ENVIRONMENTAL OCCURRENCE AND CONCERNS OF ANTIFOULING BIOCIDES

CARISMA Project: an example of integrated approach in the study of the adverse effects posed by antifouling agents in the Southern Adriatic Sea

In the framework of CARISMA project – which aims to assess the quality of the Southern Adriatic Sea area between Italy (Apulia) and Albania, and the impact due to the use of antifouling paints – a preliminary survey in ports and marinas along coastal areas of both countries was conducted. Chemical analyses were complemented with ecotoxicological assays. In addition, in order to assess potential adverse ecological effects posed by selected antifouling agents on non-target marine organisms, Ecological Risk Assessment was applied

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Introduction

Carisma (Characterization and ecological risk analysis of antifouling biocides in the Southern Adriatic Sea), a project funded the by the Italian Ministry of Foreign Affairs, aims to assess the quality of the portion of the Adriatic Sea between Italy (Apulia region) and Albania and, specifically, the impact due to the use of antifouling paints.

Antifouling (AF) paints are routinely used to prevent any living organisms from undesirably adhering to the submerged surfaces of ships, boats and aquatic structures; they act realising effective biocides from the coated surface.

Formulations containing organotin (OT) compounds (e.g., tributyltin, TBT) were the most successful against biofouling but they were banned in 2008, due to their detrimental impact on sea life. Currently, most antifouling paints contain copper or zinc as an active ingredient and a "booster" biocide, such as Irgarol and Diuron, to strengthen the effectiveness of the formulation. The toxicity of AF biocides can also be exerted on non-target species, after their release in water column. Likewise, copper and zinc at high concentrations and in a bioavailable form can be toxic to algae and other water organisms [1]. Therefore, these AF agents need to be monitored in order to assess the possible environmental damage related to their use.

A preliminary survey was carried out on the occurrence of Diuron, Irgarol, OT compounds and some heavy metals, in ports along the Apulia (Italy) and Albania coasts.

The sampling strategy was limited to harbors and marinas as they can represent the worst scenario for the exposure of marine organisms to AF compounds. In fact, such sites are usually characterized by intense boat traffic and by a conformation that does not favour water exchange, so that contaminants tend to accumulate, reaching higher levels than in the open sea.

As far as we know, no monitoring data of organic booster biocides are available for Albanian marine waters whereas previous studies have been carried out in Italy (e. g., Di Landa et al.) [2].

Moreover, to assess the toxicity of biologically available contaminants [3], even those not taken into account or detected by chemical analyses [4], as well as their action as mixtures [5,6], toxicological assays were performed [7,8].

Lastly, a deterministic Ecological Risk Assessment (ERA) has been accomplished for assessing potential adverse ecological effects posed by AF biocides (i.e., TBT, Irgarol, Diuron) to non-target marine organisms in the studied area. Through this ERA approach, high-risk or low-risk situations can be identified by the estimation of the numerical hazard quotient (HQ).

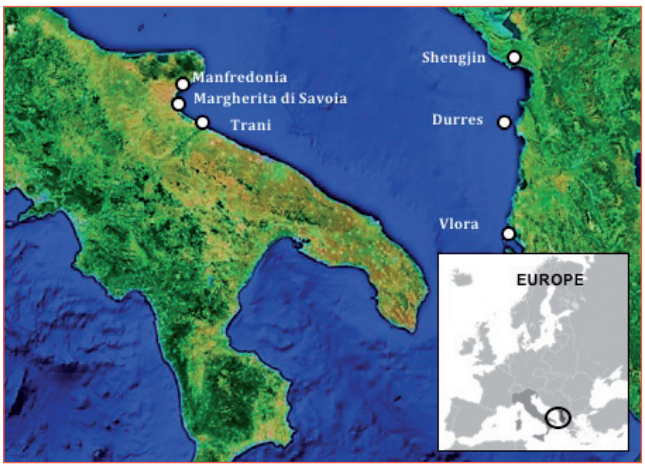

FIGURE 1 Italian and Albanian monitored sites

Study areas

Three ports from medium to large size – Manfredonia, Trani and Margherita of Savoia – were selected north of Apulia (Italy). This region is located right in front of Albania, from which it is separated by the Adriatic sea, with distances ranging between 72 and 290 km. The ports of Trani and Margherita of Savoia mainly host fishing boats and pleasure crafts. The port of Manfredonia, instead, is frequented by ferries, commercial ships, fishing boats, and pleasure crafts.

