OECD Environmental Health and Safety Publications

Series on Emission Scenario Documents No. 13

EMISSION SCENARIO DOCUMENT ON ANTIFOULING PRODUCTS

ANNEX

Environment Directorate

Organisation for Economic Co-Operation and Development

2005

CONTENTS

Annex I

Description of existing calculation models for estimating the emission from service life from the use of antifouling biocides on ship hulls

INTRODUCTION

In this annex an overview is given of 3 models which can be used to predict environmental concentrations of antifoulings used in coatings for ship hulls: USES, REMA and MAM-PEC. Both REMA and MAM-PEC have recently been developed specifically for antifoulings. Other fate models can be used for the same purpose. Examples are EXAMS, ECOS and DELWAQ. However, these models need to be adapted to accommodate the main features of the emission patterns that are deemed important for antifoulings (like shipping characteristics and leaching rates). Besides, many models need to be modified or linked to another tailor-made model to deal with complex hydraulic processes of typical marine environments. In both the REMA and MAM-PEC project it was decided after an evaluation of the available chemical fate models, to develop a new model for antifoulings. The models are not described in detail in this chapter. Described are the prototype environments modelled which is important for the selection of environmental emissions scenarios in the next chapter.

REMA

The REMA model provides predictions of antifoulant concentrations in marinas and estuaries based on the quantitative water-air sediment interaction (QWASI) model developed by Mackay et al. (1983). The model uses partition data obtained from laboratory experiments.

The model requires a large number of input variables describing discharges, physico-chemical properties and environmental parameters. Therefore the model, in its initial form, was considered unsuitable for routine use or for use by inexperienced operators. The model was set up for several UK marinas and estuaries. These cover a number of scenarios, with estuaries of varying sizes and dynamics and marinas of different types (e.g. locked, open, pontooned etc.). Using this approach, the only information a user needs to input would be the properties of the antifoulant and the number of vessels in each marina. The following range of estuary types was specified:

- a small estuary that dries out;
- a well mixed estuary, with a narrow mouth;
- a well mixed estuary, with a wide mouth;
- a large, complex estuary.

Each estuary type is divided into three estuary segments each containing a marina as shown in figure A1.1.
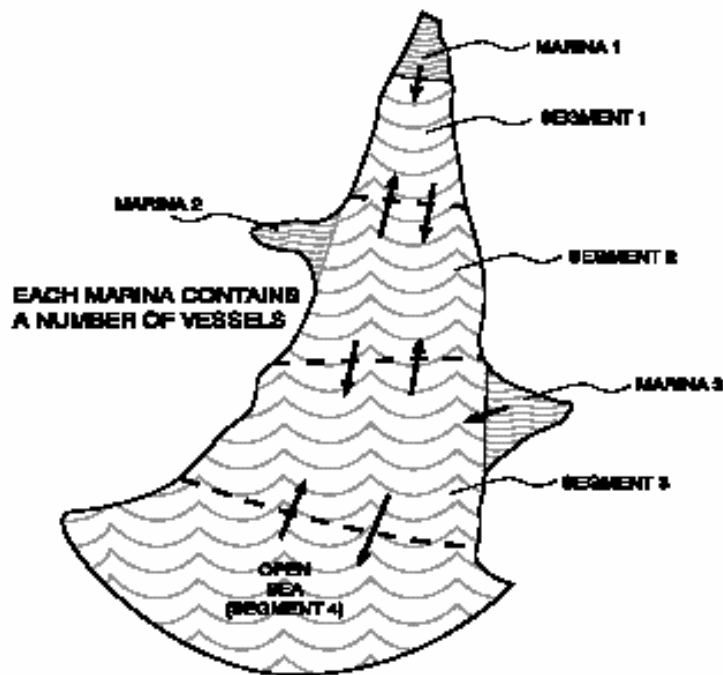
Figure A1.1 **Schematic drawing of the estuary in the REMA-model: estuary with three segments each containing a marina**

Each estuary segment has an inflow from a river, which itself may have a known concentration of the biocide. The open sea at the mouth of the marina may be seen as the fourth segment. A marina and an estuary type can be chosen from default lists. Most of the parameters can be changed by the user. However, the user should do this with caution, because e.g. the size of a default marina is based on real situations.

