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Origine:	Secrétariat général du Conseil
Destinataire:	Comité des représentants permanents (1re partie)
Nº doc. préc.:	15234/2/21 REV 2
Objet:	Projet de soumission conjointe des États membres et de la Commission à la 9e session du Sous-comité de la prévention de la pollution et de l'intervention de l'Organisation maritime internationale informant des modifications suggérées aux trois directives associées à la Convention internationale sur le contrôle des systèmes antisalissure nuisibles sur les navires (AFS) – *Approbation*

I. INTRODUCTION

1. Le 20 décembre 2021, la Commission a transmis au Conseil un document informel contenant un projet de soumission à la 9e session du Sous-comité de la prévention de la pollution et de l'intervention (PPR 9) de l'Organisation maritime internationale (OMI), informant des modifications suggérées aux trois directives associées à la Convention internationale sur le contrôle des systèmes antisalissure nuisibles sur les navires (Convention AFS) suite à l'adoption des mesures de contrôle de la substance cybutryne par l'OMI. Le délai pour transmettre la soumission au secrétariat de l'OMI est le 28 janvier 2022.

2. Plusieurs études scientifiques ont démontré que la cybutryne est toxique, persistante et nuisible pour le milieu marin. Dans l'Union, la mise à disposition sur le marché et l'utilisation des peintures antisalissure contenant de la cybutryne sont interdites[1].

3. À sa soixante-seizième session, tenue en juin 2021, le Comité de la protection du milieu marin de l'OMI a adopté des amendements à l'Annexe 1 de la Convention AFS afin d'y inclure des mesures de contrôle sur la cybutryne. Suite à cette adoption, les États membres et la Commission ont proposé, en décembre 2021, de réviser le texte de trois directives distinctes, à savoir les Directives pour un bref échantillonnage des systèmes antisalissure sur les navires (résolution MEPC.104(49)), les Directives de 2010 pour les visites et la délivrance des certificats concernant les systèmes antisalissure sur les navires (résolution MEPC.195(61)) et les Directives de 2011 pour l'inspection des systèmes antisalissure sur les navires (résolution MEPC.208(62))[2].

4. L'objectif de la présente soumission est d'expliquer au PPR 9 les modifications proposées dans le document PPR 9/6 soumis par les États membres et la Commission.

II. TRAVAIL DES INSTANCES PREPARATOIRES DU CONSEIL

5. Le groupe "Transports maritimes" a examiné le projet de soumission lors de ses réunions du 7 et du 14 janvier 2022. À l'issue de cette dernière réunion, des modifications ont été apportées au texte afin d'obtenir un consensus; ces modifications figurent dans la version finale en annexe.

6. Le groupe a convenu que la présidence pourrait indiquer au secrétariat de l'OMI, lors de la transmission de la soumission, que celle-ci peut être rendue publique avant le PPR 9.

7. La question de savoir qui devrait transmettre le projet de soumission reste toutefois non résolue. La Commission considère que la soumission devrait être transmise par "la Commission européenne au nom de l'Union européenne", tandis que les États membres sont de l'avis qu'elle devrait être transmise au nom des États membres et de la Commission européenne.

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[1] Décision d'exécution (UE) 2016/107 de la Commission du 27 janvier 2016 n'approuvant pas la cybutryne en tant que substance active existante destinée à être utilisée dans des produits biocides du type de produits 21 (JO L 21, 28.1.2016, p. 81).

[2] Document 14990/21 (document OMI : PPR 9/6).

8. Vu l'importance et l'urgence de la soumission, le groupe a décidé de suggérer qu'elle soit transmise au nom des États membres et de la Commission européenne, en prenant bonne note de la position de la Commission.

III. CONCLUSION

9. Compte tenu de ce qui précède, le Comité des représentants permanents est invité à approuver le projet de soumission en vue de sa transmission par la présidence à l'OMI le 28 janvier 2022 au plus tard.

