Use of Biocides in Evaporative Cooling Systems – Risk Mitigation and Procurement Proposals

Photo credit: DanielChang76/Shutterstock.com

Study author:
Dr. Manfred Klade Technical Office Klade

On behalf of the
Vienna Ombuds Office for Environmental Protection

September 2023

CONTENT

SUMMARY

Problem outline and aim of the study

The climate crisis is causing the cooling demand for buildings and industrial processes to increase significantly. Estimates by the City of Vienna, for example, assume that Vienna's electricity consumption for air conditioning has increased more than tenfold between 1995 and today[1] and will triple again by 2040 to a good 1000 GWh[2] per year.

Open evaporative cooling systems are used for the air conditioning of buildings such as hospitals, large office complexes or data centers as well as in the context of industrial cooling processes and in the commercial sector (e.g. in the automotive, paper, food or pharmaceutical industries). [3] These systems, also known as "open or wet cooling towers", release the heat dissipated from the system into the ambient air through the evaporation of cooling water. If pathogenic germs such as Pseudomonas and especially legionella are present in the cooling water, these are also released into the environment.

Legionella (Legionella pneumophila) are bacteria that prefer to multiply in artificial water systems (water pipes or cooling systems) at temperatures between 25 °C and 45 °C. Inhaling aerosols contaminated with legionella or pseudomonas can lead to severe pneumonia, such as "legionnaires' disease", also known as legionellosis. For this reason, biocides are constantly added to cooling towers during operation, usually in the form of regular shock disinfection.

Nevertheless, evaporative cooling systems or cooling towers are well documented as sources of infection. For example, 19 outbreaks of legionellosis with a death rate of 6% took place in 12 countries over a period of 11 years, which could be attributed to cooling towers. The homes of infected persons were up to 12 km away from the turbines. Legionellosis is a notifiable disease in Austria and is recorded by the Agency for Food Safety (AGES) as the national reference centre. Including an estimated number of unreported cases estimated by experts, it is assumed that there are about 1000 cases per year in Austria [4]. The data presented in AGES show that about 50% of all cases cannot be assigned to a specific source of infection. In 2007, severe cases of legionellosis occurred in Vienna[4] , which were directly associated with an open cooling tower. A report by the control office suggested at the time that there were about 70 locations of cooling towers in Vienna, while a representative of the Austrian Refrigeration and Air Conditioning Association (ÖKKV) estimated the number of open cooling towers in Vienna at around 1,000 in 2007.

In Germany, with a similar starting point, the mandatory registration of evaporative cooling systems in a separate cadastre was introduced in 2017 in order to create more transparency[5] . The keeping of a company diary is also required there. Among other things, the results of microbiological controls and the use of biocides must be documented. Figures from the city of Düsseldorf show that with the

---

[1] Vienna Energy Report 2014 Energy Consumption in Vienna - Energy Reports

[2] waerme-und-kaelte-2040.pdf (wien.gv.at) Chapter 3

[3] Areas of application are: foundries, semiconductor industry, refineries, chemical industry, energy producers, textile industry, paper manufacturers and printers, packaging industry, building material manufacturers, glass industry, ice rinks, airports and cold stores.

[4] https://www.stadtrechnungshof.wien.at/berichte/2008/lang/03-02-KA-VI-15-1-8.pdf

[5] 42nd Federal Immission Control Ordinance (42nd BImSchV)

expiry of the reporting deadline in 2018, the number of known and thus controllable cooling towers increased more than twentyfold.

In Austria, there are still no regulations that would be comparable to the German 42nd Federal Immission Control Ordinance. The number of domestic evaporative cooling systems can therefore only be estimated.

Part of the biocide-containing cooling water is regularly discharged into the sewer. The "General Wastewater Emission Ordinance", the "Wastewater Emission Ordinance for Refrigeration Systems and Steam Generators" and the "Indirect Discharger Ordinance" are relevant for the approval under water law in the context of the construction and operation of evaporative cooling systems. There is an obligation to report to the sewer operator. In practice, however, apparently only a fraction of the systems are reported and there is no obligation on the part of the sewer operator to actively research them.

In Vienna, evaporative cooling systems are approved at district level by decision of the respective municipal district office, the building police or the department for social affairs, social and health law or for trade law, data protection and civil status, including the MA36 (commercial engineering), the MA15 (health authority) and other departments. The complexity of responsibilities has so far prevented data from converging in one place.

The biocidal active substances discharged into the Vienna Canal from cooling towers and their actual quantity are therefore insufficiently known. The Vienna Environmental Ombudsman Board heads the disinfection working group as part of the ecological procurement programme ÖkoKauf Wien and commissioned this study to bring this environmentally relevant topic more into the public eye.

The present study primarily focuses on the biocides used in refrigeration systems and their potential hazards for health and the environment. It identifies the most frequently used active ingredients and estimates the quantities used as well as possible emissions. Based on the available data from the European Chemicals Agency ECHA, their hazard potential for the environment and health was collected and compared.

As part of a series of [6] interviews with experts and responsible authorities, the legal framework for the operation of evaporative cooling systems in Austria and Germany was also surveyed, as well as the advantages and disadvantages of individual biocidal active ingredients in practical use.

The following example from the interview part of the study illustrates that economic and ecological optimization can complement each other: For example, a cooling tower in a Viennese office complex caused an annual use of chemicals worth 95,000 euros. These were salted into the canal together with 50,000 m³ of water per year. After a successful conversion of disinfection to an ozone system in 2021, practically no chemicals are discharged into the wastewater, as both the use of wastewater-relevant biocides and corrosion inhibitors can be dispensed with. (See chapter Ozone)

In addition to a survey of the current situation, the aim of the study is to develop recommendations on how negative effects of biocide use in evaporative cooling systems can be minimised in the best possible way.

---

[6] Information on interviewees or main topics can be found in the chapter "Interviews", statements are assigned to chapters according to their content.

Results

The following insights could be gained:

The respective effectiveness of biocides for legionella control or other pathogenic germs such as Pseudomonas aeruginosa is strongly dependent on the technical and chemical conditions in the respective cooling system. A simple, comparative assessment of the effectiveness of individual biocidal active substances, as well as the concrete effects on employee protection and the environment, does not seem to make much sense without taking into account the operating conditions and maintenance status of the plant.

The following general recommendations emerge from the synopsis of the inherent, hazardous properties of frequently used biocides with the practical experiences of the interviewees:

1. Good structural design and sufficient maintenance of evaporative cooling systems are essential: Even though manufacturers of biocidal products sometimes convey to potential users that their products guarantee largely maintenance-free operation, one thing is certain: Regular maintenance, calibration and measurement of important parameters of the cooling system is essential to keep microbiological load and the formation of biofilms low. In open systems, dirt particles from the air are also continuously introduced into the cooling water and serve as nutrients for microbes. High-quality, regularly cleaned filter systems, such as full-flow filters, can improve hygienic safety under suitable conditions. The interviews have shown that microbiological derailments, especially in small plants that are maintained by in-house, poorly trained staff, are unfortunately not uncommon. The structural design should also enable a uniform flow through all plant components so that the biocidal active ingredients can be distributed throughout the system in sufficient concentration.

2. Less chemistry is more: In addition to the biocides already mentioned, chemicals are also added to circulating cooling water for pH value stabilization, as well as against (limescale) deposits and corrosion. In the safety data sheets of the mixtures offered, only those ingredients are specified that must be named due to their hazardous properties. When added, unwanted interactions with the biocidal active ingredients can occur. In addition, in addition to specific advantages, all biocidal active ingredients also have various disadvantages, such as a strong loss of effectiveness in the event of pH value fluctuations, gaps in the effectiveness of certain germs or biofilms, risks of germs developing resistance or a high volatility during evaporation in the cooling tower (so-called stripping). For this reason, biocidal products for cooling water disinfection are often on the market that contain several biocidal active ingredients. Such products in particular carry an increased risk of entering into an unwanted interaction with the other added chemicals, which can have a negative impact on the hygiene and material protection of the surfaces in the cooling system. It is therefore recommended by experienced practitioners not to lower the pH value of the cooling water below 8, to use as few environmentally toxic corrosion inhibitors as possible and not to use several biocides at the same time. In some systems, long-term operation is possible with only one active ingredient – often based on chlorine. Others require the addition of non-oxidizing biocides at certain intervals, for example at temperatures above 30°C, which have greater stability and thus a long stay in the cooling water. However, with high cooling capacities with a daily change of the entire cooling water, this is by no means necessary and expedient.

3. The research carried out as part of this study has shown that probably only 10 - 20% of the evaporative cooling systems know the location. Microbiological tests by authorities hardly take place and the awareness of the operators of the danger that these plants can pose to the health of the residents can be classified as low among some of the operators. In addition, environmental aspects play practically no role in the selection of the biocides used. From a legal point of view, the present study therefore leads to the recommendation to align the legal requirements for the operation of evaporative cooling systems in Austria with those of Germany[7]. The latter prescribe the mandatory reporting of evaporative cooling systems in a cadastre and the keeping of an operating diary nationwide. Such a measure would bring evaporative cooling systems out of anonymity. All plants would have to keep records of operation and results from the microbiological controls. In the event of outbreaks of legionellosis, this would offer better control of surrounding cooling towers and would prevent microbiological derailments overall. In Germany, maintenance by experienced and well-trained external personnel has increased due to the entry into force of the 42nd BImschV. A corresponding legal regulation could also favor the systemic approach of chemical leasing models . This would result in a relevant ecological and economic efficiency potential, because the changed nature of the business model would mean that savings in the use of biocides would be in the mutual interest of the person responsible for the plant and the external service provider. If the biocides used (and possibly other, hazardous chemicals) were also to be entered in an Austrian online register for evaporative cooling systems, Austria would also have an overview of the quantity and type of biocidal active ingredients used and could influence the use in a more targeted manner in the direction of more environmental and employee protection.

4. It should be noted that the cooling technology of the future, at least on the part of the City of Vienna, is not seen in evaporative cooling systems that additionally warm up the outdoor space during hot periods. Rather, cooling technologies should be used more in the future, in which the waste heat is fed into a network or stored in the ground so that it can be used immediately or at a later date.

Conclusions for commonly used biocides

Only biocidal active substances that have been registered with the European Chemicals Agency ECHA for approval may be used. Of the[8] 64 active ingredients currently in the EU approval procedure for the corresponding product type 11, only 5 have currently been approved[9.10] The interviews showed that good experiences have been made especially with the use of chlorine dioxide and mixtures of hypochlorous acid and sodium hypochlorite produced electrolytically from sodium chloride. For large plants in Germany and Switzerland, the use of monochloramine was also described as a new trend

---

[7] Laws into which a corresponding ordinance authorisation could be integrated in Austria would be, for example, the Epidemics Act or the Air Pollution Control Act.

[8] "Protective agents for liquids in cooling and process systems"

[9] CMIT/MIT, peracetic acid and glutaraldehyde as well as the active ingredients MIT and PHMB, which are less important for cooling towers, are approved.

[10] See Annex Table 1

due to its many advantages. To date, no approval has been granted for any of the above-mentioned procedures. Of the non-oxidizing active ingredients, the already approved CMIT/MIT is used, often in combination with bromine compounds such as bronopol.

Based on a detailed analysis, the study recommends that the use of the biocidal active ingredients CMIT/MIT, DBNPA, glutaraldehyde and active chlorine from chlorine gas or sodium hypochlorite be kept to a minimum or replaced by alternatives:

CMIT/MIT has already been approved by ECHA for product type 11. However, splashes of the application solutions can lead to blindness and poorly healing wounds. Due to the high sensitizing potential, early retirements are known. It has a high aquatic toxicity and is poorly degradable.

The expert interviews also showed that the conditions required by ECHA for the safe use of CMIT/MIT are not always met in practice. Since the active ingredient is particularly often used in small plants, maintenance personnel are not always aware of the dangers of CMIT/MIT, especially when untrained personnel handle it in cases of vacation or illness.

In addition, the degradation rates quoted by manufacturers do not correspond to the real conditions. The active ingredient often behaves more stably than assumed. In Austria, the Wastewater Emission Ordinance for cooling systems prohibits the discharge of isothiazoles into the sewer. Despite discussions with the competent authorities, it could not be determined whether this ban also includes CMIT/MIT, and thus isothiazolinones.

In Austria, CMIT/MIT measurements are not carried out either at wastewater discharge or in sewers, in the inlet and outlet of sewage treatment plants or in surface waters. The actual pollution of water bodies is therefore unknown. According to this study, measurements in order to be able to assess the current water pollution with CMIT/MIT in Austria, especially in Vienna, should be carried out as part of a priority programme on inputs of biocides from cooling plants. Despite the approval by ECHA, the information collected in the course of this study suggests that the use of CMIT/MIT should be avoided as far as possible.

DBNPA is sensitizing and shows chronic toxicity in animal experiments, the target organ is the respiratory tract. DBNPA is believed to have an endocrine effect on humans and non-target organisms caused by the degradation product bromide. DBNPA therefore fulfils the criteria for substitution under Article 5 of the Biocidal Products Regulation. Due to the health hazards such as skin sensitization and chronic toxicity for the respiratory tract, as well as a controversially discussed endocrine hazard potential due to the secondary or degradation product bromide, its use is not recommended. DBNPA is preferred as a non-oxidizing biocide in smaller plants.

Glutaraldehyde is classified as "life-threatening if inhaled" as well as skin and respiratory sensitizing and has a high hazard potential from the point of view of employee protection. Due to its properties as an inhalation allergen, the active substance meets the criteria of Article 10 of the Biocidal Products Regulation. It is therefore only authorised for a limited period of time and is classified by ECHA as an "active substance to be replaced".

Active chlorine from chlorine gas or sodium hypochlorite (and the alternatives: active chlorine from sodium chloride by electrolysis and chlorine dioxide)

The active ingredient "active chlorine" is present in a pH-dependent balance of hypochlorous acid, chlorine and sodium hypochlorite. There are several methods of producing active chlorine in cooling water from starting products. It is commonly produced from chlorine gas, bleach/sodium hypochlorite and table salt by electrolysis. The hazard potential of "active chlorine" results proportionately from the chlorine gas present in equilibrium, or the chlorine bleach solution (sodium hypochlorite). Chlorine bleach is corrosive (H314), chlorine gas is life-threatening if inhaled (H330). A sensitizing, mutagenic, carcinogenic, toxic to reproduction or chronic toxic effect is not assumed, so that only a locally irritating or corrosive effect can be assumed for the aqueous solution. The effects on the aquatic environment are determined by the high reactivity of active chlorine with organic matter. For active chlorine itself, rapid degradation is assumed. The formation of (organic) derivatives is influenced by several factors: the composition of the cooling water, pH value, biocide dosage, operating temperature or residence time. As far as the sum parameter AOX, which describes the extent of (halogenated) derivatives, is concerned, interview statements indicate that AOX formation is comparatively low or better controllable in the active ingredient/manufacturing combination "active chlorine produced from sodium chloride by electrolysis". In addition, this form of application does not come into contact with concentrates and thus human exposure to hazardous substances is low. Chlorine gas and sodium hypochlorite are mainly used because of the lower costs (e.g. compared to chlorine dioxide).

In view of the dangers to the environment (high AOX pollution) and to worker protection (chlorine gas exposure), processes in which active chlorine is produced from sodium chloride by electrolysis and the use of chlorine dioxide are preferable.

Hydrogen peroxide and ozone as alternatives

In Switzerland and Germany, catalyzed hydrogen peroxide (mostly with silver) is used more widely. For this active ingredient, the formation of the enzyme catalase by microorganisms and the associated reduction in effectiveness is an issue. In Austria, hardly any plants using hydrogen peroxide could be found during the research. According to interview statements, ozone is also very rarely used in Austria. An exception is the promising deployment in the Vienna Twin Tower. Holland and Sweden have more experience with the use of ozone, according to interview statements. From a water ecology point of view, the use of hydrogen peroxide with very low silver use and ozone would be welcome due to the rapid decomposition without wastewater-relevant by-products.

Overview tables for drug evaluation

The following tables provide an overview of classifications and the assessment of frequently used biocidal active substances derived from them. The following color code ("ABC categorization") is used:

RED (very high concern): The colour code indicates proven mutagenic, carcinogenic, toxic for reproduction, chronic toxic, sensitising or highly toxic to the environment. Even in low concentrations, these properties can damage health or kill aquatic life.

YELLOW (significant concern): This colour code indicates a potential hazard for health and the aquatic environment. This applies, for example, to acutely toxic or environmentally toxic properties. Data gaps are indicated by a question mark and rated YELLOW for certain hazards (except irritating or corrosive properties).

WHITE (low concern): This colour code indicates that existing hazardous properties (e.g. corrosive) can be controlled sufficiently well by protective equipment. If hazards are largely ruled out, this circumstance is indicated with the color code WHITE

The color code is assigned based on H-phrases (or relevant data gaps) in 6 hazard categories. An explanation of the ABC categorization can be found in the section "Detailed analysis" and in the appendix, all active ingredient evaluations are contained in Tables 1 and 2 in the appendix.

Wirkstoff	Eintrag in ECHA	CAS	Akute Giftigkeit	Reiz-, Ätzwirkung	Sensibilisierung	Kanzerogene, mutagene, reproduktionstoxische und chronisch toxische Eigenschaften	Gewässertoxizität (akut)	Gewässertoxizität (chronisch)	Bewertungsrelevant
Monochloramin (erzeugt aus…)	Aus Ammoniak und einer Chlorquelle erzeugtes Monochloramin	-	?	?	?	?	?	?	Unzureichende Datenlage; Relevantes Ausgangsprodukt: Monochloramin (chronisch toxisch bei Inhalation)
	Aus Ammoniumcarbamat und einer Chlorquelle erzeugtes Monochloramin	-	?	?	?	?	?	?	
	Aus Ammoniumchlorid und einer Chlorquelle erzeugtes Monochloramin	-	?	?	?	?	?	?	
	Monochloramin, hergestellt aus Ammoniumsulfat und einer Chlorquelle	-	?	?	?	?	?	?	
Chlordioxid (hergestellt aus…)	Chlordioxid	10049-04-4	H330	H314, H318	-	-	H400 (M10)	H411	Chlordioxid: Giftig bei Inhalation; Relevantes Reaktions- bzw. Abbauprodukt: Chlorit (Verdacht auf chronische Toxizität)
	Chlordioxid, hergestellt aus Natriumchlorat und Wasserstoffperoxid in Gegenwart einer starken Säure	-	?	?	?	?	?	?	
	Chlordioxid, hergestellt aus Natriumchlorit durch Säuerung	-	?	?	?	?	?	?	
	Chlordioxid, hergestellt aus Natriumchlorit durch Elektrolyse	-	?	?	?	?	?	?	
	Chlordioxid, hergestellt aus Natriumchlorit durch Oxidation	-	?	?	?	?	?	?	
Aktivchlor (hergestellt aus…)	Aktivchlor, hergestellt aus Natriumchlorid durch Elektrolyse	-	EUH031, H331	H314	-	-	H400 (M100)	H410 (M1)	Ökotoxische Folgeprodukte
	Aktivchlor, freigesetzt aus Chlor	7782-50-5	H330	H315, H319, H335	-	-	H400 (M100)	-	Potenzielle Gefährdung bei der Anwendung (Chlorgas, Natriumhypochlorit); ökotoxische Folgeprodukte
	Aktivchlor, freigesetzt aus Natriumhypochlorit	7681-52-9	EUH031	H314, H318	-	-	H400 (M10)	H410 (M1)	
Aktivbrom (hergestellt aus…)	Aktivbrom, hergestellt aus Bromchlorid	-	?	?	?	?	?	?	Unzureichende Datenlage; relevantes Ausgangs- bzw. Folgeprodukt: Natriumbromid (reproduktionstoxisch & chronisch toxisch); ökotoxische Folgeprodukte
	Aktivbrom, hergestellt aus Hypobromsäure und Harnstoff sowie Bromharnstoff	-	?	?	?	?	?	?	
	Aktivbrom, hergestellt aus Natriumbromid und Calciumhypochlorit	-	?	?	?	?	?	?	
	Aktivbrom, hergestellt aus Natriumbromid und Chlor	-	?	?	?	?	?	?	
	Aktivbrom, hergestellt aus Natriumbromid und Natriumhypochlorit	-	?	?	?	?	?	?	
	Aktivbrom, hergestellt aus Natriumbromid durch Elektrolyse	-	?	?	?	?	?	?	
	Aktivbrom, hergestellt aus Natriumhypobromit, N-Bromsulfamat und Sulfaminsäure	-	?	?	?	?	?	?	

Wirkstoff	Eintrag in ECHA	CAS	Akute Giftigkeit	Reiz-, Ätzwirkung	Sensibilisierung	Kanzerogene, mutagene, reproduktionstoxische und chronisch toxische Eigenschaften	Gewässertoxizität (akut)	Gewässertoxizität (chronisch)	Bewertungsrelevant
BCDMH	Bromchlor-5,5-dimethylimidazolidin-2,4-dion (BCDMH/Bromchlordimethylhydantoin)	32718-18-6	H302	H314	H317	?	H400 (M?)	H410 (M?)	als sensibilisierend eingestuft, ökotoxische Folgeprodukte
DBNPA	2,2-Dibrom-2-cyanacetamid (DBNPA)	10222-01-2	H301, H330	H315, H318	H317	H372 (Atemtrakt)	H400 (M1)	H410 (M1)	als sensibilisierend und chronisch toxisch eingestuft
Bronopol	2-Brom-2-nitropropan-1,3-diol (Bronopol)	52-51-7	H301, H312, H331	H315, H318, H335	-	-	H400 (M10)	H410 (M1)	Hinweise auf hautsensibilisierendes Potenzial und die Bildung persistenter Folgeprodukte
CMIT/MIT	Gemisch aus 5-Chlor-2-methyl-2H-isothiazol-3-on (Einecs 247-500-7) und 2-Methyl-2H-isothiazol-3-on (Einecs 220-239-6) (Gemisch aus CMIT/MIT)	55965-84-9	H301, H310, H330	EUH071, H314, H318	H317	-	H400 (M100)	H410 (M100)	Hohe akute Toxizität, hautsensibilisierend; hohe aquatische Toxizität
Wasserstoffperoxid (Zusatz von Silber)	Wasserstoffperoxid	7722-84-1	H302, H332	H314	-	-	-	-	Lokal reizende Eigenschaften
	Silber (Pulver)	7440-22-4	-	-	-	?	H400 (M10)	H410 (M10)	Eintrag eines persistenten Stoffes in die Umwelt
Ozon	Ozon	10028-15-6	H330	H314, H318, EUH071	-	H341, H351, H372 (Atemtrakt)	H400 (M100)	H410 (M1)	Hohe akute Toxizität, Verdacht auf mutagene, kanzerogene und chronisch toxische Wirkung
Peressigsäure	Peressigsäure	79-21-0	H301, H310, H330	EUH071, H314	-	-	H400 (M10)	H410 (M100)	Hohe akute und aquatische Toxizität
Benzalkoniumchloride (QAV)	Alkyl (C12-16) dimethylbenzyl ammoniumchlorid (ADBAC/BKC (C12-C16))	68424-85-1	H302	H314, H318	-	-	H400 (M10)	H410 (M1)	Hinweise, das Benzalkoniumchloride nicht leicht abbaubar sind, in der aquatischen Umwelt an Sedimentent adsorbieren bzw. im anaeroben Milieu persistieren.
	Alkyl (C12-18) dimethylbenzyl ammoniumchlorid (ADBAC (C12-C18))	68391-01-5	H302, H312	H314, H318	?	?	H400 (M?)	H410 (M?)	
	Alkyl (C12-14) dimethyl(ethylbenzyl) ammoniumchlorid (ADBAC (C12-C14))	85409-23-0	H302	H314, H318	-	-	H400 (M10)	H410 (M1)	
	Alkyl (C12-14) dimethylbenzylammoniumchlorid (ADEBAC (C12-C14))	85409-22-9	H302	H314, H318	?	?	H400 (M?)	H410 (M?)	
Glutaraldehyd	Glutaraldehyd	111-30-8	H301, H330	H314, EUH071	H317, H334	-	H400 (M1)	H411	Hohe akute Giftigkeit, sensibilisierend für Haut und Atemwege

Comments on statements of the study in a very dynamic environment

As the implementation of the above-mentioned Regulations – and in particular the EU Biocidal Products Regulation – has not been completed, the data and classifications used in this report are provisional. New data from the ongoing approval procedures can quickly lead to the fact that assessments made in this study are no longer up-to-date. This circumstance must be taken into account when interpreting the assessments made in the report. At the time of writing the report (November 2022), the status quo is as follows: Of the 64 active substances in the EU approval process[11] , 5 are approved for product type 11, namely glutaraldehyde, CMIT/MIT, peracetic acid, MIT and PHMB. If active substances are approved for other types of products or if approval is imminent, corresponding active ingredient reports are used to assess hazards. This applies to the active ingredients active chlorine (produced or released from...) and hydrogen peroxide.

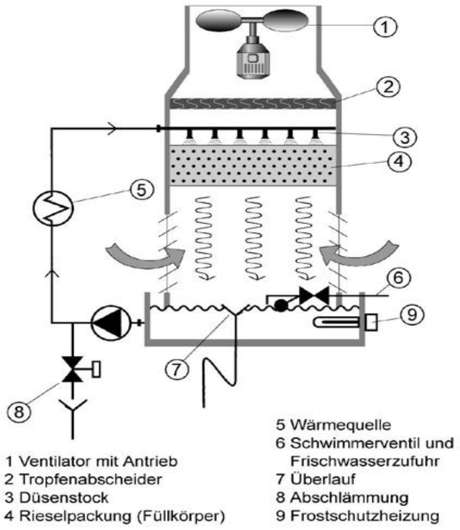
At the present time, the approval procedure has not been completed for the following frequently used active ingredients or groups of active ingredients: DBNPA, active bromine (produced or produced from...), benzalkonium chlorides, BCDMH, bronopol, chlorine dioxide, silver, ozone. The researched classifications of the respective active substances could still be supplemented as part of the approval procedure and the approval is not secured. Currently, however, the active ingredients mentioned are established or common "basic active ingredients" for cooling water conditioning in practice. In addition, authorisation can only be refused if exclusion criteria according to Article 5 of the Biocidal Products Regulation apply: these are proven CMR properties, endocrine efficacy or criteria for persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB). For example, the endocrine efficacy of the active substances DBNPA and peracetic acid is still pending.

---

[11] See Annex Table 1

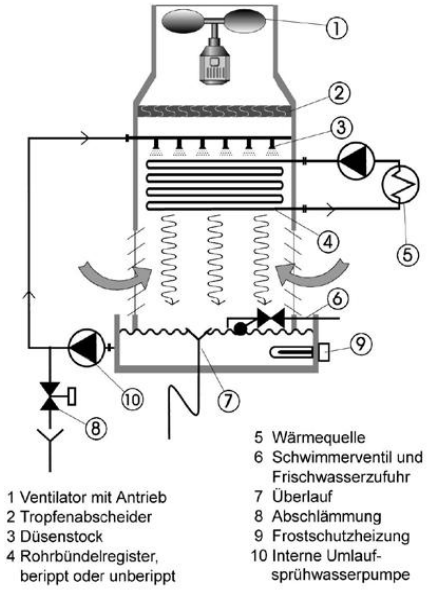
EVAPORATIVE COOLING SYSTEMS

Evaporative cooling systems are operated "open", "closed" or "hybrid", with the distinction referring to the coolant circuit. In an open system, the coolant water comes into direct contact with the ambient air. This is the most effective way to transfer heat, as there is no additional transformer involved between air and water. On the other hand, the cooling tower acts like an air washer and dirt particles remain in the water:



Evaporative cooling system with open circuit [1]

In a closed system, the heat transfer medium and cooling circuit are separated. Closed evaporative cooling systems have an internal cooling water circuit or spray circuit. The advantage of the closed system is the better controllability of the cooling water due to lower cooling water volume and shorter, hardly branched pipelines for the cooling water flow:



Closed-circuit evaporative cooling system [1]

In addition, a combination of an open and a closed system ("hybrid system") is common. Hybrid systems can be operated "dry" at low outside temperatures. Dry coolers are used to cover the base load and an evaporative cooling system is only switched on during peak loads, when the cooling demand is particularly high or the cooling capacity of the dry cooling system is too low [3]. In this case, the open circuit is emptied and the closed circuit is cooled only with air. In dry driving with spraying (adiabaticism), the intake air is cooled down by fine atomization of water in front of the radiator. The performance of the dry cooler is slightly improved by spraying: In open systems or in the open part of hybrid systems, biocides, hardness stabilizers, corrosion inhibitors and dispersants are usually added. For a closed system, usually only corrosion inhibitors and dispersants are used, biocides are needed less frequently.

Due to the evaporation of cooling water, chemical, mineral and microbiological components accumulate in the cooling tower basin. This enrichment is reset by regular blowdown or "desalination". This means that thickened circulating water is drained into the sewer and clean additional water is replenished. The discharge of the chemicals used for cooling tower conditioning pollutes wastewater treatment plants and receiving waters with potentially adverse effects on the aquatic ecosystem.

If the cooling water is not treated with biocides, microorganisms can multiply and form biofilms in a short time. There are several reasons to prevent the proliferation of microorganisms or the formation of biofilms:

- Biofilms reduce the effectiveness of the heat exchanger. For example, a 1 mm thick layer of biofilm reduces the cooling capacity by 30%.
- Certain microorganisms cause corrosion through acid formation.
- Legionella (or Pseudomonas) can enter the environment from the plant as dangerous aerosols and cause serious infections.

The latter circumstance is referred to in this report as the "legionella problem" and its aspects are addressed. From the point of view of the legionella problem, both open and closed systems meet the requirements of a possible hazard, even if biocides are less frequently needed in closed systems.

LEGIONELLA PROBLEM

Legionella are widespread bacteria in nature, occur naturally in groundwater, surface water and moist soil and can also enter drinking water in low concentrations. In poorly designed drinking water heating systems, poorly insulated cold water systems, poorly maintained pool baths, cooling towers and similar systems, legionella can multiply in biofilms at temperatures between 25 and 45 °C and stagnant water. Legionella only die quickly at temperatures above 60 °C. Drinking water contaminated with legionella does not pose a health risk. However, this occurs when water containing legionella is inhaled as an aerosol. Inhalation of aerosols contaminated with Legionella can lead to severe pneumonia ("Legionnaires' disease"), and the case mortality rate varies between 4 and 14 percent. Legionella is one of the most dangerous pathogens of pneumonia. In 2016, 161 cases of Legionnaires' disease were registered by the national reference centre of AGES in Austria. Between 2016 and 2021, the reported cases increased almost continuously and for 2021, AGES reports 278 cases [4]. It can be assumed that the number of unreported cases is high and that more than 1000 cases of Legionnaires' disease occur in Austria every year.

Sources of infection in Austria

Since Legionnaires' disease is notifiable in Austria, data from the national reference centre of AGES is collected in (annual) reports [5]. Potential sources of infection are:

- nosocomial or due to a stay in a hospital
- Travel-associated
- Outpatient, i.e. in a private or professional environment

The 2018 annual report lists 1838 cases for the period 1996 to 2017. Of these, 158 cases (8.6%) are associated with health care facilities, 503 cases (27.4%) are travel-associated and 1177 cases (64%) are acquired on an outpatient basis. The latter contain a significant proportion (1005) that is shown as "presumably acquired on an outpatient basis" and is not assigned to a specific source of infection[12]. Thus, the actual source of infection is unknown in about 50% of all cases.

Cooling towers as a source of infection

Introduced into the evaporative cooling system with the replenishment of cooling water, legionella can multiply strongly there in a short time. Since legionella as a pathogen is only relevant when inhaled, the hazard arises primarily from the discharge of cooling water containing legionella in the form of aerosols. Due to the widespread spread of aerosols in cooling water clouds, the number of potentially affected people is high in any case. In a review, the outbreaks of legionellosis caused by cooling towers were systematically documented and evaluated [6]: In 12 countries, 19 outbreaks of legionellosis were recorded over a period of 11 years, with 1609 confirmed infections and an average death rate of 6%. Legionella pneumophila of serogroup 1 was by far the most frequently identified as a pathogenic germ. In 10 outbreaks, a temporal relationship with poor maintenance of cooling systems is reported. This refers to suboptimal disinfection measures, high-pressure cleaning or a restart after maintenance work. The legionella concentrations in the cooling water varied between 103 and 1010 colony-forming units per litre. The majority of the eruptions took place in the warm season and in humid weather conditions. The places of residence of the infected persons were up to 12 km away from the cooling towers. Between 2007 and 2009, AUVA sampled "wet" cooling towers in 24 companies throughout Austria and tested them for legionella. Legionella was found in 57% of the samples, 22% of which were highly contaminated. The use of biocides is an important parameter for the reduction of Legionella in cooling towers: All samples with high bacterial counts of Legionella, i.e. more than 1000 CFU per 100 ml, had in common that no biocide had been added to the cooling tower according to the questionnaire evaluation. In the study, the authors emphasise the great importance of regular investigations and analyses of process water in order to ensure healthy workplaces [7].

As far as the regulatory measures to reduce the risk of legionella in evaporative cooling systems are concerned, there is a considerable difference between Austria and Germany. While in Germany, the 42nd Federal Immission Control Ordinance (42nd BImSchV) is a central set of rules that sets out the immission control requirements for evaporative cooling systems, there is no comparable regulation in Austria. This point is addressed in the chapter "Legal requirements".

The following statements on the legionella problem can be found in an interview that are relevant for working with evaporative cooling systems and legionella problems (Inwatec GmbH: Interview 8):

- Legionella needs a longer contact time with the biocide to inactivate than many other bacteria.
- In the case of legionella, immunization is not possible or only possible to a very limited extent. There is a high number of unreported cases. The mild form (Pontiac fever) is often not recognized.

---

[12] The sources of infection listed in the document are: workplace, car wash, bath water from baths, potting soil, leisure facility, prison, household, barracks, cooling tower, drinking water heating system of baths. The source of infection "cooling tower" is assigned 14 cases.

- In Germany, a total of 30,000 to 40,000 cases per year is assumed, with the more severe form of the course of the case of 3,000 to 4,000 cases with several hundred to almost four-digit death rates. The disease must be reported to the Robert Koch Institute.

