Antifouling Biocides in German Marinas: Exposure Assessment and Calculation of National Consumption and Emission

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ABSTRACT
The authorization of biocidal antifouling products for leisure boats is the subject of the European Union Biocides Regulation 528/2012. National specifics may be regarded by the member states in their assessment of environmental risks. The aim of this survey was to collect corresponding data and to create a database for the environmental risk assessment of antifouling active substances in German surface waters. Water concentrations of current antifouling active substances and selected breakdown products were measured in a single-sampling campaign covering 50 marinas at inland and coastal areas. Increased levels were found for Zn, Cu, and cybutryne. For the latter, the maximum allowable concentration according to Directive 2013/39/EU was exceeded at 5 marinas. For Cu, local environmental quality standards were exceeded at 10 marinas. Base data on the total boat inventory in Germany were lacking until now. For that reason, a nationwide survey of mooring berths was conducted by use of aerial photos. About 206,000 mooring berths obviously used by boats with a potential antifouling application were counted. The blind spot of very small marinas was estimated at 20,000 berths. Seventy-one percent of berths were located at freshwater sites, illustrating the importance of navigable inland waterways for leisure boat activities and underlining the need for a customized exposure assessment in these areas. Moreover, the national consumption of all antifouling products for leisure boats was calculated. The total amount of 794 tonnes/annum (t/a) consisted of 179 t/a of inorganic Cu compounds, 19 t/a of organic cobiocides, and 49.5 t/a of Zn. With regard to weight proportion, 141 t/a Cu and 40 t/a Zn were consumed. Assuming an emission ratio of 50% during service life, 70.5 t/a of Cu amounted to 15% of all external sources for Cu release to German surface waters. These figures highlight the need for mitigation measures.

INTRODUCTION
Fouling is generally understood as the process of adsorption, colonization, and development of microorganisms, algae, and small invertebrates on underwater surfaces (Clare 1996) and has deleterious impacts on the technical underwater surfaces. One of the most important problems is the high operational cost of shipping due to increasing fuel consumption as well as possible transport of invasive species (van Hattum et al. 1999). Therefore, antifouling paints containing biocides are widely used to prevent fouling in commercial shipping. These substances impair or even kill potential fouling organisms that come into close contact with the submerged boat hull. Moreover, during service life biocides are permanently released into the aquatic environment and may harm additional aquatic organisms (Guardiola et al. 2012).

Several years before the final ban of tributyltin-based antifouling products in 2008 by the International Maritime Organization (IMO), various new products were developed which consisted to a high extent of Cu metal oxides in combination with other organic cobiocides (van Hattum et al. 1999; Guardiola et al. 2012). Apart from the application in commercial shipping, highly effective antifouling products (AFP) are also used for leisure boats. High concentration of biocides in water and sediment, especially in marinas with high numbers of berths and low water exchange, may occur (Eklund et al. 2010; Biggs and D’Anna 2012), due to leaching of biocides from antifouling coatings and the sedimentation of paint particles.

In addition to this biocide-driven approach, which has the largest market shares at present (Dafforn et al. 2011), new
products are rising on the market which are based on different mechanisms: Foul-release coatings (FRC) allow fouling organisms to settle on the hull surface and start colonization. However, due to the slippery coatings’ surface, their attachment is so weak that they peel away by hydrodynamic shear forces during normal vehicle operation (Callow and Callow 2011). Nano- or silicone-based coatings have been available for a number of years, even for leisure boats, but have not established on the market. At least temporarily, some of these products contained nano Ag or Cu, which can exert specific toxic effects to fouling organisms (Watermann et al. 2010) such as other biocidal AFP.

In the European Union, the authorization of biocidal AFP is the subject of Biocidal Products Regulation No 528/2012 (EU 2012) in order to ensure sufficient efficacy while protecting both human health and the environment. Each biocidal active substance and its product must be authorized by passing 2 steps before being placed on the European Union market. Firstly, the approval of the active substance must be given at the European Union level. Secondly, the authorization of the biocidal product must be done at the national level. On this level, country-specific characteristics on a sound basis may be regarded.

One important element within this authorization process is the exposure and effect assessment on nontarget organisms (ECHA 2015). The exposure assessment of antifouling (AF) biocides comprises emission during the life cycle, including direct releases into surface waters during service life as well as releases caused by onshore activities via maintenance and repair. For marinas, 5 emission scenarios for coastal sites are available, whereas for inland waters only 1 scenario is published so far (van de Plassche and van der Aa 2004).

For Germany, reliable national background data are lacking to verify the applicability of these marina scenarios. The present study was carried out with a detailed analytical screening on the antifouling active substances currently on the national market at 50 selected marinas in order to fill this gap of knowledge. Moreover, a large-scale inventory of the total stock of German marinas was performed, including their numbers of mooring berths, physical structure, and additional marina facilities that may be relevant for potential additional releases of antifouling biocides. Finally, the national consumption of biocidal active substances and products was roughly calculated for recreational crafts, and the figures were compared with those of other European countries. Furthermore, the total emissions of inorganic Cu and Zn oxide released during service life from leisure boats into German surface waters were estimated for the first time.

**MATERIALS AND METHODS**

**Screening**

A detailed survey of 50 marinas at 34 freshwater, 11 brackish, and 5 saltwater sites was carried out from June to August 2013. Different types of marinas were selected nationwide, representing a wide range of physical (size, number of berths) and hydrological characteristics. Number of berths varied from 28 to 2100 (median 151). The regional share of marinas followed approximately the stock ratio of freshwater, brackish, and saltwater marinas determined by means of the census.

One-time water sampling was carried out in the center of the marina at 0.5 m water depth. At 14 sites, 17 additional samples were taken outside the marinas if further emission sources were assumed. For example, upstream sampling was done at rivers with a noticeable water flow, whereas at more or less stagnant flow conditions, additional sampling was done in the center of the water body or close to the assumed emission source.

Single water samples were filled up in prerinseed 1-L Veral glass bottles. Samples for metal analyses were filtered immediately (0.45 µm mesh size, TNC, Schleicher & Schuell) and filled into polypropylene vials by adding ultrapure nitric acid. The transport of the cooled samples was done by courier service.