The output of the model is expressed as the steady state concentration in bulk water and sediment for both the marinas and the estuary segments. No calculations are made for changes in the open sea segment as this is assumed to stay constant.

The outputs of the REMA-model were validated against monitoring data. The model has been shown to produce predicted environmental concentrations for two UK estuaries, which are close to measured values for the selected antifoulants.
[Source: REMA-report]

MAM-PEC

This section gives a short description of the characteristics of the MAM-PEC-model. In chapter 5 the default scenarios within the MAM-PEC-model will be discussed and compared with possible scenarios in practice (see **Error! Reference source not found.**) and, when necessary, with comparable default scenarios from other calculation models.

The MAM-PEC model generates predicted environmental concentrations for fixed default marine environments. During the MAM-PEC project a choice was made between a generic model for a few standard environments (with flexibility for adaptation to mimic local conditions) or a region-specific model (based on e.g. existing models for North Sea, Baltic,

Mediterranean). Because of (a.o.) the facts that in the case of a region specific model adaptation to other regions can only be done with large effort and standardisation is complex, the choice was made for the following five standard or prototype environments:

- Commercial harbour;
- Estuary with small harbour;
- Marina;
- Open sea;
- Shipping lane.

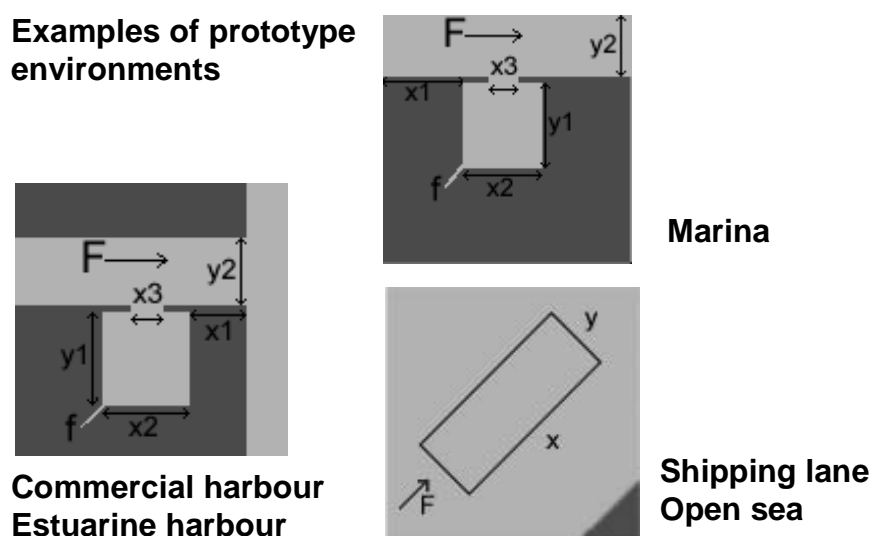In figure A1.2 these prototype environments are depicted.

Figure A1.2   **The prototype environments included in the MAM-PEC Model (from Van Hattum et al., 2002).**

According to MAM-PEC these represent the most important existing marine scenarios. The commercial harbour is situated along a large estuarine river at a distance of 2 km from the mouth of the river. The estuarine harbour is similar and differs in dimensions and the size of the harbour. The marina is an enclosed area situated directly at the coast. An additional poorly flushed marina was added as a default scenario to mimic conditions with low tidal exchange (e.g. Baltic, Mediterranean). Both marina, commercial and estuarine harbour may have additional flushing from a small river or urban drainage system discharging at the rear end of the harbour.

As described earlier the defined standard environments can be adapted to local situations and added. The model takes into account emission factors (e.g. leaching rates, shipping intensities, residence times, ship hull underwater surface areas), compound related properties and processes (e.g. Kd, Kow, Koc, volatilisation, speciation, hydrolysis, photolysis, bacterial degradation), and properties and processes related to the specific environment (e.g. currents, tides, salinity, suspended matter load).

There is a broad distinction between organic and inorganic compounds both in the mechanisms and relative importance of the processes. For instance for copper, processes such as sorption, speciation- and redox reactions have a prominent role in the fraction of freely bioavailable and potentially toxic Cu^{2+}.

