

Review Articles

Multidimensional Risk Analysis of Antifouling Biocides

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Abstract. In order to improve the orientation about the long-term sustainability of the use of the antifouling biocides tributyltin (TBT), copper, Irgarol® 1051, Sea-Nine™ 211 and zinc pyrithione, used for the protection of fouling in sea-going ships, the risks posed to the marine biosphere due to their use are evaluated. The newly presented method of risk analysis uses release rate, spatiotemporal range, bioaccumulation, bioactivity and uncertainty as 5 dimensions of ecotoxicological risk. For each dimension, a scoring procedure is briefly described. The resulting risk profiles of the antifouling biocides show characteristics of the different substances, but also indicate where further information is required. Application of the method is proposed as a decision support in the integrated development of products, informed purchasing and for regulatory purposes.

Keywords: Antifouling; biocides; copper; fouling protection; Irgarol 1051; risk analysis; Sea-Nine 211; sustainable products; tributyltin; zinc pyrithione

Abbreviations:

K_d	Equilibrium coefficient for the distribution of substances between water and sediment
K_{OM}	Equilibrium coefficient for the distribution between water and organic matter
EC_{50}	Concentration, where 50% of the tested organisms show a defined effect after a certain exposure time
NOEC	No-observed-effect concentration

1 Introduction

A global ban of the application of organotin compounds in antifouling coatings for sea-going vessels has found wide support [1]. In the European Union, Council Directive 98/8/EC concerning biocidal products [2] obligates the member states to implement national laws, installing an approval procedure for biocides in antifouling coatings (antifouling biocides) based on extensive data requirements until May 2000. However, the outline of sustainable antifouling concepts designed for wide application in sea-going vessels remains unclear. The environmentally motivated wish to generally dispense with the use of biocides in fouling protection seems unrealistic in the short term. In this situation, there is scientific, public and commercial interest in prospective understanding of advantages and risks resulting from the use of alternative biocides.

Following the terminology of N. Luhmann, the usage of the term "risk" supposes that a damage possibly occurring can

be assigned to a decision causing that possibility. If this is not the case, the potential damage is a "danger" [3]. Since the environmental effects of antifouling biocides, especially tributyltin, are widely discussed, nearly every decision influencing their release can be qualified as a *risk* managing decision.

There is a wide consensus between national and international regulatory authorities, scientists and chemical industry, that the relevant dimension for judging the acceptability of a specified release of a chemical is the quotient of exposure and the effect level in the relevant environmental compartments [4,5,6]. These concentrations may be experimentally observed or estimated using exposure models and various extrapolations. Uncertainty is often being accounted for by uncertainty factors (UF, formerly safety factors) which have been suggested some three decades ago without a sound scientific basis and in expectation of further refinements [7].

The idea underlying this concept is to ensure that no organism is exposed to a concentration which is expected to cause "inacceptable" effects. This strategy, however, is corrupted by the variability of exposure in space and time, as well as by the variability of susceptibility in different species. The increased use of probability distributions accounting for the natural variability of exposure and effects, but also for uncertain parameters, requires extensive data. Another important point of criticism is the fact that effects occurring at the eco-system level can only be estimated from effects on individual organisms in simplified cases due to inherent limitations of the modelling of eco-systems [8].

In order to provide a robust scientific basis for risk-managing decisions, a method for the comparative risk analysis of antifouling biocides has been developed. It aims at representing available relevant data of very different quantity and quality. As it focuses on the evaluation of biocides, conclusions about the comparative environmental risks of antifouling coating systems containing such biocides can not be drawn directly.

2 Five Indicators for the Risk Analysis of Antifouling Biocides

Rejecting the conception of the possibility of "zero risk", as well as the necessity of representing risk in a single quantity, indicators were sought for a multidimensional description. The notion that persistent, bioaccumulative, and toxic (PBT) chemicals are of special concern was adapted, additionally

considering the importance of quantities released, of spatial aspects and of uncertainty.

For every dimension described below, an indicator was constructed with the possibility of 4 comparative scores, 1 being the lowest and 4 being the highest score. The scoring scales are intended to cover the whole range possibly covered by antifouling biocides. Due to the use of the same ordinary scale (1 to 4) for evaluating different criteria, one might be tempted to calculate an average representing the risk as a single number. The underlying assumption that the criteria have equal weights is rejected by the authors. The risk profile set up by the five criteria should not to be reduced any further.

For every one of the first four criteria, uncertainty is represented by lower-case letters from a to d, where a stands for very low, b for low, c for high and d for a very high uncertainty. These uncertainties are combined to form the fifth criterion, the overall uncertainty of the evaluation (see below). The evaluations are subjective and changeable since newly received data can result in scoring adjustments. Using the method is normative inasmuch as that a selection of relevant measures of risk has taken place.

The method presented here is not a classification system, nor does it claim to provide a measure for the acceptability to use or to release any certain amount of any certain chemical. Rather, it aims at a comparative communication of risks posed to the environment by different substances, independent of a specific decision context. As other methods of risk analysis, it strongly depends on the sources of data accessed and subjective scoring choices. The heterogeneity of the chemicals (organic, organometallic and inorganic), of data and data contexts has discouraged the development of a scoring scheme with rules applying to every possible scoring situation. In the following, a general outline of the scoring criteria is given for the case of antifouling biocides.