Albania has a 472 km coastline, but there are few relevant ports, all destined to freight and passenger traffic as well as to mooring of fishing vessels, while recreational boating is still very poorly developed. So low environmental loading is expected for AF agents.

Sampling was carried out in the three main Albanian ports: Durres, Vlora and Shengjin. Durres has currently 78% of maritime trade at the national level and is also a key location for transit networks and passenger ferries. Shengjin houses mainly fishing vessels and Vlora has two distinct ports, one dedicated to goods and passenger traffic, and the other one to fishing boats. Only the latter was sampled in this preliminary campaign.

Figure 1 shows the Italian and Albanian sites selected for monitoring, while in Table 1 the geographic coordinates and the main characteristics of the sampled points are reported.

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Sampled harbors	Abbreviation	Position	Site description	Berths
Italy				
Manfredonia	MN1	41°37'27.94" N - 15° 55' 13.490"E	harbor; marina	365
Manfredonia quay	MN2	41°37'30.73" N –15°54' 53.600"E		
Margherita di Savoia	MDS1	41°23'17.19"N - 16°08'2.770"E	marina; fishery port	200
Margherita di Savoia quay	MDS2	41°23'02.63"N – 16°07'55.190"E		
Trani	TR1	41°16'51.399"N - 16°25'17.234"E	marina; fishery port	550
Trani quay	TR2	41°16'44.966"N - 16°25' 10.346"E		
Trani reference [a]	TRref	41° 17' 30.000"N - 16°26'6.000"E		
Albania				
Shengjin	SH1	41°48'42.900"N - 19°35'17.400"E	fishery port	28 [b]
Shengjin quay	SH2	41°48'49.320"N - 19°35'11.400"E		
Durres	DR1	41°18'22.800"N - 19°27'19.740"E	harbor	98 [b]
Durres quay	DR2	41°18'10.440"N - 19°27'14.100"E		
Vlora	VL1	40°29'4.800"N - 19°25'58.200"E	fishery port	61 [b]
Vlora quay	VL2	40° 29'3.300"N - 19°25' 51.720"E		
Vlora reference [a]	VLref	40°28'25.920"N-19°24'38.640"E		

[a] Blank seawater samples, collected 1 mile offshore; [b] Registered fishery vessels

TABLE 1 Description of sampling sites

Variables	Sampling stations											
	MN1	MN2	MDS1	MDS2	TR1	TR2	SH1	SH2	DR1s	DR2	VL1	VL2
	Seawater											
Organic compounds												
Diuron (ng/L)	12.9	12.4	16.5	583.5	448.7	68.9	1.9	8.4	78.8	93.9	28.8	33.3
Irgarol (ng/L)	10.0	8.9	0.6	14.7	5.1	16.1	< 0.2	0.5	0.8	0.7	8.5	9.3
TBT (ng/L, as cation)	76.0	105.0	12.0	110.0	24.0	22.0	5.0	22.0	24.0	24.0	34.0	44.0
Physical parameters												
T (°C)	28.5		27.3		26.7		26.0		25.4		26.7	
O2 (% saturation)	81		39		65		84		85		108	
Salinity	34.9		36.6		36.6		37.7		38.3		38.1	
pH	7.95		7.81		7.87		7.88		8.04		8.00	
Ecotoxicological assays												
A. salina (% effect)	17	23	13	6	18	16	11	26	10	15	4	4
D. tertiolecta (% effect)	66	76	79	100	75	62	99	87	85	85	88	88
P. lividus (% effect)	34	47	43	76	34	32	27	37	43	40	47	40
V. fischeri (% effect)	- 31.6	2.7	-19.6	-34.4	29.9	-24.8	-39.0	-44.7	-11.0	-25.0	-31.2	-33.0
HQ (Risk Analysis)												
Diuron	0.004	0.004	0.005	0.187	0.144	0.022	0.001	0.003	0.025	0.030	0.009	0.011
Irgarol	0.053	0.047	0.003	0.078	0.027	0.085	0.001a	0.003	0.004	0.003	0.045	0.049
TBT	25.333	35.000	4.000	36.667	8.000	7.333	1.667	7.333	8.000	8.000	11.333	14.667

