alternatives, beside other aspects, will be considered for existing systems that are to be renovated and for new industries.

Moreover, in the future the use of biocides has to be included in the integral environmental reports, in order to enable the licensing authority to monitor the use of biocides at a local level [Second Chamber, 1997].

3.3 Anti-fouling coatings

3.3.1 Introduction

Anti-fouling coatings prevent growth of bacteria, algae, diatoms, seaweed, sea acorns and crustaceans (such as mussels) on hulls. After the application of anti-fouling coatings onto the hull, active ingredients are released from the coating into the surrounding water, which prevent the growth of the abovementioned organisms [Tas et al., 1996].
Fouling may lead to technical and economic loss because of damage to the preserving layer on the ship and an increased fuel consumption and/or longer sailing times.
In Table 2.3 in Appendix 2 the selected substances are given, which have been considered further.

3.3.2 Sources, use and emissions

In The Netherlands copper compounds (which also contain triazines, thiram and ziram), TBT-compounds, dichlofluanid and diuron in combination with coal tar have been admitted since 1962.
TBT is often applied in combination with copper. Copper and TBT compounds and possibly coal tar oil distillates are the most widely used active substances in anti-fouling systems. Because of PAH problems the use of coal tar will be run down and in 1997 this will be terminated on account of the Decree on coatings which contain PAH. Alternatives are bitumen and properly preserving epoxy-based coatings [Second Chamber, 1997].

The shipping industry can be divided into three categories: ocean shipping, inland shipping and pleasure cruising.
Tributyltin-containing coatings and to a lesser extent copper-containing coatings [Gids working group Copper, 1996] are mainly used in ocean shipping. Over 90% of TBT-containing coatings is used in the coasting and ocean shipping industry [Second Chamber, 1997]. These substances do not pollute the fresh surface water used for the collection of drinking water.
Therefore these "sources" will not be considered further.
In the inland shipping industry mainly tar products are applied. Copper-containing coatings are mainly applied in the pleasure cruising industry. Therefore these products are important for the collection of drinking water [GIDS working group Copper, 1996].

Until recently the most widely used biocides were copper(I)oxide and organotin compounds [CIW, CUWVO, to be published]. The use of copper compounds is somewhat higher than that of organotin compounds (particularly tributyltin) [Tas et al., 1996]. The latter group is no longer on the market in the private sector as from January 1, 1990.
The application of organotin onto ships shorter than 25 m is prohibited within the scope of the Pesticides Act. The European prohibition on the application of anti-fouling agents which contain organotin has been in force since 1992.
Copper-containing anti-fouling coatings are applied onto a great part of the 250,000 recreation ships in The Netherlands (approx. 65%) [CIW, CUWVO, to be published]

Emissions may occur during application of anti-fouling coatings, by leaching during residence time in water, and during hosing the ships after they have been taken out of the water for maintenance purposes. Hosing of recreation ships takes place on shipyards, winter storage sites and marinas [CUWVO, 1991a].

Copper
Little data are available on the use of copper. According to the Second Chamber [1997] 200 tonnes/year of copper are used in anti-fouling coatings, of which 40 tonnes/yr are used in pleasure cruising and the remainder in the shipping industries. However, in seawater copper exists in a less toxic form, brought on by the salt content.

Various inventories pointed out that the contribution of copper-containing anti-fouling coatings to the copper emission into surface water is substantial (40%). Copper is applied in a broad range of products. Anti-fouling coatings is the main emission source of copper into surface water in The Netherlands (in 1993 44 tonnes). Another important emission source (25%) is the leaching of copper from water pipes (in 1993 26 tonnes) [Gids working group Copper, 1996].
According to calculations, emissions of copper to surface water by pleasure cruising amounts to 7.5 tonnes/year [CIW, CUWCO, to be published].
According to RIVM [1995, substance flow analyses), leaching of copper from anti-fouling coatings amounts to 16 tonnes/year [Gids, Working group Copper, 1996]. In 1985 pleasure cruising was responsible for 17% of the total diffuse copper emission caused by leaching [CUWVO, 1991a].
The contribution of hosing ships to the copper emission is negligible compared to leaching from anti-fouling coatings [CUWVO, 1991a].
99% of the copper emission from anti-fouling coatings is caused by leaching. The amount of copper released during hosing ships, based on recent data, is estimated

on approx. 550 kg/yr [CIW, CUWVO, to be published].

Table 5 Copper emissions into surface water

Emission source	Type of emission	Emission to surface water in tonnes/yr	Percentage of total emission to surface water
Anti-fouling coatings	total leaching by pleasure cruising hosing of pleasure cruising	44 (1993)[1] 16[1]; 9[2] 0,55[2]	41,4%[1] 17%[1]; 41%[3] 0,4%[3]
Water pipes	Leaching	26 (1993)[1]	25,1%[1]

1 Gids working group Copper, 1996
2 CIW/CUWVO, to be published
3 99% leaching 1% water hosing [CIW/CUWVO, to be published] derived from 41,4% [Gids working group Copper, 1996]
4 Slooff et al., 1990b

Zinc

The main emission source of zinc into the compartment water is the corrosion of zinc and galvanised steel (> 85%) [Janus et al., 1994]. In principle, zinc borate and zinc oxalate do not pollute the surface water [AMECO, 1996].

Remaining anti-fouling agents

Copper-free anti-fouling coatingss (approx. 15,000 l/yr) usually contain other biocides, such as f.i. dichlofluanid. The environmental impact of these biocides, compared to copper-containing anti-foulings is yet unknown [CIW, CUWVO, to be published].
A normal application of barium metaborate does not pollute the surface water [AMECO, 1996].
No data on usage and emission are available on metaborate, bitumen and the organic compound 2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine.

3.3.3 Analysis and detection methods

Copper
The total amount of copper is determined by electrolytic or iodometric methods. Residues can be determined by reaction with concentrated sulphuric acid and colorimetric estimations of derivatives or by AAS [Worthing, 1987]. The usual analysis techniques are spectrometry (ICP-AES, AAS) and dissolution voltametry (DPASV). Neutron activating analysis (NAA) can be applied as well. The detection limits for these techniques are in the range of 1-100 ng/g and 0.1-1.0 µg/l. Prior to analysis the filtrate has to be acidified up to pH = 2, followed by a decomposition procedure of the undissolved fraction with a mixture of acids. Poorly soluble salts, oxides and copper can only be determined after decomposition with hydrofluoric acid [Slooff et al., 1990b.

AAS, ICP (inductive coupled plasma) and the neocuproine method (detection limit 3-6 µg of Cu) are recommended because of their independence of interferences. The bathocuproine method can be used for drinking water (detection limit of 20 µg/l) [Eaton et al., 1995].

Zinc
The zinc content in water can be determined by voltametry and atomic absorption. Cathodic stripping voltametry (absorption voltametry) is a very sensitive and specific method (detection limit 10^{-10} to 10^{-11} mol/l).
The analysis of zinc in fresh surface water can be carried out by AAS after decomposition with acid, and by ICP-AES (inductive coupled plasma-atomic emission spectrometry) after decomposition with acid [Cleven et al., 1992].
BKH [1996] describes detection limits for AAS (NEN 6443) and ICP-AES (NEN 6426) of 2 and 6 µg/l, respectively.
AAS and ICP (1 µg of Zn) are recommended. The dithizon method is used for potable water and the zincon method for any kind of water [Eaton et al., 1995].

Barium
Analysis are carried out by means of AAS or ICP [Eaton et al., 1995].

Remaining substances
No data have been found on barium metaborate, bitumen and 2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine.

3.3.4 Concentrations in the environment

An estimation of the concentration in surface water caused by leaching from anti-fouling coatings has only been made for 2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine, [Tas et al., 1996]. This estimation, however, is unreliable since leaching numbers are absent and it is based on an assumed leaching value. The estimated concentration in water amounted to 0.09 mg/l [Tas et al., 1996]
No measurements or estimations of the concentrations in water caused by leaching are available on the remaining anti-fouling agents.

For copper and zinc, however, measurement results are available. The concentrations in surface water are, however, not connected with leaching from anti-fouling agents.
The main rivers are the main source of copper. The copper concentration in regional waters in 1985 ranged from 2.3 to 22 µg/l and in governmental waters from 1.5 to 6.7 µg/l [Slooff et al., 1990b]. The total zinc concentration ranged from 17 to 61 µg/l [1991] and the dissolved zinc concentration ranged from 10 to 41 µg/l [BKH, 1993].

No data on concentrations of metaborate and bitumen in water were found.

3.3.5 Behaviour in the environment

Copper
Copper salts are degradable, but heavy metal ions persist in the environment. Copper adsorbs in water to suspended particles. A small part of the substance is

present in water as free metal ion. This adsorption depends i.a. on pH, redox potential and the presence of suspended particles. Copper accumulates strongly (BCF >1,000), particularly in shell fish. Biomagnification does not take place [Slooff et al., 1990b].

