European Maritime Safety Agency

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ADDING CYBUTRYNE TO THE GUIDELINES SUPPORTING THE IMO'S AFS CONVENTION

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REPORT

Study to support the amendment of the "Guidelines for brief sampling of anti-fouling systems on ships" to include controls on Cybutryne

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Executive Summary

This study is to support the amendment of the "Guidelines for brief sampling of anti-fouling systems on ships" to include controls on Cybutryne. It covers several aspects of the existing Guidelines (that only cover organotin compounds), that need to be assessed and revised in order for the Guidelines to also be used for anti-fouling systems containing cybutryne. Concretely, the objectives of this study are to:

1. *Propose the highest concentration (**threshold**) of cybutryne that could be present in an antifouling system (AFS) for the coating system to remain in compliance with the AFS Convention.*

Presently, the "Guidelines for brief sampling of anti-fouling systems on ships" only cover organotin compounds. The threshold and sampling tolerance values are defined in the existing Guidelines as 2 500 mg + 500 mg (Sn) / kg dry paint. This value is due to the "chemical catalyst" function of organotin compounds. This rational, to allow a threshold value for non-biocidal use is not applicable for cybutryne. Cybutryne is present in anti-fouling systems only with the purpose of working as a biocide. For defining a threshold for cybutryne in an anti-fouling system, this study focussed on the partially depleted antifouling system when it reaches the end of its service life (as new application and repaint are both banned), to determine the threshold value for cybutryne concentration in anti-fouling systems that will not trigger a negative impact to the aquatic environment.

The ratio between the Predicted Environment Concentration (PEC) and the Predicted No Effect Concentration (PNEC) is used to evaluate the impact a certain chemical pose on the environment. If the ratio is equal or less than one, then it is expected that there is no negative impact to the environment. The IMO document[1], defines the **PNEC** for cybutryne in the aquatic environment as **2ng/L**. This implies that any concentration of cybutryne above 2 ng/L in water would have a negative effect on algae species. Consequently, it would have a negative impact on the marine environment as they provide the food base for most marine food chains.

Using the **MAMPEC** (Marine antifoulant model to predict environmental concentrations), a software used for predicting the leaching of biocides from anti-fouling paints, it is possible to estimate the cybutryne concentrations (PEC) in water. The "Surface area" parameter of the model can be used to represent the emissions of cybutryne at the end of the service life of the hull. Considering also the different receiving marine environments, a compliance value of 1000 mg/kg of cybutryne per kg of dry paint is defined as the threshold value for cybutryne. Below this value, emissions of cybutryne from the ship hull to the marine environment are expected not to create a negative impact on the environment.

2. *Amend the present IMO "Guidelines for Sampling[2]" to include sampling and analysis methods suited for antifouling paint containing cybutryne.*

In the organotin case, the definition of compliance is based on a two-step analytical procedure. The samples are taken from several sampling points along the hull. The number of sample points and specimens vary according to the method. Step 1 is used to determine the total tin (Sn), this is a fast method that can be done at port. If step 1 produces positive results, then Step 2 analysis is done in the laboratory using GC/MS analytical technique. The sampling strategy and analysis methodologies used for organotin were tested to check if these could be used for cybutryne.

[1] PPR6/INF.7 2018 *Information presenting scientific evidence for the adverse effects of cybutryne to the environment*.

[2] Guidelines for Brief Sampling of Anti-Fouling Systems on Ships (Resolution MEPC.104(49)) https://www.register-iri.com/wp-content/uploads/MEPC_Resolution_10449.pdf

Unfortunately, no fast test method for Step 1 was found to be reliable for determining the cybutryne concentration in the anti-fouling paint. Therefore, for cybutryne, determination the sample must be sent to the laboratory for GC/MS analysis. In Appendix 2 to this report, the exact procedure is described in detail. In case of investigating the presence of both organotin compounds and cybutryne, some simplifications can be made by skipping Step 1 for organotin and going directly to Step 2. One single preparation procedure is therefore possible for analysis of both chemicals to be detected in one run.

3. *Find a tolerance range for the threshold value.*

The tolerance range connected with the measurement uncertainty (U) at the 95% confidence level was determined specifically for the new method. This uncertainty is a result of all steps in the analytical chain such as sampling, sample preparation and analysis. The experimentally determined measurement uncertainty was found to be 25%. For the proposed method, it is not considered necessary to have a lower uncertainty.

Tolerance value = 250 mg cybutryne / kg dry paint

4. *Provide evidence on the effectiveness of sealant coatings to prevent cybutryne from being released into the marine environment from antifouling systems.*

In the case of organotin compounds, Annex 1 of the AFS convention, includes the possibility to cover the anti-fouling paint with a "sealant" coating on the non-compliant ship hull. The sealant forms a barrier to prevent organotin compounds leaching. This study tested if a similar strategy could also work for cybutryne. The standard method **ISO 15181 (**equivalent to **ASTM D 6903)** was used to measure the release rate of cybutryne into artificial seawater. Triplicate samples with and without (a total of 6 samples) sealant coating, were tested and the results for the release rate of cybutryne were compared. The efficacy of the sealant ("Mistral Fondo" from Boero S.p.A.) to reduce the cybutryne release was measured to be 96%. The results show feasibility of using a sealant as an alternative to remediation for non-complying hulls.

These results support the future work to revise the "Guidelines for brief sampling of anti-fouling systems on ships" to include controls on Cybutryne. In addition, the use of sealants to prevent cybutryne from being released into the marine environment from antifouling systems as foreseen in Annex 1 of the AFS Convention was tested and the results show that it is effective.

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Introduction and background on the rationale for this study:

The International Convention on the Control of Harmful Anti-fouling Systems on Ships, which was adopted on 5 October 2001, prohibits the use of harmful organotin compounds in anti-fouling paints used on ships and will establish a mechanism to prevent the potential future use of other harmful substances in anti-fouling systems. […] At its seventy-first session in July 2017, MEPC approved a new output to amend Annex 1 to the AFS Convention to include controls on cybutryne. While work on this matter is ongoing in the Sub-Committee on Pollution Prevention and Response (PPR), the scientific data presented so far indicates that cybutryne causes significant adverse effects to the environment, especially to aquatic ecosystems [text extracted from IMO website Anti-fouling systems (imo.org)]

This study is to support the amendment of the "Guidelines for brief sampling of anti-fouling systems on ships" to include controls on Cybutryne. It covers several aspects of the existing Guidelines (that only cover organotin compounds), that need to be assessed and revised in order for the Guidelines to also be used for anti-fouling systems containing cybutryne.

Aspects such as the threshold of, and the sampling tolerance for, cybutryne in paint. The threshold is the maximum allowed concentration of cybutryne in antifouling systems, which must be assessed to determine if the anti-fouling system is compliant with the AFS Convention. In addition, this study defines and describes the analysis needed for cybutryne determination, the techniques and protocols, and their consequent tolerance values, to be applied on samples taken from the hulls for compliance verification.

In addition to addressing the threshold, the sampling tolerance, the analytical techniques used, and the protocols for cybutryne, this study also includes an efficiency test for a so called "sealant" formulation to be applied on non-compliant ship hulls. The rationale of this test is to investigate the efficiency of such a temporary remediation method already adopted in the organotin compound's cases and to check it for the newly introduced controls on cybutryne.

Annex 1of the Convention states that by an effective date of 1 January 2003, all ships shall not apply or re-apply organotin compounds which act as biocides in anti-fouling systems, and by 1 January 2008 (effective date), ships either: shall not bear such compounds on their hulls or external parts or surfaces; or shall bear a coating that forms a barrier to such compounds leaching from the underlying non-compliant anti-fouling systems. [extracted from the IMO website Anti-fouling systems (imo.org)]

1. Cybutryne threshold

Previous banned biocides:

For organotin compounds such as tributyltin (TBT) the threshold concentration in paints for compliance with the Anti-Fouling System (AFS) Convention is set to 2'500 mg Sn/kg dry paint plus a relative detection tolerance (500 mg Sn/g dry paint) to account for uncertainties in sampling and analytical methods. This is reported in the "Guidelines for Brief Sampling of Anti-Fouling Systems on Ships" (Resolution MEPC.104(49))[1]. The rationale for the threshold value being set at 2'500 mg/kg for organotin compounds is based on the evidence that these compounds can be found in some paint systems acting as chemical catalysts (such as mono and disubstituted organotin compounds). The TBT compounds in these products at this concentration are referred to as "*not acting as biocides*".

Cybutryne in paints:

Two important aspects need to be highlighted concerning cybutryne and the "Guidelines for Brief Sampling of Anti-Fouling Systems on Ships" (Resolution MEPC.104(49))[2]:

- The cybutryne compound is not reported to have any other role in paint formulations than its biocide role. Thus, no concentration level of cybutryne detected in paint can be claimed to be there for other purposes. This is not the case for Tri-butyl Tin, where in addition to a biocide role the chemical can also be present as a chemical catalyst.
- In general, the biocide based antifouling systems used in the last decades are either "Soluble Matrix" or "Self-Polishing Coatings" (SPC) (see details in paragraph (1.1) and in Figure1.). These systems are designed to reach and maintain a target leaching rate (amount of biocide emitted from the paint to the environment per area (cm^2) and time (day)) during the paint entire service life. This is achieved with a soluble matrix or an erodible matrix in seawater, making possible for the levels of biocide and paint to be diminished in a synced manner, therefore the biocide concentration in the paint layer during entire service life is kept at almost constant level. The SPC systems being better in keeping the concentration in paint layer stable until the end of life compared to "Soluble Matrix" Systems.

These two preliminary considerations have high impact on the rational for setting and estimating the threshold concentration for cybutryne that defines compliance with the AFS Convention. The rationale for defining the maximum allowed concentration for cybutryne in an old AFS in order for it to still comply with Annex 1 of the Convention, cannot be based on the present argument of "*not acting as biocide*" as used for TBT. Cybutryne has in fact, no other use in a marine anti fouling paint than acting as a biocide.

In this study, the proposed rationale for the cybutryne threshold values will thus be the maximum concentration of cybutryne present in dry paint layers not causing a negative impact on the surrounding aquatic environment. Thus, the Predicted Environment Concentration (PEC) is estimated and compared with the Predicted No Effect Concentration (PNEC).

Given the biocide concentration in the AFS is kept almost constant in both "Soluble Matrix" and "SPC" AF systems, the real parameter to follow for predicting the leaching rate and consequential PEC is the percentage of painted area still present on the hull and the correlation between this area and the biocide concentration (see paragraph 1.2). This will become a key parameter in the estimation of PECs and thus the threshold value.

Additionally, it is well-known that antifouling systems (both soluble matrix and SPC) do not erode in a homogeneous way on the hull. It will depend on the geometry of the hull and different exposure to seawater and induced shear forces. This will be discussed in paragraph 1.2 of this chapter.

As described later in this chapter, it has been possible to correlate hull paint coverage (%) to the cybutryne concentration in paint and thus, to cybutryne predicted environment concentration (PEC). This correlation has been used to find the threshold value.

Concentrations and relative PECs of cybutryne have been estimated for several different emission and environment scenarios (See paragraph 1.8).

Threshold concentration and PEC/PNEC ratio

The predicted environmental concentration (PEC) is an indication of the expected concentration of a compound in the environment, considering the amount initially present, its distribution, and the plausible modes and rates of emission to environment together with environmental degradation and removal, either forced or natural.

The predicted no effect concentration (PNEC) is the concentration of a chemical which marks the limit at which below no adverse effects of exposure in an ecosystem are measured. PNEC values are intended to be conservative and predict the concentration at which a chemical will likely have no toxic effect.

The predicted no effect concentration (PNEC) for cybutryne in the aquatic environment is, according to a risk assessment methodology, the value that any concentration above that in water, would have a negative effect on algae species and consequently a potential effect on the ecosystem, as algae are the pillar for the ecosystem structure and function as they provide the food base for most marine food chains.

The threshold to define compliance with the guidelines (i.e., the maximum allowed concentration of cybutryne in antifouling paints) will lead to a certain predicted concentration of cybutryne (PEC) in the environment that must be lower than the predicted no effect concentration (PNEC) for cybutryne.

Threshold = PEC/PNEC ≤ 1

The PNEC for cybutryne in seawater is reported in the IMO document (*PPR6 /INF7 - 10 December 2018)*[1]. The document established the PNEC of cybutryne in the marine environment to 2ng/L. The next paragraphs focus on how the PECs for cybutryne in different situations and scenarios have been estimated.

1.1. Cybutryne concentration in antifouling coatings

Table 1 and 2 below summarize a Swedish report from 2007 (Woldegiorgis et al., 2007)[3] which contains data on antifouling products approved by the Swedish Chemicals Agency containing cybutryne (commercial name Irgarol 1051).

Antifouling products, for pleasure boats, containing cybutryne approved (in 2006) in Sweden.

Product Cat.3 = for pleasure boats <12m length	**cybutryne (% w/w)**
Cruiser	2,41
Cruiser White	1,89
Micron WQ	2,2
Micron WQ White	1,97
Mille White SE	3,5
Trilux	2,18
Trilux Prop-o-Drev	0,87
Trilux White	1,87
VC17New Technology	0,6
Average	***1,94***

Table 1 adapted from (Woldegiorgis et al., 2007)[3.]

Antifouling products for professional ships, containing cybutryne approved (in 2006) in Sweden.

Product (Cat. 1&2) for professional ships >12m length	**cybutryne (% w/w)**
Antifouling Sargasso AL KNM	2
Hempel's Antifouling Combic ALU 71800	1,1
Interspeed Extra BWO 500 Red	2
Interspeed Premium Antifouling Black	2,3
Average	***1,85***

Table 2 adapted from (Woldegiorgis et al., 2007)[3.]

From Table 1 and 2, it is possible to calculate an average concentration of cybutryne for "cat. 2" (1,8% (w/w)) and "cat. 3" (1,94% (w/w)) products. These values were used as the starting point for defining the average concentration of a typical cybutryne paint present on the market. Based on the reported

[3] "*Results from the Swedish Screening Programme 2006*"
https://www.ivl.se/download/18.34244ba71728fcb3f3f758/1591704449797/B1764.pdf

concentration, a conservative 2% (w/w) was used as a starting concentration of cybutryne for globally available products i.e., 20'000 mg/kg of cybutryne per kg of dry paint.

It is not only the type and concentration of biocide(s) that will determine the efficacy and toxicity of an AF paint, but also the way the active substance(s) is incorporated into the product and consequently released during use. The paint "binder" is the component that holds the paint matrix together and is often considered to be the most important ingredient of the paint. Along with the biocide's inherent solubility limitations, it is the properties of the binder which will control the manner and speed at which the biocide is released to the water.

There are 3-main biocidal Antifouling System types (the A "insoluble matrix" one is not used anymore). These systems differ in how they react with seawater and create "leached layers". Leaching layer is when water migrates into the paint film, the matrix reacts with sea water and becomes more soluble, and the biocide is leached out. The surface then dissolves, and film thickness is lost. The differences in the Antifouling System types comes thus from the material used and reflects how well biocide leaching and erosion are synced. This will influence the reliability and service life of the same thickness of different antifouling technologies. The materials used in SPC are more expensive than the materials used for an insoluble and soluble matrix. Consequentially the different technologies are often used depending on the intended use of the ship, such as pleasure boats, professional boats, ships etc.

- Insoluble matrix paints, also known as contact leaching paints or hard paints, contains a binder which does not erode when immersed in seawater (fig. 1A). With time, the soluble biocidal pigments leach from the surface of the paint, leaving behind a depleted, porous matrix in this area (high leached layer). As the leached layer increases in thickness, the diffusion of biocides from the paint film will decrease over time diminishing the antifouling efficacy of the paint. These systems are not reported to be used with cybutryne.
- Soluble matrix paints, also known as erodible or ablative paints, have a seawater soluble colophony-based binder (a natural resin, such as rosin or abietic acid). The paint erosion and subsequent release of biocide is thus controlled by the dissolution of both the binder and the biocidal pigments (fig. 1B).
- Self-polishing copolymer (SPC) are based on acrylic polymers which undergo hydrolysis or ion exchange. The consequent continuous surface renewal of the AFS yields a smooth paint surface with a theoretically steady release of biocides over the service life of the paint (fig. 1C).

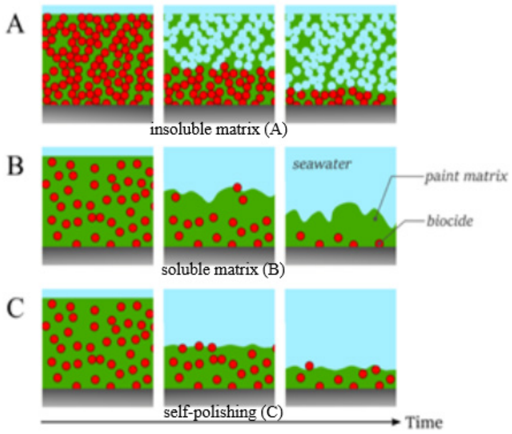

Figure 1 Schematics representation of different paint types and their erosion and release of biocides over time.[4]

1.2. Cybutryne paint systems and correlation biocide concentration and painted area

The products found in Table 1 and 2 are still present in the Swedish Chemical Directorate (KemI) database. In the product description page, the main ingredients are described. For all the products the ingredients list includes typical ingredients found in Soluble Matrix or SPC paint systems (see fig.1B and 1C). Private communication with paint industry has confirmed that cybutryne is used in both Soluble Matrix and SPC type of coatings.

(Figure 1B) In a soluble matrix paint system, water migrates into the paint film and dissolved rosin and biocides leach into the sea. Insoluble components remain present in the matrix and are left in the leached layer. The dissolution gradually slows down over time due to the accumulation of the insoluble component in leached layer. The maximum effective life of a soluble matrix systems is typically 36 months. Soluble matrix systems are not as effective as SPC systems and are suitable for use in low fouling areas or for ships with short drydocking intervals.

(Figure 1C) Self polishing copolymers (SPCs) (see figure 1C) undergo a reaction (hydrolysis) with sea water to make it soluble. This results in thinner "leached layers" which provides an excellent control of biocide leaching. These reactions continue with the film getting thinner through polishing. The coating stops working when it has all polished away. Predictable polishing rates enable specifications to be tailored to the ship type and operational profile, giving capability for long drydocking intervals of up to 60 months with inherent self-smoothing.

Both systems keep (with different performance) the cybutryne concentration in paint almost constant until end of service life. In the SPC case the end of service life is also the point when paint is polished away. In Soluble Matrix paints end of life can happen when a very thin leached layer is still on the hull.

In the SPC case in theory there would be no need for a threshold value because the cybutryne concentration will drop from start concentration (i.e., 2%(w/w)) to null as the paint layers will be totally polished away. In practice there are several aspects making necessary the analysis of the paint layer after service life. It is in fact evident from published literature that erosion on some parts of the hull occurs more slowly than other areas, hence not all the active substance would be released at the end of the service life of both SPC and even more realistically Soluble Matrix systems. A correlation between percent of painted area and biocide concentration left in paint has been discussed in an OECD

[4] (Maria Lagerström 2019)" Occurrence and environmental risk assessment of antifouling paint biocides from leisure boats" http://su.diva-portal.org/smash/record.jsf?pid=diva2%3A1298662&dswid=3106

document 2006[5]. Thus, even if the area painted could be estimated on some occasion by visual inspection of the hull, the definition of a threshold concentration will make possible to check for compliance, because will account for both SPC and soluble matrix systems and for the visible and the non-visible part of the hull, like in niche or less exposed areas of the hull, where paint could be still present.

The assumption of the presence of painted areas after service life for at least 10% of the hull, and thus 10% of initial biocide left, is reflected in the equation used for the mathematical mass balance calculation "***ISO 10890:2010***"[6] of the leaching rate during service life. In the method is assumed the presence of at least 10% of the biocide left in the paint at end of service life. This mathematical method and other methods for estimating the leaching will be discussed in detail in paragraph (1.7).