The following antifouling active ingredients and degradation products (DP) were analyzed. Chemical Abstract Service number (CAS-No), supplier, and chemical purity are given in parentheses:

- zineb, due to its rapid breakdown, analyzed only by the DP ethylene thiourea (ETU) (96-45-7; Dr Ehrenstorfer; 98.5%) and ethylene urea (EU) (120-93-4; Sigma-Aldrich; 99.5%) 
- dichlofluanid (1085-98-9; Dr Ehrenstorfer; 98.5%) and DP N,N-dimethyl-N-phenylisothiocyanate (DMSA) (4710-17-2; Dr Ehrenstorfer; 99%) 
- tolyfluanid (731-27-1; Dr Ehrenstorfer; 98.5%) and DP N,N-dimethyl-N-phenylsulphamide (DMST) (66840-71-9; Dr Ehrenstorfer; 99.5%) 
- 4,5-dichloro-2-ocetyl-isothiazolone (DCOIT) (Sea-Nine 211®) (64359-81-5; Dow; 99%) and DP N-(n-octyl) malonamic acid (NNOMA) (-/-; Dow: 96.5%), N-(n-octyl) acetamide (NNOA) (-/-; Dow: 99.5%), N-(n-octyl) oxamic acid (NNOAA) (-/-; Dow: 99.95%) 
- Cu pyrithione (CuPt) (14915-37-8; Campro Scientific; 95%) and Zn pyrithione (ZnPt) (13463-41-7; Sigma-Aldrich; 95%) as pyrithione sulfonic acid (PSA) (-/-; Sigma-Aldrich; 97%) 
- cybutryne (Irgarol 1051®) (28159-98-0; Sigma-Aldrich; 98.4%) and DP M1 (GS 26575) (-/-; Asca; ≥95%)

The following substances were used as internal standards (IS):

- atrazine-d5 (1912-24-9; 98.5%), isoproturon-d6 (34123-59-6; 97.5%), metolachlor-d6 (51218-45-2; 97.7%), mecoprop-d6 (7085-19-0; 98%), and propylene thiourea (2122-19-2; 98%) were supplied by Dr Ehrenstorfer;
- 13C6-perfluorooctanoic acid (-/-; 99%) was obtained from Wellington Laboratories; and
- 13C3-propazine (-/-; 99%) was obtained from Cambridge Isotopes.

Unfiltered water samples were used for analyses of all organic co biocides. For the analysis of cybutryne and the
break-down products (BP) M1, 0.5 L water samples were spiked with \( ^{13} \text{C}_3 \)-propazine (IS) and enriched by solid-phase extraction (SPE) (ENV+, IST Biotage; 200 mg/6 mL; conditioning with acetone, methanol, and purified water). After drying in an N gas flow, the column was eluted with acetone. Squalane was added to check the solvent volume. An aliquot was evaporated and resolved in iso-octane, adding 4,4'-dibromooctafluorobiphenyl (DBOFB) for solvent volume control. Quantification was done by use of GC–MS in single ion monitoring (SIM) mode (HP6890/5973 with split-splitless-injector, Hewlett Packard; column Optima 17, Macherey & Nagel; 0.25 mm, 0.25 \( \mu \)m, 30 m) (Target ions: cybutryne \( m/z \) 253, M1 \( m/z \) 198; \( ^{13} \text{C}_3 \)-propazine \( m/z \) 217, squalane \( m/z \) 127, DBOFB \( m/z \) 456). A 5-point calibration was used. Limits of quantification (LOQs) were calculated for each analytical sequence, whereas cybutryne had a median LOQ of 2 ng/L and M1 of 3 ng/L. Recovery rates at 10 ng/L were between 105% and 124% for cybutryne and between 94% and 113% for M1. The repeatability was close to 7% for both analytes.

All the other organic biocides and their DP were analyzed by use of an HPLC-system (Symbiosis Pico, Spark Holland) coupled to am MS/MS (MS 325 TripleQuad, Varian) with electrospray ionization (ESI). Equidistant 10-point calibrations were run. The LOQs were calculated by use of repeated 5-fold measurements of low-level samples according to DIN 32645:2008-11 (DIN 2008). Blanc and control values were always measured. The target compounds are as follows, with substance-specific quantifier and qualifier for the multiple reaction mode, retention time (RT), as well as LOQs given in parentheses: Dichlofluanid (332.6→122.8, 332.6→123.8, RT 6.5 min), DMDSA (201→92, 201→137, RT 4.1 min), tolyfluanid (346.8→137, 346.8→237.8, RT 7.1 min), DMST (215→79, 215→106, RT 4.7 min), DCOIT (281.9→169.9, 283.8→171.9, RT 8.2 min), NNOOA (172.1→60.1, 172.1→57.2, RT 6.3 min), as well as the IS atrazine-d5 (221→179, RT 5.2 min), isoprotoron-d6 (213→78, RT 5.3 min), and metolachlor-d6 (290→258, RT 6.6 min) were enriched by use of online SPE (Symbiosis Pico System, C18 HD, 7 \( \mu \)m; HySphere, Spark Holland). Cartridges were preconditioned with 1 mL methanol, followed by 1 mL water. The analysis was done according to DIN EN ISO 11369:1997-11 (DIN 1997) by use of aerial photos from governmental and census 2015). The background concentration of Zn was set by conducted by use of the full Biotic Ligand Model (BLM). The water parameters were analyzed according to DIN EN ISO 17294-2:2005-02 (DIN 2005). The mobile phase was a gradient prepared from 100 mL 0.1% formic acid, 10 mL acetonitrile, and 390 mL LC-MC water (eluuent A) and methanol (eluuent B) with a flow rate of 0.3 mL/min (Sample volume 10 \( \mu \)L). The gradient program followed also the same procedure as for dichlofluanid (LOQ: 10 ng/L).

Ethylene thiourea (103→44, 103→86, RT 0.4 min) and EU (87→44, 87→70, RT 0.4 min), both DPs of zineb, and the IS propylene thiourea (111→58, 111→60, RT 0.4 min) were analyzed according to DIN EN ISO 11369:1997-11 (DIN 1997). Isocratic separation was done by 50% of 0.02% ammonium acetate solution and 50% methanol (Sample volume 10 \( \mu \)L). Positive ionization mode was used (LOQ: 1000 ng/L).

