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**Occurrence and distribution of triclosan in the  
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# 1 Occurrence and Distribution of Triclosan in the German Bight (North Sea)

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7  
8 The potential of triclosan (TCS) acting as an endocrine disruptor has led to growing  
9 concern about the presence of TCS in the environment. In this study, seawater samples were  
10 collected from the German Bight during sampling campaigns conducted with the German  
11 research ship *Gauss* and *Ludwig Prandtl*. TCS was determined both in the dissolved phase  
12 and in the suspended particulate matters with concentrations ranging 0.8-6870 pg L<sup>-1</sup> and <1-  
13 95 pg L<sup>-1</sup>, respectively. High concentrations of TCS were present in the estuaries of the Elbe  
14 and the Weser, indicating significant input of TCS by the river discharge. The correlation  
15 coefficient ( $R^2$ ) between the dissolved concentration and salinity was 0.79 for the data obtained  
16 from the Gauss cruise, showing an obvious declining trend from the coast to the open sea. The  
17 mean partitioning coefficient ( $\log K_{OC}$ ) is  $4.85 \pm 0.30$ , suggesting partitioning to suspended  
18 particulate matter and sedimentation are important processes to control the fate of TCS in the  
19 coastal area.

20 *Keywords:* Triclosan; occurrence; water-particulate partitioning; North Sea

21 *Brief:* Investigation with coastal survey reveals distribution and partitioning of triclosan in  
22 marine waters.

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### 3 **1. Introduction**

4 Triclosan (5-chloro-2-[2,4-dichloro-phenoxy]-phenol) (TCS) is widely used as  
5 antimicrobial agent in personal care products and pharmaceuticals (Sabaliunas, 2003). It is  
6 also added to textiles to prevent odor, and to plastic products such as cutting boards. The  
7 production of TCS has been relatively stabilizing in recent years, which is used  $\sim 350$  t year<sup>-1</sup>  
8 in the EU (Environment Agency of UK). Studies have shown that TCS present in surface  
9 water may be toxic to certain algae species (e.g. *Scenedesmus subspicatus*) with a reported  
10 no-observer-effect concentration (72-h growth NOEC) of  $500$  ng L<sup>-1</sup> (Orvos et al., 2002;  
11 Reiss et al., 2002). Considering the commonly used safety factor of 10, a predicted no effect  
12 concentration (PNEC) of  $50$  ng L<sup>-1</sup> is obtained (Singer et al., 2002). Moreover, recent studies  
13 have shown that TCS blocks bacterial lipid biosynthesis by specifically inhibiting the enzyme  
14 enoyl-acyl carrier protein reductase which led to concerns of the possible development of  
15 bacterial resistance to TCS (McMurry et al., 1998; Levy et al., 1999). Thus, it is necessary to  
16 investigate the occurrence and fate of TCS in the environment.

17 The review studies (Heberer, 2002; Samsøe-Petersen et al., 2003) showed that TCS is  
18 degradable under aerobic conditions in wastewater treatment plants (WWTPs) and is  
19 extensively degraded and removed in activated-sludge systems. Results have shown about 70-  
20 90% of TCS is removed in the sewage and wastewater treatment plants (McAvoy et al., 2002;  
21 Singer et al., 2002; Bester, 2003; Ying and Kookana, 2007; Stasinakis et al., 2007), the  
22 remaining fraction is discharged with the effluent into the river and partly enters into the  
23 coastal water. Studies regarding photolysis of TCS in surface water have demonstrated that  
24 this may be a significant pathway in the upper layers of lakes, while TCS is quite stable for  
25 hydrolysis (Tixier et al., 2002; Aranami and Readman, 2007).

1 Studies in Europe, North America, Australia and China have reported the widespread  
2 occurrence of TCS with concentrations ranging 1-10  $\mu\text{g L}^{-1}$  for influent, 0.04-2  $\mu\text{g L}^{-1}$  for  
3 effluent and 0.01-0.1  $\mu\text{g L}^{-1}$  in the surface water (Singer et al., 2002; Weigel et al., 2004;  
4 Halden and Paull, 2005; Ying and Kookana, 2007; Wu et al. 2007). TCS and its methyl  
5 metabolite have also been detected in fish in surface waters (Adolfsson-Erici et al., 2002;  
6 Böhmer et al., 2004; Balmer et al., 2004) and in algae in a north Texas wastewater treatment  
7 plant receiving stream (Coogan et al., 2007). Although studies have demonstrated the  
8 ubiquitous distributions of TCS, little information is available for coastal waters.

9 The objective of the present study was to understand distribution levels of TCS in surface  
10 seawater of the German Bight. Spatial variations of TCS in the coastal waters were discussed.  
11 This study provided reliable data to understand the fate of TCS in coastal waters.

## 12 **2. Experimental Section**

### 13 *2.1. Water sampling*

14 Seawater samples were collected in the German Bight during BSH routine monitoring  
15 cruise in 29/2-10/3 2004 with research ship 'Gauss', and during a coastal survey 'NUTEX-5'  
16 with research ship 'Ludwig Prandtl' in 27/6-15/7 2005.

17 Seawater samples were collected from a stainless steel pipe at 5 m-depth onboard *Gauss*  
18 (30-400 L) and at 1 m-depth onboard *Ludwig Prandtl* (10-50 L), using the ship's water circuit  
19 located in the keel. The average flow rate was about 0.7  $\text{L min}^{-1}$ . Both suspended particular  
20 matter (SPM) and dissolved seawater phases were collected using a GFF (GFF 52 with 0.7  
21  $\mu\text{m}$  of nominal pore size) and a 95 mL PAD-2 resin column respectively. Field blanks of  
22 water sampling were prepared onboard. Details of the seawater samples are shown in Table 1  
23 and mean sampling position are shown in Figures 1 and 2, respectively.

24 PAD-2 columns were pre-cleaned by consecutive Soxhlet extractions with acetone and  
25 dichloromethane, rinsed with copious amounts of water and were capped and sealed in

1 polyethylene bags. GFFs were combusted at 450 °C for 12 hours and wrapped in aluminum  
2 foil. After sampling, PAD-2 columns and GFFs were respectively stored at 4°C and -20 °C  
3 until analysis. Samples were treated in clean-room facilities.