SUB-COMMITTEE ON POLLUTION PREVENTION AND RESPONSE
9th session
Agenda item 6

PPR 9/INF.xx
XX XXXX 2022
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REVISION OF GUIDELINES ASSOCIATED WITH THE AFS CONVENTION AS A CONSEQUENCE OF THE INTRODUCTION OF CONTROLS ON CYBUTRYNE

Information on possible revision of the *Guidelines for brief sampling of anti-fouling systems on ships,* the *Guidelines for survey and certification of anti-fouling systems on ships* and the *Guidelines for inspection of anti-fouling systems on ships*

Submitted by Austria, Belgium, Bulgaria, Croatia, Cyprus, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden and the European Commission

SUMMARY

Executive summary:	This document provides information on suggested modifications to the three guidelines associated with the AFS Convention as a consequence of the introduction of controls on cybutryne: the guidelines for brief sampling of anti-fouling systems on ships (resolution MEPC.104(49)), the 2010 guidelines for survey and certification of anti-fouling systems on ships (resolution MEPC.195(61)) and the 2011 guidelines for inspection of anti-fouling systems on ships (resolution MEPC.208(62)).
Strategic direction, if applicable:	2
Output:	2.19
Action to be taken:	Paragraph 7
Related documents:	Resolution MEPC.104(49), Resolution MEPC.195(61), Resolution MEPC.208(62), PPR 6/INF.7, PPR 6/20, PPR 7/6/1, PPR 7/22, MEPC 75/18 (paragraph 10.17 and Annex 7), MEPC 76/3/3, Resolution MEPC.331(76), PPR 9/6

Background

1 The Marine Environment Protection Committee adopted resolution MEPC.331(76), the amendments to Annex 1 to the AFS Convention at its 76th session in June 2021.

2 In view of the upcoming introduction of controls on cybutryne, three different guidelines would need to be revised:

a. Guidelines for brief sampling of anti-fouling systems on ships (resolution MEPC.104(49));
b. 2010 Guidelines for survey and certification of anti-fouling systems on ships (resolution MEPC.195(61));
c. 2011 Guidelines for inspection of anti-fouling systems on ships (resolution MEPC.208(62)).

3 The output for this work, output 2.19, has been renamed to '*Revision of guidelines associated with the AFS Convention as a consequence of the introduction of controls on cybutryne*'. The target completion year was extended to 2022 at MEPC 75.

4 The Sub-Committee invited interested Member States and international organizations to submit proposals to PPR 8 on the establishment of a correspondence group on the revision of the guidelines associated with the AFS Convention. As PPR 8 did not discuss the topic, this submission is presented to PPR 9 with the aim of finalising the guidelines.

5 It should be noted that, with the adoption of the amendments to Annex 1 to the AFS Convention, there is limited time to have the guidelines ready before the amendment enters into force on 1 January 2023. Only at PPR 9 there will be an opportunity to discuss the guidelines before the introduction of controls on cybutryne. Therefore, the modifications of the three guidelines should be considered as a package in order to move forward efficiently with the revision work that remains to be done.

6 This document includes detailed explanations on the suggested modifications to the guidelines. The suggested textual revisions to the three guidelines are provided in document PPR 9/6 (Austria et al.).

Action requested of the Sub-Committee

7 The Sub-Committee is invited to note the information provided and take action, as appropriate.

ANNEX

Suggested modifications to the guidelines associated with the AFS Convention as a consequence of the introduction of controls on cybutryne

1. Introduction

The amendments to Annex 1 to the AFS Convention will introduce controls on the use of cybutryne in anti-fouling systems of ships. For existing ships bearing an anti-fouling system that contains cybutryne in the outermost coating layer of their hulls or external parts or surfaces, on 1 January 2023, a sealer coating can be used to prevent the release of cybutryne to the marine environment or the anti-fouling system must be removed. Ships may, in any port, shipyard, or offshore terminal of a Party, be inspected to determine whether the ship is in compliance with the Convention. Such inspection is based on verification, when required, of an on-board International Anti-fouling System Certificate or a Declaration on Anti-fouling System and/or based on a brief sampling of the ship's anti fouling system.

The above amendments to Annex 1 to the AFS Convention will necessitate a revision of the three guidelines linked to the AFS Convention that presently cover only organotin compounds. The suggested modifications to the three guidelines will set up a framework of sampling activities and verification steps with the objective to also include verification of compliance with the AFS Convention with respect to anti-fouling systems containing cybutryne. The users of these guidelines are the national administrations and recognized organizations, port and flag state control authorities, companies, shipbuilders, and manufacturers of anti-fouling systems.

Compliance with Annex 1 to the AFS Convention would be assumed if the anti-fouling system contains cybutryne at a level that does not provide a biocidal effect, using the same principle of compliance mentioned in the existing guidelines for Guidelines for brief sampling of anti-fouling systems on ships and in the Guidelines for inspection of anti-fouling systems on ships (APPENDIX I) for organotin compounds.