SEWAGE

In evaporative cooling systems, a number of chemicals are used for the purpose of cooling water conditioning, which are used as such or as degradation products in sewers, sewage treatment plants or wastewater treatment plants. receiving waters. In the chapter "Cooling Water Conditioning", literature sources ([1], [8], [9], [10], [11], [12], [13]) are evaluated with regard to biocides, dispersants, hardness stabilizers and corrosion inhibitors. There are only a few sources of material loads from evaporative cooling systems. Gartiser & Ulrich cite an annual consumption of 4100 t of oxidative biocides (chlorine, chlorine releasers, BCDMH, hydrogen peroxide) and 125 t of non-oxidative biocides (isothiazolinones, DBNPA, QAV) for Germany [12]. The study also addresses the genetic and ecotoxicity of cooling water: In cooling water samples from 7 farms, a genotoxic effect was found in one sample, which is explained by the presence of isothiazolinones and bronopol. In a Dutch study cited in [12], the cooling water of 14 companies was examined and a correlation between the concentration of the active ingredient and the ecotoxicity of cooling water samples was determined. In general, the cooling waters treated with isothiazolinone, DBNPA, β-bromine, β-nitrostyrene and methylene bisthiocyanate showed higher toxicities than the oxidative biocides sodium hypochlorite and ozone. The extent of the overall environmental impact of biocides is the subject of a publication by the German Federal Environment Agency [3]: Depending on possible entry pathways into water bodies and sediments, suspected substances are identified on the basis of a prioritization concept[13] and sampling and measurements are recommended. The study also mentions active substances of product type 11[14] such as the isothiazoninon derivatives BIT, MIT, OIT as well as the mixture CMIT/MIT as well as quaternary ammonium compounds (QAV). The substances mentioned should be examined in accordance with the estimated emissions, the ecological effect and the behaviour in the environment in the effluents of sewage treatment plants as well as in urban separate sewerage systems[15]. The following relevant statements can be found in the interviews regarding wastewater and discharge into the sewer system:

- At the operator of the Vienna sewer system and in the Vienna sewage treatment plant, no CMIT/MIT measurements are currently being carried out (Wien Kanal: Interview 1).
- Only annual loads of substances imposed by decision and priority substances of the EU Water Framework Directive are entered into the Emission Register for Surface Water Bodies (Emission Register Ordinance Federal Law Gazette II 207/2017) of the Federal Ministry of Agriculture, Forestry, Regions and Water Management. So there is currently no data basis to assess the pollution of our waters with CMIT/MIT (Federal Ministry of Agriculture, Forestry, Regions and Tourism: Interview 2).

---

[13] Criteria of the prioritisation concept are: emission quantity, ecological impact as well as input and behaviour in environmental compartments

[14] Annex V of the Biocidal Products Regulation, which regulates the authorisation of biocides in the EU, classifies biocidal products into 22 product types. Product type 11 covers protective agents for liquids in cooling and process systems.

[15] The status of the monitoring or whether such a monitoring is planned could not be found out at the time of preparation of the present report.

- Due to the high stability in the cooling system (especially with decreasing pH value and increasing water hardness), the highly ecotoxic active ingredient CMIT/MIT can lead to a strong concentration and the half-life can be several days with a strong increase in toxicity (fluorescent bacterial toxicity, GL value)(see also: Detailed analysis of CMIT/MIT) (Inwatec GmbH: (Interview 8)

EMPLOYEE PROTECTION

In order to prevent work-related health hazards, the present study includes the inherent properties of substances that are potentially detrimental to human health – in particular the acutely toxic, allergenic, mutagenic, reprotoxic, carcinogenic and chronically toxic hazard potential – in the assessment of the biocides. Insofar as cooling systems and their process waters are discussed with regard to occupational safety, there is usually a focus on the microbiological contamination of the cooling water as a potential source of danger in the workplace [e.g. 7]. In the literature, the hazard potential of biocides for cooling water conditioning during handling, storage and operation of the plant is only occasionally discussed: Occupational health and safety in the operation of evaporative cooling systems is addressed by Sinder et al., for example, in the sense of a comprehensive risk assessment [1]. Chemical effects caused by the substances used are one aspect of the workplace assessment, which is documented in the form of operating instructions, safety analyses, procedural instructions, work area analyses and job or task descriptions. Müller & Bleck investigated workloads when using biocidal products in a BAUA research project [14]. This also includes biocides for product type 11. Professional users were, among others, persons for whom the handling of biocides is an essential part of their professional activity. One aim of the project was to describe alternative ways of dealing with reduced exposure as well as "best available techniques". A guideline from the German Chemical Industry Association provides a template for risk assessment prior to commissioning or recommissioning of evaporative cooling systems [15]. A possible hazard due to e.g. substance input, lack of disinfection, contamination or disruption of plant operation due to technical defects should also be assessed.

In the literature and in the interviews, the following statements can be found that are relevant for prevention when working with hazardous substances in evaporative cooling systems:

- An increased risk can be particularly present if employees use high-pressure cleaners for cleaning and maintenance work (e.g. on separators) and are exposed to the "germ-contaminated" spray mists (aerosols) without protection. Cleaning the cooling towers is a critical activity that should usually be carried out with a protective suit, gloves and respiratory protection. The naïve and often uncontrolled use of biocides, which is often used especially in aqueous systems, is not the method of choice. Rather, biocides may only be handled in such a way that no chemical hazards arise. According to the manufacturer, only competent personnel may add biocides [66].
- Employees should be better trained in accordance with VDI 2047 Part 2 on symptoms and prevention (FFP3 mask), this also applies to cleaning staff (Inwatec GmbH: Interview 8).
- Working with biocides in small plants without a dosing pump and without a dosing station is not safe. When dosing from original containers without decanting (with suction lances), contact must be avoided at all costs. Usual 1.4% CMIT/MIT mixtures can lead to blindness in the case of splashes into the eye. If the CMIT/MIT application solution added to the cooling system comes into contact with the skin, wounds that are very difficult to heal can occur (Weidner Wassertechnik GmbH: Interview 5)

- Cases up to incapacity for work due to the sensitizing effect of isothiazolinone are known (Inwatec GmbH: Interview 8).
- The metabolic products of bacteria can trigger allergies and inflammation when they occur in air conditioning systems, for example. This phenomenon is known as Sick Building Syndrome. Such effects can also occur if bacteria are emitted in addition to legionella in poorly maintained cooling systems (Sanosil AG: Interview 7)

LEGAL REQUIREMENTS

During the data collection and in particular in the course of interviews with experts and representatives of public authorities, it became apparent that the legal requirements for the operation of evaporative cooling systems can have a significant impact on the questions of the study. Therefore, this chapter deals with the legal requirements for the operation of evaporative cooling systems in Austria and Germany. In Germany, the introduction of the 42. Federal Immission Control Ordinance (42.BImSchV), the operation of evaporative cooling systems is systematically regulated. The regulation came into force in 2017 and is a response to outbreaks of legionellosis caused by evaporative cooling systems, including fatal consequences. In Austria, there is no regulation comparable to the 42nd BImSchV for the operation of evaporative cooling systems. For plants that are subject to the permit requirement under water law, the Wastewater Emissions Ordinance AEV provides for discharge bans and restrictions on cooling systems and steam generators.

Austria

Wastewater Emission Ordinance AEV Cooling Systems and Steam Generators

According to the Water Rights Act, the Wastewater Emission Ordinance AEV Cooling Systems and Steam Generators regulates the discharge of wastewater from evaporative cooling systems [16]. If the plant is to be approved under water law, the discharge of the following substances is not permitted:

1. Inorganic compounds of chromium from corrosion protection
2. inorganic compounds of mercury
3. Organometallic compounds
4. Merkaptobenzthiazoles and isothiazoles
5. Nitrites
6. Organic working and auxiliary materials that have a total degradability by aerobic microorganisms in an aqueous environment of not greater than 80% after a test period of 28 days (method regarding "degradability – DOC process" according to Annex A Section II of the Water Method Ordinance (WMD), Federal Law Gazette II No. 129/2019 in the applicable version) except phosphonates and polycaroxylates
7. Biocides from the continuous control of organism growth with the exception of peroxygen compounds (e.g. hydrogen peroxide, ozone)
8. Biocides from the discontinuous control of organism growth (shock treatment) excluding chlorine, bromine, chlorine, brominated or splitting biocides, glutaraldehyde or peroxygen compounds

In addition, no inorganic zinc compounds from cooling water conditioning may be introduced into main circulation cooling systems of thermal power plants. The prohibition of discharge shall be deemed to have been complied with if it can be proven that the materials and auxiliary materials used do not contain the substances mentioned. When discharging into a watercourse or a public sewer system, emission limits must be observed, e.g. for free chlorine. If chlorine dioxide or bromine is used instead of chlorine, a corresponding emission limitation converted to chlorine must be observed. The use of chlorine- or bromine-containing or bromine-releasing biocides is only permitted as impact treatment. During impact treatment, the installation or part intended for impact treatment must be kept closed. In addition, limit values for temperature and bacterial toxicity must be observed.

Standards

Strictly speaking, the standards are not legal requirements per se, but they can be listed in water rights notices.

ÖNORM B 5020: Requirements for microbiological water quality in evaporative recooling systems [53]

The standard is aimed at operators, maintenance staff, testing bodies and competent authorities. The microbiological examination in the laboratory includes the aerobic bacterial count, legionella and Pseudomonas aeruginosa. In the case of newly erected open, wet recooling structures, regular inspections in accordance with ÖNORM are prescribed by administrative decision. It is irrelevant whether the cooling water is used directly as a cooling medium in the process or whether the process heat is transferred from a primary cooling circuit to a water cooling circuit via heat exchangers. At the time of the study, ÖNORM B 5020 was under revision (Committee for Standardization on the Revision of ÖNORM B 5020: Interview 12)

ÖNORM M 7744 (draft) [17]

The standard is still a draft or not fully developed. The validity should apply to existing and new installations where water is trickled or sprayed or can otherwise come into contact with the atmosphere and which is circulated. The plant monitoring described in the draft was intended to enable appropriate control and monitoring of chemical water quality. However, for installations that are subject to the permit requirement under water law, the Wastewater Emission Ordinance AEV Cooling Systems and Steam Generators provides for discharge bans or restrictions in Austria. In Vienna, evaporative cooling systems must be approved by decision in accordance with § 61 of the Vienna Building Code. In terms of environmental pollution, however, only noise emissions are considered in this context. There is no obligation to report to a register or cadastre.

Germany

42nd Federal Immission Control Ordinance (42nd BImSchV)

In Germany, the obligations of responsible companies for the monitoring of legionella in evaporative cooling systems are comprehensively regulated by the 42nd Federal Immission Control Ordinance [2] and the VDI 2047 series of guidelines [18]. The ordinance came into force in 2017 and is a response to outbreaks of legionellosis caused by open evaporative cooling systems in Warstein (2013), Jülich (2014) and Bremen (2016) with a total of 8 deaths. This means that the ordinance was issued primarily to protect against legionella. Evaporative cooling systems within the meaning of the ordinance are systems in which heat is dissipated into the ambient air by evaporation of water, in particular consisting of a trickling or sprinkler device for cooling water and a heat exchanger. Cooling towers with a cooling capacity of more than 200 megawatts per air outlet are excluded. The vast majority of systems therefore fall into the category of evaporative cooling systems. The regulation applies to the construction, nature and operation of evaporative cooling systems, cooling towers and wet separators in which water is trickled or sprayed or may come into contact with the atmosphere. Key points are:

- Official notification obligation for existing and new systems. The notification of affected systems in the form of geocoordinates is made in the online portal "Cadastre of evaporative cooling systems"
- General requirements for the construction of the plant according to the state of the art

- Creating and maintaining a company diary
- At least every two weeks in-house inspection of chemical, physical and microbiological parameters of the industrial water
- Regular laboratory analysis of industrial water to determine microbiological contamination with a focus on legionella concentrations. Sampling must be carried out by a hygienically competent person and laboratory testing by an accredited laboratory
- Preparation of a risk assessment and measures in the event of limit values being exceeded
- Inspection of the plant operation every 5 years by a sworn expert
- Official reporting and information obligation in the event of exceeding measures for legionella in industrial water

European Union

BAT Leaflet

A BREF is a document issued by the European Commission that describes the best available techniques (BAT) for preventing and mitigating the environmental impact of an industry and must be taken into account when approving installations by authorities in the European Union (source: Wikipedia). A corresponding document was prepared for cooling systems in 2001[16] , and a revision is to begin in 2023. Austrian experts are also taking part in this revision (Interview 2). In the view of the author of the study, a parallel survey of the state of the art of cooling systems in Austria by the Federal Ministry for Climate Protection seems to make sense.

Interview statements on legal requirements

The following statements refer to the legal requirements in Austria regarding the operation of and discharges from evaporative cooling systems

- There is room for interpretation or clarification in the formulation of the discharge ban of "isothiazoles" in AEV cooling systems and steam generators. The question is whether this also refers to isothiazolinones (e.g. Kathon – mixture of CMIT/MIT). This could not be clearly clarified in the discussions with the Austrian interview partners. The fact is that CMIT/MIT has been approved by the ECHA as a biocidal active ingredient in product type 11 (i.e. also for the disinfection of cooling systems) and is often used in practice (Wien Kanal: Interview 1; Federal Ministry of Agriculture, Regions and Tourism: Interview 2)
- As part of the Water Status Monitoring Ordinance, regular monitoring of flowing waters takes place, among other things. As part of this monitoring, there are also special measurement programs, e.g. for pharmaceuticals or pesticides. Cooling system chemicals have not been included so far. However, this could be suggested under the focus on "industrial chemicals". If the measurement results show a relevant contamination, e.g. with CMIT/MIT, Austria could advocate more measurements at EU level in a further step. For example, it would be conceivable for CMIT/MIT to be included in the watch list for suspected substances of the EU Water Framework Directive (Federal Ministry of Agriculture, Regions and Tourism: Interview 2)

---

[16] Best Available Techniques in Industrial Refrigeration Systems Reference Document December 2001

- In an interview with hygiene experts, it is pointed out that there is no standard in Austria that specifies the technical requirements for refrigeration systems in more detail. ÖNORM B 5020 covers the microbiological requirements for make-up water/filling water and circulating water/circulation water and is currently being revised. Unfortunately, the regulation of the technical requirements with the working title ÖNORM 7744 failed a few years ago. In Germany, there is a practicable standard, VDI 2047-2. There is nothing comparable in Austria (Institute of Hygiene and Applied Immunology at MedUni Vienna: Interview 4).

The following statements refer to the existing state of knowledge in Austria regarding the locations of evaporative cooling systems:

- Presumably, only 10 to 20 % of all cooling towers (in Austria) are known (expert for water hygiene, interview 6).
- The operator of the Vienna sewer system currently has 14 operators registered according to AEV Cooling Systems and Steam Generators. That's probably only a fraction. One reason is that office buildings and companies without production that use cooling towers do not see themselves as operational wastewater dischargers and thus overlook the fact that the discharge of wastewater from cooling towers must nevertheless be approved by the sewer company. There is no obligation on the part of the sewer operator to actively identify dischargers (Wien Kanal: Interview 1).

In interviews, reference is made to the establishment of a cooling tower cadastre in Austria as follows:

- In terms of infection prevention, it is essential from the point of view of hygiene and public health that a reporting obligation is introduced for the construction and operation of evaporative recooling systems, i.e. those that release aerosols into the environment, and that a corresponding register is set up (Institute of Hygiene and Applied Immunology at MedUni Vienna: Interview 4).
- The establishment of a cooling tower cadastre analogous to Germany would be very desirable (expert for water hygiene, interview 6)

The following interview statements refer to the (improved) state of knowledge or to observed "effects" after the implementation of the 42nd Federal Immission Control Ordinance:

- While we were aware of 15 turbines in the Düsseldorf area before the 42nd BImSchV came into force, there are now 350 turbines in our area of responsibility. But probably not all plants have been reported yet, we estimate the missing reports at about 20%. In the cadastre, the facilities are provided with geodata. If legionellosis cases occur, they are reported to us. Then we check whether there are evaporative cooling systems within a radius of 1 km from the outbreak of infection. We take a targeted look at these and have the test reports presented to us. To date, we have not been able to establish a connection between a plant and a reported legionellosis. But this procedure was not possible before. We also inspect facilities where exceedances of legionella have been reported. In accordance with 42.BImSchV, the plants must be inspected by an expert every 5 years. We will then also receive the test reports. Based on these, locations for inspections are also selected. Another important side effect of the BImSchV or the plant register is that we now also know of significantly more dischargers of cooling water into the sewer who had not applied for a permit for discharge before the 42nd BImSchV came into force (Office for Environmental and Consumer Protection Düsseldorf: Interview 11).

In the interview, VDI 2047 Part 2 is described as the "tool of the 42nd BImSchV". An updated version puts more emphasis on employee training. Also, as an effect of the 42nd BImSchV, a dynamic towards closed systems or hybrid cooling systems or adiabatic cooling systems is perceived, at least in the case of smaller cooling requirements (both types, however, fall fully under the 42nd BImSchV). Such dynamics are not perceived in larger cooling towers (Inwatec GmbH: Interview 8).

EVAPORATIVE COOLING SYSTEMS IN VIENNA

The City of Vienna estimates that Vienna's electricity consumption for air conditioning has increased more than tenfold between 1995 and today[17] and will triple again by 2040 to a good 1000 GWh[18] per year. The most common coolant is water. Various system variants are available for the recooling of the heated water but also of classic refrigerants from cooling systems , e.g. evaporative cooling systems with open or closed circulation and adiabatic systems, in which air cooling is supplemented by wet cooling with water in times of increased cooling demand. For a long time, the construction of evaporative cooling systems in Vienna was not subject to any special conditions, although these systems can pose a health risk to personnel and surrounding residents in the event of poor management and maintenance.

Evaporative cooling systems as a potential emission source for legionella

In the years 2002 to 2007, 129 legionellosis cases were registered or documented in Vienna by the Municipal Department 15, Department of Infection Prevention[19]. The data show that the number of annual infections in Vienna remained about the same in the period from 2002 to 2005 and increased slightly in 2006. In the late summer of 2007, more cases of Legionnaires' disease were diagnosed in Vienna than usual. In the course of the investigation into the causes, AGES also sampled open evaporative cooling systems and was able to establish a connection with some cases of legionellosis with a severe course. In 2008, the Control Office therefore carried out an audit of the Municipal Department 15 (responsible for hygiene) with regard to cases of Legionella infections in Vienna [19]. Inspection of the documents showed that in 41% of the cases the place of residence or "unknown" was given as the cause, or in a second selection in 56% of the cases the place of residence, "unknown" and another, albeit very uncertain, possible source were mentioned. In summary, there was therefore no or only a very vague assignment to a possible source of infection in about half of the cases, which also corresponds to the data situation for Austria [5].

Activities of the Vienna Control Office

After the microbiological investigations of open evaporative cooling systems of AGES in 2007, the control office proposed a systematic recording in a cadastre. The lack of a federal law in this regard was identified as a fundamental problem. The research showed that the large number of legal matters, the different responsibilities and the distribution of competences between the federal government and the province of Vienna make the implementation of a cadastre considerably more difficult. In an official meeting in November 2007, the proposal was made to survey the locations of wet cooling towers with the help of applications for a reduction in sewer junction fees (at that time the municipal department 30 was responsible). This proposal is based on the assumption that the sewer junction fee is proportional to the water consumption, but in the case of wet cooling towers, part of the water used evaporates and thus does not enter the sewer system. A corresponding list of the former Municipal

---

[17] Vienna Energy Report 2014 Energy Consumption in Vienna - Energy Reports

[18] waerme-und-kaelte-2040.pdf (wien.gv.at) Chapter 3

[19] Since 2001, there has been an obligation to report every suspected case of illness and death from the title of legionellosis to the competent district administrative authority (health department). Since 2006, only cases of illness and death have been subject to notification.

Department 30 (Vienna Canal) showed 70 locations[20]. However, according to estimates by a representative of the Austrian Refrigeration and Air Conditioning Association (ÖKKV), the actual number of wet cooling towers in Vienna in 2007 was around 1,000[21]. The control office recommended initiating a project to create a cooling tower register. Within the framework of this project, legal issues, questions of responsibilities, maintenance of cadastral data, linking to infection data and a procedure in the event of an incident were to be developed. It was also recommended to identify other cooling towers on the basis of aerial photographs of Vienna (or the MA 41). However, the locations and number of wet cooling towers in the city of Vienna that were erected before 2007 remain unknown to this day. In September 2013, Univ. Prof. Günter Wewalka from AGES[22] pointed out in his lecture "Requirements for the microbiological water quality of evaporative cooling systems – new ÖNORM B 5020" that it is very difficult to investigate cooling towers as such. since there is no location register for them [20]. In his conclusion, he recommended a register for wet cooling towers at local authorities or a nationwide legal obligation to report them.

So far, however, only an audit list has been drawn up, in which the approximately 70 locations collected via Wien Kanal have been entered. The respective operators were required to carry out regular microbiological checks of the plants.

Commercially used evaporative cooling systems are currently approved by the respective municipal district office (MBA) with the involvement of the Department of Commercial Engineering, Fire Police and Events (MA36) and the Vienna Health Service (MA15).

Non-commercial systems for cooling the buildings of office buildings, data centres, banks, insurance companies, hotels, nursing homes, schools, etc. are approved by the Vienna Building Police (MA37) on a district-by-district basis in accordance with §61 of the Vienna Building Code. An expert report is prepared by the MA36 with the involvement of the MA15, but the conditions for the approval are significantly lower. There is also no data on the number of plants approved in this way, as they do not converge centrally under an easily assignable title.

Evaporative cooling systems in healthcare facilities are approved by the MA40 (social, social and health law) via the Vienna Hospitals Act, those for the recooling of refrigeration systems by the MA63 (trade law, data protection and civil status).

Due to the complex responsibilities alone, it is difficult to see the stock of evaporative cooling systems together. The MA15 is responsible for each district within the framework of the permits, so that data does not converge in one place there either. Overall, however, open evaporative cooling systems are rather expensive and also microbiologically more sensitive compared to adiabatic systems or dry

---

[20] In 2008, this site list was reviewed by MA 63 and for all those plants where regular, microbiological quality control was not prescribed in the notice, such a check was subsequently prescribed. The legal basis was §79 of the Trade Regulation Act (internal information of the Vienna State Health Directorate).

[21] According to the Düsseldorf Office for Environmental and Consumer Protection (Interview 11), 350 evaporative cooling systems are currently registered in Düsseldorf (approx. 0.6 million inhabitants) according to the mandatory notification according to the 42nd BImSchV. Extrapolated to the population of Vienna (approx. 1.9 million), this corresponds to approx. 1100 turbines. Thus, 1000 is more of a lower limit. A current inquiry at the guild for mechatronics engineers also came to the conclusion that between 750 and over 1000 systems in Vienna is still a realistic number.

[22] Institute of Medical Microbiology and Hygiene Vienna, National Reference Centre for Legionella Infections

cooling. The many services contacted in the study report that open evaporative cooling systems are rarely replaced by new ones and that relatively few new systems are built.

Evaporative cooling systems are probably most commonly found in large office buildings with limited space on the roof[23], banks, insurance companies, large food warehouses with refrigeration, data centers, hospitals, nursing homes, or ice skating rinks. Since the report of the Control Office, microbiological checks have been required at regular intervals for all installations built thereafter. These should be carried out by civil engineers.

For healthcare facilities, regular microbiological tests in evaporative cooling systems are generally required in accordance with ÖNORM B 5020.

This was also stated in the Hygiene Guideline No. 4, as of 18 October 2017. However, this is also currently being revised.

With regard to possible inspections of evaporative cooling systems in Vienna, it was found that if several legionellosis cases were reported to AGES in a certain area of Vienna, it could at least be investigated via aerial photographs whether an evaporative cooling system is nearby. Then a report would be sent to the Vienna Health Service to examine the plant microbiologically. In such a case, the Testing, Inspection and Certification Body of the City of Vienna (MA39) is responsible for immediate sampling and the samples would be returned to AGES for further examination. However, discussions with the MA39 have shown that they cannot remember that this has ever happened in practice.

This suggests that evaporative cooling systems outside the aforementioned revision list, which according to MA36 should contain a maximum of one or two systems per district, are practically never sampled by the health authority. This circumstance is unlikely to contribute to the fact that all operators are sufficiently aware of the risk that their installations may pose to human health. Hygiene experts have also confirmed to us that most systems are very rarely microbiologically sampled and even less often shut down and professionally cleaned due to high germ counts.

Activities of the Vienna Environmental Ombuds Office and ÖkoKauf Wien

Since the use of biocides in evaporative cooling systems is relevant beyond the legionella problem in terms of emissions into the sewer system and sewage treatment plants and also for occupational health and safety, the Vienna Environmental Ombudsman's Office (WUA) in the person of DI Marion Jaros researched this topic from 2017 onwards and contacted responsible persons and experts. The aim was to support plant operators or those responsible in selecting the optimal biocides or processes for their technical conditions and/or operating the plant in such a way that the most environmentally friendly chemicals possible are used in the smallest possible quantities.

- In order to estimate biocide loads from this area occurring in Vienna, the WUA submitted an inquiry to Wien Kanal in February 2017. The following findings of fact were made: Only the discharge of wastewater from cooling systems and steam generators in which halogen-releasing biocides are used is subject to authorisation under water law. At the time of the answer, 10 indirect discharges from cooling systems and steam generators in which halogen-releasing biocides are used had been approved under water law. The average amount of water from these discharges was about 614 m3, the total load to AOX was about 96 kg per day [21], [54].

---

[23] Because dry coolers need more space.

- Since no data are available for the total material load for Vienna, an estimate based on the number of inhabitants was made on the basis of an extrapolation for Germany [12] (Germany: 83 million; Vienna: 1.9 million). This results in an annual load of 94 tonnes of oxidative and 2.9 tonnes of non-oxidative biocides for Vienna.
- As a further activity initiated by WUA, some biocides or their formulation and application concentration were entered and evaluated in the WIDES disinfectant database in 2017 . It was found that with the vagueness of the evaluation system used and the theoretical assumptions regarding the amount and frequency of dosing, only a rough estimate of the environmental consequences is possible and more detailed information from practical application would be necessary.

Finally, the present study was commissioned by ÖkoKauf Wien for a more comprehensive analysis of the current situation, as well as for researching effective reduction measures for biocide use.

COOLING WATER CONDITIONING AND OPERATION

Literature review

The section evaluates 9 studies, reports, reference books and guidelines, which among other things address cooling water conditioning with chemicals or biocides. The naming of biocidal active substances, consumption quantities, occurrence in products, genotoxicity and other conditioning agents are taken into account. The documents are arranged according to publication date.

Tauschek [10], [71]: The guide lists frequently used active ingredients as well as corrosion inhibitors.

Nocker et al. (2020) [9]: The study deals with the inactivation of biocides during sampling for the purpose of determining legionella in cooling water.

Sinder, Gringel, Hardt & Langerbein (2019) [1]: The textbook deals with the causes and prevention of outbreaks of legionellosis in evaporative cooling systems and cooling towers. Requirements from statutory (42nd Federal Immission Control Ordinance) and technical (VDI 2047) regulations are discussed in detail.

VDI 2047 Part 2 (2019) [18]: The guideline supports the goal of ensuring the safety of evaporative cooling systems. Topics such as construction methods, occupational health and safety and health risks – in connection with the spread of legionella and pseudomonas – are dealt with, and common biocides are also listed.

Scharf et al. (2016) [13]: The report deals with the use of biocides in cooling water circuits and the consequences for drinking water supply. The advantages and disadvantages of the individual active substances, especially from the point of view of drinking water supply and with regard to their importance for the environment, are assessed in summary.

Rajagopal et al. (2012) [61]: The textbook addresses operational issues related to industrial cooling water systems with a focus on "biofouling control". Common biocidal active ingredients are also listed.

Aquaprox (2007) [11]: The reference book deals with problems with cooling water systems and also addresses the use of biocidal active ingredients.

Paulus (2005) [8]: The US standard work for biocides provides an overview of the most frequently used biocidal active ingredient for cooling water treatment.

Gartiser & Ulrich (2002) [12]: As part of the study, inputs of cooling water chemicals into surface waters of the Federal Republic of Germany were collected. Chemicals were identified from product documentation, entries on consumption data in refrigeration systems were balanced, and data was researched for an assessment of environmental relevance. Cooling water samples and products were examined for genotoxic effects. The study cites consumption data for Germany.

Biocidal active ingredients

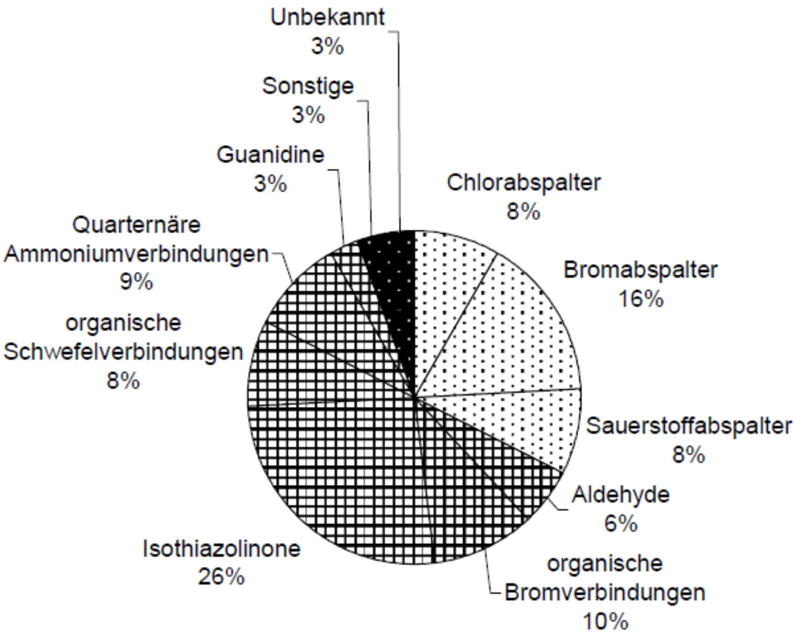
In the above-mentioned literature, the following biocidal active substances are mentioned several times:

OXIDATIVE BIOCIDES	
Chlorine dioxide	[1], [8], [10], [11], [13], [18], [61]
"Chlorine" (chlorine; chlorine bleach; electrochemical)	[1], [8], [10], [11], [12], [13], [18], [61]
"Bromine" (sodium bromide/sodium hypochlorite)	[8], [11], [12], [18], [61]
Bromochlorodimethylhydantoin (BCDMH)	[8], [10], [12], [13], [18], [61]
Ozone	[1], [8], [10], [11], [12], [13], [18], [61]
Hydrogen peroxide	[8], [10], [12], [13], [18], [61]
Peracetic acid	[8], [12], [18], [61]
NON-OXIDATIVE BIOCIDES	
DBNPA (2,2-dibromo-2-cyanacetamide)	[8], [9], [10], [11], [12], [13], [18]
Bronopol (2-Bromo-2-nitropropane-1,3-diol)	[9], [10], [12], [13], [18]
Isothiazolinones (CMIT/MIT)	[8], [9], [11], [12], [13], [18]
Benzalkonium chlorides (quaternary ammonium salts, QAV)	[8], [9], [10], [11], [12], [13], [18], [61]
Glutaraldehyde	[8], [10], [11], [12], [13], [18]

The following active ingredients are mentioned in some cases: tetrakis (hydroxymethyl)-phosphonium sulphate (THPS); Peroxomonosulfate; Dichloroisocyanuric acid; β-bromine-β-nitrostyrene; Methylene bisthiocyanate; Dodecyl guanidine hydrochloride

Biocidal active ingredients contained in products

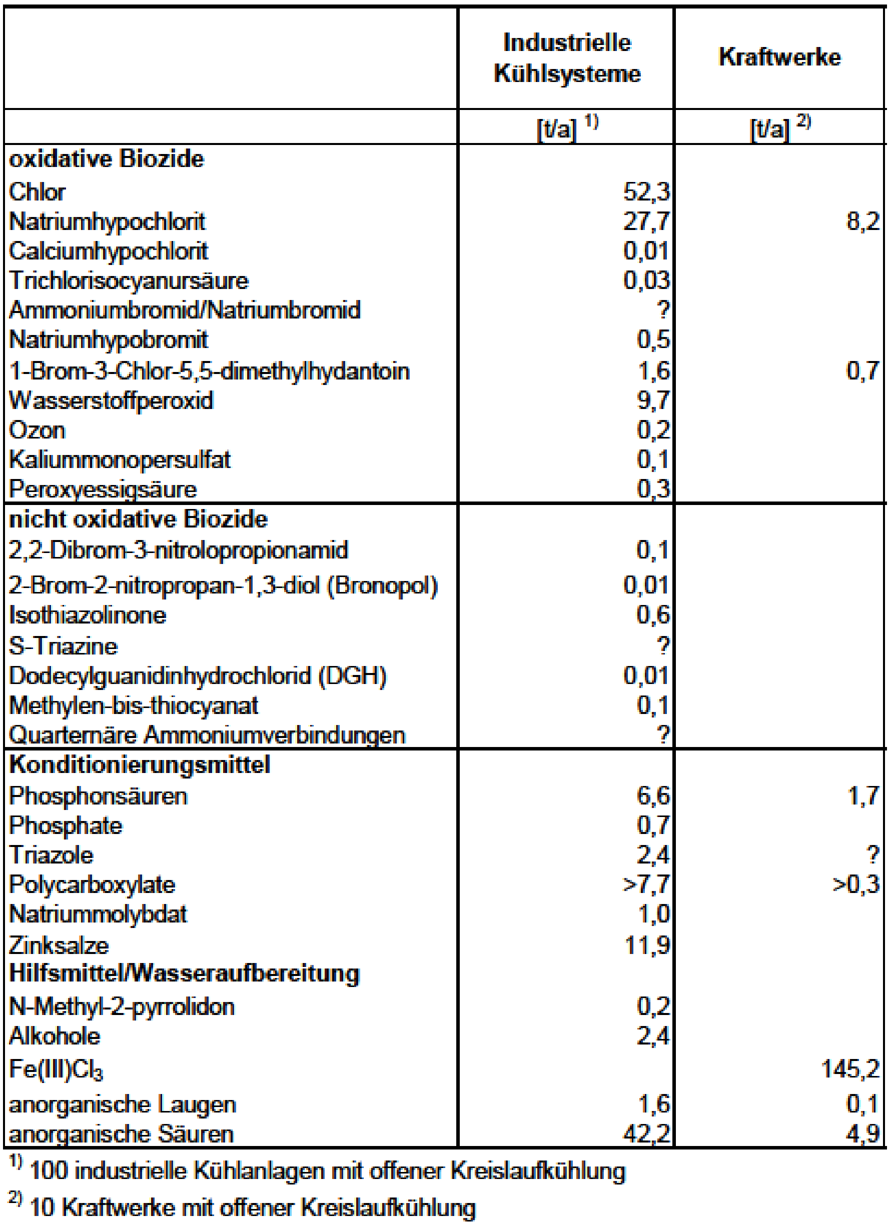
Gartiser & Ulrich (2002) evaluated about 100 products with biocidal active ingredients. According to the study, 80% of the total (German) market was covered [12]:



Among other things, five biocides and one corrosion inhibitor were tested for genotoxicity. Two biocides with isothiazolinone as the active ingredient showed mutagenic and genotoxic effects, respectively. In cooling water samples from seven plants, a genotoxic effect was found in one sample, which was explained by the presence of isothiazolinones and bronopol. In this context, the study cites a Dutch study in which the cooling water of 14 companies was examined and a clear correlation between the concentration of the active ingredient and ecotoxicity was determined. For example, cooling waters treated with the biocidal active substances isothiazolinone, DBNPA, β-bromo-nitrostyrene β-nitrostyrene and methylene bisthiocyanate had higher toxicities (necessary dilution by a factor of 769) than those treated with the oxidative biocides sodium hypochlorite and ozone (necessary dilution by a factor of < 2).