Copper and Zn were quantified by means of their common isotopes \( ^{64} \text{Cu}, ^{65} \text{Zn}, ^{63} \text{Cu}, \) and \( ^{65} \text{Cu} (\text{IS: } ^{103} \text{Rh}) \) in by use of coupled plasma mass spectrometry in kinetic energy discrimination (KED) mode (XSeries 2, Thermo Scientific USA) according to DIN EN ISO 17294-2:2005-02 (DIN 2005) by use of online SPE (Symbiosis Pico System, C18 HD, 7 \( \mu \)m; HySphere, Spark Holland). Cartridges were preconditioned with 1 mL methanol, followed by 1 mL water. The analysis was done according to DIN EN ISO 11369:1997-11 (DIN 1997) by use of a Pursuit 3 C18-A column (3 \( \mu \)m, 50×2.2 mm, Varian, Agilent). The mobile phase was a gradient prepared from 390 mL liquid chromatography mass spectroscopy (LC-MS) water, 10 ML acetonitrile, and 100 mL 0.1% ammonium acetate solution (eluuent A) and methanol (eluuent B) with a flow rate of 0.3 mL/min. The gradient program was 100% A at 0 min, 60% A + 40% B at 1 min, held for 7 min, switched to 100% B at 8 min, and switched back at 11 min to 100% A for 4 min (Sample volume 1 mL). Detection was done by positive ion mode (LOQ: 10 ng/L).

Copper pyrithione (316→141.9, 316→188.9, RT 6.6 min) and the IS metolachlor-d6 (290→258, RT 6.6 min) were analyzed according to DIN EN ISO 11369:1997-11 (DIN 1997) by use of a Monochrom column (5 \( \mu \)m, 100 × 2 mm) (Varian, Agilent) and an isocratic separation by use of 20% of 0.02% formic acid solution (eluuent A) and 80% methanol (eluuent B) (Sample volume 10 \( \mu \)L). Detection was done by positive ionization (LOQ: 1000 ng/L).

PSA (158→80, 158→94, RT 1.6 min) as a DP of Cu and Zn pyrithione and the IS \( ^{13} \text{C}_3 \)-perfluorooctanoic acid (421→376, RT 1.6 min) were analyzed following DIN 38407:2010-10 (DIN 2010) by use of a Monochrom column (5 \( \mu \)m, 100 × 2 mm) (Varian, Agilent) and an isocratic separation by 5% of 0.02% formic acid solution and 95% acetonitrile (Sample volume 10 \( \mu \)L). Quantification was done in negative ionization mode (LOQ: 1000 ng/L).

Together with the IS mecoprop-d6 (216→144, RT 4.5 min, NNOOA (200→127.8, 200→171.7, RT 5.0 min) and NNOMA (214→169.7, 214→58, RT 4.9 min), both DPs of DCOIT, were enriched by use of the same HPLC and detection system (incl. column) in negative ion mode as used for dichlofluanid. Cartridges of the online SPE system were preconditioned with 1 mL methanol, followed by 1 mL 0.1% formic acid solution. Analyses were done following DIN 38407:2010-10 (DIN 2010). The mobile phase was a gradient prepared from 100 mL 0.1% formic acid, 10 mL acetonitrile, and 390 mL LC-MC water (eluuent A) and methanol (eluuent B) with a flow rate of 0.3 mL/min (Sample volume 10 \( \mu \)L). The gradient program followed also the same procedure as for dichlofluanid (LOQ: 10 ng/L).

The bioavailability of Cu and Zn was calculated by use of the spreadsheet Bio-met Bioavailability Tool V. 3.4 (http://bio-met.net; Arche, Belgium; WCA, Great Britain) based on the full Biotic Ligand Model (BLM). The water parameters DOC, Ca, and pH were sampled in parallel and measured according to standard methods (for details, see Watermann et al. 2015). The background concentration of Zn was set by default to 1 \( \mu \)g/L.

Census

A large-scale census over all the German territory was conducted by use of aerial photos from governmental and commercial geo-information internet providers. The inventory was done by 4 supervised operators, which had to follow defined standards. Cross-checks of parallel counting by 4 operators revealed a mean variation coefficient of 4.9%.
(range: 2.1%–15.5%) on a subset of 6 randomly selected marinas (N berths = 67–166).

Marinas with more than 10 berths were always identified. Only berths of leisure boats being relevant for AF application were recorded. Thus, berths or stock yards for smaller leisure boats such as dinghies and rowing boats were excluded. Berths for visitors or residents were not differentiated. Additional data sources such as marina guides, harbor books, nautical charts, and internet homepages were also used for verification. In case of inconsistent berth numbers, the final decision was made by expert judgment or in individual cases by personal contact to the harbor master or owner. In addition, marina-specific characteristics such as the number of berths, the size of the marina, the extent of embankment, and the geographic position were recorded. Due to the occurrence of different fouling communities, all marinas were categorized according to their salinity into freshwater (salinity <0.1%), brackish (0.1%–1.8%), and saltwater (>1.8%) sites.

Extrapolation to nationwide consumption of antifouling products

For the extrapolation to nationwide consumption of antifouling products in Germany, data were needed as underwater hull surfaces (UWS) of leisure boats, product range, market share, and quantity of biocidal active substances of antifouling products. The UWS of leisure boats were calculated by use of a standard equation published by manufacturers such as AkzoNobel (International 2014) to calculate antifouling paint consumption:

\[ UWS = ff \times LOA \times (B + D), \]  

with \( LOA \) = length overall (m); \( LWL \) = length water line (m); \( B \) = beam (max. width) (m); \( D \) = draft (m); \( ff \) = correction factor for distinction between sailing and motor boats, and the ratio of \( LOA \) to \( LWL \).

Table 1. Calculated underwater hull surface of different length classes of motor and sailing boats according to the formula 

\[ UWS = ff \times LOA \times (B + D) \]

B = beam; \( D \) = draft; \( ff \) = correction factor for distinction between sailing and motor boats; \( LOA \) = length overall; \( UWS \) = underwater hull surface.

| LOA (m) | Sailing boat UWS (m²) | Motor boat UWS (m²) |
|--------|----------------------|---------------------|
| <6     | \( ff \times 5 \times (1.80 + 0.90) \) = 8.78 | \( ff \times 5.5 \times (2.10 + 0.55) \) = 11.15 |
| 6–8    | \( ff \times 7 \times (2.30 + 1.20) \) = 15.93 | \( ff \times 7 \times (2.60 + 0.63) \) = 17.3 |
| 8–10   | \( ff \times 8 \times (2.90 + 1.50) \) = 22.88 | \( ff \times 9 \times (3.15 + 0.80) \) = 27.19 |
| 10–15  | \( ff \times 11.5 \times (3.70 + 1.90) \) = 41.86 | \( ff \times 12.5 \times (3.93 + 1.10) \) = 48.1 |
| 15–20  | \( ff \times 15.5 \times (4.70 + 2.40) \) = 71.53 | \( ff \times 17.5 \times (4.70 + 1.40) \) = 81.66 |