#### 4 2.2. *Extraction and clean-up*

5 The PAD-2 columns and GFFs (Nutex-5) were spiked with 20 ng of AHTN D<sub>3</sub> after  
6 sampling (if the column was not spiked before sampling) and 20 ng of internal standard  
7 dibenzyl phthalate (Dr. Ehrenstorfer GmbH, Augsburg, Germany). They were extracted with  
8 soxhlet extractor for 16 h using 150 mL of dichloromethane. 20 ng of AHTN D<sub>3</sub> was spiked  
9 in the *Gauss* samples before analysis. All extracts were concentrated by rotary evaporation to  
10 1 mL using hexane as keeper. The extracts were cleaned on a 2.5 g silica gel column (5% H<sub>2</sub>O  
11 deactivation), eluted with 15 mL of hexane (F1), 25 mL of hexane/diethyl ether (3:1 v/v) (F2),  
12 25 mL of hexane/diethyl ether (1:1 v/v) (F3) and 20 mL of hexane/acetone (1:1 v/v) (F4). F2  
13 and F3 were combined and concentrated down to 100 µL. 100 µL of N,O-  
14 bis(trimethylsilyl)trifluoroacetamide with 1% Trimethylchlorosilane (BSTFA+1%TMCS)  
15 (Macherey-Nagel GmbH, Düren, Germany) was added for derivatization of TCS.

#### 16 2.3. *Gas chromatography-mass spectrometry (GC-MS)*

17 Sample analyses were performed with an Agilent 6890 GC-5973 quadrupole mass  
18 selective detector (MSD) with electron impact ionization. Analytes were separated on a 30-m  
19 HP-5ms column with 0.25 i.d. and 0.25 µm film thickness with helium as carrier gas (1.0 mL  
20 min<sup>-1</sup>). The oven temperature program was 80 °C for 1 min, 30 °C min<sup>-1</sup> to 130 °C, 3 °C min<sup>-1</sup>  
21 to 240 °C, 10 °C min<sup>-1</sup> to 300 °C, and then 300 °C for 5 min. The quadrupole and the ion  
22 source temperature were maintained at 150 °C and 230 °C, respectively. The electron energy  
23 was 70 eV. One microliter of the sample was injected into GC-MS by pulse splitless mode  
24 with a pulse pressure of 20 psi for 2 min and inlet temperature of 280°C.

25 The following masses were used for confirmation and quantification: m/z = 345, 347, 200  
26 for derivative of TCS, m/z = 246, 261 for surrogate standard AHTN D<sub>3</sub> and m/z = 225 for

1 internal standard dibenzyl phthalate. The response factor was derived from the calibration  
2 curve (6-points) made for response ratio between TCS (0-500 ng mL<sup>-1</sup>) (Dr. Ehrenstorfer  
3 GmbH, Augsburg, Germany) and surrogate standard AHTN D<sub>3</sub> (100 ng mL<sup>-1</sup>).

#### 4 2.4. Quality control

5 Three break-through tests were performed by filtering water through two PAD-2 columns  
6 in series during NUTEX-5 cruise. Sample volumes were 22 and 50 L. Concentrations of TCS  
7 on the back-up columns were not detectable, suggesting that break-through was not a major  
8 concern for this cruise. We have not done break-through test during the *Gauss* cruise.  
9 However, the recoveries of two surrogate standards, e.g. 4-n-octylphenol (4-n-OP) and 4-n-  
10 nonylphenol (4-n-NP) spiked prior to sampling, were 76±9% and 71±10% for the water  
11 sampling (Xie et al., 2006). As the physicochemical properties of TCS (log K<sub>OW</sub>=4.8, water  
12 solubility: 12 mg L<sup>-1</sup> (20 °C)) is similar to those of 4-n-OP (K<sub>OW</sub> =4.12, water solubility: 12.6  
13 mg L<sup>-1</sup> (20 °C)) and 4-n-NP (K<sub>OW</sub> =4.8, water solubility: 4.48 mg L<sup>-1</sup> (20 °C)), the achieved  
14 recoveries of 4-n-OP and 4-n-NP may suggest that the break-through of TCS is not of concern  
15 for samples collected during the *Gauss* cruise. The mean recovery of TCS was 99.8±0.1% for  
16 the clean-up and 98 ± 2% from spiked columns (n=3), respectively.

17 The instrumental limit of detection (LOD) was determined by the signal to noise ratio  
18 (S/N=3), which was 0.25 pg. The method detection limits (MDLs) were derived from three  
19 times the standard deviation (3σ) of field blanks. Mean blank mass of TCS was calculated  
20 from the field blanks and subtracted from the sample masses, which is 160±50 pg sample<sup>-1</sup> on  
21 PAD-2 column. There is no detectable TCS on field blanks of GFFs, therefore the method  
22 detection limit was derived from the LOD. The MDLs of TCS were 0.5-15 pg L<sup>-1</sup> for  
23 dissolved concentration, and 0.2-5 for TSM. Two measurements for TCS in the air of clean-lab  
24 showed concentrations of 570 pg m<sup>-3</sup> and 280 pg m<sup>-3</sup>, indicating that indoor air is a potential risk  
25 for contamination. Necessary modifications have been made for the laboratory equipments to  
26 eliminate contamination during sample preparation (Ebinghaus and Xie, 2006).

1

## 2 **3. Results and discussion**

### 3 *3.1. Dissolved TCS*

4 Concentrations of dissolved TCS ( $[TCS]_{diss}$ ) measured from the *Gauss* cruise was  $61 \text{ pg L}^{-1}$   
5 from the estuary of the Elbe,  $\sim 15 - 20 \text{ pg L}^{-1}$  around Helgoland, and declined to  $1 - 5 \text{ pg L}^{-1}$   
6 in the north of the German Bight. Figure 1 shows the spatial distribution profile from the  
7 coast to the open sea which agrees well with the distribution pattern of alkylphenols  
8 determined during this cruise (Xie et al., 2006).  $[TCS]_{diss}$  determined from the NUTEX-5  
9 cruise in 2005 ranged from 8 to  $6870 \text{ pg L}^{-1}$ , which varied by 3 orders of magnitude (Figure 2  
10 and Table 1). High concentrations of TCS were determined in the Elbe estuary and its plume  
11 ( $1210-6870 \text{ pg L}^{-1}$ ).  $[TCS]_{diss}$  ranged from 18 to  $615 \text{ pg L}^{-1}$  for the Weser estuary, and ranged  
12 from  $12-113 \text{ pg L}^{-1}$  for the Ems estuary. Generally, the concentration of TCS decreased  
13 greatly from estuaries to the outer German bight, which suggests significant input of TCS  
14 from river discharge.

