Council of the
European Union

Brussels, 29 June 2018
(OR. en)

10538/18

MAR 86
OMI 29
ENV 471
CLIMA 118

COVER NOTE

From:	Secretary-General of the European Commission, signed by Mr Jordi AYET PUIGARNAU, Director
date of receipt:	29 June 2018
To:	Mr Jeppe TRANHOLM-MIKKELSEN, Secretary-General of the Council of the European Union
No. Cion doc.:	SWD(2018) 372 final
Subject:	COMMISSION STAFF WORKING DOCUMENT for the Council Shipping Working party IMO - Union submission to be submitted to the 73rd session of the Marine Environment Protection Committee (MEPC 73) of the IMO in London from 22 – 26 October 2018 concerning additional information on environmental concentrations observed worldwide and scientific evidence for the adverse effects of CYBUTRYNE to the marine environment and to human health

Delegations will find attached document SWD(2018) 372 final.

Encl.: SWD(2018) 372 final

EUROPEAN
COMMISSION

Brussels, 29.6.2018
SWD(2018) 372 final

COMMISSION STAFF WORKING DOCUMENT

For the Council Shipping Working party

IMO - Union submission to be submitted to the 73rd session of the Marine Environment Protection Committee (MEPC 73) of the IMO in London from 22 – 26 October 2018 concerning additional information on environmental concentrations observed worldwide and scientific evidence for the adverse effects of CYBUTRYNE to the marine environment and to human health

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COMMISSION STAFF WORKING DOCUMENT
For the Council Shipping Working party

IMO - Union submission to be submitted to the 73rd session of the Marine Environment Protection Committee (MEPC 73) of the IMO in London from 22 – 26 October 2018 concerning additional information on environmental concentrations observed worldwide and scientific evidence for the adverse effects of CYBUTRYNE to the marine environment and to human health

PURPOSE

The document in Annex contains a draft Union submission to the 73rd session of the Marine Environment Protection Committee (MEPC 73) of the IMO, taking place in London from 22 – 26 October December 2018, concerning additional information on environmental concentrations observed worldwide and scientific evidence for the adverse effects of CYBUTRYNE to the marine environment and to human health. It is hereby submitted to the appropriate technical body of the Council with a view to achieving agreement on transmission of the document to the IMO prior to the required deadline of 20 July 2018[1].

Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products[2] establishes a harmonised system in the EU concerning the placing on the market and use of biocidal active substances and biocidal products. In particular, it aims at establishing at Union level a list of active substances which may be used in biocidal products. Pursuant to Article 9 of Regulation (EU) No 528/2012, decisions to approve or ban an active substance are adopted at EU level by the Commission. The non-approval Decision (EU) 2016/107[3] was adopted to ban cybutryne for use in antifouling paints, and antifouling paints containing cybutryne cannot be placed on

[1] The submission of proposals or information papers to the IMO, on issues falling under external exclusive EU competence, are acts of external representation. Such submissions are to be made by an EU actor who can represent the Union externally under the Treaty, which for non-CFSP (Common Foreign and Security Policy) issues is the Commission or the EU Delegation in accordance with Article 17(1) TEU and Article 221 TFEU. IMO internal rules make such an arrangement absolutely possible as regards existing agenda and work programme items. This way of proceeding is in line with the General Arrangements for EU statements in multilateral organisations endorsed by COREPER on 24 October 2011.

[2] OJ L 167, 27.6.2012, p. 1.

[3] OJ L 21, 28.1.2016, p. 81.

the market nor used in EU as from 27 January 2017. Cybutryne is also listed as a priority substance under the Water Framework Directive[4]. The said draft Union submission therefore falls under EU exclusive competence.

[4] OJ L 327, 22.12.2000, p.1, as amended by OJ L 226, 24.8.2013, p.1

ANNEX

MARINE ENVIROMENT PROTECTION COMMITTEE 73rd session Agenda Item 18	MEPC 73 /INF* [Date] Original: ENGLISH

ANY OTHER BUSINESS

Additional information on environmental concentrations observed worldwide and scientific evidence for the adverse effects of CYBUTRYNE to the marine environment and to human health

Submitted by the European Commission on behalf of the European Union

SUMMARY

Executive summary:	This document contains additional scientific information and results to support the position that cybutryne can be associated with adverse effects to the environment and has to be included in Annex 1 of the AFS Convention. The extensive literature presented in this paper contains results and risk assessments methodologies that could assist the Technical Group that will be established to objectively review the merits of the comprehensive proposal that will be submitted after the approval of the recommendations of PPR 5 on this subject by this Committee.
Strategic direction:	2
High-level action:	
Output:	2.19
Action to be taken:	The Committee is invited to invite the Technical Group that will be established following the MEPC's approval of the respective recommendations of PPR 5 to utilize as necessary the information contained in this document.