The yearly total AFP consumption was calculated as follows:

\[ AFP_{\text{total}} = (N_F \times OR_F \times UWS_F + N_{B+S} \times OR_{B+S} \times UWS_{B+S}) \times \text{Yield}_{\text{AFP}} \times N_{\text{appl}} \times \rho_{\text{AFP}}, \]

where \( AFP_{\text{total}} \) (kg/a) = Sum of antifouling product consumption per year; \( N = \) number of berths at freshwater (\( N_F \)) and at brackish–saltwater areas (\( N_{B+S} \)) (data obtained from the nationwide census); \( OR = \) occupancy rate at fresh (\( OR_F \)) and brackish–saltwater (\( OR_{B+S} \)) marinas, both set to 1, assuming a full capacity utilization of all recorded berths; \( UWS \) (m²) = mean of underwater hull surface of leisure boats at freshwater and overall mean at brackish and saltwater sites, set to \( UWS_F = 20 \text{ m}^2 \) and \( UWS_{B+S} = 34 \text{ m}^2 \); \( \text{Yield}_{\text{AFP}} \) (L/m²) = consumption of AFP per area and per layer, set to 0.1 L/m²; \( N_{\text{appl}} \) = number of paint coats (paint applications), set to 1/a; \( \rho_{\text{AFP}} \) (kg/L) = density of AFP, set to 1.6 kg/L.

Data on the yield and the physical density of antifouling coatings were taken from technical data sheets. To calculate on an annual basis, the consumption of AFP is based on the assumption of only 1 single paint layer. Paint manufacturers frequently recommend at least 2 paint layers with a service lifetime of 2 y. The theoretical maximal paint yield published for 25 different antifouling coating paints ranged from 7 to 14 m² UWS/L paint with a median of 10 m²/L equivalent to a \( \text{Yield}_{\text{AFP}} \) of 0.1 L/m² UWS.

Technical data on products and their classification were gained from antifouling product lists for Germany in the period from 2011 to 2013 (Daehne 2011, 2012; LimnoMar 2013). Only product lines are assessed, regardless of
different formulations for specific hull colors, amounting to between 89 to 99 products per annum. Antifouling products are classified as follows: The product type denoted as “copper” contained only inorganic Cu compounds such as metallic Cu, dicopper oxide, or Cu thiocyanate (Figure 1). Products specified as Cu plus “co-biocides” included at least one of the following boosters: tolyllfluorid, dichlofluanid, Zn- or Cu-pyrithione, zineb, DCOIT, cybutryne, and terbutryne. Products specified as “nano” followed the manufacturer’s information on nanomaterial content. Product types defined as “zinc oxide only” contained no additional biocidal active substances.

The calculation of the yearly consumption of single biocidal active substances and of Zn oxide was done by use of this formula:

$$\text{Ingsingle} = \text{AFP}_{\text{biocide+zno}} \times \left(\frac{\text{Prop}_{\text{ing}}}{100}\right) \times \text{WS}_{\text{ing}},$$

where $\text{Ingsingle}$ (kg/a): yearly consumption of single ingredient as AF active substance or Zn oxide; $\text{AFP}_{\text{biocide+zno}}$ = yearly consumption of AF containing biocides and/or Zn oxide; $\text{AFP}_{\text{biocide+zno}} = \text{AFP}_{\text{total}} \times 0.9$; correction for other nano and nonstick-based products without antifouling active substances or Zn oxide; Prop$_{\text{ing}}$ (%) = proportion of specific ingredient of the product range (average of 2011–2013); and WS$_{\text{ing}}$ (g/g) = mean weight share of specific ingredient in the products; metal ingredients were set as salt or metal organic compounds.

Due to the lack of national product-specific sales quantities, the portfolio of products offered on the German market was used to derive the consumption of single ingredients. The share of single ingredients (biocides and Zn oxide) in the product range was calculated for the period 2011–2013 (Daehne 2011, 2012; LimnoMar 2013). The typical weight share of the active substances was derived from the safety data sheets and set as follows: Inorganic Cu compounds with 30%; Zn oxide with 10%; dichlofluanid and tolyllfluorid with 6% each; cybutryne, Cu, and Zn pyrithione with 3% each; and DCOIT with 2% weight proportion. Multiple presence of inorganic compounds appeared in 5.3% of cuprous-containing products. In this case, the mass calculation was done on the basis of only 1 cuprous compound. Consumption figures of individual agents were added up for inorganic Cu compounds and for organic booster biocides. The balancing of the total yearly Cu consumption was done by adding up the cupferiferous active substances, each weighted by their specific market share and calculated as metal ion.

RESULTS

Antifouling biocides in the water analyses of 50 marinas

The breakdown products of zineb (ETU and EU), the organic ligand of Cu and Zn pyrithione, as well as DCOIT (Sea-Nine 211) and its breakdown products were below their limits of quantification (Table 2) at all locations. The same was true for dichlofluanid and tolyllfluorid, which also break down rapidly in water, whereas their degradation products DMSA and DMST were quantified in 70% and 54% of all analyzed samples, respectively. Their median concentrations were almost identical reaching 0.02 μg/L (Table 2; Figures 2A and 2B). The maximum concentration of DMSA at salt and brackish water marinas was 0.105 μg/L, whereas in freshwater 0.28 μg/L was detected. For DMST the highest level of 0.11 μg/L was observed in salt- and brackish water marinas. Accordingly, a similar maximum level of 0.10 μg/L was detected in freshwater. The levels of the reference samples taken outside the marinas (data not shown here) were almost always below their LOQs, indicating that the active substances originate from use in antifouling products. Cybutryne (Irgarol) was quantified in 78% and its breakdown product M1 in 46% of all analyzed samples. The median concentrations of cybutryne were quite similar at coastal and inland sites, with 0.005 μg/L and 0.006 μg/L, respectively. However, the maximum concentration of 0.110 μg/L was observed in a freshwater marina. Here also the highest concentration of the degradation product M1 appeared (0.071 μg/L). At brackish-marine sites, maximum concentrations were 0.029 μg/L for cybutryne and 0.005 μg/L for M1 (Table 2; Figures 2C and 2D). The metals Cu and Zn were almost ubiquitously present in the water samples. The highest levels were observed at the brackish water marinas with a maximum of 20 μg Cu/L and 26 μg Zn/L analyzed by means of filtered water samples (Table 2; Figures 2E and 2F). At marinas with an additional reference sampling, higher concentrations were detected outside at 7 of 14 sites with maximum levels of 16 μg/L for Zn and 20 μg/L for Cu. For these sites, the following site-specific types have been identified: marinas situated at or nearby the mouths of larger rivers with adjacent industrial port activities (Zn: 3 sites; Cu: 1 site), marinas with innercity location at almost stagnant flow conditions and with a local high-occupancy rate of leisure boats (Cu: 2 sites), and a marina situated at an open-cast mining lake (Cu: 1 site).