The existing three guidelines, and in particular the Guidelines for brief sampling of anti-fouling systems on ships, should not, as far as possible, be modified substantially. Rather, the aim should be to test and apply the existing guidelines to cybutryne and only make modifications where needed. This would minimise additional training needs for the users of these guidelines and provide a cost-efficient solution for testing procedures.

Having this in mind, and simultaneously considering the practical aspects of PSC (port state control) during inspections, two new testing approaches are suggested: a new procedure to determine cybutryne and a new simplified procedure for detecting both organotin and cybutryne. This latter would introduce some modifications to the existing organotin compliance criteria.

The European Maritime Safety Agency contracted the RISE Research Institutes of Sweden to gather data and complete experimental work, which was used for the suggested amendments below[3]. The research considered the benefits of a combined test and whether such a test meets the purpose of the guidelines and AFS Convention.

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3 Adding Cybutryne to the Guidelines supporting the IMO's AFS Convention http://emsa.europa.eu/publications/item/4581-adding-cybutryne-to-the-guidelines-supporting-the-imo%E2%80%99s-afs-convention.html

2. Suggested amendments to the **Guidelines for brief sampling of anti-fouling systems on ships**

2.1 Definition of compliance

The amendments to Annex 1 to the AFS Convention will introduce controls on the use of cybutryne in anti-fouling systems. Cybutryne is only used as biocide in anti-fouling systems. Therefore, by definition, the detection of cybutryne in the anti-fouling system, which forms the outermost coating layer of the hull or external parts or surfaces, should trigger non-compliance to the AFS Convention. However, using the principle of compliance as it stands in the existing guidelines for organotin compounds, it would allow the presence of cybutryne in the anti-fouling system up to a level which does not provide a biocidal effect. This implies that cybutryne may be present on the ship's hull (e.g., inner layer of an old anti-fouling system) up to a certain amount.

In order to accurately determine if a ship complies or not with the AFS Convention it is fundamental to have a reference value that can be used for comparison purposes. This value must be in line with the suggested test method and it must ensure that the release of cybutryne to the marine environment is at a level that does not cause a negative impact to the environment.

An initial approach to define a threshold value would be to find a correlation between the amount of cybutryne in anti-fouling systems in mg/kg dry paint and the release rate of cybutryne to the marine environment. However, there is no direct correlation between the amount of cybutryne in the coating and the amount of cybutryne released to water. Ideally, this correlation could be obtained by running a full range of laboratory tests using anti-fouling paints in different formulations and with different concentrations of cybutryne using the ISO 15181-1[4] test method. This method measures the average release rate with, as recommended in the standard, the application of a correction factor for the expected overestimation. This would be an adequate approach to derive an experimental correlation. However, this would be costly and time consuming and more importantly, not based on real market formulations.

Instead, this document suggests a compliance reference value by looking at the amount of cybutryne left at the end of life cycle of the anti-fouling systems using cybutryne and by estimating its predicted environmental concentration (PEC) considering different marine scenarios. The scenarios below do not take into consideration the expected emissions from the application and removal of anti-fouling systems containing cybutryne. This is because the legislative introduction of cybutryne controls assumes that anti-fouling systems containing cybutryne will no longer be applied, and that the removal operations take place in a dry dock with adequate control measures to prevent the dispersion of the anti-fouling paint particles to water.

2.1.1 Original concentration of cybutryne in anti-fouling systems

In some cases, the exact original concentration of an active substance in an AFS is difficult to obtain as these values are not disclosed due to industrial intellectual property and are only made available to public authorities for biocide testing and not to the general public. The information in the Safety Data Sheets usually present a range of cybutryne concentration in the AFS paint (from – to) in % (w/w).

The table below, from a Swedish report in 2007 (Woldegiorgis et al., 2007), presents a list of anti-fouling products containing cybutryne (commercial name Irgarol 1051). It contains the list of anti-fouling products approved by the Swedish Chemicals Agency at the time.

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[4] ISO 15181-1 - Paints and varnishes — Determination of release rate of biocides from antifouling paints

	Conc. cybutryne (% w/w)	Cat.		Conc. cybutryne (% w/w)	Cat.
Cruiser	2.41	cat. 3	Anti-fouling Sargasso AL KNM	2	cat.2
Cruiser White	1.89	cat. 3	Hempel's Anti-fouling Combic ALU 71800	1.1	cat.2
Micron WQ	2.2	cat. 3	Interspeed Extra BWO 500 Röd	2	cat.2
Micron WQ White	1.97	cat. 3	Interspeed Premium Anti-fouling Black	2.3	cat.2
Mille White SE	3.5	cat. 3	*Average*	*1.85*	
Trilux	2.18	cat. 3			
Trilux Prop-o-Drev	0.87	cat. 3			
Trilux White	1.87	cat. 3			
VC 17 New Technology	0.6	cat. 3			
Average	*1.94*				

Table 1 - Anti-fouling products containing Cybutryne approved in Sweden: pleasure boats <12m length (cat. 3); professional ships >12m length (cat.2); adapted from (Woldegiorgis et al., 2007).

