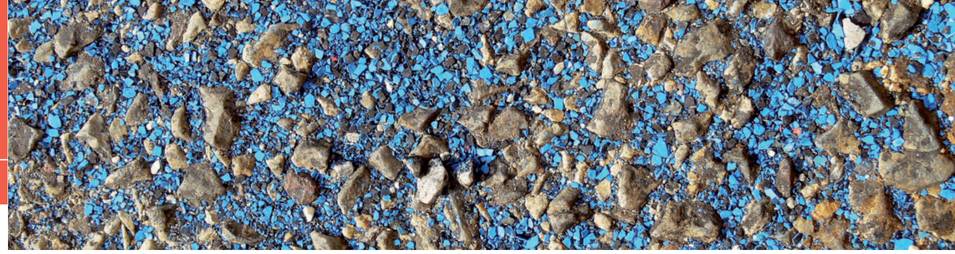

ENVIRONMENTAL OCCURRENCE
AND CONCERNS OF ANTIFOULING BIOCIDES

Ecological risk assessment and potential adverse effects posed by antifouling biocides to saltwater environments

Among human activities, the use of the antifouling paints in order to protect the ship's hull or submerged static structures from the colonization of aquatic organisms (fouling) represents a dangerous source of chemical contamination for coastal aquatic ecosystems worldwide. In recent years, the estimation of potential negative effects of biocides contained in antifouling paints upon the organisms and the aquatic ecosystems became an issue of great interest. To this aim, many ecological risk assessment (ERA) studies were conducted

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Introduction

Fouling is the successive development of a community of bacteria, protozoa, algae and invertebrates on the surfaces exposed to water. The fouling formed on the boat hulls and submerged static structures is an undesirable process with economic and environmental negative consequences; for example, boat hull fouling causes an increase in water resistance during navigation and a consequent increase in fuel demand and pollution generated by the products of fuel combustion. In order to control and minimize the progressive biofouling on submerged surfaces, antifouling paints formulated to slowly release potent biocides are usually applied. Organotin biocides, especially tributyltin (TBT), were the most used additives in antifouling paints, but the International Maritime Organization (IMO) banned the use of TBT and similar compounds starting from 2003 worldwide, due to the high toxic effects posed to various non-target aquatic species. Consequently, paint manufacturers have developed new "TBT-free" formulations; the most common being the copper-based antifouling paints, in which a herbicidal booster biocide is added to enhance the antifouling effect. Active ingredients commonly incorporated as booster biocides in antifouling paints are Irgarol 1051, Diuron, Sea-nine 211, Chlorothalonil, Zinc pyrithione, and Dichlofluanid [1].

The extensive use of these biocides in antifouling paints may be responsible of the contamination of the costal aquatic environment worldwide [1]. Chemical contamination of coastal water and sediment may constitute an important hazard for non-target aquatic species and equilibrium of ecosystems. So, the quantitative estimation of occurring biocides in the environment and the evaluation of their potentially adverse effect on the aquatic ecosystems became a question of concern

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from both, ecological and economic point of view. For the diverse and complex nature of ecosystems, a quantitative estimation of the negative consequences is often difficult and far-reaching. In this context, the Ecological Risk Assessment provides an adequate interdisciplinary approach to estimate the potential effect associated to the occurrence of biocides in the environment.

Ecological risk assessment

Ecological Risk Assessment (ERA) is defined as a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors [2]. A stressor can be any chemical, physical, or biological entity able to determine an adverse ecological effect; that is, changes that are considered undesirable because they alter important structural or functional characteristics, or components of ecological systems.
The process is used for systematically evaluating and organizing data, information, assumptions, and uncertainties, in order to understand and predict the relationships between stressors and ecological effects. There are two main advantages of ERA [3]: it comprises