Related documents:	International Convention on the Control of Harmful Anti-Fouling Systems on Ships 2001 (AFS 2001); Resolutions A.900(21),MEPC 71/14,PPR 5/INF.9, PPR 5/19, PPR 5/INF.8, PPR5/24

Introduction

1 This document is submitted in accordance with paragraph 6.12.1 of the *Guidelines on the organization and method of work of the Maritime Safety Committee and the Marine Environment Protection Committee and their subsidiary bodies* (MSC-MEPC.1/Circ.5).

2 After the decision by PPR 5 and pending the approval by this Committee, it was decided to review an additional number of scientific studies on cybutryne (also referred to as Irgarol 1051) which were conducted worldwide. The results of these studies can be used as reference when the comprehensive proposal will be prepared and submitted to the next PPR meeting. They will also be useful for the Technical Group that will be established to review the adverse effects of cybutryne on the marine environment and on human health. Furthermore, this document provides a description of the tools that have been used in addition to monitoring data to model cybutryne concentrations in ports, marinas and in the open sea. These models and the standard scenarios used have been agreed as valid tools for the exposure assessment of antifouling products in the context of the Organisation for Economic Co-operation and Development's (OECD) Biocides Program.

3 PPR 5 considered documents PPR 5/19 and PPR 5/INF.9 for the initial proposal for including cybutryne in Annex I of the AFS Convention. The sub-Committee agreed that these documents satisfied the requirements of Annex 2 of the AFS Convention and recommended to MEPC to invite for the submission of a comprehensive proposal according to the Convention's Annex 3. Document PPR 5/INF.9 includes a list of scientific publications that focus especially on the adverse effects of cybutryne and its metabolite on non-target organisms. These studies particularly describe the test methodologies used to identify the toxic components in the anti-fouling system. The present document contains supplementary information and insights from additional research including a list of peer-reviewed publications from scientific journals related to cybutryne concentrations and impacts *in vitro* as well as *in vivo* in waters and sediments from all over the world. Following concerns of IPPIC at PPR5 about a possibly limited geographical scope of the available data, particular emphasis has been put on research conducted outside European Union waters.

4 At this stage the information required for a comprehensive proposal is being collected, which will be submitted to the forthcoming PPR meeting in case this Committee approves the recommendations from PPR 5. For this purpose, a detailed study containing supporting evidence on the adverse effects of cybutryne is being drawn up. This study is being conducted in line with the requirements of Annex 3 of the Convention, and includes a

methodology for calculating cybutryne concentrations and leaching rates for specific areas monitored. Furthermore, the information contained in the study provided in the link below to fill the sections required by Annex 3 of the Convention will be used, including the physical and chemical properties of cybutryne, data on the environmental fate and effect modes of degradation/dissipation and data on unintended effects in the marine environment, particularly to marine fauna and flora, as well as the potential harmful effects on human health:
http://dissemination.echa.europa.eu/Biocides/ActiveSubstances/1281-21/1281-21_Assessment_Report.pdf

5 The mathematical model used to predict the concentrations of cybutryne in the marine environment is the Marine Antifoulant Model to Predict Environmental Concentrations (MAMPEC). MAMPEC is an integrated hydrodynamic and chemical fate model, originally developed for exposure assessments of antifouling substances (van Hattum et al.,2002)[5] that has been shown to predict the concentrations of antifoulants in the marine environment (open sea, shipping lanes, estuaries, commercial harbours, marinas and open harbours) with high accuracy. The user can define all the relevant conditions and parameters. Typically adjusted conditions are the emission factors such as the leaching rates of the substance, shipping intensities, residence times, ship hull underwater surface area, compound related properties such as volatilisation, speciation, hydrolysis, photolysis, biodegradation and properties and hydrodynamics related properties such as currents, tides, salinity, port dimensions. This model includes emission scenarios that were developed by the OECD-EU working group (OECD 2004) and agreed upon by the OECD task force on biocides as the standard environmental emission scenarios to be used for evaluation of biocides worldwide. The model has been validated for many compounds and is recognized by regulatory authorities in the EU, USA, Japan and other OECD countries that are Member States to the IMO. The use of MAMPEC to model various scenarios for ballast water has furthermore been recommended by GESAMP. More details about the model and additional documentation can be found on the following website:
https://download.deltares.nl/en/download/mampec/

6 The mathematical model described in 5 can be used in combination with available data from traffic information for different geographical areas worldwide. The information about the ship types visiting specific ports and the duration of ship's stay in the port can be used as input parameters in order to more accurately calculate the leaching rates from specific types of vessels that visited the port for a specific period.