Loads of cooling water chemicals

Gartiser & Ulrich (2002) determined the consumption quantities of cooling water chemicals among German operators of cooling systems. The total loads collected were [12]:



	Industrielle Kühlsysteme	**Kraftwerke**
	[t/a] 1)	[t/a] 2)
oxidative Biozide		
Chlor	52,3	
Natriumhypochlorit	27,7	8,2
Calciumhypochlorit	0,01	
Trichlorisocyanursäure	0,03	
Ammoniumbromid/Natriumbromid	?	
Natriumhypobromit	0,5	
1-Brom-3-Chlor-5,5-dimethylhydantoin	1,6	0,7
Wasserstoffperoxid	9,7	
Ozon	0,2	
Kaliummonopersulfat	0,1	
Peroxyessigsäure	0,3	
nicht oxidative Biozide		
2,2-Dibrom-3-nitrolopropionamid	0,1	
2-Brom-2-nitropropan-1,3-diol (Bronopol)	0,01	
Isothiazolinone	0,6	
S-Triazine	?	
Dodecylguanidinhydrochlorid (DGH)	0,01	
Methylen-bis-thiocyanat	0,1	
Quarternäre Ammoniumverbindungen	?	
Konditionierungsmittel		
Phosphonsäuren	6,6	1,7
Phosphate	0,7	
Triazole	2,4	?
Polycarboxylate	>7,7	>0,3
Natriummolybdat	1,0	
Zinksalze	11,9	
Hilfsmittel/Wasseraufbereitung		
N-Methyl-2-pyrrolidon	0,2	
Alkohole	2,4	
$Fe(III)Cl_3$		145,2
anorganische Laugen	1,6	0,1
anorganische Säuren	42,2	4,9

[1] 100 industrielle Kühlanlagen mit offener Kreislaufkühlung

[2] 10 Kraftwerke mit offener Kreislaufkühlung

Corrosion protection and hardness stabilization

Gartiser & Ulrich cite the following substances in their study for the cooling water sector [12]:

Corrosion inhibitors: phosphates, phosphonates, nitrite, silicate and molybdate. The cathodic inhibitors are zinc, calcium carbonate and orthophosphate, as well as 1,2,3-triazoles for copper alloys.

Hardness stabilizers: aminotrimethylenephosphonic acid (ATMP), hydroxyethandiphosphonic acid (HEDP), phosphonbutane tricarboxylic acid (PBTC) and polycarboxylates[24] with hardness-stabilizing effect in combination with phosphonic acids.

In one document, the following corrosion inhibitors are mentioned for cooling water circuits [71]:

Basisstoff Inhibitor	Beispiel/e:	Verwendung	Anmerkung
Zinksalze	Zinksulfat-Monohydrat	Eher selten	Abwassergrenzwert, Risiko „Zinkschwund“
Phosphate	Natrium-Tripolyphosphat	Mittel	Risiko von Calciumphosphat-ablagerungen
Phosphonate	HEPD, ATMP, HPAA, PBTC	Sehr häufig	Thermisch und chemisch sehr stabil, Nr. 1 bei Kühltürmen und Verdunstungskühlanlagen
Molybdat	Natriummolybdat	Sehr häufig	Bevorzugt bei halboffenen und geschlossenen Kühlkreisen eingesetzt. Sehr wirkungsvoll
Nitrite	Natriumnitrit	Mittel	Gefahr durch mögliche Oxidation von Nitrit, Problem Toxizität Abwasser
Silikate	Natriumsilikat	Eher selten	Risiko Calciumsilikatausfall
Azole	Benzotriazole, Totyltriazole	Sehr häufig	Nr. 1 für Korrosionsschutz von Buntmetallen (Kupfer, Messing, Rotguss etc.)
Sauerstoffbinder	Natriumbisulfit, Ascorbinsäure	Mittel	In Kühltürmen z. B. nicht sinnvoll da ständige Sauerstoffsättigung stattfindet

According to the study, sodium molybdate, azoles and phosphonates are often used as corrosion inhibitors in refrigeration systems[25]. With regard to emissions into the aquatic environment, a distinction must be made as to which of the above-mentioned substances are used in open cycles. For example, molybdate and nitrite are more likely to be used in closed cycles [72]. In any case, the human and ecotoxicological properties of corrosion inhibitors should also be taken into account in

---

[24] " Polycarboxylates" refer to compounds (polycarboxylate, polycarboxylic acid, alkylepoxycarboxylate, polyoxycarboxylic acid, polymaleic acid, maleic acid/copolymer, acrylic acid co-polymer, acrylic acid terpolymer).

[25] In an interview, it is pointed out that azoles (i.e. benzotriazole or tolyltriazole) are severely restricted in their use in Holland and Belgium due to their persistence or complex-forming properties (Inwatec GmbH: Interview 8).

conjunction with the biocide used: According to ECHA, for example, benzotriazole is currently being assessed with regard to possible persistence and endocrine properties.

Physical methods (UV, thermal disinfection)

There are indications that physical methods used in cooling water conditioning are subject to limitations:

- In an interview, for example, it is stated that the effectiveness of UV treatment is significantly reduced by turbidity. It therefore only works in systems where the clarity of the cooling water is ensured. UV treatment is therefore suitable for small systems that are used for air humidification. UV light can attack and inactivate treatment chemicals such as azoles (Inwatec GmbH: Interview 8).
- According to Sider et al. [1], thermal disinfection in the cooling water area is an exception. The reason for this is that the necessary temperatures of over 70° C cannot usually be achieved in such systems. A high energy requirement and the lack of durability of the materials used are the reasons for this.
- According to Sider et al., processes with UV light are used in evaporative cooling systems, but have a limited range of applications. These result from turbidity of the water due to dissolved or particulate components.

Efficacy of biocides used

The design of the plant and its ongoing operation are of considerable importance for the effectiveness of the biocides used. However, this is only dealt with selectively in the present study. In an interview, for example, the following general statement can be found:

- The effectiveness of biocides may depend on the pH and the interaction with other chemicals, as well as on the type of system: Is it direct or indirect cooling? If it is a dynamic plant, i.e. with a high circulation capacity in relation to the system volume, then biocides that quickly "strip" or outgas – such as chlorine dioxide – are not the means of choice. This is because if the contact time with the biocide is not sufficient, it is also not sufficiently effective against legionella. (Inwatec GmbH: Interview 8):

The structural design is relevant for the effectiveness of biocides insofar as, according to Sinder et al. [1], an even flow through all plant components should be ensured and thus the biocidal active ingredient should be available in sufficient concentrations throughout the system. The content of organic impurities and suspended solids in the cooling water is relevant for the effectiveness of oxidizing biocides. Therefore, water treatment and filtration processes are important [71]. For example, full-flow filters were cited as an effective way to eliminate contaminants[26]. The following statements can be found on the efficacy and substrates of biocides used:

- For the biocides used by industry and operators for circulating water, no information is usually disclosed about their biocidal effect, especially against Legionella and *Pseudomonas aeruginosa* . Therefore, the application concentrations stated in the product data sheets cannot be verified. An effective disinfectant should be able to achieve at least a 4-log reduction of the target microorganisms - with the intended concentration and exposure time. In a single case where the biocidal activity documentation was disclosed, it was found that the minimum

---

[26] personal conversation with Wien Energie.

concentration specified in the product data sheet was underestimated by a factor of 10. This error was then corrected by the manufacturer in the product data sheet. (Institute of Hygiene and Applied Immunology at MedUni Vienna: Interview 4)

Chemical leasing (external service providers)

On the question of whether and to what extent the maintenance of a plant can be outsourced to external service providers, there are references in the interviews (chemical leasing). In this regard , it is stated, for example,

- There are few installers of systems who offer a service with water analyses or a cleaning service. Especially in the case of small cooling systems, the system owner often leaves the maintenance to the technical service. Proper maintenance then depends on how experienced or interested the caregiver on site, such as the caretaker, is. In the event of staff changes or retirements, there may also be interruptions in regular maintenance. In small systems, overdoses are also more common according to the motto "a lot helps a lot". Due to the small size, the costs for the biocides are less significant compared to large plants. However, in large plants with hundreds of tons of cooling water, a 1 or 2 ppm higher concentration of biocides has an immediate impact. Therefore, for economic reasons alone, dosing and monitoring is usually more careful there. In principle, not every potential for reducing the use of chemicals is leveraged. Especially if plants have been able to be operated stably for many years, the maintenance personnel do not want to change the successful operational management (Sanosil AG: Interview 7).

A company operating in Germany describes its service offerings as follows:

- Chemical leasing is common practice in our company. For example, we charge plant operators for the use of biocides in maintenance contracts at a fixed price and that if legionella concentrations are complied with, i.e. a test value < 1000 CFU / 100 ml. To guarantee very low concentrations would be dubious. In addition to the biocide, the treatment flat rate per m3 of treated make-up water also includes corrosion protection and hardness stabilisation. We also offer offers for the treatment of cooling water. By desalination and recirculation of the cooling water, water consumption and the amount of wastewater can be reduced. The treatment of partial flows can also be regulated by leasing contracts in the form of treated water per m3. This is interesting for larger plant operators, for example. Smaller plant operators often do not have well-trained employees available to meet all the requirements of the 42nd BImSchV well. They are happy to conclude complete contracts that outsource the delivery and filling of chemicals as well as the operation of the plant together with the documentation obligations - i.e. operating diary, chemical analysis, legionella analysis. However, the responsibility or liability always remains with the operator. The service provider will only use as many chemicals as necessary to make the contract economical. External maintenance contracts have become very common in Germany. The introduction of the 42nd BImSchV has increased the motivation to conclude contracting models. This also has to do with the increased organizational requirements such as expert examinations, operating diaries, adhering to sampling intervals and carrying out inspections (Inwatec GmbH: Interview 8).

The authority entrusted with compliance with the 42nd BImSchV presents the situation in Germany as follows (Office for Environmental and Consumer Protection Düsseldorf: Interview 11):

- In the real estate sector, players change frequently, which is bad for the flow of information. Some of the people on site do not even know what their system is doing or where the documents are located. When it comes to building cooling, i.e. office buildings, administrative buildings, data centres, hospitals or shopping centres, around 90% of operators commission external companies to maintain the system. Some manufacturing companies still have their own specialist staff. The awareness of operators of the legionella problem has improved in recent years. In the area of building cooling, there has even been a considerable improvement.

DETAILED ANALYSIS OF BIOCIDAL ACTIVE INGREDIENTS (PRODUCT TYPE 11)

Substance data

In order to evaluate the biocidal active ingredients used in cooling systems comparatively, substance data from the database of the European Chemicals Agency ECHA were evaluated. ECHA is a driving force in the implementation of EU legislation in the field of chemicals. Biocides used as protective agents in evaporative cooling systems are processed by ECHA under the Biocidal Products Regulation in product type (PT) 11[27]. The entries for approval in PT11 (protective agents for liquids in cooling and process systems) form the starting point for the selection of active ingredients for detailed analysis. The following documents were taken into account in the selection:

- BPC statements[28] or active substance reports[29] in accordance with the EU Biocidal Products Regulation[30].
- registration dossiers under REACH,[31]
- harmonized classifications[32] according to the CLP Regulation[33].

Table 1 in the appendix contains all current entries for PT 11 together with their approval status. Substance classifications or substance data were collected as follows:

---

[27] In Annex V of the Biocidal Products Regulation, biocidal products are classified into 22 product types. Product type 11 concerns protective agents for liquids in cooling and process systems.

[28] Opinion of the Committee for Biocidal Products (BPC) in relation to various BPR processes.

[29] dossier for the approval of an active substance. It shows whether an active substance is suitable for use in biocidal products.

[30] The Biocidal Products Ordinance (BPR) regulates the approval of active substances and the authorisation of biocidal products. The testing or approval of biocidal active substances is carried out as part of a test programme. ECHA provides the status of the authorisation as well as active substance reports (BPR reports).

[31] The REACH Regulation (EC) No. 1907/2006 is the European chemicals legislation. An ECHA database records all chemicals produced and imported in the EU in quantities above one tonne per year. ECHA is the central REACH authority.

[32] In the case of particularly critical hazards (carcinogenicity, mutagenicity, reproductive toxicity [CMR] and inhalation allergens), classification and labelling should generally be harmonised across the EU in order to ensure appropriate risk management. This is done in the Harmonised Classification and Labelling (CLH) procedure. The harmonized classification and labeling can be found in the database of the C&L Directory.

[33] The CLP Regulation (EC) No. 1272/2008 regulates the classification, labelling and packaging of substances and mixtures. A core principle of the regulation is the "self-classification" of a substance or mixture by the manufacturer, importer or downstream user. The aim of self-classification is to determine whether a chemical substance or mixture is associated with physical, health and/or environmental hazards.

- On the website "Information on Biocides", PT 11 *was selected in the search function*. According to this, the authorisation status for the biocidal active substances as well as any BPC statements or active ingredient reports can be retrieved.
- Harmonised classifications and REACH dossiers can be queried on the ECHA homepage after entering the CAS number via the *Substance Infocard*. As information, the German substance name also provides information on an ongoing investigation (e.g. on endocrine activity). The classification listed on the *Substance Infocard* will be used for evaluation if no classifications are available in the above-mentioned sources.

ABC Categorization

The ABC categorization of the hazardous properties of biocides used in this study was taken from the disinfectant database WIDES[34] . It was prepared by the author of the study together with AUVA, the Austrian Federal Environment Agency and the Vienna Environmental Ombuds Office and is explained in detail in the appendix. A color code is linked to the ABC categorization. Hazards are differentiated in this way. On the basis of H-phrases (or relevant data gaps), a substance of the category

- Category A (colour code red; very high concern),
- Category B (colour code yellow; significant concern) or
- Category C (colour code white; low concern)

conjugated. Ingredients assigned to category A (red) have a property of particular concern for health or the aquatic environment. These include substances with proven mutagenic, carcinogenic, toxic for reproduction, chronic toxic, sensitizing or highly environmentally toxic properties. Even in low concentrations, these can damage health or kill aquatic life. Ingredients assigned to category B (yellow) still have a risk potential for health and the environment. For category C (white), it is assumed that the existing hazardous properties (e.g. corrosive) can be sufficiently controlled by appropriate precautionary measures (protective clothing, gloves). Category C substances should be preferred.

Active ingredient selection

The selection for the detailed analysis takes into account the mention in research reports, reference books, guidelines (see section Cooling Water Conditioning / Literature Evaluation), entries in product type 11 - Article 95 list [35] and entries in product type 11 - BAUA population register[36]

---

[34] See www.wides.at

[35] According to the Biocidal Products Regulation, biocidal products may only be marketed if the substance manufacturer/supplier or the biocidal product manufacturer/supplier is listed in the "Article 95 List" for the corresponding product type (the evaluation is not part of the report).

[36] In Germany, biocidal products must be notified or registered with the Federal Institute for Occupational Safety and Health (BAuA) before they are placed on the market. These are recorded via a publicly accessible database or can be queried.

MONOCHLORAMINE (PRODUCED FROM ...)

Identity, Admission, Classification

On the homepage of the European Chemicals Agency ECHA, the approval status of monochloramine in the product type PT11 was queried. Four in-situ production and release processes are listed on the website. At the time of the survey, all approval procedures were ongoing and no published documents were found. In addition, substance data or classifications of the starting materials mentioned in the manufacturing processes were therefore researched, and sodium hypochlorite was assumed to be the source of chlorine:

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument**
Monochloramine generated from ammonia and a chlorine source	Aus Ammoniak und einer Chlorquelle erzeugtes Monochloramin	-	laufend	-	-	-	-
Monochloramine generated from ammonium carbamate and a chlorine source	Aus Ammoniumcarbamat und einer Chlorquelle erzeugtes Monochloramin	-	laufend	-	-	-	-
Monochloramine generated from ammonium chloride and a chlorine source	Aus Ammoniumchlorid und einer Chlorquelle erzeugtes Monochloramin	-	laufend	-	-	-	-
Monochloramine generated from ammonium sulphate and a chlorine source	Monochloramin, hergestellt aus Ammoniumsulfat und einer Chlorquelle	-	laufend	-	-	-	-
Ausgangsstoffe, Folgeprodukte bei der Herstellung von Monochloramin							
Herstellungsverfahren (Referenz)	**Stoffbezeichnung**	**CAS Nummer**	**Funktion**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument**
Aus Ammoniak und einer Chlorquelle erzeugtes Monochloramin	Ammmoniak (Gas)	7664-41-7	Ausgangsprodukt	-	H314, H331, H400	EUH071, H314, H331,Sens.: keine Daten, CMR & chron.Tox.: keine Einstufung; H400 (M1), H411	-
Aus Ammoniumcarbamat und einer Chlorquelle erzeugtes Monochloramin	Ammoniumcarbamat	1111-78-0	Ausgangsprodukt		-	H302, H318, Sens. & CMR & chron.Tox.: keine Einstufung; Aq. Tox.(akut & chronisch): keine Einstufung	-
Aus Ammoniumchlorid und einer Chlorquelle erzeugtes Monochloramin	Ammoniumchlorid	12125-02-9	Ausgangsprodukt	-	H302, H319	H302, H319, Sens. & CMR & chron.Tox.: keine Einstufung; Aq. Tox. (akut & chronisch): keine Einstufung	-
Monochloramin, hergestellt aus Ammoniumsulfat und einer Chlorquelle	Ammoniumsulfat	7783-20-2	Ausgangsprodukt	-	-	keine Einstufungen lt. REACH Dossier	-
Aus… und einer Chlorquelle erzeugtes Monochloramin	Natriumhypochlorit (= Chlorquelle)	7681-52-9	Ausgangsprodukt	-	EUH031, H314, H318; H400 (M10), H410 (M1)	EUH031, H314, H318, Sens., CMR & chron. Tox: keine Einstufung; H400 (M10), H410 (M1)	-
Aus… und einer Chlorquelle erzeugtes Monochloramin	Monochloramin	10599-90-3	Folgeprodukt	bewertet hinsichtlich endokriner Wirksamkeit	-	**Lösung (2,5 - 10 g/l):** Akut. Tox., Sens.: keine Daten, H314, H335, CMR.: keine Einstufung, H372 (Atemtrakt), Aq. Tox. (akut): keine Einstufung, H412. **Lösung (< 3mg/l)**: keine Einstufung	-

ABC categorization

Since no authorisation documents or classifications are available for the manufacturing or release processes for monochloramine, only the lack of data can be used for the assessment of ABC categorisation. For example, all categories with the exception of the irritant and corrosive effect are rated "Major concern (colour yellow)" (see Annex Table 1).

The data and classifications researched from REACH dossiers for the starting materials, the chlorine source sodium hypochlorite and the monochloramine produced in-situ were also used for ABC categorisation. This results in a negligible hazard potential for ammonium carbamate, ammonium chloride and ammonium sulphate. For ammonia (gas) and sodium hypochlorite, the classifications show an acute toxic hazard potential as well as corrosive properties. Sodium hypochlorite is toxic to aquatic organisms in the short and long term.

The REACH dossier for monochloramine ("chloramides") lists a classification for the commercial aqueous solution with a concentration of 2.5 g to 10 g per litre and a classification for the concentration used in cooling systems < 3 mg/L. While hazards are excluded for the latter, the commercial solution is classified as corrosive or irritating as well as chronic toxic to the respiratory tract (STOT RE 1, H372).

Ausgangsstoffe, Folgeprodukte bei der Herstellung von Monochloramin									
Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Ammmoniak	7664-41-7	REACH Dossier	H331	EUH071, H314	-	-	H400 (M1)	H411
Ammoniumcarbamat	1111-78-0	REACH Dossier	H302	H318	-	-	-	-
Ammoniumchlorid	12125-02-9	REACH Dossier	H302	H319	-	-	-	-
Ammoniumsulfat	7783-20-2	REACH Dossier	-	-	-	-	-	-
Natriumhypochlorit (Chlorquelle)	7681-52-9	REACH Dossier	EUH031	H314	-	-	H400 (M10)	H410 (M1)
Monochloramin (2,5 - 10 g /l)	10599-90-3	REACH Dossier	?	H314, H335	?	**H372 (Atemtrakt, Inhalation)**	-	H412
Monochloramin (< 3 mg/l)		REACH Dossier	-	-	-	-	-	-

Employee protection

The hazardous substances database of the German Accident Insurance GESTIS lists the hazard potential of chloramine[37] [41] :

- As a result of the volatile nature of the water-soluble liquid, inhalation exposure is possible under normal conditions, especially to vapours. Its high irritant potential mainly affects the mucous membranes of the eyes and upper respiratory tract or in the gastrointestinal tract (after ingestion). Experience with eye irritation comes from swimming pools, for example, whose water can be disinfected by adding chloramide.
- In the secondary literature, a sensitizing potential was assumed, although this has not been proven. Probably the reason is an original work, according to which "powdered chloramine or

---

[37] Chloramine and chloramide are synonymous

solutions" are said to have triggered allergic contact urticaria. This must therefore not have been chloramide, but chloramine T.

- The inhalation of chloramide vapours (mainly caused by improper handling of hypochlorite bleach solutions) has led in a number of cases to poisoning with the symptoms of eye irritation, headache, nausea, vomiting, weakness as well as functional disorders/damage to the respiratory tract (tracheobronchitis, pneumonia, sometimes respiratory arrest) and also to long-term damage.
- An EPA evaluation of long-term drinking water studies in rodents resulted in a NOAEL for C. of 200 ppm (9.5 mg/kg x d), from which a reference dose for drinking water of 0.1 mg/kg per day was derived. The WHO guideline value is 3 mg/l.

Application (Literature)

In the evaluated literature, there are only a few references to the use of monochloramine in evaporative cooling systems. Tauschek [67] gives the following information on the active ingredient:

- Disinfection with monochloramine is generally becoming more and more popular because the product is more stable in the distribution system, minimizes the formation of disinfection by-products, can penetrate biofilms better and can kill bacteria more successfully than free chlorine. However, monochloramine also has a lower disinfection effectiveness than free chlorine and requires a much longer contact time or a higher dose if it is to be used as a primary disinfectant. Another important point that should definitely be considered when disinfecting with monochloramine is the fact that research on this product is still in its infancy. Therefore, much more research is needed to investigate the exact effect of monochloramine on the persistence and growth of Legionella within biofilms.

Application interview statements

- Active ingredient concentration: 2.5 mg/liter (measured as total chlorine) (Kurita Europe GmbH: Interview 10).

In the interviews conducted, relevant advantages and disadvantages of monochloramine in operation and the manufacturing process are described as follows:

- Monochloramine is experiencing a boom for large cooling capacities, for example in power plants. Monochloramine reacts with sulfur compounds in the bacterial membrane, so it is more selective in relation to other biocides. Compared to chlorine dioxide, the consumption is lower, it is less volatile and also less corrosive. The AOX problem with monochloramine is similarly low or non-critical as with chlorine dioxide (Inwatec GmbH: Interview 8).
- Monochloramine is increasingly used in large evaporative cooling systems in Germany. The advantages are: It is very effective against legionella and biofilms and breaks down into non-critical compounds (Kurita Europe GmbH: Interview 10).
- Monochloramine is produced on-site in a reactor of chlorine bleach (sodium hypochlorite) and ammonium sulfate. The starting materials must not come into contact uncontrollably, as this would cause a strong exothermic reaction with the formation of nitrous gases. This also applies to storage. Safety mechanisms are integrated into the (in-situ) system to avoid such direct contact. For example, the system can only add additional doses when the (monitored) propellant water flow is running. Overall, this requires complex dosing technology. Simpler dosing technology is available for smaller systems. The conversion is pH-dependent, the dosed solution of the biocide is slightly alkaline, but has only a minor effect on the pH value of

the system water due to the small dosage quantity, if at all. (Kurita Europe GmbH: Interview 10).

- Monochloramine can be determined by a total chlorine measurement. Monochloramine is low corrosive and therefore protects materials. It can be combined well with hardness stabilizers or film formers. The measured AOX value is low compared to chlorine (Kurita Europe GmbH: Interview 10).

Market research: Product information and safety data sheet were provided by the supplier Kurita Europe GmbH for the Dilurit BC S system.The components Dilurit® BC S and Dilurit® cat are converted to the actual active ingredient directly at the application site with a dosing system. Dilurit® BC S is a clear to yellowish liquid of pH 5 - 6 and contains an inorganic nitrogen compound. Dilurit® cat is a colourless to slightly yellowish liquid from pH 12 - 13 and contains an inorganic chlorine compound. The Dilurit BC S system is a clear liquid with pH 9 – 10, for which the safety data sheet gives the following classification: H314, H318, H335, H400.

Conclusion

To date, no authorisation has been granted for the various production processes of monochloramine. There are currently no documents from the admission procedure available. Monochloramine is classified as chronically toxic to the respiratory tract (H372) in concentrations above 2.5 g/litre. According to Kurita Europe GmbH, the concentrations occurring in evaporative cooling systems are 2.5 mg/litre. Monochloramine is currently being evaluated for endocrine efficacy. The results are still pending. In the literature evaluated, references to its use are sparse. Overall, however, it can be concluded from the evaluated sources that the active ingredient is becoming increasingly important. The interviews also revealed that monochloramine is increasingly being used in larger plants in Germany and Switzerland. The advantages are low corrosiveness, lower consumption compared to chlorine dioxide, low AOX formation and a selective, microbial effect due to the reaction with sulfur compounds in the bacterial membrane.

The strongly exothermic reaction of the starting materials chlorine bleach and ammonium sulphate solution with the formation of nitrous gases can be regarded as a disadvantage. This requires higher safety precautions to safely avoid uncontrolled contact with the starting materials. The in-situ production of the active ingredient therefore places increased demands on operational management and plant safety.

CHLORINE DIOXIDE (MADE FROM...)

Identity, Admission, Classification

The status of chlorine dioxide was queried on the website of the European Chemicals Agency ECHA. In addition to the active ingredient itself, the approval procedure also identifies four different manufacturing processes. At the time of the survey, all approval procedures were ongoing. For chlorine dioxide with CAS 10049-04-4, a harmonised classification can be found in the ECHA database as well as a classification in the REACH dossier.

For the starting materials sodium chlorite and sodium chlorate mentioned in the manufacturing processes, substance data and classifications were also researched:

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument**
chlorine dioxide	Chlordioxid	10049-04-4	laufend	-	H314, H330; H400 (M10)	H314, H318, H330, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), H411	-
Chlorine dioxide generated from sodium chlorate and hydrogen peroxide in the presence of a strong acid	Chlordioxid, hergestellt aus Natriumchlorat und Wasserstoffperoxid in Gegenwart einer starken Säure	-	laufend	-	-	-	-
Chlorine dioxide generated from sodium chlorite by acidification	Chlordioxid, hergestellt aus Natriumchlorit durch Säuerung	-	laufend	-	-	-	-
Chlorine dioxide generated from sodium chlorite by electrolysis	Chlordioxid, hergestellt aus Natriumchlorit durch Elektrolyse	-	laufend	-	-	-	-
Chlorine dioxide generated from sodium chlorite by oxidation	Chlordioxid, hergstellt aus Natriumchlorit durch Oxidation	-	laufend	-	-	-	-
Ausgangsstoffe, Folgeprodukte bei der Herstellung von Chlordioxid							
Herstellungsverfahren (Referenz)	**Stoffbezeichnung**	**CAS Nummer**	**Funktion**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument**
Chlordioxid, in Gegenwart einer starken Säure aus Natriumchlorat und Wasserstoffperoxid hergestellt	Natriumchlorat	7775-09-9	Ausgangsprodukt	-	Vorschlag: H301	H302, Korr., Sens., CMR & chron. Tox.: keine Einstufung; Aq. Tox. (akut): keine Einstufung, H411	-
Chlordioxid, durch Säuerung aus Natriumchlorit hergestellt	Natriumchlorit	7758-19-2	Ausgangsprodukt	Stoffbewertung (CoRAP List): Verdacht auf mutagene und reproduktionstoxische Eigenschaften	-	H301, H310, H314, H373 (betroffenes Organ: Milz), Sens. & CMR : keine Einstufung; H400 (M1), H412	-

ABC categorization

For the ABC categorization of chlorine dioxide with CAS 10049-04-4, the classification of the REACH dossier can be used. It classifies chlorine dioxide with H330 ("danger to life if inhaled") and as corrosive to skin and eyes (H314, H318). No data are available for the production processes with sodium chlorite and sodium chlorate.

For an ABC categorization of the starting materials sodium chlorite and sodium chlorate, researched classifications from REACH dossiers are used: Both substances show an acute toxic hazard potential, sodium chlorite is classified as corrosive. Sodium chlorite is suspected to have a chronic toxic effect (H373). In addition, the substance is suspected of having a mutagenic or toxic effect on reproduction and is currently being evaluated in this regard (see below).

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Chlordioxid	10049-04-4	REACH Dossier	H330	H314, H318	-	-	H400 (M10)	H411
Chlordioxid, hergestellt aus Natriumchlorat und Wasserstoffperoxid in Gegenwart einer starken Säure	-	-	?	?	?	?	?	?
Chlordioxid, hergestellt aus Natriumchlorit durch Säuerung	-	-	?	?	?	?	?	?
Chlordioxid, hergestellt aus Natriumchlorit durch Elektrolyse	-	-	?	?	?	?	?	?
Chlordioxid, hergestellt aus Natriumchlorit durch Oxidation	-	-	?	?	?	?	?	?
Ausgangsstoffe, Folgeprodukte bei der Herstellung von Chlordioxid								
Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Natriumchlorat	7775-09-9	harmonisierte Einstufung, REACH Dossier	H301	-	-	-	-	H411
Natriumchlorit	7758-19-2	REACH Dossier	H301, H310	H314	-	H373 (Milz)	H400 (M1)	H412

Employee protection

The hazardous substances database of the German Accident Insurance GESTIS provides the following information [41]:

- Due to the explosive properties of chlorine dioxide, exposure opportunities in the workplace are very limited. There are two main possibilities: exposure to released gas during production and use, or direct contact with stabilized aqueous solution containing no more than 1% ClO2 (common form of trade and transport; higher concentrated solutions are explosive).
- Animal experiments indicate a low acute hazard potential for the occupational handling of highly diluted aqueous ClO2 solutions, provided that inhalation exposure through released gas or aerosol can be ruled out.
- There are no indications or test results regarding a skin sensitizing effect.
- From professional contact, only health disorders in connection with inhaled chlorine dioxide exposure were reported. In other studies and case reports, various persistent effects affecting the respiratory tract have been reported in connection with exposures to chlorine dioxide: bronchitis, pulmonary dysfunction, hyperreactivity of the airways to other irrigancies, asthmoid complaints and chronic inflammation of the nasal mucosa.

According to the Limit Values Ordinance (GVK) in Austria, the Technical Rules for Hazardous Substances (TRGS 900) in Germany, the following occupational exposure limits must be complied with for chlorine dioxide: TRGS 900: 0.1 ppm; GKV: 0.1 ppm.

Environmental behaviour / disinfection by-products (DBPs)

Rouge et al. cite the formation of disinfection by-products when chlorine dioxide is applied [42]:

- Chlorine dioxide is a powerful oxidizing agent and a common alternative disinfectant to chlorine with limited formation of organic halogenated disinfection by-products (DBPs). However, it inevitably forms chlorite ions (ClO2^{-}) through a 1-electron transfer from reactions with water matrix components and partially chlorate ions (ClO3^{-}). ClO2^{-} is a DBP with a World Health Organization (WHO) guideline value of 0.7 mg/l. It is proposed by the European Commission to set a lower value for ClO3 and ClO2 at 0.25 mg/l.
- Unlike chlorine, chlorine dioxide is not able to directly halogenate organic compounds. Although the DBPs produced by chlorine dioxide generally have much lower concentrations than the DBPs produced by chlorination , chlorine dioxide still produces its own set of DBPs such as haloacetic acids, halogen ketones and a large proportion of unknown organic halogen species.

Another publication also points to the lower potential for the formation of disinfection by-products [39]:

- Chlorine reacts (in drinking water disinfection) with certain naturally occurring organic substances to form chloroform (a trihalomethane or THM). As a consequence, the US EPA set a limit of 0.1 ppm for trihalomethanes in drinking water. Subsequently, research in the field of THM reduction in drinking water led the EPA to conclude that the use of chlorine dioxide is an effective means of controlling THMs. The application shows a significant reduction or absence of THM in systems.

The disinfection by-product sodium chlorite (CAS 7758-19-2) has been included in the Community Rolling Action Plan (CoRAP) as part of the substance evaluation[38]. This is partly due to concerns

---

[38] Community Rolling Action Plan (CoRAP) of the European Chemicals Agency (ECHA): Sodium chlorite

about the exposure of workers in connection with possible hazards from mutagenic and reprotoxic properties.