Zinc
Zinc adsorbs to sediment and suspended particles. This adsorption depends on pH and temperature. With increasing pH from 6.5 to 9 adsorption increases from 20 to 90%. In aquatic organisms zinc bioaccumulates. The BCF values vary between 100 and 1,000 and are highest for crabs, oysters and insect larvae (BCF 10,000 - 100,000). Biomagnification does not take place [Cleven et al., 1992].

Barium metaborate
No information is available on the behaviour of barium metaborate in water.

Bitumen
Bitumen is poorly degradable and its components have log Kow values >6, indicating possible bioaccumulation. However, bitumen are not likely to constitute a risk to the aquatic environment [CONCAWE, 1995].

Organic substance
According to the Syracuse program [Boethling, 1993] 2-methyl-thio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine is poorly biodegradable (see Table 4.3 in Appendix 4). Estimated log Kow amounts to -0.18 [Boethling, 1993] (see Table 5.3 in Appendix 5), indicating that the substance is hydrophilic and will not bioaccumulate.

3.3.6 **Toxicity**

Data on the toxicity of these substances are included in Appendix 3, table 3.3. For an assessment of the toxicity data the classification method described in Appendix 7 was used.

Copper
Copper compounds strongly irritate skin and mucous membranes. After resorption liver and kidney damage and anomalies of the blood picture may occur [Anonymous, 1986].
The acute oral LD50 for copper(I)oxide ranges from 140 to 470 mg/kg (see Table 3.3 in appendix 3), indicating a moderate to high toxicity to mammals.
Copper oxides are poorly soluble, resulting in a poor availability of these copper compounds in water.

Copper salts are highly toxic to water organisms [Anonymous, 1986]. The acute toxicity of copper to crustaceans and fish ranges from high to moderate and to algae the acute toxicity is low. Chronic toxicity to crustaceans and fish ranges from low to moderate (see Table 3.3 in Appendix 3).

Zinc
Toxicity of zinc oxide to mammals is very low; acute oral LD50 values being >5,000 mg/kg (see Table 3.3 in Appendix 3). Moreover, zinc oxide is poorly soluble in water (4-6 ppm Zn; see Table 5.3 in Appendix 5).
For the amphibian Bufo bufo japonicus an acute LC50 value of 3.2 mg/l has been

found, which is below the solubility limit. This indicates a moderate toxicity. No toxicity data have been found concerning zinc, oxalate and borate which are applied in anti-fouling coatings.
However, toxicity data are available for other zinc compounds (sulphide and chloride) (see Table 3.3 in Appendix 3).
Chronic aquatic toxicity to algae and crustaceans ranges from high to low and to fish this ranges from moderate to very low.

Barium metaborate
No information is available on the toxicity of barium metaborate.

Bitumen
Acute oral LD50 for rats of >5,000 mg/kg indicates a low toxicity to mammals. Bitumen is not toxic to aquatic organisms because of its high molecular weight (see Table 3.3 in Appendix 3).

Organic substance
The acute oral LD50 for 2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine amounts to 200 mg/kg (see Table 3.3 in Appendix 3), indicating a moderate toxicity to mammals.
Toxicity to crustaceans is low and to fish it is high with an acute LC50 value of 0.86 mg/l (see Table 3.3 in Appendix 3).

3.3.7 Environmental evaluation

Copper
In The Netherlands anti-fouling coatings are one of the two main diffuse sources of copper emissions into surface water (in 1996 41.4%: 43.7 tonnes/yr) [Gids working group Copper, 1996]. Inflow from abroad makes up 70% from the total copper emission into water in The Netherlands.

The main exposure routes for humans are food and drinking water. Tolerable daily intake (TDI) amounts to 140 µg/kg b.w. and the actual exposure level is 20-30 µg/kg b.w. per day. Since the TDI is not exceeded, the risk to the public health is considered to be negligible [Janus et al., 1994].
However, no concentrations in surface water caused by leaching from anti-fouling coatings are available. At a local level this might cause increased copper concentrations. Furthermore, it should be noticed that copper from water pipes causes a more direct copper contamination of drinking water than copper from anti-fouling coatings entering surface water.
Since the copper concentration in surface water by leaching from anti-fouling coatings is unknown, a risk assessment for aquatic organisms of copper as an anti-fouling agent cannot be made.

Zinc
Corrosion of zinc and galvanised steel are the main emission sources of zinc to water. Anti-fouling coatings is a minor emission source.
The intake of zinc through the total nourishment (mid eighties an average of 8-14 mg per adult per day) is lower than the Tolerable Daily Intake by a factor of 1-8 (TDI: 20-60 mg per adult per day) and approximately equal to the necessary intake of this essential element [Janus et al., 1994]. Therefore, the risk of adverse effects

to man through the intake of zinc is considered to be negligible [Janus et al., 1994]. However, no concentrations in surface water caused by leaching from anti-fouling coatings are available. At a local level this might cause increased zinc concentrations.
On a national scale the limit value for total zinc in surface water (30 µg/l) is exceeded. Since the zinc concentration in surface water caused by leaching from anti-fouling coatings is unknown, a risk assessment for aquatic organisms on zinc as an anti-fouling agent cannot be made.

Barium metaborate
No environmental pollution of surface water is caused by normal applications of barium metaborate [AMECO, 1996]. No data are available on use, emissions and toxicity, therefore a risk caused by the application of barium metaborate cannot be ruled out.

Bitumen
Bitumen contains no or only a very small amount of PAHs (polycyclic aromatic hydrocarbons) and therefore the environmental impact is lower than that of coal tar bitumen and coal tar [BKH, 1992; CUWVO VI, 1991b].
Bitumen is an oil product which contains saturated and aromatic hydrocarbons, having a chain length mainly >C25.
The available toxicity data indicate a low toxicity to man. The substance has not been classified within the scope of EEC Guideline 93/21 EEC. No evidence could be found on mutagenesis and carcinogenity.

No data are available on the toxicity to aquatic organisms, however, it will probably be low.
Bitumen is not readily degradable and its components have log Kow values >6, indicating possible bioaccumulation. Bitumen, however, is not likely to constitute a risk to the aquatic environment [CONCAWE, 1995].

Organic compounds
Tas et al., [1996] has performed a risk assessment for 2-methyl-thio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine. Since leaching data are absent, the assessment was based on default values for tributyltin. Therefore the estimated concentration in water of 0.09 mg/l is highly unreliable.
Based on this estimated concentration, exposure of humans through drinking water is estimated to be 0.0023 mg/kg b.w. per day (1.65 l/day, 65 kg). The LD50 value for mammals is 2,000 mg/kg [Tas et al., 1996]. The calculated exposure is far below this level. The substance is not likely to constitute a risk to humans through the consumption of drinking water.

The calculated PEC/NEC of 110 indicates a risk to the aquatic ecosystem. However, these values are highly unreliable since chronic toxicity data and measured concentrations in water are absent [Tas et al., 1996].

3.3.8 Behaviour during a simple water purification process

Copper, zinc and bitumen are properly eliminated by the combination of flocculation and sand filtration.
Metal oxalates are biodegraded to metal ions or oxides.

Barium metaborate is probably converted into borate and this is not adsorbed.

2-Methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine will probably have a log Kow >3 [RIWA, press release], resulting in a proper elimination by adsorption to the organic substance of the biomass in the sand filter. Based on the calculation with structural fragments [Syracuse program, see Appendix 5.3), the log Kow would be extremely low. Further investigations are therefore needed.

3.3.9 Conclusions

From the substances mentioned above, copper compounds are the most widely used anti-fouling agents.
The application of copper and zinc compounds might cause risks at a local level to aquatic organisms, but no data regarding leaching from anti-fouling coatings are available. These compounds are unlikely to constitute a risk to humans through the consumption of drinking water. Moreover, copper and zinc are properly eliminated by means of a water purification process.

For a risk assessment on barium metaborate not enough data are available. Moreover, the substance is probably not adsorbed during water purification. Further investigations are needed.

Bitumen probably does not cause a risk to both aquatic organisms and humans. This substance is also properly eliminated by means of water purification.

2-Methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine is likely to cause a risk to aquatic organisms, however not to humans. The assessment of this substance, however, is very unreliable. Moreover, elimination by means of water purification is uncertain. Therefore, further investigations are needed.

3.3.10 Remediation measures

Alternatives
Potentially likely alternatives for anti-fouling ship coatings are: cleaning and the application of non-stick coatings.
Cleaning implies the periodical removal of fouling in so-called cleaning stations.
Non-stick coatings are based on silicon polymers and their low surface energy is unattractive to fouling organisms. This causes less fouling.
The environmental impact of these coatings is probably low compared to leaching by biocides, provided the coating does not become unstuck. Application of these coatings is likely to be feasible. However, do-it-yourself application is difficult. Furthermore, these coatings sometimes contain a small amount of dibutyltin, which might leach.
Another good alternative is a combination of cleaning and non-stick coatings [Gids working group Copper, 1996].