2.1 Release rate

The amount of biocide released to the biosphere is a first indicator of a potential damage. In order to make the release of different biocides comparable, release rates per unit of protected area (service unit) are at the focus of the evaluation.

Two main influences on the release rates of antifouling biocides and their development during the lifetime of the coatings can be distinguished, the target values of the coating manufacturer and the technical possibilities to attain these target values. Due to lacking information about the price and effectiveness of different biocides, only the technical possibility of producing the desired release rate was evaluated.

Antifouling biocides can be incorporated in coatings either in a separate, inorganic phase such as the most commonly used copper pigment copper oxydul, or mixed into or bound to (in the case of tributyltin) the binder. Thus far, the best known technology to attain a release rate constant over the whole lifetime seems to be to chemically control the erosion of the binder by slow hydrolysis. Biocides mainly used in combination with this technique are rated with a release rate score of 2, expressing the remaining shortcomings of

this technique. Biocides mainly used in combination with other techniques are rated with a release rate score of 3.

For improved evaluations, release rates estimated from average biocide contents of the coatings, the maximum lifetimes of the respective coatings and, finally, the measured release rates for all biocides would have to be used. Biocide releases due to cleaning and repairing in drydocks were not included in the evaluation.

2.2 Spatiotemporal range

If a certain amount of a chemical is released to the environment, the fraction of the biosphere potentially affected depends on its persistence in time and its closely related tendency to spread in space. The *spatial range* as an indicator for the evaluation of xenobiotics has been defined as the 95%-range of its exposure distribution in a spatially resolved environmental compartment [9]. It is independent of the amount of the chemical released and can therefore be regarded as an attribute of the chemical which is valid for a specified environment. The exact determination of the spatial range of a chemical requires comprehensively observed exposure data or the performance of exposure modelling. The *temporal range* or persistence of a chemical for the case of a constant release can be described by its mean residence time [10] or by its overall decay rate.

Since spatial and temporal aspects of the fate of a chemical are closely interrelated, the aim in defining an indicator of spatiotemporal range was to combine information about both using a two-compartment model as a first approach. Therefore, the spatial aspect of spatiotemporal range does not describe a spatially resolved compartment, but rather the distribution between two compartments.

The equilibrium distribution of the chemicals between water and sediment in a system with a water to sediment ratio of 100 L/kg was chosen to represent phase ratios to be found in the coastal areas. Copper is not a xenobiotic, being present in sea and sediment in considerable background concentrations. Only the amount released by antifouling activities "on top" of possible background levels was considered. The air compartment was not considered relevant.

The score for the spatiotemporal range was determined by a combination of the expected equilibrium distribution and the persistence in water and sediment (\rightarrow Table 1, p. 107). The equilibrium distribution was described by coefficients like K_d , K_{OM} or, if none of these was available, K_{OW} . The distribution was judged by evaluating whether more than 95% of the released biocide are to be found in only one of the two compartments, or if the fraction in both compartments is greater than 5%. A half-life of one year served as a boundary value for the persistence in both seawater or sediment.

2.3 Bioaccumulation

Bioaccumulation, describing bioconcentration from the surrounding media as well as biomagnification along the food chain, describes the internal exposure of biota in relation to a given external exposure. As most ecotoxicological effects conceptually depend on internal exposure, bioaccumu-

Table 1: Matrix for evaluating the spatiotemporal range from equilibrium distribution and persistence on a scale from 1 to 4

	not persistent	only persistent in water	only persistent in sediment	persistent in water and sediment
mainly in water	1	3	2	3
mainly in sediment	1	2	3	3
significant amounts in both water and sediment	2	3	3	4

lation is a further indicator of a potential environmental damage with the advantage that it is relatively easy to assess experimentally.

The affinity of a chemical substance to organisms (\rightarrow Table 2) is commonly expressed by the bioconcentration factor BCF determined by laboratory tests with fish, or from concentrations measured in environmental samples, where the uptake by feeding is additionally possible. The BCF always contains information about the kinetics of uptake and purging processes like metabolism and excretion. The K_{OW} is of a more limited relevance for the evaluation of bioaccumulation and the relation between the two quantities ([11], only for non-ionic compounds) is not unequivocal.

Table 2: Scheme for evaluating the bioaccumulation tendency on a scale from 1 to 4

Score	1	2	3	4
BCF	< 30	30 - 100	100-1000	> 1000
log K_{OW}	< 2.8	2.8 - 3.5	3.5 - 4.8	> 4.8

2.4 Biological activity

Effect dependencies on internal doses are known only in very few cases. Consequently, for the determination of the biological activity in the marine environment, mainly information about external concentrations causing a given effect were taken into account.

The scoring range from 1 to 4 is set up to enfold the whole range of antifouling substances, starting with repellents ideally not showing acute toxicity at active concentrations, up to TBT, which is regarded as being the compound with the lowest effect concentrations ever deliberately released into the aquatic environment in large amounts.