### 15 *3.2. TCS in suspended particulate matters*

16 Concentrations of TCS in suspended particulate matters ( $[TCS]_{SPM}$ ) were only analyzed for the  
17 SPM samples collected during NUTEX-5 cruise.  $[TCS]_{SPM}$  ranged from below the MDL ( $1 \text{ ng L}^{-1}$ )  
18 to  $95 \text{ ng L}^{-1}$ . Particulate related TCS fraction ( $\phi = [TCS]_{SPM} / ([TCS]_{diss} + [TCS]_{SPM}) * 100\%$ ) is  
19 determined by the concentrations of TCS in dissolved and particulate phases, which varied  
20 from  $\sim 1$  to 48%. For a better understanding of the particle bound ability of TCS, the  
21 concentrations of particulate associated TCS were recalculated versus the SPM  
22 concentrations, which ranged from  $<0.4$  to  $12.9 \text{ ng g}^{-1}$  (Table 1). These concentrations were at  
23 a lower level as compared to those measured in marine sediments in the Mediterranean coast,  
24 Spain (Agüera et al., 2003). It may give additional information for a reliable explanation of  
25 the distribution of  $[TCS]_{diss}$ . For example,  $[TCS]_{diss}$  determined in the estuaries of the Ems  
26 (site 1) and the Weser (sites 9-12) were  $\sim 10$  times lower than those measured in the estuary of

1 the Elbe (sites 16-18), whereas the concentrations related to the SPM concentration were  
2 comparable. These results imply that, for some samples, the SPM samples collected were  
3 dominated by the local mass, while the water body was significantly affected by the tides.

4 Dilution looks like a major parameter influencing the spatial distribution of TCS in the German  
5 Bight.  $[TCS]_{diss}$  obtained from the *Gauss* cruise demonstrated a strong correlation with salinity  
6 (Figure 3a). The correlation coefficient ( $R^2$ ) was 0.79, which shows obviously declining trends  
7 from the coast to the open sea. While the correlation coefficient ( $R^2=0.21$ ) derived from data  
8 obtained by the NUTEX-5 cruise (excluding the highest concentration) was weak (Figure 3b).  
9 This result may be due to the fact that the water samples collected during the NUTEX-5 cruise are  
10 close to the coast where the river discharge mixing with the seawater is not complete, thus TCS  
11 concentrations determined are strongly influenced by the tides and the mixing process of  
12 freshwater with seawater.

13 Indeed, the North Sea currents transport the water mass along the Dutch, German and  
14 Danish coast and further to the Norwegian coast. The river discharge is diluted by fresh  
15 seawater and tides during the transport, which leads to a declining concentration profile of  
16 TCS from the estuaries to the open water. During this process, sedimentation is a fast  
17 elimination process for the SPM-associated TCS. Although  $[TCS]_{diss}$  at sampling sites 15-18  
18 showed a relatively high level, the SPM fractions calculated based on the paired  
19 dissolved/SPM concentrations were at a relatively low level (0.8-3%). Moreover,  
20 photochemical degradation may be a significant elimination pathway of TCS in surface  
21 seawater during the summer season (Tixier et al., 2002; Aranami and Readman, 2007).

### 22 3.3. Comparison with other studies in the world

23 Data on TCS in marine water are rare, while TCS has been detected at various levels from  
24 the effluent of WWTP and surface waters in many cities around the world (Table 2).  
25 Recently, TCS has been determined in seawater from Tai Po and Victoria Harbours in Hong  
26 Kong with concentrations ranging 15-110 ng L<sup>-1</sup> (Wu et al., 2007). Loos et al. (2007)

1 conducted a comprehensive survey for polar organic contaminants in surface and drinking  
2 waters around Lake Maggiore in Northern Italy. TCS was determined in lake water with  
3 concentrations ranging from below method detection limit (2 ng L<sup>-1</sup>) to 4.0 ng L<sup>-1</sup>. In  
4 Switzerland, TCS were found in the lakes and rivers with concentrations ranging from 1.4 to  
5 74 ng L<sup>-1</sup>, while the TCS concentration in groundwater was below the detection limit (<0.4 ng  
6 L<sup>-1</sup>) (Lindström et al., 2002). Similarly, TCS was detected with a mean concentration of 60 ng  
7 L<sup>-1</sup> from effluents of a WWTP in Canada, and with concentrations of 4-8 ng L<sup>-1</sup> in surface  
8 water from down streams on the Canadian shoreline of the Detroit River (Hua et al., 2005). In  
9 comparison to the results from these studies, TCS determined in the estuary of the Elbe and in  
10 the area around the island of Sylt were comparable to those in the Maggiore Lake, the Detroit  
11 River and the lower levels in Swiss lakes. TCS concentrations present in the open sea were  
12 lower by 2-3 orders of magnitude than those present in surface waters (Table 2).

### 13 3.4. Partitioning of TCS between dissolved phase and SPMs

14 The organic suspended matter partition coefficient ( $K_{OC}$ ) is an equilibrium expression  
15 commonly employed for comparing the equilibrium partitioning of semi-volatile organic  
16 compounds in different aquatic suspended matter matrices. The partitioning coefficients were  
17 calculated according to the SPMs and the fraction of organic matters ( $f_{OC}$ ). The partitioning  
18 coefficient related to organic matters can be calculated using the following equation:

$$19 \quad K_{OC} = \frac{C_s}{C_w f_{OC}} \quad (1)$$

20 where  $C_s$  is the concentration of a compound in SPMs (ng kg<sup>-1</sup>) and  $C_w$  (ng L<sup>-1</sup>) is the  
21 concentration of a compound in the dissolved phase ( $[TCS]_{diss}$ ). Generally, the water-SPM  
22 partitioning can be affected by the pH of seawater, salinity and the contents of the SPM. In  
23 the estuaries, salinity-related changes in chemical reaction rates are important by the influence  
24 of ambient ionic strength on the activities of reacting species (Zhou and Rowland, 1996). The  
25 solubility, speciation, and partition behaviour of organic contaminants may vary as result of

1 salinity-induced changes in pH. The pH related  $K'_{OC}$  can be calculated using the equation 2  
2 and then  $\log K'_{OC}$  may be derived from equation 3 (Singer et al., 2002)

$$3 \quad K'_{OC} = \frac{C_s}{C_w f_{OC}} (1 + 10^{(pH - pK_a)}) \quad (2)$$

$$4 \quad \log K'_{OC} = \log K_{OC} + \log(1 + 10^{(pH - pK_a)}) \quad (3)$$

5 where pH and  $f_{OC}$  value were measured on board, and the pKa of TCS is 8.1 (20 °C).