3.3.11 Policy

In 1994 the Ministry of VROM started an approach for anti-fouling coatings. This has been the basis for the policy plan "anti-fouling ship coatings". The emission reduction from anti-fouling coatings is unanimously endorsed.
For The Netherlands the target is a 100% reduction of emitting agents in the year 2010. This can be realised by regarding a ship as a "closed system" and applying non-stick coatings en mechanical cleaning of the hull.
A new national guideline does not exist at present. A report on the performance of the approach will be issued every 3-4 years.
Two fields requiring special attention are: the tributyltin issue and the pollution of inland waterways by copper.
An approach has been drafted for both fields [Second Chamber, 1997]:

1. For TBT the Marine Environment Protection Committee (VN-IMO-MEPC) accepted a recommendation for the reduction of the maximum leaching of TBT coatings. This resulted in the termination of the application of so-called "free association" type of coatings with a high emission of TBT. At the moment mainly "self-polishing" copolymers are being used with a lower TBT emission and a longer lifetime.
   The intention of the North Sea countries is a further reduction of TBT emissions and they are considering a prohibition on the application of the substance.
   TBT has been prohibited since 1990 on ships shorter than 25 meters [EU Guideline 89/667/EEC].
   The objective is to achieve an international termination of the application of TBT in approx. 5 years.
   For the coasting trade and ocean shipping trade the prohibition of the use of TBT was given priority over the use of copper, since copper is less problematic in seawater and is not under international discussion. Furthermore, national measures have been taken at ship yards and marinas. A more structural solution for the anti-fouling issue on the long-term is being worked on.

   The objective is to terminate the application of agents or methods which emit pesticides in approx. 15 years, for instance by applying non-stick coatings and/or periodical chemical cleaning.

   The approach for TBT comprises:
   a) optimising the possibilities to reduce emissions;
   b) developing alternatives (replace tin for copper and organic biocides, and the application of cleaning techniques);
   c) influencing international frameworks

   [Second Chamber 1997]

2. A policy has been formulated for copper within the scope of the Rhine and North Sea Action plan (RAP, NAP), stating that copper emissions have to be reduced by 50% between 1985 and 1995. On a national level measures are being taken mainly at ship yards and marinas.
   The objective is a reduction of the copper pollution of surface water by anti-fouling coatings. This needs attuning with the approach of other sources of copper contamination, such as copper drinking water pipes.
   The approach is phased. During the first phase the problem is mapped, alternatives are surveyed and information is provided. During the second phase

a decision will be taken regarding a progressive reduction of the copper contamination from coatings and a possible prohibition on copper-containing anti-fouling coatings for inland waterways [Second Chamber, 1997].

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Appendices

Appendix 1

The selection of substances

Table 1.1 The selection of wood preservatives

Substances	**Selected or reason for non-selection**
2-phenylphenol	No longer admitted in 1996
2-(thiocyano methylthio)benzothiazole	No longer admitted in 1996
4-chloro-3-methylsodiumphenolate ?	No longer admitted in 1996
ammoniumbichromate	Selected
ammoniumbifluoride	Selected
arsenic pentoxide	Selected
arsenic acid	No longer admitted in 1996
azaconazole	Selected
alkylbenzyldimethyl ammoniumchloride	No longer admitted in 1996
boric acid	Selected
borax	Selected
carbendazim	Mainly used in agriculture
carbendosulf	No longer admitted in 1996
chromium trioxide	Selected
creosote	In the future no longer admitted
cyfluthrin	Mainly used in agriculture
cypermethrin	Mainly used in agriculture
deltamethrin	Mainly used in agriculture
dichlofluanide	Mainly used in agriculture
didecyldimethylammoniumchloride	Selected
ethylhexanoate	Readily degradable and non-accumulating
fenitrothion	No longer admitted in 1996
folpet	Mainly used in agriculture
potassium bichromate	Selectedv
potassium bifluoride	Selected
copper naphtenate	Selected
copper I oxide	Selected
copper II carbonate hydroxide	Selected
copper II oxide	Selected
copper silicofluoride	Selected
copper sulphate	Selected
methylene bisthiocyanate	Readily degradable and non-accumulating
sodium arsenate	No longer admitted in 1996
sodium bichromate	Selected
sodium octaborate	Selected
sodium tetrafluoroborate	No longer admitted in 1996
n-octyl isothiazolon	No longer admitted in 1996
permethrin	Mainly used in agriculture
pentachlorophenol/sodiumpentchlorophenolate	No longer admitted in 1996
propiconazole	Selected
tebuconazole	Selected
tolylfluanide	Mainly used in agriculture
tributyltin compounds	Mainly used in agriculture
zincsilicofluoride	Selected
zincnaphtenate	No longer admitted in 1996
zineb	Mainly used in agriculture

Table 1.2 The selection of biocides for cooling water

Substances	**Selected or reason for non-selection**
ß bromo-ß nitrostyrene	Selected
1-bromo-3-chloro-5,5-dimethyldantoin	Selected
2-bromo-2-nitropropane-1,3-diol (bronopol)	Selected
5-chloro-2-methyl-4-isothiazolin-3-on	Selected
2,2-dibromo-3-nitrilo propionamide	Selected
2,2-dithiobisbenzamide	Readily degradable and non-bioaccumulating
1,2-benz isothiazolin-3-on	No longer admitted in 1996
2-methyl-4-isothiazolin-3-on	Readily degradable and non-bioaccumulating
Selected	Selected
benzalkoniumchloride	No longer admitted in 1996
bromonitrostyrene	Selected
carbendazim	Mainly used in agriculture
dazomet	Selected
didecyldimethylammoniumchloride	Selected
glutaraldehyde	Readily degradable and non-bioaccumulating
isopropanol	Readily degradable and non-bioaccumulating
methylenebisthiocyanate	Readily degradable and non-bioaccumulating
sodium chlorite	No longer admitted in 1996
sodium dichloroisocyanurate	Readily degradable and non-bioaccumulating
sodium hydroxide	Strongly reactive
sodium hypochlorite	Selected
poly[oxyethylene(dimethylimino) ethylene-(dimethyl-imino)ethylene dichloride]	Selected
trichloroisocyanic acid	No longer admitted in 1996
chlorine dioxide	Selected
sodiumbromide	Selected
ozon	Strongly reactive
hydrogen peroxide	Readily degradable and non-bioaccumulating
alkyldimethylbenzylammoniumchloride	Selected
alkyldimethylethylbenzylammoniumchloride	Selected

Table 1.3 The selection of anti-fouling agents

Substances	Selected or reason non-selection
2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine	Selected
bariummetaborate	Selected
bitumen	Selected
creosote	No longer admitted in 1996
dichlofluanide	Mainly used in agriculture
diuron	Mainly used in agriculture
folpet	Mainly used in agriculture
copper	Selected
copper I oxide	Selected
copper resinate	No longer admitted in 1996
copper thiocyanate	Selected
tributyltin compounds	Mainly used in agriculture
triphenyltinhydroxide	No longer admitted in 1996
zineb	Mainly used in agriculture
zincborate	Selected
zincoxalate	Selected
zincoxide	Selected
ziram	Mainly used in agriculture

Appendix 2

Selected substances

Table 2.1 Selected wood preservatives

Groups of substances	Selected substances
Chromium	ammonium bichromate (Cr^{6+}) potassium bichromate (Cr^{6+}) sodium bichromate (Cr^{6+}) chromium trioxide (Cr^{6+})
Boron	boric acid borax sodium octaborate
Arsenic	arsenic pentoxide
Copper	coppernaphtenate copper(I)oxide copper(II)carbonate hydroxide copper(II)oxide coppersulphate
Fluorides	copper silicofluoride potassium bifluoride zinc silicofluoride ammonium bifluoride
Organic compounds	propiconazole tebuconazole azaconazole
Quats	didecyldimethylammoniumchloride

Table.2.2 Selected biocides for cooling water

Groups of substances		Selected substances
Non-oxidative	Isothiazolines	5-chloor-2-methyl-4-isothiazolin-3-on
	Quats	didecyldimethylammoniumchloride alkyldimethylbenzylammoniumchloride alkyldimethylethylbenzylammoniumchloride poly(oxyethylene(dimethylimino)ethylene-(dimethylimino)ethylenedichloride)
	Bromine compounds	β-bromo-β-nitrostyrene 2-bromo-2-nitropropane-1,3-diol 2,2,-dibromo-3-nitrilo propionamide
Oxidative	Bromine compounds	sodium bromide
	Chlorine compounds	sodium hypochlorite chlorine dioxide sodium chlorite
	Hydantoins	1-bromo-3-chloro-5,5-dimethyldantoin
	Remaining	5-oxo-3,4-dichloro-1,2-dithiol dazomet

Table 2.3 Selected anti-fouling agents

Groups of substances	Selected substances
Copper	Copper Copper(I)oxide Copperthiocyanate
Zinc	Zincborate Zincoxalate Zincoxide
Bitumen	
Bariummetaboraat	
Organic compound	2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine

Appendix 3

Toxicity data

Table 3.1 Toxicity of wood preservatives

Groups of substances	Substances	Bacterium	EC50 algae mg/l	EC50/LC50 Crustac. Mg/l	LC50 fish mg/l	NOEC algae mg/l	NOEC Crustac. mg/l	NOEC fish mg/l	LD50 oral mg/kg
Arsenic	arsenic pentoxide			48-96h 0.8-12 As[i] 96h 0.93[g]	96h 1.1-82.4 As[i]	14d 0.01-10[i]	28d >0.973 insect/moll.[i] 14d >0.931 crustac.[i] 28d 0.97[g]	28d >=0.089[g] 28d >=0.973[g]	rat 8[c] mus 55[c]
Boron	boric acid 10043-35-3			48h 133[h] 48h 658-875[o]	72h 1020[o] 120h 1260[o]	58[o]	21d 80[o]	60d 137-503[o]	rat 2660[c,o] mus 3450[c,o] wmn LDL0 200[c] rat 2700-5100[k] rat LD0 3000-4000[o]
	borax								rat 2660[c] gpg 5330[c] mus 2000[c] rat 4500-6000[d]
	sodium octaborate								rat 2000[c] gpg 5300[c] gpg 5300[d]
Chromium	ammoniumbichromate	24h EC0 10[o]		48-96h 2-60 Cr6+/Cr3+ compounds[f]	96h 3.4-170 Cr6+[f] 48h TLM 212[o] 96h TLM 136[o] 48h LC0 50[o]				rat 350 mixture[e] rat 80[o] rat 54[o] rat 64[o]
	potassium bichromate			24h 0.5[f] 48h 0.66-34.8 mollusca[g] 48h 0.77-0.9 Daphnia[g] 48h 0.24-0.66[f] 24h 1.5[f] 0.007[f] 0.024f	96h 35.9-39.7[g] 96h 28.93[g] 96h 113-169[g] 96h 18-61[f]	4-7d 0.35-350 µg/l [f]	3w 35-350 µg/l [f]	3w-16m <0.2-6.65[f] 412d 1.0[g] 412d growth 0.0178-3.95[g] 90d 0.05[g]	mus 190[c] gpg LDL0 163[c]
	sodium bichromate	3h EC50 75.5[o] 24h EC0 100[o] 16h TT 0.7[o]	48h TT 1.2[o]	48h 0.195[o] 96h 4.4-12 Rotifera[g] 24h 1.4[o] 14d >0.0175 reprod.[o] 48h 4[o] 48h 0.122[o]	96h 3.4-65.5[g] 96h 69[o] 96h 264[o] 96h 4[g] 96h 33.2[g] 96h 10[o]		4w EC 10 µg/l[f]	4w-22m 0.02-0.522[f] 60d 0.11[o] 60d 0.29[o] 60d 0.54[o] 60d 0.05[o] 60d 0.15[o] 32d 0.01-10[g] 33d 0.1[g] 113d 0.01[g] 60d 0.52[o]	rat 50[c] rat 147[e] rat 14-21[o] rat 324[o] rat 50[o]
	chromium trioxide	24h EC0 500[o]			96h 60[o] 96h 40[o]		3w <0.05-0.5 wormen[f]	28d LC50 0.35[o] 8d LC50 2.2[o]	rat 80[c] mus 127[c]

Groups of substances	Substances	Bacterium	EC50 algae mg/l	EC50/LC50 Crustac. Mg/l	LC50 fish mg/l	NOEC algae mg/l	NOEC Crustac. mg/l	NOEC fish mg/l	LD50 oral mg/kg
					48h LC0 100[o]		3w LC50 280-550 wormen[f]	7d LC50 1.32[o] 7d LC50 0.06[o]	
Fluorides	copper silicofluoride								rat 350 mixt.[e]200 F[k]
	potassium bifluoride		96h 43 NaF[h]	48h 340 NaF[h]	96h 3.1 (KF), 5.3 (NaF), mix of 3 fish sp.[j]				rat 180 NaF
	zinc silicofluoride								rat LDL0 100[c]
	ammoniumbifluoride	EC50 2394 (98.7%) act. Sludge[o] EC50 4184 (98.7%)[o]			96h 0.8 (NH4F) mix of 3 fish sp.[i] 96h LC100 562 (98.7%)[o] 96h LC0 237 (98.7%)[o]	37% reduction 2 mg F /l[i]	3w 3.7 mg F /l[i] 3w 26 mg F /l[i]	10-20d LC100 2.3-8.5 mg F /l[i] 3w LC100 4.5 mg F /l[i]	rat 130[o] LDL0 gpg 150[o]
Copper	copper naphtenate			18 h 200 NEF mollusca[r]					mus LDL0 110[c] rat >6000[e] rat 450[k] rat 1340[o]
	copper(I)oxide		96h 65[o]	24h 1.4[o] 48h 0.51[o] 400-600 ppb [p]	48h LC100 50-150 range[o]				rat 470[c] rat 1340[o] rat 470[d,e] rat 140-300[p]
	copper(II)carbonate hydroxide								rat 159[c] rbt 159[c] mam 625[c] brd 900[c]
	copper(II)oxide								rat 700[e]
	copper sulphate			4d 0.037-2 mollusca[g] 4d 0.32-8.3 insecta[g] 2d 0.026-2.5 crustacea[g]	96h 0.025-1.5[g]	< 0.005, 0.040[q] (Cu-ion)	42d 0.008 mol-lu-sca/crustacea[g] 14d 0.032-0.56 crustacea[g] 82-100d 0.04 crustacea[g]	31-85d 0.08-0.057 growth[g] 11-85d 0.011-0.03 mortality[g]	rat 300[c, o] man LDL0 857 GIT[c] rat 960[e]
Organic compounds	propiconazole		0.76[a]	11.5[a]	3.3[a] 20[d] >100[d]	0.32[a]			1.490[a] rat 1517[d]
	tebuconazole		0.11[a]	11.8[a] 10-12[q]	4.4[a] 6.4[q] 8.7[q]	0.1[a]	0.33a	0.01[a]	625[a] rat 4000[q] mus 3000[q] quail 4438, 2912, 1988[q]
	azaconazole		67[a]	86[a]	14[a]	1.2[a]			310[a]
Quats	didecyldimethyl-ammoniumchloride								rat 84[c] mus 268[c] rat 500 quat[e]

Unless stated otherwise, only data of the mentioned substances are given

a= Tas et all., 1996
b= Baltus & Berbee, 1996
c= Sax & Lewis, 1989 ; rbt=rabbit, gpg=guinea pig; mus=mouse; wmn=woman, brd=bird, mam=mammal, scu= subcutaneous , GIT= Effects to the gastrointestinal tract, TER= teratogenic effects
d= Worthing et all., 1987
e= Anon, 1985 a en b
f= Slooff et all., 1989b
g= Mance, 1987
h= Nikunen et all., 1990
i= Slooff et all., 1990a
j= Slooff et all., 1989a
k= Anon, 1986
l= Khangarot & Ray, 1989
m= Untis et all., 1974
n= Liang et all., 1978
o= HED-sets of various substances
p= Court, 1990
q= Aquatox, 1996
r = ISIS/RISK Line, 1996.

Abbreviations:
TT= Toxic threshold
TLM= median toxic lethal concentration ~ LC50

LDL0=lowest lethal effects dose

Table 3.2 Toxicity of biocides for cooling water

Groups of substances	Substances	Inhibition sludge	EC50 algae mg/l	EC50 crustac. mg/l	LC50 fish mg/l	NOEC algae mg/l	NOEC crustac. mg/l	NOEC fish mg/l	LD50 oral mg/kg
Non-oxidative	**Isothiazolines**								
	5-chloro-2-methyl-4-isothiazolin-3-on	98% - 10 mg/l[b] 81% - 1 mg/l 61% - 0.1 mg/l[b]	MIC 0.12[b] MIC0.03[b] MIC 1[b] MIC 0.25[b] MIC 0.63[b] MIC0.03-0.5[b]	48h 0.15[b]	144h 0.54[b] 144h 0.1[b] 144h 0.12[b] 144h 0.14[b]				rat, mus 53-60[i]
	Quats								
	didecyldimethylammoniumchloride								rat 84[c] mus 268[c] rat 500 quat[h]
	alkyldimethylbenzyl ammoniumchloride		MIC 5[b]		96h 1-10[b]				
	alkyldimethylethylbenzyl ammoniumchloride								rat 300[c] mus 150
	poly[oxyethylene(dimethylimino-) ethylene-(dimethylimino)ethylenedichloride]		0.5[a]	0.16[a] 48h 0.0972[b]	0.1[a] 96h 0.26[b] 96h 0.27[b] 96h 4[b]			1.32[b]	rat 1850[a]
	Bromine compounds								
	β-bromo-β nitrostyrene	69% - 25 mg/l[b] 60% - 2.5 mg/l[b]		48h EC 0.024[b] 96h 0.051[b]	96h 0.017[b] 96h 0.027[b] 96h 0.057[b]				
	2-bromo-2-nitropropane-1,3-diol		2.6[a] MIC 6-50[b] 72h 0.02[b]	0.81[a] 48h 1.4[b] 48h 1.7[b] 48h 5.9[b]	13[a] 96h 41.2[b] 96h 35.7[b] 96h 57.6[b]	0.32[a]	48h 0.32[b]	96h 32[b] 96h 18[b] 96h 18[b]	rat 180-400[d] mus 270-400[d] dog 250[d]