The main parameters evaluated were aquatic NOEC values, preferably for reproduction, and acute EC_{50} or LC_{50} values, which were considered less relevant because of chronic exposure. Data for algae, bivalves, crustaceans and fish were preferred. Eventually, information about the effects from the molecular level up to the population level were included. Also, bacterial and fungal inhibition concentrations and genotoxic effects were taken into account where available. Because of differences in the types and amount of data considered for the different active substances, no general rule has been developed for the scoring process.

2.5 Remaining uncertainty

The last criterion is set up to clarify the limits of evaluative power of the performed risk analysis. The indicator is meant

to reflect the uncertainty remaining after the acquisition and interpretation of data. It serves as an indicator of risk, because the possibility of damage done to the marine biosphere increases with decreasing investigations. Without such investigations, potential damage cannot be communicated and transformed into risk-managing decisions.

However, investigations can only reduce the risk due to damage possibilities not yet examined, not risks that have been firmly agreed upon. Therefore, the indicator has to be interpreted in close relationship to the other indicators.

3 Risk Analysis of Five Antifouling Biocides

In the compendium "Pesticides 1998", edited by the Health and Safety Executive of the Pesticides Safety Directorate, Great Britain, around 600 different antifouling coatings are listed, containing different combinations of approximately 60 different active ingredients. TBT and copper currently are the most important biocidal components of antifouling coatings. In most cases, a combination of these agents is used. Copper is effective against both algae and calcareous fouling organisms such as barnacles, less so against some bryozoans and weeds like *Enteromorpha*. Organotin is toxic to a wider range of species, but does not work as well against algae [13], [14] cited in [15]. Due to these gaps in the effect ranges of the basic biocides, "booster" biocides are employed to inhibit the settlement of remaining organisms, also aiming at minimising the content of basic biocides in the coatings.

A literature study about available alternatives to TBT-containing products for sea-going vessels revealed that commercially promoted alternatives focus on the use of copper compounds (mostly cuprous oxide Cu_2O) in combination with synthetic organic biocides. Out of these booster biocides, three have been chosen for the risk comparison due to their occurrence in tin-free products promoted by large suppliers of marine coatings.

3.1 Tributyltin

Because of the release of tributyltin compounds (\rightarrow Fig. 1) to the environment due to use in antifouling coatings, in the protection of wood and of other materials, considerable research work on environmental fate and effects has resulted in a vast amount of publications reviewed in different contexts [16, 17, 18]. Organotin compounds were still considered environmentally harmless in 1975 since their strong bioaccumulation and their potential to disrupt the endocrine system of some organisms were not yet known [19]. The numerical ratings corresponding to the evaluations below are shown in Table 3, graphical representations of the risk profiles in Fig. 6.

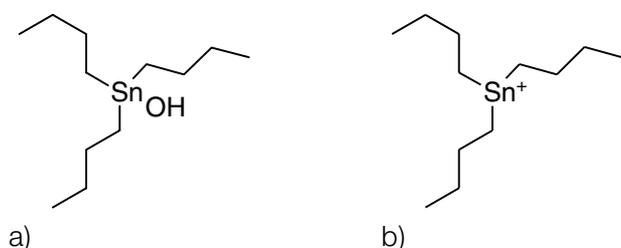


Fig. 1: Structural formulas of the tributyltin compounds a) TBTOH and b) TBT⁺ as present in natural waters [20]

Biological activity. Concentrations of TBT at which approximately 10% of the species of several groups reveal acute toxic effects, range from 5 ng/L (zooplankton) to 2 µg/L (fish) [23]. An increase in the percentage of mud snails with male reproductive organs was shown to be probable at chronic exposure with 2 ng/L TBT [24].

Release rate. Tributyltin compounds like (TBT)₂O, TBTCl or TBTf are integrated into the binder of the coating by simple mixing ("free association paints") and/or by bonding to an acrylate/methacrylate copolymer ("Self-Polishing Copolymer", SPC). Because of the steadier and longer-lasting, chemically controlled TBT-release of the second type of coating, combined with easy repair, this technology is currently preferred. TBT release rates measured with the rotating cylinder method used by the US EPA are restricted to 4(5) µg cm⁻² d⁻¹ in the U.S., Canada and Sweden (Australia, New Zealand). Release rates measured directly on the hull of a ship in the harbour with the "Navy method" are generally lower by an average factor of 13 and had an average of approximately 0.35 µg cm⁻² d⁻¹ after two to three weeks [20]. The *release rate* for TBT-SPC-type coatings is being rated *low*, with the remainder of a very low uncertainty.

For other types of TBT-containing coatings, initial release rates have to be higher because of the ageing processes. Their *release rate* is being rated *high*, with a low remaining uncertainty.