From the table above, it is possible to calculate an average concentration of cybutryne (% w/w) for "cat. 2" products 1.8% (w/w) and for "cat. 3" products 1.94% (w/w). Due to a lack of representative data for all anti-fouling products containing cybutryne on the market, it was used as the starting point for defining compliance with the AFS Convention.

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

In addition to concentration of the biocide type, the paint "binder" is of paramount importance for an anti-fouling paint. The paint "binder" is the component that holds the paint matrix together. Along with the biocide's inherent solubility limitations, the properties of the binder will control the manner and speed at which the biocide is released to the water.

In soluble matrix paint systems, seawater migrates into the paint film while dissolved rosin and biocides leach into the sea. 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. A part of insoluble components is present in the matrix and these remain in the layer left behind. This dissolution gradually slows down over time as the biocide diminishes in the leached layer. The maximum effective life of a soluble matrix system 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.

Self-polishing copolymers (SPCs) undergo a reaction (hydrolysis) with seawater to make it soluble. 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. The result is thinner "leached layers" with excellent control of biocide leaching. Reaction/solution continues 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 the end of the service life can happen when an AFS layer (below the leached layer) is still on the hull.

2.1.2 End-of-life of the anti-fouling system and expected impact to the marine environment

It is expected that the distribution of the remaining anti-fouling paint on the hull surface would not be uniform. Due to hull design and consequent action of the sea water during the service life of the paint, the paint will not have uniformly eroded, some parts on the hull may still have some paint, other parts may not have any paint left. Thus, there may be cases where although cybutryne is not acting as a biocide in technical terms however, it is still present on some parts of the hull.

If a paint contains cybutryne when applied, it is reasonable to assume that concentration of cybutryne in any remaining paint at the time of sampling could be non-compliant. Therefore, the following section proposes a suitable threshold value for compliance.

In document PPR 6/INF.7 a maximum of 2 ng/L (PNEC, Predicted No Effect Concentration) of maximum allowed concentration of cybutryne in water was proposed. Any concentration above this threshold in water, would cause significant adverse effects to certain marine species and consequently to the marine ecosystem and corresponding food chains.

The MAMPEC model 3.1.0.5 was used to estimate the Predicted Environmental Concentration (PEC) of cybutryne in water associated to the amount of cybutryne left at the end of life of the anti-fouling system.

The MAMPEC model integrates a 2D hydrodynamical and chemical fate model, based on the Delft3D-WAQ and Silthar model. It is used by regulatory authorities and applicants for exposure assessment of antifoulants in harbours, rivers, estuaries and open water. The MAMPEC model has built-in a set of agreed OECD-EU emission scenarios that the user can choose. These scenarios are based on the Emission Scenario Document (OECD, 2005), that recommends and describes the emission scenarios for anti-fouling products in OECD countries. These scenarios are intended to be used for general risk assessment and not for site specific risk assessment. The calculations are based on the initial local concentration in the primary receiving environment. The scenarios take into consideration the shipping characteristics (hull area, ships moving, ships at berth), leaching rate and the application factor i.e. the percentage of ships painted with the specific product in the environment in question.

Assuming that at the end of the life of the anti-fouling systems only a fraction of the original concentration of cybutryne is left, in a simplified manner this can be correlated with a decrease in the hull area in contact with water. The leaching rate used was 1.9µg/cm^2/day as explained in PPR 6/INF.7.

The release of cybutryne to the marine environment was estimated considering different amounts of cybutryne left at the “end of life” of the anti-fouling system. The reference point was 10 % of the original concentration (2 000 mg/kg of dry paint), as defined in the methodology outlined in ISO 10890:2010[5]. Additionally, a value of 5% (1000 mg/kg of dry paint) and 1% (200 mg/kg of dry paint) of cybutryne left were used to have a range of values to support the selection of the threshold value.