Groups of substances	Substances	Inhibition sludge	EC50 algae mg/l	EC50 crustac. mg/l	LC50 fish mg/l	NOEC algae mg/l	NOEC crustac. mg/l	NOEC fish mg/l	LD50 oral mg/kg
	2,2,-dibromo-3-nitrilo propionamide		0.3^{a} MIC 2^{b} MIC 16^{b} MIC 16^{b}	0.5^{a} 96h 0.7^{b} 48h 0.86^{b}	1^{a} 96h 6.2^{b} 96h 10.1^{b} 96h 2.3^{b} 96h 2.3^{b} 96h 8.8^{b} 24h 3^{b} 48h 2.2^{b} 72h 1.9^{b} 96h 1.8^{b}			<9.0^{b} 4^{b}	rat 308^{a}
Oxidative									
	sodiumbromide	4h NOEC 3200-4^{g} 0d NOEC 3200-.3^{g}	48h 0,008^{e} 96h 5-24 g/l^{g} 96h 8,5-72 g/l^{g}	96h LD$_{50}$ 7900^{b} 96h >2000^{b} 48h EC$_{50}$ 1^{e} 48h EC$_{50}$ 0,011^{e} 48h 13500^{e} 48h 5-40 g/l^{g} 48h >1000-40^{g}	96h >2000^{b} 96h >2000^{b} 96h 225^{b} 96h LD$_{50}$ 16479^{b} 96h 0,016^{e} 96h 24-96 g/l^{g} 96h 15-95 g/l^{g}	7d 3200-7^{g}	16d EC$_{50}$ 29^{e} 21d 10-21^{g} 21d 14-21^{g} 23d 7-23000^{g}	125d EC$_{50}$ 180-225^{e} 24d 7-124000^{g} 20d 100-20^{g} 34d 700-34000^{g} 40d 3200-40^{g}	rat 3500^{e} rat 4200^{g}
	Chlorine compounds								
	sodium hypochlorite	100% - 10 mg/l^{b} 7d EC50= 0.0316 protozoa^{g}	24h 0.4^{g} 24h 0.11^{g} 24h 0.095^{g} 24h 0.2^{g} 24h 0.33^{g}	24h 0.006^{b} 24h 0.005^{g} 24h 0.07-0.7 (12.7%)^{g} 48h 1-13.6 mollusca^{g}	48h 0.07^{e} 96h 5.9^{e} 96h 0.033-0.097^{g} 96h 0.023-0.052^{g} 96h 0.026-0.030^{g} 96h 5.9^{g}			subchr. LOEC 0.02^{e}	rat >5000 (4.7%)^{g} rat 8200 (12.5%)^{g} mus 880^{g} mus 5800 (50%)^{g}
	chlorine dioxide				96h 0.02^{b} 96h 0.17^{b} 96h 0.15^{b}				
	sodium chlorite	3h EC50 2.2^{g} 3h EC50 120^{g}		48h 0.026 (80%)^{g} 48h 0.29 (80%)^{g}	48h 50^{g} 96h 500^{g}				rat 165^{c,g} mus 350^{c,g} gpg 300^{c,g} rat 375 (50%)^{g} rat 204 (25%)^{g}
	Organic substances								
	1-bromo-3-chloro-5,5-dimethyldantoin			96h 0.46^{b} 48h 0.75^{b}	96h 0.87^{b} 96h 2.25^{b} 96h 0.40^{b} 96h 0.46^{b}				

Groups of substances	Substances	Inhibition sludge	EC50 algae mg/l	EC50 crustac. mg/l	LC50 fish mg/l	NOEC algae mg/l	NOEC crustac. mg/l	NOEC fish mg/l	LD50 oral mg/kg
	5-oxo-3,4-dichloro-1,2-dithiol								
	dazomet	TGK= 20 act.sludge^{g} 17h EC10 1.8^{g}	96h 1^{g}	96h 6 24% dazomet^{e} 48h 0.3 >90% dazomet^{g}	50-65 24% dazomet^{e,g} 24h 0.09 Thione^{e} 48h 0.045 Thione^{e} 96h 10-22 basamid-granulat (98% dazomet)^{g} 96h 0.46-1 basamid-granulat^{g} 96h 1-2.15 basamid-granulat^{g} 96h 0.16 N521 (?% dazomet)^{g} 96h 4.6-10 98% dazomet^{g}				rat 363^{c} mus 180^{c} rbt 120^{c} gpg 160^{c} rat 520^{d} rat 500^{f} mus 650^{f}

a= Tas et all., 1996
b= Baltus & Berbee, 1996
c= SAX & Lewis, 1989 ; rbt=rabbit, gpg=guinea pig; mus=mouse; wmn=woman, brd=bird, mam=mammal, scu= SUBCUTANEOUS , GIT= Effects to the gastrointestinal tract), TER= teratogenic effects
d= Worthing et all., 1987
e= Nikunen et all., 1990
f= Anon, 1986
g= HED-sets of various substances
h= Anon, 1985 a en b
i= De Bethizy, J.D. et all., 1986, Food.Chem.Toxicol. 24(1), 43-49.

Abbreviations:
TGK= Toxic limit concentration

MIC= minimal inhibiting concentration

Table 3.3 Toxicity of anti-fouling agents

Groups of substances	Substances	EC50 algae mg/l	EC50 crustac. mg/l	LC50 fish mg/l	NOEC alg mg/l	NOEC crustac. mg/l	NOEC fish mg/l	LD50 mg/kg
Copper	Copper(I)oxide	96h 65^d	400-600 ppb^b 24h 1.4^d 48h 0.51^d	48h LC100 50-150 range^d				rat 140-300^b rat 470^{c,e,f} rat 1340^d
	Copperthiocyanate							
Zinc	Zinc borate							
	Zinc oxalate							
	Zinc oxide			52h LD0 220-262 mg/kg^d 48h 3.2 Bufo bufo japonicus^d	2 wk 0.005-0.4^g Zn SO_4	1 wk-17 dg 0.008-0.4^g $ZnCl_2$	lifecycle 0.03-1.3 $ZnSO_4$	rat TDL0 6846 TER^c rat >5000^d rat >15000^d mus 7950^d
Barium metaborate								
Bitumen				nontoxic because of high mol.weights^d				rat >5000^d
Organic compound	2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine	-	49^a	0.86^a				200^a

a = Tas et all., 1996
b = Court, 1990
c = SAX & Lewis, 1989 ; rbt=rabbit, gpg=guinea pig; mus=mouse; wmn=woman, brd=bird, mam=mammal, scu= subcutaneous , GIT= Effects to the gastrointestinal tract), TER= teratogenic effects
d = HED-sets of various substances
e = Worthing, et al , 1987
f = Anon, 1985 a en b
g = Janis, 1992 (Appendix Basisdocument zinc)

Abbreviations:

TDL0=Lowest effect dose

Table 3.4 Standards for wood preservatives

Group of substances/Name	Limit value surface water Total in µg/l	Limit value surface water dissolved in µg/l	Target value surface water Total in µg/l	Target value surface water Dissolved in µg/l	Standard surface water for the intake of drinking water in µg/l	Standard for drinking water in µg/l WLB	Standard for drinking water in µg/l WHO	Indicative MTR in µg/l active subst.
Arsenic	10	8.6	5	4	20	50, cat.I	10	
Boron					1000		500 (recomm.)	
Chromium	20	2	5	0.5	50	50, cat I	50	
Fluoride	1.500				≤ 1.000	1100 cat.I	1.500	
Copper	3	1.3	3	1	≤ 50	100, cat. I	2.000	
Organic								
propiconazole					≤ 0.1 non-chloro pesticides individual	0.1 cat. I pesticides individual		
tebuconazole					≤ 0.1 non-chloro pesticides individual	0.1 cat. I pesticides individual		
azaconazole					≤ 0.1 non-chloro pesticides individual	0.1 cat. I pesticides individual		
Quats								
didecyldimethyl ammoniumchloride								

All data from VROM, 1994, Stoffen en normen

Abbreviations:

WLB	= Water Supply Act
WHO	= World Health Organisation
Cat.I	= contains substances of which the values determined in the WLB may not be exceeded.
Cat.IV	= contains substances of which the values may only be exceeded in situations where meeting the requirements cannot be demanded.

