The global fate of antifouling biocides
Implications from a box-model approach

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Introduction

The applicability of biocide-free antifouling coatings in commercial shipping is still limited. Because of the approaching global prohibition of organotin biocides, alternative substances are increasingly being discussed. A comprehensive evaluation of biosphere endangerment caused by these substances requires the consideration of data about release, spatiotemporal range, bioaccumulation, biological activity and about uncertainties [1]. In a first evaluation [2], the special significance of the spatiotemporal range was revealed. This poster shows the results of a modelling approach for quantifying the spatiotemporal range and discusses its limitations.

Biocides

Tributyltin, copper, Irgarol® 1051 und DCOI (active ingredient in Sea-Nine® 211) were characterized by degradation rate constants in water and sediment, as well as by their particle-water partitioning constants (Table 1, data from literature). The variability of these biocide-specific parameters was described by Maximum-Likelihood estimations of lognormal distributions. Non-antifouling inputs of copper into the system were also estimated on the basis of literature values.

The model

The model of the marine biosphere presented here (Fig. 1) consists of five seawater four sediment compartments that are assumed to be homogeneous and well-mixed. Biocide input into surface water compartments was estimated from the product of the wetted hull area of the world commercial fleet and typical release rates. Biocide dynamics are described by the linear processes degradation, water exchange, sedimentation of particles and sediment burial. Monte Carlo simulations were carried out with input parameters varying according to the variability of biocide data from literature.

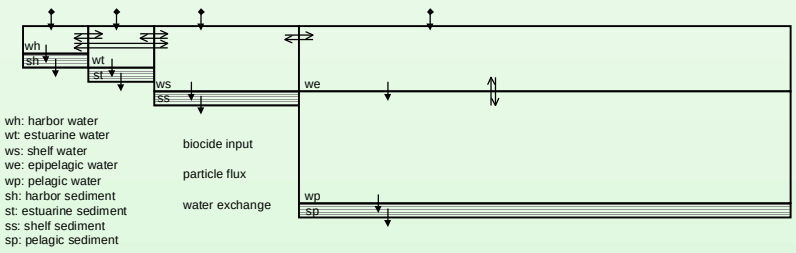

Fig. 1: Compartments and processes in the fate model

Table 1: Geometric Mean of particle-water sorption constants in water (K_{pw}) and degradation rate constants in water (k_w) as well as in sediments (k_s), the number n of data points from literature used for lognormal distribution estimations and the 5th and the 95th percentiles ($q_{0.05}$ and $q_{0.95}$) of the estimated distributions.

Substance	Parameter	n	Mean	$q_{0.05}$	$q_{0.95}$	Unit
TBT^+/TBTOH	K_{pw}	13	4.7	0.28	79	(10^3 L kg^{-1})
	k_w	13	.061	.042	.088	(day^{-1})
	k_s	4	.24	.062	.9	($year^{-1}$)
Cu^{2+}	K_{pw}	4	45.7	10.3	204	(10^3 L kg^{-1})
Irgarol® 1051	K_{pw}	1	3.1	0.36	26	(10^3 L kg^{-1})
	k_w	1	.0054[a]	.0024	.0012	(day^{-1})
	k_s	1	.0086	.0038	.19	($year^{-1}$)
DCOI	K_{pw}	2	1.1	0.13	9.3	(10^3 L kg^{-1})
	k_w	5	.44	.007	2.7	(day^{-1})
	k_s	1	6.1[b]	2.7	14	(10^3 day^{-1})

[a]photolytic rate, only used for surface water compartments [b]4.8 % to 0.7 % of the applied radioactivity as DCOI in aerobic water from days 15 to 30 was not identified and around 60 % was not extractable from the sediment. Despite the high degradation rate claimed by the manufacturers 4.8 and 2.6 % of radioactivity was reported to have been found extractable as DCOI from anaerobic sediments on days 14 and 61, respectively.