Variables	Sampling stations											
	MN1	MN2	MDS1	MDS2	TR1	TR2	SH1	SH2	DR1s	DR2	VL1	VL2
Sediments												
OT compounds												
TBT (µg/kg, as cation)	51		5		7		41		71		n.s.	
Metals												
^{52}Cr (mg/kg)	99.3		39.4		71.1		293.4		439.1		n.s.	
^{55}Mn (mg/kg)	705.9		88.6		1044.4		1041.8		537.1		n.s.	
^{63}Cu (mg/kg)	89.7		26.8		54.7		47.7		52.8		n.s.	
^{75}As (mg/kg)	15.6		5.6		21.5		13.4		11.1		n.s.	
^{114}Cd (mg/kg)	< 0.1		< 0.1		< 0.1		< 0.1		< 0.1		n.s.	
^{208}Pb (mg/kg)	49.6		17.1		34.1		11.3		17.2		n.s.	
^{78}Se (mg/kg)	< 0.1		< 0.1		< 0.1		< 0.1		< 0.1		n.s.	
^{118}Sn (mg/kg)	5.9		1.4		4.1		< 0.1		< 0.1		n.s.	
^{66}Zn (mg/kg)	168.6		49.8		126.6		112.2		117.6		n.s.	
^{121}Sb (mg/kg)	0.1		0.3		0.6		< 0.1		< 0.1		n.s.	
^{115}In (mg/kg)	< 0.1		< 0.1		< 0.1		< 0.1		< 0.1		n.s.	
^{98}Mo (mg/kg)	2.1		0.6		2.1		1.1		1.0		n.s.	
^{60}Ni (mg/kg)	45.8		13.9		38.2		205.5		226.8		n.s.	
^{51}V (mg/kg)	128.0		58.5		101.6		94.9		95.5		n.s.	
^{59}Co (mg/kg)	14.9		25.5		16.1		23.0		21.6		n.s.	
Ecotoxicological assays												
A. salina -Eluatriates (% effect)	3		4		3		10		13		n.s.	
A. salina - Pore water (% effect)	3		-		3		16		16		n.s.	
D. tertiolecta - Eluatriates (% effect)	98		98		88		95		95		n.s.	
D. tertiolecta - Pore water (% effect)	88		-		88		85		96		n.s.	
P. lividus - Eluatriates (% effect)	74		75		72		74		75		n.s.	
V. fischeri - Eluatriates (% effect)	36.2		-		-		-		-		n.s.	
V. fischeri - Pore water (% effect)	3.3		-		-		-		-		n.s.	
V. fischeri - Whole sediment (EC 50% mg /mL)	NM[b]		1.4		30.9		3.6		NM[c]		n.s.	
Mussels												
OT compounds												
TBT (µg/kg)	732		854		220		122		n.s.		n.s.	

n.s.: not sampled. NM: Not Measurable. [a] Value derived from a concentration arbitrarily set equal to one half of the detection limit. [b] Hormesis. [c] Highest toxic effect = 90%(200mg/mL)

TABLE 2 Physical, chemical and ecotoxicological data for Italian (Apulia) and Albanian ports

Sampling

Water, sediment and biota samples were collected in Italy and Albania in September 2012, when boating activity is still intense and the contamination from AF paints is expected to be significant.
At each site, water sampling was carried out in the middle of the basin and close to quay, with the aim to evaluate changes in concentration for the investigated chemicals.
Surface sediment samples were collected only at the centre of each harbor, by a stainless steel Van Veen grab sampler.
Where available, sea urchins *(Paracentrotus lividus)* and mussels *(Mytilus galloprovincialis)* were taken too.
For seawater samples, also measurements of temperature (T, °C), conductivity (mS/cm)/salinity, pH and dissolved oxygen (DO, % saturation), were performed in situ, using a portable multi-meter.

Results and discussion

All results are summarized in Table 2.