5 ISO 10890:2010 - Paints and varnishes - Modelling of biocide release rate from antifouling paints by mass-balance calculation

Three built-in scenarios in MAMPEC, based on the Emissions Scenarios Document (OECD, 2005), were used to depict the expected emissions from a ship and the receiving environment. These are the shipping lane, commercial harbour and marina scenarios. The PEC values in a marina will always be higher than in a commercial harbour, which in turn will be higher than in a shipping lane. This is due to the number of ships per m^3 due to their size and the low water exchange rates expected in a marina.

For the OECD-EU marina scenario two different sub scenarios were used: the default scenario that defines 500 ships at berth and a modified scenario with 276 boats at berth. This sub-scenario was agreed to be more realistic, see table footnote.

The table below summarises the results:

	End of life of the anti-fouling system (ng/L)								
	2 000 mg/kg 10 %			1 000 mg/kg 5 %			200 mg/kg 1 %		
Application factor	0.5	0.2	0.1	0.5	0.2	0.1	0.5	0.2	0.1
OECD-EU shipping lane	9.9 E-04	4.0 E-04	2.0 E-4	5.0 E-04	2.0 E-04	9.9 E-5	9.9 E-05	4.0 E-05	2.0 E-05
OECD-EU commercial harbour	1.9	0.8	0.4	1.0	0.4	0.2	0.2	0.08	0.04
OECD-EU Marina (default)	18	7.4	3.7	9.2	3.7	1.8	1.8	0.7	0.4
OECD-EU Marina (modified)*	10	4.1	2.0	5.1	2.0	1.0	1.0	0.4	0.2

* *In MAMPEC the OECD-Marina scenario has the following 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 m2, [Source: Final minutes of TM V 2007].*

Table 2 – Average values for different scenarios PEC values for water (nanograms per litre)

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

The adopted controls on anti-fouling systems containing cybutryne are expected to result in a gradual reduction in 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 would be reduced significantly. Five years after the introduction of cybutryne controls, the 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 of 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 is one ship that has 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 would not create a negative impact to the environment.

Assuming that the introduction of cybutryne controls will lead to a gradual reduction of emissions of cybutryne to water related to anti-fouling systems of ships, it could be concluded that a compliance value of 1 000 mg of cybutryne per kg of dry paint should be set as threshold value. Below this value emissions of cybutryne from the ship hull to the marine environment could be expected not to create a negative impact to the environment.

2.2 Sampling and testing methodologies to determine cybutryne

In the current guidelines for brief sampling of anti-fouling systems, the following generic principles for the analysis are mentioned:

'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.'

These principles have been followed as much as possible for the suggested amendments described below.

The guidelines, include two methods (Method 1 and Method 2) for organotin determination. Method 1 is more detailed than Method 2. However, the guidelines do not provide any recommendation on the method selection nor explanations concerning their differences. It is stated in the guidelines that these methods only serve as examples of sampling and analytical methods and other sampling methods may be used subject to the satisfaction of the Administration or the port State.

The starting point for the revision of these guidelines is to test if the sampling and testing methodologies described in the guidelines were adequate or appropriate for cybutryne. If required, modifications are suggested having in mind the cost efficiency of the testing methodologies and minimisation of training needs of the guidelines' users. The points below justify the modifications to include cybutryne in the scope of the guidelines.

The inspector, after checking the on-board International Anti-fouling System Certificate or a Declaration on Anti-fouling System should decide if the brief sampling is needed and if so if the brief sampling analysis should focus only on one of the substances listed in Annex 1 of the AFS Convention or all substances listed in Annex 1. Therefore, the inspector will have three scenarios to choose from:

Case A. Analysis of organotin only

Case B. Analysis of cybutryne only

Case C. Simplified approach to detect organotin and cybutryne

This third case aims at a significant simplification of the brief sampling procedures by checking both substances simultaneously. Instead of checking each substance separately, Case A and Case B, a simplified approach to detect organotin and cybutryne is suggested. This approach (Case C) requires a smaller number of samples to be collected and prepared and a substantial smaller number of GC-MS analysis to be performed.

2.2.1 Strategy

The guidelines state that the precision of the sampling method, the analytical requirements, costs, and required time and the purpose of the sampling, depend on the sampling strategy. They define that triplicate specimens of paint at each sampling point should be taken in close proximity to each other on the hull (e.g., within 10 cm of each other).

Method 1 mentions a minimum number of eight independent samples to be collected. For each sample point three specimens: 'specimen A' for STEP 1 analysis, Specimen B for STEP 2 analysis and a third specimen for storage/back-up.

The description of Method 2 is not as detailed as method 1. The record sheet for method 2 indicates four sample points (four sampling points are also mentioned as a minimum in the brief sampling guidelines). It then states that at each sampling point, three sets of sampling, or more if necessary, should be carried out to obtain at least six specimens. Note that the sampling device might have three or two rotating rods, resulting in six or nine specimens.