1.3. How to estimate the Predicted Environment Concentration (PEC) by MAMPEC

The PEC for a marine antifoulant can be calculated using modelling software and the most used for this purpose is the freeware Marine Antifoulant Model to Predict Environmental Concentrations (MAMPEC)[7]. This model is recognized and used by regulatory authorities in EU, USA, and other OECD countries for antifouling substances, and by the IMO for ballast water discharges. MAMPEC is an integrated 2D hydrodynamic and chemical fate model, based on the Delft3D-WAQ and Silthar mode and was originally developed to predict environmental concentrations (PECs) of antifoulants in harbours, rivers, estuaries, and open water. The MAMPEC model has also been adapted and is being used for exposure assessment in freshwater systems and to assess the impact of discharges of chemicals in ballast water. It is an easy-to-use and freely available model which was developed by Deltares and the Institute for Environmental Studies with continuing support of the European Council of the Paint, Printing Ink, and Artist's Colours Industry (CEPE).

MAMPEC needs three different sets of inputs from the user to calculate the PEC for a material or biocide leaching from antifouling pain:

-The *environment* receiving the pollutant

-The *compound*/*pollutant* and the source of

-The *emissions scenarios* (number and class of boats/ships present; number of boats moving/ at berth per day/ area of the hull painted in m^2; application factor etc)

"Environment module"

[5] OECD 2006 "*Harmonisation of leaching rate determination for antifouling products under the Biocidal Products Directive*" https://echa.europa.eu/documents/10162/16908203/pt21_leaching_workshop_en.pdf
[6]"ISO 10890:2010" Modelling of biocide release rate from antifouling paints by mass-balance calculation"
[7] MAMPEC – available here: https://www.deltares.nl/en/software/mampec/

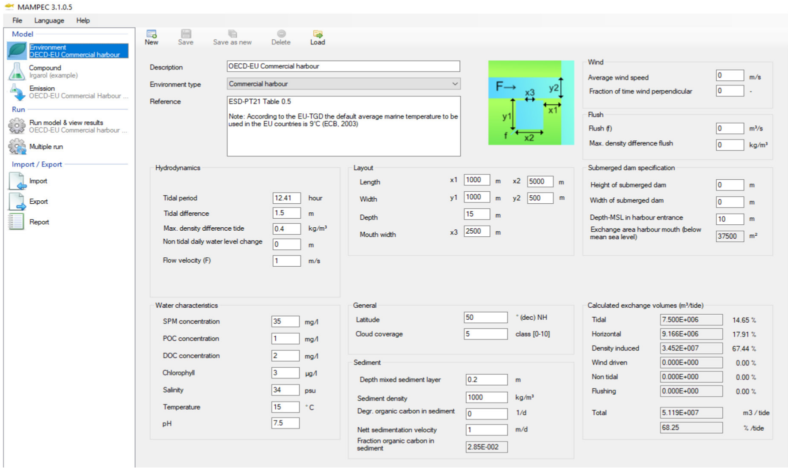

Figure 2 MAMPEC 3.1.0.5 Environment module

Different environments (marina, harbour etc) can be found in the MAMPEC database and can be chosen (see figure 2). For an antifouling paint system to be used on pleasure boats usually the marina scenario (i.e., EU OECD Marina or similar) is a suitable environment. For an antifouling paint system used on commercial ships the commercial harbour scenario (i.e., EU OECD Commercial Harbour or similar) is a more appropriate choice. These modules are used to define the environments where the emission will take place (e.g., amount of water exchanged, temperature, etc.). The total emissions of biocide will be used by the algorithm to calculate the PEC. The term total emission will be defined later in the "emission module" part.

"Compound Module"

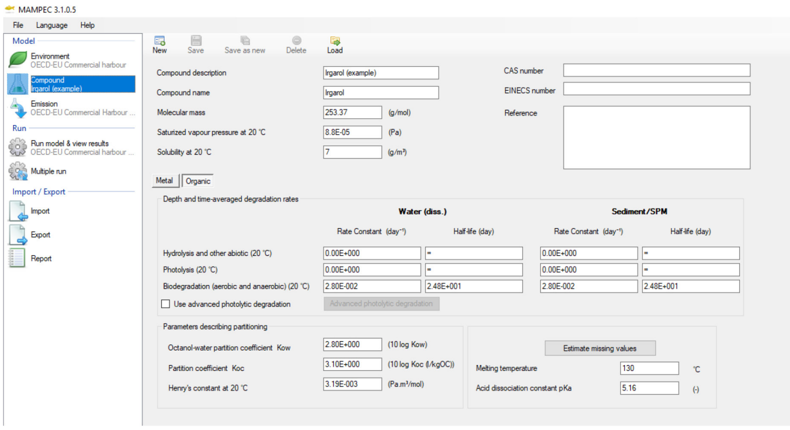

Figure 3 MAMPEC 3.1.0.5 Compound module

The compound section of MAMPEC contains the specific properties of the biocide, allowing accurate modelling of the biocide fate upon release into the environment and its potential environmental accumulation levels once released. For many biocides, including cybutryne (commercial name Irgarol 1051®), these properties are already available in the MAMPEC database. (Figure 3).

"Emission Module"

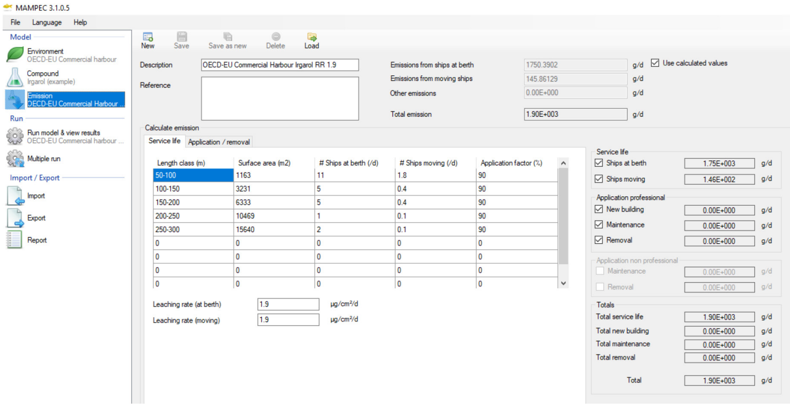

Figure 4 MAMPEC 3.1.0.5 Emission module

The emission section of MAMPEC (figure 4) sets the boundaries of the scenario being evaluated and defines where and how the emission from hull and other release sources of the compound are contributing to the total emission.

The submerged hull surface area (m^2) for each vessel class and the number of ships moving and/or at berth are needed to define the scenario. These values are entered into the model, together with the Application Factor (%) which defines the percentage of the ships painted with the product evaluated over the total number of ships present in the emission scenario. The leaching rate of the biocide also needs to be defined and added into the model. Leaching rates ($\mu g/cm^2/day$) are the mass of biocide released per square centimetre of painted area.

The difference between leaching rate and emission (ship at berth; moving ships; other emission) is that the leaching is a quantity of biocide emitted by painted area per day, and it is a value characteristic of the paint system under evaluation (mass/area/time). The emissions from ships are instead depending on the different inputs present in this module, such as the number of ships at berth or moving, the hull's area of the different ship class. So, the emission is represented by mass/day and is typical of the scenario under evaluation and not only the paint.

Regarding the other emissions, in the MAMPEC it is possible to account for other sources of biocide emission such as maintenance and repair. For example, biocide emission to the environment during paint application can arise from overspray i.e., paint droplets not reaching the target and instead being dispersed by wind in the surrounding environment. This can occur especially if no containment systems are in place during spray painting in open and windy conditions. Similar emissions can arise during different removal operations. All these sources of pollution can be accounted for in MAMPEC. The sum of all these emissions sources is called "Total Emission". In this study, as the cybutryne containing paints are no longer be present on the market (in the EU) or cannot be used globally after the ban, the "other emissions" part of this module has been left empty. In fact, with no cybutryne paint present on the market, both repainting and/or maintenance done with cybutryne paint are not to be expected.

Note: The contribution of cybutryne PEC coming from removal activities of non-complying paint layers is beyond the scope of this study. In chapter 3, an alternative to removal of non-complying cybutryne paint is explored and an efficacy test of sealant paints on cybutryne are presented.

1.4. PNEC for cybutryne

In the IMO document (*PPR6 /INF7 - 10 December 2018)*[1], the PNEC for cybutryne in the water column is reported to be **2 ng/L**. This implies that any concentration of cybutryne in the water column above 2 ng/L would exert a negative effect on algal species, and consequently also potential trophic effects on the receiving ecosystem. This is because algae are the pillar of the marine ecosystem structure and function by providing the foundation for most marine food chains.

1.5. "Leaching rate" for cybutryne containing paint.

The typical leaching rate for cybutryne containing paints during the service life of the AFS (from freshly painted until the end of the claimed service life) has been reported in the IMO document[1] to be **1,9 µg/cm²/d**. It is specified that this can be used as a conservative figure both for ships at berth and those that are moving. This value has been used in this study as the standard leaching rate in MAMPEC emission module.

1.6. PEC for paints in "service-life"

For any antifouling paint present on the market, the supplier needs to specify a proven service life related to the thickness of the dry paint film. This is the duration the paint works in service. After this time, the coating will lose its antifouling effect mainly due to erosion of the layer and/or depletion of biocide in paint.

The PEC for AFS containing cybutryne has been calculated using the MAMPEC 3.1.0.5 model by employing the compound "Irgarol" (market name of cybutryne). The following emission scenarios and environments has been respectively tested: OECD-EU Shipping Lane; OECD-EU Commercial Harbour; and two different marinas, OECD-EU Marina (500 boats) and OECD-EU Marina (276 boats). The latter is a modified version of the OECD-EU marina as also reported in a MAMPEC note: "*The number of boats in the ESD marina scenario, Table 0.6, should be reduced to 276 to reflect a more realistic boat density of 1.38 boats / 100 m^2" and as discussed in (TM IV 07 in Arona, October 2007)*[8]

The complete results for all the concentrations the emission scenarios and application factors are attached in Appendix 1 to this document. The "PECs" for freshly painted AF systems containing 2% cybutryne (w/w) (i.e., 20'000mg cybutryne/Kg dry paint) are presented in (Table 3) assuming 90% of all ships present in the selected emission scenario are painted with AFS containing cybutryne.

Emission Scenario	**Average Concentration cybutryne (ng/L)**
OECD-EU Marina (500 boats)	331
OECD-EU Marina (276 boats)	183
OECD Commercial Harbour	34,8
OECD-EU Shipping Lane	0,0178

Table 3 PECs for 2%(w/w) cybutryne paints as "average concentration of cybutryne in water" for the different emission scenarios calculated by MAMPEC[*]

[8] Final Minutes of the Biocides Technical Meeting (TM IV 07 in Arona, October 2007), https://echa.europa.eu/documents/10162/21863589/biocides_tecnical_meeting_4_2007_en.pdf

The values in table 3, are based on the MAMPEC model using a leaching rate of 1,9 µg/ cm^2/day (as reported in the IMO - PPR6 /INF7 - 10 December 2018)[1].

As shown in Table 3, with the exception of the "*OECD-EU Shipping Lane,* the cybutryne PECs for the 2% (w/w) paints are all above the **PNEC of 2 ng/L**. This illustrates that the predicted environment concentrations in water are higher than the PNEC. This was expected as reported in the IMO document PPR6 /INF7 - 10 December 2018[1].

1.7. PECs for paint after "service-life"

As discussed previously, the "leaching rate" is a key input parameter needed to calculate PEC with MAMPEC. The value of **1,9 µg/cm^2/day** reported in the IMO document[1] is valid during the service-life of a coating. The cybutryne concentration in paint and the leaching rate will not change much during the service-life, while a reduction of both is expected after the service life. Once the paint layer ends its service life, the leaching rate will be reduced to <1,9 µg/cm^2/day and will not be sufficient for maintaining the efficacy of the antifouling.

There are several available methods to estimate the leaching rate of biocides from antifouling paints and two methods are mentioned by OECD[9]:

-The Mass Balance Model described in **ISO 10890:2010**[6]

-The "Rotating Cylinder Method" (**ISO 15181** or **ASTM D 6903**)[10]

The Mass Balance Model **ISO 10890:2010** is very useful for regulatory reasons such as aquatic hazard and risk assessment for the antifouling biocide products. The method requires paint specific inputs normally obtained from the paint supplier, but unfortunately one of the key information needed is the **service life**. The method calculates the mean leaching rate for the product by dividing the amount of total biocide in 1cm^2 of paint (knowing the thickness) by the days claimed for the service life. In this study, as the leaching rate we need to estimate is for low biocide concentration left in the paint after **service life**, this key input value would be missing, i.e., no days left in service life (if service life is 36 months, after service life this value should be put as 0 or negative number) and neither is it possible to estimate the time left before the complete depletion of the leftover biocide. Thus, this method is easy, fast, and cheap but unfortunately impossible to be used for this study. According to the method itself the service life of a paint will finish when ≤10% of initial biocide concentration is left in the paint. Using this method for calculating the leaching rate and thus PECs, will mean to obtain a constant value until at least 10% of original concentration of biocide is still left in the paint. This constant value is similar to the freshly painted cybutryne 2% (weight/weight), which according to IMO document (IMO PP6/INF7 – 2018)[1] is not acceptable from an environmental point of view (see values for freshly painted in Table 3).

The **ISO 15181** laboratory method (or equivalent **ASTM D 6903**) could potentially be used to determine the leaching rate and consequentially the PECs for cybutryne concentration in paints. To do this, we should produce several "ad hoc"-formulated cybutryne paints with a gradient of concentration starting from 2%(w/w) and decreasing. Then measure the leaching rates of all these formulations in triplicates for 45 days. So, these methods are labour intensive, time and money consuming. These methods are very valuable for specific product leaching rate estimation, or comparison between two

[9] " Possible approach for developing data to estimate leaching rates of biocidal active substances from antifouling coating films"
http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=ENV/JM/MONO(2012)6&doclanguage=en
[10] ISO 15181-1:2007 "Determination of release rate of biocides from antifouling paints"
https://www.iso.org/standard/42867.html

formulations during product development. For a screening purpose like the one we face in this study these are less useful and too expensive. In fact, for each experimental paint in triplicates during the study of 46 days, 13 samples points would be taken and analysed. For i.e., 4 formulations only this would mean a total of 156 samples to be analysed by costly techniques. Therefore, for the large screening study we need to perform in this case, an alternative method for the leaching rate calculation is needed. These methods can be used, if possible, only afterwards, to validate the leaching rate of the cybutryne threshold in paint.

An alternative solution is to use the correlation discussed in paragraph (1.2) between the percent of area still painted with AFS but not yet eroded by the action of water, and the biocide amount still left in the paint system after service life is therefore crucial for the scope of this study. This allows MAMPEC to calculate the cybutryne PECs for the old paint's layer after service life and thus establish the threshold.

In fact, in MAMPEC there is the possibility to modify the "Surface area" of the hull in contact with water. Reducing the surface area for each ship class to e.g., 10% in the "Emission module" (se fig.5 and 6) will yield the corresponding PEC for the case where 10% of biocide is left in the paint. The reduction has been done for each ship category, as can be seen in Figure 5 and 6 allowing MAMPEC to work with the standard number of ships in each class, both moving or at berth.

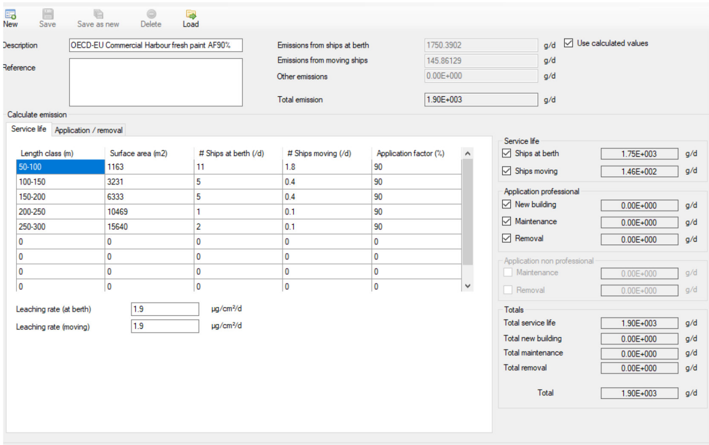

Figure 5 100% area painted as per definition of the OECD EU Harbour emission scenario. Five different ship categories are present in this scenario each with a specific hull area painted.

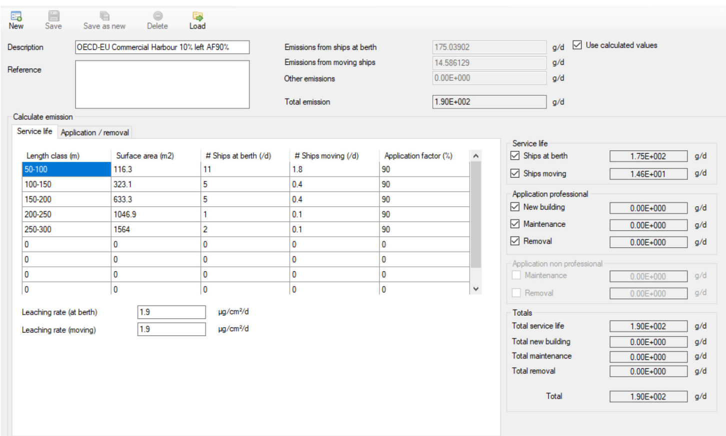

Figure 6 Emission Scenario used to calculate PEC with 10% of biocide remaining in the paint. The reduction of biocide has been translated in an area reduction to 10% compared to the OECD EU Harbour emission scenario. Five different ship categories are present in this scenario, each with a specific hull area painted reduced by 10%.

1.8. Finding the threshold

As described in the previous paragraph, we have used the hull area in contact with water and we have not estimated leaching rates to model the different PECs of cybutryne containing paint at different concentrations. The leaching rate of the cybutryne coating is kept fixed at 1,9 µg/cm^2/day. In the MAMPEC screening exercise (See Appendix 1 to this report), area and not leaching rates, has been used to correlate the amount of biocide left in paint with the amount of paint left on the hull.

Moreover, variation of the "application factor" (i.e., the number of ships painted with the cybutryne containing paint on the total number of boats present in the emission scenario) has also been tested by MAMPEC. The application factors evaluated were 90%; 50% 20% and 10%. These decreasing application factor tests were performed to reflect the progressive diminishing number of ships expected to carry cybutryne after the global ban of cybutryne.

The concentration of cybutryne left in the paint varied from the original starting concentration of 2%(w/w) (referred as "freshly painted" in Table 4) to situations where 10%, 5% and 1% remain in the AFS (Table 5-7). The original 2% (w/w) concentration was included to verify that the values obtained by this model were in line with what was expected and as reported in PPR6 /INF7 - 10 December 2018[2].

Here under the results of the MAMPEC screening exercise reported in 4 different tables (one per "emission scenario" from Shipping Lane to marina). In bold and green the PEC values < 2ng/l and thus passing the PEC:PNEC ratio ≤ 1 threshold.