Spatiotemporal range. The affinity of TBT to particulate matter is only moderate. Distribution constants K_d between seawater/freshwater and sediment mainly range between 1×10^3 and 3×10^3 L/kg [18]. Therefore, in the equilibrium model described above, 3.2 to 9 percent of the total amount will be present in the water. The distribution of TBT was classified as "significant amounts in both water and sediment". The degradation of TBT in seawater generally takes place with a half-life of a few days to a few weeks, decreasing with temperature. TBT has also been shown to degrade in marine sediments, but half-lives in marine sediments range from weeks to 4-6 months [21], estimations based on sediment core analysis go up to several years [17]. TBT was classified as persistent neither in sediment nor in seawater. According to the scoring scheme in Table 1, the resulting *spatiotemporal range* is *low*. The neglect of adsorption to dissolved and particulate organic matter in the water column, and of the complex interplay between hydrophobic and ionic interaction potential of TBT, result in a remaining uncertainty which was rated comparably low.

Bioaccumulation. Bioconcentration factors BCF vary highly between types of organisms. BCF for fish and algae have been reported with high and very high values above 100/1000. For filtering molluscs, values above 100,000 have been reported [22]. The ability to metabolise TBT has been stated to be the greatest in higher animals, particularly in vertebrates [18]. Biomagnification of TBT along the food chain has been considered to be insignificant [17]. The *bioaccumulation* potential of TBT is rated *very high* with very low remaining uncertainty.

Biological activity. Concentrations of TBT at which approximately 10% of the species of several taxonomic groups reveal acute toxic effects, range from 5 ng/L (zooplankton) to 1 µg/L (fish) [23]. An increase in the percentage of mud snails with male reproductive organs was shown to be probable at chronic exposure with 2 ng/L TBT [24]. Trace concentrations of TBT compounds cause significant detrimental effects on the level of populations in a variety of mussels and snails. Biochemical modes of action in µmolar concentrations include membrane toxicity in fish hepatoma cells, disturbance of Ca²⁺-homeostasis and induction of apoptosis in thymocytes (immunotoxicity), inhibition of oxidative phosphorylation and photophosphorylation (ATP-synthesis in mitochondria and chloroplasts), inhibition of ion pumps including the Na⁺/K⁺-ATPase and inhibition of the cytochrome P₄₅₀ system. The combination of a positive charge with high lipophilicity seems to be responsible for the strong effects on different ion channels of membranes [18]. The *biological activity* is classified as *very high*, with a remaining uncertainty which is very low.

Remaining uncertainty. Publications and accessible data about almost all of the aspects relevant to the risk evaluation are abundant. Few questions about bioconcentration and spatiotemporal range remain to be answered. The overall *remaining uncertainty* is rated very low.

3.2 Copper

Copper is used in antifouling coatings as copper metal, oxides, thiocyanates or sulfides. The most commonly used copper(II)oxide, Cu₂O, is a red pigment, other colours are obtained by using CuSCN (white) or Cu₂S (black) [25]. Reviews about the risks posed by copper in the marine environment include reports of governmental institutions [26, 27,28] and scientific reviews [29,30].

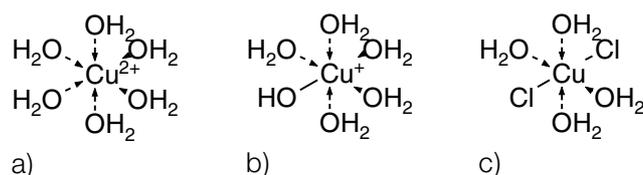


Fig. 2: a) "Free" Cu²⁺, b) a Cu(OH)⁺-complex and c) a Cu(Cl)₂⁰-complex

Release rate. The lower toxicity of copper compared to TBT causes the necessity of higher amounts of copper to be incorporated in and released from antifouling coatings in order to warrant sufficient fouling protection. Recent developments advertise with the absence of tin combined with

self-polishing properties. Apparently, all of these products, if containing biocides at all, contain copper. The comparability of the copper-acrylate system to the TBT-acrylate system has been questioned [31]. This is supported by the fact that copper contents are usually far higher than the TBT contents of antifouling coatings. For Cu-acrylate systems, a hydrolytically controlled release of copper was stated [32], but for one coating the "reduced formation of a leached layer" [33] is an indication of a certain amount of washing-out which, in turn, indicates a decrease in biocide release with increasing age. Release rates were not found accessible. With very high remaining uncertainty, the *release rate* from Cu-copolymers is rated high.

The *release rate* for copper from hydrophilic coatings can be evaluated with a low uncertainty as being *very high*.