Amount of mooring berths and marinas and their regional distribution

The nationwide census revealed an inventory of 146 000 berths in freshwaters (71.0% of total stock) and 54 000 berths (26.2%) in brackish waters such as the Baltic Sea, including...
fjords and inner bays as well as river estuaries of the North Sea (Figure 3). Only 5800 mooring sites (2.8%) were directly situated at the North Sea coast, defined here as saltwater areas. In total about 206 000 mooring berths were assessed at 3091 marinas. Eighty percent of the marinas were situated at freshwater, 18% at brackish, and 2% at saltwater sites. The total stock numbers presented here are neither corrected for the amount of very small marinas nor for their berths, which were hard to identify by means of aerial views.

Agglomerations of marinas with at least 10 000 berths were identified along the Baltic Sea coast (approximately 43 000 berths) and along the North Sea coast with its estuaries (10 500), in total amounting to 26% of all berths in Germany (Figure 3). At the freshwater sites, 5 high-density areas of numerous clusters of marinas were identified at areas that are rich in lakes and rivers near major cities. In total, these agglomerations reached about 102 500 berths, which is almost 50% of the total stock (Figure 3).

On the local scale, small-sized inland marinas are often tightly packed to each other, forming inventories of more than 1000 leisure boats at lakefronts and riverbanks. At the North Sea coast, a typical marina represents a well-diked “safe haven” with a median number of 70 mooring sites and comprehensive infrastructure facilities (Figure 4). At maximum, 270 mooring sites were observed at the German North Sea coast. Here, 70% of the coastal marinas at saltwater sites are well embanked at least from 3 sites and often constructed with only a small harbor entrance. In contrast, 79% of the freshwater inland marinas were more or less directly exposed to their adjacent water bodies. German freshwater marinas have a median number of 40 berths and are used exclusively for water sport activities. Marinas at brackish sites have a mid-position in respect to the grade of embankment as well as to the number of berths. The sizes of marinas in fresh and brackish waters may vary from single landing stages to major marinas with more than 1000 berths (Figure 4).

In total, UWS of 12 207 leisure boats (38% motor and 62% sailing boats) were determined on the basis of aerial photos from the 50 marinas that had been selected for the screening campaign. This number represents almost 6% of total national stock. The largest leisure boats appeared at brackish sites, whereas boats anchoring in freshwaters were markedly smaller as indicated by their mean UWS. Depending on the vessel type, freshwater boats had only a hull surface of 19 and 22 m², respectively, compared to 34 to 35 m² at brackish sites. Even leisure boats positioned at the North Sea were smaller, reaching only 28 and 32 m², respectively (Table 3).

Consumption of antifouling products, biocides, and Zn oxide for leisure boats

The yearly consumption of about 794 t antifouling products was calculated for Germany by both the use of the total stock of mooring berths, set as the total amount of leisure boats that are relevant for antifouling application, and by the use of

| Antifouling compound          | Degradation product                                      | Salt- + brackish water | Freshwater |
|------------------------------|----------------------------------------------------------|------------------------|------------|
| Dichlofluanid                 | N,N-dimethyl-N-phenylsulphamide (DMSA)                   | <0.010                 | <0.010     |
|                              | Dimethylamino-sulfotoluclid (DMST)                        | 0.025 (0.110)          | 0.020 (0.100) |
| Tolyfluanid                   | N-(n-Octyl) acetamid (NNOA)                              | <0.010                 | <0.010     |
|                              | N-(n-Octyl) oxamid acid (NNOOA)                           | <0.010                 | <0.010     |
|                              | N-, N-(n-Octyl) malonimid acid (NNOMA)                    | <0.010                 | <0.010     |
| DCOIT (SeaNine 211)           | Pyrithione sulfinic acid (PSA) as sum of CuPt + ZnPt     | <0.05                  | <0.05      |
| Copper (CuPt) and zinc pyrithione (ZnPt) | Pyrithione sulfinic acid (PSA) as sum of CuPt + ZnPt     | <1.0                   | <1.0       |
| Zineb                         | Ethylene thiourea (ETU)                                  | <1.0                   | <1.0       |
|                              | Ethylene urea (EU)                                       | <1.0                   | <1.0       |
| Cybutryne (Irgarol 1051)      | GS26575 (M1)                                             | 0.005 (0.029)          | 0.006 (0.110) |
| Cu (filtered)                |                                                         | 5 (20)                 | 4 (14)     |
| Zn (filtered)                |                                                         | 6 (27)                 | 3 (10)     |

n. d. = not determined.
*Values shown in μg/L.
Figuers with “<” = below limit of quantification.

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typical product-specific properties. Furthermore, the calculation was specified according to different regional boat sizes and their corresponding hull surfaces. Although nano- and nonstick-based products reached in sum about 14% of the product range (Figure 1), their sales quantities were estimated to be far below the 10% threshold in the relevant period. However, the market share of the foul release products was set to 10% in order to avoid being overprotective in the calculation of the consumption figures for antifouling products and to consider the high dynamics of the market development in general. Therefore, the remaining 90% referred to 715 t/a, addressing the consumption of products with biocides plus Zn oxide, which is not regarded as a biocide.

By adding up single ingredients, approximately 179 t amounted to inorganic Cu compounds and approximately 19 t to organic cobiocide consumption, whereas Zn oxide as the commonly used nonbiocidal paint component reached 49.5 t yearly. Considering the weight proportion of the metals only, approximately 141 t/a Cu and approximately 40 t/a Zn were applied onto hulls of leisure boats in Germany.