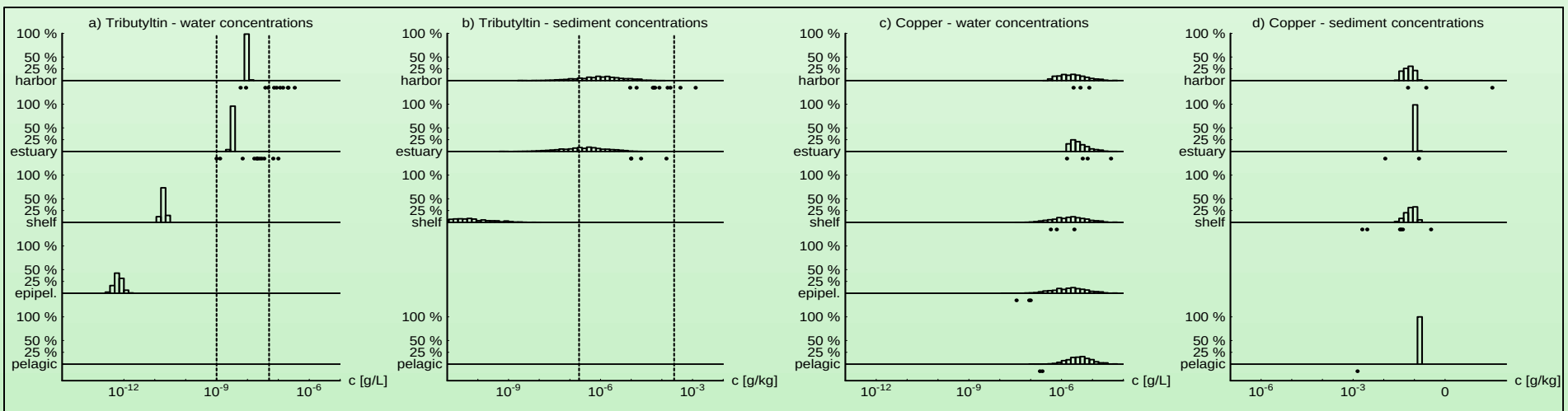

Fig. 2: Comparison of simulated distributions (histograms) of TBT and copper concentrations with measured values (•). Dotted vertical lines in a) and b) depict a typical range of detection limits for TBT

Results

Model calculations for steady-state suggest that the major part of TBT released from commercial ships is present in the water of estuaries influenced by harbors and above the continental shelf. The estimated release of copper amounts to about 5 % of total copper inputs into the marine biosphere represented by the model (data not shown). A tentative validation of the model is shown in Fig. 2.

A comparison of the simulated residence times of the four biocides (Fig. 3) shows that there are significant differences in the timescale of possible comsequences. The residence time of copper in the system is largely controlled by the sediment burial rate of the pelagic sediment. Out of the remaining biocides, Irgarol® seems to be least favorable as far as the fate is concerned. Although the mean of the simulated DCOI residence times is clearly lower than for TBT, the strongly varying data suggest that no final conclusion concerning this point is yet possible.

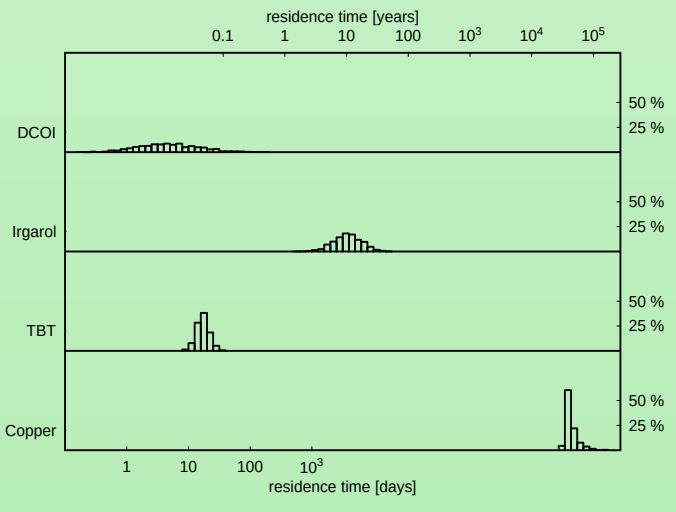

Fig. 3: Histograms of the calculated residence times of four antifouling biocides in the model system

Perspectives

The results presented, if used for evaluation purposes, should not be used in an isolated manner. Uncertainties due to the model structure have to be kept in mind as well as the different uncertainties in the input parameters. In order to facilitate the communication of these uncertainties, uncertainty scores on a scale from A (lowest uncertainty) to D (highest uncertanity) were attributed to the evaluation of the spatiotemporal range of each biocide:

Copper: A Irgarol® 1051: C Tributyltin: C DCOI: D

Literature

[1] Ranke J, Stock F, Jastorff B (2000) Multidimensional risk analysis of chemicals. Platform 7B, 11th annual meeting of SETAC-Europe 5-10 May 2001 in Madrid, Spain
[2] Ranke J, Jastorff B (2000) Multidimensional risk analysis of antifouling biocides *Environmental Science and Pollution Research* **7**(2), 105-114