Spatiotemporal range. Copper(II) is generally persistent in seawater. Under anoxic conditions, it can be reduced to copper(I). Since the biological activity of copper(I) is not well known, the two species are treated as equivalent with respect to the spatiotemporal range of copper in this first approach. In the sediment, copper(II) is bound to organic matter, but the sorption to mineral surfaces is probably quantitatively more important [29]. In anoxic, strongly reducing sediments, practically insoluble copper sulfides are formed. However, due to the possibility of a remobilisation by sediment-dwelling organisms, copper was also rated as persistent in sediment. The determination of a spatiotemporal range of copper is complicated by the fact that copper is present in the world seas, because of the development of an oxidic atmosphere [34]. In the present context, only the amount of copper that is additionally released to the biosphere is considered to be relevant for the spatiotemporal range (2.2). A release of 25 t copper from antifouling coatings per annum was estimated for the Netherlands [35]. The Baltic sea (20,000 km³) roughly contains 10,000 t copper, taking 0.5 µg/L as a mean concentration [36]. This demonstrates the possibility of a significant increase of copper concentrations by antifouling in regions with low water exchange rates and high antifouling activities. The distribution of copper in the environmental compartments was judged based on concentrations measured in the Baltic sea, because this empirical information appeared more relevant for the judgement of the spatial range than using theoretical distribution coefficients. Using seawater concentrations of 0.5 µg/L and sediment concentrations of 10-80 mg/L [29], only about 1×10⁻³ of total copper is approximated to be present in the water phase of the described model system, therefore it is expected to be present mainly in the sediment compartment. From the above, the *spatiotemporal range* is rated *high*. Considering the presently unknown stability of biologically active complexes of copper(II) with other antifouling biocides like pyriithione and thiram, but also with natural dissolved organic compounds apt to increase the bioavailability of copper, the remaining uncertainty is very high.

Bioaccumulation. Bioconcentration factors vary in an unknown function of the chemical composition of water and particles, as well as of other factors. In algae, animal plankton, molluscs and crustaceans, BCF values greater than 1000 are found for some algae, macroalgae and bivalves (e.g. *Crassostrea virginica*: 28,000) and crustaceans greater than 10,000

[35]. The lower values for fish (150-700) can be rationalised by the fact that fish and higher invertebrates are able to regulate copper by active excretion [37]. Correspondingly, a bio-magnification of copper along the food chain was generally not found [28,35]. In spite of the very high enrichment in the majority of organisms, the *bioaccumulation* was rated only high, with very low remaining uncertainty. The data supporting the evaluation of this criterion is comprehensive.

Biological activity. Of the metal ions naturally occurring in seawater, copper(II) is toxic at the lowest concentrations. Compared with TBT, Cu-effect concentrations, but also non-observable effect concentrations are generally greater by at least one order of magnitude. The much greater difference in fish toxicity is consistent with the fact that fish are able to regulate copper. Complex formation with different chelate ligands has been shown to lower the effect concentrations for copper with respect to bacteria, planktic algae and *Daphnia* [38]. Some antifouling biocides like thiram or pyriithione are known or suspected to increase the lipophilicity of copper(II) in seawater. Only scarce information was found concerning the stability of such complexes and about components of naturally occurring dissolved organic matter DOM capable of increasing the bioavailability of copper. The *biological activity* of copper in seawater was rated *high*, with a high remaining uncertainty.

Remaining uncertainty. Copper is an essential trace element for all living organisms. The optimum concentration range neither causing deficiency nor detrimental effects is generally quite small. For some bivalves, Verburgh [39] showed that this concentration range only spans one order of magnitude (factor 10). Total copper concentrations in the world seas are about 0.15 µg/L, in the Baltic Sea approximately 0.3 to 0.8 µg/L. However, the comparability of total copper concentrations in seawater with data from toxicity tests is questioned by the differences in the composition of the water matrices with respect to complexing capacities. Generally, only part of the total amount of copper is bioavailable and therefore potentially harmful to living organisms [40]. The speciation of copper is very controversially discussed in the literature. The overall risk analysis for copper as an antifouling biocide is connected with a *high remaining uncertainty*.

3.3 Irgarol 1051

Irgarol® 1051, in brief Irgarol, belongs to the class of symmetric triazines inhibiting the photosynthesis by binding to the D1-protein of the photosystem II. In water with a low fouling pressure by the macroorganisms, the fouling protection by copper and Irgarol has been sufficient before the invention of copper acrylate systems. Due to the growing use of Irgarol, environmental concentrations and effects have been studied in a number of publications (e.g. [41,42]).

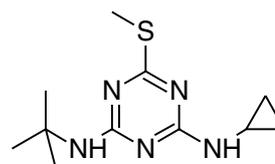


Fig. 3: Structural formula of Irgarol® 1051

Release rate. A special mode of release control for Irgarol in antifoulings is not known. Its *release rate* was rated *low*, with a very high uncertainty.

Spatiotemporal range. The distribution coefficient between water and sediment K_d of 3.4 [42] indicates an equilibrium fraction in water of about 4% in the model described above. Except for the stability of Irgarol with respect to hydrolysis and the occurrence of photolysis which was considered irrelevant, no data about the degradation in natural waters was found, so that Irgarol was considered to be persistent in natural waters. In saltwater sediments, a half-life of approximately 100 d has been stated (Ciba Geigy 1995, cited in [43]). Irgarol was consequently classified as not persistent in sediment. The products of transformation, mainly of oxidation or displacement of the methylthio-entity as well as N-dealkylation, are being considered significantly less biologically active. Ring-cleavage was not reported. These evaluations indicate a *low spatiotemporal range*, with a high remaining uncertainty.