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[5] Computer model to generate predicted environmental concentrations (PECs) for antifouling products in the marine environment 2nd edition accompanying the release of Mam-Pec version 1.4 *B. van Hattum, A.C. Baart*, J.G. Boon*,2002*

Moreover, it will be tried to extend the model to ensure that other conditions in seawater across the globe will not alter the findings showing that the concentrations both found in the scientific literature and estimated using MAMPEC exceed the environmentally acceptable levels of cybutryne, whereby causing a real concern for the environment.

7 Finally the Annex of this paper lists a number of publications on cybutryne concentrations and the substance's effects, either published in peer-reviewed scientific journals or by government agencies along with a short summary of their content. This list includes studies from all continents, allowing for the conclusion that cybutryne contamination of the marine environment is a worldwide reality. Therefore, this problem is brought to the attention of the International Community once again and especially to the member states of this Organization. Cybutryne contamination is not only a regional problem that concerns only the EU Member States, but rather affects many areas around the globe. As a result, measures to protect waters and especially coastal areas from the detrimental effects of this antifouling agent need to be taken on a global scale.

Action requested by the Committee

8 The Committee is invited to note the information contained in this document and to invite the Technical Group that will be established following the MEPC's approval of the respective recommendations of PPR 5 to utilize as necessary the information contained in this document.

ANNEX

2 SCIENTIFIC PUBLICATIONS MEASURING THE CONCENTRATIONS OF CYBUTRYNE

Asia:

Basheer, Tan and Lee, Organotin and Irgarol-1051 contamination in Singapore coastal waters, *Marine Pollution Bulletin*, 2002

Seawater samples were taken from 26 locations (Oct – Nov 2000) measuring TBT, TPhT, and Cybutryne. Cybutryne (also known under its trademark name Irgarol 1051) was found in 13 samples. The highest concentration detected was 4.0 µg/L (highest ever detected level) and at four other locations above 2.5 µg/L. (In this context it should be noted that the Dutch National Institute of Public Health determined the Environmental Risk Limit (ERL) as 24ng/L.) The concentrations of Irgarol 1051 were higher in samples obtained from eastern Straits of Johor than the Singapore Straits. This is has been the result of to the presence of potential sources of antifouling leachates from Sembawang shipyard, Punggol Marina and Pasir Gudang, a Malaysian port located in the eastern Straits of Johor. The paper is trying to raise concerns on the increase in use of Irgarol 1051 and other similar chemicals as antifoulants as a result of the TBT ban. The paper makes reference to other documents of similar studies conducted in Europe and specifically at Beaulieu Marinas (Mediterranean Coast) since there was an increase of the measured Irgarol 1051 almost 30 times higher than it used to be in previous years. Therefore, the authors supported that cybutryne as a substance that is highly toxic to non-target marine algae has likely become the substitute for the banned TBT, causing an undesirable increase on a worldwide scale.

Okamura *et al*, Antifouling herbicides in the coastal waters of western Japan, *Marine Pollution Bulletin*, 2003

A large number of samples from subsurface waters in harbours and marinas in western Japan were examined for this study in 1999. The occurrence of Diuron was positively identified, for the first time, in the Japanese aquatic environment, accompanied by residues of both Irgarol and M1. Detection frequency of the substances in the 142 water samples was 86% for Diuron, 60% for Irgarol, and 28% for M1. The highest detected concentration of Irgarol was 262 ng/L, while 9 of the 142 measurements were above 100 ng/L. The concentrations of Irgarol were almost identical to those found in a previous survey made in 1997–1998, although concentrations of M1 were lower. These results suggest that antifouling paints containing Diuron and Irgarol have been used for pleasure boats, fishing boats, and small craft in the study area.

Harino, Mori *et al,* Monitoring of Antifouling Booster Biocides in Water and Sediment from the Port of Osaka, Japan, *Arch Environ. Contam. Toxicol.*, 2005

This study examined Irgarol 1051 concentrations in the port of Osaka, and found wide contamination as well as an increase in concentrations during Summer time. The highest values of Irgarol 1051 concentration detected was 267 ng/L, and in six out of eight locations levels above 24 ng/L were detected at least once.