As copper is an ingredient in many antifouling products, a specific module has been introduced in the MAM-PEC model which calculates Cu-speciation and predicts expected ranges of free Cu^{2+} ion concentrations.

The outputs of the model consist of the average, median, minimum, 95-percentile and maximum concentrations for the different default environments for the dissolved concentration, the total aqueous concentration, the concentration on particulate matter and the sediment. As sediment processes are slow and attaining steady state may take years to decades, the model calculates sediment concentrations for different time periods (1, 2, 5 and 10 year). It is the responsibility of the user to determine which statistics need to be used. Maximum values, for example, only occur directly below the emissions, which are situated e.g. in the rear end of the harbour.

For a selected number of compounds model-predictions for specific environments were compared with measured concentrations in order to evaluate the validity of the model. The model predictions appeared to be reasonably in line with results from monitoring studies. [Source: MAM-PEC-report]

USES

In this section the USES-model is described. This model consists of a single default scenario. In chapter 5 the characteristics of this scenarios will be discussed and compared with possible scenarios in practice (see **Error! Reference source not found.**) and, when necessary, with comparable default scenarios from other calculation models.

For calculating the emissions of antifoulants in the aquatic environment a middle size yacht-basin was modelled. This scenario that is incorporated in USES 3.0 (Uniform System for the Evaluation of Substances) is derived from the original scenario of Luttik et al. 1993. USES 3.0 has been developed by the RIVM in the Netherlands (Linders and Jager 1997).

The emission is calculated from the mean leaching rate of the antifoulant and the total ship area. The emission is converted to a concentration in the water with help of the water volume per ship and the residence time of water in the basin. The concentration is calculated applying equilibrium partitioning over the water phase and suspended matter using a solids-water partitioning coefficient.

In the USES-model, only the concentrations for the water phase (including suspended matter) in the yacht basin are calculated.

The results of model calculations were compared with monitoring data from three sample sites in Sweden and two sample sites in the Netherlands. This was done for tributyltin, copper, irgarol and diuron. Based on these measurements it was concluded that in some cases the model calculates too high values in comparison with the measured values, but that they are not unrealistic high. However, applying the defaults regardless of the antifoulant and the environment to be assessed will result in data with very little relevance. [Source: USES 3.0 and Council of Europe, 1996]

Annex II

Provision of biocide Leaching rate data for Anti-Fouling Products. A Discussion Document from the Anti-Fouling Working Group of CEPE. April 2003.

PROVISION OF BIOCIDE LEACHING RATE DATA FOR ANTI-FOULING PRODUCTS

A Discussion Document from the Anti-Fouling Working Group of CEPE

CEPE Anti-Fouling Working Group, April 2003

1. Introduction

For anti-fouling coatings, a significant route of exposure into the environment is entry of active substances into the aquatic environment as they are leached from the paint film. The **biocide leaching rate** is therefore a critical parameter in an environmental risk assessment. This issue has been the focus of discussion with several regulatory authorities and standards organisations (eg. ASTM, ISO). The following chapter describes the position of Anti-Fouling Coatings Manufacturers who are members of CEPE[1] to the issue.

1.1 Biocide leaching rate from anti-fouling coatings

Release rates of biocides from anti-fouling paints (AF) are required by a number of regulatory authorities to review/regulate the release of biocides into the aquatic environment. An accurate biocide release rate value is essential when conducting an environmental risk assessment. There has been much debate over experimentally derived release rate data, with some methods generally considered overly conservative and not believed to assess the actual environmental loading of the biocide into the environment. This document summarises the current situation.

1.2 Present Methods

1.2.1 Laboratory methods

The following recognised standard methods have been developed to measure the release rate of biocides from AF paints:

ASTM D5108-90	Organotin release rates from A/F coating systems in sea water
ASTM D6442-99	Copper release rates from A/F coating systems in seawater
ISO 15181-1	Determination of release rate of biocides from A/F paints – General method for extraction of biocides
ISO 15181-2	Determination of release rate of biocides from A/F paints - Determination of copper-ion concentration in the extract and calculation of the release rate

These methods are standardised laboratory methods using a rotating cylinder device measuring the release rates during a given time of immersion (45 days) under specified conditions (T: $25^{o}C$ +/- 1; salinity: 33 – 34 parts per thousand; pH: 7,9 - 8,1).