OECD-EU Shipping Lane	PEC ng/L	PEC ng/L	PEC ng/L	PEC ng/L
Application factor	90%	50%	20%	10%
2%(w/w) freshly painted (20'000mg/Kg dry paint)	**1,78E-02**	**9,89E-03**	**3,96E-03**	**1,98E-03**
10% left (2'000mg/Kg dry paint)	**1,78E-03**	**9,89E-04**	**3,96E-04**	**1,98E-04**
5% left (1'000mg/Kg dry paint)	**8,91E-04**	**4,95E-04**	**1,98E-04**	**9,90E-05**
1%left (200mg/Kg dry paint)	**1,78E-04**	**9,89E-05**	**3,96E-05**	**1,98E-05**

*Table 4. PEC values for cybutryne in the OECD-EU Shipping Lane at different concentration of cybutryne in paint and different application factors. In **bold** and **green** the values < 2ng/l passing the PEC:PNEC ratio threshold.*

OECD-EU Commercial harbour	PEC ng/L	PEC ng/L	PEC ng/L	PEC ng/L
Application factor	90%	50%	20%	10%
2%(w/w) freshly painted (20'000mg/Kg dry paint)	34,80	19,30	7,73	3,87
10% left (2'000mg/Kg dry paint)	3,48	**1,93**	**0,77**	**0,39**
5% left (1'000mg/Kg dry paint)	**1,74**	**0,97**	**0,39**	**0,19**
1%left (200mg/Kg dry paint)	**0,35**	**0,19**	**0,08**	**0,04**

*Table 5. PEC values for cybutryne in the OECD-EU Commercial harbour, at different concentration of cybutryne in paint and different application factors. In **bold** and **green** the values < 2ng/l passing the PEC:PNEC ratio threshold.*

OECD-EU Marina (276 boats) *	PEC ng/L	PEC ng/L	PEC ng/L	PEC ng/L
Application factor	90%	50%	20%	10%
2%(w/w) freshly painted (20'000mg/Kg dry paint)	183,0	102,0	40,6	20,3
10% left (2'000mg/Kg dry paint)	18,3	10,2	4,1	**2,0**
5% left (1'000mg/Kg dry paint)	9,2	5,1	**2,0**	**1,0**
1%left (200mg/Kg dry paint)	**1,9**	**1,0**	**0,4**	**0,2**

*Table 6. PEC values for cybutryne as in the OECD-EU Marina modified[$], at different concentration of cybutryne in paint and different application factors. In **bold** and **green** the values < 2ng/l passing the PEC:PNEC ratio threshold.*

[*] The **OECD-EU Marina** modified according to the MAMPEC note: "*The number of boats in the ESD marina scenario, Table 0.6, should be reduced to 276 to reflect a more realistic boat density of 1.38 boats / 100 m^2*" as discussed in (TM IV 07 in Arona, October 2007)[8]

OECD-EU Default Marina (500 boats)	PEC ng/L	PEC ng/L	PEC ng/L	PEC ng/L
Application factor	90%	50%	20%	10%
2%(w/w) freshly painted (20'000mg/Kg dry paint)	331,0	184,0	73,6	36,8
10% left (2'000mg/Kg dry paint)	33,1	18,4	7,4	3,7
5% left (1'000mg/Kg dry paint)	16,6	9,2	3,7	**1,9**
1%left (200mg/Kg dry paint)	3,3	**1,9**	**0,7**	**0,4**

*Table 7. PEC values for cybutryne as in the OECD-EU Marina, at different concentration of cybutryne in paint and different application factors. In **bold** and **green** the values < 2ng/l passing the PEC:PNEC ratio threshold.*

The 64 results from which the PEC values were extracted and reported in Table 3 are available in full version in Appendix 1 to this document.

With the cybutryne ban, anti-fouling systems containing cybutryne will no longer be applied to ship hulls. For ships that have an anti-fouling system with cybutryne they can keep the anti-fouling system until the next dry-docking period (or up to 5 years since the application of an anti-fouling system containing cybutryne). At the next dry-dock, these ships will have to remove the anti-fouling system that contains cybutryne or apply a sealant to prevent the release of cybutryne to the marine environment.

The cybutryne ban will result in a gradual reduction of the number of ships bearing an anti-fouling system with cybutryne in the external coating layer of their hulls. This means that the market share of ships with cybutryne will be reduced significantly. Five years after the ban, emissions of cybutryne to water related to anti-fouling systems of ships should be zero. This can be transposed to the MAMPEC estimations by changing the application factor (i.e., percentage of ships with cybutryne).

From the table above, it is possible to conclude that a threshold of 2'000 mg/kg (corresponding to 10% of cybutryne left at the end of life of the AFS) might still lead to a negative impact if the receiving environment is a marina (the most sensitive scenario) as the PEC/PNEC >1 despite using a low application factor (i.e., percentage of ships with cybutryne).

Reducing the threshold to 1'000 mg/kg (corresponding to 5% of cybutryne left at the end of life of the anti-fouling system) and using an application factor range of 0,20-0,10, the MAMPEC results show that for all scenarios the PEC/PNEC<1. This means that if there are 10 ships berthed at a marina and there are one or two ships that have 5% left of the anti-fouling systems containing cybutryne, no negative impact to the marine environment is expected.

The results from the table above must be interpreted with caution. The scenarios used are generic and therefore the results should be read as indicative. The aim is to understand at which level the presence of any remaining cybutryne in the hull will not create a negative impact to the environment.

If the cybutryne ban scheme will lead to a gradual reduction of emissions of cybutryne to water related to anti-fouling systems of ships, **we can conclude that a compliance value of 1'000 mg/kg of cybutryne per kg of dry paint should be set as the threshold value**. Below this value emissions of cybutryne from the ship hull to the marine environment are expected not to create a negative impact to the environment.

It should be noted that for biocide products still present on the market, the total local emission is a sum of the paint service life emissions (leaching of biocide from the ship hull moving or at berth) and the contribution from other paint operations such as during newbuilding, maintenance, and removal. In the case of cybutryne containing coatings these latter contributions have not been considered because of the cybutryne global ban. It is expected that future operations made with the same product will not be possible.

For the same reason it was considered relevant to include different application factors in the MAMPEC exercise. The application factor is the ratio of ships/boats painted with cybutryne compared to the total number of boats present in each emission scenario during the simulation.

Chapter 3 of this report contains a laboratory study on the efficacy of sealant coatings as verified according to ISO1518.

2. Sampling strategy, analytical method, and tolerance

This report includes possible changes that need to be made to the guidelines[11] for these to become suitable for detecting and checking compliance for AFS containing cybutryne. This chapter covers some possible new methodologies that can be used to supplement, simplify, or improve the existing ones and could ideally apply for detecting both cybutryne and organotin compounds in AFS.

2.1. Sampling strategy

The important difference between an organotin compound such as TBT and cybutryne has been introduced in chapter 1. In the case of the organotin compound threshold, single values can be representative for intrinsic characteristics of the paint system and confirm or exclude if organotin compounds detected in that specific paint system have been employed as a biocide, which is not permitted by the guidelines, or as a catalytic agent, which is permitted (see reference 1).

In the cybutryne case, the difference between the use and role of a cybutryne molecule is not discussed. There is no reported other use of cybutryne than it being a biocide. In the first chapter of the study, the rationale for setting a threshold is coupled with the predicted environment concentration of cybutryne and based on the MAMPEC calculation using a standardized size and number of ships in different marina and harbour scenarios. This difference must be reflected and taken into consideration for the sampling strategy and most of all for the method adopted to prove compliance or not with the guidelines. The cybutryne concentration for the examined hull will need to represent as much as possible the entire hull. This threshold concentration needs to be compared with the average value from the all the samples taken from the hull and not only relying on single or just few concentrations of cybutryne in some of the samples. As described earlier in the previous chapter, paint systems erode in different rates on different parts of the hull due to the erosive action of seawater. This is influenced by many factors, among which is the hull's geometry. Therefore, it is expected to find spot/areas with higher, and spot/areas with lower, concentrations of biocide in an old cybutryne containing paint layer on a hull. For this reason, an average value derived from samples collected at several sampling points along the hull should be a more appropriate way to decide compliance or not of the paint system with the Antifouling Guideline in the specific cybutryne case.

For all these reasons, sampling strategy could remain similar between organotin and cybutryne guidelines, but in case the objective of the test includes cybutryne control, an average value of cybutryne concentration derived from all the samples collected at several points would be a more representative value to work with. Relying on one or just a few sample points that do not comply with the threshold is still correct for the organotin compounds, but risk being misleading for a cybutryne test.

Moreover, it's suggested that an inspector should not rely only on visual inspection of the hull for establishing non-compliance, as cybutryne is used not only in SPC paint systems (where the concentration is expected to be around 2%(w/w) (20'000 mg/kg dry paint) until the paint is totally polished away). Cybutryne is also used in soluble matrix paint systems, where paint may still be visible on large parts of the hull, nevertheless compliant with the amended regulations for cybutryne if the concentration of cybutryne in paint is below the threshold.

[11] Resolution MEPC.104(49) - adopted on 18 July 2003 – "Guidelines for brief sampling of antifouling systems on ships" https://www.mpa.gov.sg/web/wcm/connect/www/36298c78-32fd-4f30-ab55-ed8efa8cd8d6/sc08-22c.pdf?MOD=AJPERES

2.2. New analytical method for determination of cybutryne in AF paints

A new method has been developed and verified for the determination of cybutryne (Appendix 2, "*Analytical method for determination of Cybutryne in AF paint"*) in AFS paints. The method is based on GC/MS and sample work-up by extraction. It is proposed to add this method, or a similar method with, at least, the same measurement uncertainty, to the Guidelines.

In the current *Guidelines for Brief Sampling of Anti-Fouling Systems on Ships*[12] the following criteria are stated for analytical methods to be used in general:

4.9 The analysis of the antifouling system should ideally involve minimal analytical effort and economic cost

4.10 The analysis should be conducted by a recognized laboratory meeting the ISO 17025 standard or another appropriate facility at the discretion of the Administration or the port State.

4.11 The analytical process should be expeditious, such that results are rapidly communicated to the officers authorized to enforce the Convention.

4.12 The analysis should produce unambiguous results expressed in units consistent with the Convention and its associated Guidelines. For example, for organotin, results should be expressed as: mg tin (Sn) per kg of dry paint

In order to include control on cybutryne in the Guidelines for Brief Sampling of Anti-Fouling Systems on Ships, several methods for detecting this specific biocide with "*minimal analytical effort and economic cost*" has been evaluated. The goal was to keep same analytical approach as for organotin compounds in the present guidelines, which is a cheap and fast "Step 1", or "first-stage analysis" followed, if necessary, by a more specific and precise "Step 2" or "second phase" analysis.

In the cybutryne case the fast and cheap methods could be based on colour-reactions detection and/or easy separation (TLC, Thin-Layer Chromatography) of cybutryne from paint compounds. Unfortunately, all the tested methods, once tested in laboratory, gave too many false positives not complying with general criteria 4.12 in the guidelines for *unambiguous results*. Thus, these minimal analytical effort and economic methods were to be excluded from the analytical strategy for cybutryne in antifouling systems. Therefore, it is recommended to go directly for a specific and reliable GC/MS method similar to the ones described as "Step 2" or "Second phase" methods for organotin compounds in the current Guideline.

This means that, for compliance with the Convention, samples are needed to be sent to a laboratory using ISO 17025 to analyse cybutryne levels. Possibly a portable GC/MS can be used to perform the analysis of cybutryne at the ship (in order to comply even better with point 4.11 of the general part of the present guidelines). The results from ad-hoc experiments undertaken under this study, using thermal extraction directly on dry paint, are promising. This could make it possible to check compliance with the Convention for both compounds (cybutryne and organotin compounds) in a more flexible way by the port authority or similar.

2.3. Tolerance or uncertainty range

The uncertainty is denoted (U) and is often expressed as the expanded measurement uncertainty at the 95% confidence level. This uncertainty is a result of all steps in the analytical chain such as sampling, sample preparation, and analysis. The uncertainty can be improved (lowered) by more analytical work including, more replicates, other calibrations etc. As a starting point in discussions regarding measurement uncertainty of chemical analysis of any type, an educated guess would be U = -/+20%. A

[12] Guidelines for Brief Sampling of Anti-Fouling Systems on Ships (Resolution MEPC.104(49)) https://www.register-iri.com/wp-content/uploads/MEPC_Resolution_10449.pdf

reference guide to measurement uncertainty (GUM) can be found at Bureau International des Poids et Mesures (BIPM.org). In the analytical work performed on the determination of cybutryne containing paints (see Appendix 2 – "*Analytical method for determination of Cybutryne in AF paint*") an experimental estimation of U was determined to be 25%. This includes sampling of laboratory paint samples and the analytical work, excluding the uncertainty coming from sampling of real ships. From this reasoning, two arguments are put forward to set 25% as the "range" in the guidelines.

1. The experimentally measurement uncertainty was determined to be 25%. It is therefore, at this point, unwise to set stricter values determined, i.e., lower target value.
2. For the proposed method it is not considered necessary to have a lower uncertainty. The average cybutryne concentration in AF products is 2% (w/w) in a freshly prepared Antifouling paint and with a threshold of 0,1% (w/w) (corresponding to 1000mg cybutryne/ kg dry paint) means that the threshold results in a non-complying paint if it is above 0,1%+0,025% =0,125% (w/w). This is considered far from the new/active concentration of 2%.

For the analytical method presented in Appendix 2 to this document, the relative analytical uncertainty (range) has been determined to be ± 25%. This means that compliance should be achieved at a measured concentration < (threshold + range) i.e., 1000 + 250 mg cybutryne / kg dry paint.

2.4. Differences in the current guideline (Method 1 VS Method 2)

From a sampling perspective Method 1 and Method 2 are different.

Number of sample points differs between the methods. In the "Guidelines for Brief Sampling of Anti-Fouling Systems on Ships (Resolution MEPC.104(49))"[2] Method 1 states that specimens should be taken from at least eight sample points at different parts of the hull. Method-2 is unclear on how many samples are to be taken but indicates a maximum of four sample points in the "record sheet for the sampling and analysis of AF systems on ship hulls".

Number of replicate specimens at each sample point differs. Method 1 states that three specimens should be taken from each sample point (specimen A, B and C). They are analysed with different methods (e.g., GC/MS or XRF) or kept for record, meaning that only one specimen analysed at each sampling point. Method 2, on the other hand, states that six or nine replicates should be sampled at each sample point. The analysis of these replicates is performed on all of these samples as a first-stage analysis (XRF) and evaluated. Thereafter, the samples are sent to a second-stage analysis (if the first stage is deemed non-compliant). It is unclear if all samples, from all sample points, are sent or if it is only samples from the non-complying sample point that are sent to second-stage analysis.

The difference in *Number of samples points* and *Number of replicate specimens* results in different uncertainty for the different methods. Method 1 is better to describe the average biocide concentration on the hull whereas Method 2 is better to describe the biocide concentration at an individual sample point (lower measurement uncertainty).

The criteria for the definition of the compliance differ. For Method 1, all samples are included in the decision whereas Method 2 omits the highest and lowest value for the first-stage analysis. It is also unclear if all replicate specimens from all sample points should be analysed at the second stage for Method 2 or if it is only the samples from the non-complying first-stage sample point(s) that should be sent for second-stage analysis.

The analytical procedure for determination of total tin differs. For Method 1 any scientifically recognized procedure (e.g., ICP-MS, XRF, ICP-OES, AAS) can be used for determination. For Method 2 only XRF can be used.

The analytical procedure for determination of organic tin differs. For Method 1, "any equally reliable method" (as GC/MS) can be used for determination. For Method 2 only GC/MS can be used. Both methods are unclear regarding sample work-up and GC analysis.

All in all, a harmonisation, simplification, and clarification on the number of sample points, the number of replicates, the criteria for compliance and the analytical procedures would promote the use and interpretation of the Guidelines.

2.5. Additions to Method 1 and Method 2 to include cybutryne.

- Number of sample points:
  - No changes, specific to cybutryne, but needs to be clear in the methods. Possibly the number of sample points could be increased depending on the length of the ship.
- Number of replicates:
  - At least one extra specimen (abrasive pad) for each sampling point should be added. Two extra specimens for each sample point if separate backup specimens are required for organotin compounds and cybutryne.
- Analytical procedure:
  - The proposed method (Appendix 2) or any other method with an expanded measurement uncertainty ≤ 25% can be used.
- Compliance criteria:
  - It is proposed to use the average concentration of the samples analysed to represent the concentration of cybutryne in the hull surface. As discussed in chapter 1 the threshold rational for cybutryne is based on the percent of paint on the hull still carrying cybutryne more than the percent of cybutryne in the paint itself. So, this is best reflected from an average of the different sampling points along the hull, thus a threshold based on single points could be misleading with respect to the threshold rational. The average value of all samples must be below the threshold plus the tolerance range, i.e., 1'250 mg of cybutryne per kg of dry paint for compliance.

2.6. Alternative strategies for sampling, analysis, and cost reduction

Two steps or a single step analysis?

Since no Step-1/First-stage analysis can be made for cybutryne, the analysis of both cybutryne and organotin compounds on the same hull, using the current strategy, is less economically beneficial. It is suggested that the sampling pads are sent directly to the laboratory for GC/MS analysis for both organotin and cybutryne. This may result in reduction of costs of the GC/MS analysis for two biocides, as it will use similar extraction and sample preparation work. Both expenses and the need for complex operations at the harbour can potentially be reduced by eliminating the need for Step 1. The possibility to collect only one specimen (sample disc) for both compounds is discussed below.

The approximate costs, per chemical analysis, for the different steps and analyses are estimated in the table below. If the new proposed criteria (average values) for "compliance/non-compliance" is accepted, all 8 cybutryne samples (for Method 1) could be pooled and thus only one sample work-up and analysis is needed. If the current compliance criteria for organotin compounds should apply, then each sample point on the hull must be evaluated individually and therefore each sample needs to be analysed separately. So, the approximate cost needs to be multiplied for the number of samples to be analysed separately.

Step #	Method name	Approx. Cost per analysis
Total tin (Step-1)	ICP or XRF for total tin	**150 Euro**[1]
Organo-tin (Step-2)	GC/MS for organotin	**350 Euro**[1]
cybutryne	GC/MS for cybutryne	**350 Euro**[2]
Simultaneous cybutryne/organo-tin	GC/MS for both cybutryne and organotin (*)	**450 Euro**[3]

Table 8. Price approximation for the analytical steps

[1]In the guideline, for Method 1, each sample point needs to be analysed separately for organo-tin, i.e., 8 analyses are required.
[2]For cybutryne, the average value is the basis for compliance. Therefore, the 8 different sample points can be pooled and analysed as one sample, i.e., only one analysis is required.
[3]For simultaneous GC/MS-determination of cybutryne and organo-tin (if analytically possible), 8 analyses are required if the current compliance decisions apply.

Possible cost-saving strategies

As stated before, most probable cost savings and simplifications could be achieved by eliminating the need for several specimens.
Since no quick or "at the ship" method has been found reliable to detect cybutryne, any detection strategy must include a laboratory capable of performing analytical chemical work with at least ISO 17025 quality standard. These laboratories can most likely perform many analytical procedures and are flexible when coming to the use of methods.

If the PSC (Port State Control) officer decides that only organo-tin compounds are to be measured, the existing Guidelines are followed, meaning that, for Method 1, 24 abrasive discs (8 sample points in triplicate, of which 8 are used for the Step 1 analysis, 8 for the Step 2 analysis and 8 as backup) are sampled. If only cybutryne is to be measured, 16 abrasive discs (8 sample points in duplicate, of which 8 are used for analysis and 8 as backup) are sampled. If both organo-tin compounds and cybutryne are to be measured, 40 abrasive discs are sampled.
In the case where both organo-tin and cybutryne are to be determined, cost-saving strategies (given that Method 1 is used) could be:

1. Omit the step 1 analysis: 32 sample discs needed.
    - 8 for organo-tin (8 backup), 8 for cybutryne (8 backup)
2. Divide the sample discs in half and omit the step 1 analysis: 16 sample discs needed.
    - 8 halves for organo-tin, 8 halves for cybutryne (8 for backup, cybutryne/organo-tin)
3. Split the organic solvent extracts during sample work-up in two and omit the step 1 analysis: 16 sample discs needed.
    - 8 discs for both organo-tin and cybutryne (8 discs for backup)
4. Simultaneous GC/MS-determination of cybutryne and organo-tin and omit the step 1 analysis: 16 sample discs needed.
    - 8 discs for both organo-tin and cybutryne (8 discs for backup)

For point 2, the trade-off is a higher Limit of Quantification (LOQ) and the added uncertainty of dividing the sample discs, i.e., it would require verification that the measurement uncertainty is acceptable. Point 3, the solvent selected must be compatible with the Grignard reagent. No carbonyl containing solvents can be used, instead inert solvents such as toluene should be used. The feasibility of Point 4 is tested in section 2.5.3 below and indicate a successful strategy.