Application (Literature)

Active ingredient concentration

mg/l (ppm)	Source / Product	Comment
0,1 - 5	Brenntag	Chlorine dioxide, produced from sodium chlorite by oxidation
0,5 - 2	Beluga	Chlorine dioxide, produced from sodium chlorite by adding acid

A manual lists properties of chlorine dioxide relevant for cooling water treatment [11]:

- Since chlorine dioxide is a volatile gas, it is more practical if it is produced close to the place of use.
- In contrast to chlorine, chlorine dioxide as a biocide offers two advantages: it does not react with ammonia and its biological activity is only slightly affected by pH fluctuations between 6 and 10.
- As an algaecide, it is a little superior to chlorine. The chlorophyll of the algae is destroyed by chlorine dioxide. Water escapes from the protoplasm, which causes the algae to die. However, it is more expensive than chlorine.

Simpson et al. evaluate the biocidal properties of chlorine dioxide in application as follows [39]:

- Unlike chlorine, chlorine dioxide remains a true dissolved gas. The lack of a significant reaction of chlorine dioxide with water is partly responsible for the fact that it retains biocidal efficacy over a wide pH range. This feature makes it a logical choice for cooling systems operating in the alkaline pH range or cooling systems with poor pH control
- One possible reason for the slow regrowth of bacteria after sterilization by chlorine dioxide is its ability to penetrate and disperse biofilms. The effective killing and removal of biofilms allows bacteria to regenerate much more slowly
- Chlorine dioxide works exceptionally well in systems contaminated with ammonia and is very effective in cooling systems with a high degree of organic contamination.

According to AEV Cooling Systems and Steam Generators [16], a limit value of 0.19 mg/l chlorine dioxide (calculated as ClO2) must be complied with when discharging wastewater from evaporative cooling systems into a flowing water or a public sewer system, which is approved under water law

Application interview statements

Chlorine dioxide can be produced in on-site plants or chlorine dioxide solutions can be purchased and used ready-to-use – for smaller plants, for example.

A manufacturer describes the operation of a plant for the production of chlorine dioxide from sodium chlorite by adding acid (chlorite-acid process) on site as follows (Weidner Wassertechnik GmbH: Interview 5):

- The reactor is filled with the two feedstocks, followed by a reaction time of 10 to 15 minutes. The reactor contents are then ejected into the cooling water with a submersible pump. This cycle is repeated a maximum of four times for a total of two hours, so that a concentration of 0.2 – 1 ppm chlorine dioxide can be maintained in the cooling water. The two-hour shock treatment is carried out two to three times a week when the system is not loaded. If the cooling water system is (organically) loaded, the shock treatment is carried out daily.

Companies cite the following as advantages and disadvantages of chlorine dioxide in plant operation:

- Chlorine dioxide in cooling water can be measured online. Thus, the desalination can be controlled with simple measurement technology in such a way that chlorine dioxide has already reacted before the desalination is reopened. This significantly reduces wastewater pollution with biocide and increases environmental friendliness (Weidner Wassertechnik GmbH: Interview 5).
- When chlorine dioxide is used, very little AOX is produced compared to chlorine or sodium hypochlorite, while at the same time it is highly effective (Inwatec GmbH: Interview 8).

Chlorine dioxide begins to outgas strongly in the cooling tower at over 30°C. We have seen with customers that with a system that is stable in itself, the legionella concentration begins to fluctuate strongly at higher (outdoor) temperatures. This also increases the risk of corrosion of the system components that come into contact with the exhaust air. In these cases, the outgassing can also be noticed by the smell when you stand directly next to the generator system (Innowatech GmbH: Interview 9) Ready-to-use, stabilized one-component systems release chlorine dioxide when the pH is lowered. The following information is given in the interview:

In a stabilized one-component mixture, sodium chlorite is mixed with the oxidizer at a high pH. Chlorine dioxide is only produced in-situ after addition to the cooling water by the pH value drop to 7 to 9. This results in an excess of chlorine and slightly more AOX than in the production of chlorine dioxide (Inwatec GmbH: Interview 8). In addition, the interviews point out that chlorine dioxide should be presented as pure as possible on site in order to keep the AOX values as low as possible during desalination. Chlorine dioxide is also referred to as "the best solution" in connection with microbiological cooling water conditioning (Standardization Committee ÖNORM B 5020: Interview 12)

Market research

- Clorious2 is offered by Brenntag as a ready-to-use solution: *In contrast to conventional chlorine dioxide concepts, Clorious2 is the only highly concentrated, ready-to-use chlorine dioxide solution that is both stable and transportable.*
- The supplier Weidner Wassertechnik: describes its plant for in-situ production as follows: *The chlorine dioxide plant Beluga produces the chlorine dioxide in a newly developed reactor, which is sunk into the water to be treated. The potentially explosive and highly reactive chlorine dioxide is thus produced exclusively under water. An explosion or health hazard to employees is thus ruled out. These only come into contact with the starting substances hydrochloric acid and sodium chlorite. The following are required for production: hydrochloric acid (9%), sodium chlorite (7.5%)*

Conclusion

Chlorine dioxide is a reddish-yellow gas that is known for its high toxicity when inhaled. The substance database GESTIS reports on health disorders in connection with inhaled chlorine dioxide exposures from occupational interactions. The application has advantages over chlorine gas or chlorine bleach: chlorine dioxide quickly penetrates biofilms and destroys them. Itis dissolved as a gas and does not react with ammonia. Its activity is only slightly impaired by pH fluctuations and the development of resistance is negligible due to its properties as an oxidizing biocide. Disadvantages are safety concerns due to the toxicity of the gas and the explosiveness, the high tendency to outgassing in the cooling tower, especially at temperatures above 30 °C, the considerable corrosiveness and the higher costs compared to chlorination.

The gas is either used as a stabilized solution (especially in small plants) or produced from the precursor substances sodium chlorite or sodium chlorate by adding acid or oxidizing agent in a plant on site. Chlorite (ClO2-) is relevant as a reaction or degradation product. This is currently being evaluated in an EU CoRAP process with regard to potential CMR properties, as its widespread use poses the possibility of exposure at the workplace. In the literature, there is a reference to the fact that no trihalomethanes are formed when chlorine dioxide is applied, but adsorbable organic halogen compounds (AOX) are formed. Overall, however, AOX formation is significantly lower, so that in combination with a measurement before desalination and the use of chlorine dioxide produced as pure as possible, the environmental impact can be classified as low.

An active ingredient approval has not yet been granted.

The results of literature research and interviews show that chlorine dioxide has many advantages over chlorine gas or chlorine bleach, especially ecological ones. Human exposure to ClO2 as well as chlorite during production or application should be avoided as far as possible.

ACTIVE CHLORINE (PRODUCED OR RELEASED FROM…)

Identity, Admission, Classifications

On the homepage of the European Chemicals Agency ECHA, the approval status of "active chlorine" was queried. On the website, 6 production or release processes are listed. At the time of the survey, all approval procedures for product type 11 were ongoing. For "Active chlorine produced from sodium chloride by electrolysis", there is an active ingredient report for product type 2, among others [28]. For "Active chlorine released from chlorine" and "Active chlorine released from sodium hypochlorite", there is an opinion of the Committee for Biocidal Products [30] [31]. In the above-mentioned documents as well as in REACH dossiers, there are classifications that are used for ABC categorization.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
Active chlorine generated from seawater (sodium chloride) by electrolysis	Aktivchlor, hergestellt aus Meerwasser durch Elektrolyse	-	laufend	-	-	-	-
Active chlorine generated from sodium chloride by electrolysis	Aktivchlor, hergestellt aus Natriumchlorid durch Elektrolyse	-	laufend	-	-	-	Wirkstoffbericht (PT2): EUH031, (H314), H331, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M100), H410 (M1)
Active chlorine generated from sodium N-chlorosulfamate	Aktivchlor, hergestellt aus Natrium N-Chlorsulfamat	-	laufend	-	-	-	-
Active chlorine released from calcium hypochlorite	Aktivchlor, freigesetzt aus Calciumhypochlorit	7778-54-3	laufend	-	EUH031, H302, H314; H400 (M10)	EUH031, H302, H314, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), Aq. Tox. (chronisch): keine Einstufung	-
Active chlorine released from chlorine	Aktivchlor, freigesetzt aus Chlor	7782-50-5	laufend	-	H315, H319, H331, H335; H400 (M100)		BPC Stellungnahme (PT2): H315, H319, H330, H335; H400 (M100)
Active chlorine released from sodium hypochlorite	Aktivchlor, freigesetzt aus Natriumhypochlorit	7681-52-9	laufend	-	EUH031,H314, H318; H400 (M10), H410 (M1)	EUH031, H314, H318, Sens., CMR & chron. Tox: keine Einstufung; H400 (M10), H410 (M1)	BPC Stellungnahme (PT2): EUH031, H314, H400 (M10), H410 (M1)

ABC categorization

No classifications are available for the active ingredient "active chlorine" because "active chlorine" cannot be isolated and tested as a pure substance. The classifications are therefore derived from the starting materials chlorine gas or chlorine bleach (sodium hypochlorite). Chlorine bleach is classified as corrosive (H314), chlorine gas as life-threatening if inhaled (H330). A sensitizing, mutagenic, carcinogenic, toxic to reproduction or chronic toxic effect is not assumed. The hazard to the aquatic environment is determined by chlorinated degradation and derived products.

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Aktivchlor, hergestellt aus Meerwasser durch Elektrolyse	-	-	?	?	?	?	?	?
Aktivchlor, hergestellt aus Natriumchlorid durch Elektrolyse	-	Wirkstoffbericht Report (PT2)	EUH031, H331	H314	-	-	H400 (M100)	H410 (M1)
Aktivchlor, hergestellt aus Natrium N-Chlorsulfamat	-	-	?	?	?	?	?	?
Aktivchlor, freigesetzt aus Calciumhypochlorit	7778-54-3	REACH Dossier Calciumhypochlorit	EUH031, H302	H314	-	-	H400 (M10)	-
Aktivchlor, freigesetzt aus Chlor	7782-50-5	BPC Stellungnahme (PT2)	H330	H315, H319, H335	-	-	H400 (M100)	-
Aktivchlor, freigesetzt aus Natriumhypochlorit	7681-52-9	BPC Stellungnahme (PT2), REACH Dossier	EUH031	H314, H318	-	-	H400 (M10)	H410 (M1)

The further analysis takes into account active ingredient/manufacturing combinations insofar as they appear to be relevant for use in evaporative cooling systems, namely:

- Active chlorine, produced from sodium chloride by electrolysis
- Active chlorine, released from chlorine
- Active chlorine, released from sodium hypochlorite

Active chlorine, produced from sodium chloride by electrolysis

Active Ingredient Specification, Worker Protection

The authorisation report [28] and the statement [29] based on it specify as follows:

- It is an equilibrium mixture that is strongly dependent on the pH value and whose components cannot be isolated. In the electrolysis cell, chloride (Cl^-) is oxidized to chlorine (Cl2), which rapidly hydrolyzes to form hypochlorous acid (HOCl), chloride and hypochlorite (OCl^-). "Active chlorine" refers to the forms of available chlorine mentioned above.
- The concentration of active chlorine depends on electrolyte concentration, temperature and pH value. At pH 7.5, the ratio of hypochlorite to hypochlorous acid is 1:1, at higher pH values hypochlorite dominates. The "active chlorine" produced by electrolysis consists of 99.5% water, the content of available chlorine (Cl2 + hypochlorous acid + sodium hypochlorite) is about 300 mg/l
- Active chlorine, which is obtained from sodium chloride by electrolysis, does not have any dangerous physicochemical properties. It is non-explosive, non-flammable or flammable. It has an oxidizing mode of action, but it is not classified as an oxidizing agent due to the dominance of water properties. Due to the physicochemical properties of the product, no risk is expected
- The toxicological profile is linked to that of sodium hypochlorite, hypochlorous acid and chlorine gas. On the basis of available toxicological data covering the standard information requirements for biocides and some observational data in humans, it was concluded that the only obvious toxicological problem is the irritating potential of solutions of sodium hypochlorite for the eyes, skin and respiratory tract.

Active chlorine, released from chlorine

Active Ingredient Specification, Worker Protection

The opinion of the Biocidal Products Committee makes the following statement [30]:

- When used, chlorine releases active chlorine by reacting in water to form hypochlorous acid and hydrochloric acid. Furthermore, hypochlorous acid partially dissociates to the hypochlorite anion. The ratio of chlorine, hypochlorous acid and the hypochlorite anion in the aqueous equilibrium solution is pH and temperature dependent.
- The rating is based on the evaluation of chlorine (a gas at room temperature and ambient pressure) and the active ingredient active chlorine, as an aqueous equilibrium solution
- Chlorine gas is handled exclusively in closed systems and exposure to the gas is only incidental. Due to its gaseous state of aggregation, inhalation is the only possible route of exposure.

The effects on human health are primarily due to the local mode of action of chlorine gas, and possible systemic effects are secondary to its direct irritating reactivity.

Active chlorine, released from sodium hypochlorite

In its opinion, the Biocidal Products Committee states [31].

- When applied, sodium hypochlorite releases active chlorine by hydrolyzing it in water to form hypochlorous acid, which can react to chlorine depending on the pH. The ratio of chlorine, hypochlorous acid and hypochlorite anion in the aqueous equilibrium solution is pH and temperature dependent

- The primary mode of action of active chlorine released from sodium hypochlorite in aqueous solutions is characterized by local irritation/corrosion and oxidation at the site of first contact, triggered by direct chemical reactivity. All systemic effects observed in animal studies are considered secondary to local irritation/corrosion.

Resistance development

In the opinion of the Biocidal Products Committee on the authorisation of "active chlorine produced by electrolysis from sodium chloride", a possible development of resistance is assessed as follows [29]:

The resistance of pathogens to active chlorine is not very likely. The resistance of pathogens to active chlorine is no higher than that of other active substances with a general mode of action (oxidation). No specific resistance management strategies are required for active chlorine-based disinfectants

Environmental behaviour and disinfection by-products (DBPs)

In the opinions of the Biocidal Products Committee, the following (unanimous) statements can be found with regard to the threat to the aquatic environment [29], [30], [31]:

- For the chemical reactivity in an aqueous solution with the same active chlorine concentrations and the same pH conditions, it is irrelevant whether active chlorine is produced either from chlorine gas, calcium hypochlorite, sodium hypochlorite or from sodium chloride by electrolysis. Therefore, all studies on aqueous hypochlorite solutions were used for the evaluation of active chlorine.
- In terms of the aquatic environment, algae proved to be the most sensitive species in the long-term test. Active chlorine is highly reactive and reacts quickly with organic matter in the sewer, in the sewage treatment plant, in surface water and in the soil. Where organic material is present, active chlorine acts as a highly reactive oxidizing agent. Active chlorine degrades rapidly in all environmental compartments.
- Active chlorine forms disinfection by-products (DBPs), the risks of which should be assessed during product approval.
- Active chlorine released from chlorine is not believed to have endocrine disrupting properties.

With regard to degradation and derivatives of active chlorine, ECHA's guidance on the risk assessment of disinfection by-products (DBPs) makes the following findings [32]:

- The use of halogenated biocides leads to the formation of disinfection by-products (DBPs). These have been shown to contain substances that may pose a risk to human health or the environment
- Several known (groups of) DBPs are biologically active, and some are (suspected) carcinogens or mutagens (e.g., chloroform, halogenated methane, bromate). In addition, most DBPs are more stable than the biocide itself. Therefore, a risk assessment of DBPs is required in the context of the authorisation of biocidal products
- The formation of DBPs is often characterized by measurement (the increase) of group parameters such as TOX (total organic halogens) or AOX (adsorbable organic halogens). AOX is the part of TOX that can be adsorbed on activated carbon, which is the case with most DBPs. However, the composition of AOX and its relationship to ecotoxicity is unknown and can change even if absolute amounts remain the same. Therefore, there is too little information

to define an acceptable AOX value that can be used as a trigger for a risk assessment in terms of ecotoxicological impacts

- Key parameters determining the type and amount of DBPs likely to be formed during the use of an active halogen biocide are pH, the type of substrates present, the dose applied, the contact time, and the temperature.
- In terms of pH, it can be assumed that at pH 6 and higher, there may be slight shifts in the relative proportions of specific by-products (e.g., increased THM [39]formation as pH increases), but the overall hierarchy will not change. This means that THM will be dominant, followed by HAA[40], followed by halo aldehydes, halo ketones, and halo acetonitriles, followed by smaller groups. At pH > 6, there is no significant formation of polyhalogenated dioxins, furans, etc.
- Influence of the substrate: When comparing substrates, it is important to consider whether the substrate is dominated by proteins, carbohydrates and/or fats (e.g. surface cleaning, swimming pools) or by natural organic matter (groundwater)
- Dose, contact time and temperature: An increase in the applied dose, contact time and temperature generally leads to increased DBP formation. The extent to which this happens depends on the (persistent) presence of suitable substrates, and a threshold can be reached quickly
- The known DBP groups that should at least be included in the risk assessment are: trihalomethanes (THMs), halogenated acetic acids (HAAs), halogenated acetonitriles (HANs), bromate, halogenated phenols and halogenated amines
- Based on the literature on this topic, trihalomethanes (THMs) and trichloramine are considered volatile DBPs
- In principle, exposure to non-volatile DBPs is possible through aerosol formation. It should be noted that this pathway (aerosol) is unimportant for overall exposure to DBP.

Statements on application from literature and interviews

Active ingredient concentrations (application):

	mg/l (ppm)	Source /Link/Manufacturer
Active chlorine, produced from sodium chloride by electrolysis	0,5 – 1,5	Danish clean water
Active chlorine, released from sodium hypochlorite	0,5 – 5	[9]
Limit value for discharge into public sewer system	0,3	[16]

Active chlorine, produced from sodium chloride by electrolysis

The following statements can be found in literature or interviews:

- In one process, a low-concentration, hypochlorous acid is produced by electrolysis of sodium chloride, water and electric current. The in-situ method is implemented directly at the user's site. For this purpose, drinking water is usually softened, enriched with a saline solution and fed into a reactor. The resulting biocide is dosed directly into the cooling water via a stacking container. Active ingredient-dependent proportional dosages or controls via the redox value

---

[39] Tri- or tetra-halomethane

[40] Haloacetic acids

are easy to implement. Hypochlorous acid is effective against various microorganisms and also attacks biofilms [1].

- Chlorine – which can now be elemental chlorine or chlorine gas, sodium hypochlorite, hypochlorous acid or hypochlorite – forms chlorinated organic substances together with organic substances, which are recorded as AOX. This means that the formation of AOX is just as possible in an electrolysis plant. However, if active chlorine is produced locally by electrolysis from sodium chloride, the stockpiling of hazardous substances can be avoided (Inwatec GmbH: Interview 8).

A supplier characterizes its plant for the production of active chlorine by saline electrolysis as follows (Innowatech GmbH: Interview 9)

- The plant operates without hazardous materials in that only saline tablets, drinking water and electricity are required for electrolysis. The manufacturing costs are low. For a medium-sized plant, about one ton of salt per year is needed.
- The concentrate produced by the plant contains 250 – 1500 ppm of free chlorine, and the cooling water itself contains between 0.1 and 0.3 ppm of free chlorine. The buffer tank is dimensioned in such a way that the concentrate is only stored for a short time or consumed quickly.
- The treatment is permanent, and there is no provision for alternating with other biocides. Resistance problems are not known in practice.
- AOX do not cause any problems due to the low dosage in the cooling water.
- The chlorine content is permanently measured and documented together with pH, conductivity and temperature. The cooling water does not show a chlorine smell. The active ingredient breaks down biofilms very well. If limit values are exceeded, a fault message is given. The systems also work well at pH 8.5 to 9, no pH adjustment with acid is needed.
- A hardness stabilizer is added when very hard source water is used.
- A specially provided corrosion inhibitor is available for operation. Other corrosion inhibitors can be used, but must be tested for compatibility.

Active chlorine, released from sodium hypochlorite or chlorine gas

In addition, the following statements can be found in literature or interviews about the operation or the advantages and disadvantages of using it:

- Commercial solutions of sodium hypochlorite contain around 15% effective chlorine. At the pH values of over 8, which are common in cooling circuits, the biocidal effect of chlorine in water decreases sharply. The application of chlorine can lead to the formation of a number of undesirable by-products. Organic chlorine compounds (AOX) are particularly relevant here [10].
- The advantages of sodium hypochlorite are easy handling and inexpensive purchase without high investment costs. The disadvantages are space requirements for logistics and storage, the formation of AOX and attacks on materials [13].
- Sodium hypochlorite and chlorine (gas) are less effective at high pH. The strengths are cost-effectiveness. There are safety concerns about chlorine as a toxic gas; Sodium hypochlorite has limited stability [8].
- The hypochlorous acid is most effective at pH less than 8. If the pH value rises, the equilibrium shifts to sodium hypochlorite, which is much less effective. In order to maintain the effectiveness with rising pH, more chlorine is required and correspondingly more AOX is generated. Therefore, for an economical as well as low-AOX operation, it is important to

maintain a pH of 7.5 to a maximum of 8 (case-by-case consideration) (Inwatec GmbH: Interview 8).

- By spraying the cooling water in the cooling tower and the associated discharge of CO2, the pH value rises above 8.5 without permanent dosing of acid. If there is a lack of monitoring, this can lead to a lot of chlorine having to be added and AOX is produced accordingly. Chlorine is only effective in a limited pH value range between pH 7 – 7.3. Above pH 7.3, the effect is only about 50% and from pH 8 only at about 10% of the dosed amount used. For this reason, sulphuric acid, for example, is added to set a pH value of 7.3 to 7.4 (Weidner Wassertechnik GmbH: Interview 5).

In Austria, the following emission limits are set when the discharge of wastewater from open recirculating cooling systems into a watercourse or a public sewer system is approved under water law:

- Free chlorine calculated as Cl2: 0.3 mg/l (discharge into flowing waters or public sewerage) [16].

Market research

Two suppliers of plants for the production of active chlorine from table salt by electrolysis were researched. These are the supplier Novochem GmbH with the Novoclean Ox technology and the provider Danish Clean Water with the NEUTHOX technology. In this context, it is worth mentioning case studies published in the USA that address the reduction of water, energy and chemical consumption in evaporative cooling systems [33], [34], [35]. In one case, this involves the electrolysis of table salt.

Conclusion

The active ingredient "active chlorine" is present in a pH-dependent balance of hypochlorous acid, chlorine and sodium hypochlorite. The hazard potential of "active chlorine" results proportionately from the chlorine gas present in equilibrium, or the chlorine bleach solution (sodium hypochlorite). Chlorine bleach is corrosive (H314), chlorine gas is life-threatening if inhaled (H330). A sensitizing, mutagenic, carcinogenic, toxic to reproduction or chronic toxic effect is not assumed, so that the aqueous solution can only be assumed to have a locally irritating or corrosive effect. The effects on the aquatic environment are determined by the high reactivity of active chlorine with organic substances, while active chlorine itself is assumed to degrade rapidly. The formation of (organic) follow-up products is influenced by several factors, such as: composition of the cooling water, pH value, dosage of the biocide, operating temperature or residence time. In the context of the present study, derivatives are not evaluated in detail, but a human and ecotoxic effect can generally be assumed. As far as the sum parameter AOX, which describes the extent of (halogenated) derivatives, is concerned, interview statements indicate that AOX formation is comparatively low or better controllable in the active ingredient/manufacturing combination "active chlorine produced from sodium chloride by electrolysis". In addition, this form of application does not come into contact with concentrates and thus human exposure to hazardous substances is low. Chlorine gas and sodium hypochlorite are mainly used because of the lower costs (e.g. compared to chlorine dioxide). In view of the associated dangers for the environment (such as high AOX exposure) and for worker protection (chlorine gas exposure), processes in which active chlorine is produced from sodium chloride by electrolysis are definitely preferable.

ACTIVE BROMINE (MADE FROM …)

Identity, Admission, Classification

On the homepage of the European Chemicals Agency ECHA, the approval status of active bromine was queried. Of the 7 manufacturing processes shown, all approvals were ongoing at the time of the survey. In addition, substance data and the classifications of the mentioned starting materials, including bromine, were researched:

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument
Active bromine generated from bromine chloride	Aktivbrom, hergestellt aus Bromchlorid	-	laufend	-	-	-	-
Active bromine generated from hypobromous acid and urea and bromourea	Aktivbrom, hergestellt aus Hypobromsäure und Harnstoff sowie Bromharnstoff	-	laufend	-	-	-	-
Active bromine generated from sodium bromide and calcium hypochlorite	Aktivbrom, hergestellt aus Natriumbromid und Calciumhypochlorit	-	laufend	-	-	-	-
Active bromine generated from sodium bromide and chlorine	Aktivbrom, hergestellt aus Natriumbromid und Chlor	-	laufend	-	-	-	-
Active bromine generated from sodium bromide and sodium hypochlorite	Aktivbrom, hergestellt aus Natriumbromid und Natriumhypochlorit	-	laufend	-	-	-	-
Active bromine generated from sodium bromide by electrolysis	Aktivbrom, hergestellt aus Natriumbromid durch Elektrolyse	-	laufend	-	-	-	-
Active bromine generated from sodium hypobromite and N-bromosulfamate and sulfamic acid	Aktivbrom, hergestellt aus Natriumhypobromit, N-Bromsulfamat und Sulfaminsäure	-	laufend	-	-	-	-
Ausgangsstoffe, Folgeprodukte bei der Herstellung von "Aktivbrom"							
Aktivbrom, hergestellt aus Natriumbromid und …	Natriumbromid	7647-15-6	Ausgangsprodukt	-	Vorschlag: H360FD, H362, H336, H372	Akut. Tox., Korr., Sens., Muta, Karz.: keine Einstufung; H361, H373 (Zentralnervensystem), Aq. Tox. (akut & chronisch): keine Einstufung	-
Aktivbrom, hergestellt aus… und Natriumhypochlorit	Natriumhypochlorit	7681-52-9	Ausgangsprodukt	-	EUH031, H314, H318; H400 (M10), H410 (M1)	-	-
Aktivbrom, hergestellt aus… und Calciumhypochlorit	Calciumhypochlorit	7778-54-3	Ausgangsprodukt	-	EUH031, H302, H314; H400 (M10)	EUH031, H302, H314, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), Aq. Tox. (chronisch): keine Einstufung	-
Aktivbrom, hergestellt aus Natriumhypobromit, N-Bromsulfamat und Sulfaminsäure	Natriumhypobromit	13824-96-9	Ausgangsprodukt	-	-	-	-
	N-Bromosulfamat	-	Ausgangsprodukt	-	-	-	-
	Sulfaminsäure	5329-14-6	Ausgangsprodukt	-	H315, H319, H412	Akut.Tox., Sens, CMR & chron. Tox.: keine Einstufung; Aq. Tox. (akut): keine Einstufung, H412	
Aktivbrom, hergestellt aus Bromchlorid	Bromchlorid	13863-41-7	Ausgangsprodukt	H314, H331, H400 (M?)	-	-	-
Aktivbrom, hergestellt aus Hypobromsäure und Harnstoff sowie Bromharnstoff	Hypobromsäure	13517-11-8	Ausgangsprodukt	-	-	-	-
	Harnstoff	57-13-6	Ausgangsprodukt	keine Einstufung	-	-	-
	Bromharnstoff	-	Ausgangsprodukt	-	-	-	-
	Brom	7726-95-6		-	H314, H330, H400	H330, H314, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M100), Aq. Tox. (chronisch): keine Daten	-

ABC categorization

For the starting materials and bromine, the researched classifications were used for an ABC categorization:

Ausgangsstoffe, Folgeprodukte bei der Herstellung von "Aktivbrom"								
Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Natriumbromid	7647-15-6	REACH Dossier (Vorschlag harmonisierte Einstufung)	-	-	-	**H361 (H360), H373 (H372) (Zentralnerven system)**	-	-
Natriumhypochlorit	7681-52-9	REACH Dossier	EUH031	H314	-	-	H400 (M10)	H410 (M1)
Calciumhypochlorit	7778-54-3	REACH Dossier	EUH031	H314	-			
Natriumhypobromit	13824-96-9	-	?	-	?	?	?	?
N-Bromosulfamat	-	-	?	-	?	?	?	?
Sulfaminsäure	5329-14-6	REACH Dossier	-	H315, H319	-	-	-	H412
Bromchlorid	13863-41-7	ECHA Infocard	H331	H314	-	-	H400 (M?)	-
Hypobromsäure	13517-11-8	-	?	-	?	?	?	?
Harnstoff	57-13-6	ECHA Infocard	-	-	-	-	-	-
Bromharnstoff	-	-	?	-	?	?	?	?
Brom	7726-95-6	REACH Dossier	H330	H314	-	-	H400 (M100)	?

No data are available for sodium hypobromite, N-bromine sulphate, hypobromic acid and bromineeas, but hazards can be ruled out for sulfamic acid and urea. Sodium and calcium hypochlorite are acutely toxic by inhalation and are classified as corrosive. In the case of sodium bromide, the classifications in the REACH dossier and the proposal for a harmonised classification indicate a high risk due to reprotoxic and chronic toxic properties. In the case of bromine, the classification shows a considerable risk during inhalation.

Further analysis takes into account the following active ingredient/manufacturing combination:

Active bromine produced from sodium bromide and sodium hypochlorite

Employee protection

The hazardous substances database of the German Accident Insurance GESTIS provides the following information on the hazard potential of the starting substance sodium bromide [41], which is relevant for employee protection:

- Repeated (oral) exposure leads to an accumulation of bromide ions in the blood. This is accelerated when the amount of chloride absorbed at the same time is reduced. Effects include: Slurred speech, sensitivity to touch, memory impairment and visual disturbances.
- A TWA (time weighted average) value for the inhalation of aerosols of 7 mg/m3 anda maximum concentration of 3.2 ppm in cooling water systems was proposed.

Mode of action

A manual [58] explains the mechanism of action of active bromine starting from the hypobromic acid via a pH-dependent equilibrium:

- Hypobromic acid can be produced relatively easily by reacting a bromide with hypochlorous acid ($HOCl + Br^- \rightarrow HOBr + Cl^-$). In practice, an appropriate amount of bromide salt (sodium bromide) is added to a solution of sodium hypochlorite.
- Hypobromic acid is a strong biocide and dissociates analogously to hypochlorous acid: $HOBr \rightarrow H+ + OBr^-$. Due to a smaller dissociation constant, the hypobromous acid is present in the interest, i.e. slightly alkaline pH range of 8 to 9 to a much higher proportion in the undissociated form. It is therefore much more suitable for alkaline cooling water. In addition, hypobromite has a stronger biocidal effect than hypochlorite.

Active ingredient concentration: 4.5 - 9 mg/l (ppm) total bromine content. Source : Nalco STABREX ST 40 Safety Data Sheet

Market research: Nalco STABREX ST 40 (SDS). Active ingredients in the product: Sodium hypochlorite: 6.36%; Sodium bromide: 9.23%. The supplier is advertising the product for industrial and commercial recirculating cooling water systems.

Application (literature & interview statements)

Bromination or the use of active bromine in cooling water treatment is described in a manual [11] as a "promising alternative to chlorination" that is "increasingly being used". According to this, the following starting materials can be used: gaseous bromine, bromine chloride, 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDHM), bromine salts and sodium bromide together with sodium hypochlorite. The advantages of bromination compared to chlorination are given as follows:

- Active bromine is not as volatile as active chlorine and can therefore remain in solution longer
- Active bromine is more effective at elevated pH levels and acts faster than active chlorine
- the reaction of active bromine with nitrogen and ammonia derivatives is identical to that of active chlorine, but the bromines formed are not stable compounds
- Active bromine is less corrosive than active chlorine

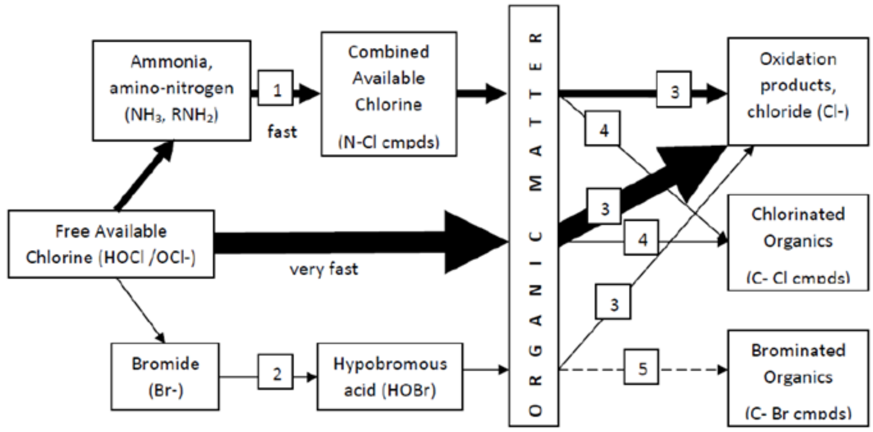
The disadvantage mentioned is that active bromine causes higher costs.

In an interview, the possibilities of producing active bromine in a plant are described as follows:

- There are stabilized ready-to-use mixtures and in-situ processes. In the in-situ process, sodium bromide and chlorine bleach are mixed together, whereby the ratio or their setting is important. At high pH, operation with hypobromic acid is favorable, also because it is less volatile than chlorine or chlorine dioxide. However, if the dosage is too high, the stabilizer contained in the finished mixture in the cooling water prevents the turnover and the added biocide does not work well (Inwatec GmbH: Interview 8).

Environmental behaviour, derivatives and degradation products

The European Chemicals Agency's ECHA guideline on disinfection by-products (DBPs) provides an overview of the degradation pathways of active chlorine and active bromine [32]:



The main statements are:

- Most of the information about DBPs is related to chlorination, but in general, the principles apply to bromination as well. The extent to which different compounds are formed may vary depending on the competition between bromine and chlorine in substitution reactions. If bromine is used as an active ingredient, pathways 3 and 5 gain in importance (see graph above).
- The formation of brominated organic compounds becomes more important when bromide is present in the treated water.
- As data clearly show, brominated and chlorinated DBPs are interchangeable in the sense that, depending on the source content of active chlorine or active bromine in the treated water, the formation of either chlorinated or brominated trihalomethanes dominates.