**DISCUSSION**

*Survey on antifouling active substances in the water samples from 50 marinas*

The screening data at 50 marinas revealed no clear indication for the use of DCOIT and zineb in antifouling

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**Figure 2.** Water concentration of antifouling biocides and specific degradation products in coastal (salt + brackish water) and freshwater marinas. DMSA (A), DMST (B), cybutryne (C), M1 (D), Cu (E), Zn (F). For box-whisker plot details, see Figure 2B. aM = arithmetical mean.
products for leisure boats because all samples were below the LOQ. This is in line with findings from a current national market analysis (LimnoMar 2013) according to which these biocides are mainly applied by the commercial shipping industry, whereas only a small number of AF products with these biocides is recently available for leisure boats in Germany.

Based on a 3-y market survey from 2011 to 2013 of the different antifouling active substances in antifouling products (Daehne 2011, 2012; LimnoMar 2013), dichlofluanid and tolyfluanid were the most commonly detected cobiocides, reaching 21.1% and 16.2% (Table 4). Other cobiocides were contained in less than 6% of the antifouling products.
In the present survey, tolyfluanid and dichlofluanid could not be detected in water samples, but their actual use is indicated by their frequently detected breakdown products DMSA and DMST. Levels of up to approximately 0.1 mg/L and more were observed for DMSA and DMST, especially at brackish and freshwater marinas. However, the concentration levels of both breakdown products were far below the threshold concentrations of adverse ecotoxicological effects on water organisms as indicated by the risk assessment for tolyfluanid (EC 2009) with a predicted no-effect concentration (PNEC) of 140 μg/L for DMST in aquatic ecosystems. The water concentration of the persistent cybutryne, monitored in this single-sampling campaign, indicated risks for water organisms: According to the European Union directive 2013/39/EU (EU 2013), at 35 of 50 marinas the actual concentrations were above the environmental quality standard (EQS) of 0.0025 μg/L which should not be exceeded as annual average (AA-EQS). At 5 marinas the concentrations were even above the maximum acceptable concentration (MAC-EQS) of 0.016 μg/L. Again the highest concentrations appeared at brackish and in particular at freshwater sites, with a maximum concentration of 0.110 μg/L.

In a recent survey on organic AF biocides at 10 selected Austrian marinas (Hauzenberger et al. 2015), a very similar pattern was observed for dichlofluanid and tolyfluanid, also just ascertained by their breakdown products. The DCOIT was detected to be above the limit of detection only once at a city harbor with mixed municipal and private use. There was no analytical proof of the use of zineb. In contrast to the present study, cybutryne was below LOQ in water samples at any site, but frequently detected in the sediment, which might be an indication that in Austria cybutryne has been phased out recently.

Higher levels of Cu and Zn in filtered water samples were observed in relatively large, well-embanked marinas situated at coastal sites and adjacent estuaries. Large-sized and well-embanked marinas with higher levels of Cu and Zn indicate that both metals were applied in antifouling products for leisure boats. Altogether, inorganic Cu compounds reached an overall presence of nearly 89% (Table 4). High frequencies of the total sum of inorganic Cu or co-biocide compounds are attributed to the fact that multiple active substances appeared in single products.

On the German market, Zn is present in more than two-thirds of biocidal products and biocide-free coatings with Zn oxide only, whereas zineb and Zn pyrithione reached in total 6.2% only (Table 4). Additional sampling outside the marinas revealed higher concentrations of both metals at some sites, indicating that there are further emission sources (EC 2008). Additional relevant inputs of Zn can also originate from sacrificial anodes (Boxall et al. 2000). Although Zn oxide is present in many antifouling products for several reasons (binder, white pigment, UV stabilizer, etc.), it is not classified as a biocide according to the European Union regulation. However, Zn oxide has antifouling properties, stocks on the Zn levels in aquatic systems (EC 2008), and therefore should be considered for risk assessment in the future. Concentrations presented here were analyzed by means of filtrated water samples, excluding the particle bound metal fraction. Due to partitioning processes in the waterbody, metal ions bind to some extent at suspended matter which will be deposited and accumulate in the long run in the sediment of the marinas and the adjacent areas (Comber et al. 2002).

Besides the releases from antifouling products during service life, further relevant inputs may occur from maintenance and repair activities onshore. There, for example, high-pressure cleaning of the hull surface nearby the slipway may generate flaking of paint particles, which may be flushed into the harbor basin in the case of the lack of wash-down separating systems (Turner 2010). After sedimentation a new equilibrium between water and particle phase appears and may stock on the metal content in the waterbody. However, local inputs due to maintenance activity onshore as well the interaction between sediment and water body inside the

![Figure 4. Box-whisker plots of number of berths per marina at salt-, brackish, and freshwater sites.](image)

| Type of boat     | Saltwater | Brackish water | Salt- + brackish water | Freshwater |
|------------------|-----------|----------------|------------------------|------------|
| Motor boat       | 31.2 (257)| 33.5 (893)     | 33.0 (1150)            | 21.7 (3455)|
| Sailing boat     | 27.8 (332)| 34.9 (2975)    | 34.2 (3307)            | 18.7 (4295)|
| Motor + sailing boat | 29.3 (589)| 34.6 (3868)    | 33.9 (4457)            | 20.2 (7750)|

*Arithmetical mean shown in m².*

*Nr boats = mean weighted by number.*
The present study, identification of marinas and counting of berths was done by use of aerial photo analysis. Thereby, only in-water berths were addressed, assuming these boats were painted with antifouling products. Comparable studies on the total German stock of leisure boats are scarce. Official data predicted a total stock of 750,000 boats (including all boat classes) for 2012 (BMVI 2014) without quoting data sources. These uncertainties occur because in Germany motorized leisure boats are not centrally registered. Aerial photo interpretation had to be taken as a surrogate method for a nationwide inventory on leisure boats due to the absence of central registration or comprehensive surveys of private ownership. Some imponderabilities are associated with its use. On the one hand, very small marinas or single anchoring boats are hard to detect at photo shots in summer when riparian vegetation is standing in full leaf. The same is true for single boat houses. The amount of trailer boats without permanent mooring places cannot be recorded, either. Thus, approximately 20,000 leisure boats (10% of the total stock) were not recorded. On the other hand, a clear allocation of berths for boats of guests and residents based on aerial photos is impossible. Regarding the nationwide inventory, the co-recording of guest berths may overestimate the total national boat stock, but may balance out to some extent the underestimation of very small marinas. On the scale of single marinas, the inclusion of guest boats represents the situation at high season on site and is therefore relevant for local risk assessment of biocidal AF active substances. In conclusion, the actual nationwide census can be regarded a valuable and reliable estimate.