Bioaccumulation. Determinations of 1-octanol-water partitioning constants by contract laboratories have resulted in values from 2.8 (GLP study) to ≥ 3.95 . A recalculation of the raw data carried through in KEMI, Sweden, even added uncertainty to the data. BCFs around 200 [44, 45] for fish indicate a high affinity to organisms. However, the credibility of the very high affinity to macrophytes concluded in [43] is the subject of discussion due to the very low detection limit of 0.3 ng/L given for aqueous concentrations in this study. BCFs of at least 1000, nevertheless, seem realistic for macrophytes. *Bioaccumulation* is rated *high*, with a high remaining uncertainty.

Biological activity. Like the related triazine-herbicides, Irgarol has a very specific inhibitory effect on the photosystem II. The effects on photosynthesis rates of algae populations were shown for concentrations as low as 0.1 $\mu\text{g/L}$. Effects on organisms not photosynthetically active were reported only for concentrations around 1 mg/L. The NOECs for such organisms were slightly lower, in one case considerably so [44]. *Biological activity* was rated *low*, with a low remaining uncertainty.

Remaining uncertainty. The overall *remaining uncertainty* was classified as *high*.

3.4 Sea-Nine 211

Sea-Nine™ 211, in brief C-9211 (\rightarrow Fig. 4) has been used as a fungicide, among other targets against mildew. The substance has been chosen for antifouling applications by the producer Rohm & Haas through the screening of various isothiazolones using the parameters algae toxicity, barnacle toxicity and water solubility (slow leaching) [46]. Because of its lower persistence in the environment and lower toxicity towards humans in comparison with TBT, the company won the "presidential green chemistry award" of the U.S. EPA in the category "designing safer chemicals". However, in Sweden, the use of C-9211 is subject to some restrictions and the biocide has the same regulatory status as the biocide diuron [47].

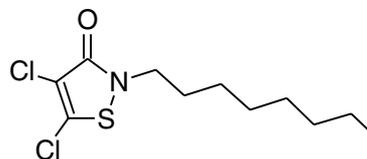


Fig. 4: Structural formula of Sea-Nine™ 211

Release rate. The use of encapsulation and of a reservoir-membrane have currently been researched at the University of New Hampshire [48]. Current *release rates* are rated *low*, with a very high remaining uncertainty.

Spatiotemporal range. The distribution of C-9211 in the marine environment is difficult to evaluate. The distribution in water-sediment systems is governed by the superimposition of transformation and transport processes. The occurrence of bound residues indicates the possibility that the fast disappearance in the aqueous phase is caused by an irreversible association to particulate organic matter to a significant degree, above all as a result of organic matter in the sediment. Persistence in natural waters is low, while there are contradictory reports concerning the persistence in sediments. After the extraction of sediments with different solvents, high fractions of "bound residues" were found which were apparently quite persistent. Due to the high lipophilicity, it seems possible that these residues may be reversibly bound, although only extracted from the sediment in small amounts. Knowledge about the structure of metabolites is comparatively small. The persistence in sediments is classified as high. A *high spatiotemporal range* with a *high* remaining uncertainty is the consequence.

Bioaccumulation. Experimental values for $\log K_{ow}$ span from 2.3 to 6.4. Estimations carried out with quantitative structure-activity relationships published by Meylan et al. and Hansch and Leo (as in [51]) indicate a $\log K_{ow}$ value above 6. The assessments of BCFs indicate an associating reaction of C-9211 with body tissues. The lipophilicity, which is assumed to be high, is consistent with the high BCFs > 100 . The uptake of the substance is presumably accompanied with metabolic transformations. The *bioaccumulation* is rated *high*, with high remaining uncertainty due to lacking bioconcentration data for organisms other than fish.

Biological activity. The biological activity of C-9211 results in critical effects for all tested organisms at concentrations between 1 and 30 $\mu\text{g/L}$, with the exception of protozoae in sewage sludge, possibly due to the strong association of C-9211 to organic substance, and of the fiddler crab *Buca pugilator*. Since it is being used as a fungicide and since a high activity against a broad spectrum of bacteria was found for 3(2H)-isothiazolones [52], it is to be regarded as a broad-range biocide with high toxic activity. Effect concentrations towards algae are comparable to the respective values for Irgarol, whereas in one publication an even lower effect concentration was to be found for C-9211 [53]. Only very little data is available about chronic effects. Known values in combination with common interspecies variabilities lead to the assumption that relevant effects for some species will occur at concentrations around

100 ng/L. The *biological activity* is being rated *high*, with very high remaining uncertainty.

Remaining uncertainty. The overall *remaining uncertainty* was classified as *high*.

3.5 Zinc pyrithione

The zinc salt of pyrithione (\rightarrow Fig. 5), known in brief as ZnPT, is not only used as a fungicide in anti-dandruff shampoos but, due to its low solubility in water, is also known as an antifouling pigment. Here, it acts especially well in combination with Cu_2O or CuSCN [54]. Complexes with Cu, Hg and Ag are stable. The copper complex (\rightarrow Fig. 5b) is of special interest since it is formed during the release from copper-containing antifouling coatings [55]. No investigations about the synergistic effects of Cu and ZnPT have been found. Aside from ZnPT (zinc omadine[®]), copper pyrithione (copper omadine[®]) is provided as an antifouling pigment by the former Olin Corporation, now Arch Chemicals. Copper pyrithione is not registered for use in the U.S. by way of the U.S. Environmental Protection Agency and is therefore only sold in other parts of the world.