This results in a complex formation of disinfectant by-products comparable to "active chlorine" for the use of "active bromo". These include brominated methane, brominated acetic acids or bromate.

Conclusion

To date, no authorisation has been granted for the production processes of 'active bromine'. A common production method of "active bromine" is the formation of hypobromous acid by mixing a solution of sodium hypochlorite with sodium bromide. Hypobromic acid is a strong biocide and dissociates at higher pH values compared to hypochlorous acid or "active chlorine", which is why the former is better suited for alkaline cooling water. Other advantages include lower corrosiveness and lower volatility. From the point of view of employee protection, the acute toxic hazard when inhaled as well as the corrosive properties of sodium hypochlorite and a high reproductive toxic and chronic toxic hazard potential of sodium bromide are relevant. This is relevant if a concentrate of sodium hypochlorite and sodium bromide is stored on site and added to the plant. The formation or release of brominated organic derivatives is to be assumed analogous to "active chlorine" and, in addition to chlorinated substances, includes tribromethane, brominated acetic acids and bromate.

BCDMH (BROMOCHLORODIMETHYLHYDANTOIN)

Identity, Admission, Classification

On the website of the European Chemicals Agency ECHA, the status of the approval procedure of the biocidal active ingredient 1-bromo-3-chloro-5,5-dimethylhydantoin or BCDMH was queried. At the time of the survey, the approval process was still ongoing for all product types. For the active substance, the ECHA database only contains an evaluation of all registrations with regard to their classification as substance information.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)**
Bromochloro-5,5-dimethylimidazolidine-2,4-dione (BCDMH/Bromochlorodimethylhydantoin)	Bromchlor-5,5-dimethylimidazolidin-2,4-dion (BCDMH/Bromchlordimethylhydantoin)	32718-18-6	laufend	H302, H314, H317, CMR & chron.Tox.: keine Daten verfügbar; H400 (M?), H410 (M?)	-	-	-

ABC categorization

For ABC categorisation, the H-phrases mentioned by ECHA are used.

Stoffbezeichnung (Edukt)	**CAS**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächengewässer (Aq. Tox. akut)	Gefährdung Oberflächengewässer (Aq. Tox. chronisch)
Bromchlor-5,5-dimethylimidazolidin-2,4-dion (BCDMH/Bromchlordimethylhydantoin)	32718-18-6	ECHA Infocard	H302	H314	H317	?	H400 (M?)	H410 (M?)

Employee protection

BCDMH is classified as skin sensitizing with H317 and as corrosive (H314). No classifications are available with regard to carcinogenic, mutagenic, reprotoxic and chronic toxic effects, but such can not yet be ruled out due to the current lack of data.

Environmental behaviour and application

Degradation behaviour, degradation, derivatives: Classification with H410 indicates a long-term toxic effect on aquatic organisms. There are no classifications for this link in ECHA's REACH dossier or short- or long-term hazards to the aquatic environment are excluded.

Active ingredient concentration: 3.4 mg/l (ppm; Median) [12]

Mechanism of action: BCDMH is classified as an oxidizing biocide, because the reaction with water releases hypobromous or hypochlorous acid with a time delay, which are the actual active ingredients.

BCDMH is mainly used in smaller plants, but occasionally related compounds such as 1,3-dichloro-5,5-dimethylhydantoin or 1,3-dichloro-5-ethyl-5-methylhydantoin are also used. Various sources cite advantages and disadvantages of using it [8], [10], [12], [13], [39]:

- ➢ Simple dosing of the solids ("tablets") via a cooling water partial flow
- ➢ Time-shifted effect, which makes it easier to reach less flooded areas

- Lasting efficacy at higher pH caused by the release of hypobromous acid and overall high biocidal efficacy compared to chlorine releasers.

The disadvantages mentioned are:

- Dust generation when using small amounts of material.
- Formation of halogenated degradation and derivatives (analogous to active bromine or active chlorine)
- Not cost-effective

Conclusion

An evaluation of BCDMH within the framework of the EU active substance approval is pending and there is insufficient data available to rule out hazards. For employee protection, the sensitizing and corrosive properties must be taken into account. No conclusions can be drawn about the aquatic hazard potential from the available water toxic classifications. "Active bromine" or "active chlorine" are released from BCDMH by hydrolysis, so it can be classified as oxidizing biocides. In addition to the simple possibility of dosing, the attractiveness of BCDMH is mainly explained by the high biocidal efficacy of active bromine even at higher pH values and the delayed release. BCDMH is preferably used in smaller systems and is dosed via a separate partial flow. The formation or release of brominated organic derivatives can be assumed by analogy with active chlorine and active bromine. In addition to the formation of chlorinated compounds of tribrommethane, this refers to brominated acetic acids and bromate.

DBNPA (2,2-DIBROMO-2-CYANACETAMIDE)

Identity, Admission, Classifications

The status of the authorisation procedure for the biocidal active ingredient 2,2-dibromo-2-cyanacetamide or DBNPA (CAS 10022-01-2) was queried on the website of the European Chemicals Agency ECHA. At the time of the survey, the approval procedure was ongoing. The database contains a proposal for a harmonised classification as well as a classification in the opinion of the Committee for Biocidal Products for authorisation in product type PT4.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene**
2,2-dibromo-2-cyanoacetamide (DBNPA)	2,2-Dibrom-2-cyanacetamid (DBNPA)	10222-01-2	laufend	bewertet hinsichtlich endokriner Wirksamkeit	Vorschlag: H301, H330, H315, H317, H318, H372 (Atemtrakt), H400 (M1), H410 (M1)	-	BPC Stellungnahme (PT4): H301, H330, H315, H317, H318, H372 (Atemtrakt); H400 (M1), H410 (M1)

ABC categorization

For ABC categorization, the H-phrases of the proposal for harmonized classification are used [27]. DBNPA is classified as H330 ("danger to life if inhaled") and as skin sensitizing (H317), as well as with STOT RE 1, H372 ("damages the organs during prolonged and repeated exposure") with the target organ respiratory tract. The opinion of the Biocidal Products Committee [26] assumes endocrine activity against humans and non-target organisms.

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
2,2-Dibrom-2-cyanacetamid (DBNPA)	10222-01-2	harmonisierte Einstufung (Vorschlag)	H301, H330	H315, H318	**H317**	**H372 (Atemtrakt)**	H400 (M1)	H410 (M1)

Employee protection

DBNPA is skin sensitizing. The classification "Damages the organs through prolonged and repeated exposure" (STOT RE 1, H372) is justified by effects on the respiratory tract. In addition, the Committee for Biocidal Products (BPC) states in its opinion that there is an endocrine activity in humans [27]:

- The conclusion is based on the observed side effects in the thyroid gland in the studies in rats and dogs in combination with data from a literature review on bromide effects on the thyroid gland. Bromide can replace iodide in transport processes in the thyroid gland, resulting in a relative iodide insufficiency in the synthesis of thyroid hormones. This shows an association between the observed adverse effects on the thyroid gland and endocrine activity, which is relevant for humans and non-target organisms

Candidate for substitution according to the Biocidal Products Regulation (BPR), endocrine efficacy : The evaluation of the endocrine efficacy of DBNPA is based on the sequelae or degradation product bromide. Together with the above statement [27], documents have been published that controversially discuss the application of Article 5 (substitution requirement) in connection with endocrine activity to non-target organisms (minority positions of the Swedish Chemical Agency and the Federal Institute for Occupational Safety and Health BAuA). According to the opinion, DBNPA fulfils the exclusion criteria under Article 5 of the Biocidal Products Regulation due to its endocrine properties and is a candidate for substitution. This means that DBNPA can only be approved under very specific exceptional conditions (applies to product type 4) [26].

Application and environmental behaviour (according to literature)

In the literature, the non-oxidizing biocide DBNPA is described as a biocide used especially in smaller plants. It is unstable at pH > 7.5 and hydrolyzes rapidly. Its advantages are uncomplicated storage and handling [9]. In addition to rapid hydrolysis, toxic by-products are also described as disadvantages.

Active ingredient concentration: 4 - 8 mg/l [9] or 1 - 4.8 mg/l (PDB Nalco 7320)

Mechanism of action: DBNPA is a fast-acting biocide and exerts its biocidal action immediately after its application via bromine, which inactivates enzymes by converting functional -SH groups into the oxidized S-S form. This reaction irreversibly disrupts the function of cell surface components, interrupts transport through cell membranes and inhibits important biological functions [26]. However, DBNPA is sensitive to UV radiation and nucleophiles, so that the substance is sometimes decomposed within seconds. The resulting reaction products are sometimes toxic to a considerable extent and are also not harmless to humans.

Development of resistance: The risk of developing resistance to the active ingredient is estimated to be low due to the mode of action, which affects several cellular targets [26].

Degradation behavior, degradation, derivatives: According to its chemical properties, DBNPA can be degraded in two ways: hydrolysis and nucleophilic reaction. DBNPA is finally degraded to oxalic acid, malonic acid and bromide [12], [27].

Market research: According to the safety data sheet, Nalco 7320 contains 10 – 30% of 2,2-dibromo-3-nitrilopropionamide (CAS 10222-01-2) (SDS)

Conclusion

DBNPA is sensitizing and shows chronic toxicity in animal experiments, the target organ is the respiratory tract. DBNPA is believed to have an endocrine effect on humans and non-target organisms caused by the degradation product bromide. DBNPA therefore fulfils the criteria for substitution under Article 5 of the Biocidal Products Regulation. Due to the health hazards (skin sensitization, chronic toxicity for the respiratory tract) as well as a (controversially discussed) endocrine hazard potential due to the secondary or degradation product bromide, its use is not advisable. DBNPA, a non-oxidizing biocide, is preferred in smaller plants.

BRONOPOL (2-BROMO-2-NITROPROPANE-1,3-DIOL)

Identity, Admission, Classification

The status of the authorisation procedure for 2-bromo-2-nitropropane-1,3-diol or BNPD (CAS 52-51-7) was queried on the website of the European Chemicals Agency ECHA. At the time of the survey, the approval process was still ongoing for all product types. For the active substance, the proposal for a harmonised classification and a REACH dossier with manufacturer classification can be found in the database of the European Chemicals Agency ECHA.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)**
Bronopol	2-Brom-2-nitropropan-1,3-diol	52-51-7	laufend	-	Vorschlag: H301, H312, H315, H318, H331, H335, H400 (M10), H411	H301, H312, H315, H318, H331, H335, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), H410 (M1)	-

ABC categorization

For ABC categorisation, the H-phrases of the manufacturer classification of the REACH dossier are used:

Stoffbezeichnung (Edukt)	**CAS**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
2-Brom-2-nitropropan-1,3-diol (Bronopol)	52-51-7	REACH Dossier	H301, H312, H331	H315, H318, H335	-	-	H400 (M10)	H410 (M1)

Employee protection

Bronopol is classified as H331 ("Toxic by inhalation") and H318 ("Causes serious eye damage"), among others. Sensitizing, carcinogenic, mutagenic, toxic to reproduction and chronic toxic properties are excluded according to the REACH dossier and there are no classifications in these hazard categories in ECHA's C&L Inventory. However, there is evidence that bronopol, as a widely used preservative in skincare products, has some skin-sensitizing potential. In any case, the German Contact Allergy Group (DKG) has noticed an increasing number of sensitizations since 2003 [59], [60].

Application and Environmental Behavior (Literature)

Active ingredient concentration: 5 – 50 mg/l (ppm) Source: [9]

Mechanism of action: In addition to the slow release of formaldehyde, the effect of bronopol is based on the inactivation of thiols, as they are present in the active centers of various enzymes. The biocidal effect increases with increasing pH and higher temperature, although the decay rate also increases [9]. The formaldehyde released in the alkaline medium contributes only to a small extent to the biocidal efficacy [12].

Degradation behaviour, degradation, derivatives, ecotoxicity:

The following information can be found in the literature:

- Hydrolysis increases with increasing pH value and temperature, degradation products are bromide, nitrite, bromonitroethanol and formaldehyde [12].
- The genotoxic effect in the cooling circuit of a company is therefore most likely due to the biocide [...], whereby the effects can be explained by both isothiazolinones and bronopol [12].
- In their publication, Cai et al. [40] find that in natural waters, some reversible degradation pathways of bronopol led to a complex mixture of degradation products. 2-bromo-2-nitroethanol (BNE) and bromonitromethane (BNM) proved to be more persistent than bronopol with simultaneous aquatic toxicity [40].

According to the ECHA website, Bronopol is evaluated for its endocrine activity. There are no further indications or results on the proceedings. It can be assumed that the evaluation refers to the degradation product bromide.

Conclusion

Conclusion: Bronopol is often used in combination with other active ingredients such as CMIT/MIT in cooling circuits. An evaluation within the framework of the EU active ingredient approval is pending. Bronopol is classified as toxic and corrosive. There is evidence in the literature that bronopol – although not classified – has skin sensitizing potential. In addition, there are indications that persistent and ecotoxic degradation products can form in the aquatic environment despite rapid hydrolysis of bronopol.

CMIT/MIT

Identity, Admission, Classification

According to the European Chemicals Agency ECHA, the *mixture of 5-chloro-2-methyl-2H-isothiazole-3-one (Einecs 247-500-7) and 2-methyl-2H-isothiazole-3-one (Einecs 220-239-6) (mixture of CMIT/MIT)* with CAS number 55965-84-9 is approved as an active ingredient in the product type PT11 (*protective agent for liquids in cooling systems*). The ECHA database contains a harmonised classification as well as a classification in the active substance report for authorisation.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch (Edukt)**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)**
Mixture of 5-chloro-2-methyl-2H- isothiazol-3-one (EINECS 247-500-7) and 2-methyl-2H-isothiazol-3-one (EINECS 220-239-6) (Mixture of CMIT/MIT)	Gemisch aus 5-Chlor-2-methyl-2H-isothiazol-3-on (Einecs 247-500-7) und 2-Methyl-2H-isothiazol-3-on (Einecs 220-239-6) (Gemisch aus CMIT/MIT)	55965-84-9	**ZUGELASSEN**	-	EUH071, H301, H310, H314, H317, H318, H330; H400 (M100), H410 (M100)	-	Wirkstoffbericht (P11): H301, H310, H314, H317, H318, H330, CMR & chron. Tox.: keine Einstufung; H400 (M100), H410 (M100)

ABC categorization

CMIT/MIT is classified as H330 ("danger to life if inhaled") and H310 ("danger to life if in contact with the skin"), has a corrosive effect on the respiratory tract (EUH071) and is skin sensitizing (H317). Carcinogenic, mutagenic, toxic to reproduction and chronic toxic properties are excluded according to the active ingredient report. The classification with H410 in combination with an M-factor[41] of 100 shows a high toxicity against aquatic organisms.

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Gemisch aus 5-Chlor-2-methyl-2H-isothiazol-3-on (Einecs 247-500-7) und 2-Methyl-2H-isothiazol-3-on (Einecs 220-239-6) (Gemisch aus CMIT/MIT)	55965-84-9	harmonisierte Einstufung, Wirkstoffbericht	H301, H310,H330	EUH071, H314, H318	**H317**	-	H400 (M100)	**H410 (M100)**

Employee protection

The hazardous substances database of the German Accident Insurance GESTIS presents the hazard potential for CMIT/MIT as follows [41]:

- Skin contact with Kathon[42] formulations is considered to be superficial in the vast majority of possible exposures
- It is generally accepted that Kathon CG is a sensitizer whose sensitization frequency is high and whose sensitization potential is moderately pronounced. Kathon has now been included

---

[41] M is a multiplication factor that weights highly water-toxic substances accordingly

[42] Kathon is a general trade name for products with CMIT/MIT

in the standard series of sensitizing substances. A clear correlation between test dose and sensitization achieved was demonstrated in both human and animal experiments. The lowest concentration of CMIT/MIT in Kathon-containing cosmetic products, which caused sensitization in some of 200 uncontaminated individuals, was 7.5 mg/l of water. In people already sensitized to Kathon, 1.5 mg/l was already sufficient to cause a positive reaction.

- Differentiated studies with 5-chloro-2-methyl-2H-isothiazole-3-one showed that its sensitizing potential significantly exceeds that of 2-methyl-2H-isothiazole-3-one. Recent research has shown that 4,5-dichloro-2-methylisothiazolin-3-one, which occurs as an impurity in Kathon, is much more effective.

The opinion of the Biocidal Products Committee states that the following risk mitigation measures are necessary to avoid dermal exposure [48]:

- The containers are designed in such a way that spillage can be avoided during decanting
- Use of automated systems that prevent contact with the product
- Standard procedures prevent contact and spillage
- Use of chemical-resistant coveralls, gloves, shoes and face masks
- Users are informed about the dangers and trained in safe handling

Application and environmental behaviour (according to literature)

Active ingredient concentration: Typical application concentrations of C(M)IT/MIT are between 0.2 and 1 mg active ingredient/l with continuous dosing and 2 mg/l with shock dosing [48].

Mechanism of action: The biocidal effect is based on the one hand on a rapid inhibition of bacterial growth and metabolism (within minutes) and on the other hand on the irreversible damage to the cells (within hours). The inhibition of the metabolism is based, among other things, on the damage to dehydrogenases and the synthesis of ATP. Cell death is caused by the destruction of thiol groups of proteins and the formation of free radicals [9].

Development of resistance: The opinion of the Committee for Biocidal Products on the authorisation in PT 11 [48] states: C(M)IT/MIT has been used as a commercial antimicrobial agent since 1980, during which time microbial resistance to C(M)IT/MIT was described in the literature. C(M)IT/MIT is often used in combination with or in exchange with other biocides, which can avoid the potential risk of resistance development. Particular attention should be paid to the development of resistance during product authorisation.

Environmental monitoring: In a publication by the German Federal Environment Agency, suspected substances were identified on the basis of a prioritization concept[43] with regard to a possible entry path into water bodies and sediments and sampling and measurements were recommended [57]. Among other things, systematic monitoring is proposed for CMIT/MIT. The active ingredient mixture is to be investigated in effluents of sewage treatment plants as well as in urban separation sewer systems[44].

Application notes according to interview statements

---

[43] Criteria of the prioritisation concept are: emission quantity, ecological impact as well as input and behaviour in environmental compartments

[44] The status of the monitoring or whether such a monitoring is planned could not be found out at the time of preparation of the present report.

Advantages and disadvantages of CMIT/MIT for the operation of evaporative cooling systems as well as risks when handling the active ingredient are described in the interviews conducted as follows:

- CMIT/MIT is a highly effective broad-spectrum biocide that is often used in smaller plants, but it is too expensive for large plants. The manufacturer specifies a theoretical decay time of 2 hours, but this is not always given in practice, which can be proven with the luminescent bacteria test. In the case of a continuous dosage - such a dosage is not actually provided for - resistance problems arise. CMIT/MIT cannot be measured online, but only in the laboratory (Weidner Wassertechnik GmbH: Interview 5)
- Isothiazolinones are more stable in cooling water than oxidizing biocides, but are less effective and tend to have a bacteriostatic effect in cooling water (Sanosil AG: Interview 7).
- CMIT/MIT is effective against Legionella only in high concentrations and relatively slowly. Full effectiveness is only achieved after 15 to 20 hours. At low pH, it is stable in cooling water for a relatively long time. CMIT/MIT therefore has a certain depot effect, which is particularly helpful for cooling systems with longer service lives. In systems without rapid water changes, the high half-life of the active ingredient can lead to a concentration of the active ingredient in the cooling water at moderate pH in the course of the shock dosing. This increases both the ecotoxicity of the blowdown and the risk of resistance formation. According to VDI 2047, the active ingredient should be changed after some time to avoid the formation of resistance. Therefore, it is often used in combination, in such a way that one does a shock dosage with CMIT/MIT about every 14 days or 4 weeks, but the standard dosage is carried out with an oxidizing biocide (Inwatec GmbH: Interview 8).
- Isothiazolinones are used in about half of the smaller plants. One reason is that there is no risk of damage to the system even in the event of poor maintenance (Kurita Europe GmbH: Interview 10).
- Working with biocides in small plants without a dosing pump and without a dosing station is not safe. When dosing from original containers without decanting (with suction lances), contact must be avoided. Usual 1.4% CMIT/MIT mixtures can lead to blindness in the case of splashes into the eye. If the CMIT/MIT application solution dosed into the cooling system comes into contact with the skin, wounds that are difficult to heal can occur (Weidner Wassertechnik GmbH: Interview 5).
- Cases of incapacity for work due to the sensitizing effect of isothiazolinone are known (Inwatec GmbH: Interview 8).
- A far-reaching renunciation of the active ingredient CMIT/MIT would be welcome (Standardization Committee ÖNORM B 5020: Interview 12)

Market research: The product Acticide 14 from the supplier Thor is a colourless to slightly yellow liquid and contains CMI/MIT in a concentration of 13.9 – 14.3%. According to the supplier, Acticide 14 is suitable for the preservation of water circuits, cooling lubricant emulsions and paper treatments. Usual bet quantities are, depending on the system and the customer's objectives, between 0.005 and 0.0025 %.

CONCLUSION

According to expert interviews, CMIT/MIT is a frequently used biocide, especially in small plants. It is often found in biocidal products combined with other non-oxidizing active ingredients.

The stability in cooling water is higher than with oxidizing biocides, it has only a minor effect against biofilms and has more of a bacteriostatic, but very broad effect overall. Resistance to germs is known. It is low corrosive, so that hardly any damage to the cooling system is to be expected, even in the event of maintenance defects. The system costs are low and the operating costs are in the middle of the field. The stability can easily lead to overdosing or a gradual concentration in the cooling water. Its concentration in the cooling or blowdown is not directly measurable, but can only be determined by means of a luminescent bacteria test.

CMIT/MIT is classified as "danger to life if inhaled", as well as corrosive and skin sensitizing. According to the GESTIS substance database, the frequency of sensitization is high and its sensitization potential is estimated to be medium. In the expert interviews, frequent early retirements due to sensitization were reported. Common 1.4% CMIT/MIT mixtures can quickly lead to blindness in the case of splashes into the eye. If the CMIT/MIT application solution added to the cooling system comes into contact with the skin, wounds that are very difficult to heal can occur. The classification with H410 in combination with a multiplication factor of 100 shows the high toxicity against aquatic organisms.

CMIT/MIT is one of the few active ingredients that has already been approved by ECHA for use in cooling systems. According to this, professional use in the cooling water sector ("manual mixing and loading") is rated as "acceptable" if skin contact - for example by splashes - can be avoided at all times by means of an automatic dosing system and protective clothing. Likewise, emissions from cooling circuits are "acceptable" in the context of the risk assessment, provided that they are carried out in a wastewater treatment plant. CMIT/MIT is identified in the assessment report as not readily biodegradable and without bioaccumulation potential, and the metabolites are quickly biodegraded.

Assessment: The expert interviews showed that the conditions required by ECHA for safe use are not always met in practice. Since it is often used in small plants, maintenance personnel are not always aware of the dangerous nature of CMIT/MIT, especially when untrained personnel handle it during vacation and sick leave. The degradation rates reported by manufacturers do not correspond to the real conditions, where the active ingredient often behaves more stably than assumed. In Austria, the Wastewater Emission Ordinance for cooling systems prohibits the discharge of isothiazoles into the sewer. Despite discussions with the competent authorities, it could not be determined whether this ban also includes CMIT/MIT, i.e. isothiazolinones.

Conclusion:
Measurements in order to be able to assess the current water pollution with CMIT/MIT in Austria should be carried out as part of a priority programme on inputs of biocides from cooling systems. Despite the authorisation by ECHA, the information collected in this study suggests that the use of CMIT/MIT should be avoided as far as possible due to the risk of accidents, high sensitising potential and high aquatic toxicity and poor degradability.

We also recommend (especially for Vienna as a hot spot of cooling demand) to take measurements of CMIT/MIT in the sewer, as well as in the inlet and outlet of sewage treatment plants in order to estimate the real water pollution. Since this substance was often mentioned to us as a popular one, especially in the interviews with Austrian experts, it cannot be ruled out that ecotoxicologically relevant quantities end up in the waters. The Federal Environment Agency will soon be able to carry out technical measurements of CMIT/MIT in wastewater samples. If the measurement results show a relevant contamination, e.g. with CMIT/MIT, Austria could advocate more measurements at EU level in a further step. For example, it would be conceivable for CMIT/MIT to be included in the watch list for suspected substances of the EU Water Framework Directive (Federal Ministry of Agriculture, Regions and Tourism: Interview 2)

HYDROGEN PEROXIDE (INCLUDING THE ADDITION OF SILVER)

Identity, Admission, Classification

The status of the authorisation procedure for the biocidal active ingredient hydrogen peroxide (CAS 7722-84-1) and available classifications were queried on the website of the European Chemicals Agency ECHA. At the time of the survey, the active ingredient was approved in product types PT 1, 2, 3, 4, 5, 6, but not in product type 11. For hydrogen peroxide, the database of the European Chemicals Agency ECHA contains a harmonised classification in addition to the classification in the active substance report and a classification in the REACH dossier.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
Hydrogen peroxide	Wasserstoffperoxid	7722-84-1	laufend		H302, H314, H332	H302, H314, H332, H335, Sens., CMR & chron. Tox.: keine Einstufung; Aq. Tox (acute): keine Einstufung, H412	Wirkstoffbericht (PT1-6): H302, H314, H332, Sens., CMR & chron. Tox.: keine Einstufung, Aq.Tox. (akut, chronisch): keine Einstufung

Hydrogen peroxide is often used in combination with silver in evaporative cooling systems, so the status of silver (CAS 7440-22-4) was also queried. At the time of the survey, the authorisation procedure for product type 11 was ongoing, and in the REACH dossier there are classifications for "silver powder > 99.9% (does not meet the criteria for nano form)" and for "silver in nano form (average particle size < 100 nm)".

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
Silver	Silber	7440-22-4	laufend	aktuell bewertet hinsichtlich endokriner Wirksamkeit	-	Silber Pulver (> 99,9%, erfüllt nicht Kriterien für Nano Form): Akute Tox., Korr., Sens., CM & chron.Tox.: keine Einstufung, Repro.: keine Daten verfügbar; H400 (M10), H410 (M10) Silber in Nano-Form (mitlere Partikelgröße < 100 nm): Akute Tox., Korr., Sens., CM & chron.Tox.: keine Einstufung, Repro.: H360D; H400 (M1000), H410 (M1000)	-

ABC categorization

Hydrogen peroxide has a corrosive effect (H314) and is classified as "harmful by inhalation" (H332). Skin sensitizing, carcinogenic, mutagenic, toxic to reproduction and chronic toxic properties are excluded in the active ingredient report.

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Wasserstoffperoxid	7722-84-1	Wirkstoffbericht (PT1 bis 6)	H302, H332	H314	-	-	-	-

For the ABC categorization, the nanoform is taken into account in addition to microscale silver powders: Microscale silver has[45] a high toxicity against aquatic organisms with H410 and M-factor 10. In comparison, the nanoform shows a significantly higher aquatic hazard or is classified as toxic to reproduction with H360D ("May harm the child in the womb"):

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Silber	7440-22-4	REACH Dossier (Silberpulver)	-	-	-	?	H400 (M10)	H410 (M10)
		REACH Dossier (Silber in Nanoform)	-	-	-	**H360 D**	**H400 (M1000)**	**H410 (M1000)**

The use of nanocal silver (or silver as a nanomaterial) as a biocide is prohibited in a 2021 Commission Implementing Decision[46] for product types PT 2, 4 and 9. It is not known whether nanoscale silver is used in products for evaporative cooling (PT11). The manufacturer Sanosil AG argues that this is not the case for its product.

Worker Protection Hydrogen Peroxide

In its opinion, the Committee for Biocidal Products makes the following statements [44]:

- The adverse effects of hydrogen peroxide in humans are limited to local effects at the site of first contact with the body and embolisms in rare cases at very high concentrations.
- No clear systemic effects were observed, which is plausible given the mode of action, i.e. the direct chemical reactivity leading to rapid degradation.
- Corrosion and/or irritation of the skin and mucous membranes are the most prominent observations in the large number of animal studies. These effects are concentration-dependent and do not or only slightly depend on the duration of exposure.

The hazardous substances database of the German Accident Insurance GESTIS presents the concentration-dependent effect of hydrogen peroxide as follows [41]:

---

[45] M is a multiplication factor that weights highly water-toxic substances accordingly

[46] Commission Implementing Decision (EU) 2021/1283 of 2 August 2021 on the non-approval of certain active substances in biocidal products.

- The lowest eye irritation concentration for most people is considered a 0.01% solution. 8% solutions showed moderate to strong irritation effects on the rabbit's eye. 30% solutions set epithelial defects in addition to corneal opacity, even more concentrated ones have a strong corrosive effect.

Environmental behaviour of hydrogen peroxide and silver

The degradation and environmental behaviour of hydrogen peroxide described in the active substance report can be summarised as follows [45]:

- Hydrogen peroxide shows very rapid biodegradation in sewage sludge and rapid degradation has also been observed in surface waters and soil compartments.
- The decomposition of hydrogen peroxide is catalyzed abiotically by transition metal ions. In addition to biotic degradation, the half-life in surface water also includes abiotic catalysis.
- There are no relevant metabolites.

A research report assesses the environmental exposure of silver ions from biocidal products as follows [46]:

- The risk assessment for silver compounds is subject to uncertainty.
- On the basis of the determined exposure concentrations, the determined effect values and the assumptions made for the extent of free silver ions in the environment, the risk of an unacceptable impairment for the compartments "water" and "sewage sludge" due to the expected sorption or formation of poorly soluble silver salts is classified as low.
- With regard to the risk to soil and its functions, it should be borne in mind that the input of persistent substances, including silver, is not desirable in the context of precautionary soil protection. Since no degradation can take place for such substances, an accumulation in the environment will take place. In the event of changing environmental conditions or new findings, undesirable consequences cannot be ruled out. This would mean that the entry must be minimized. Since sewage sludge is likely to be the main pathway into the soil, the corresponding concentrations in this medium should be limited. , sewage sludge with significant amounts of silver should therefore not be released for agricultural use.

Application (Literature)

Active ingredient concentration: Hydrogen peroxide is used in high concentrations of active ingredients (up to 50 mg/l) and is often used continuously [12].

Hydrogen peroxide can be inactivated by Legionella with the help of the enzyme catalase or converted to oxygen and hydrogen, resulting in a tolerance range to Legionella [1].

The following are mentioned as advantages in the application [10]:

- Effectiveness against biofilms: Microorganisms are not only killed, but biofilms are also easily detached from surfaces and can be rinsed out, for example.
- Harmless decomposition products (water and oxygen) or no formation of organic chlorine compounds.

Application of hydrogen peroxide in combination with silver (market research, interview statements)

Documents on the biocide concentrate Sanosil C were researched at the manufacturer Sanosil AG. According to the manufacturer, Sanosil C is *a highly concentrated water disinfectant for use in large cooling water systems (open and closed).* According to the safety data sheet, the concentrate contains hydrogen peroxide (30-50%) and silver (< 0.05%). In addition, the manufacturer was asked about the application and explains the advantages of using it as follows (Sanosil AG: Interview 7):

- For shock disinfection – such is indicated for systems that are already contaminated with germs – up to 1000 ppm Sanosil is used. This means that a germ reduction of 4 log levels can be achieved within 1 hour.
- Maintenance disinfection is carried out in a dosage of 20 and 50 ppm, with an average of 30 ppm.
- Silver acts as a catalyst in Sanosil and enhances the effect by 8 times by accelerating the breakdown of hydrogen peroxide into oxygen radicals. Silver would have a bacteriostatic effect in higher concentrations, but in the present case this effect is negligible.
- Silver reacts with chlorides to form inert silver chloride and enters the sewage sludge via wastewater.

In addition, the manufacturer notes: The silver contained in Sanosil for the catalytic enhancement of ROS formation from H2O2 and thus the oxidizing effect in the presence of organic material is explicitly microscale, i.e. it can be visually recognized as "flakes" with a very good microscope.

A German service provider describes the application (Inwatec GmbH: Interview 8):

- Systems with continuous cooling may only use oxygen separators, i.e. ozone and hydrogen peroxide. Hydrogen peroxide is used as a catalyst both with and without silver.
- Hydrogen peroxide without silver, similar to chlorine, can only be used at a low pH range. At a higher pH value, the variant catalyzed with silver (formation of oxidizing OH radicals) is needed to get by with small amounts.
- Legionella can be well controlled with hydrogen peroxide. However, a problem arises from the fact that Legionella catalase is positive. This means that the active ingredient is broken down more quickly. With ready-to-grow culture media, it is possible to check whether catalase-positive bacteria are present in the cooling water (spontaneously strong gas formation when the colonies are exposed to a 3% solution of hydrogen peroxide – in the case of dip slides by simply filling the tube with peroxide solution). Then an alternative active ingredient should be used for 2 or 3 months.

Conclusion

Hydrogen peroxide poses a health hazard due to locally irritating or corrosive properties, systemic effects are not known. A low hazard can be assumed for the aquatic environment due to a rapid decay into harmless metabolites accelerated by catalysis. The addition of silver increases the effectiveness of hydrogen peroxide, but causes the entry of a persistent substance into the environment. Hydrogen peroxide is effective against biofilms, but its application requires a high concentration of active ingredients. Legionella can increase their enzymatic degradation activity compared to hydrogen through selection, which is associated with a reduction in effectiveness. In the course of the research for the study, we did not come across any evaporative cooling systems in Austria that use hydrogen peroxide.

OZONE

Identity, Admission, Classification

According to the European Chemicals Agency ECHA, the approval procedure for ozone in the product type PT11 is ongoing. The ECHA database contains a proposal for a harmonised classification for ozone [62], as well as classifications in a REACH dossier and in an opinion of the Biocidal Products Committee. In addition, there is a note that ozone is currently being evaluated with regard to its endocrine activity.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)**
Ozone generated from oxygen	Aus Sauerstoff erzeugtes Ozon	10028-15-6	laufend	aktuell bewertet hinsichtlich endokriner Wirksamkeit	Vorschlag: H330, H341, H351, H370, H372, Korr. : Daten nicht eindeutig; Hautsens: nicht anwendbar (Gas); H400 (M100), H410 (M1)	H330, H314, H318, Sens & CMR: Keine Einstufung, H372 (Atemtrakt); H400 (M100), H410 (M1)	BPC Stellungnahme (PT11): H330, H341, H351, H370, H372, Repro. Tox.: keine Einstufung notwendig; H400 (M100), H410 (M1)

ABC categorization

All classification sources are taken into account for the ABC categorization: Ozone is uniformly classified as H330 ("danger to life if inhaled") and H372 ("damages the organs during prolonged or repeated exposure"). The damage affects the respiratory tract, but also the heart, circulatory and nervous systems [62]. Skin sensitizing properties are excluded.