Table 3.5 Standards for biocides for cooling water

Group of substances/Name	Limit value surface water Total in μg/l	Limit value surface water dissolved in μg/l	Target value surface water Total in μg/l	Target value surface water Dissolved in μg/l	Standard surf.water for the intake of drinking water in μg/l	Standard for drinking water in μg/l WLB	Standard for drinking water in μg/l WHO	Indicative MTR in μg/l active substance
Non-oxidative								0.1[a]
Isothiazolines								
Quats								
Bromine compounds								
β-bromo-β-nitrostyrene								0.02[a]
2-bromo-2-nitro-(1,3)-propanediol								0.2[a]
2,2-dibromo-3-nitrilopropionamide								7[a]
Oxidative								
Bromine compounds								
sodium bromide	8.000[b]							
Chlorine compounds								
sodium hypochlorite	200000 chloride[b]				≥ 200000 chloride[b]	150000, cat. IV,chloride[b]		0.3[a]
sodium chlorite	200000 chloride[b]				≥ 200000 chloride[b]	150000, cat. IV, chloride[b]		0.3[a]
chlorine dioxide	200000 chloride[b]				≥ 200000 chloride[b]	150000, cat. IV, chloride[b]		
Organic substances								
1-bromo-3-chloro-5,5-dimethyl hydantoin								
5-oxo-3,4-dichloro-1,2-dithiol								
dazomet								
Standard for pesticides				≥ 0.1 non-chlorine pesticides individual[b]	0.1 cat. I pesticides[b] individual			

a Baltus & Berbee, 1996
b Stoffen en normen

Abbreviations:

WLB = Water Supply Act
WHO = World Health Organisation
Cat.I = contains substances of which the values determined in the WLB may not be exceeded.
Cat.IV = contains substances of which the values may only be exceeded in situations where meeting the requirements cannot be demanded.

Table 3.6 Standards for anti-fouling agents

Group of substances/Name	Limit value surface water Total in µg/l	Limit value surface water Dissolved in µg/l	Target value surface water Total in µg/l	Target value surface water Dissolved in µg/l	Standard surface water for the intake of drinking water in µg/l	Standard drinking water in µg/l WLB	Standard drinking water in µg/l WHO	Indicative MTR in µg/l active substance
Copper	3	1.3	3	1	≤ 50	100, cat. I	2.000	
Zinc	30	2	9	2	≤ 200	100, cat. IV	5.000	
Bitumen								
Barium metaborate								
2-methylthio-4-t-butyl-amino-6-cyclo-propyl-amino-s-triazine					≤ 0.1 non-chlorine pesticides individual	0.1 cat. I pesticides individual		

All data from VROM, 1994, Stoffen en normen

Abbreviations:

WLB = Water Supply Act
WHO = World Health Organisation
Cat.I = contains substances of which the values determined in the WLB may not be exceeded.
Cat.IV = contains substances of which the values may only be exceeded in situations where meeting the requirements cannot be demanded.

Appendix 4

Degradability

Table 4.1 Degradability of wood preservatives

Substance	Hydrolysis half life	DT50 hydrolysis in days	Evap. From water in days	DT50 water/sed. in days	Photodegradation/photolysis half life in days	Biodegradation	Biodegradation Syracuse[a,c]	Expected persistence
Arsenic								
arsenic pentoxide								
Boron								
boric acid								
borax								
sodium octaborate								
Chromium								
ammoniumbichromate								
potassium bichromate								
sodium bichromate								
chromium trioxide								
Fluorine								
coppersilicofluoride								
potassium bifluoride								
zinc silicofluoride								
ammonium bifluoride								
Copper								
coppernaphtenate								
copper(I)oxide								
copper(II)carbonate hydroxide								
copper(II)oxide								
copper sulphate								
Organic substances								
azaconazole			298.7 yr[a]		0.68 (12h, 1.5E6 OH/cm^3)[a]		lineair p=-0.64 non-lineair p=0 ultimate =1.89	
propiconazole			136.3 yr[a]	57[b]	0.39 (12h, 1.5E6 OH/cm^3)[a]		lineair p=-0.66 non-lineair p=0 ultimate =1.8	
tebuconazole				365[b]				
Quats								
didecyldimethylammoniumchloride								
Remaining								
methylene bisthiocyanate					2.3 hrs (12h, 1.5E6 OH/cm^3)[a]		lineair p=0.69 non-lineair p =0.76 ultimate p=2.9	
ethyl hexanoate					1.3 d (12h, 1.5E6 OH/cm^3)[a]		lineair p=0.86 non-lineair p=0.97 ultimate =3.5	

[a] Boethling et all., 1993

[b] Tas et all., 1996

[c] If both p-values are >0.5, the substance is readily degradable, ultimate indicates degradation took place at 5 in hours, at 4 in days, at 3 in weeks, at 2 in months en at 1 longerj; thus, ultimate = 3.54 means that degradation takes place within some days to some weeks.

Table 4.2 Degradability of biocides for cooling water

Substance	Hydrolysis-half life	DT50 hydrolysis in days	DT50 water/sed. in days	Photodegradation/ photolysis	Biodegradation	Biodegradation Syracuse^{a,d}	Expected persistence
Non-oxidative							
1,2-benz isothiazolin-3-on				0.042 d (12h, 1.5E6 OH/cm3)^{a}		lineair p=1.02 non-lineair p=0.98 ultimate = 2.42	
isothiazolines	100d - pH 4-4.5 - 7°C^{c} 83 d - pH 8 - 7°C^{c} 11.4d - pH 8 - 25 °C^{c} 6.8d - pH 8 -30°C^{c} 2.6d - pH 8 - 40°C^{c} 8.2d - pH 11 - 7 °C^{c} 0.072d - pH 11 - 40 °C^{c} river water > 100d^{c}			UV 5-11d^{c}	river water possibly <1 d^{c}	lineair p=0.56 non-lineair p=0.28 ultimate =2.70 5 chloro-2-methyl-4-isothiazolin-3-on lineair p=0.69 non-lineair p=0.80 ultimate =2.94 2 methyl-4-isothiazolin-3-on	< 1 d^{c}
Bromine compounds							
β-bromo-β-nitrostyrene	6h - pH 5 - 25°C^{c} 4.8h - pH 7 - 25°C^{c} 0.6h - pH 6-7 - 50°C^{c} 1.5h - pH 8.5 - 25°C^{c} <0.1h - pH 9 - 50°C^{c}			-	-	lineair p=0.72 non-lineair p=0.05 ultimate =2.75	-
2-bromo-2-nitro-(1,3)-propanediol	>6 y - pH 6 - 5°C^{c} 6 y - pH 6 - 22-25°C^{c} > 4mth - pH 6 - 30°C^{c} 4 mth - pH 6 - 40°C^{c} 36h - pH 6 - 60°C^{c} 6 mth - pH 8 - 5°C^{c} 4 mth - pH 8 - 22-25°C^{c} 14d - pH 8 - 30°C^{c} 8d - pH 8 - 40°C^{c} 3h - pH 8 - 60°C^{c}		1.000^{b}	24 h -pH 4 -25°C^{c}	poor	lineair p=0.74 non-lineair p=0.02 ultimate =2.89	> 1 w^{c}
2,2-dibromo-3-nitrilopropion amide	38d - pH 6 - 10°C^{c} 12d - pH 6 - 20°C^{c} 3d - pH 6 - 30°C^{c} 20h - pH 6 - 40°C^{c} 13h - pH 8 - 10°C^{c} 3h - pH 8 - 20°C^{c} 1h - pH 8 - 30°C^{c}	1^{b}	1.000^{b}	-	-	lineair p=0.87 non-lineair p=0.02 ultimate =2.37	< 1 d - < 1 w^{c}

Substance	Hydrolysis-half life	DT50 hydrolysis in days	DT50 water/sed. in days	Photodegradation/ photolysis	Biodegradation	Biodegradation Syracuse^{a,d}	Expected persistence
	0.2h - pH 8 - 40°C^{c} 1.5h - pH 9 - 10°C^{c} 0.5h - pH 9 - 20°C^{c} 0.15h - pH 9 - 30°C^{c}						
Quats	-			-	reasonable within 1 month^{c}		some days to 1 month^{c}
Remaining							
2,2-dithiobisbenzamide						lineair p=1.02 non-lineair p=0.98 ultimate =2.42	
glutaric aldehyde				2.7 h (12h, 1.5E6 OH/cm^{3})^{a}	88% after 5 d	lineair p=1.27 non-lineair p=1.0 ultimate =3.02	
methylene bisthiocyanate	stable - pH - 24°C 21h - pH - 24°C 2.2h - pH - 24°C			2.3 h (12h, 1.5E6 OH/cm^{3})^{a}		lineair p=0.69 non-lineair p=0.76 ultimate =2.91	
sodium hydroxide				76.4 d (12h, 1.5E6 OH/cm^{3})^{a}		lineair p=0.73 non-lineair p=0.92 ultimate =3.1	
Oxidative							
Bromine compounds							
sodium bromide		half-life of free bromium = some minutes; small res.. present for up to some hrs					very short; persistence of free bromium is very short
Chlorine compounds							
sodium hypochlorite		half-life of free chlorine = some minutes; small res. present for up to 24 hrs					very short; persistence of free chlorine is very short
chlorine dioxide	evaporation from water; half-life = 2.4 hrs^{a}						very short
sodium chlorite							
Organic substances							
1-bromo-3-chloro-5,5-dimethyldantoin							