Ali, Arifin, Sheikh *et al*, Occurrence and distribution of antifouling biocide Irgarol-1051 in coastal waters of Peninsular Malaysia, *Marine Pollution Bulletin*, 2013

The study aimed to provide baseline data on Irgarol 1051 concentrations in selected coastal waters surrounding Malaysia. Strong temporal variations were detected, with only one sampling station detecting levels above the Environmental Risk Limit (ERL) of 24ng/L in water, set by the Dutch National Institute of Public Health in November 2011, but 92 percent of station detecting levels above this limit in April. The highest detected concentration was 2021 ng/L, with 25 out of 28 measurements exceeding 350 ng/L.

Kim, Hong *et al*, Distribution of butlytins and alternative antifouling biocides in sediments from shipping and shipbuilding areas in South Korea, *Marine Pollution Bulletin*, 2015

In this 2015 Korean study, high Irgarol 1051 concentrations were found in Korean sediment samples from shipping and shipbuilding areas. 40 percent of measurements in bays and 20 percent of samples from harbours exceeded the Environmental Risk Limit for sediment set by the Dutch National Institute for Public Health at 1.4 ng/g. Overall, Irgarol 1051 was detected at 15 of 34 stations. In one fishing port, sediment levels of 11.8 ng/g were found, exceeding the ERL by 800 percent.

Saleh, Molaei, Fumani and Abedi, Antifouling paint booster biocides (Irgarol 1051 and diuron) in marinas and ports of Bushehr, Persian Gulf, *Marine Pollution Bulletin,* 2016
For this publication and analysis of seawater and sediment samples was performed in Bushehr, Iran. The highest Irgarol-1051 level concentration in seawater was 63.4 ng/L. The highest concentration in soil was 35.4 ng/g.

The Americas:

Gardinali *et al*, Occurrence of Irgarol 1051 in coastal waters from Biscayne Bay, Florida, USA, *Marine Pollution Bulletin*, 2002
In this paper the contamination of the antifouling compount Irgarol 1051 has been documented in the USA. The area studied was the Biscayne Bay coastal waters, with samples having been collected from different coastal locations. The Antifoulant was detected in 80% of the locations that were sampled. Altghough the overall concentrations reported were low when compared to the European and Japanese waters, the consistent detection of the substance at concentrations that were ranging from 1 to 61 ng/l indicate the potential contatmination of US coastal waters. Furthermore, the studies have confirmed the presence of the metabolite M1 along the Biscayne Bay and the Miami River. The paper concluded that the findings along with the data generated from this investigation provide a set of basic tools for managing the biocide in coastal waters of Biscayne Bay, and will help to assess the potential environmental risk associated with present and future use of Irgarol 1051 within US coastal waters.

Owen, Knap *et al*, Inhibition of coral photosynthesis by the antifouling herbicide Irgarol 1051, *Marine Pollution Bulletin*, 2002
This study examined Irgarol 1051 concentrations in marinas in Bermuda and Florida, and furthermore reports on results of incubation experiments from the coral *Madracis mirabillis*. Of the sixteen examined coastal areas, Irgarol 1051 concentrations in 12 exceeded the ERL of 24 ng/L, while for 4 locations concentrations above 100 ng/L were detected. Photosynthesis of the coral was measurably reduced at levels as low 63 ng/L.

Carbery, Owen, Frickers *et al*, Contamination of Caribbean coastal waters by the antifouling herbicide Irgarol 1051, *Marine Pollution Bulletin*, 2006
Seawater samples from several sites at six different coastal areas on three different days in Puerto Rico and the U.S. Virgin Islands were examined, with 85 per cent of the samples testing positive for Irgarol 1051. Concentrations varied widely between and also within the different sites. Concentrations were above 24 ng/L at overall nine points (of three different

harbours). Concentrations above 200 ng/L were found at three sites of one harbour, which were above this threshold at all three time points. The highest level detected was 1300 ng/L.

Hall Jr., Killen *et al*, Ecological risk of Irgarol 1051 and its major metabolite in coastal California and reference areas, *Marine Pollution Bulletin*, 2006

The study aimed to determine ecological risk and measured concentration of Irgarol in coastal marinas. Risk from exposure was evaluated and found to be low, although levels exceeded the predicted no effect concentration (PNEC) accepted by the responsible EU bodies and the ERL, which would place them in the high risk category. The highest measurement was 323 ng/L; 34 measurements exceeded 24 ng/L, four measurements exceeded 100 ng/L, and three of those were above 200 ng/L.