However the following limitations should be taken into consideration when using data generated following the above mentioned standardised laboratory methods:
The Laboratory methods above (with the rotating cylinder device) were primarily developed and validated for organotin copolymer-containing and first generation TBT-free copper-containing A/F paints.

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[1] CEPE is the European Association of Paint Manufacturers

The results obtained from 'round robin' tests of the methods above show a significant level of variation between different experimental laboratories for organotin copolymer containing paints and a high level of variation for first generation tin-free copper containing formulations.

The ASTM and ISO methods specify that release rates are to be measured in fully saline water (33-34 parts per thousand) and at a seawater temperature of 25^0C +/-1. Release rates at lower salinity and/or at lower temperatures, such as those generally prevalent in Finnish waters (Gulf of Finland) and the Baltic Sea, are expected to be lower.

In some cases the short testing period in the standard methods above generates release rate data which is too high and does not necessarily represent the release rate of a biocide during the in-service lifetime of an anti-fouling coating. For example it is well known that the copper leaching rate for soluble-matrix type paints decays exponentially with time. In these cases, the ASTM/ISO 'pseudosteady state' release rates measured for days 21-45 is <u>clearly</u> an overestimate of the 'average' release rate over the paint's specified lifetime. In some cases leaching rate data derived from the methods above, if representative of product on ships hulls, would suggest that that there will be no biocide remaining in the paint after a few months in service. This is clearly not the case.

1.2.2 Field tests

The Space and Naval Warfare Systems Center, San Diego (SSCSD), has developed a field method for measuring in-situ organotin release rates using a dome placed on the painted surface of an immersed hull. A fixed volume of water sampled through this device was analysed and the organotin release rate results obtained by this method were found to be an order of magnitude lower than results obtained using the standardised laboratory methods described above.

SSCSD has recently used the dome method to measure in situ copper release rates from immersed panels and the published results demonstrate that the release rates measured in the field by this technique are also significantly lower than those measured using laboratory methods.

These results suggest that the laboratory methods above may overestimate organotin and copper release rates from anti-fouling paints and hence the environmental loading into the aquatic environment. Therefore interpretation and use of the derived release rates, as direct input into environmental risk assessments should only be done with caution.

It should be noted that it is stated in the published ASTM (D5108-90) method for determination of leaching rate for organotin, that the test method only serves as a guide for the organotin leach rate in service. It is further stated in the ASTM method for determination of copper release rates (D 6442-99) that '*the test method has not yet been validated to reflect in-situ copper release rates for anti-fouling paints and therefore should not, at present, be used in the process of generating environmental risk assessm*ents', and '*this test method serves only as a guide for characterisation of the early release pattern as well as estimating the steady state release of copper from anti-fouling coatings*'. Further it is stated in ISO method for copper (ISO 15181-1), that '*actual release rate of biocides from ship's hulls into the environment will depend on many factors such as ship operating schedules, length of service, berthing conditions, paint condition, as well as temperature, salinity, pH, pollutants and bacterial content*'.

1.2.3 Mass balance method - Calculation method (See Appendix 1)

The European Paint Industry (CEPE) has developed a calculation method for the determination of leaching rates based on the assumption that the total release of biocide can never exceed the amount incorporated into the coating. Data generated by this method has been accepted as an interim solution by some countries' authorities (Norway, and The Netherlands) as the method used for submission of release rate data with a product application.

Data calculated by this method for the release of copper from an organotin copolymer paint shows good agreement with copper release rates measured via the ISO method, although that agreement was less good for copper release from rosin-based paints, and there is no data currently available for other biocides. The calculation method has, on recommendation from CEPE been placed on the agenda in ISO/TC35/SC9/Working Group 27, for further discussion.

The method is a simplified generic model of biocide release, which is based on the assumption that the majority of biocide in the paint that is applied is released at a constant rate during the specified lifetime.