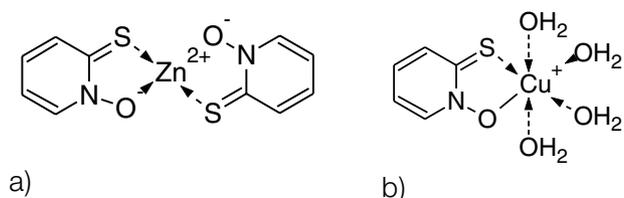


Fig. 5: Structural formulas of a) zinc pyrithione (1:2-complex) and b) copper(II)-pyrithione (1:1-complex)

Almost no literature has been found about the behaviour of pyrithione in the environment. An estimation of the speciation of pyrithione in seawater with respect to complexation with metals was calculated as follows. Assuming a background concentration of 0.4 $\mu\text{g/L}$ for Zn [56], the fraction of pyrithione complexed 1:1 with zinc can be calculated using the stability constant $\log K \cong 5.8$ [57] as being ca. 0.2%. The stability constant for copper pyrithione complexes is assumed to be of the same order of magnitude as the one provided for zinc above. Of the background concentration in seawater which reveals about 0.15 $\mu\text{g/L}$ for total copper, only about 1% is assumed to be present as Cu^{2+} [29]. This leads to the conclusion that the fraction of pyrithione occurring as copper 1:1-complex CuPT is considerably smaller than the fraction of ZnPT. The biological activity of CuPT is subject only to speculation.

Release rate. Typical *release rates* of pyrithione are rated *low*, with a very high uncertainty remaining.

Spatiotemporal range. It has been shown that photodecomposition requires a $\text{pH} < 6$ and only the undissociated fraction of pyrithione ($\text{pK}_a = 4.6$) is subject to photolysis [58]. However, photolysis half-lives between 15 min and > 10 days for depths between up to 3 m have been presented at the 10th International Congress on Marine Corrosion and Fouling [59]. Considering that the neutral fraction of pyrithione ($\text{pK}_a = 4.6$

[58]) is $< 0.1\%$ at $\text{pH} 8$ and, based on the assumption that the partitioning of the pyrithione anion from water is negligible, the distribution constant $\log D_{\text{ow}}$ is expected to be < -2 . Therefore, it is expected to mainly occur in water. With very high remaining uncertainty, the *spatiotemporal range* was rated *high*, considering the assumptions of its main occurrence in water and its assumed persistence in this compartment.

Bioaccumulation. The very low lipophilicity of free pyrithione discussed above suggests a correspondingly low bioaccumulation. The biological activity at very low concentrations, on the other hand, indicates an affinity to organisms that is significantly higher. It is suspected that the bioavailable compound is not free pyrithione. Since 1:1 complexes will occur [57] in the presence of small concentrations of pyrithione and metal cations, these complexes might be responsible for pyrithione uptake. Such complexes carrying a single positive charge could exhibit high lipophilicity and the corresponding high affinity to organisms, in analogy to Cu-oxine complexes [60]. *Bioaccumulation* is rated *low* with a very high uncertainty.

Biological activity. Related to the use of anti-dandruff shampoos, some studies about biological effects (e.g. [61]) and mechanisms of action [62] have been reported. ZnPT as well as pyrithione alone, which is also used as an ionophore for Zn^{2+} , are active. ZnPT is accumulated in cell membranes and free pyrithione is mainly found in the cytoplasm [63]. Obviously, it is a broad-range antimicrobial agent with high activity. The only data on algae toxicity indicates inhibitory activity at concentrations as low as 10 $\mu\text{g/L}$ [54]. Acute toxicity [64] and embryotoxicity [65] towards fish was found at concentrations of 3 and 10 $\mu\text{g/L}$. The *biological activity* of ZnPT is rated *high*, with very high uncertainty remaining.

Remaining uncertainty. The overall *remaining uncertainty* was classified as *very high*.

4 Comparative Risk Assessments

It is inherent in the presented method of risk analysis that it does not produce a definite ranking or scoring of the biocides. It can be assured that no single aspect of environmental risk will be used in the isolation of other aspects. The following verbal comparison of the biocides will serve to complement the graphical representations in Fig. 6 (\rightarrow p. 112), based on the scores in Table 3 (\rightarrow p. 112).

Interestingly, a positive comparative judgement of the spatiotemporal range of TBT provides a reminiscence of the optimistic early judgement of its degradability by Evans and Smith [19]. It has to be kept in mind that a half-life of 1 year is a relatively tolerant value for the evaluation. Furthermore, metabolites were not considered. The extremely high bioaccumulation and biological activity of TBT are not shared by any of the other biocides evaluated here. Also, even if its release rate per unit ship area is controlled considerably, its global application as a standard biocide for sea-going vessels still causes a very high overall release. The low uncertainty about this risk shows that a decision concerning only TBT would involve a very low uncertainty of risk knowledge.