Testing feasibility for simultaneous GC/MS determination of cybutryne and organo-tin (see point 4 costs saving strategies)

The determination of cybutryne in AF paint can be performed using extraction and GC/MS as specified in the newly developed method described above. The determination of TBT in the current amendment is also based on similar extraction, sample work up and GC/MS analysis. Two schematic TBT-methods are described in the current amendment. To test if the cybutryne and TBT methods could be compatible, experiments were performed by adding cybutryne to general methods for TBT derivatization with Grignard reagents and by heating cybutryne in sodium hydroxide solution to determine its stability. The Grignard experiment was performed in toluene and ethyl magnesium bromide. The sodium hydroxide experiment was performed in 2 M NaOH overnight. Cybutryne was shown to be stable in both the Grignard and sodium hydroxide experiments (T-test, 95%). Data are shown below.

These tests suggest that the new cybutryne and the existing organotin compounds -method are compatible. However, the selection of a solvent must be adjusted in the new cybutryne method to a solvent that is inert to the Grignard reagent. Toluene is the proposed alternative solvent, which also has high solubility for cybutryne.

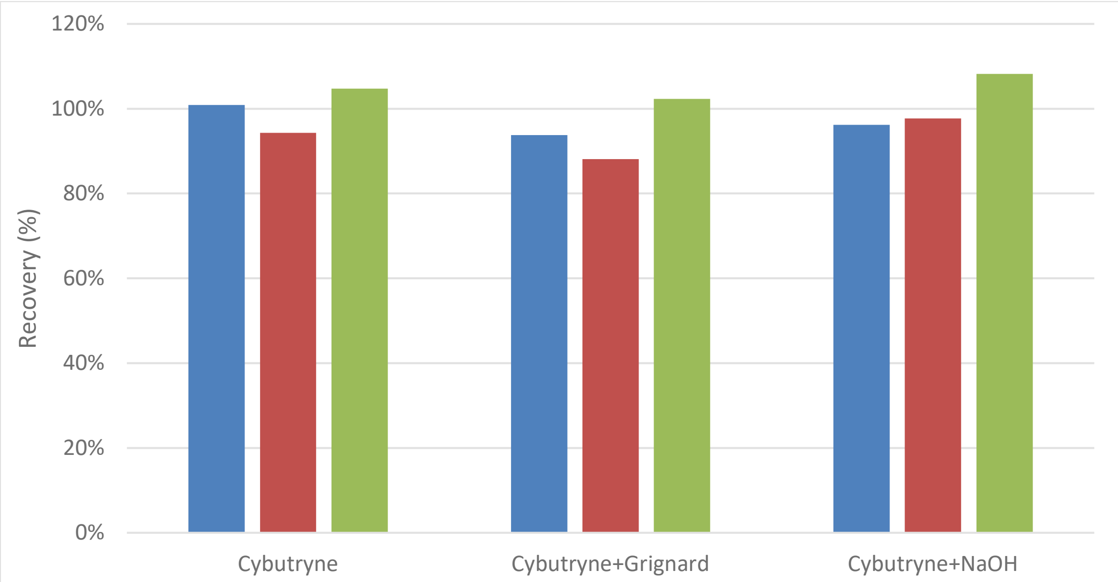

Figure 7 Stability of cybutryne shown as recovery% from GC/MS different sample preparation methods present in the actual guidelines for organo-tin compounds. The plot shows recovery rate of cybutryne with no derivatisation (Cybutryne), using the Grignard reaction derivatisation (Cybutryne + Grignard) and the NaOH derivatisation (Cybutryne + NaOH). The three colour bars represent the recovery rates for triplicate experiments.

Note: As can be seen in figure 7, the recovery% is sometime higher than 100%. This is strange in theory but normal in practice. It is a direct consequence and a demonstration of the measurements uncertainty (U) described in paragraph (2.3). A recovery above 100% is normal in recovery tests. In theory 100% is max but this in not theory, it's a practical experiment. The recovery is within the measurement uncertainty (U) estimated to 25% for the method itself. This mean that theoretically the recovery% of cybutryne with this analytical method and sample strategy would be in the 100% +/- 25% as stated in paragraph 2.3.

3. Effectiveness of sealant coatings on cybutryne AFS

This chapter focuses on one specific temporary remediation allowed in Annex 1 of the AFS Convention. It allows ships bearing an anti-fouling system containing cybutryne on the external coating layer of their hull or external parts or surfaces, to apply a coating that forms a barrier to this substance leaching from the underlying non-compliant anti-fouling system.

This possibility of sealing the non-complying hull with sealant coatings was also foreseen in the past for the organotin compounds.

The sealing efficacy study presented in this chapter has been performed on a general sealant product already present on the market.

3.1. Leaching rate measurement method

To verify the efficiency of the sealant over cybutryne containing AFS, the strategy has been simply to compare the leaching rate of a SPC paint with 2% (w/w) cybutryne versus the exact same paint but covered by a sealant coating. The choice for SPC has been taken because of the reliability of a steady state release rate from such systems, as explained earlier in this study in chapter 1.

As previously mentioned in chapter (1.7) when it comes to compare two antifouling paints the laboratory method called **ISO 15181 (**or the equivalent **ASTM D 6903)** is particularly suitable.

The rotating cylinder (ISO and ASTM) method for determining the release rate is summarised below: Triplicate test cylinders (6,4 cm diameter, 17,5 cm length) painted with a test-coating (typically a 200 cm^2 painted area) are immersed in a **holding tank** (see figure 14) containing standardised artificial seawater under controlled conditions of temperature (25ºC +/- 1ºC), salinity (33% - 34%), and pH (7,9 – 8,1). On specified measurement days, each cylinder is transferred to a **release rate measuring container** containing 1,5L of artificial seawater and rotated at a surface velocity of 0,2 m/s (about 0,4 knots) for up to 1h (for the dimensions of test cylinders used this is 60rpm). The cylinders are then returned to the **holding tank** until the next measurement point and the concentration of biocide in the **release rate measuring** at the end of the rotation period is determined analytically. Testing is continued twice weekly for a minimum of 45 days. From knowledge of the painted surface area, the rotation time, and the resulting biocide concentration after rotation, the release rate at each measurement point can be determined. These individual results are arithmetically treated to generate data for cumulative release (units: $\mu g/cm^2$), the average leaching rate from day 21 to day 45 (units: $mg/cm^2/d$). The analytical protocol provides a measure of the total release rate.

The method explicitly states that ''*This test method has not been validated to reflect in situ release rates for antifouling products and, therefore should not be used in the process of generating environmental risk assessments. In-service release rates of antifouling (AF) coatings change with natural variability in seawater chemistry, temperature, and hydrodynamic regime*.'' This has previously been recognised by the US Environmental Protection Agency (EPA) which has acknowledged that release rate results generated using this method ''are not expected, or intended, to correlate with actual, in-service leach rates'' (Naval Sea Systems Command, US Department of the Navy, Office of Water, US Environmental Protection Agency, 2003).

In Alistair Finnie (2006)[13] correlation between laboratory methods and measuring release rate in-service are compared. From those results, regulators have accepted the use of default correction factor 5,4 to be applied to values obtained from these methods if one wants to estimate more realistic values. Among the conditions not replicable in laboratory giving rise to this difference by 5,4 time are the biological conditions. For example, at in-service conditions, the accumulation of biofilm on the painted surfaces can slow down the release of biocide compared to the artificial water conditions.

[13] Alistair A. Finnie (2006) Improved estimates of environmental copper release rates from antifouling products, Biofouling, 22:5, 279-291, DOI: 10.1080/08927010600898862

In this study, the ability of the sealant to reduce leaching of cybutryne is verified by comparison, rather than by absolute values. Therefore, in this exercise the values have been used as is and not reduced by the application of any correction factor.

3.2. Cybutryne AFS and sealant coating

Cybutryne AFS

Starting from a detailed list for suppliers of antifouling paints containing cybutryne, the study team contacted several companies in the EU to obtain samples, with no success. The main reason was due to the fact that antifouling paints containing cybutryne are no longer authorised to be placed on the market in the EU and thus are no longer present or available for purchase. When contacting non-EU suppliers, the fact that export to the EU is not allowed also posed a strong barrier to obtain the samples.

Based on the above, it was decided to perform this study with a laboratory made antifouling paint containing cybutryne. An SPC coating "Magellan 630 Extra"[14] was kindly supplied by the Italian paint company "Boero Bartolomeo S.p.A." (Genova, Italy). The Magellan 630 Extra has been used as a base paint, as it does not contain any cybutryne and is very similar in matrix and formulation to some of the SPC paint containing cybutryne presented in chapter 1 and to the ones present on the non-EU market.

Cybutryne

Cybutryne (CAS 28159-98-0), trade name "Irgarol 1051" was purchased from Merck. The product was dissolved in solvent (xylene) and mixed to the base paint to a final concentration in wet paint corresponding to a concentration in dry paint of 2% (w/w) i.e., 20'000 mg Cybutryne / kg dry paint. The ratio between the concentration in wet paint and the concentration in dry paint has been calculated using the specific gravity of the paint (ca.1,5Kg/L) and the solid per volume 48% (±2%) available from the technical datasheet for "Magellan 630 Extra"[12].

Sealant Coating

After communication with different paint producers, it was clarified that "sealant coatings" are generally primer coatings. In order to test the possibility to use sealant products already present on the market and widely spread globally, the sealant choice was a primer called "Mistral Fondo"[15] kindly supplied by the Italian paint company "Boero Bartolomeo S.p.A."

3.3. Sample preparation

The surface of 7 polycarbonate cylinders 160mm*70mm diameter (see figure 8) was cleaned, rinsed, and then abraded with 200 grit sandpaper to promote paint adhesion. The abraded surface was then wiped and washed with Milli-Q® water and left to dry. The base paint which included cybutryne up to 20'000 mg/kg dry paint was added. This resembles the formulation "2%(w/w) freshly painted (20'000 mg/kg dry paint)" and was applied on 6 out of 7 cylinders. The height of the painted area on each cylinder was 100 mm leaving 20 mm unpainted to the bottom and 40 mm to the top. This gave a total painted area of 219,8 cm^2. Three out of 6 painted cylinders were applied with "Mistral Fondo"[12] on top of the "20'000 mg/dry paint" cybutryne formulations once these were cured.

[14] "Magellan 630 Extra" Boero Bartolomeo S.p.A. (Genova, Italy) Technical Data Sheet: https://www.boeroyachtcoatings.com/fileadmin/documents/Schede%20tecniche%20eng/Magellan_630_Extra_TDS_e.pdf

[15] "Mistral Fondo" Boero Bartolomeo S.p.A. (Genova, Italy) Technical Data Sheet: https://www.boeroyachtcoatings.com/fileadmin/documents/Schede%20tecniche%20eng/Mistral_Fondo_TDS_e.pdf

The cylinders were marked as cylinder 1; 2; 3; for the triplicate set "sealed freshly painted cybutryne 20'000 mg/kg dry paint" and as cylinder 4; 5 and 6 for the non-sealed "freshly painted cybutryne 20'000 mg/kg dry paint". An extra cylinder was marked as cylinder 7 as a "blank".

The cylinders were weighted before painting. The paint was applied by roller on a rotating cylinder to achieve a homogenous paint film thickness. The application has been repeated until the calculated thickness was inside the range specified from the standard method (see next paragraph for dry film thickness calculation). According to the ISO 15181-1, the cylinders were left to dry in a fume hood for one week before the start of the study.

3.4. Dry film thickness

The information on 2% (w/w) cybutryne AFS formulation from the paint producers was used to calculate the dry density of the paint.

Dry film density = [NV × Dp × Ds] / [100 × **Ds** – (100-**NV**) × **Dp**] (Eq.1)

Where:

NV = percent of Non-Volatile solids measured per standard method,

Dp = density of the wet paint measured per standard method

Ds = density of the solvent (in this case water-based paint so **Ds**=1).

Input:

density wet paint (g/ml) [Dp] = 1,45

NV = solid content (in%) [NV] = 48

Density of the Solvent (Ds)= 0,88

Dry film density calculated

(2%(w/w) cybutryne AFS) = [NV × Dp × Ds] / [100 × Ds – (100-NV) × Dp]

= (48 x 1,45 x 0,88) / (100 x 0,88-(100-48) x 1,45) = 4,86g/cm^3

The film thickness was calculated knowing the weight of the paint on the cylinder and dividing it by the specific "dry film" weight (which is the specific weight per µm of thickness of a particular paint). Knowing the painted area (219,8 cm^2) and the dry film density 4,86 g/cm^3, the dry film weight expressed in g/µm was calculated as follow:

Dry film weight = film density (g/cm3) x area (cm2) = dry film weight (g/cm)

4,86g/cm3 x 219,8cm2 = 1068,43 (g/cm). Transforming this in g/µm makes it more usable in painting normal thick films (usually in the range of hundreds of µm). Thus, the values will be divided by 10'000 to be 0,106 (g/µm) which was used to control the thickness by just using a laboratory precision balance after each layer was cured. The balance used for this study is a Sartorius ED224S: Readability 0,0001(g); Repeatability (STD) ≤ ± 0,0001(g); Linearity ≤ ± 0,0002g. The instrument is calibrated at regular intervals of one year, according to the ISO 17025.

In Table 8, the calculated film thickness is reported. The cylinder has been weighed before paint application, after paint application (dry film condition) and before the start of the experiment. Additionally, for the sealant covered samples, the operation of weighing was repeated for both paint and sealant application and before the start of experiment. This gave the possibility to account for both paint and sealant thickness as a minimum thickness is required from the standard test in order to make the test results reliable.

Sample name	thickness paint (µm)	thickness sealant (µm)
cylinder 1	53,0	84,6
cylinder 2	66,1	111,6
cylinder 3	65,3	109,4
cylinder 4	76,2	--
cylinder 5	81,1	--
cylinder 6	97,9	--
cylinder 7 (blank)	0,0	--

Table 9 Cylinders sample name; dry film thickness before start

3.5. ISO 15181-1 Method description.

Test cylinders (figure 8) painted with antifouling paint are immersed, together with reference cylinder, in a holding tank (figure 14) containing artificial seawater (prepared according to *ASTM D 1141-98(2003) Standard Practice for the Preparation of Substitute Ocean Water*) for 45 days. At specified time intervals, the cylinders are removed and exposed for a defined period (1 hour) in individual polycarbonate release rate measuring containers (figure 9) containing 1,5L of fresh artificial seawater (ASTM D 1141-98(2003). At the end of the one-hour exposure in the release rate measuring containers, the cylinders are replaced in the holding tank. The concentration of the biocide released into the 1,5L of artificial sea water is then determined by appropriate analysis technique. This operation is repeated at defined time intervals (day: 2; 8; 10; 14; 21; 24; 28; 31; 35; 38; 42; 45) for all the cylinders, and hence the release rate of the biocide under the specified laboratory conditions can be calculated.

3.6. Materials

Figure 8 - Test Cylinder used

The test cylinders used were 8 centrifuge bottles with screw caps. Volume 500 ml, Diameter ×Length: 70mm×160mm, Polycarbonate by Nalgene®

The release rate measuring containers were 2L containers in Polycarbonate H. 21,6cm and D. 14,5cm, the "release rate measuring container". A new container for each measurement and each cylinder so that no contamination from previous measurements was possible.

Figure 9 - "Release rate measuring container" in PC

Figure 10 - Filter system used for the holding tank water.

The filter system used was an active coal filter and two iminodiacetic acid chelating cation exchange resins to lower and control the cybutryne concentration in the holding tank. The maximum limit of organic biocide in the holding tank, according to the ISO 5181-1 is 100µg/L.

The recirculating filter system consisted of a combined ion-exchange resin → activated-charcoal filter → an ion-exchange resin" (see figure 10). The cartridge containers were made in Styrene acrylonitrile resin (308mm*122mm).

Figure 11 - Ion exchange resin (left), cartridge nylon (middle) and activated charcoal cartridge (right)

For the iminodiacetic acid ion-exchange-resin, a nylon cartridge *(see figure 11 (centre*) with net-mash 80µicron; max flow 3500 L/h at 20°C; max pressure 6 bar and max temperature 50°C, has been used as filter/holder for the ion-exchange-resin itself "*Amberlite® IRC-748 ion-exchange resin*" from *Acros Organics (see figure 11 (left)*.

In between two iminodiacetic filters, one activated-charcoal filter was used as purchased. Particle size of 20µicron; maximum flow at 20°C 216(L/h); maximum pressure 6bar; max temperature 50°C (*see figure 11 (right)*).

Figure 12 - Water bath 160L

A thermostatically controlled water bath was used to control the temperature in the holding tank (aquarium) by immersing the holding tank in a SÆPLAST 160L tub (figure 12). The temperate water bath was kept at 25°C during all the duration of the experiment, 45 days.

Figure 13 – Temperature control unit, heat element

The temperature in the water bath has been controlled during the entire duration of the test by the use in combination of a Lauda ETK30 calibrated cooling element and an IKA ICC electronic controlled heat element (figure 13). All the system was thermostatically calibrated to reach and maintain the 25°C±1°C in the holding tank immersed in the water bath

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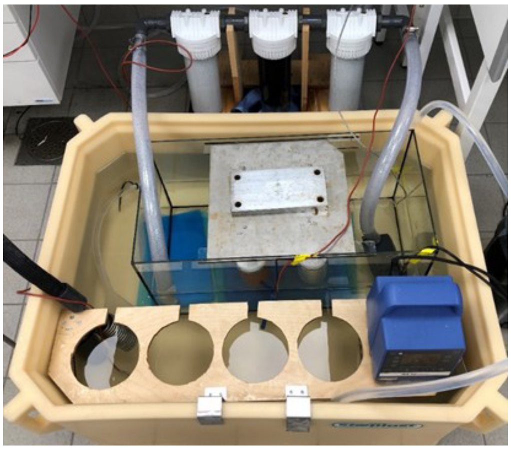


Figure 14. Set up for the controlled temperature of holding tank for ISO 15181-1 using a water bath.

In a 160 L water bath (figure 14), deionized water was thermostatically controlled at 25°C ± 1°C and recirculated. Inside this water bath, a 30L "*holding tank*" (an aquarium) containing substitute ocean water (SOW) prepare according to ASTM D1141-98 was kept at constant 25°C during the whole study (45 days). The 7 cylinders remained immersed in the "holding tank" for the whole duration of the experiment (45 days).

Prior to each measurement 1,5L of fresh SOW was put into the "*release rate measuring containers"* (figure 9). These release rate measuring containers were also immersed in the controlled bath using the wooden support (see figure 14) to allow the temperature of the SOW of the release rate measuring container be the same as the one in the holding tank i.e., 25°C ±1°C.

The painted and blank cylinders were then moved from the holding tank and mounted on a rotating device, then immersed in the "release rate measuring containers" and rotating at a speed of 60 (±1) round/min (RPM) (see figure 15). After one hour, 50 ml of SOW was taken from each of the release rate measuring container and sent to analysis for cybutryne concentration determination.

At each day, (day 2; 8; 10; 14; 21; 24; 28; 31; 35; 38; 42; 45), 50 ml of SOW and a sample of water from the holding tank (the aquarium) was collected, to check for cybutryne concentration. According to the ISO standard 15181-1 organic biocide limit allowed in holding tank is 100µg/L. The active carbon filter used is particularly suited to capture organic biocides and keep the concentration in the holding tank under this limit.

Extraction & Analysis procedure

The test started on the $2^{nd\ of}$ November 2020 (Day 0) and finished on the 17^{th} of December 2020 (day 45). According to the ISO 1518-1 the experiment period has been 45 days long. The extraction of samples was done, as described, at specific intervals, and more precisely at day2; 8; 10; 14; 21; 24; 28; 31; 35; 38; 42 and 45.

Figure 15. From left to right, from up do down: The release rate measuring tanks; the rotating device for biocide extraction at 60 rpm; the cylinder painted on a 200cm2 area and the extraction moment in the water bath at 25°C± 1°C.