Substance	Hydrolysis-half life	DT50 hydrolysis in days	DT50 water/sed. in days	Photodegradation/ photolysis	Biodegradation	Biodegradation Syracuse[a,d]	Expected persistence
5-oxo-3,4-dichloro-1,2-dithiol							
dazomet						lineair p=0.54 non-lineair p=0.38 ultimate =2.54	
Remaining							
sodium dichloroisocyanurate				3.6 d (12h, 1.5E6 OH/cm^3)[a]		lineair p=0.64 non-lineair p=0.47 ultimate =2.71	
isopropanol	evaporation from water 3.9 d[a]			1.47 d (12h, 1.5E6 OH/cm^3)[a]		lineair p=0.88 non-lineair p=0.96 ultimate =3.23	
sodium hydroxide							very short
hydrogen peroxide				1.34 d (12h, 1.5E6 OH/cm^3)[a]			very short
ozone		half-life of free ozone = some minutes; small res. present for up to 30 min					short persistence

a Boethling et all., 1993

b Tas et all., 1996

c Baltus & Berbee, 1996

d If both p-values >0.5 the substance is readily degradable, ultimate indicates that at 5 degradation took place in hours, at 4 in days, at 3 in weeks, at 2 in months and at 1 longer; hence, ultimate = 3.54 means the the substance is degraded within some days to some weeks.

Table 4.3 Degradability of anti-fouling agents

Substance	Hydrolysis-half-life	DT50 hydrolysis in days	DT50 water/sed. in days	Photolysis	Biodegradation	Biodegradation Syracuse^{a,c}	Expected persistence
Copper							
copper(I)oxide							
copper thiocyanate						thiocyanate is rapidly degraded: lineair p=0.72 non-lineair p=0.90 ultimate = 3.07	
Zinc							
zinc borate							
zinc oxalate						oxalate is readily degraded: lineair p=0.85 non-lineair p=0.95 ultimate = 3.73	
zinc oxide							
barium metaborate							
bitumen	inert, in sea water persistent for 50 years^{b}			highly resistent against sunlight^{b}		non biodegradable^{b}	
Organic substance							
2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine				0.13d calc. (1.5e6OH/cm^{3};12h)^{a}		lineair p=0.87 non-lineair p=0.009 ultimate =2.08	

a Boethling et all., 1993

b HED-sets of various substances

c If both p-values >0.5 the substance is readily degradable, ultimate indicates that at 5 degradation took place in hours, at 4 in days, at 3 in weeks, at 2 in months and at 1 longer; hence, ultimate = 3.54 means the the substance is degraded within some days to some weeks.

Appendix 5

Physical/chemical data

Table 5.1 Physical/chemical data of wood preservatives

Substance	CAS nr	Mol weight	Melting point °C	Solubility (mg/l)	LogKow Syracuse	Vapour tension Pa	Henry coëfficiënt Pa.m^{3}/mol
Arsenic							
arsenic pentoxide	1303-28-2			alc/wat=65.8/ 100 at 20 °C^{a}			
Boron							
boric acid	10043-35-3	61.84^{d}	171^{d}	47.2 g/l (20°C)^{d}	-0.76 (25°C) exp.^{D}		
borax	1303-96-4						
sodium octaborate	?12007-46-4?						
Chromium							
ammonium bichromate	7789-09-5	252.06^{d}	>180^{d}	360 g/l (20°C)^{d}			
potassium bichromate	7778-50-9		390^{d}	49 g/l (0°C)^{d} 115-130 g/l (20°)^{d} 1020 g/l (100°)^{d}			
sodium bichromate	10588-01-9	264.1^{d}	-48-80/356^{d}	very sol in water^{a} 2355 g/l (20°C)^{d} 75-100 vol% (20C)^{d}			
chromium trioxide	1333-82-0		196^{d}	61.7g/100cc (0 °C)^{a} 67.45 g/100cc (100 °C)^{a} 62.5% w/w (20°C)^{d}			
Fluoride							
copper silicofluoride							
potassium bifluoride	7789-29-9						
zinc silicofluoride	16871-71-9						
ammonium bifluoride	1341-49-7	57.04^{d}	126^{d}	630 g/l (20°C)^{d}		100 (20°C)^{d}	
Copper							
copper naphtenate	1338-02-9						
copper (I) oxide	1317-39-1	80^{d}	1235°C^{d}	<0.007 (25°C)^{d}			
copper (II) carbonatehydroxide	12069-69-1						
copper (II) oxide	1317-38-0	143.1^{d}	1226-1326°C^{d}	not soluble^{d}			
copper sulphate	7758-98-7	249^{d}	200^{d}	200 g/l (20°C)^{d}			

Substance	CAS nr	Mol weight	Melting point °C	Solubility (mg/l)	LogKow Syracuse	Vapour tension Pa	Henry coëfficiënt Pa.m^3/mol
Organic substances							
propiconazole	60207-90-1	342.2^c	173^b	110^c	3.5 exp^b 3.65^c	‘1.3 e-4^c	‘1.66 e-7^c
tebuconazole	107534-96-3	307.8^c	105^c	32^c	3.7^c	‘9.6 e-7^c	‘3.8 e-9^c
azaconazole	60207-31-0	300.1^c	100^c	300^c	2.32^b exp 2.36^c	‘5.3 e-7^c	‘2.18 e-10^c
Quats							
didecyldimethylammoniumchloride	7173-51-5				4.66^b		

a Sax, 1989
b Boethling et all., 1993
c Tas et all., 1996
d HED-sets of various substances

Table 5.2 *Physical/chemical data of biocides for cooling water*

Substance	CAS nr	Mol weight	Melting point °C	Solubility (mg/l)	LogKow Syracuse	Vapour tension Pa	Henry coëfficiënt Pa.m^3/mol
Non-oxidative							
Isothiazolines							
5-chloro-2-methyl-4-isothiazolin-3-on	26172-55-4	149.6	54-55		-0.34^b		
Quats							
didecyldimethylammoniumchloride	7173-51-5				4.66^b		
alkyldimethylbenzylammoniumchloride	8001-54-5				5.4^b		
alkyldimethylethylbenzylammoniumchloride	?				6.43^b		
poly[oxyethylene(dimethylimino) ethylene-(dimethylimino-) ethylene dichloride]	31075-24-8	123.5^c	-15^c	1.000^c			....
Bromine compounds							
ß bromo-ß nitrostyrene see bromonitrostyrene	7166-19-0				2.34^b		
2-bromo-2-nitropropane-1,3-diol (bronopol)/ 2-bromo-2-nitro-1,3-propanediol	52-51-7	200^c	130^c	1.000^c	-0.64^b		....
2,2-dibromo-3-nitrilo propionamide	10222-01-2	241.8^c	123^c	1.500^c	1.0^b	'1.3 e+3^c	'8.62 e-2^c
Oxidative							
Bromine compounds							
sodium bromide	7647-15-6	102.9^b	755^d	1116 mg/l 50°C^d	0.36^b	'0.0000010 25°C^d	
Chlorine compounds							
sodium hypochlorite	7681-52-9	74.4^d	-20/-30^d	completely misc.^{d}	-3.42^b	17400-2000 (20°C)^d 2.9 e-6 mm Hg^b	
sodium chlorite	7758-19-2		>170^d	500-800 g/l^d			
chlorine dioxide	10049-04-4	67.5^b	-145^b	1000 g/l (25°C)^b	-3.22^b	1110 mm Hg^b	2.45 e-2 atm.m3/mol^b
Organic substances							
1-bromo-3-chloro-5,5-dimethyldantoin	32718-18-6						
5-oxo-3,4-dichloro-1,2-dithiol							
dazomet	533-74-4	162.28^d	102-105^d	3.6 g/l (20°C)^d	1.4 exp^b	'4.e-4 (20°C)^d	

a Sax, 1989
b Boethling et all., 1993
c Tas et all., 1996
d HED-sets various substances

Table 5.3 Physical/chemical data of anti-fouling agents

Substance	CAS nr	Mol weight	Melting point °C	Solubility (mg/l)	LogKow Syracuse	Vapour tension Pa	Henry coëfficiënt Pa.m^{3}/mol
copper							
copper(I)oxide	1317-39-1	80^{d}	1235°C^{d}	<0.007 (25°C)^{d}			
copperthiocyanzinc							
zinc							
zincborate							
zincoxalate							
zincoxide	1314-13-2	81.37^{d}	1000-1970^{d}	almost insoluble^{a,d} 4-6 ppm Zn (25°C)^{d} 10-300 mg Zn of 100g ZnO/l dissolves^{d}			
barium metaborate							
bitumen	8052-42-4		30-130^{d}	solubility negligible^{d}	>5 calc.^{d}	volatility negligible^{d}	
organic							
2-methylthio-4-t-butyl-amino-6-cyclopropyl-amino-s-triazine	?	253.3^{c}	130^{c}	7^{c}	-0.18 calc.^{b}	'8.8 e-5^{c}	'1.31 e-6^{c}

a Sax, 1989
b Boethling et all., 1993
c Tas et all., 1996
d HED-sets of various substances