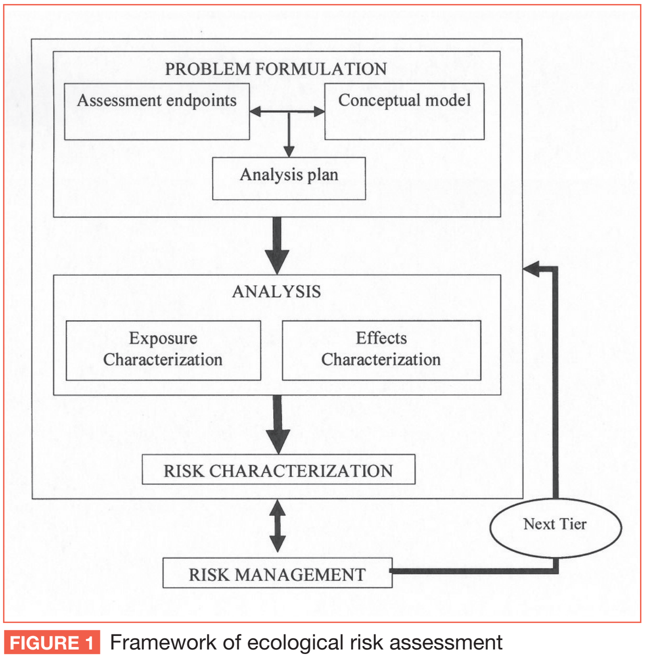

FIGURE 1 Framework of ecological risk assessment

a framework that supports the environmental decision making, and it considers the natural high variability of ecosystems, or rather the aleatory uncertainties (which can never be fully eliminated), in estimating the adverse effects of stressors.
The final outcome of a risk assessment may range from qualitative judgments to a quantitative estimate of the possible risk associated to a stressor.
ERA can be used both in assessing whether effects are caused by past exposure to stressors (retrospective assessment) and in predicting the likelihood of future adverse effects (prospective assessment). The evaluation of the risk linked to the historic contamination of coastal seawaters from TBT, provides an excellent example of retrospective ERA while the evaluation of the risk posed by the new biocides formulation carried out before releasing in the environment is a typical case of prospective assessment.
The most common approach is described in the Guidelines for ERA from USEPA; it is worked out again in a compatible way in the ASTM (American Society for Testing and Materials) standard guide E 2205-02 for Eco-RBCA (Risk-Based Corrective Action for protection of Ecological resources), and consists in a three-stage methodology (Figure 1): 1) problem formulation 2) analysis 3) risk characterization. The process is more often iterative than linear, in fact one or more phases of the risk assessment can be revaluated integrating new data and new information. In the following paragraphs, the three phases of the procedure will be analyzed and the key issues related to ERA of biocides used in antifouling paints will be summarized.

Problem formulation

In the problem formulation, the goals that have to be addressed in the risk evaluation phase are identified; to this end all the available information on sources, stressor, effects and the ecosystem are collected; then, from the integration of this information, assessment endpoints are selected, and the conceptual model is prepared. The selection of appropriate assessment endpoints is a basic element of the risk evaluation process. Assessment endpoints are "explicit expression of the environmental value that is to be protected, operationally defined by an ecological entity and its attributes" [2]. An ecological entity can be considered as a very important ecological receptor. It may include, for example, species or communities protected or rare, recreational, or commercial, or cultural important resources, specific valued habitat, species or communities that are important in maintaining the integrity and biodiversity of the environment [4]. Once the potential entity of concern has been identified, it is necessary to define what are the priority measurable attributes (i.e., survival, growth or reproduction endpoints) to be protected and potentially at risk. Generally the appropriate measures that have to be used in assessment endpoints are identified during the conceptual model development. The conceptual model is defined on the basis of the preliminary information about the ecosystem at risk, stressor characteristics, exposure pathways and ecological effects on assessment endpoints. The goal consists in defining the working hypothesis and developing an exposure diagram that describes the possible exposure and effect scenarios (Figure 2).