Sampling
A sample of 50 ml was collected in a polypropylene tube, taken from the 1,5L "release rate measuring containers". The samples were frozen at -20°C. The maximum period of storage at -20°C has been from 2nd November 2020 to 17th of December 2020, thus 45 days. This procedure has been validated prior the experiment in order to be sure no organic biocide was lost during the time in freezer.

3.7. Analysis

The samples were thawed overnight, in the fridge, and diluted prior to analysis by LC/MS/MS[16]. The LC/MS/MS instrument was a Waters Acquity UPLC I-class LC-system and a Waters Xevo TQ-XS mass spectrometer. A Waters Acquity UPLC CSH C18, 2.1 mm × 100 mm, 1.7 µm column was used for chromatographic separation of the analytes by a linear gradient from 95% of mobile phase A (95:5 purified water: Acetonitrile, containing 0,1% formic acid) to 80% of mobile phase B (Acetonitrile containing 0,1% formic acid).

3.8. Calculation and Results

The organic biocide concentration was calculated in each treated subsample based on the instrument response for samples and blanks.

Calculation of the **Release Rate at Each Data Point** (Sampling Day):

The Release Rate (µg/cm²/d) for each individual test cylinder was calculated at each data point (sampling day) as follow:

$$R_{cyl} = (C_{biocide} \times V \times D)/(T \times A)$$

$$= (C_{biocide} \times 1{,}5 \times 24) / (1 \times 220)$$

$$= (C_{biocide} * 0{,}163) \text{ for } 220\ cm^2 \text{ paint area}$$

where:

$C_{biocide}$ = concentration of biocide in substitute ocean water, µg L^{-1},

V = substitute ocean water volume in measuring container, L,

D = hours per day (24),

T = rotation period, h, and

A = area of paint, cm^2.

Input:

T = 1 hour the cylinders were rotating inside the form the 1,5L "release rate measuring containers"

A = 220cm^2 paint area of the cylinders

The **mean cybutryne concentration at each data point** (sampling day) was calculated for each set of triplicate test cylinders. Standard deviation for the mean cybutryne concentration was also e calculated and reported in the results. The **mean release rate at each data point** (sampling day) was calculated

[16] **LC/MS/MS system**
Liquid chromatographic system (LC), Waters Acquity UPLC i-class. Mass spectrometer (MS), Waters Xevo TQXS triple quadrupole. Column, Waters Acuity UPLC CSH C18, 2.1 x 50mm 1.7µm. Mobile phase A, 95:5 purified water: Acetonitrile, containing 0.1% formic acid. Mobile phase B, Acetonitrile containing 0.1% formic acid. Cybutryne and the internal standard were separated by a linear gradient from 95% of mobile phase A to 80% of mobile phase B.

for each set of triplicate test cylinders. Standard deviation for the mean release rate was also calculated and reported in the results.

The mean cybutryne concentration and the mean cybutryne release rate at each time point for the "**Freshly painted cybutryne coatings (20'000mg Cybutryne/kg dry paint)"** and "**Sealed freshly painted cybutryne coatings (20'000mg Cybutryne/kg dry paint)"** are reported respectively in Table 10 and Table 11.

The mean release rate for the triplicate samples of the sealed and un-sealed cybutryne paint as a function of time during the 45 days release rate study are shown in Figures 16 and 17, respectively.

Day	**Mean cybutryne conc. (µg/l)**	**STD (± µg/l)**	**Mean release rate of cybutryne (µg*cm^{-2}*d^{-1})**	**STD (± µg*cm^{-2}*d^{-1})**
2	11.313	0.677	1.792	0.046
8	15.071	1.544	2.385	0.172
10	16.446	1,915	2.600	0.209
14	19.739	2.723	3.119	0.328
21	24.479	1.631	3.876	0.080
24	26.511	2.679	4.193	0.243
28	28.259	3.805	4.463	0.411
31	26.835	2.285	4.252	0.288
35	29.638	2.747	4.691	0.283
38	39.592	8.633	6.229	1.063
42	32.850	3.022	5.203	0.375
45	36.361	3.577	5.955	0.586

*Table 10. The mean cybutryne concentration (for triplicate cylinders at each sampling day) as identified with LC/MS-MS for the "**Freshly painted cybutryne coating (20'000mg Cybutryne/Kg dry paint)"** and the mean cybutryne release rate (for triplicate cylinders at each sampling day) for the same samples.*

Day	Mean cybutryne conc. (µg/l)	STD (± µg/l)	Mean release rate of cybutryne (µg*cm^{-2}*d^{-1})	STD (± µg*cm^{-2}*d^{-1})
2	6.841	0.852	1.120	0.140
8	3.507	0.615	0.574	0.101
10	3.200	0.628	0.524	0.103
14	2.413	0.329	0.395	0.054
21	1.863	0.212	0.305	0.035
24	1.676	0.275	0.274	0.045
28	1.466	0.224	0.240	0.037
31	1.330	0.249	0.218	0.041
35	1.138	0.130	0.186	0.021
38	1.119	0.265	0.183	0.043
42	0.985	0.256	0.161	0.042
45	0.904	0.239	0.148	0.039

Table 11. The mean cybutryne concentration (for triplicate cylinders at each sampling day) as identified with LC/MS-MS for the ***Sealed Freshly painted Cybutryne coating (20000mg Cybutryne/Kg dry paint)*** *and the mean cybutryne release rate (for triplicate cylinders at each sampling day) for the same samples.*

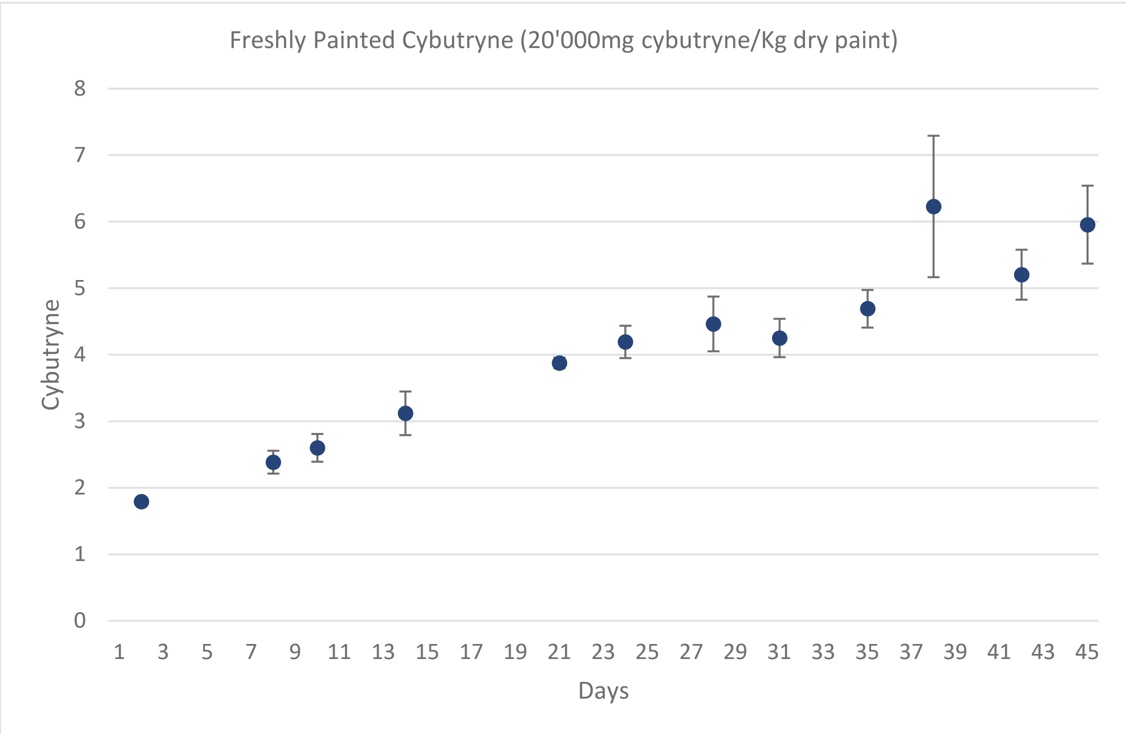


*Figure 16 - The plot shows the mean release rate of cybutryne for the "**Freshly painted Cybutryne coatings (20'000 mg Cybutryne/Kg dry paint)**" during the 45 days of the study. Mean release rates values are plotted as a function of time.*

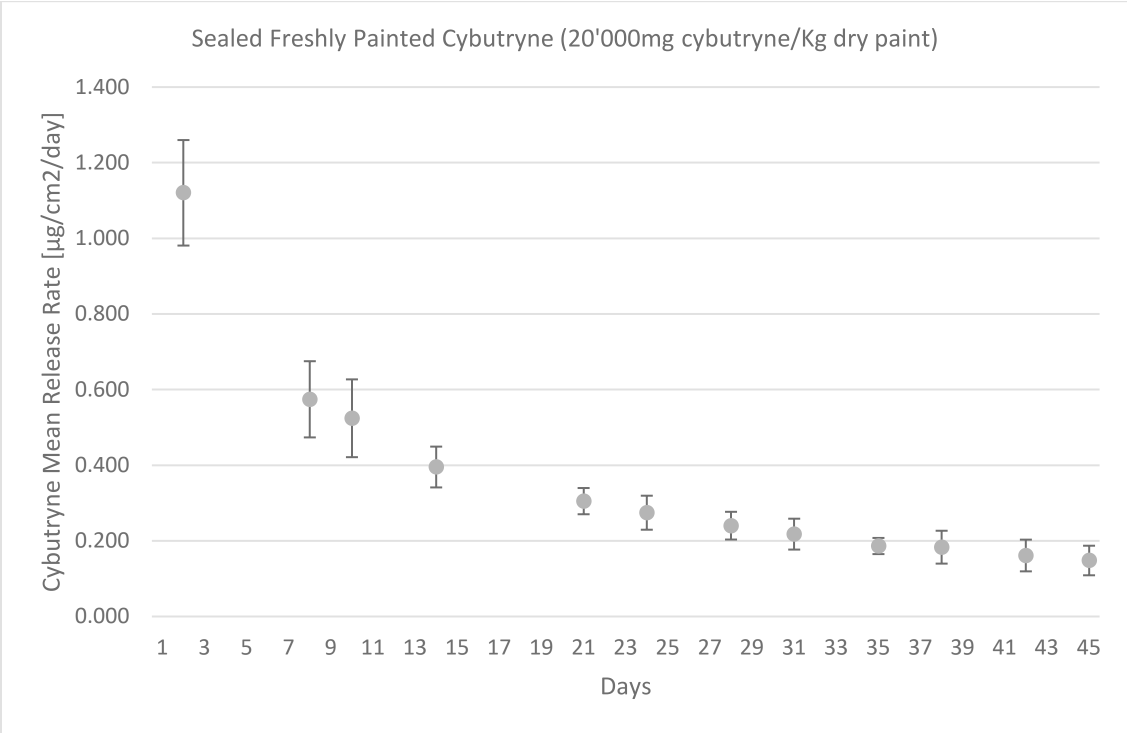


*Figure 17 the plot shows the mean release rate of cybutryne for the "**Sealed Freshly painted Cybutryne coatings (20'000mg Cybutryne/Kg dry paint)"** during the 45 days of the study. Mean release rates values are plotted as a function of time.*

In the plots above, it can be noted that although the release rates values for the two cases (sealed and un-sealed) start with a similar order of magnitude (between 1 and 2 µg/cm2/day), they diverge during the experiment.

While the un-sealed SPC cybutryne paint increases the mean release rate from 2µg/cm2/day to 5-6 µg/cm2/day in the last week of the study, the sealed cylinders show instead a clear decrease or leaching rate

Calculation of the **weighted mean release rate from day 21 to final test day** (µg of organic biocide $cm^{-2}\ d^{-1}$) as follows:

$$\bar{R}_{21,end} = \frac{\sum \bar{R}_{i,j}\,(j-i)}{\sum\,(j-i)} = \frac{\sum \frac{(R_i+R_j)}{2}(j-i)}{\sum\,(j-i)}$$

$\mathbf{R_{21,\,end}}$ **= µg/cm²/day**

where:

$\bar{R}_{21,\,end}$ = mean release rate (µg of organic biocide $cm^{-2}\ d^{-1}$) between Day 21 and the last day of sampling,

$\bar{R}_{i,\,j}$ = mean release rate (µg of organic biocide $cm^{-2}\ d^{-1}$) between consecutive sampling Days i and j for all data points from Day 21 through the last day of sampling, *i and j* = time elapsed (days) since the start of the trial for each pair of consecutive data points, specifically Days 21 and 24, 24 and 28, 28 and 31, and so forth, respectively, and

R_i and R_j = mean release rates (µg of organic biocide cm^{-2} d^{-1}) for each triplicate set of test cylinders for each pair of consecutive data points from Day 21 through the last day of sampling, specifically Days 21 and 24, Days 24 and 28, Days 28 and 31, and so forth, respectively.

Note: this equation calculates the weighted mean release rate, considering any differences in time between test days, and is a more valid treatment of the data than calculation of the simple arithmetic average of the data.

The values for the $R_{21, end}$ for the two studied cases are calculated using the above equation and resulted in the following:

$R_{21, end}$ (Cybutryne Paint (2%w/w)) = 4,58 µg/cm²/day

$R_{21, end}$ (Sealed Cybutryne Paint (2%w/w)) = 0,21 µg/cm²/day

The concentration of cybutryne in the holding tank (aquarium) was monitored under the whole experiment. The upper limit of organic biocide concentration in holding tank during the ISO 15181-1 is 100µg/L water. As can be seen in Table11 the filtration worked well and the concentration have been kept way below this 100µg/L limit.

Table 12. Concentration of cybutryne (µg/L) in the holding tank (aquarium) under the whole experiment and sampled during sampling days.

Day	Aquarium cybutryne concentration (µg/l)
2	0,647
8	0,339
10	0,447
14	0,616
21	0,694
24	0,667
28	0,835
31	0,835
35	0,998
38	1,299
42	1,326
45	1,727

3.9. Leaching Rate Results

The sealant efficacy can be calculated as the relative decrease of cybutryne release rate between the "freshly painted paint containing 2%(w/w) cybutryne" and the same paint with the sealant.

In the plots, it can be noted that although the release rates values for the two cases (sealed and un-sealed) start with a similar order of magnitude (between 1 and 2 µg/cm^2/day), they diverge during the experiment.

Typically, an AFS paint once immersed in water for the first time, show an unstable release rate period (known as boost effect) where the paint needs to start reacting with seawater and the "leaching layer" (chapter 1.1) needs to form. This is the reason why the calculations are normally done after day 21, when the system is stable. In fact, 21 or even 45 days, cannot be considered as "a long period" for an antifouling system to stabilize, as their lifetime can be from 3-5 years.

The efficacy of the sealant on (20 000 mg cybutryne / kg dry paint) was calculated as follows:

Efficacy (%) = 1 – ($R_{21,\,end}$ (Sealed Cybutryne Paint (2% w/w)) / $R_{21,\,end}$ (Cybutryne Paint (2%w/w))) * 100 = 1- ((0,21 µg/cm^2/day) / (4,58 µg/cm^2/day)) * 100 = (1 - 0,04) * 100 **= 96%**

Taking the efficacy of **96%** and reducing the PECs values in Tables 4, 5, 6 and 7, one can calculate new PEC values and create new tables, this time for sealed hulls. These results indicate that sealants applied to SPC anti-fouling paints containing cybutryne, act as a barrier.
The sealant layer prevents the leaching of cybutryne from the inner layer. The use of sealants can be considered as an option as it forms a barrier preventing the leaching of cybutryne from an underlying non-compliant anti-fouling system. It works as a remediation instead of removing the anti-fouling system containing cybutryne.

Important: the absolute values for the leaching rates generated using the ISO standard method 15181-1 **(**equivalent to **ASTM D 6903)** such as

$R_{21,\,end}$ (Cybutryne Paint (2%w/w)) = 4,58 µg/cm^2/day
$R_{21,\,end}$ (Sealed Cybutryne Paint (2%w/w)) = 0,21 µg/cm^2/day

are reliable and very useful to compare different paint systems (including same paint systems with and without sealant) but are not to be considered to reflect expected values in real conditions of use. As stated in paragraph 3.1 and in Alistair Finnie (2006)[17] correlation between laboratory methods and measuring release rate in-service has been compared and from the results, regulators have accepted the use of default correction factors, i.e., 5,4 for copper, to be applied to values obtained from these methods if one wants to estimate more realistic values.

Taking the value obtained in this study from the ISO 15181-1 **4,58µg/cm^2/day** for an in service cybutryne paint and comparing it with the value for the same system **1,9µ/cm^2/day** reported in "PPR6/INF.7 2018 *Information presenting scientific evidence for the adverse effects of cybutryne to the environment*" one can notice that in this case the correction factor should be 2.4. This can be considered as normal overestimation factor even if not in line with the 5.4 from Finnie as 1) the 5.4 refer to copper as biocide and not organic biocide, 2) the overestimation value can change in different laboratory and 3) the value 1,9 is a value calculated on several different paint system used during the years in different parts of the world while 2% was an average value of these different commercial present biocide paint. Considering these difference, a factor of 2.4 between

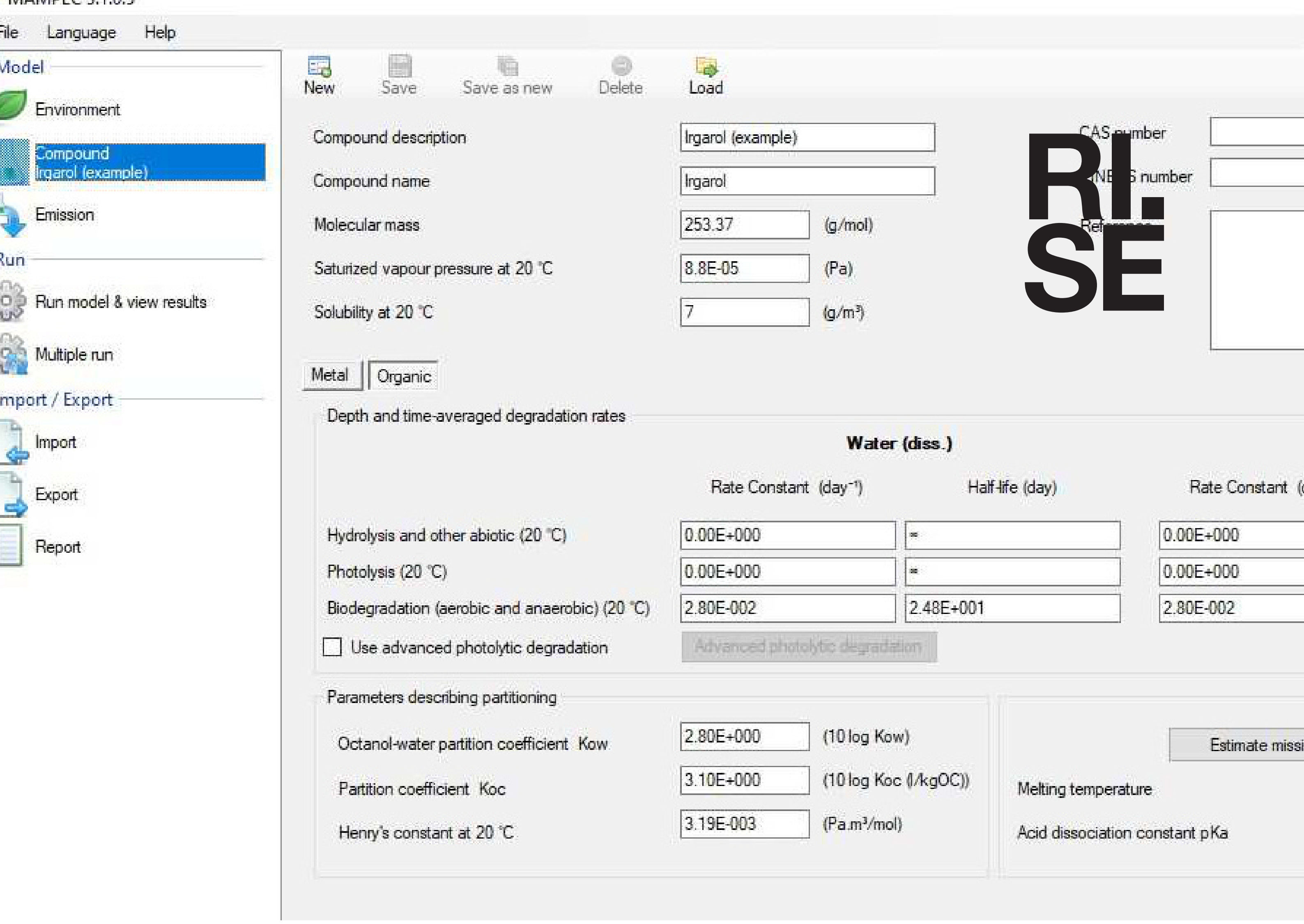
[17] Alistair A. Finnie (2006) Improved estimates of environmental copper release rates from antifouling products, Biofouling, 22:5, 279-291, DOI: 10.1080/08927010600898862

the values obtained by laboratory method used in this study and the leaching rate in PPR6/INF.7 2018, can be considered still a good demonstration of the ground principle about overestimation and shall not be taken as a value to base any regulation decision on but only for comparison between "with sealant" and "without sealant" as it has been reported and used in this study.