Data on leisure boat inventories or berth stocks of other European countries are rarely published or hard to find. Leisure boats with combustion engines were estimated for Denmark at approximately 59,000 in 2001 (Lassen et al. 2001) and for Sweden at approximately 669,000 in 2010 (MIND Research 2010). In Switzerland, where inventories have been conducted annually, about 92,000 motor crafts and sailing boats were recorded in 2014 (VKS 2014). In the Netherlands, a stock of approximately 166,000 leisure boats with antifouling products was reported for 2013 (Rijkswaterstaat-WVL 2015). Summarized European Union wide data on leisure boat stock are lacking, to our knowledge.

The amount of leisure boats at German freshwater sites scored highly with 71% and emphasizes the high relevance of inland waters with a waterway network of approximately 10,000 km for leisure boat activities. The results at hand substantiate the relevance of an environmental risk assessment of biocidal AFP also for freshwater sites in Germany. Local data on size and number of berths provide a sound database for the derivation of a specific inland scenario (Figure 3). Besides the assumption for a single freshwater marina, there is also the need to assess AF releases of clusters of marinas to adjacent rivers or lakes. In Berlin, Germany, marina berths often are fused like pearls on a necklace to more than 1000 boats. If stagnant or low-flow conditions are
given, an increase of biocide concentration may occur in adjacent water bodies outside the marina. This increase may be favored by clusters of free-floating landing stages along the shore. In case of cybutryne this had been shown for inner-city lakes in Berlin (UBA 2007). However, for the interpretation of monitoring data, releases from other emission sources also must be taken into account.

National consumption of biocidal active substances and Zn oxide

Restricted by lack of national sales quantities of specific active substances, the calculation in the present study followed Rijkswaterstaat-WVL (2015), assuming that the market share of active ingredients is similar to the product range. This approach was advisable due to the outstanding market dominance of cuprous compounds and their comparatively high weight proportion in the products. The same was true for Zn oxide. The situation was different for the organic cobiocides, due to their lower individual market presence and their quite low weight proportion in the products. For getting a robust calculation, these weight proportions of active substances were added up as organic cobiocides. Cluster formation was also done for inorganic Cu compounds. In the period from 2011 to 2013 about 78% of the antifouling products available on the German market contained biocides according the European Union biocides regulation, whereas the rest (22%) are specified as products with Zn oxide only, with nano compounds, and other foul-release coatings (Figure 1).

Data on inventories of leisure boats together with consumption figures of antifouling products in Europe are rarely published (Table 5). In Germany, the annual consumption with 198 t/a for both inorganic cuprous compounds and organic cobiocides seems higher compared to the other countries, with the exception of Denmark. Nevertheless, these data reveal that there is no simple relationship between the national boat stock and the consumption of biocidal antifouling active substances: For Switzerland the mean underwater hull surface for leisure boats was valued 10 m², whereas leisure boats located at the coasts of the North and Baltic seas and their estuaries were noticeably larger, reaching 34 m² on the average (the present study).

In the present study, underwater surface areas of more than 12 000 leisure boats were calculated by measuring boat lengths on the basis of aerial images and a simplified approach based on a formula recommended by international antifouling paint producers. In light of the type diversity of leisure boats, large deviations can be expected. However, the method applied here was developed in order to derive averages for bulks of boats from different regions. For calculation of the wet surface area of hulls, a couple of formulas with different complexity are published. Van Hattum et al. (2002) compared 2 similar linear models, one with 2 (length, beam) and the other with 3 independent variables (length, beam, draught). For the smallest length class of 11 to 100 m, the 2-variables model reached only 94% of the other one. In a further study on large commercial vessels (NNWB 2008), 3 more complex approaches were compared with one used by van Hattum et al. (2002). For the latter a clear trend to smaller values was obvious, reaching only 84% of the surface compared to the others. This may indicate that by use of the method at hand an underestimation of the underwater surface area might be possible. In any case further investigations are needed in order to develop a simple method for the determination of the underwater surfaces of leisure boats applicable for the analysis of aerial images.

Obviously, local consumption was influenced by local bans. In Sweden, the use of antifouling products for leisure boats is regionally regulated: At the west coast, products with high Cu content are allowed, at the east coast the one with a lower Cu content may be used, whereas at freshwater sites all biocides have been banned (Ytreberg et al. 2010). These restrictions demonstrate the possibility to adjust the biocidal content of antifouling products to the minor fouling pressure in freshwater areas. Similar restrictions are also relevant for Denmark (Hansen et al. 2014). In the Netherlands, a ban of Cu-based antifouling products lasted from 2000 to 2004 (Rijkswaterstaat-WVL 2015) and resulted in decreasing Cu content of antifouling products to the minor fouling pressure (Rijkswaterstaat-WVL 2015). For calculation of the wet surface area of hulls, a couple of formulas with different complexity are published. Van Hattum et al. (2002) compared 2 similar linear models, one with 2 (length, beam) and the other with 3 independent variables (length, beam, draught). For the smallest length class of 11 to 100 m, the 2-variables model reached only 94% of the other one. In a further study on large commercial vessels (NNWB 2008), 3 more complex approaches were compared with one used by van Hattum et al. (2002). For the latter a clear trend to smaller values was obvious, reaching only 84% of the surface compared to the others. This may indicate that by use of the method at hand an underestimation of the underwater surface area might be possible. In any case further investigations are needed in order to develop a simple method for the determination of the underwater surfaces of leisure boats applicable for the analysis of aerial images.

Table 5. Stock of leisure boats and use of antifouling agents (excluding ZnO) and amount of cuprous compounds

| Country   | Stock of leisure boats | Use of AF agents (t/a) | Amount of cuprous compounds (%w/w) | Year       | References                                      |
|-----------|------------------------|------------------------|-----------------------------------|------------|------------------------------------------------|
| Denmark   | 59 000                 | 53                     | 94                                | 2000–2001  | Lassen et al. 2001                              |
| Switzerland | 92 000               | 7.8–13                 | 66–74                             | 2011       | Burkhardt and Dietschweiler 2013; VKS 2014     |
| Netherlands | 166 000              | 34                     | 53                                | 2013       | Rijkswaterstaat-WVL 2015                        |
| Germany   | 206 000                | 198                    | 90                                | 2012–2013  | the present study                               |
| Sweden    | 669 000                | 148                    | 93                                | 2012       | KEMI 2013; MIND Research 2010                   |

AF = antifouling; t/a = tonnes/annum; %w/w = %weight/weight.
specific national product range. Furthermore, this has an impact on the total consumption figures due to the high physical density of cuprous compounds and their high mass fraction in the product. Actual studies on XRF measurements of Sn, Cu, and Zn in antifouling paints coated on leisure boats demonstrated a significantly thicker antifouling layer on German leisure boats compared to Swedish boats indicating a higher consumption of antifouling paints (B Eklund, Department of Applied Environmental Science, Stockholm University, Sweden, personal communication).