Occurrence of booster biocides

The two most persistent booster biocides, Diuron and Irgarol, were monitored in seawater. Analyses were performed according to the method described in Di Landa et al. [9].
Concentrations of Irgarol and Diuron in Italy were almost always higher than in Albania.
Diuron was detected in all the surveyed Italian and Albanian harbors and always exhibited higher concentrations than Irgarol, and the Diuron/Irgarol concentration ratios ranged from 1.3 to 87.7 in Apulia and from 3.6 to 145.1 in Albania.
Since Diuron is largely used in agriculture as herbicide as well as for weed control in non-agricultural applications, we suppose that seawater contamination by Diuron is also due to these uses in addition to antifouling paints, in both countries.
Average concentrations for Diuron in ports of Apulia were comparable to those reported by other authors (<7 and 366 ng/L) [10,11], but lower than those measured elsewhere in the world (up to 2160 ng/L) [1].
Albanian levels were similar to those recorded in Seto Inland Sea, Japan (10-62 ng/L) [12] and in California (<2-68 ng/L) [13].
Irgarol was found in all samples from the ports of Apulia while, as regards Albania, it was below the detection limit (< 0.2 ng/L) at Shengjin.
Irgarol concentrations in samples from Apulia were considerably lower than those detected in harbors and marinas worldwide, where levels up to 1300 ng/L have been achieved [2, 14].
Unlike the ports of Apulia, the Albanian ones are characterized by basins with good water circulation, hence both Irgarol and Diuron concentrations were quite similar in samples collected from quayside and centre of basin. The greatest differences in concentrations were registered at MDS. Moreover, it is interesting to note that in the harbor of Trani, contrary to what is usually observed, Diuron levels in the dock (68.9 ng/L) were much lower than those at the centre of the port (448.7 ng/L), probably because of a contamination source nearby.

Occurrence of OT compounds

Despite the total ban of TBT-based paints, TBT was still a commonly encountered contaminant [15] and we found it in all samples collected from both Albanian and Italian coastal areas.
The highest TBT concentrations in water were observed in samples collected near quayside in both a large commercial harbor (MN) and a little marina (MDS).
Monitored sites of Apulia's coastal area resulted more contaminated with TBT (range 12– 110 ng/L as cation) than Albanian sites (range 5 – 44 ng/L as cation). The results are in agreement with recent studies in marine environment [15], where maximum concentrations in water rarely exceed 100 ng/L.
Environmental Quality Standards (Directive on EQS, 2008/105/EC) identified TBT as a priority hazardous substance and set the maximum allowable concentration (MAC-EQS) at 1.5 ng/L as cation. TBT levels found in this work were not negligible compared to its MAC-EQS.
TBT concentrations in sediment samples ranged between 5 and 71, with almost all results higher than the EQS for sediment (5 µg/kg, Legislative Decree 219/2010).

Mussel analyses confirmed that TBT is ubiquitous, with higher pressure on the coast of Apulia.
TBT concentrations found in both sediments and mussels were in agreement with the results reported in literature for countries [15] where the TBT has been banned.

Metals

Concentration levels of As, Cd, Co, Cr, Cu, In, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, and Zn were determined in sediments collected in the ports of Apulia and Albania.
Cd, In and Se were always below the detection limit (0.1 mg/kg).
Very low amounts were found for Sb (≤ 0.6 mg/kg) and Mo (0.6 -2.1 mg/kg).
By comparing the results obtained for Italian ports with the quality standards (QS) reported in the DM 260/2010, a good ecological status was found only for the sediment sample collected at MDS. Conversely, sediments from MN and TR showed higher values than QS for Pb (QS 30 mg/kg dry weight, d.w.), As (QS 12 mg/kg, d.w.), Ni (QS 30 mg/kg, d.w.) and, mostly, for Cr (QS 50 mg/kg d.w.). Very high levels, up to 1044 mg/kg, were measured also for Mn, the main sources of which are from industrial processes, agricultural activities and combustion of coal. The Mn levels detected in this work are in accordance with the results found by other authors in the Adriatic sea [16].
Quality standard limits for Cu and Zn in sediments are not available in the Italian legislation, but the National Oceanic and Atmosphere Administration (NOAA) [17] indicated 34 mg/kg for Cu and 150 mg/kg for Zn as the concentrations below which adverse effects rarely occur. However, the results reported in literature showed that even lower concentrations can be toxic to aquatic organisms [18,19,20].
Levels of Sn, largely used in the past in AF paint based on OT compounds, ranged from 1.4 to 5.9 mg/kg in the Italian harbors, where they may also indicate unknown mineralisation or contamination by industrial activities. As regards sediments from Albanian ports (SH and DR), Sn was always below the detection limit and also Pb amounts were lower than in Apulia. Instead, As, Co, V, Mn, Cu and Zn exhibited concentrations comparable to Italian ports. Finally, Cr and Ni showed significantly higher levels than those detected in the Italian sediment samples. These high amounts may be due to agricultural and industrial activities (metallurgical and chemical plants for Cr, refineries, sewage sludge and phosphate fertilizers for Ni), producing discharges transported into the sea by rivers flowing across the country. In addition, the Albanian territory is characterized by the rich deposits of Cr and Ni, which might contribute to the high levels found for these two elements.