4. Conclusions

TRESHOLD VALUE
• Using the **MAMPEC** model for predicting the **PREDICTED ENVIRONMENTAL CONCENTRATION (PEC) values** for cybutryne leaching from antifouling paints at the end of service life to water, it was possible to identify the maximum concentration value for cybutryne in paint which would give a PEC below the **PREDICTED NO EFFECT CONCENTRATION** in marine environment (PNEC) stated in a previous study to be set at 2 ng/L. • **This Threshold concentration is 1000mg cybutryne/kg dry paint.** This **gives**, according to this study, a ratio between what is predicted and what is the limit (PEC/PNEC) less than 1 in different emission scenarios. This mean that the PEC will be lower than the limit of 2ng/L in marine environment, and thus not posing risk to the marine environment. • Thus, 1000mg cybutryne/Kg dry paint can be identified as a threshold concentration.
SAMPLING AND ANALYTICAL STRATEGY
• The sampling strategies and the analytical methodologies described in the AFS guidelines have been studied and validated for the control of anti-fouling systems containing cybutryne. • Unfortunately, **no Step 1 fast screening method has been found reliable to determine cybutryne in paint**. • **The current Step 2**, designed for the organotin compounds, **could be used for the analysis of cybutryne with some adjustment**. • In **Appendix 2 to this report the exact procedure is described in detail**. • In case the inspector is investigating the presence of both organotin compounds and cybutryne, there are some potential savings by skipping Step 1 for organotin and taking the sample for the ship hull directly to Step 2 analysis. One single preparation procedure and analysis can be used for the analysis of both chemicals.

TOLERANCE VALUE
• The tolerance range connected with the measurement uncertainty (U) at the 95% confidence level was determined specifically for the new procedure described in Appendix 2. This uncertainty is a result of all steps in the analytical chain such as sampling, sample preparation and analysis. The uncertainty was determined to be 25%. For the proposed method it is not considered necessary to have a lower uncertainty. • Tolerance value is thus 25% (of the 1 000 mg threshold) = **250 mg cybutryne / kg dry paint**
SEALANT EFFICACY
• **Method**: In order to test and validate the efficacy of the sealant for cybutryne containing antifouling systems, an experimental antifouling paint with 20 000 mg cybutryne per kg dry paint has been formulated as representative paint and applied on cylinders to be processed according to the standard method **ISO 15181 (**equivalent to **ASTM D 6903)** to measure the release rate of cybutryne into artificial seawater. • Three cylinders applied with this paint and three applied with both this paint and covered by sealant coating were compared to each other in term of release rate of the cybutryne. • In the plots, it can be noted that although the release rate values for the two cases (sealed and un-sealed) start with a similar order of magnitude (between 1 and 2 µg/cm2/day), they diverge during the experiment. • The efficacy of the sealant to reduce cybutryne release was measured to be 96%. The result shows high effectiveness for the sealant to prevent the leaching of cybutryne from the anti-fouling system to the surrounding water. • Therefore, a sealant can be considered as a possible remediation for non-complying hulls. **Important note on the release rate values in chapter 3:** • As already mentioned in previous studies[1], for a typical cybutryne paint (at the concentration studied here) the leaching rate value in real life conditions is expected to be 1,9µg/cm^2/d. The standard method used in this study is very reliable in order to compare different formulations (such as in this case with and without sealant) but is well known from literature and as stated in the standard document itself, to overestimate the absolute values of release rate in real life. In literature and in regulation procedure for product authorisation it is therefore conceded to use a default "correction factors" for the values obtained with the ASTM/ISO rotating cylinder method of 5,4 (A. Finnie 2006)



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APPENDIX 1 TO

Study to support the amendment of the "Guidelines for brief sampling of anti-fouling systems on ships" to include controls on Cybutryne

All the PEC values as calculated by MAMPEC for the different siatuation of use and concentration of cybutryne in paints

RISE REPORT

EMILIANO PINORI (RISE)
EMILIANO.PINORI@RI.SE

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – Freshly painted Cybutryne AFS
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane Freshly painted Cybutryne AFS App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.17	ng/l
95 % concentration	0.14	ng/l
Average concentration	0.02	ng/l
Median concentration	0.00	ng/l
Minimum concentration	0.00	ng/l

-- Freely dissolved --

Maximum concentration	0.17	ng/l
95 % concentration	0.14	ng/l
Average concentration	0.02	ng/l
Median concentration	0.00	ng/l
Minimum concentration	0.00	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – Freshly painted Cybutryne AFS
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane Freshly painted Cybutryne AFS App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.09	ng/l
95 % concentration	0.08	ng/l
Average concentration	0.01	ng/l
Median concentration	0.00	ng/l
Minimum concentration	0.00	ng/l

-- Freely dissolved --

Maximum concentration	0.09	ng/l
95 % concentration	0.08	ng/l
Average concentration	0.01	ng/l
Median concentration	0.00	ng/l
Minimum concentration	0.00	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – Freshly painted Cybutryne AFS
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane Freshly painted Cybutryne AFS App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.038	ng/l
95 % concentration	0.030	ng/l
Average concentration	0.004	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- Freely dissolved --

Maximum concentration	0.038	ng/l
95 % concentration	0.030	ng/l
Average concentration	0.004	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – Freshly painted Cybutryne AFS
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane Freshly painted Cybutryne AFS App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.019	ng/l
95 % concentration	0.015	ng/l
Average concentration	0.002	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- Freely dissolved --

Maximum concentration	0.019	ng/l
95 % concentration	0.015	ng/l
Average concentration	0.002	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **10% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **10% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.017	ng/l
95 % concentration	0.014	ng/l
Average concentration	0.002	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- Freely dissolved --

Maximum concentration	0.017	ng/l
95 % concentration	0.014	ng/l
Average concentration	0.002	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **10% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **10% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.009	ng/l
95 % concentration	0.008	ng/l
Average concentration	0.001	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- Freely dissolved --

Maximum concentration	0.009	ng/l
95 % concentration	0.008	ng/l
Average concentration	0.001	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **10% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **10% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.004	ng/l
95 % concentration	0.003	ng/l
Average concentration	0.000	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- Freely dissolved --

Maximum concentration	0.004	ng/l
95 % concentration	0.003	ng/l
Average concentration	0.000	ng/l
Median concentration	0.000	ng/l
Minimum concentration	0.000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **10% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **10% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.0019	ng/l
95 % concentration	0.0015	ng/l
Average concentration	0.0002	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- Freely dissolved --

Maximum concentration	0.0019	ng/l
95 % concentration	0.0015	ng/l
Average concentration	0.0002	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **5% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **5% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.0084	ng/l
95 % concentration	0.0068	ng/l
Average concentration	0.0009	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- Freely dissolved --

Maximum concentration	0.0084	ng/l
95 % concentration	0.0068	ng/l
Average concentration	0.0009	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **5% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **5% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.0047	ng/l
95 % concentration	0.0038	ng/l
Average concentration	0.0005	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- Freely dissolved --

Maximum concentration	0.0047	ng/l
95 % concentration	0.0038	ng/l
Average concentration	0.0005	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **5% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **5% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --
-- Total conc. --

Maximum concentration	0.0019	ng/l
95 % concentration	0.0015	ng/l
Average concentration	0.0002	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- Freely dissolved --

Maximum concentration	0.0019	ng/l
95 % concentration	0.0015	ng/l
Average concentration	0.0002	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **5% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **5% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --
-- Total conc. --

Maximum concentration	0.0009	ng/l
95 % concentration	0.0008	ng/l
Average concentration	0.0001	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- Freely dissolved --

Maximum concentration	0.0009	ng/l
95 % concentration	0.0008	ng/l
Average concentration	0.0001	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **1% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **1% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.0017	ng/l
95 % concentration	0.0014	ng/l
Average concentration	0.0002	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- Freely dissolved --

Maximum concentration	0.0017	ng/l
95 % concentration	0.0014	ng/l
Average concentration	0.0002	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **1% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **1% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.0009	ng/l
95 % concentration	0.0008	ng/l
Average concentration	0.0001	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- Freely dissolved --

Maximum concentration	0.0009	ng/l
95 % concentration	0.0008	ng/l
Average concentration	0.0001	ng/l
Median concentration	0.0000	ng/l
Minimum concentration	0.0000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **1% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **1% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.00038	ng/l
95 % concentration	0.00030	ng/l
Average concentration	0.00004	ng/l
Median concentration	0.00000	ng/l
Minimum concentration	0.00000	ng/l

-- Freely dissolved --

Maximum concentration	0.00037	ng/l
95 % concentration	0.00030	ng/l
Average concentration	0.00004	ng/l
Median concentration	0.00000	ng/l
Minimum concentration	0.00000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Shipping Lane – **1% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Shipping Lane	
Emission	OECD-EU Shipping Lane **1% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.00019	ng/l
95 % concentration	0.00015	ng/l
Average concentration	0.00002	ng/l
Median concentration	0.00000	ng/l
Minimum concentration	0.00000	ng/l

-- Freely dissolved --

Maximum concentration	0.00019	ng/l
95 % concentration	0.00015	ng/l
Average concentration	0.00002	ng/l
Median concentration	0.00000	ng/l
Minimum concentration	0.00000	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – Freshly painted Cybutryne AFS
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour fresh paint App. Fact.90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- **Harbour** --

-- *Total conc.* --

Maximum concentration	63.70	ng/l
95 % concentration	63.20	ng/l
Average concentration	34.80	ng/l
Median concentration	35.00	ng/l
Minimum concentration	4.10	ng/l

-- Freely dissolved --

Maximum concentration	63.60	ng/l
95 % concentration	63.10	ng/l
Average concentration	34.70	ng/l
Median concentration	34.90	ng/l
Minimum concentration	4.10	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – Freshly painted Cybutryne AFS
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour fresh paint App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration		
95 % concentration	35.10	ng/l
Average concentration	19.30	ng/l
Median concentration	19.40	ng/l
Minimum concentration	2.28	ng/l

-- Freely dissolved --

Maximum concentration	35.40	ng/l
95 % concentration	35.00	ng/l
Average concentration	19.30	ng/l
Median concentration	19.40	ng/l
Minimum concentration	2.28	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – Freshly painted Cybutryne AFS
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour fresh paint App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	14.20	ng/l
95 % concentration	14.00	ng/l
Average concentration	7.73	ng/l
Median concentration	7.77	ng/l
Minimum concentration	0.91	ng/l

-- Freely dissolved --

Maximum concentration	14.10	ng/l
95 % concentration	14.00	ng/l
Average concentration	7.72	ng/l
Median concentration	7.76	ng/l
Minimum concentration	0.91	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – Freshly painted Cybutryne AFS
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour fresh paint App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	7.08	ng/l
95 % concentration	7.02	ng/l
Average concentration	3.87	ng/l
Median concentration	3.89	ng/l
Minimum concentration	0.46	ng/l

-- Freely dissolved --

Maximum concentration	7.07	ng/l
95 % concentration	7.01	ng/l
Average concentration	3.86	ng/l
Median concentration	3.88	ng/l
Minimum concentration	0.46	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – 10% left cybutryne in paint
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 10% left App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	6.37	ng/l
95 % concentration	6.32	ng/l
Average concentration	3.48	ng/l
Median concentration	3.50	ng/l
Minimum concentration	0.41	ng/l

-- Freely dissolved --

Maximum concentration	6.36	ng/l
95 % concentration	6.31	ng/l
Average concentration	3.47	ng/l
Median concentration	3.49	ng/l
Minimum concentration	0.41	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **10% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 10% left App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	3.54	ng/l
95 % concentration	3.51	ng/l
Average concentration	1.93	ng/l
Median concentration	1.94	ng/l
Minimum concentration	0.23	ng/l

-- Freely dissolved --

Maximum concentration	3.54	ng/l
95 % concentration	3.50	ng/l
Average concentration	1.93	ng/l
Median concentration	1.94	ng/l
Minimum concentration	0.23	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **10% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 10% left App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	1.42	ng/l
95 % concentration	1.40	ng/l
Average concentration	0.77	ng/l
Median concentration	0.78	ng/l
Minimum concentration	0.09	ng/l

-- Freely dissolved --

Maximum concentration	1.41	ng/l
95 % concentration	1.40	ng/l
Average concentration	0.77	ng/l
Median concentration	0.78	ng/l
Minimum concentration	0.09	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **10% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 10% left App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.71	ng/l
95 % concentration	0.70	ng/l
Average concentration	0.39	ng/l
Median concentration	0.39	ng/l
Minimum concentration	0.05	ng/l

-- Freely dissolved --

Maximum concentration	0.71	ng/l
95 % concentration	0.70	ng/l
Average concentration	0.39	ng/l
Median concentration	0.39	ng/l
Minimum concentration	0.05	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **5% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 5% left App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	3.19	ng/l
95 % concentration	3.16	ng/l
Average concentration	1.74	ng/l
Median concentration	1.75	ng/l
Minimum concentration	0.21	ng/l

-- Freely dissolved --

Maximum concentration	3.18	ng/l
95 % concentration	3.15	ng/l
Average concentration	1.74	ng/l
Median concentration	1.75	ng/l
Minimum concentration	0.21	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **5% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 5% left App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	1.77	ng/l
95 % concentration	1.76	ng/l
Average concentration	0.97	ng/l
Median concentration	0.97	ng/l
Minimum concentration	0.11	ng/l

-- Freely dissolved --

Maximum concentration	1.77	ng/l
95 % concentration	1.75	ng/l
Average concentration	0.97	ng/l
Median concentration	0.97	ng/l
Minimum concentration	0.11	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **5% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 5% left App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.71	ng/l
95 % concentration	0.70	ng/l
Average concentration	0.39	ng/l
Median concentration	0.39	ng/l
Minimum concentration	0.05	ng/l

-- Freely dissolved --

Maximum concentration	0.71	ng/l
95 % concentration	0.70	ng/l
Average concentration	0.39	ng/l
Median concentration	0.39	ng/l
Minimum concentration	0.05	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **5% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 5% left App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.35	ng/l
95 % concentration	0.35	ng/l
Average concentration	0.19	ng/l
Median concentration	0.19	ng/l
Minimum concentration	0.02	ng/l

-- Freely dissolved --

Maximum concentration	0.35	ng/l
95 % concentration	0.35	ng/l
Average concentration	0.19	ng/l
Median concentration	0.19	ng/l
Minimum concentration	0.02	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **1% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 1% left App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.64	ng/l
95 % concentration	0.63	ng/l
Average concentration	0.35	ng/l
Median concentration	0.35	ng/l
Minimum concentration	0.04	ng/l

-- Freely dissolved --

Maximum concentration	0.64	ng/l
95 % concentration	0.63	ng/l
Average concentration	0.35	ng/l
Median concentration	0.35	ng/l
Minimum concentration	0.04	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **1% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 1% left App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.35	ng/l
95 % concentration	0.35	ng/l
Average concentration	0.19	ng/l
Median concentration	0.19	ng/l
Minimum concentration	0.02	ng/l

-- Freely dissolved --

Maximum concentration	0.35	ng/l
95 % concentration	0.35	ng/l
Average concentration	0.19	ng/l
Median concentration	0.19	ng/l
Minimum concentration	0.02	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **1% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 1% left App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.14	ng/l
95 % concentration	0.14	ng/l
Average concentration	0.08	ng/l
Median concentration	0.08	ng/l
Minimum concentration	0.01	ng/l

-- Freely dissolved --

Maximum concentration	0.14	ng/l
95 % concentration	0.14	ng/l
Average concentration	0.08	ng/l
Median concentration	0.08	ng/l
Minimum concentration	0.01	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Commercial Harbour – **1% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Commercial Harbour	
Emission	OECD-EU Commercial Harbour 1% left App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.07	ng/l
95 % concentration	0.07	ng/l
Average concentration	0.04	ng/l
Median concentration	0.04	ng/l
Minimum concentration	0.00	ng/l

-- Freely dissolved --

Maximum concentration	0.07	ng/l
95 % concentration	0.07	ng/l
Average concentration	0.04	ng/l
Median concentration	0.04	ng/l
Minimum concentration	0.00	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276)– Freshly painted Cybutryne AFS		
Application Factor	90% of the ships		
MAMPEC Version	3.1.0.5		

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) Freshly painted Cybutryne AFS App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	269	ng/l
95 % concentration	269	ng/l
Average concentration	183	ng/l
Median concentration	204	ng/l
Minimum concentration	31	ng/l

-- Freely dissolved --

Maximum concentration	269	ng/l
95 % concentration	269	ng/l
Average concentration	183	ng/l
Median concentration	204	ng/l
Minimum concentration	31	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276)– Freshly painted Cybutryne AFS
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) Freshly painted Cybutryne AFS App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	150	ng/l
95 % concentration	150	ng/l
Average concentration	102	ng/l
Median concentration	113	ng/l
Minimum concentration	17	ng/l

-- Freely dissolved --

Maximum concentration	149	ng/l
95 % concentration	149	ng/l
Average concentration	101	ng/l
Median concentration	113	ng/l
Minimum concentration	17	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276)– Freshly painted Cybutryne AFS
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) Freshly painted Cybutryne AFS App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	60	ng/l
95 % concentration	60	ng/l
Average concentration	41	ng/l
Median concentration	45	ng/l
Minimum concentration	7	ng/l

-- Freely dissolved --

Maximum concentration	60	ng/l
95 % concentration	60	ng/l
Average concentration	41	ng/l
Median concentration	45	ng/l
Minimum concentration	7	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276)– Freshly painted Cybutryne AFS
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) Freshly painted Cybutryne AFS App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	30	ng/l
95 % concentration	30	ng/l
Average concentration	20	ng/l
Median concentration	23	ng/l
Minimum concentration	3	ng/l

-- Freely dissolved --

Maximum concentration	30	ng/l
95 % concentration	30	ng/l
Average concentration	20	ng/l
Median concentration	23	ng/l
Minimum concentration	3	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **10% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **10% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	27	ng/l
95 % concentration	27	ng/l
Average concentration	18	ng/l
Median concentration	20	ng/l
Minimum concentration	3	ng/l

-- Freely dissolved --

Maximum concentration	27	ng/l
95 % concentration	27	ng/l
Average concentration	18	ng/l
Median concentration	20	ng/l
Minimum concentration	3	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **10% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **10% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	15	ng/l
95 % concentration	15	ng/l
Average concentration	10	ng/l
Median concentration	11	ng/l
Minimum concentration	2	ng/l