The classification sources are not uniform in terms of CMR properties: The proposal for harmonised classification and the opinion on authorisation classify ozone with H341 ("suspected of causing genetic effects") and H351 ("likely to cause cancer"), such properties are excluded in the REACH dossier. The skin-irritating or corrosive properties of ozone are also inconsistent: only the REACH dossier classifies ozone with H314 ("causes severe burns to the skin and severe eye damage").

The (uniform) classification with H400 in combination with an M-factor[47] of 100 indicates a high acute toxicity against aquatic organisms.

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Aus Sauerstoff erzeugtes Ozon	10028-15-6	harmonisierte Einstufung, REACH Dossier, BPC Stellungnahme (PT11)	H330	H314, H318, EUH071	-	**H341, H351, H372 (Atemtrakt)**	H400 (M100)	H410 (M1)

Employee protection

---

[47] M is a multi-complication factor that weights highly water-toxic substances accordingly

The hazardous substances database of the German Accident Insurance GESTIS assesses the inhaled intake or effect of ozone as follows [41]:

- At rest, 40 - 50% of the inhaled ozone is already absorbed by the mucous membranes of the nose, mouth and throat by humans.
- Acute main effects are irritation and damage to the mucous membranes of the eyes, chronic main effects are lung dysfunction and lung damage.
- At lower concentrations of 0.8 to 1 mg/m3, proteins, inflammatory cells and inflammatory mediators could be detected in the nasal and lung fluid of healthy volunteers after only 2 hours.
- A concentration level of 0.2 to 0.4 mg/m3 triggers mucosal irritation, odor nuisance and changes in lung function (decrease in vital and second capacity).
- Ozone can damage the resistance of lung cells to infections. Animal experiments resulted in the assessment that ozone has an immunotoxic effect.

Environmental behaviour (literature).

In the opinion on the approval of ozone for cooling water treatment, the behaviour of ozone in the (aquatic) environment is described as follows [69]:

- No risk has been identified for any of the applications within PT11 with release into the sewer system, as ozone depletes rapidly.
- However, depending on the amount of blowdown, direct emission into surface waters when used as a cooling water biocide can lead to unacceptable risks to the aquatic environment if no additional measures are taken to reduce the ozone concentration.
- However, ozone can lead to disinfection by-products that can pose a potential risk to the environment. However, the information currently available is not sufficient to draw definitive conclusions about the risks of disinfection by-products. These must be taken into account during product approval.

The Committee for Biocidal Products makes the following concluding statement:

- Safe use for human health and the environment is identified for all intended uses. An exception is the direct discharge of cooling water from large cooling systems into the surface water.
- Due to the rapid depletion of ozone in the cooling water, these unacceptable risks to surface waters could be mitigated, for example, by increasing the retention time of the blowdown in the sewer or by installing a settling basin.

Application

<u>Active ingredient concentration</u>: 0.1 – 0.3 mg/l (ppm) [49]

In the technical literature, properties and production are described as follows [11], [39], [49].

- Ozone is unstable due to its high reactivity and therefore cannot be stored and is therefore produced locally.
- For ozone production, air or oxygen is passed between two electrodes between which a high-voltage alternating potential is maintained (ozonizer). The dissolution of ozone in the water is one of the key elements of a well-functioning system. Temperature has a major influence on the degree of dissolution of the gas.
- The disinfection efficiency of ozone, like that of chlorine dioxide, is relatively pH-independent.
- The abreaction of ozone in "dirty" systems causes a shortened half-life
- Compared to other oxidants, ozone is not very selective because it reacts with many substances.

The following statements can be found on the advantages and disadvantages of using it [8], [10], [13].

- The advantages are easy on-site generation, decay or abreaction within a very short time, low operating costs and high toxicity to target organisms.
- High investment costs and unmanageable reaction products (non-specific oxidation) are disadvantageous, and it may not be possible to cover all areas in the plant with a short residence time.
- One advantage of ozone is that it produces fewer environmentally harmful by-products compared to comparable oxidants and disinfectants.
- Ozone is corrosive and incompatible with almost all additives, PVC and copper[48]. Due to the high oxidizing power of ozone, organic conditioning agents as well as plastic and wooden fixtures can be attacked.
- To avoid side reactions, the cooling water should have the lowest possible organic matter content when using ozone.

The interviews also mentioned:

- Ozone is the most effective biocide, a major disadvantage is the expensive system, the toxicity and the risk of massive corrosion processes in the cooling system in the event of overdosing. (Weidner Wassertechnik GmbH: Interview 5)
- Ozone represents a potential hazard for smaller farms. Ozone is not smelled in high concentrations, only in low concentrations in the indoor air. Therefore, indoor air monitoring is mandatory. The processes for on-site generation hold potential for employee protection. It is a highly efficient biocide, but non-specifically reactive and quite volatile. 0.3 ppm is already a high concentration. The application is declining and is limited to those farms where ozone has proven itself or has proven itself in clean systems without high organic pollution and thus without the formation of disinfection by-products) (Inwatec GmbH: Interview 8)

Conclusion

The EU approval procedure is still ongoing for all product types. The proposal for the harmonised classification provides for ozone to be classified as corrosive, with H341 (presumably mutagenic), H351 (presumably toxic to reproduction) and H372 (long-term organ damage in relation to the respiratory tract). Ozone is classified as very toxic to aquatic life with short-term and long-term effects. However, the Committee for the Authorisation of Biocides excludes a risk to the aquatic environment due to the rapid degradation, provided that ozone does not enter the surface water directly from large cooling plants. For cooling water treatment, ozone is produced in plants on site, which involves a process engineering effort or requires investment. Although it is considered one of the most effective biocides, its disadvantages are high corrosiveness or material incompatibility as well as considerable sensitivity to organic stress (cooling water). As a result, and in combination with its potential hazard to human toxicity, the requirements for operational management and occupational safety are considerable.

However, the following practical example (as of 2023) shows that ozone systems can be very successful in reducing the use of wastewater-relevant chemicals. For example, a cooling tower of the Vienna Twin Tower caused an annual use of chemicals worth 95,000 euros. These were salted into the canal together with 50,000 m³ of water per year. After a successful conversion of disinfection to

---

[48] And according to the company KOFEC, ozone is also incompatible with polyethylene. (Silicone) seals must also have a defined quality in order not to be attacked.

an ozone system[1], no chemicals have been discharged into wastewater for four years, as the use of biocides relevant to wastewater as well as (mostly environmentally harmful) corrosion inhibitors can be dispensed with. The ozone is generated directly on the roof and introduced into a recirculating water reservoir by means of a hydrophysical colloid reactor with a redox potential of 700mV. This hydrophysical treatment also raises the pH value, so that the use of stabilizers can be dispensed with. Under these conditions, microorganisms die within seconds. The ozone system, which is expensive in itself, also paid for itself in two to three years, as the operating costs could be reduced to 25,000 euros per year (for electricity requirements and regular maintenance) without the high use of chemicals. The use of ozone can therefore ensure a high level of hygiene, save costs despite additional safety technology, and (according to the current state of knowledge) protect water bodies from the discharge of high quantities of environmentally toxic chemicals.

---

[1] The ozone system mentioned comes from the company KOFEC (www.ko-fec.com)

PERACETIC ACID

Identity, Admission, Classification

According to the ECHA database, peracetic acid is authorised for product type 11. Peracetic acid is classified harmonised, and there is a proposal for a revision [63]. There is also an active substance report [51] and an opinion of the Committee for Biocidal Products on the authorisation [50]. On the ECHA website, in addition to a REACH dossier, there is a note that peracetic acid is assessed with regard to its endocrine activity. Final results are not yet available.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch (Edukt)	CAS	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
Peracetic acid	Peressigsäure	79-21-0	**ZUGELASSEN**	aktuell bewertet hinsichtlich endokriner Wirksamkeit	Stellungnahme des RAC: EUH071, H301, H310, H314, H330; H400 (M10), H410 (M100)	40% wässrige Lsg: H301, H312, H314, H330, Sens. & CMR & chron.Tox.: keine Einstufung; H400 (M1), H410 (M10)	BPC Stellungnahme (PT11): H302, H312, H314, H332, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M?), H410 (M10)

ABC categorization

The proposal to revise the harmonized classification [63] is a priority for ABC categorization: In it, peracetic acid is classified with regard to its acute toxic effect with H330 ("danger to life if inhaled"), H310 ("danger to life in contact with skin") and as corrosive (EUH071: "corrosive to the respiratory tract; H314: "causes severe skin burns and severe eye damage"). There are no indications of sensitizing, carcinogenic, mutagenic, toxic to reproduction or chronic toxic effects in the classifications. The classification with H410 in combination with an M-factor[49] of 100 means a very high toxicity against aquatic organisms with long-term effects. Peracetic acid is discussed by the ECHA ED Expert Group with regard to an endocrine effect , while an endocrine effect is still excluded in the opinion on the authorisation [50].

Stoffbezeichnung (Edukt)	CAS	Datenquelle(n) für ABC Kategorisierung	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Peressigsäure	79-21-0	harmonisierte Einstufung (Vorschlag)	H301, H310, H330	EUH071, H314	-	-	H400 (M10)	H410 (M100)

Employee protection

---

[49] M is a multiplication factor that weights highly water-toxic substances accordingly

Aqueous peracetic acid consists of peracetic acid, hydrogen peroxide and acetic acid. Based on the evaluated information, peracetic acid is the most critical component of aqueous solutions in terms of potential health risks. The opinion of the Biocidal Products Committee on the authorisation makes the following statements [50].

- The effects of peracetic acid in humans are limited to local effects at the site of first contact with the body. No clear systemic effects of peracetic acid have been observed, which is plausible given the mode of action, i.e. the direct chemical reactivity that leads to rapid degradation of peracetic acid.
- Irritation and chemical burns of the skin or mucous membranes are the most prominent observations in the available animal studies. The effects are concentration-dependent and do not depend or only slightly on the duration of exposure. In addition, peracetic acid causes sensory irritation of the respiratory tract.
- Personal protective equipment is required due to the corrosive properties of the concentrated solution of peracetic acid.
- Breathing apparatus is also required for manual handling.
- Secondary drift exposure from cooling towers is acceptable.

This is confirmed in interview statements (Stockmeier Group: Interview 3)

- For the personnel on site, there are health risks, especially when preparing the solution or diluting the concentrated peracetic acid. Maintenance personnel must wear protective clothing during these operations.

Application and environmental behaviour

Active ingredient concentration: 5 mg/l (ppm) [51]

Development of resistance: The risk is low due to the non-specific reactions [50].

The opinion on the authorisation characterises the application as follows [50]:

- Peracetic acid contributes most to the biocidal efficacy of the application solutions, as peracetic acid has a significantly higher biocidal activity than hydrogen peroxide, but synergy effects cannot be ruled out.
- In the concentrations common in application solutions, acetic acid does not contribute to effectiveness.
- Although peracetic acid is classified as highly toxic to water with a long-term effect, it decomposes quickly in all environmental compartments, i.e. in surface waters, soil, air and activated sludge. In addition, peracetic acid and hydrogen peroxide decompose in cooling systems and wastewater before they reach the wastewater treatment plant.
- The degradation products of peracetic acid are oxygen, acetic acid and hydrogen peroxide. Acetic acid and hydrogen peroxide are further degraded to water, carbon dioxide and oxygen

Peracetic acid has a corrosive effect on numerous metals such as iron, zinc, brass, copper, magnesium. Low (concentrate) to almost no corrosion (application solution), on the other hand, occurs with aluminum and alloy (stainless) steel. No corrosion is described in glass, porcelain, glazed earthenware, as well as plastics such as polyethylene and polyvinyl chloride [70].

Peracetic acid is not very volatile because it is water-soluble. If organic particles are present in the air, peracetic acid degrades within minutes. Overall, the use of peracetic acid in the cooling water sector is described as rare and rather in closed systems. In principle, there is the possibility of continuous dosing as well as shock dosing (Stockmeier Group: Interview 3).

Market research: The manufacturer Stockmeier Group researched documents on a biocide concentrate for use in the cooling water sector (PT 11), among other things. According to this, Lerasept Peracetic Acid is *a foam-free disinfectant based on peracetic acid (12%).*

Conclusion

Peracetic acid is not considered to have a sensitizing, chronically toxic or CMR hazard potential. As far as acute toxicity is concerned, there is currently a proposal for a harmonised classification in which peracetic acid is classified as H330 ("danger to life if inhaled") and as corrosive to the respiratory tract, skin and eyes. These classifications underline the need for personal protective measures to avoid skin contact and inhalation during handling as well as during use. Although peracetic acid is classified as highly toxic to water with a long-term effect, it decomposes quickly in all environmental compartments, i.e. in surface waters, soil, air and activated sludge. In addition, peracetic acid and hydrogen peroxide decompose in cooling systems and wastewater before they reach the wastewater treatment plant. Peracetic acid is corrosive to certain materials and is rarely used in open cooling systems.

BENZALKONIUM CHLORIDES (QAV)

Identity, Admission, Classifications

For approval, there are 4 entries for benzalkonium chlorides in the database of the European Chemicals Agency ECHA, and the approval procedures for product type 11 are still ongoing. Only the benzalkonium chloride ADBAC/BKC (C12-16) is approved for other product types or an active ingredient report is available for product type 1. For ADEBAC (C12-C14) there is a classification in the REACH dossier, harmonised classifications are not available in any case.

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch (Edukt)	CAS	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Aussschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
Alkyl (C12-16) dimethylbenzyl ammonium chloride (ADBAC/BKC (C12-16))	Alkyl (C12-16) dimethylbenzyl ammonium chloride (ADBAC/BKC (C12-C16))	68424-85-1	laufend	-	-	-	Wirkstoffbericht (PT1): H302, H314, H318, H335, Sens., CMR & chron.Tox.: keine Einstufung; H400 (M10), H410 (M1)
Alkyl (C12-18) dimethylbenzyl ammonium chloride (ADBAC (C12-18))	Alkyl(C12-18)dimethylbenzyl ammoniumchlorid (ADBAC (C12-18))	68391-01-5	laufend	H302, H312, H314, H318, Sens., CMR & chron. Tox.: keine Daten verfügbar; H400 (M?), H410 (M?)	-	-	-
Alkyl (C12-C14) dimethyl(ethylbenzyl) ammonium chloride (ADEBAC (C12-C14))	Alkyl(C12-C14)dimethyl(ethyl benzyl)ammonium chlorid (ADEBAC (C12-C14))	85409-23-0	laufend	-	-	H302, H314, H318, Sens., CMR & chron.Tox.: keine Einstufung; H400 (M10), H410 (M1)	-
Alkyl (C12-C14) dimethylbenzyl ammonium chloride (ADBAC (C12-C14))	Alkyl (C12-C14) dimethylbenzyl ammoniumchlorid (ADBAC (C12-C14))	85409-22-9	laufend	H302, H312, H314, H318, Sens., CMR & chron.Tox.: keine Daten verfügbar; H400 (M?), H410 (M?)	-	-	-

ABC categorization

For the ABC categorization, the classification of benzalkonium chloride with CAS 68424-85-1 from the active ingredient report [64] is used as a reference, especially since the classifications of the other QAVs do not differ significantly from this: The benzalkonium chlorides are classified as corrosive, there are no indications of sensitizing, carcinogenic, mutagenic, toxic to reproduction or chronic toxic effects. The classification with H410 in combination with an M-factor[50] of 1 shows a medium toxicity against aquatic organisms.

---

[50] M is a multiplication factor that weights highly water-toxic substances accordingly

Stoffbezeichnung (Edukt)	**CAS**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Alkyl (C12-16) dimethylbenzyl ammonium chloride (ADBAC/BKC (C12-C16))	68424-85-1	Wirkstoffbericht (PT1)	H302	H314, H318	-	-	H400 (M10)	H410 (M1)
Alkyl(C12-18)dimethylbenzylammonium chlorid (ADBAC (C12-18))	68391-01-5	ECHA Infocard	H302, H312	H314, H318	?	?	H400 (M?)	H410 M?)
Alkyl(C12-C14)dimethyl(ethylbenzyl) ammoniumchlorid (ADEBAC (C12-C14))	85409-23-0	REACH Dossier	H302	H314, H318	-	-	H400 (M10)	H410 (M1)
Alkyl (C12-C14) dimethylbenzylammonium chlorid (ADBAC (C12-C14))	85409-22-9	ECHA Infocard	H302	H314	?	?	H400 (M?)	H410 (M?)

Employee protection

The opinion of the Biocidal Products Committee makes the following statement [36] for the already authorised ADBAC/BKC (C12-16):

- The main critical effects associated with alkyl(C12-16)-dimethylbenzylammonium chloride are due to its corrosive properties. For professional use, the potential risks associated with local impacts are acceptable for all uses.

The hazardous substances database GESTIS [41] confirms the irritating or corrosive effect of solutions containing QAV and also reports a case-by-case occurrence of allergic reactions:

- In individual cases, the occurrence of allergy-related contact dermatitis has been reported from professional use, mostly after the use of BAC (i.e. QAV) containing cleaning agents and disinfectants in the medical field.

However, against the background of very frequent use, the allergenic potency is considered low and the intensive irritating effect on the skin is seen in the foreground.

Environmental performance

The opinion of the Biocidal Products Committee assesses the environmental performance of ADBAC/BKC (C12-16) as follows [36]:

- Alkyl(C12-16)-dimethylbenzylammonium chloride is readily biodegradable, the substance is neither persistent nor does it produce problematic metabolites. The substance is hydrolytically stable, and hydrolytic processes do not contribute to its degradation in the environment. It is not volatile, nor is it expected to be present in the air.

In specialist literature and studies, there are sufficient indications that it does suggest that benzalkonium chlorides remain in the environment. An overview study commissioned by the Nordic Council of Ministers[51] from 2014 summarizes [38]:

- Different types of QAVs – a total of 17 compounds – were measured in wastewater and sludge from wastewater treatment plants, sediments and fish.

---

[51] https://de.wikipedia.org/wiki/Nordischer_Ministerrat.

in general, there was a widespread occurrence of QAVs in all included matrices. The concentration in the wastewater varied over a large area. A large part of the "highly concentrated" wastewater had concentrations that could pose a risk to the aquatic environment, even after tenfold dilution.

In an Austrian study, a broad-based environmental risk characterization and assessment of selected benzalkonium chlorides was carried out with a special focus on the situation in Austrian rivers. Water samples with high suspended solids loads showed concentrations of benzalkonium chloride (C12 or C14) above 1 mg/L. In some cases, high concentrations have also been found in sediments of rivers such as the Liesing and Inn [68].

A scientific article justifies the occurrence of QAV in the environment as follows [65]:

- The industrial and private use of products containing QAV are the main source of their occurrence in wastewater treatment plants, surface waters and sediments. The pollution of wastewater and surface waters is in the order of ng/L to µg/L, that of sludge and sediments in the order of µg/L to mg/L. Although QAVs are degradable under aerobic conditions, their sorption occurs faster than degradation. Therefore, significant amounts of QAV can be accumulated, especially in anoxic/anaerobic compartments. The presence of QAVs in the environment not only endangers aquatic and terrestrial organisms, but also increases the likelihood of antibiotic resistance selection in bacteria.

Due to the abnormalities in the material behaviour of QAVs in combination with the significant emissions, the German Federal Environment Agency proposes to include QAVs in systematic environmental monitoring [57]. The list includes three of the four QAV biocides listed. The active substances are to be investigated according to the estimated emissions, the ecological effect and the behaviour in the environment in effluents of sewage treatment plants as well as in urban separation sewer systems[52].

Application (literature & interview statements)

Active ingredient concentration: 1 – 10 mg/l [9]

The reference book "Cooling Water Treatment" describes the advantages and disadvantages of using QAV in cooling water treatment as follows:

- They are effective in controlling algae development,
- can cause foaming when injected into the circuit,
- are not compatible with anionic polymers (polyacrylates) used as dispersants,
- can dissolve or dissolve protective layers (biofilms) in combination with chlorine, and thus increase its effect when chlorine is used at the same time.

It is reported that quarternary ammonium compounds can only be used effectively against algae [12].

Another source mentions the following points regarding the application [13]:

- The handling of the waxy mixture is usually uncomplicated and harmless,
- advantageous is its effectiveness in alkaline,
- They are not easily biodegradable and relatively expensive.

When using the QAV, overdosing due to the resulting foaming should be avoided. If the coolant is not clean, QAVs are not a good option, as they experience a sharp drop in performance due to dirt, oil

---

[52] The status of the monitoring or whether such a monitoring is planned could not be found out at the time of preparation of the present report.

and solids [8], [13]. In an interview, the effect and application context of the QAVs is described as follows:

- QAVs degrade slowly, so they are used. However, their effect is rather bacteriostatic. They tend to have a basic effect and are also used to administer shock doses with oxidizing biocides such as chlorine and bromine. (Sanosil AG: Interview 7).

Their effect against legionella is described as "not good", but they are effective algaecides in "the lowest concentration" (Inwatec GmbH: Interview 8).

Conclusion

Benzalkonium chlorides are particularly effective in controlling the development of algae. When injected into the circuit, foaming can occur. They are also effective in the alkaline environment, but are rather more expensive biocides to purchase. Due to their low effectiveness against biofilms, they are only used in combination with oxidizing biocides. The four non-oxidizing and surface-active biocidal active ingredients summarized here under "benzalkonium chlorides" are classified as hazardous to health and corrosive. From the point of view of employee protection, their application is associated with a low risk. They are not classified as sensitizing, although a "case-by-case occurrence of allergic reactions" is reported. The benzalkonium chloride with the CAS number 68424-85-1 is reported in the active substance report as readily biodegradable and non-persistent, but there are sufficient indications in the literature that benzalkonium chlorides remain permanently in the environment, where they absorb sediments and persist in the anaerobic environment. For their occurrence, for example in wastewater treatment plant effluents, systematic monitoring is therefore also proposed.

GLUTARALDEHYDE

Identity, Admission, Classification

According to the ECHA database, glutaraldehyde is authorised for product type 11. In addition to the classification in the active substance report, a harmonised classification and a classification in a REACH dossier are available for glutaraldehyde.

Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
Glutaraldehyd	111-30-8	**ZUGELASSEN**	-	EUH071, H301, H314, H317, H330, H334; H400 (M1), H411	EUH071, H301, H314, H317, H330, H334, CMR & chron. Tox.:keine Einstufung; H400 (M?), H411	Wirkstoffbericht (PT11): EUH071, H301, H314, H317, H330, H334, CMR & chron. Tox.:keine Einstufung; H400 (M1), H411

ABC categorization

Glutaraldehyde is classified as H330 ("danger to life if inhaled"), has a corrosive effect on the respiratory tract (EUH071) and is skin and respiratory sensitizing (H317, H334). Carcinogenic, mutagenic, toxic to reproduction and chronic toxic properties are excluded. The H411 classification indicates moderate toxicity to aquatic organisms.

Stoffbezeichnung (Edukt)	CAS	Datenquelle(n) für ABC Kategorisierung	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Glutaraldehyd	111-30-8	Wirkstoffbericht (PT11)	H301, H330	H314, EUH071	H317, H334	-	H400 (M1)	H411

Employee protection

The opinion of the Biocidal Products Committee for the authorisation of glutaraldehyde points out that glutaraldehyde fulfils the criteria of Article 10 of the Biocidal Products Regulation due to its nature as an inhalant allergen and is therefore classified as an 'active substance to be replaced'[53].

---

[53] Authorisations for active substances that are found to meet the criteria (of Article 10) are only valid for 7 years. When applying for an extension, alternatives will be examined. Provided that there are no significant economic or practical disadvantages, the competent authority may refuse the authorisation.

Application and environmental behaviour

Active ingredient concentration: 1 - 200 mg/l (ppm) [12]

Glutaraldehyde, although currently still used, is only approved as an "existing active ingredient" or its use is only permitted until 2026 [9]. The following information on the advantages and disadvantages of using it can be found in the literature [8], [12], [13]:

- Easy handling and dosing
- Need for higher dosage and therefore higher costs
- Effective against sulfate-reducing bacteria and algae
- decreased activity in systems with high ammonia content, high temperature and pH
- easy biodegradability, relatively harmless to aquatic organisms, few by-products (during degradation)

Conclusion

Glutaraldehyde is classified as "life-threatening if inhaled" as well as skin and respiratory sensitizing and has a high hazard potential from the point of view of employee protection. Due to its nature as an inhalation allergen, the active substance meets the criteria of Article 10 of the Biocidal Products Regulation, is therefore only authorised for a limited period of time and is classified as an "active substance to be replaced".

OTHER BIOCIDAL ACTIVE SUBSTANCES

For the detailed analysis, biocidal active substances were selected as relevant on the basis of criteria (evaluated literature, entries Article 95 list or BAuA register). However, the evaluated literature also mentions individual active substances that were not included in the detailed analysis. This is because it was concluded that these active ingredients were of secondary importance. This applies to, for example:

- Tetrakis (hydroxymethyl)-phosphonium sulfate (THPS); Peroxomonosulfate; Dichloroisocyanuric acid; β-bromine-β-nitrostyrene; Methylene bisthiocyanate; Dodecyl guanidine hydrochloride

For these and other active substances, however, classifications or ABC categorization can be queried in the Appendix Tables 1 & 2. For example, for tetrakis (hydroxymethyl)-phosphonium sulfate (THPS), the following entries can be found in Tables 1 & 2:

Eintrag ECHA "information on biocides" (Abfrage: November 2022)	**Stoffbezeichnung in Deutsch**	**CAS Nummer**	**BPR Zulassung PT11**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)**
Tetrakis(hydroxymethyl)phosphonium sulphate (2:1) (THPS)	Tetrakis(hydroxymethyl)phosphoniumsulfat (2:1) (THPS)	55566-30-8	laufend	-	-	H302, H317, H318, H330, H361, Muta., Karz., chron. Tox.: keine Einstufung; H400 (M1), H411	-

Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
Tetrakis(hydroxymethyl) phosphoniumsulfat (2:1) (THPS)	55566-30-8	REACH Dossier	H302, H330	H318	**H317**	**H361**	H400 (M1)	H411

From the entries, it can be concluded that for THPS

- the approval process (as of Nov. 2022) is ongoing,
- a substance classification from a REACH dossier is available and in it
- the substance is classified as acutely toxic by inhalation, corrosive, skin sensitizing and presumably toxic to reproduction.

With the help of the tables in the appendix for active substances of product type 11 not included in the detailed analysis, the authorisation status, the available database (in the sense of classifications) can be researched or the hazard potential can be estimated. However, this requires an appropriate identification of the active ingredient.

In addition, not every production or release process was explicitly dealt with in the detailed analysis. For example, for the "Active chlorine, produced or released from..." six manufacturing or release processes have been applied for approval, three of which have been selected as relevant for the detailed analysis. The same applies to the oxidative biocidal active ingredients monochloramine, chlorine dioxide and active bromine.

INTERVIEWS

The aim of the interviews with experts from administration and manufacturer representatives was to address regulatory practice, wastewater and occupational health and safety problems and biocide assessment. The interviews were conducted online and documented in writing:

No.	Interviewees (institution or company)	Thematic priority	Date
1	Otto Krenek (Vienna Canal)	Situation City of Vienna	29.7.22
2	Heide Müller-Rechberger, Peter Weilgony, Aron Frei (Federal Ministry of Agriculture, Regions and Tourism); Gertraud Moser (Federal Environment Agency)	Regulatory status quo	2.8.22
3	Boris Hinz (Stockmeier Group)	Peracetic acid	5.9.22
4	Regina Sommer, Elisabeth Holzhammer; Michael Reiter (Institute of Hygiene and Applied Immunology; MedUni Vienna)	Regulatory status quo	6.9.22
5	Marc Müllen (Weidner Wassertechnik GmbH)	Chlorine dioxide, biocides	8.9.22
6	Michael Vogl (Standards Committee for the Revision of ÖN B 5020, Expert for Water Hygiene)	Regulatory status quo	19.9.22
7	Daniel Rüegg (Sanosil AG)	Hydrogen peroxide incl. silver	21.9.22
8	Holger Ohme (Inwatec GmbH)	Plant operation, biocides	26.9.22
9	Volker Fischer, Christoph Feil (Innowatech GmbH)	Active chlorine, biocides	28.9.22
10	Anja Friedrich, Erik Schlander, Stefan Mantler, Louisa Maria Alleta (Kurita Europe GmbH)	Monochloramine, biocides	4.10.22
11	Cornelia Wollman, Britta Greve-Scheidt (Office for the Environment and Consumer Protection Düsseldorf)	42.BImSCHV, Cooling Tower Cadastre	19.10.22
12	Arno Sorger (Standardization Committee for the Revision of ÖNORM B 5020)	Biocides	14.9.22
13	Bernhard Benka, Alexander Indra, (AGES)	Legionellosis, situation in Austria	23.2.23
14	Sigrid Kiermayr, Irene Kászoni-Rückerl, Esther Ayasch (Federal Ministry of Social Affairs, Health, Care and Consumer Protection)	Legionellosis, situation in Austria	24.3.23

In addition, on 29.08.2023, an ozone-powered cooling tower system was visited at the Twin Towers (participants: Manfred Klade, Marion and Peter Koch / KOFEC GmbH).

BIBLIOGRAPHY

[1] Sinder, Cristoph; Gringel Meinolf; Hardt, Hartmut; Langerbein, Hermann: Legionella risks in evaporative cooling systems and cooling towers: causes and avoidance. 2019. Beuth Verlag.

[2] Ordinance on Evaporative Cooling Systems, Cooling Towers and Wet Separators (42nd BImSchV), Federal Law Gazette I p. 2379. Effective Date: August 19, 2017

[3] Federal Environment Agency (ed.): Recommendation of the Federal Environment Agency for a procedure for the investigation of environmental pollution caused by biocides. UBA-Texte 15/2017

[4] Legionella folder: Austrian Agency for Health and Food Safety AGES.
https://www.ages.at/themen/krankheitserreger/legionellen/

[5] National Reference Centre for Legionella Infections: Annual Report 2018.
https://www.ages.at/themen/krankheitserreger/legionellen/

[6] Walser, S.M. et al.: Assessing the environmental health relevance of cooling towers – A systematic review of legionellosis outbreaks. Int. J. Hyg. Environ. Health 217 (2014) 145 -154

[7] Schrammel B, Hinker M. Legionella in process wastewater: Project results.

[8] Paulus, Wilfried (Ed.): Directory of Microbicides for the Protection of Materials. A Handbook. 2005. Springer Verlag.

[9] Andreas Nocker, Gabriele Schaule, Martin Strathmann, Kathrin Wiede. Inactivation of biocides during sampling for legionella analysis in cooling water of evaporative cooling systems and cooling towers. UBA-Texte 05/2020

[10] Tauschek J. Operation of open and closed cooling circuits: Guide to cooling circuits, cooling water and cooling towers.

[11] Aquaprox (ed.): Kühlwasserbehandlung. 2007. Springer Verlag Heidelberg.

[12] Gartiser, S., Ulrich, E. (2002). Use of environmentally friendly chemicals in cooling water conditioning. UBA-Texte 70/02. Hydrotox GmbH, Freiburg, Federal Environment Agency, Berlin.

[13] Scharf, J. Fleig, M. Brauch, HJ., Sacher, F. Evaluation of the risks of biocides and similarly toxic feedstocks from the operation of open cooling towers for drinking water supply. DVGW Water Technology Centre. 2016.

[14] Müller, A. & Bleck, D. Workplace burdens in the use of biocidal products. Part 2: Safe handling of concentrates". Project F 1703. On behalf of the Federal Institute for Occupational Safety and Health.

[15] German Chemical Industry Association (VCI): Template for the preparation of a risk assessment in accordance with the 42nd BImSCHV.

[16] Ordinance of the Federal Minister for Agriculture, Forestry, Environment and Water Management on the Limitation of Wastewater Emissions from Cooling Systems and Steam Generators (AEV Cooling Systems and Steam Generators), Federal Law Gazette II No. 266/2003. Version of 11.10.2021.

[17] Information for refrigeration, air conditioning and heat pump manufacturers, No. 57, 28.05.2019: ÖNORM M 7744: Planning, execution, operation, maintenance and monitoring of evaporative cooling systems (draft)

[18] VDI 2047 Part 2. Ensuring the hygienic operation of evaporative cooling systems (VDI cooling tower rules). January 2019.

[19] Control Office of the City of Vienna: MA 15, cross-sectional examination with regard to the legionella problem in Vienna; public health sector. Activity Report 2008.

[20] Wewalka G.: Requirements for microbiological water quality in evaporative cooling systems – new ÖNORM B 5020.

[21] Pollutant loads in Vienna's sewer system: Letter of reply from Wien Kanal to the Vienna Environmental Ombudsman's Office. 6.3.2017

[22] DIN EN 13623:2020-12: Chemical disinfectants and antiseptics - Quantitative suspension test for the determination of the bactericidal activity against Legionella of chemical disinfectants for water-bearing systems - Test methods and requirements (phase 2, stage 1); German version EN 13623:2020

[23] Introduction to the evaluation grid. Download at Vienna Disinfectant Database (WIDES Database)

[24] Federal Institute for Occupational Safety and Health (Baua):Article 95

[25] "Authorisation of biocidal products – legal situation": Lecture held online by Dr. Peter Schindler (Federal Environment Agency) on the occasion of the DESNET Meeting on 11.11.2021

[26] BPC opinion on application for approval of the active substance 2,2-Dibromo-2-cyanoacetamide (DBNPA). PT 4. ECHA/BPC/300/2021

[27] RAC Opinion proposing hCL of 2,2-dibromo-2-cyanoacetamide (DBNPA) adopted 13.06.2019 CLH-O-0000001412-86-289/F

[28] EU Assessment Report for evaluation of active substances in Regulation 528/2012: Active chlorine generated from sodium chloride by electrolysis; Product-type PT July 2, 2020; Slovak Republic

[29] BPC opinion on application for approval of the active substance Active chlorine generated from sodium chloride by electrolysis PT 2. ECHA/BPC/251/2020

[30] BPC opinion on application for approval of the active substance Active chlorine released from chlorine PT 2. ECHA/BPC/136/2016

[31] BPC opinion on application for approval of the active substance Active chlorine released from sodium hypochlorite PT 2. ECHA/BPC/128/2016

[32] ECHA: Guidance on the BPR: Guidance on Disinfection By-Products. Version 1.0 January 2017.