Sapozhnikova, *et al,* Antifouling pesticides in the coastal waters of Southern California, *Marine Pollution Bulletin*, 2007

The study examined occurrence of Irgarol-1051 in surface waters in several marinas in the area of San Diego, CA. Irgarol-1051 was detected in all samples; for 17 of 30 samples, the Irgarol concentrations measured were above 24 ng/L, and in five of 30 samples the levels were above 100 ng/L. The highest level of Irgarol-1051 was 304 ng/L.

Knutson, Downs and Richmont, Concentrations of Irgarol in selected marinas of Oahu, Hawaii and effects on settlement of coral larvae, *Ecotoxicology*, 2012

Seawater samples from selected marinas and coral reefs on the islands of Oahu, Hawaii were collected and examined, and effects of Irgarol on coral larvae (*Porites hawaiiensis*) were evaluated in laboratory tests. Irgarol was not detected in offshore reefs, but levels in marinas exceeded 100ng/L and 200 ng/L in eight and two samples, respectively (highest concentration detected: 283 ng/L). The coral settlement bioassays showed statistically significant reductions in coral larvae settlement at concentrations of 100 ng/L and higher ($P > 0.05$). EC_{50} was found to be 1738 ng /L.

Batista-Andrade et al, From TBT to booster biocides: Levels and impacts of antifouling along coastal areas of Panama, Environmental Pollution, 2017

The paper investigated the contamination of a number of biocides including Irgarol 1051. Irgarol 1051 was detected in eight and Diuron in four out of eleven sites, with levels higher than the environmental limits proposed by the Dutch and Norwegian authorities. This indicates that toxic effects to marine organisms, especially reef communities and benthic organisms, are probably taking place. DCOIT levels were detected in association to antifouling paint particles, specifically near shipyards in Colon port and Flamenco Marina. It was clear that paint particles are acting as important secondary sources of antifouling biocides contamination to Panamanian coastal environments. The present study reported simultaneous inputs and impacts of current and old generations of antifouling biocides, and included an urgent call by its authors for immediate action by the environmental authorities of Panama.

Africa:

Hannachi, Elarbaoui, Khazri et al, Impact of the biocide Irgarol on meiofauna and prokaryotes from the sediment of the Bizerte lagoon—an experimental study, *Environ Sci Pollut Res*, 2016
Sediments from up to 15 cm below sediment surface of the Bizerte lagoon in Tunisia were collected and the meiofauna and procaryotes were examined as well as incubated with Irgarol. Irgarol was shown to be toxic for both meiofauna and bacteria inhabiting the sediments, causing drastic decreases in the abundance of nematodes and an increase in the number of oligochaetes. The high Irgarol concentrations in parts of the lagoon thus could potentially affect biodiversity, leading to a clear reduction of it in the *in vitro* experiments.

Australia:

Antifouling biocides in Perth coastal waters: a snapshot at select areas of vessel activity: *Government of Western Australia Department of Water May 2009*
This report is presenting a survey of antifouling biocides that was carried out in Perth coastal waters. The study was funded by the Australian Government and the purpose was to undertake a preliminary scoping study of chemicals that have not usually included in such investigations, and link these to vessel activity or related industries. Eight sites, including commercial harbours, recreational boat harbours, ship-building facilities, sailing clubs and boatlifts/slipways, were chosen to represent a broad range of intensive vessel activities. The project found significant contamination by unregistered biocides including Irgarol 1051 at a number of sites in Perth coastal waters. Irgarol 1051 was at the time not registered for use in antifouling paints in Australia.

Arctic

Kottuparambil et al, Comparative assessment of single and joint effects of diuron and Irgarol 1051 on Arctic and temperate microalgae using chlorophyll a fluorescence imaging *Ecological Indicators 2017*
This study presents the adverse effects of antifouling biocides such as diuron and Irgarol 1051 to the polar environment showing that the ecological risk of these biocides could be higher in the polar ecosystems than in temperate regions. The tested chemicals were equally toxic to the Arctic strains and the authors concluded therefore, that there is a need to closely monitor anthropogenic stress factors including shipping and ice breaking activities.

Europe:

Zhou et al., **Seasonal distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber Estuary and Humber coastal zone, *Marine Pollution Bulletin*, 1996**
This study examined the concentrations of a number of antifouling substances including Cybutryne in the Humber Estuary and coastal zone in the United Kingdom. The concentrations detected were ranging from between <1 to 39 ng/L with the majority being below the Environmental Risk Limit (ERL) of 24ng/L, set by the Dutch National Institute of Public Health. Cybutryne levels peaked in April, fell over the summer and increased again in September.