Appendix 6

Applied quantities

Table 6.1 Dosage data of wood preservatives

Substance	Dosage curative[a] g/m^2	Dosage saturation[a] kg/m^3	Dosage impregnation[a] kg/m^3
Arsenic			
arsenic pentoxide			
Boron			
boric acid			
borax			
sodium octaborate			
Chromium			
ammonium bichromate			
potassium bichromate			
sodium bichromate			
chromium trioxide			
Fluoride			
copper silicofluoride			
potassium bifluoride			
zincsilicofluoride			
ammoniumbifluoride			
Copper			
copper naphtenate			
copper(I)oxide			
copper(II)carbonate hydroxide			
copper(II)oxide			
coppersulphate			
Organic substances			
azaconazole	12	0.1	0.45
propiconazole	2.88	0.36	0.36
tebuconazole	-	-	0.04
Quats			
didecyldimethylammoniumchloride			

[a] Tas et all., 1996

Table 6.2 Dosage data for biocides for coolingwater

Substance	Dosage in active subst.[b] mg/l	Dosage[a] mg/l
Non-oxidative		
isothiazolines	1-5	
quats	3-50	
poly(oxyethylene-dimethylimino)..)		10
Bromine compounds		
β-bromo-β-nitrostyrene	1-5	
2,2-dibromo-3-nitrilopropionamide	4-10	2.4
2-bromo-2-nitropropane-1,3-diol	1-25	100
Oxidative		
Bromine compounds		
sodium bromide	depend.dosage chlorine. (1:1)	
Chlorine compounds		
sodium hypochlorite	0.1-0.2	
chlorine dioxide		
sodium chlorite		
Organic substances		
1-bromo-3-chloro-5,5-dimethylhydantoin	2-7	
5-oxo-3,4-dichloro-1,2-dithiol		
dazomet		

a Tas et all., 1996

b Baltus & Berbee, 1996

Appendix 7

Classification of toxicity

CLASSIFICATION OF TOXICITY

Aquatic toxicity (classified as used by RIZA)

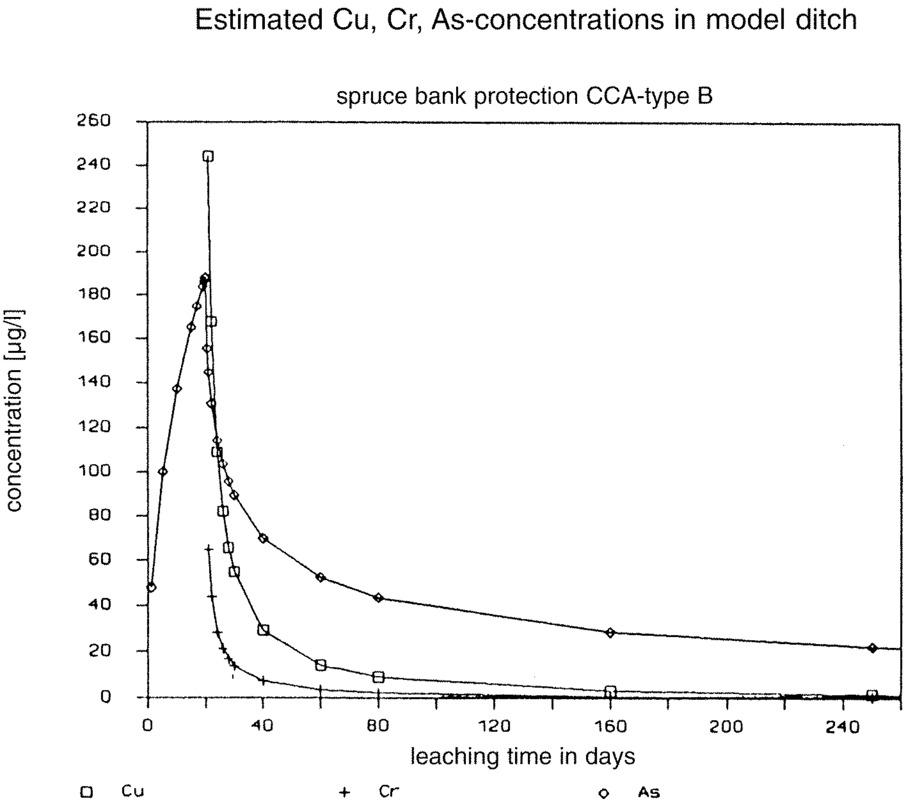
	Acute	Chronic
Highly toxic	<1 mg/l	<0.01 mg/l
Moderately toxic	1-10 mg/l	0.01-0.1 mg/l
Little toxic	10-100 mg/l	0.1-1 mg/l
Very little toxic	>100 mg/l	>1 mg/l

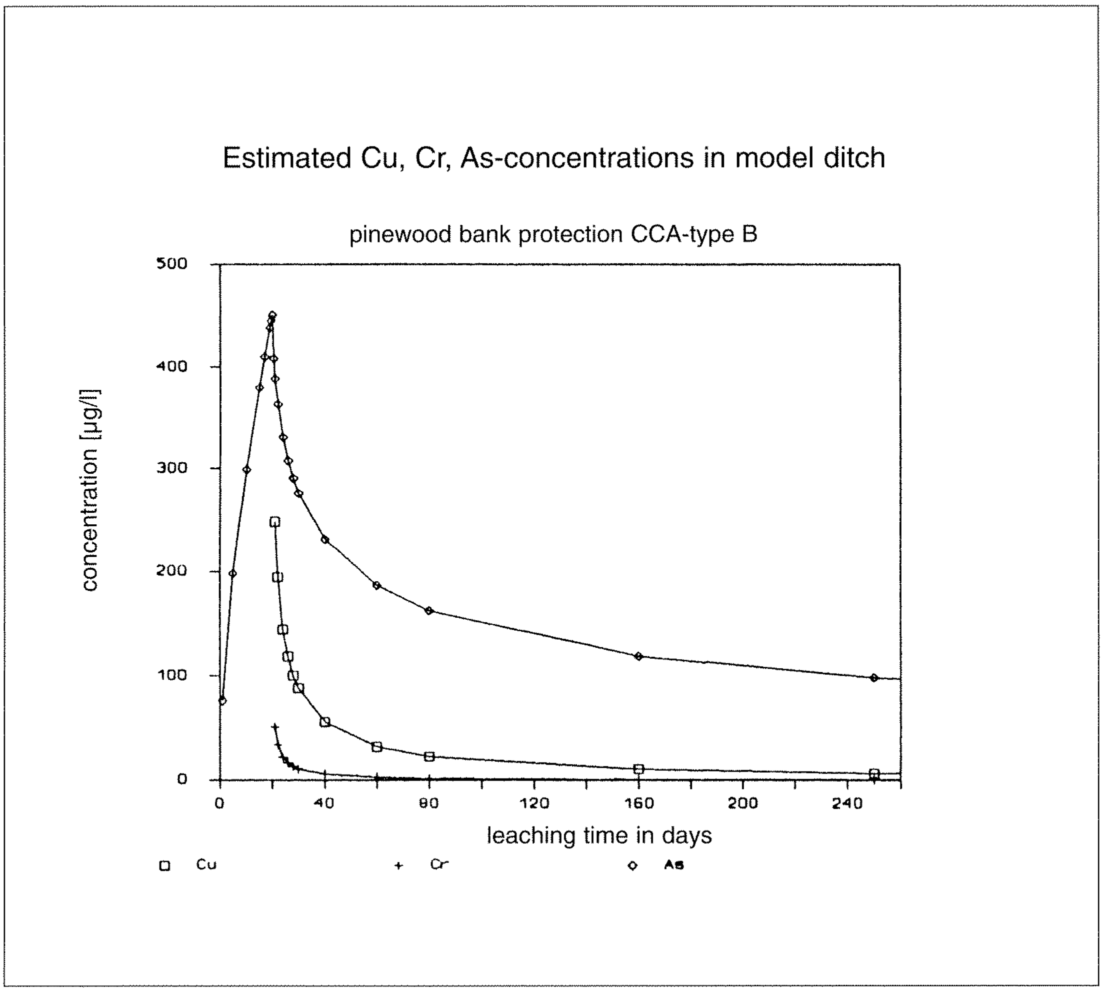
Toxicity (expert judgement)

Highly toxic	<200 mg/kg
Moderately toxic	200-2.000 mg/kg
Little toxic	>2.000 mg/kg

Appendix 8

Leaching from preserved wood


Estimated Cu, Cr, As-concentrations in model ditch
spruce bank protection CCA-type B
concentration [µg/l]
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0
40
80
120
160
200
240
leaching time in days
Cu
Cr
As


Estimated Cu, Cr, As-concentrations in model ditch
pinewood bank protection CCA-type B
concentration [µg/l]
500
400
300
200
100
0
0
40
80
120
160
200
240
leaching time in days
Cu
Cr
As

Colophon

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