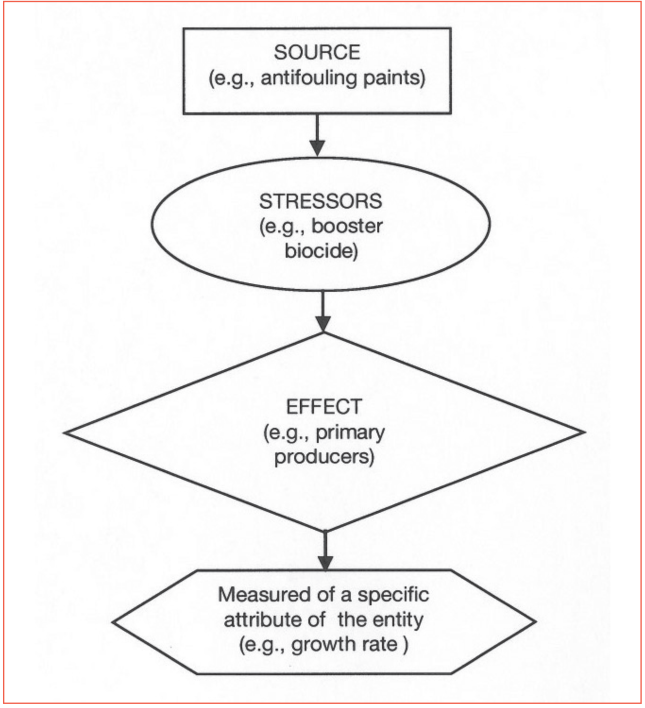

FIGURE 2 Flow diagram of the conceptual model

In the estimation of risk associated to the occurrence of antifouling biocides in aquatic ecosystem, the conceptual model can be based on the hypothesis that the use of antivegetative paint (i.e., source) on the submerged structures has contributed to the environment contamination through the release of these active substances; so, the booster biocides can be identified as primary chemical stressors. In addition, albeit banned from many years, also the tributyltin (TBT) represents an hazardous chemical stressor; in fact various studies showed that TBT contamination is still an actual problem for the environment, since its degradation in sediment (ranging from months to years) is much slower than in water (that is on the order of days), and sediments may then continue to be a source for the water column exposure [5].

Hence, the assessment consists in determining how these chemical stressors might have adverse effects towards the specific assessment endpoint. Some studies show that in the aquatic environment the most susceptible organisms to these substances, used as algaecide, are the plant species which may be directly affected rather than animal species, which may be affected indirectly. Consequently, to ensure a conservative approach the appropriate endpoint of concern is generally identified among non-target aquatic species of primary producers (Phytoplancton and Macrophite species), with the aim of evaluating the long-term viability of aquatic communities (plant, fish, invertebrates, etc.) and the integrity of the ecosystem's structures and functions [6-10]. Just in a few cases, marine invertebrate species [11] or both, aquatic plants and animals (i.e., Phytoplancton, Zooplancton, benthic and fish species) were considered. This is the case of TBT, since it has a significant tissue burden in many taxa with the highest bioaccumulation factor into the mollusks (minimal metabolic potential) [5].

Finally, the problem formulation step ends with the production of an investigation plan that has to be developed in the following "analysis" phase of ERA.

Analysis

The analysis phase includes the exposure and effect characterization. This step is aimed at determining how

exposure to stressors may occur (i.e., exposure characterization) and what are the possible adverse ecological effects that may occur under exposure to this stressor themselves (i.e., effects characterization).
The objective of the exposure characterization is to produce an exposure profile that identifies the receptor (i.e., the exposed ecological entity), describes the paths of stressors from the source(s) to receptors (i.e., the exposure pathway), and evaluates – in terms of intensity, space and time – the stressors-receptors contact, or the co-occurrence of both. Estimation of exposure concentrations may be determined by using measured environmental concentration (MEC), obtained from monitoring studies, or predicted environmental concentration (PEC), obtained from computer simulations. Single exposure data can be used for a deterministic ERA, or to develop the distribution of P/MEC used in the probabilistic approach.
A synthesis of literature data related to exposure characterization as maximum environmental concentration of worldwide marinas, and the 90th percentile used as exposure benchmarks for different biocides were summarized in Table 1.
Literature data used in the exposure characterization of the most common booster biocides showed that, as expected, in open water areas the biocide concentrations were low or non-detected, while in enclosed or semi-enclosed marinas areas, higher biocide concentrations were found.
To complete the analysis phase, it is necessary to produce an accurate effect characterization. To this aim, the relationship between stressor levels and ecological effects, together with the plausibility that effects may occur, or are occurring as a result of exposure to stressors have to be examined [2]. Finally, these results were summarized in a stressor dose-response profile.
Identifying the appropriate ecotoxicological benchmark is another important step into effect characterization. The ecotoxicological benchmark is defined as the concentration of a chemical that is not likely to pose unacceptable adverse risks to the exposed biota [4]. In other words, it is the concentration value for which the ecosystem may be considered protected.
The reference value can be obtained by applying an assessment factor (AF) to ecotoxicological data, or also by the statistical extrapolation method, based on