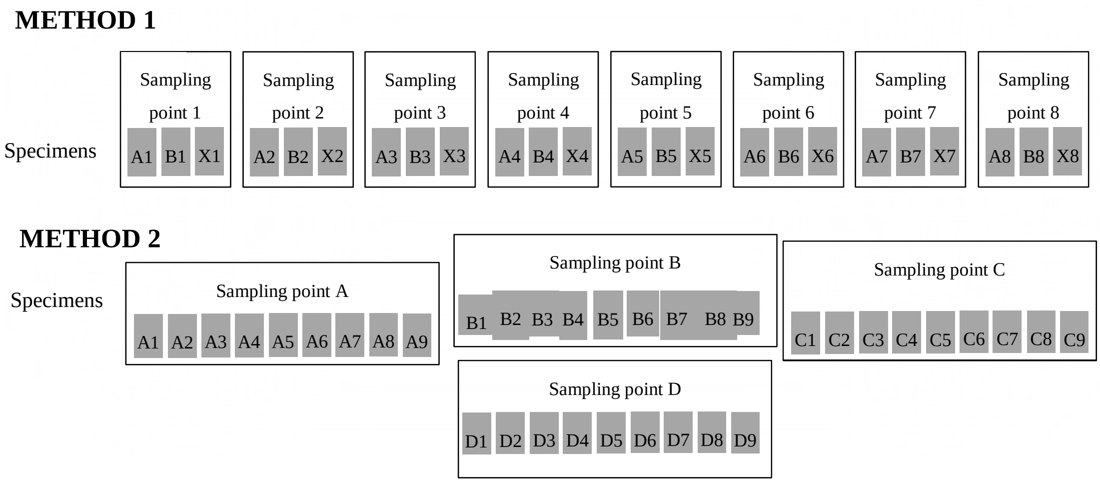

Figure 1 – current sampling strategy, only for organotin analysis

The difference in sampling points and number specimens at each sampling point results in different uncertainty for each of methods. Method 1 is better suited to describe the average biocide concentration on the hull, whereas Method 2 is better suited to describe the biocide concentration at an individual sample point (lower measurement uncertainty). Despite the differences, it is suggested not to change the number of sample points for Method 1 and Method 2.

Depending on the purpose of the inspection to investigate one or two substances, the number of specimens for analysis will vary:

For '*Case A. Analysis of organotin only'* the number specimens is kept at each sampling point:

Method 1: *'every sample should be taken in triplicate'.*

Method 2: *'at each sampling point, three sets of sampling, or more if necessary, should be carried out to obtain at least six specimens.'*

For '*Case B. Analysis of cybutryne only'*, the number of specimens is reduced as the cybutryne analysis is done in a single step (see below point 2.2.1).

Method 1: *'every sample should be taken in duplicate.'*

Method 2*: 'at each sampling point, three sets of sampling, or more if necessary, should be carried out to obtain at least six specimens.'*

For '*Case C. Simplified approach to detect organotin and cybutryne',* the number of specimens is reduced as the organotin and cybutryne analysis is done in a single step (see below point 2.2.1):

Method 1: 'every sample should be taken in duplicate.'

Method 2: 'at each sampling point, three sets of sampling, or more if necessary, should be carried out to obtain at least six specimens.'

Proposal for simplification

Cases B and C should enable the sampler to reduce the number of specimens to be collected for method 1.

2.2.1 Step-wise approach

The first approach was to replicate the step-wise approach in the existing guidelines (both in Method1 and Method 2): a STEP 1 to check the presence of total cybutryne and then a STEP 2 only applied when STEP 1 produces positives results. The STEP 2 analysis is done at an ISO 17025 accredited laboratory using the GC/MS (Gas Chromatography/Mass Spectrometry) analytical technique. The STEP 2 analysis is more costly and time consuming than STEP 1 analysis.

Unfortunately, not having a metal to detect with ICP/MS (inductively coupled plasma/mass spectrometry) and XRF (X-ray fluorescence analysis) methods (as for organotin compounds), prevented the development of a quick reaction test method to detect cybutryne. The methodologies tested were based on colour-reactions and easy separation (i.e. TLC Thin Layer Chromatography). Unfortunately, they gave too many false positives to be considered relevant as candidates. The use of a portable GC/MS analyser with thermal extraction directly on dry paint was also considered. However, this is an expensive option and the equipment is not widely available.