Ecological risk assessment

In the present study the ERA procedure, developed by US-EPA and described in detail in the Guideline for Ecological Risk Assessment [21] and elsewhere in this journal [22], was applied.
The numerical hazard quotients (HQ) were obtained as the ratio of the measured exposure concentrations to the 5th percentile of species sensitivity distributions, used as toxicity benchmarks.
The estimated 5th percentile from literature toxicity data was 189 ng/L, 3126 ng/L and 3 ng/L for Irgarol, Diuron and TBT, respectively.
HQ lower than 1 were obtained for Diuron (0.001-0.187) and Irgarol (0.001-0.085), considered as both single contaminants and a mixture.
For TBT, instead, the individual HQ values were always higher than 1 (1.67-36.67): it means that even if TBT has been banned, deleterious effects on aquatic exposed organisms can still be exerted.

Ecotoxicity

The organisms used for the tests responded to the samples showing a different sensitivity. The D. tertiolecta algae test on seawater samples, always showed the highest effects with peaks registered at MDS2 (EC50 of 3%) for the Italian samples and at VL2 (55%) for the Albanian ones. This peculiar sensitivity, ascribed to the chronic exposure (72 hours, ISO 10253), was also evidenced in other studies with different matrices [23,24]. For all seawater samples, *V. fischeri* showed biostimulation, with the only exception of TR1 (30%); *A. salina* showed an effect lower than 20%, while the *P. lividus* spermiotoxicity test evidenced high toxicity.
The algal test for sediments (aqueous matrices)

always showed the highest effect in Apulia with values near to 100% for MDS and MN elutriates, while, pore waters exerted low effects in all samples. Despite the general view of a higher contaminant concentration in aqueous matrices deriving from sediment compared to seawaters, this never happened for our Albanian and Italian samples. This can be ascribed to a recent contamination that mainly affected algae populations, while presumably in these sediments, contaminants were of different nature [25, 26] or strongly stuck to particles; for example, Irgarol in sediments can be present in association with paint particles and this fact restricts its bioavailability [27].

A. salina always showed an effect lower than 20% for both elutriates and pore waters, while *V. fischeri* evidenced higher toxicity in the elutriates. *P. lividus* test, carried out only on elutriates, always showed effect values over 50%.

Except for MN, for which hormesis was detected, toxic effects (90%) were observable with *V. fisheri* in all whole sediments, while generally they were not found in the corresponding aqueous matrices (elutriates and pore water). This can be linked to the occurrence of some low soluble chemicals, scarcely released during the elutriation treatment. Actually, in sediment toxicity evaluation, since toxicity is evaluated on both dissolved and adsorbed contaminants, the test with whole sediments can be considered more ecologically relevant than the test performed with elutriates or pore waters [28].

Considerations on chemical, ecotoxicological, and risk analyses results

Water chemical analyses showed a different extent of contamination by Irgarol and Diuron between Albania and Apulia, the latter exhibiting higher levels for both biocides, as expected since marine traffic in Albania is much lower.

However, HQ calculated by ERA indicated that, in both countries, the risk posed by Irgarol and Diuron to aquatic organisms was always low, even when their mixture was considered. Conversely, a very high risk was determined for TBT in water. This biocide was detected in all the sampling sites but, differently from Irgarol and Diuron, its levels in water were comparable to those observed in Albania, except in a few cases. In particular, in the waters of MN and in the inner channel of Margherita di Savoia (MDS2), especially high concentrations of TBT (31-45 ng/L) were recorded.

It is worth noting that MDS2 was a hotspot for all the AF biocides investigated. This was due to the particular lay of the harbor, having an inner channel with a high density of moored boats and a very poor water exchange in contrast to the middle of the port, free of berths and connected to the open sea (MDS1).