6 Selected samples from the NUTEX-5 cruise were used to calculate the partitioning  
7 coefficients that are listed in Table 1. The individual  $\log K'_{OC}$  values calculated varied in a  
8 wide range and distributed in two groups, the lower level of 4.01 –4.53 and the higher level of  
9 4.86-5.32. The mean  $\log K'_{OC}$  of TCS was  $4.89 \pm 0.30$ , which is slightly higher than the value  
10 of 4.67 determined in the WWTP in Switzerland (Singer et al., 2002) and the value of 4.76  
11 estimated based on the equation  $\log K_{OC} = 1.029 \log K_{OW} - 0.18$  (Bonazountas and Wagner,  
12 1984). The difference can be addressed to the combined effect of the increased pH and  
13 salinity of the estuaries. As TCS is a weak base (pKa of 8.1), increased pH may lead to a high  
14 fraction of undissociated TCS which is supposed to be the active form for sorption (Synger et  
15 al., 2002), thus increased  $K'_{OC}$  is expected. However, the correlation between the estimated  
16  $\log K'_{OC}$  and the pH of water samples is not significant (Table 1), which suggests that the  
17 effect of pH on the sorption of TCS is complicated. For instance, pH changes could have  
18 altered, to some extent, the electrokinetic property of either the organic compound or the  
19 surface of SPM (Zhou and Rowland, 1996).

20 Salinity has a very strong effect upon equilibrium partition coefficients of organic  
21 compounds on organic matters. As it is shown in Figure 4, a good correlation ( $R^2=0.50$ ) is  
22 present between the salinity and the  $\log K'_{OC}$ . TCS likely partitions to SPM with increasing  
23 salinity. This trend has been observed for enhanced adsorption of phthalates and permethrin in  
24 the presence of salt or in seawater (Al-Omran and Preston, 1987; Zhou and Rowland, 1996).  
25 A reasonable explanation is to assume that the influence of salting-out on the aqueous

1 solubility of TCS in seawater, which has been quantitatively described by the empirical  
2 Setschenow relationship (Schwarzenbach et al., 1993). When salinity increases, the TCS may  
3 become less soluble, leading to increased sorption on SPMs and on sediment. In this study the  
4  $\log K_{SC}$  values increased from 4.86 to 5.32 for the salinity range of 31.5-34.0‰. The lower  
5  $\log K_{SC}$  values may result from a non-equilibrium state of the water mass which contains  
6 more or less SPMs originating from the rivers discharge.

7 The result of partitioning of TCS between water phase and SPMs suggests that the  
8 particulate combination could play a significant role in the transport of TCS from  
9 contaminated estuaries into the vast aquatic environments. Moreover the high  $\log K_{OC}$  value  
10 of TCS implies that TCS may likely be uptaken by marine organisms and fish (Adolfsson-  
11 Erci et al., 2002; Böhmer et al., 2004).

### 12 *3.5. Transport of TSC into the German Bight*

13 In Germany, Bester (2003) studied a sewage treatment plant that processes 200,000 m<sup>3</sup> of  
14 wastewater per day. The concentration of TCS determined was ~1000 ng L<sup>-1</sup> in the influent  
15 water and was 50 ng L<sup>-1</sup> in the effluent water. Weigel et al. (2004) reported TCS  
16 concentration of 120 ng L<sup>-1</sup> in the effluent of a wastewater treatment plant in Hamburg. TCS  
17 concentrations in the Itter were between 30 ng L<sup>-1</sup> in upstream of a WWTP at Solingen-Ohligs  
18 and 90 ng L<sup>-1</sup> downstream of the WWTP (Wind et al., 2004). These studies suggest a baseline  
19 level of TSC in the German rivers ranging ~10 to ~100 ng L<sup>-1</sup> which are comparable to the  
20 concentrations (21-94 ng L<sup>-1</sup>) predicted with geo-referenced exposure model GREAT-ER  
21 (Geo-referenced Regional Environmental Assessment Tool for European Rivers) (Wind et al.,  
22 2004). Given the mean fresh water discharges 509 m<sup>3</sup> s<sup>-1</sup> for the Elbe, 196 m<sup>3</sup> s<sup>-1</sup> for the  
23 Weser and 51.2 m<sup>3</sup> s<sup>-1</sup> for the Ems, an annual input of TCS to the German Bight was ca. 500  
24 kg year<sup>-1</sup> using the low level of  $PEC_{catchment}$  of 21 ng L<sup>-1</sup>. These results suggest that the  
25 German Bight is a significant sink for TCS, which accounts for ~1.2% of the annual market  
26 consumption of TCS in Germany (~40 t year<sup>-1</sup>).

1 Wedekind and Främcke (1991) have derived the transfer factor of concentrations ( $F_{TC}$ ) of  
2 contamination between the German Bight and its tributary waters (Rhine, Elbe, Weser, and  
3 Ems) from measured tritium and Cs-137 activity concentrations.  $F_{TCS}$  are 0.003 (Ems), 0.013  
4 (Weser) and 0.030 (Elbe) at salinity of 31‰, and are 0.008 (Ems), 0.031 (Weser) and 0.069  
5 (Elbe) at salinity of 29‰. TCS concentrations at different water mass may be estimated using  
6 these  $F_{TCS}$  and the concentration in the rivers (21 ng L<sup>-1</sup>), which gave estimated  
7 concentrations 63 –170 pg L<sup>-1</sup> in the Ems estuary, 270-650 pg L<sup>-1</sup> in the Weser estuary and  
8 630-1450 pg L<sup>-1</sup> in the Elbe estuary. These predicted concentration profiles fit very well to the  
9 measured environmental distribution, such as 30-113 pg L<sup>-1</sup> for the Ems estuary, 101-615 pg  
10 L<sup>-1</sup> for the Weser estuary and 40-6867 pg L<sup>-1</sup> for the Elbe estuary.

11 In conclusion, the concentrations of TCS measured in the German Bight were lower by 1-3  
12 orders of magnitude than the predicted no-effect concentration (PNEC) of 50 ng L<sup>-1</sup> for TCS  
13 in surface water (Singer et al., 2002). Although the presence of TCS in the German Bight is  
14 not significant risk based on the current knowledge, more systematic investigation on the fate  
15 of TCS and its metabolites is necessary to understand their chronic effect to the marine  
16 organisms and to conduct a comprehensive environmental risk assessment.