Stressor	Maximum values (ng l^{-1})	90th percentile (ng l^{-1})	Site investigated	Years	References
Irgarol	4000	-	-	-	[11]
	173	61	Gulf of Napoli, Italy	2005-2006	[9]
	1693	133	European countries	1992-1997	[6]
	1816	745	Chesapeake Bay, U.S.	2003	[14]
	182	64	Southeast Florida, U.S.	1999-2001	[7]
	85	48	Carolinian Province, U.S.	2004	[14]
	2427	-	East Anglia, UK	-	[8]
	186	-	Brittany, France	-	[10]
	410	-	Pearl Harbour Estuary	-	[15]
	620	-	Hong Kong Waters	-	[15]
Diuron	3050	-	Japanese waters	-	[16]
	430	-	Dutch waters	-	[17]
	1380	741	Gulf of Napoli, Italy	2005-2006	[9]
	249	-	East Anglia, UK	-	[8]
	268	-	Brittany, France	-	[10]
Chlorothalonil	1400	-	-	-	[11]
Sea-Nine	3700	-	-	-	[11]
Dichofluanid	5800	-	-	-	[11]
TBT	1801	387	Chesapeake Bay U.S.	1985-1996	[5]

TABLE 1 Maximum Environmental concentration and 90th percentile exposure benchmarks for biocide stressors

sensitivity species distribution (SSD). For example the Predicted Non Effect Concentration (PNEC) can be obtained from measured or extrapolated effects concentration, such as the L/EC50 (lethal/effective median concentration), or NOEC (no-observed effect concentration), divided by an AF that ranges from 10 to 1000.

Stressor	Organisms	Data type - Water type	Toxicity benchmarks (ng l-1) – (method)		References
Ingarol	Plant species	L/EC50 - SW+FW	251	10th Percentile	[7]
	Plant species	L/EC50 - SW+FW	297	10th Percentile	[9]
	Plant species	EC50 - FW	40.9	10th Percentile	[15]
		EC50 - SW	346.9		
		NOEC - SW	43.9		
	Invertebrate species	EC10^{a} - SW	80000	PNEC	[11]
		EC10^{b} – SW	290000		
		EC10^{c} - SW	92000		
	Plant species	EC50 - FW	130	5th Percentile	[10]
		NOEC - FW	5		
		EC50 - SW	110		
		NOEC - SW	4		
		EC50 - SW+FW	108		
		NOEC - SW+FW	3.7		
Diuron	Plant species	L/EC50 - SW+FW	4846	10th Percentile	[9]
	Plant species	EC50 - FW	2000	5th Percentile	[10]
		EC50 - SW	2900		
		NOEC - SW	260		
		EC50 - SW+FW	2300		
		NOEC - FW+SW	55		
Chlorothalonil	Invertebrate species	EC10^{a} - SW	450	PNEC	[11]
		EC10^{b} – SW	430		
		EC10^{c} - SW	1200		
Sea-Nine	Invertebrate species	EC10^{a} - SW	710	PNEC	[11]
		EC10^{b} – SW	590		
		EC10^{c} - SW	5800		
Dichlofluanid		EC10^{a} - SW	5200	PNEC	[11]
		EC10^{b} – SW	28000		
		EC10^{c} - SW	22000		
TBT	Plant+Animal species	L/EC50 - SW	320	10th Percentile	[5]
		L/EC50 – FW	103		
	Invertebrate species	L/EC50 - SW	5		
		L/EC50 – FW	102		

^{a} EC10 – *M. edulis*, ^{b} EC10 – *P. lividus*, ^{c} EC10 – *C. intestinalis*

TABLE 2 Different toxicity benchmarks estimated for freshwater (FW) and saltwater (SW) organisms from different types of toxicity data