Therefore, it is suggested that a one-step approach is added to the existing guidelines in order to determine the amount of cybutryne present in the sample (Case B) which would be carried out at a laboratory using the GC/MS analytical method.

In the case where the port sate control officer wishes to verify the presence of both organotin and cybutryne (Case C), there is potential to reduce costs using the one step approach. For this case, it is advantageous to send the samples directly to a laboratory for GC/MS analysis to determine both the cybutryne and organotin compounds at the same time, skipping STEP 1 for organotin.

Suggested simplification

One-step approaches are added to the existing guidelines in order to determine the amount of cybutryne present in the sample (Case B) as well as for the determination of organotin and cybutryne (Case C).

2.2.3 Extraction

To quantify the amount of cybutryne present in the abrasive material, cybutryne needs to be extracted from the paint in the abrasive material to a solvent. It is suggested that the sample is extracted with 10 ml of ethyl acetate using an internal standard (see below justification for solvent and internal standard choice).

2.2.4 Internal standard

The optimal internal standard for Mass Spectometry detection is isotopically labelled cybutryne. This substance is available on the market, but at a very high price. Therefore, another triazine with the same secondary amines and sulphur chemistries as cybutryne is proposed, ametryn (CAS No. 834-12-8). This substance is readily available at a reasonable price and is chemically very similar.

2.2.5 Solvent

For Case B, the solubility of both ametryn and cybutryne was determined to be above 20 mg/ml in acetone for ethyl acetate, dichloromethane and toluene. Based on: safety, health and environmental (SHE) aspects; extraction efficiency tests; and, solubility / selectivity tests, ethyl acetate can be used as solvent (for more information see report[3]).

For Case C, it is proposed the use of toluene as ethyl acetate reacts with one of the reagents used in the derivatisation procedure for the organotin analysis. Although it presents additional safety, health and environmental (SHE) issues in comparison to ethyl acetate, it is inert, it does not react with the derivatisation reagents and the solubility of cybutryne in toluene is high.

2.2.6 Separation and detection with GC/MS method

It is recommended to use the GC/MS analytical method to quantify the amount of cybutryne[6], Case B. The calibration and maintenance of the GC/MS system should be performed according to ISO

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6 It is suggested to do a splitless injection of 1 µl etyl acetate extract 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. For the separation a typical temperature program of 35 °C for 5 min, ramp to 325 °C at 10 °C/min should be used. It is suggested to do the detection of the baseline between the analyte and the internal standard using

17025. For Case C, it is also suggested to use the GC/MS analytical method to quantify in the same GC/MS analysis organotin and cybutryne. Laboratory tests were performed by adding cybutryne to the general methods for organotin derivatization described in the existing guidelines. The results show that cybutryne remained stable, after the derivatization procedures. Therefore, it is possible to detect in the same GC/MS analysis both cybutryne and organotin. However, the selection of solvent must be adjusted (see point 2.2.5 above). Toluene is the proposed alternative solvent for case C, which also has high solubility for Cybutryne.

2.2.7 Calculation and reporting

It is suggested to calculate the concentration of cybutryne in the paint sample using the internal standard approach. The results should be reported individually and as an average value.

2.2.8 Limit of quantification

In order to determine the limit of quantification for the above test method for cybutryne quantification, duplicate samples of two dried paints one with SPC mechanism and another one with ablative mechanism containing 0,02 weight % cybutryne (wet basis) were tested. The samples were collected with an abrasive material, extracted and analysed with GC/MS analysis according to the method described above and in guidelines. The RMS signal (s/n) to noise was 200. This means that it is possible to perform analytical work at least one order of magnitude below, at 0,002 %, giving a limit of quantification of 20 mg/kg.

2.2.9 Measurement uncertainty and tolerance range

In order to test the uncertainty of the test method, dry paint (with 2% cybutryne) was sampled and analysed in duplicate but reported as single sample determinations. Several paints were used. The precision was calculated as the relative standard deviation of the repeatability (rsd r) and the trueness is based on the recovery. The relative standard deviation of the repeatability 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 corresponds to a tolerance range of 0,025% (250 mg/kg) for the method.

For the suggested analytical method, the range of uncertainty to be considered on the measured value is 25%. This means that compliance should be achieved at measured concentration lower than the threshold plus the tolerance range) i.e. 1 000 plus 250 mg cybutryne / kg dry paint.