17

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## 1 **References**

- 2 Adolfsson-Erici, M., Pettersson, M., Parkkonen, J., Sturve, J., 2002. Triclosan, a commonly  
3 used bactericide found in human milk and in the aquatic environment in Sweden.  
4 *Chemosphere* 46, 1485-1489.
- 5 Agüera, A., Fernandez-Alba, A.R., Piedra, L., Mezcua, M., Gomez, M.J., 2003. Evaluation of  
6 triclosan and biphenol in marine sediments and urban wastewaters by pressurized liquid  
7 extraction and solid phase extraction followed by gas chromatography mass  
8 spectrometry and liquid chromatography mass spectrometry. *Analytica Chimica Acta*  
9 480, 193-205.
- 10 Al-Omran, L.A., Preston, M.,R., 1987. The interaction of phthalate esters with suspended  
11 particulate material in fresh and marine waters. *Environmental Pollution* 46, 177-186.
- 12 Aranami, K., Readman, J.W., 2007. Photolytic degradation of triclosan in freshwater and  
13 seawater. *Chemosphere* 66, 1052-1056.
- 14 Balmer, M.E., Poiger, T., Droz, C., Romanin, K., Bergqvist, P.A., Müller, M.D., Buser, H.R.,  
15 2004. Occurrence of methyl triclosan, a transformation product of the bactericide  
16 triclosan, in fish from various lakes in Switzerland. *Environmental Science and*  
17 *Technology* 38, 390-395.
- 18 Bester, K., Triclosan in a sewage treatment process-balances and monitoring data. *Water*  
19 *Research* 37, 3891-3896.
- 20 Bonazountas, M, Wagner, J., 1984. SESOIL: a seasonal soil compartment model Arthur D.  
21 Little, Inc., Cambridge.
- 22 Böhmer, W., Rüdell, H., Wenzel, A., Schröter-Kermani, C. 2004. Retrospective monitoring of  
23 triclosan and methyl-triclosan in fish  
24 Results from the german environmental specimen bank. 2004, 17 S.  
25 International Symposium on Halogenated Environmental Organic Pollutants and POPs,  
26 Berlin.

1 Coogan, M.A., Edziyie, R.E., La Point, T.W., J. Venables, B., 2007. Algal bioaccumulation of  
2 triclocarban, triclosan, and methyl-triclosan in a North Texas wastewater treatment  
3 plant receiving stream. *Chemosphere* 67, 1911-1918.

4 Ebinghaus, R.; Xie, Z., 2006. Occurrence and air/sea-exchange of novel organic pollutants in  
5 the marine environment. *J. Physique* 139, 211-237.

6 Environment Agency UK. Triclosan briefing. [http://www.environment-  
8 agency.gov.uk/commondata/acrobat/triclosanbriefing\\_886859.pdf](http://www.environment-<br/>7 agency.gov.uk/commonddata/acrobat/triclosanbriefing_886859.pdf).

9 Gómez, M.J., Martínez Bueno, M.J., Lacorte, S., Fernández-Alba, A.R., Agüera, A., 2007.  
10 Pilot survey monitoring pharmaceuticals and related compounds in a Sewage treatment  
11 plant located on the Mediterranean coast. *Chemosphere* 66, 993-1002.

12 Halden, R.U., Paull, D.H., 2005. Co-occurrence of triclocarban and triclosan in U.S. water  
13 resources. *Environmental Science and Technology* 39, 1420-1426.

14 Hua, W.Y., Bennett, E.R., Letcher, R.J., 2005. Triclosan in waste and surface waters from the  
15 upper Detroit River by liquid chromatography-electrospray-tandem quadrupole mass  
16 spectrometry. *Environmental International* 31, 621-630.

17 Heberer, T., 2002. Occurrence, fate, and removal of pharmaceutical residues in the aquatic  
18 environment: a review of recent research data. *Toxicology Letter* 131, 5-17.

19 Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B.,  
20 Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater  
21 contaminants in U.S. streams, 1999-2000: a national reconnaissance. *Environmental  
22 Science and Technology* 36, 1202-1211.

23 Levy, C.W., Roujeinikova, A., Sedelnikova S., Baker, P.J., Stuitje A.R., Slabas, A.R., Rice,  
24 D.W., Rafferty J.B., 1999. Molecular basis of triclosan activity. *Nature* 398, 383-384.

25 Lindström, A., Buerge, I.J., Poiger, T., Bergqvist, P.A., Müller, M.D., Buser, H.R., 2002.  
26 Occurrence and environmental behavior of the bactericide triclosan and its methyl

1 derivative in surface waters and in wastewater. *Environmental Science and Technology*  
2 36, 2322-2329.

3 Loos, R., Wollgast, J., Huber, T., Hanke G., 2007. Polar herbicides, pharmaceutical products,  
4 perflouroctanesulfonate (PFOS) perfluorooctanoate (PFOA), and nonylphenol and its  
5 carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in  
6 Northern Italy. *Analytical Bioanalytical Chemistry* 387, 1469-1478.

7 McAvoy, D.C., Schatowitz, B., Jacob, M., Hauk, A., Eckhoff, W.S., 2002. Measurement of  
8 triclosan in wastewater treatment systems. *Environmental Toxicology Chemistry* 21,  
9 1323-1329.

10 McMurry L.M., Oethinger, M., Levy, S.B., 1998. Triclosan targets lipid synthesis. *Nature*  
11 394, 531-532.

12 Orvos, D.R., Versteeg, D.J., Inauen, J., Capdevielle, M., Rothenstein, A., Cunningham, V.,  
13 2002. Aquatic toxicity of triclosan. *Environmental Toxicology Chemistry* 21, 1338-  
14 1349.

15 Reiss, R., Mackay, N., Habig, C., Griffin, J., 2002. An ecological risk assessment for triclosan  
16 in lotic systems of following discharge from wastewater treatment plants in the United  
17 States. *Environmental Toxicology Chemistry* 21, 2483-2492.

18 Sabaliunas, D., Webb, S.F., Hauk, A., Jacob, M., Eckhoff, W.S., 2003. Environmental fate of  
19 triclosan in the river Aire basin, UK. *Water Research* 37, 3145-3154.

20 Samsoe-Petersen, L., Winther-Nielsen, M., Madsen, T., 2003. Fate and effects of triclosan.  
21 Environmental Project No. 861. Copenhagen: Danish Environmental Protection  
22 Agency.

23 Schwarzenbach, R.P., Gschwend, P.M., Imboden; D.M. 1993. *Environmental Organic*  
24 *Chemistry*; John Wiley and Sons: New York.