Toxicity Benchmarks corresponding to protection different levels as 95% (5th percentile), or 90% (10th percentile) of the species that composes the investigated ecosystem, can be obtained based on the effects concentration distribution derived from point estimates of acute or chronic toxicity values [12].
In Table 2, literature toxicity benchmarks are reported for the most commonly used biocides. Toxicity characterization studies highlight that autotrophic groups of species (i.e., macroalgae, microalgae, or cyanobacteria) are much more sensitive to Irgarol (43.9 ng l^{-1}) than the other biocides. In particular, results show that Irgarol 1051 is generally more toxic to the microalgae than to macroalgae, while the toxic response of Cyanobacteria to irgarol is still largely unknown [15], even if they are important primary producers in marine ecosystems and serve as essential food for many herbivores. By looking at Table 2, we can observe that very high values of sensitivity are presented by invertebrate saltwater species toward the TBT (5 ng l^{-1}).
Finally, based on the PNEC values, the considered biocides may be ranked in the following order from the highest to lowest toxicity: Chlorothalonil, Sea-Nine, dichlofounid and Irgarol.

Risk characterization

Risk characterization is the final phase of ERA. During this step, the information obtained from all of the previous phases are integrated and presented in a comprehensive way for non-specialists to make the communication of key information possible for supporting decision-makers. The information contents should include a description of the nature, the risk magnitude for ecological resources, and also a qualitative and quantitative characterization of uncertainty [2].
Two specific methods are generally used to evaluate the adverse ecological effects of pollutants to organisms and ecosystem: (1) the hazard quotient calculation and (2) the probabilistic approach [2]. Numerical hazard quotient (HQ), or deterministic method is defined as the ratio of the MEC or PEC of the stressor, divided by a toxicant reference value as PNEC. If the resulting value is higher than one, a potential negative effects towards ecological receptors may be expected.

Main advantages of the quotient method are the easiness and velocity of use, and that risk assessors and managers are familiar with its application. In addition it provides an efficient, inexpensive tool for identifying high- or low-risk situations even if it may result useless when quantification of risk is needed. Moreover, in most cases, the quotient method does not explicitly consider the uncertainty. Therefore, in recent literature the use of probabilistic analysis has become preferable [7, 13].
The probabilistic analysis is a quantitative approach based on the comparison between exposure distribution for chemical stressors and a point estimate of effects or a distribution of effects. So, the full range of variability in the exposure and in the effect data is adequately represented.
Figure 3 shows that the likelihood that a certain percentage of species may be adversely affected, is indicated: in case (1), by the proportion of exposure distribution where concentration values exceed the effect levels of concern; instead in case (2), by the degree of overlapping of the curves of effect and exposure distribution (i.e., % of probability exceedence).
Results of the probabilistic ERA on antifouling biocides are reported for different water areas of the world. In European waters, the probability of exceedence of plant 10th percentile for Irgarol 1051 is evaluated in Cote d'Azur (France) with a maximum of 40% of exceedence. As expected, the highest value of exceedence occurred in marinas (24%) more than in the estuaries (1%) and in the coastal type stations (<1%) [6]. Viceversa, the ecological risk from exposure to Irgarol can be considered in the low risk range (0.1%-4%) for various marinas, ports, rivers, bay/embayments, open ocean and channel areas in the United States' surface waters (Chesapeake Bay, southeast Florida and Carolinian Province) [7, 14].
In this area, an exception occurs in Port Annapolis's marina (Chesapeake Bay), where in two different studies significant risk levels for both contaminants, Irgarol and TBT, are found. The analysis results suggest that TBT may pose a risk to aquatic biota with a 12% exceedence [5], whereas the annual probability of exceedence for Irgarol 1051 is extremely high, 99% in 2003 and 82% in 2004, even if additional measures of various