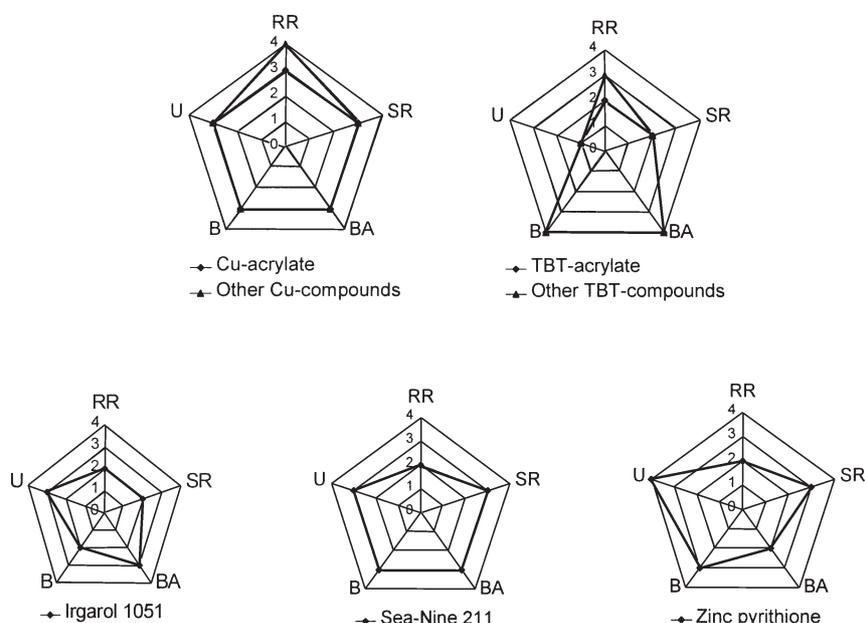


Fig. 6: 5-dimensional risk comparison of five antifouling biocides. High risk scores are located on the outside of the graph, low risk scores towards the center. RR = Release rate, SR = Spatiotemporal range, BA = Bioaccumulation, B = Biological activity, U = Uncertainty

Table 3: Scoring of the risk indicators for the five biocides on a scale from 1 to 4. Letters behind the numerical scores represent the uncertainty of judgement, where a is the lowest and d the highest uncertainty

	Release rate	Spatiotemporal Range	Bioaccumulation	Biological activity	Remaining uncertainty
TBT acrylate	2a	2b	4a	4a	1
Other TBT compounds	3b	2b	4a	4a	1
Cu acrylate	3d	3d	3a	3c	3
Other Cu compounds	4c	3d	3a	3c	3
Irgarol 1051	2d	2c	3c	2b	3
Sea-Nine 911	2d	3c	3c	3d	3
Zinc pyrithione	2d	3d	2d	3d	4

The lower biological activity and bioaccumulation of *copper* is partially compensated by the uncertainty of the evaluation. This might be surprising, because extensive literature about ecotoxicological effects of copper exists. Nevertheless, copper speciation, and its consequences for bioaccumulation and biological activity, are challenging questions to current research. Surprises in both directions cannot be ruled out.

The comparative profile of *Irgarol* can be described as combining a low biological activity due to the selectivity of action with a comparatively low remaining uncertainty about the risk. For *Sea-Nine*, high ratings in almost all of the dimensions regarded seem to be characteristic. Certainly, a decrease in uncertainty is desirable. *Zinc pyrithione* shows a much more heterogeneous risk profile, where the bioaccumulation and release are rated low, but the very high remaining uncertainty is an important characteristic pertaining to all of the other indicators.

5 Conclusions

A method of risk evaluation has been proposed aiming at the demands of a) the possibility of intersubjective agreement about its results independent of the evaluating context and background, b) operability, c) effectivity with respect to the revelation of at least the present state of knowledge and d) completeness regarding all advantages and disadvantages, as well as problems and effects relevant to the context of the evaluation [66]. Depending on a very heterogeneous data basis, the method has been applied to five antifouling biocides of commercial and environmental importance. The resulting risk profiles are to be regarded as preliminary, especially since the implementation of the EU Biocides Directive will oblige producers and importers of antifouling products to present the respective data necessary for such comparative risk profiles.

The ratings of release rates reflect only very limited knowledge. However, this indicator is very relevant, especially in the context of a comparative evaluation of antifouling coatings. The concept of a spatiotemporal range proved to be useful for integrating the information about distribution and persistence.

The use of the method to compare the evaluations of chemicals in various other applications seems to be possible. However, the current basic status of method development will demand considerable resources for the choice and development of adequate scoring.

Since the consequences to be drawn from the risk profile are not part of the scientific concept, a broad context-dependent use by different parties is possible. Examples for such parties are public authorities in charge of the regulatory treatment of biocides or harbour authorities afflicted by the consequences of biocide release in harbours. Further, the application in the development process for new antifouling coatings or even for internal evaluations by biocide producing companies is possible. Last, but not least, any person purchasing or applying any of the biocides might be interested in learning about risk-related properties of the substances.

The work presented here is also a pledge for an open discussion of risks regarding the competence of all parties affected by or otherwise interested in the topic.

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