[33] Dean J, Tomberlin G, Silverstri. GSA Guidance – Alternative Water Treatment Systems for Cooling Towers. National Renewable Energy Laboratory. US Department of Energy. 2020.

[34] Tomberlin G, Dean J, Deru M. Electrochemical Water Treatment for Cooling Towers. National Renewable Energy Laboratory. US Department of Energy. 2018.

[35] Dean J, Tomberlin G, Cutler D, Elsworth J. Demonstration and Evaluation of an Advanced Oxidation Technology for Cooling Water Treatment. National Renewable Energy Laboratory. US Department of Energy. 2018.

[36] BPC Opinion on the application for approval of the active substance: Alkyl (C12-16) dimethyl benzyl ammonium chloride; PT 3. ECHA/BPC/267/2020

[37] Project Biomics: Biocides as Micropollutants in Wastewater and Waters. Subproject 2. Material Flow Analysis for Switzerland: Quaternary Ammonium Compounds. GEO Partner AG. 2007.

[38] Lennart, K., Wallberg, P., Brorström-Lundén, E.: Quaternary ammonium compounds. Analyses in a nordic cooperation on screening. TemaNord 2014:556. North.

[39] Simpson, G. D., Miller R. F., Laxton G. D. Clements W. R.: A Focus on Chlorine Dioxide: The "Ideal" Biocide. Unichem International Inc.

[40] Cui, N. et al. Toxicity profile of labile preservative bronopol in water: the role of more persistent and toxic transformation products. Environmental Pollution 2011: 159, 609 – 615

[41] GESTIS substance database of the Institute for Occupational Safety and Health of the German Social Accident Insurance

[42] Rouge, V. et al. In situ formation of free chlorine during ClO2 Treatment: Implications on the formation of disinfection bgyproducts. Environ. Sci. Technol. 2018: 52, 1321 - 1349

[43] BPC Opinion on the application for approval of the active substance: Glutaraldehyde; PT 11. ECHA/BPC/023/2014

[44] BPC Opinion on the application for approval of the active substance: Hydrogen peroxide; PT 2. ECHA/BPC/40/2015

[45] EU Assessment Report for evaluation of active substances in Regulation 528/2012: Hydrogen peroxide; Product-types PT 1-6. March 2015; Finland

[46] Hund-Rinke, K. Marscheider-Weidemann, F. Kemper, M. Assessment of the total environmental exposure of silver ions from biocidal products. Research Report 360 04 020 UBA-FB 001212. 2008. Federal Environment Agency.

[47] EU Assessment Report for evaluation of active substances in Regulation 528/2012: C(M)IT/MIT; Product-type PT May 11, 2015; France

[48] BPC Opinion on the application for approval of the active substance: Reaction mass of 5-chloro-2-methyl-2h-isothiazole-3-one and 2-methyl-2h-isothiazole-3-one (3:1); PT 11. ECHA/BPC/47/2015; latest download: 17.05.2022

[49] BKG Water Solutions: Fundamentals of Cooling Water Treatment. Technical Information 117.

[50] BPC Opinion on the application for approval of the active substance: Peracetic acid; PT 11. ECHA/BPC/106/2016

[51] EU Assessment Report for evaluation of active substances in Regulation 528/2012: Peracetic acid; Product-type PT 11, August 12, 2016; Finland

[52] Federal Institute for Occupational Safety and Health (Baua): Search for biocidal products eBIOMELD

[53] ÖNORM B 5020: Requirements for microbiological water quality in evaporative recooling systems (date of issue 1.11.2013)

[54] Minutes of the WIDES core team meeting on 8.9.2017 (unpublished)

[55] Buser, A.: Analysis of isothiazolinones in wastewater (diploma thesis). Department of Environmental Sciences ETH Zurich. 2005

[56] Silva, V. Silva, C., Soares, P., Garrido. E.M. Borges, F & Garrido, J.: Isothiazolinone Biocides: Chemistry, Biological, and Toxicity Profiles. Molecules. 2020: 25(4): 991

[57] Federal Environment Agency: Recommendation Lists for the Investigation of Environmental Pollution by Biocides. Update of the substance lists of the UBA-Texte 15/2017 report. October 2021.

[58] BKG Water Solutions: Technical Information Cooling Water Manual. Basics of cooling water treatment. Last update: 07.09.2009

[59] Lange, M., Geier, J.: Ingredients of skin protection, skin cleansing and skin care preparations. An allergological commented market overview. Dermatology in Profession and Environment (2005): 53, 167-171.

[60] Mahler, V. et al.: Justification of the assessment of the effects of an allergy to bronopol. Dermatology in Profession and Environment (2009): 57, 36-37.

[61] Rajagopal, S. et al. (eds.): Operational and Environmental Consequences of Large Industrial Cooling Water Systems. 2012. Springer.

[62] CLH Report - Proposal for Harmonised Classification and Labelling: Ozone. Version number: 2.0 December 2021. Dossier submitter: Federal Institute for Occupational Safety and Health (BAuA).

[63] RAC opinion proposing harmonised classification and labelling of peracetic acid ...%. CLH-O-0000007133-82-01/F; Adopted 2 June 222

[64] EU Assessment Report for evaluation of active substances in Regulation 528/2012: Alkyl (C12-16) dimethylbenzyl ammonium chloride; Product-type 1, December 2021; Italy

[65] Zhang, C. et al: Quaternary ammonium compounds (QACs): A review on occurrence, fate and toxicity in the environment. Sciene of the Total Environment (2015): 518-519, 352-362.

[66] DGUV Information 209-054: Activities with contact with biological agents in the wood and metal industry. German Social Accident Insurance March 2023.

[67] Tauschek, J.: Ratgeber - Legionellen kampf und elimination. Important measures and many tips against legionella in the cooling tower, cooling water, cooling circuit and the evaporative cooling system.

[68] Grillitsch, B. Gans, O. Kreuzinger, N. Scharf, S. Uhl, M. & Fuerhacker, M.: Environmental risk assessment for quaternary ammonium compounds: a case study from Austria. Water Sci. Technol. 2006; 54(11-12): 111-8

[69] BPC Opinion on the application for approval of the active substance: Ozone generated from Oxygen; Product type: PT 11 ECHA/BPC/353/2022

[70] Federal Ministry of Food and Agriculture: Directive on means and procedures for the implementation of disinfection in certain animal diseases. Version 1.0 from 20.03.2023

[71] Tauschek, J.: Water treatment and water treatment of open, semi-open and closed process, service and cooling circuits. Guide with many tips on cooling circuits, cooling water, cooling towers, and evaporative cooling systems. February 2023.

[72] Technical Information 117: Basics of Cooling Water Treatment. BKG Water Solutions

ANNEX TABLE 1 PT 11BIOCIDES & PRECURSORS: CLASSIFICATIONS

Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
Reaktionsprodukte aus Ethylenglycol und Paraformaldehyd (EGForm)	3586-55-8	laufend	-	-	H302, H315, H318; Sens., CMR & chron.Tox.: keine Einstufung; Aq. Tox. (akut & chronisch): keine Daten verfügbar	-
1,2-Benzisothiazol-3(2H)-on (BIT)	2634-33-5	laufend	-	H302, H315, H317, H318; H400	H302, H315, H317, H318; CMR & chron.Tox.: keine Einstufung; H400 (M1), H411	BPC Stellungnahme (PT6): H302, H317, H318, H330; H400 (M1), H410 (M1)
2,2-Dibrom-2-cyanacetamid (DBNPA)	10222-01-2	laufend	bewertet hinsichtlich endokriner Wirksamkeit	Vorschlag: H301, H330, H315, H317, H318, H372 (Atemtrakt), H400 (M1), H410 (M1)	-	BPC Stellungnahme (PT4): H301, H330, H315, H317, H318, H372 (Atemtrakt); H400 (M1), H410 (M1)
2,2′,2″-(Hexahydro-1,3,5-triazin-1,3,5-triyl)triethanol (HHT)	4719-04-4	laufend	-	H302, H317	H302, H330, H317, H319, H372 (Atemtrakt), Muta., Repro: keine Einstufung; Karz: keine Daten verfügbar; Aq. Tox. (akut & chronisch): keine Einstufung	-
2-Methyl-2H-isothiazol-3-on (MIT)	2682-20-4	**ZUGELASSEN**	-	EUH071, H301, H311, H314, H317, H330; H400 (M10), H410 (M1)	EUH071, H301, H311, H330, H314, H317, CMR & chron. Tox.: keine Einstufung; H400 (M10), H410 (M1)	BPC Stellungnahme (PT11): entspricht harmonisierte Einstufung
2-Octyl-2H-isothiazol-3-on (OIT)	26530-20-1	laufend	-	EUH071, H301, H311, H314, H317, H330; H400 (M100), H410 (M100)	-	BPC Stellungnahme (PT8): H301, H311, H331, H314, H317, H335; H400 (M100), H410 (M1000)
4,5-Dichlor-2-octylisothiazol-3(2H)-on (4,5-Dichlor-2-octyl-2H-isothiazol-3-on (DCOIT))	64359-81-5	laufend	-	EUH071, H302, H314, H317, H318, H330; H400 (M100), H410 (M100)	-	Wirkstoffbericht (PT21): H302, H314, H317, H330, CMR & chron. Tox.: keine Einstufung; H400 (M100), H410 (M100)

Continued Table 1

Nr	Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
8	Active bromine generated from bromine chloride	Aktivbrom, hergestellt aus Bromchlorid	-	laufend	-	-	-	-
9	Active bromine generated from hypobromous acid and urea and bromourea	Aktivbrom, hergestellt aus Hypobromsäure und Harnstoff sowie Bromharnstoff	-	laufend	-	-	-	-
10	Active bromine generated from sodium bromide and calcium hypochlorite	Aktivbrom, hergestellt aus Natriumbromid und Calciumhypochlorit	-	laufend	-	-	-	-
11	Active bromine generated from sodium bromide and chlorine	Aktivbrom, hergestellt aus Natriumbromid und Chlor	-	laufend	-	-	-	-
12	Active bromine generated from sodium bromide and sodium hypochlorite	Aktivbrom, hergestellt aus Natriumbromid und Natriumhypochlorit	-	laufend	-	-	-	-
13	Active bromine generated from sodium bromide by electrolyse	Aktivbrom, hergestellt aus Natriumbromid durch Elektrolyse	-	laufend	-	-	-	-
14	Active bromine generated from sodium hypobromite and N-bromosulfamate and sulfamic acid	Aktivbrom, hergestellt aus Natriumhypobromit, N-Bromsulfamat und Sulfaminsäure	-	laufend	-	-	-	-
	Ausgangsstoffe, Folgeprodukte bei der Herstellung von "Aktivbrom"							
	Aktivbrom, hergestellt aus Natriumbromid und …	Natriumbromid	7647-15-6	Ausgangsprodukt	-	Vorschlag: H360FD, H362, H336, H372	Akut. Tox., Korr., Sens., Muta, Karz.: keine Einstufung; H361, H373 (Zentralnervensystem), Aq. Tox. (akut & chronisch): keine Einstufung	-
	Aktivbrom, hergestellt aus… und Natriumhypochlorit	Natriumhypochlorit	7681-52-9	Ausgangsprodukt	-	EUH031, H314, H318; H400 (M10), H410 (M1)	-	-
	Aktivbrom, hergestellt aus… und Calciumhypochlorit	Calciumhypochlorit	7778-54-3	Ausgangsprodukt	-	EUH031, H302, H314; H400 (M10)	EUH031, H302, H314, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), Aq. Tox. (chronisch): keine Einstufung	-
	Aktivbrom, hergestellt aus Natriumhypobromit, N-Bromsulfamat und Sulfaminsäure	Natriumhypobromit	13824-96-9	Ausgangsprodukt	-	-	-	-
		N-Bromosulfamat	-	Ausgangsprodukt	-	-	-	-
		Sulfaminsäure	5329-14-6	Ausgangsprodukt	-	H315, H319, H412	Akut.Tox., Sens, CMR & chron. Tox.: keine Einstufung; Aq. Tox. (akut): keine Einstufung, H412	
	Aktivbrom, hergestellt aus Bromchlorid	Bromchlorid	13863-41-7	Ausgangsprodukt	H314, H331, H400 (M?)	-	-	-
	Aktivbrom, hergestellt aus Hypobromsäure und Harnstoff sowie Bromharnstoff	Hypobromsäure	13517-11-8	Ausgangsprodukt	-	-	-	-
		Harnstoff	57-13-6	Ausgangsprodukt	keine Einstufung	-	-	-
		Bromharnstoff	-	Ausgangsprodukt	-	-	-	-
		Brom	7726-95-6		-	H314, H330, H400	H330, H314, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M100), Aq. Tox. (chronisch): keine Daten	-

Continued Table 1

Nr	Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
15	Active chlorine generated from seawater (sodium chloride) by electrolysis	Aktivchlor, hergestellt aus Meerwasser durch Elektrolyse	-	laufend	-	-	-	-
16	Active chlorine generated from sodium chloride by electrolysis	Aktivchlor, hergestellt aus Natriumchlorid durch Elektrolyse	-	laufend	-	-	-	Wirkstoffbericht (PT2): EUH031, (H314), H331, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M100), H410 (M1)
17	Active chlorine generated from sodium N-chlorosulfamate	Aktivchlor, hergestellt aus Natrium N-Chlorsulfamat	-	laufend	-	-	-	-
18	Active chlorine released from calcium hypochlorite	Aktivchlor, freigesetzt aus Calciumhypochlorit	7778-54-3	laufend	-	EUH031, H302, H314; H400 (M10)	EUH031, H302, H314, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), Aq. Tox. (chronisch): keine Einstufung	-
19	Active chlorine released from chlorine	Aktivchlor, freigesetzt aus Chlor	7782-50-5	laufend	-	H315, H319, H331, H335; H400 (M100)		BPC Stellungnahme (PT2): H315, H319, H330, H335; H400 (M100)
20	Active chlorine released from sodium hypochlorite	Aktivchlor, freigesetzt aus Natriumhypochlorit	7681-52-9	laufend	-	EUH031,H314, H318; H400 (M10), H410 (M1)	EUH031, H314, H318, Sens., CMR & chron. Tox: keine Einstufung; H400 (M10), H410 (M1)	BPC Stellungnahme (PT2): EUH031, H314, H400 (M10), H410 (M1)
21	Alkyl (C12-16) dimethylbenzyl ammoniumchloride (ADBAC/BKC (C12-16))	Alkyl (C12-16) dimethylbenzylammoniumchlorid (ADBAC/BKC (C12-16))	68424-85-1	laufend	-	-	-	Wirkstoffbericht (PT1): H302, H314, H318, H335, Sens., CMR & chron.Tox.: keine Einstufung; H400 (M10), H410 (M1)
22	Alkyl (C12-18) dimethylbenzyl ammoniumchloride (ADBAC (C12-18))	Alkyl(C12-18) dimethylbenzylammoniumchlorid (ADBAC (C12-18))	68391-01-5	laufend	H302, H312, H314, H318, Sens., CMR & chron. Tox.: keine Daten verfügbar; H400 (M?), H410 (M?)	-	-	-
23	Alkyl (C12-14) dimethyl(ethylbenzyl) ammoniumchloride (ADEBAC (C12-14))	Alkyl(C12-C14) dimethyl(ethylbenzyl) ammoniumchlorid (ADEBAC (C12-14))	85409-23-0	laufend	-	-	H302, H314, H318, Sens., CMR & chron.Tox.: keine Einstufung; H400 (M10), H410 (M1)	-
24	Alkyl (C12-14) dimethylbenzylammonium chloride (ADBAC (C12-14))	Alkyl (C12-C14) dimethylbenzylammonium chlorid (ADBAC (C12-14))	85409-22-9	laufend	H302, H312, H314, H318, Sens., CMR & chron.Tox.: keine Daten verfügbar; H400 (M?), H410 (M?)	-	-	-

Continued Table 1

Nr	Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
	Ammonium bromide			nicht mehr unterstützt				
	Ammonium sulfate			nicht mehr unterstützt				
25	Bromide activated chloramine (BAC) generated from ammonium bromide and sodium hypochlorite	-	-	laufend	-	-	-	-
	Bromine chloride			nicht mehr unterstützt				
26	Bromochloro-5,5-dimethylimidazolidine-2,4-dione (BCDMH/Bromochlorodimethylhydantoin)	Bromchlor-5,5-dimethylimidazolidin-2,4-dion (BCDMH/Bromchlordimethyl hydantoin)	32718-18-6	laufend	H302, H314, H317, CMR & chron.Tox.: keine Daten verfügbar; H400 (M?), H410 (M?)	-	-	-
27	Bronopol	2-Brom-2-nitropropan-1,3-diol	52-51-7	laufend	-	Vorschlag: H301, H312, H315, H318, H331, H335, H400 (M10), H411	H301, H312, H315, H318, H331, H335, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), H410 (M1)	-
	Chlorine dioxide			nicht mehr unterstützt				
28	chlorine dioxide	Chlordioxid	10049-04-4	laufend	-	H314, H330; H400 (M10)	H314, H318, H330, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M10), H411	-
29	Chlorine dioxide generated from sodium chlorate and hydrogen peroxide in the presence of a strong acid	Chlordioxid, hergestellt aus Natriumchlorat und Wasserstoffperoxid in Gegenwart einer starken Säure	-	laufend	-	-	-	-
	Chlorine dioxide generated from sodium chloride by electrolysis			nicht mehr unterstützt				
	Chlorine dioxide generated from sodium chlorite & sodium persulfate			nicht mehr unterstützt				
30	Chlorine dioxide generated from sodium chlorite by acidification	Chlordioxid, hergestellt aus Natriumchlorit durch Säuerung	-	laufend	-	-	-	-
31	Chlorine dioxide generated from sodium chlorite by electrolysis	Chlordioxid, hergestellt aus Natriumchlorit durch Elektrolyse	-	laufend	-	-	-	-
32	Chlorine dioxide generated from sodium chlorite by oxidation	Chlordioxid, hergstellt aus Natriumchlorit durch Oxidation	-	laufend	-	-	-	-
	Ausgangsstoffe, Folgeprodukte bei der Herstellung von Chlordioxid							
	Herstellungsverfahren (Referenz)	**Stoffbezeichnung**	**CAS Nummer**	**Funktion**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)**
	Chlordioxid, in Gegenwart einer starken Säure aus Natriumchlorat und Wasserstoffperoxid hergestellt	Natriumchlorat	7775-09-9	Ausgangsprodukt	-	Vorschlag: H301	H302, Korr., Sens., CMR & chron. Tox.: keine Einstufung; Aq. Tox. (akut): keine Einstufung, H411	-
	Chlordioxid, durch Säuerung aus Natriumchlorit hergestellt	Natriumchlorit	7758-19-2	Ausgangsprodukt	Stoffbewertung (CoRAP List): Verdacht auf mutagene und reproduktionstoxische Eigenschaften	-	H301, H310, H314, H373 (betroffenes Organ: Milz), Sens. & CMR : keine Einstufung; H400 (M1), H412	-

Continued Table 1

Nr	Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
33	Copper	Kupfer	7440-50-8	laufend	aktuell bewertet hinsichtlich endokriner Wirksamkeit	H411	Kupferspäne: Akute Tox., Korr., Sens., CMR & chron. Tox.: keine Einstufung; H400 (M1), H411	-
34	DCEMH	DCEMH	-	laufend	-	-	-	-
35	Didecyldimethylammonium chloride (DDAC (C8-10))	Didecyldimethylammoniumchlorid (DDAC (C8-10))	68424-95-3	laufend	-	-	H301, H314, H318, Sens.: keine Einstufung, CMR & chron.Tox.: keine Daten verfügbar; H400 (M10), H411	-
36	Didecyldimethylammonium chloride(DDAC)	Didecyldimethylammoniumchlorid	7173-51-5	laufend	-	H302, H314	-	BPC Stellungnahme (PT3): H301, H314, H335, Sens, CMR & chron. Tox.: keine Einstufung; H400 (M10), H411
	Disilver oxide			nicht zugelassen				
37	Dodecylguanidine monohydrochloride	Dodecylguanidinmonohydrochlorid	13590-97-1	laufend	H302, H314, H318, H330, Sens, CMR & chron.Tox: keine Daten verfügbar; H400 (M?), H410 (M?)	-	-	-
	Formic acid			nicht mehr unterstützt				
38	Free radicals generated in situ from ambient air or water	Freie Radikale, die in situ aus Umgebungsluft oder Wasser erzeugt werden	-	laufend	-	-	-	-
39	Glutaral (Glutaraldehyde)	Glutaraldehyd	111-30-8	**ZUGELASSEN**	-	EUH071, H301, H314, H317, H330, H334; H400 (M1), H411	EUH071, H301, H314, H317, H330, H334, CMR & chron. Tox.:keine Einstufung; H400 (M?), H411	Wirkstoffbericht (PT11): EUH071, H301, H314, H317, H330, H334, CMR & chron. Tox.:keine Einstufung; H400 (M1), H411
40	Hydrogen peroxide	Wasserstoffperoxid	7722-84-1	laufend	-	H302, H314, H332	H302, H314, H332, H335, Sens., CMR & chron. Tox.: keine Einstufung; Aq. Tox (acute): keine Einstufung, H412	Wirkstoffbericht (PT1-6): H302, H314, H332, Sens., CMR & chron. Tox.: keine Einstufung, Aq.Tox. (akut, chronisch): keine Einstufung
	Metam-sodium			nicht mehr unterstützt				
41	Mixture of 5-chloro-2-methyl-2H-isothiazol-3-one (EINECS 247-500-7) and 2-methyl-2H-isothiazol-3-one (EINECS 220-239-6) (Mixture of CMIT/MIT)	Gemisch aus 5-Chlor-2-methyl-2H-isothiazol-3-on (Einecs 247-500-7) und 2-Methyl-2H-isothiazol-3-on (Einecs 220-239-6) (Gemisch aus CMIT/MIT)	55965-84-9	**ZUGELASSEN**	-	EUH071, H301, H310, H314, H317, H318, H330; H400 (M100), H410 (M100)	-	Wirkstoffbericht (P11): H301, H310, H314, H317, H318, H330, CMR & chron. Tox.: keine Einstufung; H400 (M100), H410 (M100)

Continued Table 1

Nr	Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
42	Monochloramine generated from ammonia and a chlorine source	Aus Ammoniak und einer Chlorquelle erzeugtes Monochloramin	-	laufend	-	-	-	-
43	Monochloramine generated from ammonium carbamate and a chlorine source	Aus Ammoniumcarbamat und einer Chlorquelle erzeugtes Monochloramin	-	laufend	-	-	-	-
44	Monochloramine generated from ammonium chloride and a chlorine source	Aus Ammoniumchlorid und einer Chlorquelle erzeugtes Monochloramin	-	laufend	-	-	-	-
	Monochloramine generated from ammonium chloride and sodium hypochlorite			nicht mehr unterstützt				
45	Monochloramine generated from ammonium sulphate and a chlorine source	Monochloramin, hergestellt aus Ammoniumsulfat und einer Chlorquelle	-	laufend	-	-	-	-
	Ausgangsstoffe, Folgeprodukte bei der Herstellung von Monochloramin							
	Herstellungsverfahren (Referenz)	**Stoffbezeichnung**	**CAS Nummer**	**Funktion**	**Stoffinformation ECHA "Substance Infocard"**	**harmonisierte Einstufung**	**Einstufung REACH Dossier**	**BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)**
1	Aus Ammoniak und einer Chlorquelle erzeugtes Monochloramin	Ammmoniak (Gas)	7664-41-7	Ausgangsprodukt	-	H314, H331, H400	EUH071, H314, H331,Sens.: keine Daten, CMR & chron.Tox.: keine Einstufung; H400 (M1), H411	-
2	Aus Ammoniumcarbamat und einer Chlorquelle erzeugtes Monochloramin	Ammoniumcarbamat	1111-78-0	Ausgangsprodukt		-	H302, H318, Sens. & CMR & chron.Tox.: keine Einstufung; Aq. Tox.(akut & chronisch): keine Einstufung	-
3	Aus Ammoniumchlorid und einer Chlorquelle erzeugtes Monochloramin	Ammoniumchlorid	12125-02-9	Ausgangsprodukt	-	H302, H319	H302, H319, Sens. & CMR & chron.Tox.: keine Einstufung; Aq. Tox. (akut & chronisch): keine Einstufung	-
4	Monochloramin, hergestellt aus Ammoniumsulfat und einer Chlorquelle	Ammoniumsulfat	7783-20-2	Ausgangsprodukt	-	-	keine Einstufungen lt. REACH Dossier	-
5	Aus… und einer Chlorquelle erzeugtes Monochloramin	Natriumhypochlorit (= Chlorquelle)	7681-52-9	Ausgangsprodukt	-	EUH031, H314, H318; H400 (M10), H410 (M1)	EUH031, H314, H318, Sens., CMR & chron. Tox: keine Einstufung; H400 (M10), H410 (M1)	-
6	Aus… und einer Chlorquelle erzeugtes Monochloramin	Monochloramin	10599-90-3	Folgeprodukt	bewertet hinsichtlich endokriner Wirksamkeit	-	**Lösung (2,5 - 10 g/l):** Akut. Tox.: keine Daten, Sens.: keine Daten, H314, H335, CMR.: keine Einstufung, H372 (Atemwege, Inhalation), Aq. Tox. (akut): keine Einstufung, H412 ; **Lösung (< 3mg/l)**: keine Einstufungen lt. REACH Dossier	-

Continued Table 1

Nr	Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
46	N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (Diamine)	N-(3-aminopropyl)-N-dodecylpropan-1,3-diamin	2372-82-9	laufend	-	-	H301, H314, H373 (Niere), Sens. & CMR: keine Einstufung; H400 (M10), H410 (M10)	-
47	Ozone generated from oxygen	Aus Sauerstoff erzeugtes Ozon	10028-15-6	laufend	aktuell bewertet hinsichtlich endokriner Wirksamkeit	Vorschlag: H330, H341, H351, H370, H372, Korr. : Daten nicht eindeutig; Hautsens: nicht anwendbar (Gas); H400 (M100), H410 (M1)	H330, H314, H318, Sens & CMR: Keine Einstufung, H372 (Atemtrakt); H400 (M100), H410 (M1)	BPC Stellungnahme (PT11): H330, H341, H351, H370, H372, Repro. Tox.: keine Einstufung notwendig; H400 (M100), H410 (M1)
48	Peracetic acid	Peressigsäure	79-21-0	**ZUGELASSEN**	aktuell bewertet hinsichtlich endokriner Wirksamkeit	Stellungnahme des RAC: EUH071, H301, H310, H314, H330; H400 (M10), H410 (M100)	40% wässrige Lsg: H301, H312, H314, H330, Sens. & CMR & chron.Tox.: keine Einstufung; H400 (M1), H410 (M10)	BPC Stellungnahme (PT11): H302, H312, H314, H332, Sens., CMR & chron. Tox.: keine Einstufung; H400 (M?), H410 (M10)
	Peracetic acid gen. from tetra-acetylethylenediamine (TAED) and sodium percarbonate			abgebrochen				
49	Performic acid generated from formic acid and hydrogen peroxide	Perameisensäure, hergestellt aus Ameisensäure und Wasserstoffperoxid	-	laufend	-	-	-	-
	polyhexamethylene biguanide hydrochloride with a mean number-average molecular weight (Mn) of 1415 and a mean polydispersity (PDI) of 4.7 (PHMB(1415; 4.7))			nicht mehr unterstützt				
50	polyhexamethylene biguanide hydrochloride with a mean number-average molecular weight (Mn) of 1600 and a mean polydispersity (PDI) of 1.8 (PHMB(1600;1.8))	-	27083-27-8	**ZUGELASSEN**	-	H302, H317, H318, H330, H351, H372 (Atemtrakt); H400 (M10), H410 (M10)	-	Wirkstoffbericht (PT11): H302, H317, H318, H330, H351, H372, Muta. & Repro.: keine Einstufung; H400 (M10), H410 (M10)
51	Polymer of N-Methylmethanamine (EINECS 204-697-4 with (chloromethyl) oxirane (EINECS 203-439-8)/Polymeric quaternary ammonium chloride (PQ Polymer)	Polymer aus N-Methylmethanamin (Einecs 204-697-4) mit (Chlormethyl)oxiran (Einecs 203-439-8)/Polymeres quaternäres Ammoniumchlorid (PQ Polymer)	25988-97-0	laufend	H302, H319, H332; H400 (M?), H410 (M?)	-	-	-
52	Potassium dimethyldithiocarbamate	Kaliumdimethyldithiocarbamat	128-03-0	laufend	-	-	H315, Acute Tox., Sens., CMR & chron.Tox.: keine Einstufung; H400 (M?), Aq. Tox. (chronisch): keine Daten verfügbar	-
	Reaction mass of titanium dioxide and silver chloride			zurückgenommen				
53	Reaction products of 5,5-dimethylhydantoin, 5-ethyl-5-methylhydantoin with bromine and chlorine (DCDMH)	Reaktionsprodukte aus 5,5-Dimethylhydantoin, 5-Ethyl-5-methylhydantoin mit Brom und Chlor (DCDMH)	-	laufend	-	-	-	-
54	Reaction products of paraformaldehyde and -2-hydroxypropylamine (ratio_1:1)	α,α',α''-trimethyl-1,3,5-triazine-1,3,5(2H,4H,6H)-triethanol	25254-50-6	laufend	-	-	-	Wirkstoffbericht (PT11): EUH071, H302, H314, H317, H332, H341, H350, H373 (Gastrointestinaltrakt, Atemtrakt), Repro. & Aq.Tox. (akut): keine Einstufung, H411
55	Reaction products of paraformaldehyde and -2-hydroxypropylamine (ratio_3:2)	3,3′-Methylenbis[5-methyloxazolidin] (Oxazolidin/MBO)	-	laufend	aktuell bewertet hinsichtlich endokriner Wirksamkeit	-	-	Wirkstoffbericht (PT11): EUH071, H302,H311, H314, H317, H332, H341, H350, H373 (Gastrointestinaltrakt, Atemtrakt), Repro., Aq.Tox. (acute): keine Einstufung, H411

Continued Table 1

Nr	Eintrag ECHA "information on biocides" (Abfrage: November 2022)	Stoffbezeichnung in Deutsch	CAS Nummer	BPR Zulassung PT11	Stoffinformation ECHA "Substance Infocard"	harmonisierte Einstufung	Einstufung REACH Dossier	BPR Dokument: Stellungnahme des Ausschusses für Biozidprodukte (BPC) bzw. Wirkstoffbericht für jeweils zugelassene Produktart (PT)
56	Silver	Silber	7440-22-4	laufend	aktuell bewertet hinsichtlich endokriner Wirksamkeit	-	Silber Pulver (> 99,9%, erfüllt nicht Kriterien für Nano Form): Akute Tox., Korr., Sens., CM & chron.Tox.: keine Einstufung, Repro.: keine Daten verfügbar; H400 (M10), H410 (M10) Silber in Nano-Form (mitlere Partikelgröße < 100 nm): Akute Tox., Korr., Sens., CM & chron.Tox.: keine Einstufung, Repro.: H360D; H400 (M1000), H410 (M1000)	-
	Silver chloride			nicht mehr unterstützt				
57	Silver nitrate	Silbernitrat	7761-88-8	laufend	-	Vorschlag: H300, H314, H317, H341, H360; H400 (M1000), H410 (M100)	H314, Akute Tox., Hautsens., chron. Tox, Muta: keine Einstufung; Karz & Repro. Tox: keine Daten verfügbar; H400 (M1000), H410 (M100)	-
	Sodium bromide			nicht mehr unterstützt				
58	Sodium dichloroisocyanurate dihydrate	Natriumdichlorisocyanurat Dihydrat	51580-86-0 (2893-78-9)	laufend	-	EUH031, H302, H319, H335; H400 (M?), H410 (M?)	EUH031, H302, H314, Sens., CMR & chron.Tox.: keine Einstufung; H400 (M?), Aq. Tox. (chronisch): keine Daten verfügbar	-
59	Sodium dimethyldithiocarbamate	Natriumdimethyldithiocarbamat	128-04-1	laufend	-	-	Acute Tox., Korr., Sens., CMR & chron. Tox.: keine Einstufung; H400 (M100), H410 (M10)	-
60	Symclosene	-	87-90-1	laufend	-	EUH031, H302, H319, H335, H400 (M?), H410 (M?)	EUH031, H302, H319, H335, Sens., CMR & chron.Tox: keine Einstufung; H400 (M?), H410 (M?)	-
61	Tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazole-2,5 (1H,3H)-dione (TMAD)	Tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazol-2,5(1H,3H)-dion (TMAD)	5395-50-6	laufend	-	-	H317, H350, H411; Akute Tox., Korr., Muta & chron.Tox.: keine Einstufung; Repro.: keine Daten verfügbar; Aq. Tox. (akut): keine Einstufung	-
62	Tetrakis(hydroxymethyl)phosphonium sulphate (2:1) (THPS)	Tetrakis(hydroxymethyl)phosphoniumsulfat (2:1) (THPS)	55566-30-8	laufend	-	-	H302, H317, H318, H330, H361, Muta., Karz., chron. Tox.: keine Einstufung; H400 (M1), H411	-
63	Troclosene sodium	-	2893-78-9	laufend	-	EUH031, H302, H319, H335, H400 (M?), H410 (M?)	H302, H314, H318, Sens, CMR & chron.Tox: keine Einstufung; H400 (M?), Aq. Tox. (chronisch): keine Daten verfügbar	-
64	Willaertia subsp. magna, C2c.Maky	-	-	laufend	-	-	-	-

Explanation of Table 1 & 2

Acute tox.	Harmful effect that occurs when a substance is administered orally or dermally in a single dose or inhaled.
Corr.	Classification based on the results of animal experiments as irritating or corrosive.
Sens.	Classification as a skin and/or inhalation allergen
CMR	Carcinogenic, mutagenic and fertility-endangering substances or properties
Karz	Carcinogenic or increasing the incidence of cancer
Muta.	Mutations in the germ cells that can be passed on to the offspring.
Repro.	Impairment of sexual function and fertility in males and females, and developmental toxicity in offspring.
Chron. Tox.	Acts on a target organ with repeated exposure, thus affecting the health of exposed persons.
Aq. Tox. (acute)	Substances classified as aquatic acute 1, H400.
Aq. Tox. (chronic)	Substances classified as aquatic chronic 1, H410 or H411.
No classification	The available data rule out a potential hazard.
No data available	The available data are not sufficient to rule out a potential hazard.