Tolosa et al., **Contamination of Mediterranean (Côte d'Azur) coastal waters by organotins and Irgarol 1051 used in antifouling paints, *Marine Pollution Bulletin,* 1996**
This study examined the concentrations of a number of antifouling substances along the French Mediterranean Coast. Cybutryne was detected in almost all locations and samples, with concentrations ranging from <1.5 to 17 ng/L in open waters and 14 to 640 ng/L in marinas and ports; being the highest concentrations detected in marinas with a high density of small pleasure crafts.

Tolosa and Readman, **Simultaneous analysis of the antifouling agents: tributyltin, triphenyltin and IRGAROL 1051 in marina water samples, *Analytical Chemic. Act.*, 1996**
Using a new sampling method that allows for the simultaneous detection of several antifouling substances in samples, this article examined the concentration of different organotin and booster antifouling substances in a port and marina in Monaco. Cybutryne levels in Monaco Port were found to be 132 ng/L and 275 ng/L in Fontvieille Marina.

Ferrer et al., **Pilot Survey for Determination of the Antifouling Agent Irgarol 1051 in Enclosed Seawater Samples by a Direct Enzyme-Linked Immunosorbent Assay and Solid-Phase Extraction Followed by Liquid Chromatography−Diode Array Detection, *Environmental Science and Technology*, 1997**
This study used an enzyme-linked immunosorbent assay (ELISA) to determine Cybutryne concentrations along the Spanish Eastern Mediterranean coast. Concentrations were found to be between 7 ng/L and 325 ng/L. In the majority of samples, Cybutryne levels were found to exceed the ERL of 24 ng/L. The highest concentrations of the antifouling agent were detected in April, followed by the concentrations measured in the second half of September.

Scarlett et al., **Occurrence of the marine antifouling agent irgarol 1051 within the Plymouth Sound locality: Implications for the green macroalga Enteromorpha intestinalis, *Marine Pollution Bulleting, 1997***
Scarlett et al. measured cybutryne concentrations in and around Sutton Harbour, and assessed the effects on a green macroalgae species. Their survey showed that about one in

five boats used antifouling substances containing cybutryne. Concentrations in 12 of 18 samples from four of the six locations were found to be above the ERL, the highest value of 127 ng/L was measured in Sutton Harbour Marina. The no effect concentration EbC_0 for *Enteromorpha intestinalis zoosporis* was calculated to be 22 ng/L, with slowly increasing levels of growth inhibition and, at higher levels, increasing cell death.

Scarletta et al., Risk posed by the antifouling agent Irgarol 1051 to the seagrass, *Zostera marina*, *Aquatic Toxicology*, 1999

This publication examines the short-term and long-term effects of cybutryne concentrations on the seagrass *Zostera marina*, while also measuring concentrations in a number of estuaries in South Western England. Water concentrations were found to range between <30ng/L and 10 ng/L. Dry weight Zostera tissue concentrations, however, were up to 25000 times higher than the water concentrations, indicating accumulation in the plant. While short-term effects were only detected at levels higher than ever detected in harbours, long-term differences in photosystem II activity between cybutryne-exposed and sample cultures were detected at levels as low as 180 ng/L, a concentration commonly found in UK marinas at the time.

Ferrer and Barceló, Simultaneous determination of antifouling herbicides in marina water samples by on-line solid-phase extraction followed by liquid chromatography–mass spectrometry, *Journal of Chromatography A,* 1999

In this publication, samples were taken at the Ebre Delta (April 1998 – Dec 1998) and Masnou Marina (April '96 – January '99) and analysed using on-line solid-phase extractions and liquid gas-mass spectrometry. In the Masnou Marina, the highest cybutryne level detected was 325 ng/L, with a majority of samples above the ERL, but below 100 ng/L. In the Ebre Delta, all samples were found to have cybutryne levels above 50 ng/L, the highest being found in June '98 with a cybutryne concentration of 280 ng/L.

Martínez et al., Part-per-trillion level determination of antifouling pesticides and their by-products in seawater samples by off-line solid-phase extraction followed by high-performance liquid chromatography–atmospheric pressure chemical ionization mass spectrometry, *Journal of Chromatography A,* 2000

As part of the research for this publication, concentrations of organotin and booster antifouling substances were measured along the Catalan coast in the Spanish Mediterranean Sea. High diuron and Sea Nine 211 (DCOIT) concentrations were detected, while only comparably low levels (<100ng/L) were measured. Concentrations of cybutryne by-products (M1) were found to be higher than those of cybutryne itself, with no precise concentrations being stated in the article.