The calculated release rate derives from the volume of dry paint film applied, the loading of biocide in the paint, and the specified lifetime of the product.

The model assumes that:
- the biocide release rate falls linearly for the first 14 days following immersion;
- the biocide release rate is thereafter constant from day 14 until the last day of the coating's specified life-time;
- the ratio of the cumulative amount of biocide released during the first 14 days following immersion to the average release rate during the remainder of the coating's specified lifetime is 30;
- 30% of biocide is retained in the paint film at the end of its specified lifetime.

Based on these assumptions, and from knowledge of the biocide content of the paint, specified dry film thickness and its specified lifetime, it is possible to calculate

X: Amount of biocide released during first 14 days ($\mu g/cm^2$)
Y: Average leaching rate during the rest of the lifetime ($\mu g/cm^2$ pr day)

(See Appendix 1: Figure A1.1)

In common with release rate data which is generated by the ASTM/ISO experimental methods described above, it is probable that the calculated average release rate will overestimate the release rate under static conditions, *i.e.* when the vessel is idle in a harbour (*static release rate*). This is the typical situation for many pleasure craft, which are only sailing for a small amount of time during a season, and for ocean-going vessels when they are in port. Conversely, both the calculated and measured average release rate will most probably underestimate the release rate when the ship is in operation (*dynamic release rate*), as would be the case when a vessel is at sea. Release rates higher than the calculated or experimentally measured average release rates will therefore mostly occur in deep-sea areas under conditions of high dilution, rather than in shallow in-shore or coastal waters.

1.3 Development of Leach Rate Test Methods within ASTM and ISO

ASTM is currently working on draft documents at sub committee level for three biocides: Sea-Nine 211, Irgarol, and Zinc Omadine.

ISO has just initiated work at Working Group (WG) level for three biocides: Zineb, Dichlofluanid (Preventol A4) and Pyridine-Triphenyl Borane.

It is likely that the resulting ISO/ASTM standard methods will be laboratory methods based on the existing release rate methods for organotin and copper.

In the long-term it is envisaged that more accurate and reproducible experimental methods to determine the release rate of biocides from anti-fouling paints will be established.

2. Conclusion

Internationally accredited standard methods exist for measuring the release rates of copper and tin biocides from anti-fouling paint films and additional methods are currently being developed for a number of organic biocides. However, the relationship between biocide release rates obtained by these laboratory test methods and the true environmental inputs of biocides from anti-fouling paints is uncertain and release rate data from these methods cannot be reliably used for environmental risk assessment. A calculation method has been used to estimate biocide release rates from anti-fouling coatings, based on the assumption that 70% of the biocide is released during the lifetime of the coating. Also, for this method there is no direct relationship between the environmental input at a certain moment in time and the calculated average release of biocide.