25 Singer, H., Müller, S., Tixier, C., Pillonel, L., 2002. Triclosan: occurrence and fate of a  
26 widely used biocide in the aquatic environment: field measurements in wastewater

1 treatment plants, surface waters, and late sediments. *Environmental Science and*  
2 *Technology* 36, 4998-5004.

3 Stasinakis, A.S., Petalas, A.V., Mamais, D., Thomaidis, N.S., Gatidou, G., Lekkas, T.D.,  
4 2007. Investigation of triclosan fate and toxicity in continuous-flow activated sludge  
5 systems. *Chemosphere* 68, 375-381.

6 Tixier, C., Singer, H., Canonica, S., Müller, S.R., 2002. Phototransformation of triclosan in  
7 surface waters: A relevant elimination process for this widely used biocide-laboratory  
8 studies, field measurements, and modeling. *Environmental Science and Technology* 36,  
9 3482-3489.

10 Weigel, S., Berger, U., Jensen, E., Kallenborn, R., Thoresen, H., Hühnerfuss, H., 2004.  
11 Determination of selected pharmaceuticals and caffeine in sewage and seawater from  
12 Tromsø/Norway with emphasis on ibuprofen and its metabolites. *Chemosphere* 56, 583-  
13 592.

14 Wedekind, C., Främcke, G., 1991. Transfer factors of contamination between the German  
15 Bight and its tributary waters derived from measured tritium and Cs-137 activity  
16 concentrations. *Ocean Dynamics* 44, 59-75.

17 Wind, T., Werner, U., Jacob, M., Hauk, A., 2004. Environmental concentrations of boron,  
18 LAS, EDTA, and triclosan simulated with GREAT-ER in the river Itter. *Chemosphere*  
19 54, 1135-1144.

20 Wu, J.L., Lam, N.P., Marten, D., Kettrup, A., Cai, Z.W., 2007. Triclosan determination in  
21 water related to wastewater treatment. *Talanta* 72, 1650-1654.

22 Xie, Z.; Lakaschus, S.; Ebinghaus, R.; Caba, A.; Ruck, W. 2006. Atmospheric concentrations and  
23 air-sea exchanges of nonylphenol, tertiary octylphenol and nonylphenol monoethoxylate in  
24 the North Sea. *Environmental Pollution* 142, 170-180.

25 Ying, G.G., Kookana, R.S., 2007. Triclosan in wastewaters and biosolids from Australian  
26 wastewater treatment plants. *Environment International* 33, 199-205.

1 Zhang, S.Y., Zhang, Q., Darisaw, S., Ehie, O., Wang, G.D., 2007. Simutaneous quantification  
2 of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and  
3 pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New  
4 Orleans, Louisiana, USA. *Chemosphere* 66, 1057-1069.

5 Zhou, J.L., Rowland, S.J., 1996. Evaluation of the interactions between hydrophobic organic  
6 pollutants and suspended particles in estuarine waters. *Water Research* 31, 1708-1718.

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1 **Figure caption**

2 **Figure 1.** Spatial distribution of the dissolved TCS in the German Bight determined from  
3 water sampling with *Gauss* cruise in 2004. The bars are placed on the average position for  
4 each water sample

5 **Figure 2.** Spatial distribution of the dissolved TCS in the German Bight determined from  
6 water sampling with NUTEX-5 cruise in 2005

7 **Figure 3.** Change in dissolved TCS concentrations with salinity gradients for sampling  
8 conducted with *Gauss* (a) and NUTEX-5 cruises (b)

9 **Figure 4.** Effect of salinity on the water-particulate partitioning of TCS in the German Bight

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**Table 1.** Summary of results of TCS in dissolved ( $[TCS]_{diss}$ ) and suspended particulate matters ( $[TCS]_{SPM}$ ) measured in the German Bight during the NUTEX-5 cruise, particulate associated fractions ( $\phi$ ), water-particulate partitioning coefficient ( $Logk'_{oc}$ ) and sample collecting data; water sample numbers of the sampling sites are marked on Figure 2

Sample site	Longitude (E)	Latitude (N)	Depth (m)	Temperature (°C)	Salinity (‰)	pH	SPM (mg L <sup>-1</sup> )	$f_{oc}$ (%)	$[TCS]_{diss}$ (pg L <sup>-1</sup> )	$[TCS]_{SPM}$ (pg L <sup>-1</sup> )	$\phi$ (%)	$TCS]_{SPM}$ (ng g <sup>-1</sup> )	$Logk'_{oc}$
1	6.96	53.4	11	18.6	25.2	7.84	18.4	18	113	27	19	1.5	4.86
2	6.5	53.62	11	16.7	32.5	8.02	8.7	24	89	3.5	4	0.4	4.27
3	7.08	53.82	20	15.2	33.7	8.32	2	50	12	<1	-	-	-
4	7.16	53.74	5	16.7	33.4	8.18	4.6	35	30	n.a.	-	-	-
5	7.42	53.87	23	15.6	33.5	8.29	2	70	18	<1	-	-	-
6	7.42	53.78	10	17	32.9	8.27	3	47	8	1.5	16	0.5	4.47
7	7.64	53.87	22	15	33.6	8.26	3.5	40	18	6	25	1.7	4.58
8	8.03	53.79	28	15.5	33.1	8.32	2	60	19	n.a.	-	-	-
9	8.23	53.47	2.5	18.9	31.8	8.05	58.2	15	101	95	48	1.6	5.03
10	8.18	53.51	13	18.5	32.8	8.07	18.7	17	142	29	17	1.6	4.81
11	8.17	53.59	17	17.1	31.8	8.34	9.9	23	115	9.3	7	0.9	4.55
12	8.29	53.71	2.5	19.7	22.3	7.79	25	18	615	29	5	1.2	4.02
13	8.02	53.92	12.5	14.9	34	8.26	6	23	33	2.3	7	0.4	4.70
14	8.22	53.98	22	14.2	34	8.26	2.6	46	10	n.a.	-	-	-
15	8.32	54.02	8	16	32.4	8.30	4.5	38	6870	58	0.8	13	3.69
16	8.70	54.12	13	18.2	27.9	8.40	13.2	26	1868	46	2.4	3.5	3.86
17	8.91	54.11	2	18.7	27.6	8.19	54.6	11	3198	88	3	1.6	3.66
18	8.73	54.12	9.5	18.6	28	8.42	14.2	24	1212	22	2	1.5	3.73
19	8.34	54.32	11	18	31.5	8.33	2	60	139	13	9	6.5	4.89