In agreement with chemical results, the growth inhibition test with seawater samples performed on the marine algae *D. tertiolecta* showed the highest effect (100%) right at MDS2 as well as the spermiotoxicity test with sea urchin *P. lividus,* which showed an effect about as twice (76%) as that observed in all the other sampling stations (32-47%).

In contrast to the results of chemical analyses, an effect near to 100% was determined in the algal test with elutriates from MDS1, a site exhibiting a low degree of contamination in sediments, as regards TBT and selected heavy metals, and also in water, as regards Irgarol, Diuron and TBT.

These results suggest the presence of contaminants not taken into account by chemical analyses.

Again, differently from chemical results, the algal test highlighted slightly higher toxic effects for Albanian seawaters (average 86.8%) than for Italian ones (average 76.3%). In particular it should be noted that, despite the less contaminated waters from the monitored biocides, SH exhibited a very high toxic effect for algae (99%) and the major response from bacteria in bioluminescence tests (- 44.7%).

Spatial distribution assessment of Irgarol, Diuron and TBT within each port evidenced different concentrations for seawater samples collected from the quay and from the centre of the basin in Italy, except at Manfredonia, while in Albania the spatial variability was rarely observed.

In agreement with chemical findings, ecotoxicological bioassays, carried out on seawater samples, evidenced

higher toxic effects at the quay in the ports of Apulia, whereas in Albania similar values were obtained.
The same distribution was observed for the monitored AF biocides at MDS, with higher levels at the dock. However, the pattern distribution was not always similar for the investigated AF agents, thus suggesting that the concentration changes could be due to the proximity of pollution sources in addition to the dynamics of the currents. For example, at MN both Irgarol and Diuron exhibited comparable levels in the two sampling points, while TBT showed a higher concentration in the dock. At Trani, the opposite was true: Diuron and Irgarol, to a much lesser extent, showed a spatial variability, while TBT did not. In particular, for Diuron, a much higher level was found in the centre of the harbor (TR1), while in all the other ports it was always observed the opposite. Similarly, the ecotoxicological test showed that the water sample from TR1 was more toxic than the one from the dock. Furthermore, TR1 seawater was the only one eliciting 30% toxic effect for *V. fischeri,* which usually exhibited biostimulation.
At Shengjin, water concentrations of Diuron and TBT were higher in the dock while no variation in Irgarol concentrations was observed. Conversely, higher toxic effects have been found at the centre of the port (SH1), once again suggesting the presence of not analysed toxicants.
The high concentrations of Ni and Cr found in all analyzed sediments, together with the high levels frequently determined for TBT, could contribute to the high toxic effect (> 70%) obtained for all elutriates with the *P. lividus* test, and to the even higher toxic effect (> 90%) recorded for all samples (whole sediment) with the *Vibrio fischeri* test.
Sediments should always be taken into account when assessing the quality of an aquatic ecosystem to determine the most polluted areas which demand treatment and remediation. In fact, contamination of sediments in a water body not only results in water quality deterioration but also involves a continuous and long-term risk for ecosystems and human health due to the diffusion and re-suspension in pore water and in the water column of contaminants, and to the transfer of pollutants at different trophic levels through the food chain.

Conclusions

This work gives an example of how the combined use of diverse and complementary methodologies enables a deep and robust interpretation of data, allowing to capture different aspects of the system.
In the coastal areas of the Southern Adriatic Sea, we evaluated the occurrence of Irgarol, Diuron, TBT and some heavy metals, their effects by ecotoxicological assays, and their associated risk by ERA. The chemical characterization showed that coastal waters in Albania were less polluted than in Apulia with regard to Irgarol and Diuron. In contrast, the algal test highlighted slightly higher toxic effects in Albania than in Italy. This result suggests the presence of contaminants not taken into account by chemical analyses. With reference to sediments, instead, two hot spots were identified by the algal test in Italy, at MDS and MN.
Surprisingly, TBT was detected in all the sampling sites and in all samples (water, sediments and mussels), even at concentrations by far higher than the fixed quality standard limits, although it has been banned for years. Moreover, ERA indicated a high likelihood of adverse effects for TBT, while for Irgarol and Diuron no risk was found.
Therefore there is an urgent need for further investigation on the spread of TBT in the marine environment and the frequency of exceedence of TBT quality standards (MAC-EQS), in order to both evaluate the associated risk and to understand the possible sources of this dangerous biocide.

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