Emission of biocidal AF active substances and Zn oxide

Commercial shipping aims to have an extended interval between dry dockings for maintenance and repair. For that reason, remaining AF-paint layers are minimal (Haslbeck and Ellor 2005). For leisure boats the situation is more complex. Release rates and release mechanisms are affected by different types of boats and AF products (Yebra et al. 2004; Dafforn et al. 2011), the water quality, and the highly variable activity patterns of the users. Therefore, a bottom-up approach for calculating total emission by use of short-term laboratory tests ASTM Method D6442-99 (ASTM 2002) is inappropriate and would overestimate releases even if natural water is used (Schiff et al. 2004). In-situ release tests of some active substances are available but were carried out at saltwater sites only and mostly focused on Cu-based antifouling products (Haslbeck and Ellor 2005; Finnie 2006; Ytreberg et al. 2010). Furthermore, there are no data available on the application rate of different antifouling products and on the nationwide intensity of boat operations by the different owners. Therefore, the robust approach published by Rijkswaterstaat-WVL (2015) for the Netherlands was used by assuming an emission to surface water of 50% of the consumed AFP for leisure boats during service life. As a consequence, the emission data published here may be regarded only as an estimate of the order of magnitude. Therefore, yearly consumption figures outlined here were halved, resulting in a total emission of 124 t/a, parted into 89.5 t/a inorganic cuprous-based antifouling active substances, 25 t/a Zn oxide, and 9.5 t/a organic booster biocides. By recalculating to the metal content, about 70.5 t Cu and 20 t Zn were released on an annual basis into German surface waters. The release of almost 10 t of booster biocides seems to be negligible compared to the outstanding mass of persistent metals released annually and to biocidal active substances like zineb, DCOIT, and others which may break down quite rapidly. However, some existing substances are still in use and are quite persistent and highly toxic, such as cybutryne (Mohr et al. 2008). Meanwhile the European Union has rejected the further use of cybutryne from end of January 2017 (Commission Implementing Decision [EU] 2016).

Compared to the total nationwide Zn input into water bodies via diffuse and point sources into German catchments of 2756 t/a for 2003–2005 (Fuchs et al. 2010), the additional release of Zn from underwater coatings of leisure boats was below 1%. For the same period the total Cu emission into German water bodies was estimated by these authors to amount of 461 t/a. It must be stressed that additional inputs via flaking paint particles are not quantified here. Based on the leisure boat inventory of 2012, the yearly releases of inorganic Cu from AFPs reached about 15% of total input of 2003–2005, emphasizing the relevance of this emission route on the national scale.

For Switzerland AF-based Cu releases into surface water reached only about 5% of the total input of 49 t/a in 2000 (von Arx 2006). However, the market share of Cu-based AFPs is quite low in Switzerland compared to Germany (Table 4; Burkhardt and Dietschweiler 2013). In the Netherlands, about 17 t of the 34 t/a AF active substances were released by leisure boats in 2013, whereas Cu inputs provided the highest share with about 9 t. Prior to the temporary ban for Cu products, inputs from AFPs reached 72 t and 62 t yearly in 1995 and 2000, respectively (Rijkswaterstaat-WVL 2015).

The ongoing European Union-funded research project CHANGE concerning the Baltic Sea aims at the enforcement of the current regulations and the reduction of biocidal active substance emissions from into water bodies (Kononen 2013). Products with reduced release rates are currently on the market in Sweden and Denmark.

CONCLUSION

The analytical screening on actually permitted antifouling active substances in water samples of 50 marinas located all over the country reflected the use of biocidal products currently on the market. High water concentrations of the persistent active substances Zn, Cu, and cybutryne inside the marinas were observed for a number of sites. In some cases, environmental risks by Cu and cybutryne were identified. The use of dichlofluanid and tolyfluanid could only be demonstrated by the presence of their breakdown products. Further active substances could not be detected, most probably due to their low application rate at this time, their rapid degradation, the high limits of quantification for some of their degradation products, and the 1-time sampling at each site.

Results of the nationwide inventory of mooring berths revealed an outstanding importance of leisure boat activities at German inland waters. Freshwater sites amounted to 71% of the total boat stock, assuming that the number of berths is equal to the number of leisure boats. About 50% of the total nationwide stock was concentrated in regional agglomerations at inland areas. Clusters of closely packed marinas up to 1000 boats could be encountered even on a local scale. By use of structural data on marina size, emission scenarios for German freshwater marinas as well as for waterbodies adjacent to clusters of harbors should be tailored for environmental risk assessment in the near future.

The calculated yearly consumption of antifouling products in Germany reached 794 t/a. Although the German stock of leisure boats was less than one-third of the Swedish one, its calculated yearly consumption of biocidal active substances was higher, exceeding the Swedish by one-third. In our view, Swedish regional bans and restrictions on the use of Cu-based antifouling products are important drivers to reduce application and emission of biocidal active substances.
Furthermore, the first tentative estimation of antifouling based Cu emission by leisure boats during service life reached about 15% of total Cu emission from diffuse and point sources into German water bodies. If the Cu emission to surface waters should be reduced in general, the use of cuprous compounds in antifouling products of leisure boats also must be reduced, and countermeasures such as restrictions or bans are on the agenda. Nordic countries such as Sweden, Finland, or Denmark set a good example here, indicating that a reduction of Cu consumption is feasible. Moreover, new nonbiocidal antifouling products based on various operating principles are rising (Norioglu et al. 2015) but still have to prove their efficacy in practice.

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Data Accessibility—The data referenced in this paper is publicly available; the report and raw data are available from http://www.umweltbundesamt.de/sites/default/files/medien/378/publikationen/texte_68_2015_sicherung_der_verlaesslichkeit_der_antifouling_0.pdf

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