<b>20</b>	8.52	54.37	14.5	19.1	31.6	8.13	8.9	24	40	n.a.	-	-	-
<b>21</b>	8.22	54.47	10	19.1	31	8.28	4.7	30	1640	n.a.	-	-	-
<b>22</b>	8.27	54.70	15	18.4	31.9	8.16	21.3	17	1352	n.a.	-	-	-
<b>23</b>	8.40	55.07	7.5	20.5	31.2	8.10	3.7	32	1266	9.6	1	2.6	3.81
<b>24</b>	8.33	55.09	6	19.2	31.6	8.14	2.4	58	747	n.a.	-	-	-

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**Table 2.** Comparison of TCS concentrations in water and SPM measured in this study with concentrations in surface water reported from other locations in the world

<b>Location</b>	<b>[TCS]<sub>diss</sub> (ng L<sup>-1</sup>)</b>	<b>[TCS]<sub>SPM</sub> (ng g<sup>-1</sup>)</b>	<b>References</b>
<b>U.S. streams, U.S.</b>	140	-	Kolpin et al., 2002
<b>Aabach Mönchaltorf River, Switherland</b>	20	-	Singer et al., 2002
<b>Swiss lakes, Switzerland</b>	<0.4-74	<2	Lindström et al., 2002
<b>Almeria, Spain</b>		0.27-130.7	Agüera et al., 2003
<b>Dortmund, Germany</b>	43-59	-	Bester, 2003
<b>Hamburg, Germany</b>	120	-	Weigel et al., 2004
<b>Itter, Germany</b>	30-90		Wind et al., 2004
<b>Detroit River, Canada</b>	4-8	-	Hua et al., 2005
<b>Texas, United States</b>	50-200	-	Coogan et al., 2007
<b>Mississippi River, U.S.</b>	8.8-34.9	-	Zhang et al., 2007
<b>Lake Maggiore, Italy</b>	<2.0-4.0	-	Loos et al., 2007
<b>Mediterranean coast, Spain</b>	80-400	-	Gómez et al., 2007
<b>Australia</b>	<3-75	-	Ying and Kookana, 2007
<b>Hong Kong, China</b>	15-110	-	Wu et al., 2007
<b>German Bight</b>	0.001-6.87	<0.4-13	This study