Given the present level of uncertainty with all approaches, until internationally agreed guidelines are developed, approved and validated, care must be taken when selecting a release rate value to use in an environmental risk assessment. However, as several regulatory authorities demand that an environmental risk assessment is performed, the best available release rate data, either experimental, calculated, or both, should be used taking due account of the limitations stated in this document. A proposed testing strategy for obtaining release rates for biocides from anti-fouling paints is given in Figure A.2.1 below.
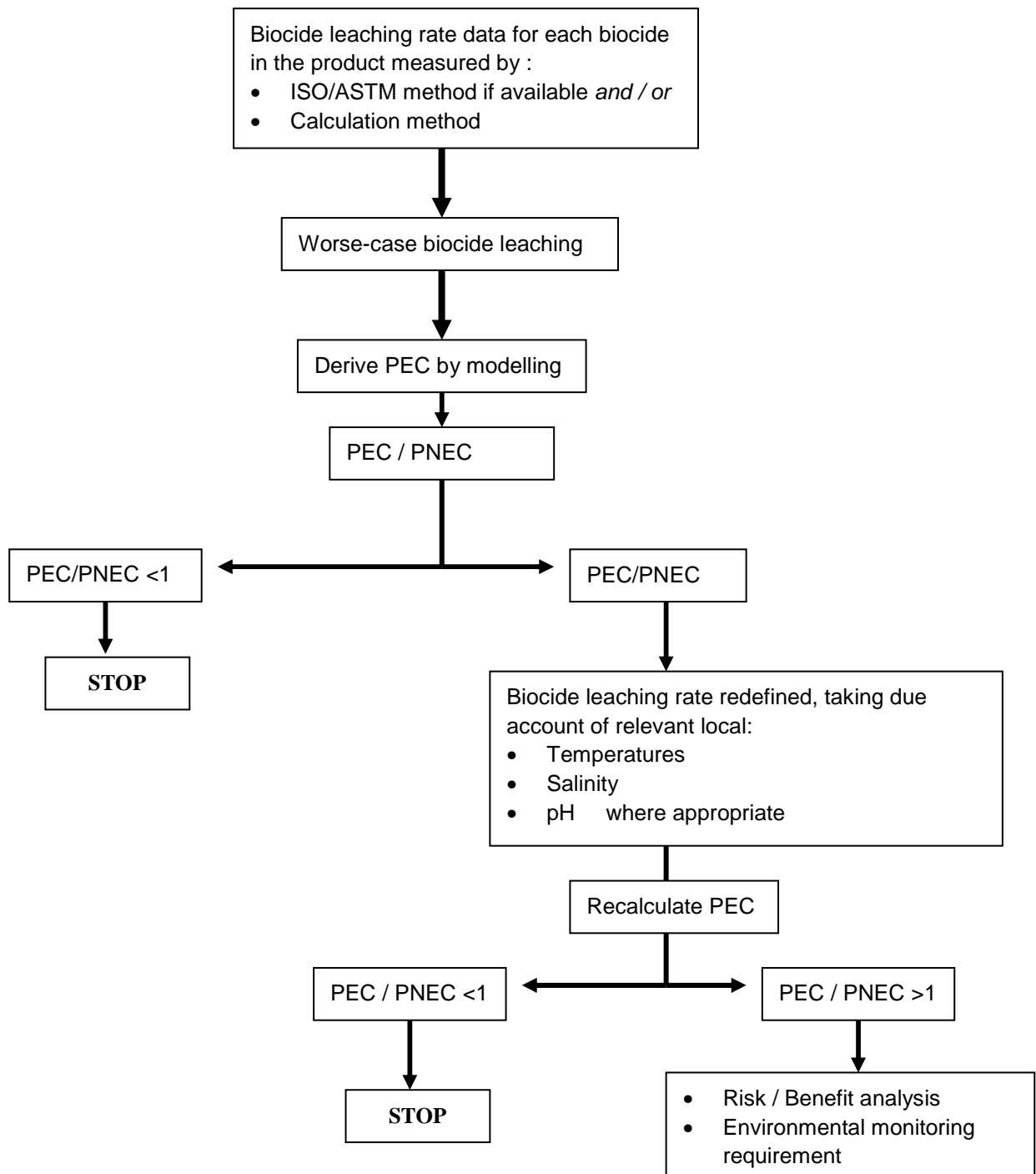
Biocide leaching rate data for each biocide in the product measured by :
- ISO/ASTM method if available *and / or*
- Calculation method

↓

Worse-case biocide leaching

↓

Derive PEC by modelling

↓

PEC / PNEC

← →

PEC/PNEC <1

↓

STOP

PEC/PNEC

↓

Biocide leaching rate redefined, taking due account of relevant local:
- Temperatures
- Salinity
- pH   where appropriate

↓

Recalculate PEC

← →

PEC / PNEC <1

↓

STOP

PEC / PNEC >1

↓

- Risk / Benefit analysis
- Environmental monitoring requirement

Figure A2.1   Proposed Testing Strategy for Release Rate of Biocides From Anti-Fouling Paints

APPENDIX 1
A METHOD FOR CALCULATING THE RELEASE RATE OF BIOCIDES FROM ANTI-FOULING PAINTS

Definitions
X = Amount of biocide released during first 14 days ($\mu g/cm^2$)
Y = Average leaching rate during the rest of the lifetime ($\mu g/cm^2$ pr day)