Sargent et al., Levels of antifoulant irgarol 1051 in the Conwy Marina, North Wales, *Chemosphere*, 2000

This study was carried out at Conwy Marina in Wales, UK, from January to March 1999. The levels detected ranged between 7 ng/l to 543 ng/L, and were found to be correlated with density of boating activity, but not water temperature, salinity or pH. Cybutryne levels above the ERL of 24 ng/L were found in the majority of samples. The study also concluded that a large number of sites must be sampled to obtain a representative picture of cybutryne concentrations.

Voulvoulis et al., Occurrence of Four Biocides Utilized in Antifouling Paints, as Alternatives to Organotin Compounds, in Waters and Sediments of a Commercial Estuary in the UK, *Marine Pollution Bulleting*, 2000
For this study, cybutryne concentrations were measured at the Blackwater estuary in southern England. Sampling was conducted between the end of the boating season 1998 until the beginning of the following boating season in June 1999. Both the highest sediment and the highest water concentrations were measured after, and not before the boating season; with sediment levels ranging between <3.1 and 222.3 ppb, and water levels between below detectable levels and 0.68 ppb.

Thomas et al., Antifouling Paint Booster Biocide Contamination in UK Marine Sediments, *Marine Pollution Bulletin*, 2000
Just before the IMO ban of TBT came into effect, sediment samples were taken at 27 different locations to determine levels of a number of antifouling agents at Southampton Waters in Southern England. The survey was conducted to detect concentrations for TBT, Irgarol 1051, the Irgarol 1051 metabolite M1, diuron, in coastal and offshore sediments. The highest cybutryne concentration detected was 110 ng/g at the Brooklands Marina, with overall low concentrations of the cybutryne metabolite M1.

Agüera et al., Multiresidue method for the analysis of five antifouling agents in marine and coastal waters by gas chromatography–mass spectrometry with large-volume injection, *Journal of Chromatography A*, 2000
The levels of five different antifouling agents in three marinas in Almería, Spain, were examined for this publication. The detected cybutryne levels all exceeded the ERL, ranging between 25 and 450 ng/L. The solid-phase extraction used for the detection was shown to be a suitable method for the simultaneous detection of a number of antifouling substances.

Thomas et al., Antifouling Paint Booster Biocides in the UK Coastal Environment and Potential Risks of Biological Effects*, Marine Pollution Bulletin, 2001*
As part of this publication, cybutryne concentrations in Crouch Estuary, Essex, Sutton Harbour, Plymouth and Southampton Water in England were taken from April to October 1998. The majority of samples showed concentrations below the ERL of 24ng/L, with the notable exception of Sutton Harbour where the average was above the ERL and the

maximum value 76 ng/L and Hythe Marina of Southampton Water, where a concentration of 1421 ng/L was found.

Martínez and Barceló, Determination of antifouling pesticides and their degradation products in marine sediments by means of ultrasonic extraction and HPLC-APCI-MS, Fresenius' *Journal of Analytical Chemistry, 2001*

In this paper a method has been developed for the simultaneous determination of antifouling pesticides and some of their degradation products, e.g. dichlofluanid, diuron, demethyldiuron, 1-(3,4-dichlorophenyl)urea, sea-nine (DCOIT), Irgarol 1051 (cybutryne) and one of its metabolites (2-methylthio-4tert-butylamino-s-triazine) in marine sediments. The analytical procedure was successfully applied to the determination of these pesticides and their degradation products in marine sediment samples from different marinas of the Catalan coast. The compounds detected were: diuron, dichlofluanid, demethyldiuron, sea-nine, and Irgarol 1051. The highest concentrations were those of diuron and Irgarol 1051 of 136 and 88 µg kg–1, respectively.

Ferrer and Barceló, Identification of a new degradation product of the antifouling agent Irgarol 1051 in natural samples, *Journal of Chromatography A,* 2001

This study also examined cybutryne and its metabolite's levels in water at the Masnou Marina. Sampling took place in 1997 and 1998, with the highest concentration of cybutryne, 119 ng/L detected in June 1998. Metabolite concentrations M1 concentrations that were detected and reported for the first time as part of this study, were lower than the parent, peaking at 23 ng/L in July 1993.

Hernando et al., Determination of traces of five antifouling agents in water by gas chromatography with positive/negative chemical ionisation and tandem mass spectrometric detection, *Journal of Gas Chromatography A*, 2001

Hernando et al focused on Cybutryne concentrations in Southeast Spain. The method applied was gas chromatography-mass spectrometry, using an ion trap mass spectrometer. The method was then tested for water samples from three marinas at Almería, Spain, detecting cybutryne levels between 50 ng/L and 1000 ng/L.