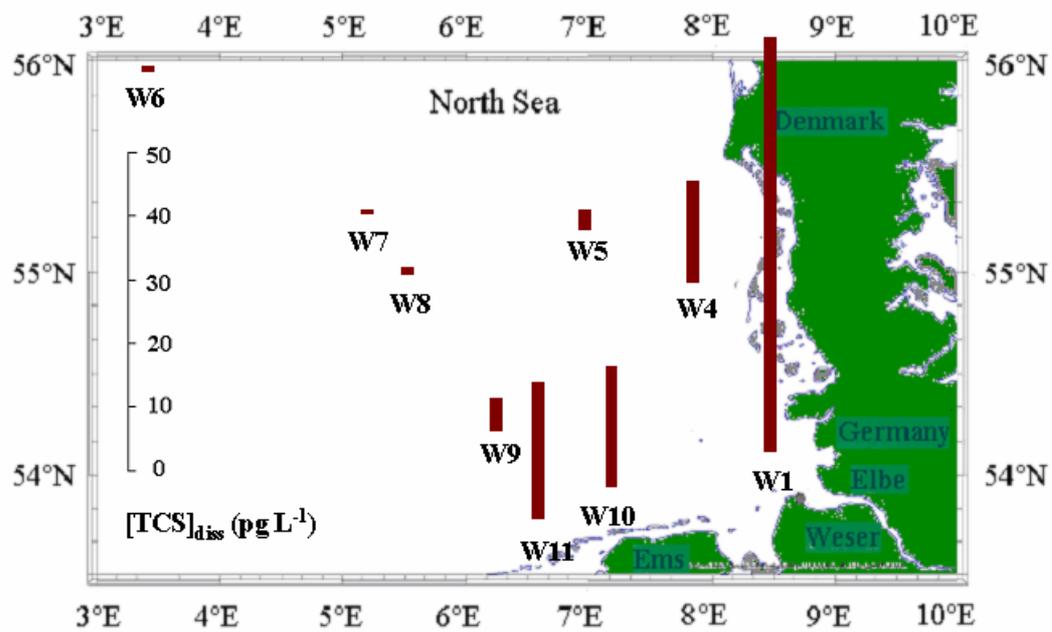


Figure 1

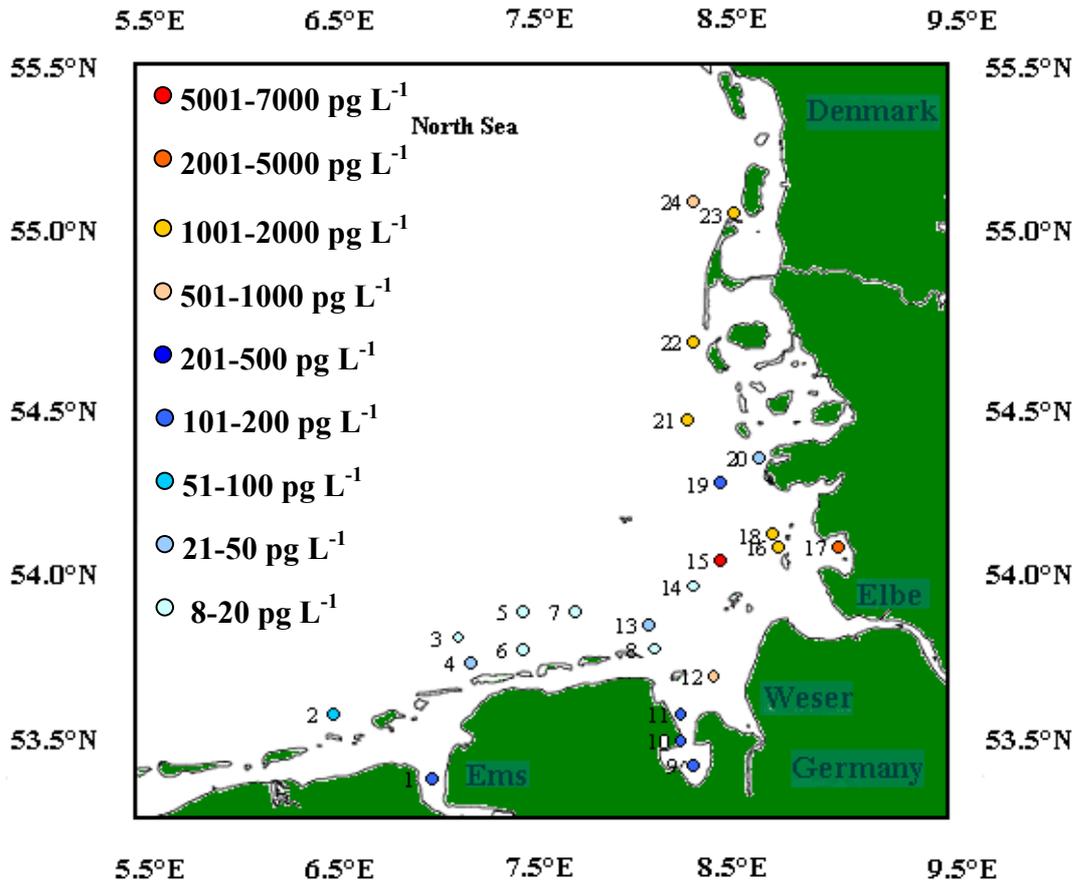


Figure 2

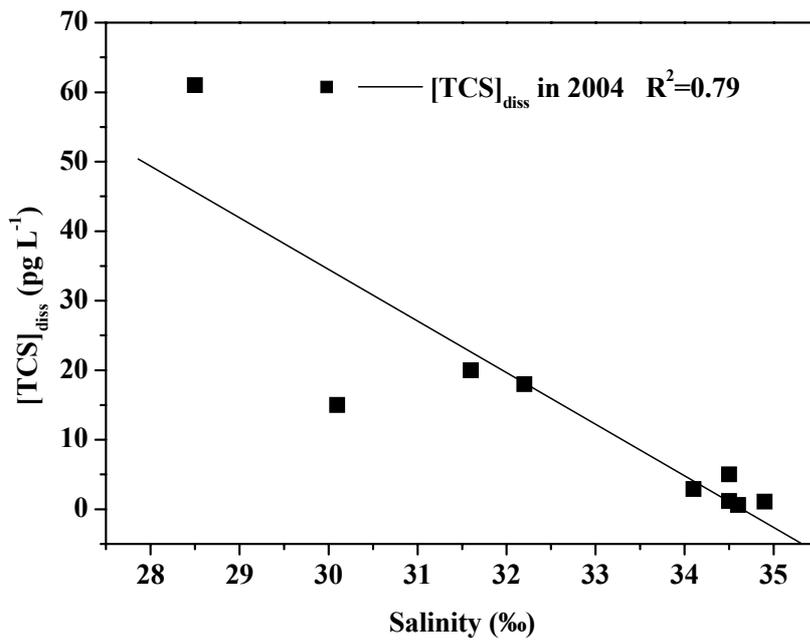


Figure 3a

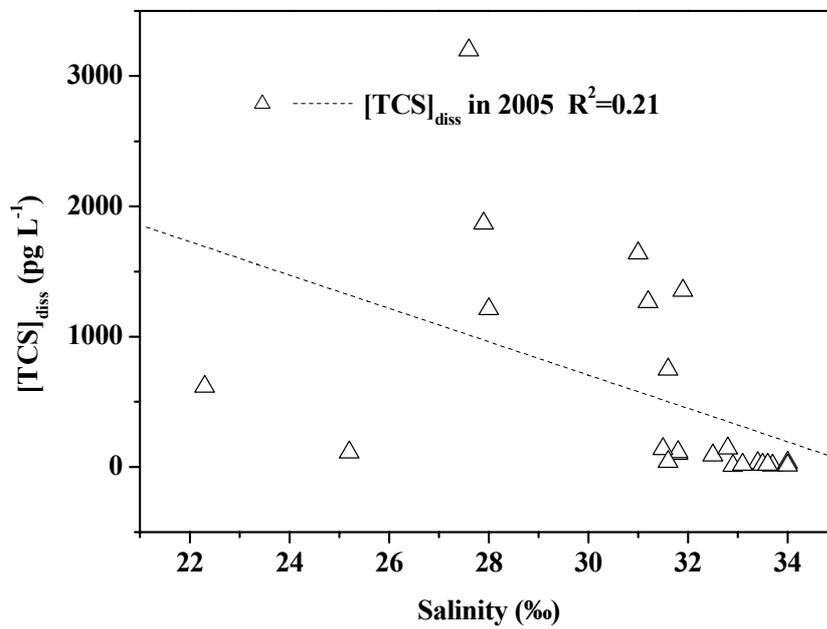


Figure 3b

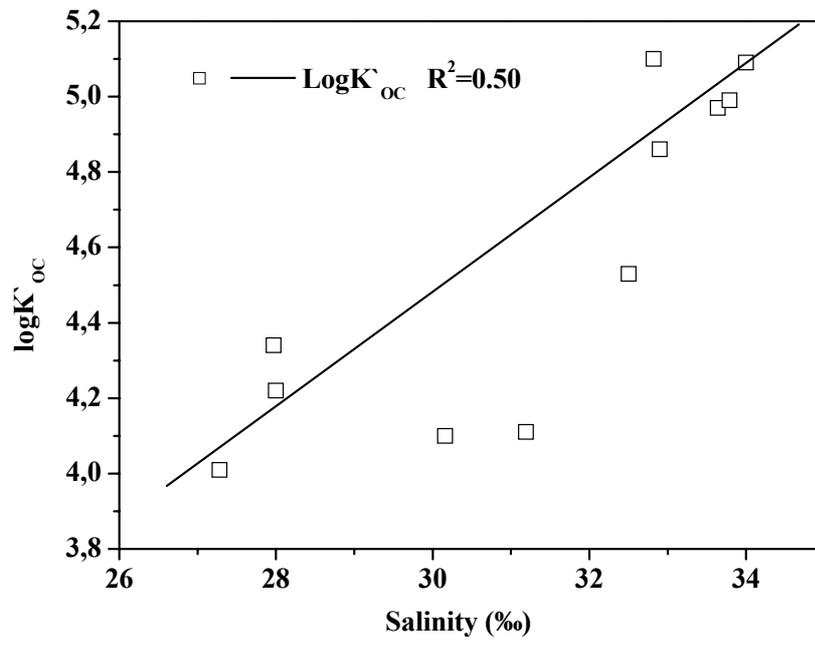


Figure 4