Assumptions:
First 14 days linear drop in release rate
Rest of the lifetime: Constant leaching rate
X/Y = 30: Constant by experience from leaching rate measurement
30% of biocide is retained in the paint film at the end of its specified lifetime (i.e. 70% is released)
See figure 1 for further details

These assumptions are based on extensive experience within the paint industry of the measured release rates of copper and tin biocides from organotin copolymer and first generation TBT-free anti-fouling paints.
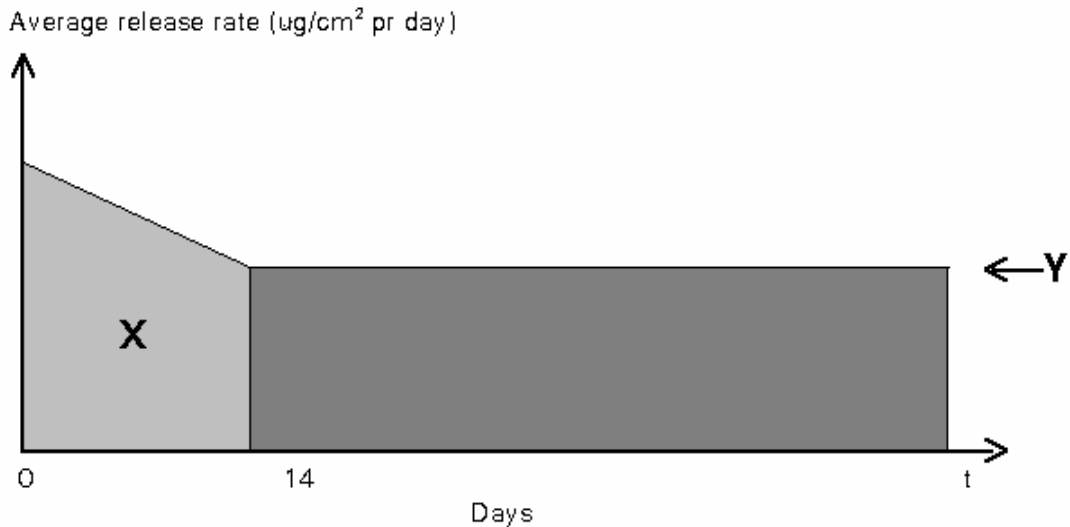

Figure A1.1

Calculations:
The calculation of total cumulative amount of biocide released during the lifetime t ($\mu g/cm^2$) is made according to the following equations:
1) $X + (t - \tfrac{1}{2}) \times 30 \times Y = L_a \times a \times W_a \times 100/SVR \times SPG \times DFT$
2) $X/Y = 30$

where:
-    **t** is the specified lifetime (months) of the paint for the dry film thickness DFT

- **30**: 1 month = 30 days
- **½**: half a month (14 days)
- L_a is the fraction of the active ingredient in the dry film released during the life time t, assumed to be 0.7. (From experience in practice L_a is estimated to be 0.7)
- **a** is the weight fraction of active ingredient in the biocide
- W_a is the concentration of biocide in the wet paint in weight %
- **100** is included to secure the units of measure in the equation
- **SVR** is the solid volume ratio (volume of dry paint versus volume of wet paint) in %
- **SPG** is the specific gravity of the wet paint (g/cm^3)
- **DFT** is the dry film thickness (in micron) specified for the lifetime t. The value to be applied depends on the type of paint

Total release of the biocide $(\mu g/cm^2)$ during the lifetime t as derived from the geometrics of figure A1.1: $X + (t-½) \times 30 \times Y$

Total release of biocide $(\mu g/cm^2)$ during the lifetime t, for the specified film thickness DFT, the concentration of biocide in the wet paint W_a and with the fraction of biocide L_a actually released during the lifetime t:

$$L_a \times a \times W_a \times 100/SVR \times SPG \times DFT$$

On the basis of equation 1 and 2 and on the basis of data on the individual anti-fouling paints and their specifications both the assumed total release during the first 14 days and the assumed average release rate of biocide during the rest of the lifetime of the product can be calculated.

Annex III

MEMBERS OF THE OECD STEERING GROUP on Anti-Fouling Products

MEMBERS OF THE OECD STEERING GROUP ON ANTI-FOULING PRODUCTS

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