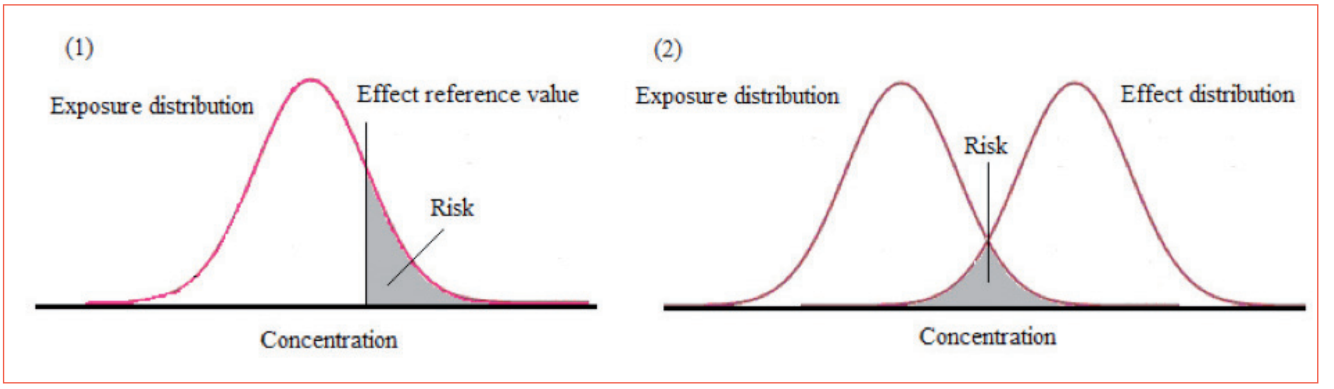

FIGURE 3 Comparison of effect distribution with a single effect value and an effect distribution

functional and structural properties of resident phytoplankton communities in this areas do not support this severe evaluation [14].

The risk posed by Irgarol 1051 and Diuron considered as single contaminants was evaluated in the bay of Vilaine area (Brittany, France) [10], and in harbours and marinas in the Gulf of Napoli (Italy) [9]. In the first study, for the examined area high risk levels were observed for both contaminants, whereas in the second one, the risk levels posed by Irgarol and Diuron were estimated as negligible (<0.001%-5.5%) or low (<0.001%-13%), respectively.

The results obtained from the computation of HQ values allowed to conclude that in 2001 the freshwater of East Anglia (UK) contained Irgarol and Diuron at levels that induce stress and reduce the growth rate in the macrophyte populations [8]. Finally, from the HQ values of more commonly used booster biocides, chlorotahalonil, Sea-Nine 211 and dichlofluanid levels in marinas are found to possibly cause deleterious effects on the marine invertebrate population exposed (1.1<HQ<26), whilst Irgarol 1051 showed no toxic effects on the exposed organisms (HQ<1) [11].

The result of risk characterization can be used by risk managers to decide on a scientific basis whether the risks are acceptable or unacceptable for the environment, and to consider whether further activities are required. Risk managers may decide on risk mitigation measures, and then develop a monitoring plan to determine whether the procedures were efficient or whether ecological recovery is occurring. Managers may also elect to conduct another planned tier or iteration of the risk assessment, if needed, to support a management decision [2].

Main considerations about antifouling biocides risk assessment

Potential ecological risk from exposure to the most common antifouling biocide was observed in many aquatic systems in Europe, the United States and other countries. However, to refine the risks conclusion and to improve the process of estimation of the potential impacts and of the level of protection for the aquatic species exposed, some critical aspects have to be much more investigated. They can be highlighted from the analysis of risk evaluation studies existing in literature.

The first critical aspect is to determine the role of marinas and of their endemic species. In fact these aquatic systems, due to their generally limited water exchange and intense yachting activity, represent the most sensitive areas where the worst case scenarios for biocides maybe applied. Hence, a key issue is to determine if the contaminated marinas systems serve as a nursery or as a refuge area for aquatic organisms and if, among potentially affected organisms, keystone species of high ecological, recreational or commercial value are included.

The second critical aspect is related to the need for determining the status of aquatic resources in marinas, also taking into account that numerous stressors coexist in these environments. Therefore, a greater effort is demanded to improve our understanding on the site-specific ecotoxicological status, which is hardly available.

In spite of these limitations, the probabilistic risk assessment remains an attractive approach that allows to focus on the more significant problems related to chemical contamination of ecological systems, and to provide a basis for comparing, ranking and prioritizing risks.

Last but not least, with the aim of better exploiting economic resources, the risk assessment results can also be used in a cost-benefit analysis, which offers an additional interpretation of the effects of an alternative management option [2].

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