Sakkas et al., Survey for the occurrence of antifouling paint booster biocides in the aquatic environment of Greece, *Environmental Science and Pollution Research*, 2001

This paper presents an extended survey of antifouling biocides including Irgarol 1051 (cybutryne) carried out in Greek ports and marinas during the period from October 1999 to September 2000. The paper describes in detail the methodology used to identify the compounds from seawater samples. The results have shown that overall the concentrations levels of the biocides where elevated throughout the sampling period from April to October 2000. Among the biocides in the study, the detection of Irgarol 1051 was the most frequently detected and ranged from 11 to 90 ng/L

The mean detected concentrations detected ranged from 10 to 41 ng/L and the higher values were found in the Piraeus Mikrolimano marina, which is the busiest enclosed marina of Piraeus. Direct contamination from the shipyard with Irgarol 1051 due to ship painting, in addition to the normal leaching rate, cannot be excluded for the case of Elefsina marina where the mean concentration value was also above the ERL (31 ng/L).

Albanis et al., Antifouling paint booster biocide contamination in Greek marine sediments, *Chemosphere*, 2002
Samples from ports and marinas located on the Eastern and Western coast of Greece were taken to measure Cybutryne concentrations in sediment for this study by Albanis et al. The three ports examined were Piraeus, Patra and Thessaloniki. Additionally, samples from seven other marinas in Greece were taken. Cybutryne levels in sediment in ports were lower, ranging from 3 to 19 ng/g: Piraeus 12-19 ng/g, Patra 8-11 ng/g, Thessaloniki 3-11 ng/L. Sediment levels in marinas were markedly elevated, ranging from 10 to 690 ng/g, with the highest concentration measured in Elefsina (690 ng/g) and Thessaloniki marina (350 ng/g).

Thomas et al., Antifouling paint booster biocides in UK coastal waters: inputs, occurrence and environmental fate, *Science of the Total Environment, 2002*
This study examined cybutryne concentrations in a number of UK docks and marinas as well as possible factors increasing cybutryne leaching into the water. Concentrations ranged from 1ng/L to 305 ng/L in the Hythe marina. Hosing was found to be a significant source of input of cybutryne into the marine environment. Cybutryne and Diuron were also found to be highly persistent in water and to accumulate in sediment, while booster biocides such as Sea Nine 211 were removed quickly and not detectable in the sediments at significant levels.

Bowman et al., Seasonal variability in the concentrations of Irgarol 1051 in Brighton Marina, UK; including the impact of dredging, *Marine Pollution Bulletin*, 2003
This publication examined cybutryne levels and fluctuations over the course of one year in the UK's largest marina in Brighton, with concentrations between <1ng/L and 960 ng/L being detected, but most measurements below 100 ng/L. Sediment concentrations ranged from <1ng/g to 77 ng/g. The highest levels were detected during the months of November to January, an increase likely associated with the increased dredging activity during these months.

Georgia Gatidou et al. Fate of Irgarol 1051, diuron and their main metabolites in two UK marine systems after restrictions in antifouling paints *"Environment International, 2007"*
The paper includes concentrations of Irgarol 1051 and diuron and their products in Shoreham Harbour and Brighton Marina in the UK during 2003-2004. The highest concentrations of Irgarol 1052 were 136 and 102 ng/L in water and 40 and 49 ng/g dry weight in sediments for

Shoreham Harbour and Brighton Marina, respectively, thus levels in both water and sediment exceeded the Dutch ERL. As the degradation product of Irgarol 1051, M1 was also widespread with the highest concentration of 59 ng/L in water and 23 ng/g in sediments in Shoreham Harbour, and 37 ng L^{-1} in water and 5.6 ng/g in sediments in Brighton Marina. The target compounds showed enhanced concentrations during the boating season (May–July), when boats were being re-painted (January–February), and where the density of pleasure crafts was high. Overall, the concentration of Irgarol 1051 decreased significantly from late 2000 to early 2004, indicating the effectiveness of controlling its concentrations in the marine environment following restricted use.

Ineris, Cybutryne EQS dossier, 2011.
This document was prepared as part of the review of the priority substances list (under the EU Water Framework Directive). It focuses on cybutryne's chemical characteristics and environmental behaviour and compiles information and data on fresh and seawater concentrations, sediment concentrations as well as toxicity for marine organisms and humans from a number of European environment agencies and numerous peer-reviewed publications. These data show that cybutryne concentrations in several European coastal areas have been found to significantly exceed EC_{50} and other risk levels for marine organisms. The collated data were the basis of the decision taken in 2013 to add cybutryne to the priority substances list, with environmental quality standards being set for both fresh and marine waters.