ANNEX TABLE 2 PT11 BIOCIDES AND STARTING MATERIALS: ABC - CATEGORISATION

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
1	Reaktionsprodukte aus Ethylenglycol und Paraformaldehyd (EGForm)	3586-55-8	REACH Dossier	H302	H315, H318	-	-	?	?
2	1,2-Benzisothiazol-3(2H)-on (BIT)	2634-33-5	REACH Dossier, BPC Stellungnahme	H302, H330	H315, H318	**H317**	-	H400 (M1)	H410 (M1)
3	2,2-Dibrom-2-cyanacetamid (DBNPA)	10222-01-2	harmonisierte Einstufung (Vorschlag)	H301, H330	H315, H318	**H317**	**H372 (Atemtrakt)**	H400 (M1)	H410 (M1)
4	2,2′,2″-(Hexahydro-1,3,5-triazin-1,3,5-triyl)triethanol (HHT)	4719-04-4	REACH Dossier	H302, H330	H319	**H317**	**H372 (Atemtrakt)**	-	-
5	2-Methyl-2H-isothiazol-3-on (MIT)	2682-20-4	harmonisierte Einstufung, BPC Stellungnahme	H301, H311, H330	H314	**H317**	-	H400 (M10)	H410 (M1)
6	2-Octyl-2H-isothiazol-3-on (OIT)	26530-20-1	BPC Stellungnahme	H301, H311, H331	H314	**H317**	-	H400 (M100)	**H410 (M1000)**
7	4,5-Dichlor-2-octylisothiazol-3(2H)-on (4,5-Dichlor-2-octyl-2H-isothiazol-3-on (DCOIT))	64359-81-5	Wirkstoffbericht (PT21)	H302, H330	H314	**H317**	-	H400 (M100)	**H410 (M100)**

Continued Table 2

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächengewässer (Aq. Tox. akut)	Gefährdung Oberflächengewässer (Aq. Tox. chronisch)
8	Aktivbrom, hergestellt aus Bromchlorid	-	-	?	?	?	?	?	?
9	Aktivbrom, hergestellt aus Hypobromsäure und Harnstoff sowie Bromharnstoff	-	-	?	?	?	?	?	?
10	Aktivbrom, hergestellt aus Natriumbromid und Calciumhypochlorit	-	-	?	?	?	?	?	?
11	Aktivbrom, hergestellt aus Natriumbromid und Chlor	-	-	?	?	?	?	?	?
12	Aktivbrom, hergestellt aus Natriumbromid und Natriumhypochlorit	-	-	?	?	?	?	?	?
13	Aktivbrom, hergestellt aus Natriumbromid durch Elektrolyse	-	-	?	?	?	?	?	?
14	Aktivbrom, hergestellt aus Natriumhypobromit, N-Bromsulfamat und Sulfaminsäure	-	-	?	?	?	?	?	?
Ausgangsstoffe, Folgeprodukte bei der Herstellung von "Aktivbrom"									
	Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
	Natriumbromid	7647-15-6	REACH Dossier (Vorschlag harmonisierte Einstufung)	-	-	-	**H361 (H360), H373 (H372) (Zentralnervensystem)**	-	-
	Natriumhypochlorit	7681-52-9	REACH Dossier	EUH031	H314	-	-	H400 (M10)	H410 (M1)
	Calciumhypochlorit	7778-54-3	REACH Dossier	EUH031	H314	-			
	Natriumhypobromit	13824-96-9	-	?	-	?	?	?	?
	N-Bromosulfamat	-	-	?	-	?	?	?	?
	Sulfaminsäure	5329-14-6	REACH Dossier	-	H315, H319	-	-	-	H412
	Bromchlorid	13863-41-7	ECHA Infocard	H331	H314	-	-	H400 (M?)	-
	Hypobromsäure	13517-11-8	-	?	-	?	?	?	?
	Harnstoff	57-13-6	ECHA Infocard	-	-	-	-	-	-
	Bromharnstoff	-	-	?	-	?	?	?	?
	Brom	7726-95-6	REACH Dossier	H330	H314	-	-	H400 (M100)	?

Continued Table 2

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächengewässer (Aq. Tox. akut)	Gefährdung Oberflächengewässer (Aq. Tox. chronisch)
15	Aktivchlor, hergestellt aus Meerwasser durch Elektrolyse	-	-	?	?	?	?	?	?
16	Aktivchlor, hergestellt aus Natriumchlorid durch Elektrolyse	-	Wirkstoffbericht Report (PT2)	EUH031, H331	H314	-	-	H400 (M100)	H410 (M1)
17	Aktivchlor, hergestellt aus Natrium N-Chlorsulfamat	-	-	?	?	?	?	?	?
18	Aktivchlor, freigesetzt aus Calciumhypochlorit	7778-54-3	REACH Dossier Calciumhypochlorit	EUH031, H302	H314	-	-	H400 (M10)	-
19	Aktivchlor, freigesetzt aus Chlor	7782-50-5	BPC Stellungnahme (PT2)	H330	H315, H319, H335	-	-	H400 (M100)	-
20	Aktivchlor, freigesetzt aus Natriumhypochlorit	7681-52-9	BPC Stellungnahme (PT2), REACH Dossier	EUH031	H314, H318	-	-	H400 (M10)	H410 (M1)
21	Alkyl (C12-16) dimethylbenzylammonium-chlorid (ADBAC/BKC (C12-C16))	68424-85-1	Wirkstoffbericht (PT1)	H302	H314, H318, H335	-	-	H400 (M10)	H410 (M1)
22	Alkyl (C12-18) dimethylbenzylammonium-chlorid (ADBAC (C12-18))	68391-01-5	ECHA Infocard	H302, H312	H314, H318	?	?	H400 (M?)	H410 M?)
23	Alkyl (C12-C14) dimethyl(ethylbenzyl)ammoniumchlorid (ADEBAC (C12-C14))	85409-23-0	REACH Dossier	H302	H314, H318	-	-	H400 (M10)	H410 (M1)
24	Alkyl (C12-C14) dimethylbenzylammonium chloride (ADBAC (C12-C14))	85409-22-9	ECHA Infocard	H302, H312	H314, H318	?	?	H400 (M?)	H410 (M?)

Continued Table 2

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
25	Bromine activated chloramine (BAC) generated from ammonium bromide and sodium hypochlorite	-	-	?	?	?	?	?	?
26	Bromchlor-5,5-dimethylimidazolidin-2,4-dion (BCDMH/Bromchlordimethylhydantoin)	32718-18-6	ECHA Infocard	H302	H314	**H317**	?	H400 (M?)	H410 (M?)
27	2-Brom-2-nitropropan-1,3-diol (Bronopol)	52-51-7	REACH Dossier	H301, H312, H331	H315, H318, H335	-	-	H400 (M10)	H410 (M1)
28	Chlordioxid	10049-04-4	REACH Dossier	H330	H314, H318	-	-	H400 (M10)	H411
29	Chlordioxid, hergestellt aus Natriumchlorat und Wasserstoffperoxid in Gegenwart einer starken Säure	-	-	?	?	?	?	?	?
30	Chlordioxid, hergestellt aus Natriumchlorit durch Säuerung	-	-	?	?	?	?	?	?
31	Chlordioxid, hergestellt aus Natriumchlorit durch Elektrolyse	-	-	?	?	?	?	?	?
32	Chlordioxid, hergestellt aus Natriumchlorit durch Oxidation	-	-	?	?	?	?	?	?
Ausgangsstoffe, Folgeprodukte bei der Herstellung von Chlordioxid									
	Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
	Natriumchlorat	7775-09-9	harmonisierte Einstufung, REACH Dossier	H301	-	-	-	-	H411
	Natriumchlorit	7758-19-2	REACH Dossier	H301, H310	H314	-	H373 (Milz)	H400 (M1)	H412

Continued Table 2

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
33	Kupfer	7440-50-8	REACH Dossier	-	-	-	-	H400(M1)	H411
34	DCEMH	-	-	?	?	?	?	?	?
35	Didecyldimethylammoniumchlorid (DDAC (C8-10))	68424-95-3	REACH Dossier	H301	H314, H318	-	?	H400 (M10)	H411
36	Didecyldimethylammoniumchlorid	7173-51-5	BPC Stellungnahme (PT3)	H301	H314, H335	-	-	H400 (M10)	H411
37	Dodecylguanidinmonohydrochlorid	13590-97-1	ECHA Infocard	H302, H330	H314, H318	?	?	H400 (M?)	H410 (M?)
38	Freie Radikale, die in situ aus Umgebungsluft oder Wasser erzeugt werden	-	-	?	?	?	?	?	?
39	Glutaraldehyd	111-30-8	Wirkstoffbericht (PT11)	H301, H330	H314, EUH071	**H317, H334**	-	H400 (M1)	H411
40	Wasserstoffperoxid	7722-84-1	Wirkstoffbericht (PT1-6)	H302, H332	H314	-	-	-	-
41	Gemisch aus 5-Chlor-2-methyl-2H-isothiazol-3-on (Einecs 247-500-7) und 2-Methyl-2H-isothiazol-3-on (Einecs 220-239-6) (Gemisch aus CMIT/MIT)	55965-84-9	harmonisierte Einstufung, Wirkstoffbericht	H301, H310,H330	EUH071, H314, H318	**H317**	-	H400 (M100)	**H410 (M100)**

Continued Table 2

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
42	Aus Ammoniak und einer Chlorquelle erzeugtes Monochloramin	-	-	?	?	?	?	?	?
43	Aus Ammoniumcarbamat und einer Chlorquelle erzeugtes Monochloramin	-	-	?	?	?	?	?	?
44	Aus Ammoniumchlorid und einer Chlorquelle erzeugtes Monochloramin	-	-	?	?	?	?	?	?
45	Monochloramin, hergestellt aus Ammoniumsulfat und einer Chlorquelle	-	-	?	?	?	?	?	?
Ausgangsstoffe, Folgeprodukte bei der Herstellung von Monochloramin									
	Stoffbezeichnung	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
	Ammmoniak	7664-41-7	REACH Dossier	H331	EUH071, H314	-	-	H400 (M1)	H411
	Ammoniumcarbamat	1111-78-0	REACH Dossier	H302	H318	-	-	-	-
	Ammoniumchlorid	12125-02-9	REACH Dossier	H302	H319	-	-	-	-
	Ammoniumsulfat	7783-20-2	REACH Dossier	-	-	-	-	-	-
	Natriumhypochlorit (Chlorquelle)	7681-52-9	REACH Dossier	EUH031	H314	-	-	H400 (M10)	H410 (M1)
	Monochloramin (2,5 - 10 g /l)	10599-90-3	REACH Dossier	?	H314, H335	?	**H372 (Atemtrakt, Inhalation)**	-	H412
	Monochloramin (< 3 mg/l)		REACH Dossier	-	-	-	-	-	-

Continued Table 2

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächengewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
46	N-(3-aminopropyl)-N-dodecylpropan-1,3-diamine	2372-82-9	REACH Dossier	H301	H314	-	H373 (Niere)	H400 (M10)	H410 (M10)
47	Aus Sauerstoff erzeugtes Ozon	10028-15-6	harmonisierte Einstufung, REACH Dossier, BPC Stellungnahme (PT11)	H330	H314, H318, EUH071	-	**H341, H351, H372 (Atemtrakt)**	H400 (M100)	H410 (M1)
48	Peressigsäure	79-21-0	harmonisierte Einstufung (Vorschlag)	H301, H310, H330	EUH071, H314	-	-	H400 (M10)	**H410 (M100)**
49	Perameisensäure, hergestellt aus Ameisensäure und Wasserstoffperoxid	-	-	?	?	?	?	?	?
50	polyhexamethylene biguanide hydrochloride with a mean number-average molecular weight (Mn) of 1600 and a mean polydispersity (PDI) of 1.8 (PHMB(1600;1.8))	27083-27-8	Wirkstoffbericht (PT11), harmonisierte Einstufung	H302, H330	H318	**H317**	**H351, H372 (Atemtrakt)**	H400 (M10)	H410 (M10)
51	Polymer aus N-Methylmethanamin (Einecs 204-697-4) mit (Chlormethyl)oxiran (Einecs 203-439-8) / Polymeres quaternäres Ammoniumchlorid (PQ Polymer)	25988-97-0	ECHA Infocard	H302, H332	H319	?	?	H400 (M?)	H410 (M?)
52	Kaliumdimethyldithiocarbamat	128-03-0	REACH Dossier	-	H315	-	-	H400 (M?)	?
53	Reaktionsprodukte aus 5,5-Dimethylhydantoin, 5-Ethyl-5-methylhydantoin mit Brom und Chlor (DCDMH)	-	-	?	?	?	?	?	?
54	α,α',α''-trimethyl-1,3,5-triazine-1,3,5(2H,4H,6H)-triethanol	25254-50-6	Wirkstoffbericht (PT11)	H302, H332	EUH071, H314	**H317**	**H341, H350, H373 (Gastrointestinal trakt, Atemtrakt)**	-	H411
55	3,3′-Methylenbis[5-methyloxazolidin] (Oxazolidin/MBO)	-	Wirkstoffbericht (PT11)	H302, H311, H332	EUH071, H314	**H317**	**H341, H350, H373 (Gastrointestinal trakt, Atemtrakt)**	-	H411

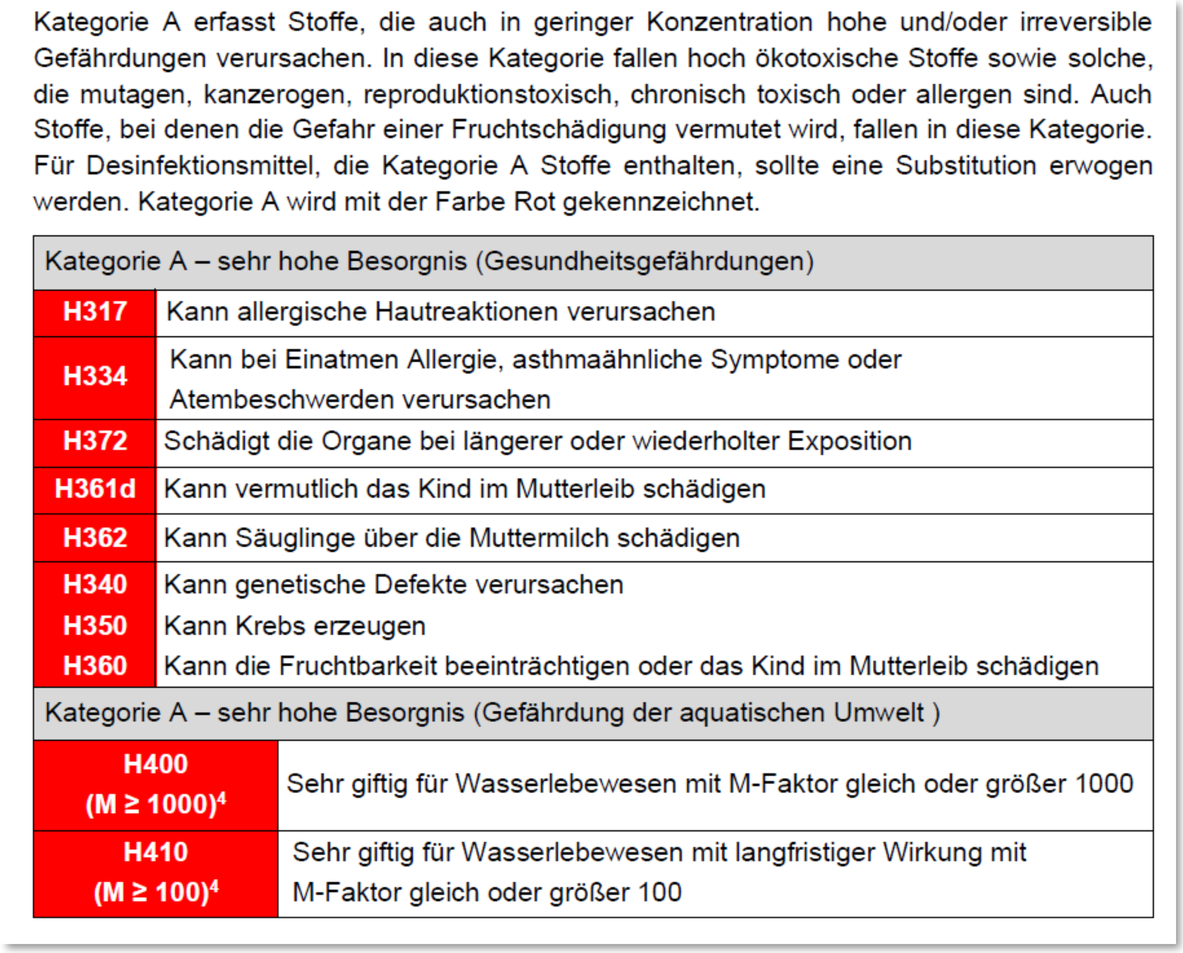
Continued Table 2

Nr	**Stoffbezeichnung**	**CAS Nummer**	**Datenquelle(n) für ABC Kategorisierung**	Akute Giftigkeit (Akut Tox.)	Reiz-, Ätzwirkung (Korr.)	Sensibilisierung (Sens.)	CMR & chronische Toxizität (CMR & chron. Tox.)	Gefährdung Oberflächen gewässer (Aq. Tox. akut)	Gefährdung Oberflächen gewässer (Aq. Tox. chronisch)
56	Silber	7440-22-4	REACH Dossier (Silberpulver)	-	-	-	?	H400 (M10)	H410 (M10)
			REACH Dossier (Silber in Nanoform)	-	-	-	**H360 D**	**H400 (M1000)**	**H410 (M1000)**
57	Silbernitrat	7761-88-8	REACH Dossier	-	H314	-	-	**H400 (M1000)**	**H410 (M100)**
58	Natriumdichlorisocyanurat Dihydrat	51580-86-0 (2893-78-9)	REACH Dossier	EUH031, H302	H314	-	-	H400 (M?)	?
59	Natriumdimethyldithiocarbamat	128-04-1	REACH Dossier	-	-	-	-	H400 (M100)	H410 (M10)
60	Symclosen	87-90-1	REACH Dossier	EUH031, H302	H319, H335	-	-	H400 (M?)	H410 (M?)
61	Tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazol-2,5(1H,3H)-dion (TMAD)	5395-50-6	REACH Dossier	-	-	**H317**	**H350**	-	H411
62	Tetrakis(hydroxymethyl)phosphoniumsulfat (2:1) (THPS)	55566-30-8	REACH Dossier	H302, H330	H318	**H317**	**H361**	H400 (M1)	H411
63	Troclosene sodium	2893-78-9	REACH Dossier, harmonisierte Einstufung	EUH031, H302	H314, H318	-	-	H400 (M?)	-
64	Willaertia subsp. magna, C2c.Maky	-	-	?	?	?	?	?	?

APPENDIX: ABC CATEGORIZATION

The classification is evaluated according to criteria of the ABC categorization – this is a simple form of substance evaluation based on the evaluation scheme of the Vienna disinfectant database WIDES [23]. The results of the ABC categorization are summarized in Appendix Table 2. The assessment is carried out in 6 hazard categories in order to highlight adverse properties for human health and the aquatic environment. Four adverse properties concern human health (acute toxicity, irritant or corrosive effect, sensitizing properties or carcinogenic, mutagenic, toxic to reproduction and chronic toxic), two adverse properties affect the aquatic environment (acute toxic or chronic toxic behavior in surface waters). The ABC categorization is linked to a color code or a distinction is made between questionable and less questionable hazards. On the basis of its H-phrases (or due to a lack of data that can rule out a hazard), a substance is assigned to category A (colour code red; very high concern), B (colour code yellow; significant concern) or C (colour code white; low concern). The corresponding data (H-phrase, data uncertainty, exclusion of a hazard) including colour codes are assigned to the hazard categories in Annex Table 2. The following figures show how categories A, B, and C are associated with H-phrases (or data gaps). Further explanations of the ABC categorization can be found after logging in to the WIDES database in the pdf document "Introduction to the Evaluation Grid" [23].

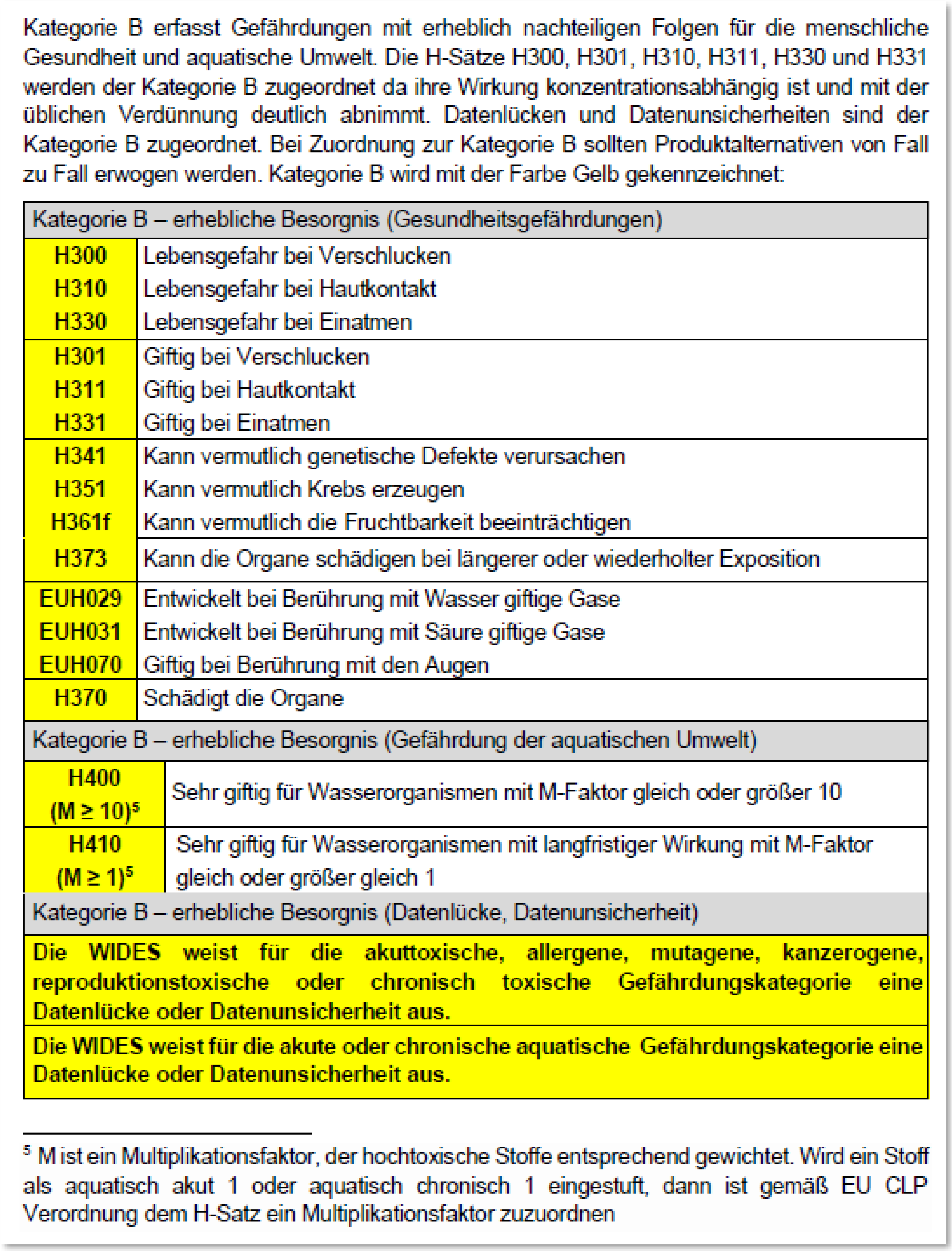
Category A



Kategorie A erfasst Stoffe, die auch in geringer Konzentration hohe und/oder irreversible Gefährdungen verursachen. In diese Kategorie fallen hoch ökotoxische Stoffe sowie solche, die mutagen, kanzerogen, reproduktionstoxisch, chronisch toxisch oder allergen sind. Auch Stoffe, bei denen die Gefahr einer Fruchtschädigung vermutet wird, fallen in diese Kategorie. Für Desinfektionsmittel, die Kategorie A Stoffe enthalten, sollte eine Substitution erwogen werden. Kategorie A wird mit der Farbe Rot gekennzeichnet.

Kategorie A – sehr hohe Besorgnis (Gesundheitsgefährdungen)	
H317	Kann allergische Hautreaktionen verursachen
H334	Kann bei Einatmen Allergie, asthmaähnliche Symptome oder Atembeschwerden verursachen
H372	Schädigt die Organe bei längerer oder wiederholter Exposition
H361d	Kann vermutlich das Kind im Mutterleib schädigen
H362	Kann Säuglinge über die Muttermilch schädigen
H340	Kann genetische Defekte verursachen
H350	Kann Krebs erzeugen
H360	Kann die Fruchtbarkeit beeinträchtigen oder das Kind im Mutterleib schädigen
Kategorie A – sehr hohe Besorgnis (Gefährdung der aquatischen Umwelt)	
H400 (M ≥ 1000)[4]	Sehr giftig für Wasserlebewesen mit M-Faktor gleich oder größer 1000
H410 (M ≥ 100)[4]	Sehr giftig für Wasserlebewesen mit langfristiger Wirkung mit M-Faktor gleich oder größer 100

Category B



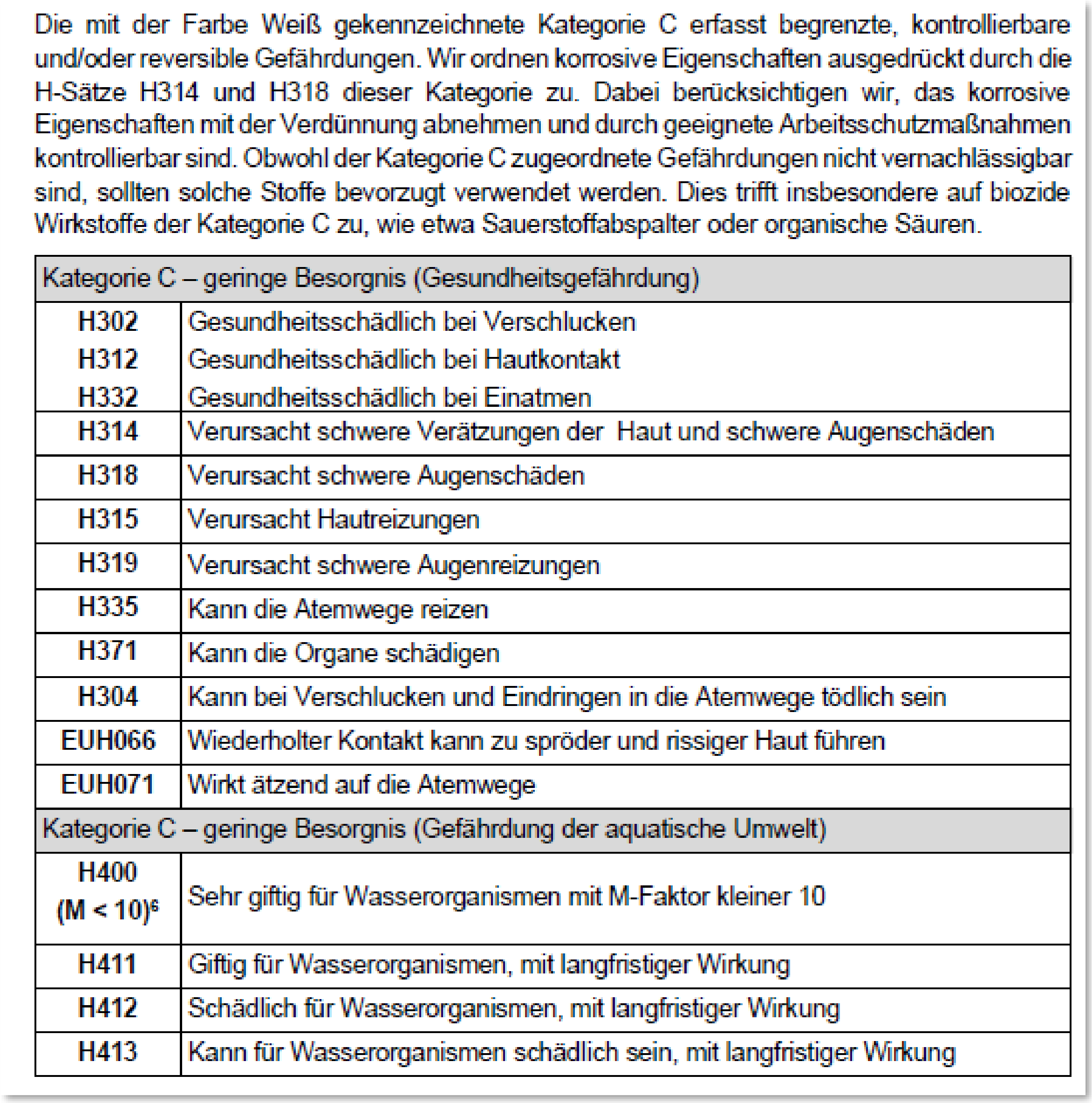
Kategorie B erfasst Gefährdungen mit erheblich nachteiligen Folgen für die menschliche Gesundheit und aquatische Umwelt. Die H-Sätze H300, H301, H310, H311, H330 und H331 werden der Kategorie B zugeordnet da ihre Wirkung konzentrationsabhängig ist und mit der üblichen Verdünnung deutlich abnimmt. Datenlücken und Datenunsicherheiten sind der Kategorie B zugeordnet. Bei Zuordnung zur Kategorie B sollten Produktalternativen von Fall zu Fall erwogen werden. Kategorie B wird mit der Farbe Gelb gekennzeichnet:

Kategorie B – erhebliche Besorgnis (Gesundheitsgefährdungen)	
H300 **H310** **H330**	Lebensgefahr bei Verschlucken Lebensgefahr bei Hautkontakt Lebensgefahr bei Einatmen
H301 **H311** **H331**	Giftig bei Verschlucken Giftig bei Hautkontakt Giftig bei Einatmen
H341 **H351** **H361f**	Kann vermutlich genetische Defekte verursachen Kann vermutlich Krebs erzeugen Kann vermutlich die Fruchtbarkeit beeinträchtigen
H373	Kann die Organe schädigen bei längerer oder wiederholter Exposition
EUH029 **EUH031** **EUH070**	Entwickelt bei Berührung mit Wasser giftige Gase Entwickelt bei Berührung mit Säure giftige Gase Giftig bei Berührung mit den Augen
H370	Schädigt die Organe
Kategorie B – erhebliche Besorgnis (Gefährdung der aquatischen Umwelt)	
H400 **$(M \geq 10)$[5]**	Sehr giftig für Wasserorganismen mit M-Faktor gleich oder größer 10
H410 **$(M \geq 1)$[5]**	Sehr giftig für Wasserorganismen mit langfristiger Wirkung mit M-Faktor gleich oder größer gleich 1
Kategorie B – erhebliche Besorgnis (Datenlücke, Datenunsicherheit)	
Die WIDES weist für die akuttoxische, allergene, mutagene, kanzerogene, reproduktionstoxische oder chronisch toxische Gefährdungskategorie eine Datenlücke oder Datenunsicherheit aus.	
Die WIDES weist für die akute oder chronische aquatische Gefährdungskategorie eine Datenlücke oder Datenunsicherheit aus.	

---

[5] M ist ein Multiplikationsfaktor, der hochtoxische Stoffe entsprechend gewichtet. Wird ein Stoff als aquatisch akut 1 oder aquatisch chronisch 1 eingestuft, dann ist gemäß EU CLP Verordnung dem H-Satz ein Multiplikationsfaktor zuzuordnen

Category C



Die mit der Farbe Weiß gekennzeichnete Kategorie C erfasst begrenzte, kontrollierbare und/oder reversible Gefährdungen. Wir ordnen korrosive Eigenschaften ausgedrückt durch die H-Sätze H314 und H318 dieser Kategorie zu. Dabei berücksichtigen wir, das korrosive Eigenschaften mit der Verdünnung abnehmen und durch geeignete Arbeitsschutzmaßnahmen kontrollierbar sind. Obwohl der Kategorie C zugeordnete Gefährdungen nicht vernachlässigbar sind, sollten solche Stoffe bevorzugt verwendet werden. Dies trifft insbesondere auf biozide Wirkstoffe der Kategorie C zu, wie etwa Sauerstoffabspalter oder organische Säuren.

Kategorie C – geringe Besorgnis (Gesundheitsgefährdung)	
H302 **H312** **H332**	Gesundheitsschädlich bei Verschlucken Gesundheitsschädlich bei Hautkontakt Gesundheitsschädlich bei Einatmen
H314	Verursacht schwere Verätzungen der Haut und schwere Augenschäden
H318	Verursacht schwere Augenschäden
H315	Verursacht Hautreizungen
H319	Verursacht schwere Augenreizungen
H335	Kann die Atemwege reizen
H371	Kann die Organe schädigen
H304	Kann bei Verschlucken und Eindringen in die Atemwege tödlich sein
EUH066	Wiederholter Kontakt kann zu spröder und rissiger Haut führen
EUH071	Wirkt ätzend auf die Atemwege
Kategorie C – geringe Besorgnis (Gefährdung der aquatische Umwelt)	
H400 (M < 10)[6]	Sehr giftig für Wasserorganismen mit M-Faktor kleiner 10
H411	Giftig für Wasserorganismen, mit langfristiger Wirkung
H412	Schädlich für Wasserorganismen, mit langfristiger Wirkung
H413	Kann für Wasserorganismen schädlich sein, mit langfristiger Wirkung