-- Freely dissolved --

Maximum concentration	15	ng/l
95 % concentration	15	ng/l
Average concentration	10	ng/l
Median concentration	11	ng/l
Minimum concentration	2	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **10% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **10% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	6	ng/l
95 % concentration	6	ng/l
Average concentration	4	ng/l
Median concentration	5	ng/l
Minimum concentration	1	ng/l

-- Freely dissolved --

Maximum concentration	6	ng/l
95 % concentration	6	ng/l
Average concentration	4	ng/l
Median concentration	5	ng/l
Minimum concentration	1	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **10% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **10% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	3	ng/l
95 % concentration	3	ng/l
Average concentration	2	ng/l
Median concentration	2	ng/l
Minimum concentration	0	ng/l

-- Freely dissolved --

Maximum concentration	3	ng/l
95 % concentration	3	ng/l
Average concentration	2	ng/l
Median concentration	2	ng/l
Minimum concentration	0	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **5% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **5% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	14	ng/l
95 % concentration	14	ng/l
Average concentration	9	ng/l
Median concentration	10	ng/l
Minimum concentration	2	ng/l

-- Freely dissolved --

Maximum concentration	14	ng/l
95 % concentration	14	ng/l
Average concentration	9	ng/l
Median concentration	10	ng/l
Minimum concentration	2	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **5% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **5% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	8	ng/l
95 % concentration	8	ng/l
Average concentration	5	ng/l
Median concentration	6	ng/l
Minimum concentration	1	ng/l

-- Freely dissolved --

Maximum concentration	8	ng/l
95 % concentration	8	ng/l
Average concentration	5	ng/l
Median concentration	6	ng/l
Minimum concentration	1	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **5% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **5% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	3	ng/l
95 % concentration	3	ng/l
Average concentration	2	ng/l
Median concentration	2	ng/l
Minimum concentration	0	ng/l

-- Freely dissolved --

Maximum concentration	3	ng/l
95 % concentration	3	ng/l
Average concentration	2	ng/l
Median concentration	2	ng/l
Minimum concentration	0	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **5% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **5% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	1.5	ng/l
95 % concentration	1.5	ng/l
Average concentration	1.0	ng/l
Median concentration	1.1	ng/l
Minimum concentration	0.2	ng/l

-- Freely dissolved --

Maximum concentration	1.5	ng/l
95 % concentration	1.5	ng/l
Average concentration	1.0	ng/l
Median concentration	1.1	ng/l
Minimum concentration	0.2	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **1% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **1% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	2.7	ng/l
95 % concentration	2.7	ng/l
Average concentration	1.9	ng/l
Median concentration	2.1	ng/l
Minimum concentration	0.3	ng/l

-- Freely dissolved --

Maximum concentration	2.7	ng/l
95 % concentration	2.7	ng/l
Average concentration	1.8	ng/l
Median concentration	2.1	ng/l
Minimum concentration	0.3	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **1% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **1% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	1.5	ng/l
95 % concentration	1.5	ng/l
Average concentration	1.0	ng/l
Median concentration	1.1	ng/l
Minimum concentration	0.2	ng/l

-- Freely dissolved --

Maximum concentration	1.5	ng/l
95 % concentration	1.5	ng/l
Average concentration	1.0	ng/l
Median concentration	1.1	ng/l
Minimum concentration	0.2	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **1% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **1% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.6	ng/l
95 % concentration	0.6	ng/l
Average concentration	0.4	ng/l
Median concentration	0.5	ng/l
Minimum concentration	0.1	ng/l

-- Freely dissolved --

Maximum concentration	0.6	ng/l
95 % concentration	0.6	ng/l
Average concentration	0.4	ng/l
Median concentration	0.5	ng/l
Minimum concentration	0.1	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina (276) – **1% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina (276)	
Emission	OECD-EU Marina (276) **1% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	0.3	ng/l
95 % concentration	0.3	ng/l
Average concentration	0.2	ng/l
Median concentration	0.2	ng/l
Minimum concentration	0.0	ng/l

-- Freely dissolved --

Maximum concentration	0.3	ng/l
95 % concentration	0.3	ng/l
Average concentration	0.2	ng/l
Median concentration	0.2	ng/l
Minimum concentration	0.0	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – Freshly painted Cybutryne AFS
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina Freshly painted Cybutryne AFS App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	488	ng/l
95 % concentration	488	ng/l
Average concentration	331	ng/l
Median concentration	369	ng/l
Minimum concentration	56	ng/l

-- Freely dissolved --

Maximum concentration	487	ng/l
95 % concentration	487	ng/l
Average concentration	331	ng/l
Median concentration	369	ng/l
Minimum concentration	56	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – Freshly painted Cybutryne AFS
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina Freshly painted Cybutryne AFS App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	271	ng/l
95 % concentration	271	ng/l
Average concentration	184	ng/l
Median concentration	205	ng/l
Minimum concentration	31	ng/l

-- Freely dissolved --

Maximum concentration	271	ng/l
95 % concentration	271	ng/l
Average concentration	184	ng/l
Median concentration	205	ng/l
Minimum concentration	31	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – Freshly painted Cybutryne AFS	
Application Factor	20% of the ships	
MAMPEC Version	3.1.0.5	

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina Freshly painted Cybutryne AFS App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	108	ng/l
95 % concentration	108	ng/l
Average concentration	74	ng/l
Median concentration	82	ng/l
Minimum concentration	12	ng/l

-- Freely dissolved --

Maximum concentration	108	ng/l
95 % concentration	108	ng/l
Average concentration	74	ng/l
Median concentration	82	ng/l
Minimum concentration	12	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – Freshly painted Cybutryne AFS	
Application Factor	10% of the ships	
MAMPEC Version	3.1.0.5	

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina Freshly painted Cybutryne AFS App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	54	ng/l
95 % concentration	54	ng/l
Average concentration	37	ng/l
Median concentration	41	ng/l
Minimum concentration	6	ng/l

-- Freely dissolved --

Maximum concentration	54	ng/l
95 % concentration	54	ng/l
Average concentration	37	ng/l
Median concentration	41	ng/l
Minimum concentration	6	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **10% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **10% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --
-- Total conc. --

Maximum concentration	49	ng/l
95 % concentration	49	ng/l
Average concentration	33	ng/l
Median concentration	37	ng/l
Minimum concentration	6	ng/l

-- Freely dissolved --

Maximum concentration	49	ng/l
95 % concentration	49	ng/l
Average concentration	33	ng/l
Median concentration	37	ng/l
Minimum concentration	6	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **10% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **10% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --
-- Total conc. --

Maximum concentration	27	ng/l
95 % concentration	27	ng/l
Average concentration	18	ng/l
Median concentration	21	ng/l
Minimum concentration	3	ng/l

-- Freely dissolved --

Maximum concentration	27	ng/l
95 % concentration	27	ng/l
Average concentration	18	ng/l
Median concentration	21	ng/l
Minimum concentration	3	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **10% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **10% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --
-- Total conc. --

Maximum concentration	11	ng/l
95 % concentration	11	ng/l
Average concentration	7	ng/l
Median concentration	8	ng/l
Minimum concentration	1	ng/l

-- Freely dissolved --

Maximum concentration	11	ng/l
95 % concentration	11	ng/l
Average concentration	7	ng/l
Median concentration	8	ng/l
Minimum concentration	1	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **10% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **10% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --
-- Total conc. --

Maximum concentration	5	ng/l
95 % concentration	5	ng/l
Average concentration	4	ng/l
Median concentration	4	ng/l
Minimum concentration	1	ng/l

-- Freely dissolved --

Maximum concentration	5	ng/l
95 % concentration	5	ng/l
Average concentration	4	ng/l
Median concentration	4	ng/l
Minimum concentration	1	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **5% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **5% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	25	ng/l
95 % concentration	25	ng/l
Average concentration	17	ng/l
Median concentration	19	ng/l
Minimum concentration	3	ng/l

-- Freely dissolved --

Maximum concentration	24	ng/l
95 % concentration	24	ng/l
Average concentration	17	ng/l
Median concentration	19	ng/l
Minimum concentration	3	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **5% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **5% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	14	ng/l
95 % concentration	14	ng/l
Average concentration	9	ng/l
Median concentration	10	ng/l
Minimum concentration	2	ng/l

-- Freely dissolved --

Maximum concentration	14	ng/l
95 % concentration	14	ng/l
Average concentration	9	ng/l
Median concentration	10	ng/l
Minimum concentration	2	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **5% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **5% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	5	ng/l
95 % concentration	5	ng/l
Average concentration	4	ng/l
Median concentration	4	ng/l
Minimum concentration	1	ng/l

-- Freely dissolved --

Maximum concentration	5	ng/l
95 % concentration	5	ng/l
Average concentration	4	ng/l
Median concentration	4	ng/l
Minimum concentration	1	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **5% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **5% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	2.7	ng/l
95 % concentration	2.7	ng/l
Average concentration	1.9	ng/l
Median concentration	2.1	ng/l
Minimum concentration	0.3	ng/l

-- Freely dissolved --

Maximum concentration	2.7	ng/l
95 % concentration	2.7	ng/l
Average concentration	1.8	ng/l
Median concentration	2.1	ng/l
Minimum concentration	0.3	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **1% left cybutryne in paint**
Application Factor	90% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **1% left cybutryne in paint** App. Fact. 90%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	4.9	ng/l
95 % concentration	4.9	ng/l
Average concentration	3.3	ng/l
Median concentration	3.7	ng/l
Minimum concentration	0.6	ng/l

-- Freely dissolved --

Maximum concentration	4.9	ng/l
95 % concentration	4.9	ng/l
Average concentration	3.3	ng/l
Median concentration	3.7	ng/l
Minimum concentration	0.6	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **1% left cybutryne in paint**
Application Factor	50% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **1% left cybutryne in paint** App. Fact. 50%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	2.7	ng/l
95 % concentration	2.7	ng/l
Average concentration	1.9	ng/l
Median concentration	2.1	ng/l
Minimum concentration	0.3	ng/l

-- Freely dissolved --

Maximum concentration	2.7	ng/l
95 % concentration	2.7	ng/l
Average concentration	1.9	ng/l
Median concentration	2.1	ng/l
Minimum concentration	0.3	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **1% left cybutryne in paint**
Application Factor	20% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **1% left cybutryne in paint** App. Fact. 20%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

-- Harbour --

-- Total conc. --

Maximum concentration	1.1	ng/l
95 % concentration	1.1	ng/l
Average concentration	0.7	ng/l
Median concentration	0.8	ng/l
Minimum concentration	0.1	ng/l

-- Freely dissolved --

Maximum concentration	1.1	ng/l
95 % concentration	1.1	ng/l
Average concentration	0.7	ng/l
Median concentration	0.8	ng/l
Minimum concentration	0.1	ng/l

-- **MAMPEC 3 - Result Sheet** --

Run name	OECD-EU Marina – **1% left cybutryne in paint**
Application Factor	10% of the ships
MAMPEC Version	3.1.0.5

-- *Input* --

Environment	OECD-EU Marina	
Emission	OECD-EU Marina **1% left cybutryne in paint** App. Fact. 10%	
Compound	Irgarol (example)	
Background conc.	0.00E+000	g/d
Using hydrodynamics v2.5	False	
Using hydrodynamics v3.1	True	

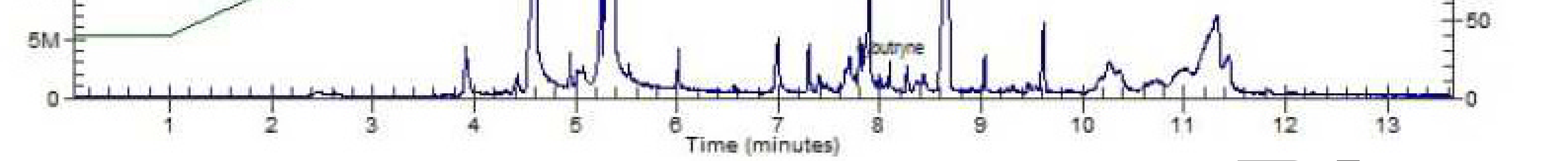
-- Harbour --

-- Total conc. --

Maximum concentration	0.5	ng/l
95 % concentration	0.5	ng/l
Average concentration	0.4	ng/l
Median concentration	0.4	ng/l
Minimum concentration	0.1	ng/l

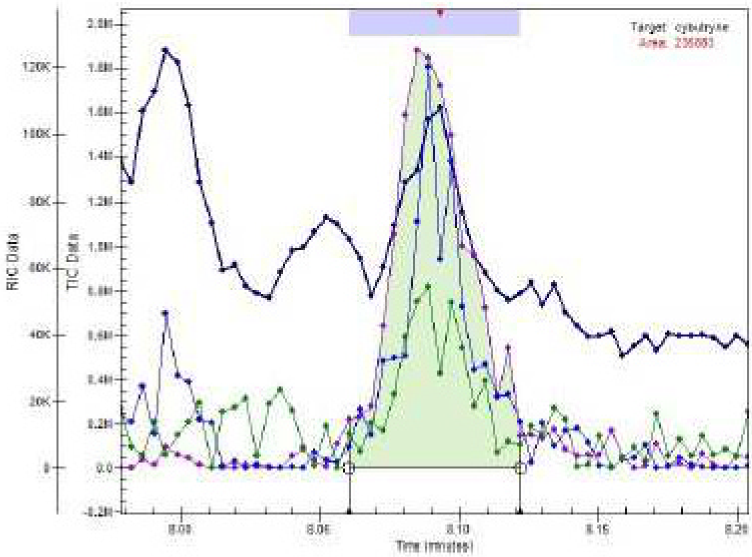
-- Freely dissolved --

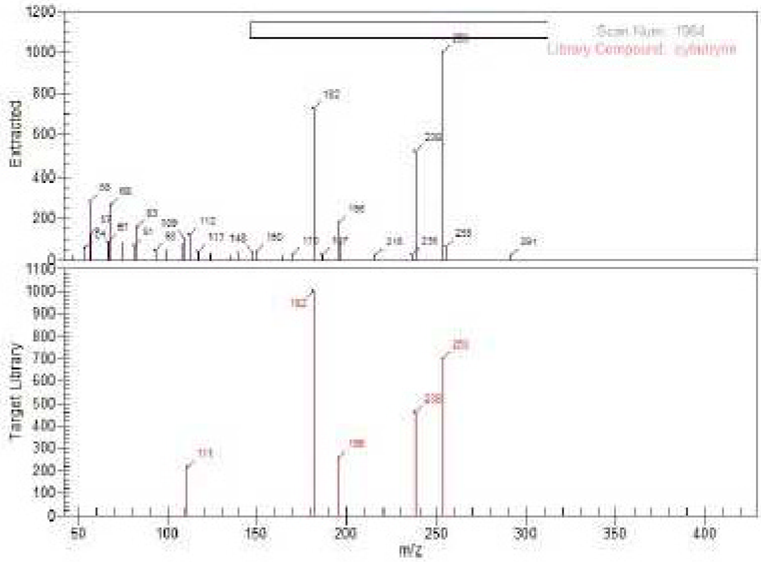
Maximum concentration	0.5	ng/l
95 % concentration	0.5	ng/l
Average concentration	0.4	ng/l
Median concentration	0.4	ng/l
Minimum concentration	0.1	ng/l



Scan Number: 1964
Ret. Time: 8.09

GMF	CAS #	Compound
95	28159-98-0	cybutryne





APPENDIX 2 TO

Study to support the amendment of the "Guidelines for brief sampling of anti-fouling systems on ships" to include controls on Cybutryne

Analytical method for determination of Cybutryne in AF paint

RISE REPORT

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REPORT

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Date
2021-04-20

Reference
2P09945-01

European Maritime Safety Agency
Praça Europa 4
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Analytical method for determination of Cybutryne in AF paint

Aim

To develop and validate an analytical chemical method for determination of the biocide Cybutryne in anti-fouling paint. The method is intended to be used in conjunction with the sampling method "Guidelines for Brief Sampling of Anti-Fouling Systems on Ships (Resolution MEPC.104(49) Guidelines for brief sampling on anti-fouling systems on ships" and adapted on paints used for both leisure boats and commercial vessels.

Paints and chemicals used

Akzo Nobel -International- Interspeed 5617 Red

Akzo Nobel -International- Interspeed 5617 Black

Akzo Nobel -International- Interspeed 5992 Black

Hempel Mille Xtra 71100

Hempel Antifouling Olympic 86951 Blue

Boero Magellan 630 Extra

Cybutryn (CAS 28159-98-0), trade name Irgarol 10510, supplier Merck.

Ametryn (CAS 834-12-8), supplier Merck.

Solvent supplier Merck.

Analytical method- description

Sampling

A sample taken by the "Resolution MEPC.104(49)" procedure result in an abrasive pad with paint adhered on to it. The amount of paint is determined by weighing and this is included in the sampling procedure. This mass is used as input for the determination of the Cybutryne concentration.

Extraction

The sampling pad with paint is folded or cut so it fits into a sample tube made of polypropylene or glass with a suitable cap. The sample is then extracted with 10 ml of

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etyhlacetate with an added internal standard (ametryn, approx. 4 µg/ml) using the following procedure:

1) vortex the sample for 5 seconds

2) extract the sample using an ultrasonic bath for 15 minutes

3) centrifuge the extracted samples at 6000 relative centrifugal force (RCF) for 5 minutes. The upper solvent phase is then transferred to a vial for further separation and detection.

Separation and detection using gaschromatography- masspectrometry (GC/MS)

Mass calibration, use and maintenance of the GC/MS system is performed according to ISO17025 laboratory practice.

A splitless injection of 1 µl etylacetate extract is performed at 300 °C using a spitless time of 30 seconds. The separating column should be a 30 meter ; 0,25 mm wide, 25 µm thick 5% phenyl 95 % methyl phase operated with helium or hydrogen as the carrier gas. A typical temperature program for the separation is 35 °C for 5 min, ramp to 325 C at 10 °C/min. Detection of the baseline separated analyte and internal standard is performed by the MS operating in Selected Ion Mode (SIM) using the m/z 253, 238 and 183 ions for Cybutyn and m/z 227, 212 and 185 ions for Ametryn.

Calculation and reporting

Calculation of the Cybutryn concentration in the paint sample is performed using the internal standard approach commonly used throughout the analytical chemical community under conditions (within linear response range of the instrument, suitable detector sampling frequency, etc) which result in an expanded (U, k=2, 95 % confidence level) measurement uncertainty of the analytical procedure (without sampling uncertainty) of 25%.

Supporting information

Paint selection

Paint with cybutryn content is forbidden in Europe. Therefore, for experimental uses, commonly used paints (list above) was added pure cybutryn to mimic cybutryn containing paint found overseas. A number of different paints, manufactures and binders (including both ablative rosin based and self polishing (SPC) binders) was chosen to represent the market.

During method development and validation of the method the following results have been collected.

Selection of an internal standard

The optimal internal standard with masspectrometric detection is the isotopically (deuterium) labelled cybutryn. This substance is available on the market, but at a very high price. Therefore, another triazine with the same secondary amines and sulfur chemistries as cybutryn was selected, Ametryn. This substance is readily available at a reasonable price, and chemically very similar.

Solubility

The solubility of both ametryn and cybutryn was determined to be above 20 mg/ml in acetone, ethylacetate, dichloromethane and toluene. The solubility was below 20 mg/ml for water, iso-propanol and pentane.

Selectivity between paint binder and analyte

Extractions of dried paint (Hempel Mille Xtra and International Interspeed 5617 Red) was performed according to the stated procedure above and evaluated with respect to the amount of binder and other interfering substances that was eluting close to the analyte or was very abundant so the short/mid term performance of the GC/MS instrument could be affected.

It was shown that all solvents with good solubility for cybutryn had similar extraction also of the matrix.

Selection of solvent

Based on the solubility and selectivity of solvents tested the final solvent (out of four), was selected based on its safety, health and environmental (SHE) aspects. The selected solvent is ethylacetate.

Extraction efficiency

Duplicate samples of all six paints containing 2 weight-% (wet basis) cybutryn was sampled with an abrasive pad and extracted according to the stated procedure three consecutive times and analysed using the state GC/MS methodology.