2.2.10 Compliance criteria

The compliance criteria for organotin compounds (Case A) is based on the analysis of each specimen, at least for Method 1. For Method 2 first stage analysis, the maximum and minimum values from the data is omitted and an average of the organotin content is calculated from the intermediate values for the representing value of the sampling point. If one or more values of the samples from the different sampling points do not meet the compliance criteria, then the sample(s) is sent to second-stage analysis. The inspector may decide to send the sample to the second stage.

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the following conditions: MS operating in Selected Ion Mode (SIM) using the m/z 253, 238 and 183 ions for Cybutryne and m/z 227, 212 and 185 ions for Ametryn.

This approach can possibly be explained with the dual function of organotin in anti-fouling systems: as biocide[7] and as chemical catalyst. Due to this dual role, small quantities of organotin compounds are allowed in the anti-fouling paint provided that they are present at a level which does not provide a biocidal effect to the coating. This has been the basis for the defining the compliance criteria in Method 1 and 2. If organotin is detected, then it must be only be for the purpose of working as a catalyst at a threshold of < 2,500 mg Sn/kg of dry paint. Only with single measurements it is possible to identify if organotin is present in the specimen as a biocide or simply as a chemical catalyst.

The compliance criteria for organotin defines that two conditions need to be met (for Method 1):

'.1 no more than 25% of the total number of samples yield results above 2,500 milligrams total tin per kilogram dry paint (2,500 mg Sn/kg of dry paint); and

.2 no sample of the total number of at least eight samples shows a concentration of total tin higher than the sum of threshold value plus the tolerance range, i.e. no sample must exceed the concentration 3,000 mg Sn/kg of dry paint.'

This requires that each specimen must be evaluated individually: prepared, extracted and analysed individually. It is proposed to keep the compliance criteria for Case A as it is.

For cybutryne only (Case B), it is suggested to use the average concentration of all paint samples as the best value to represent the content of cybutryne in the hull surface. All the samples can be pooled together and analysed as one sample, therefore only one GC-MS analysis is required. As mentioned before, the distribution of any remaining anti-fouling paint in the hull surface is not homogenous. The rational for defining the threshold for cybutryne (see chapter 2.1) is based on the percentage of paint on the hull still carrying cybutryne rather than the percent of cybutryne in the paint itself. So, this is best reflected as an average value from the different sampling points along the hull. A threshold based on single points could be misleading with respect to the threshold rational. Therefore, it is suggested that for compliance the average value of all samples is below the threshold plus the tolerance range, i.e. 1 250 mg of cybutryne per kg of dry paint.

'.1 The average value of the total number of specimens shows a concentration below the threshold plus the tolerance range i.e., 1 250 mg of cybutryne per kg of dry paint'

For Case C, a considerable modification to the existing organotin compliance criteria, described in Case A above, is suggested. Instead of quantifying the presence of organotin in each specimen, it is suggested that an average value is used instead, whilst keeping the threshold limits. Therefore, only one GC-MS analysis is required instead of eight individual analysis. This will substantially reduce the costs for the analysis. The following compliance criteria is therefore proposed:

'.1 For organotin, the average value of the total number of specimens shows a concentration below the threshold plus the tolerance range i.e. 3 000 mg Sn/kg of dry paint'

This should only be used for Case C when cybutryne and organotin are analysed at the same time[8].

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7 'organotin-containing compounds, when present in paint in order to act as a biocide, were found in concentrations up to 50,000mg Sn/kg', see method 1, point 6.5 of the guidelines for brief sampling of anti-fouling systems on ships.

8 The other option would be to quantify organotin in every specimen (Case A). However, this would not lead to significant simplifications and relevant costs savings. A total of 9 GC-MS analysis would be needed: 8 (assuming method 1) for organotin plus 1 more for cybutryne for method 1.

This compliance criteria fails to identify specific points in the hull where organotin is working as a catalyst. Nevertheless, looking at all the samples together (representing the entire hull) and using the same threshold, this approach will not significantly change the current situation. It still allows the discrimination between anti-fouling systems containing organotin acting as:

- a biocide;
- a catalyst; or,
- an anti-fouling system that does not contain organotin.

For cybutryne the same compliance criteria used in Case B is suggested.

'.2 For cybutryne, the average value of the total number of specimens shows a concentration below the threshold plus the tolerance range i.e., 1 250 mg of cybutryne per kg of dry paint'

3. Conclusions

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 brief sampling guidelines.

The suggested modifications to the brief sampling guidelines should provide the port state control officers the necessary flexibility to choose the best procedure depending on the circumstances and conditions during each ship inspection.

4. References

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