The extraction efficiency was calculated and is listed below and deemed fully acceptable as the recovery for an analytical method. The average extraction efficiency was 96%.

Paint name	Extraction efficiency (%)
Akzo Nobel -International- Interspeed 5617 Red Subsample A	93
Akzo Nobel -International- Interspeed 5617 Red Subsample A	97
Akzo Nobel -International- Interspeed 5617 Red Average	95
Akzo Nobel -International- Interspeed 5617 Black Subsample A	98
Akzo Nobel -International- Interspeed 5617 Black Subsample B	97
Akzo Nobel -International- Interspeed 5617 Black Average	97
Akzo Nobel -International- Interspeed 5992 Black Subsample A	96
Akzo Nobel -International- Interspeed 5992 Black Subsample B	98
Akzo Nobel -International- Interspeed 5992 Black Average	97
Hempel Mille Xtra 71100 Subsample A	95
Hempel Mille Xtra 71100 Subsample B	97
Hempel Mille Xtra 71100 Average	96
Hempel Antifouling Olympic 86951 Blue Subsample A	97
Hempel Antifouling Olympic 86951 Blue Subsample B	97
Hempel Antifouling Olympic 86951 Blue Average	97
Boero Magellan 630 Extra Subsample A	87
Boero Magellan 630 Extra Subsample B	95
Boero Magellan 630 Extra Average	91
Average of all paints	96

Limit of quantification

Duplicate samples of two dried paints (Boero Magellan 630 Extra (SPC mechanism) and Akzo Nobel -International- Interspeed 5617 Red (ablative mechanism)) containing 0,02 weight-% cybutryn (wet basis) was sampled with an abrasive pad and extracted according to the stated procedure followed by GC/MS analysis using the stated procedure. The RMS signal (s/n) to noise was determined to be 200. The average RMS signal to noise at the 0,02 weight-% level cybutryn is mean that it is possible to perform analytical work at least one order of magnitude below, at 0,002 % cybutryn. The methodology will be able to perform cybutryn quantifications at the suggested threshold of 0,1 % w/w (1000 mg/kg) (see MAMPEC calculation in separate documentation) and two orders of magnitude lower.

Measurement uncertainty

As an intermediate estimation of the methods measurement uncertainty, dry paint sampled (with 2% cybutryn) were sampled and analysed in duplicate but reported as single sample determinations. All paints types, above mentioned, were used. The precision was calculated as the relative standard deviation of the repeatability (rsd r) and the trueness is based on the recovery. Rsd r was determined to be 14% and the Bias to be 3%. The expanded measurement uncertainty (U) was calculated as two times (k=2) the measurement uncertainty (u), corresponding to 95% a confidence interval, and resulted in 25%.
This correspond to a “tolerance range” of 0,025% (250 mg/kg) for the method.

Feasibility to simultaneously determine TBT, tributultin

Two general procedures for determination of TBT in paint is suggested in the Resolution MEPC.104(49). These methods are also based on extraction a quantification with GC/MS. However, they include a derivatization step using a Grignard reagent. To test if the Cybutryne and TBT methods could be compatible, experiments were performed by adding Cybutrune to general methods for TBT derivatization with Grignard reagents and by heating Cyburyne in sodium hydroxide solution and determine its stability. The Grignard experiment was performed in toluene and ethyl magnesium bromide. The Sodium hydroxide experiment was performed in 2 M NaOH overnight. Cybutryne was shown to be stable in both the Grignard and sodium hydroxide experiments (T-test, 95%).

This suggest that the above described Cybutryne method and the existing TBT-methods are compatible. However, the selection of solvent has to be adjusted in the Cybutryne method to a solvent inert to the Grignard reagent. Toluene is the proposed alternative solvent, which also has high solubility of Cybutryne.

RISE Research Institutes of Sweden AB
Chemistry, Biomaterials and Textiles - Chemical Problem Solving

Performed by

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Date & Time: 2021-04-21 13:27:37 +02:00
Anders Lorén

Examined by

Signed by: Maciej Wysocki
Reason: Jag är författare till det här dokumentet
Date & Time: 2021-04-21 12:36:03 +02:00
Maciej Wysocki

Result File:	D:\510-00217\20200714-217\20200714\PSI, 0% paint_20200714_195158_30
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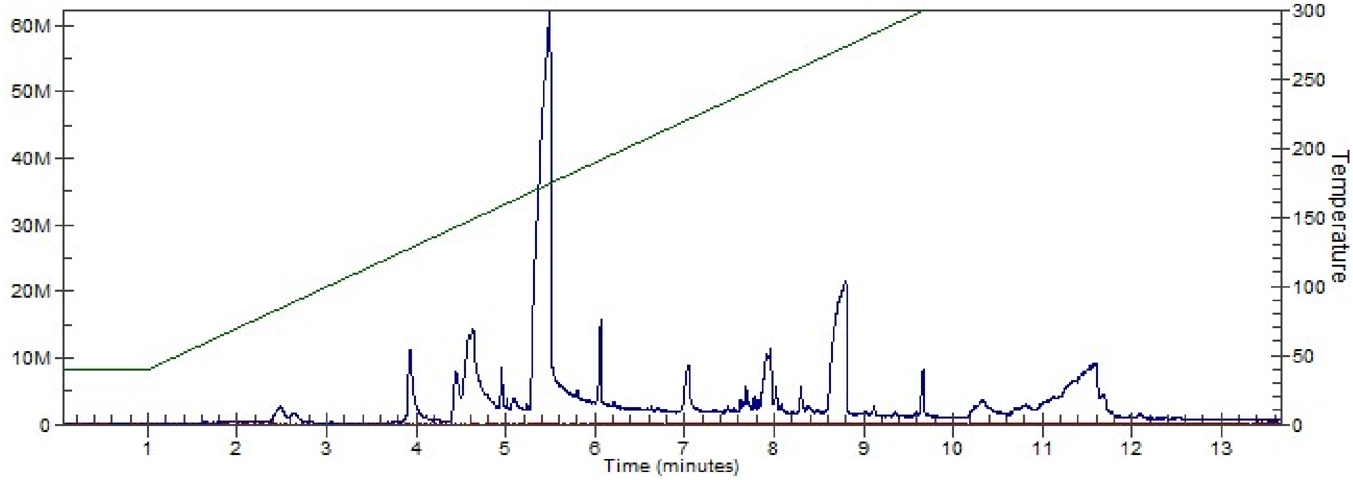

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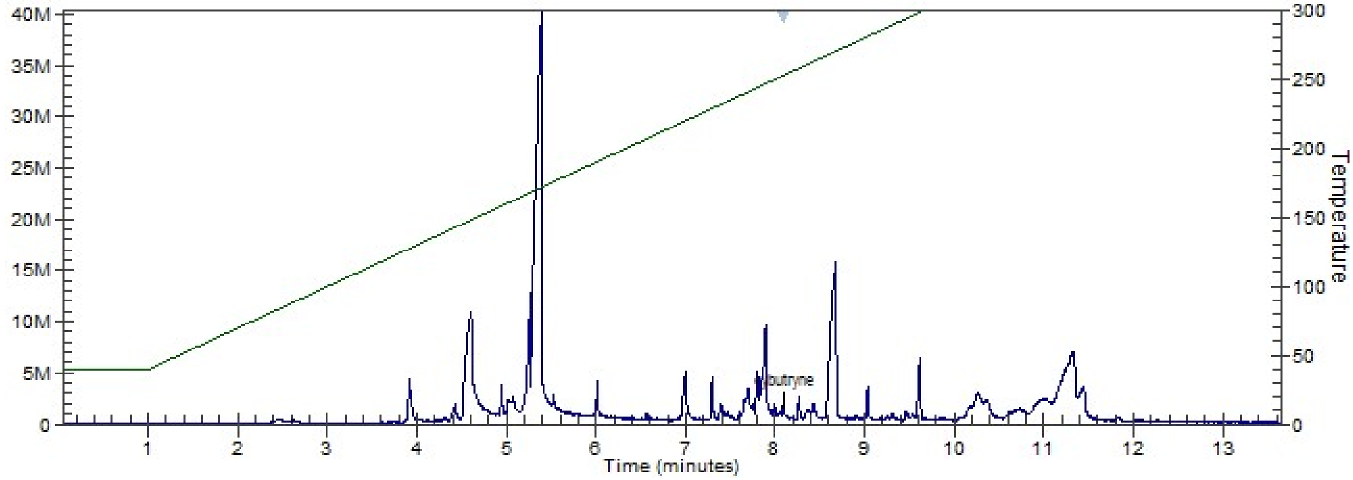

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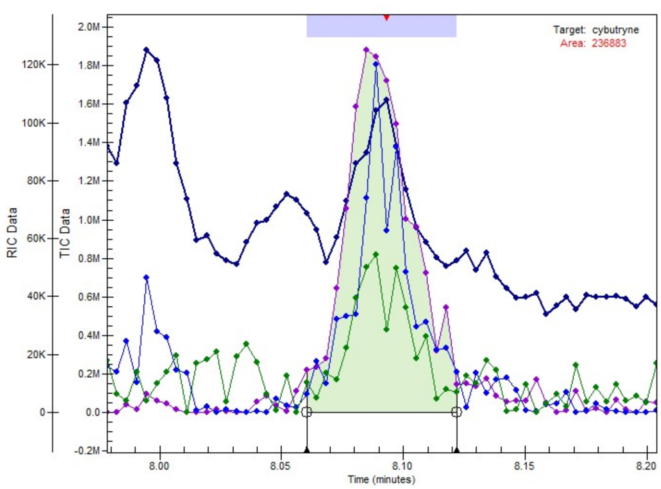
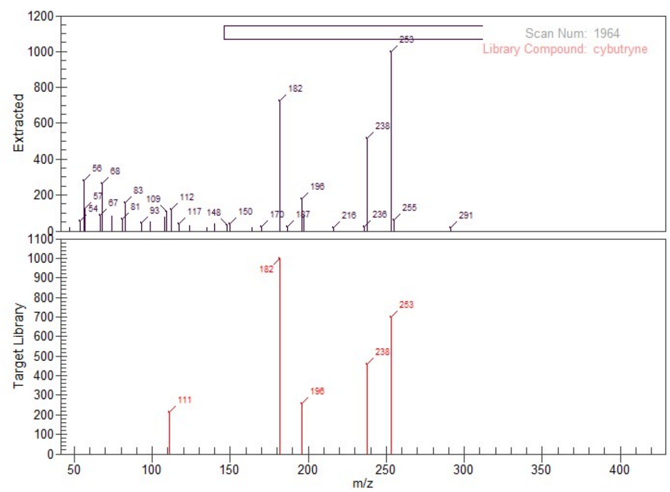
Ret. Time: 8.09

GMF	CAS #	Compound
95	28159-98-0	**cybutryne**





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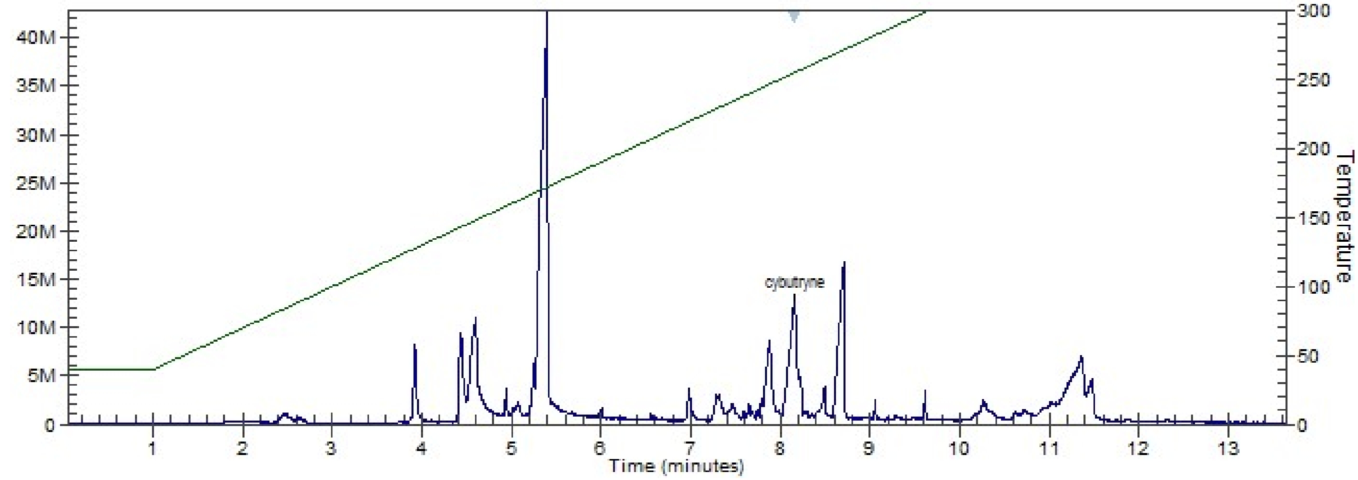
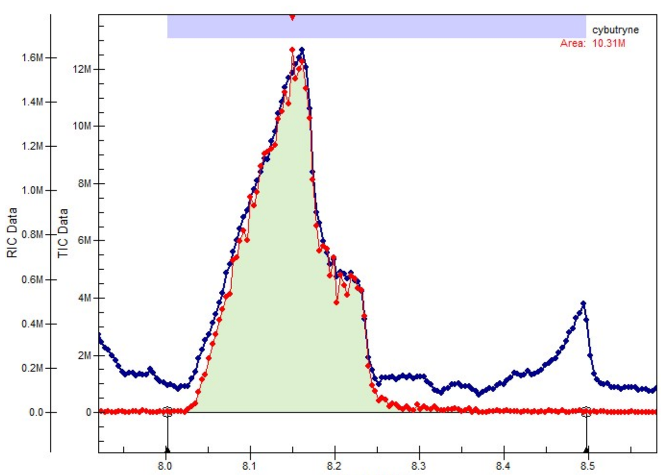
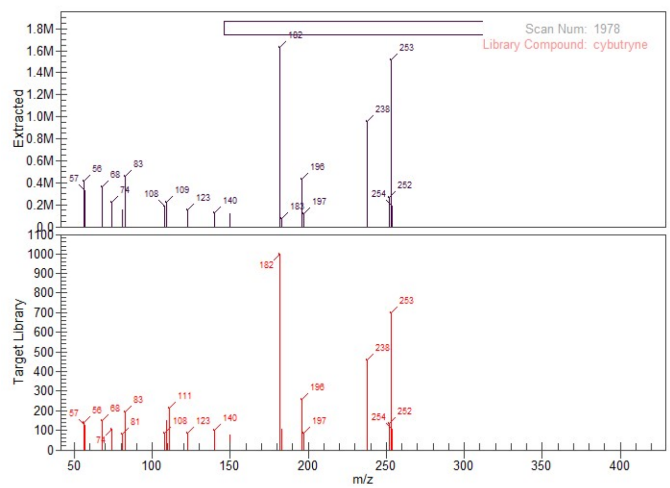
Method File: PSI method for paint
Result Date: 2020-07-14 21:05:59
Instrument: G510-00217 G510 510-00217 v1.5
Total number of targets: 1



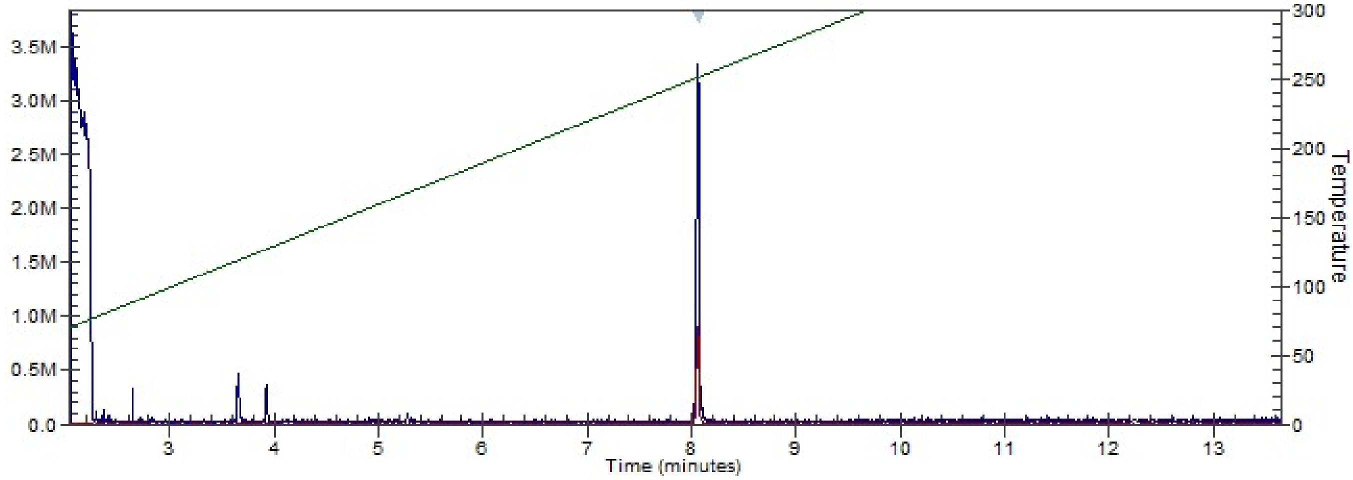
Scan Number: 1978
Ret. Time: 8.15

GMF	CAS #	Compound
95	28159-98-0	cybutryne



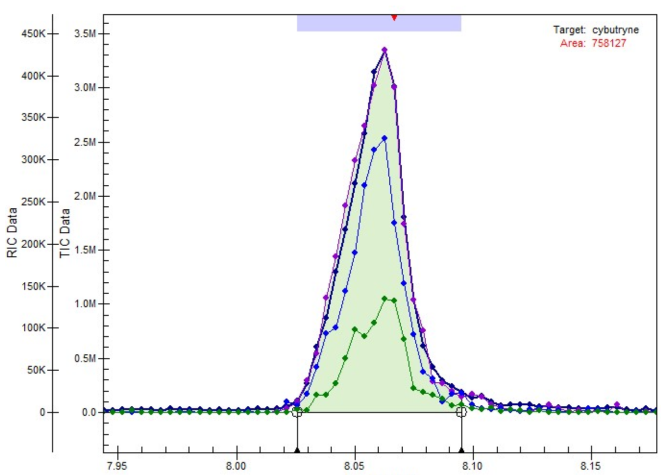


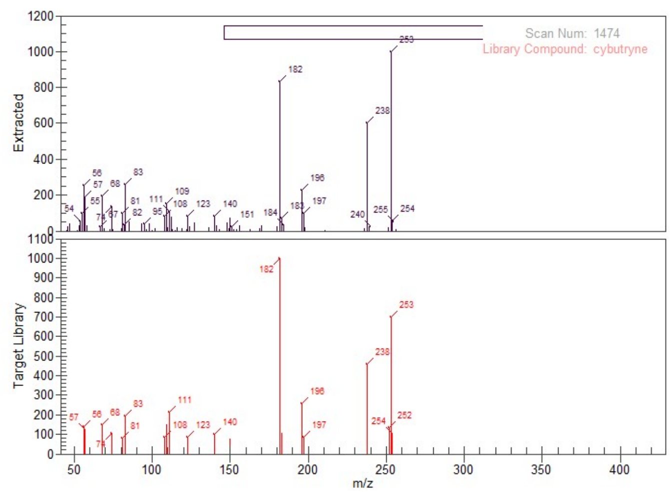
Result File: D:\510-00217\20200714-217\20200714\100 ng cybutryne, splitless, filament B_20200714_160549_18
Method File: PSI method for paint
Result Date: 2020-07-14 16:06:26
Instrument: G510-00217 G510 510-00217 v1.5
Total number of targets: 1



Scan Number: 1474
Ret. Time: 8.06

GMF	CAS #	Compound
93	28159-98-0	cybutryne





Study to support the amendment of the "Guidelines for brief sampling of anti-fouling systems on ships" to include controls on Cybutryne

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