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Occurrence, distribution and fluxes of benzotriazoles along the German large river basins into the North Sea

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ABSTRACT

Benzotriazole (BT) and tolyltriazole (TT) are high production volume chemicals which are used in various industrial and household applications. In this study, the distribution of benzotriazoles in the estuaries of different rivers of central Europe and in the North Sea was analyzed by solid-phase extraction (SPE) and liquid chromatography-mass spectrometry (HPLC-MS/MS). BT as well as TT was detected in all water samples. The concentrations for total benzotriazoles (BTs) ranged from 1.7 to 40 ng/L in the North Sea in coastal areas. Concentrations in rivers are from 200 to 1250 ng/L, respectively. The mass flux of total benzotriazoles from the major rivers of central Europe into the North Sea was calculated to 78 t/a, dominated by the Rhine with an individual flux of 57 t/a of BTs. The analysis of the distribution profile in the North Sea showed that the decrease of the concentration was mostly caused by dilution and that the benzotriazoles are poorly degradable in the North Sea. This paper presents the first report of benzotriazoles in the marine environment.

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1. Introduction

1-H-benzotriazole (BT) and 1H-methyl-benzotriazole (tolyltriazole, TT, used as a technical mixture of 4- and 5-TT) are a class of high production volume chemicals (HPVC) with broad applications in various industrial processes as well as in households. They show metal complexing properties and are used as anticorrosive additives and flame retardants in aircraft de-icers and anti-ice fluids (ADAFs) (Gruden et al., 2001), in cooling and hydraulic fluids and for silver protection in dishwashing agents (Ort et al., 2005; Janna et al., 2011). The content of BTs in ADAFs varies between 0.2 and 1.7% (WIPO, 2002). The annual production of BTs in the United States was reported to be in the range of 9000 t per year (Hem et al., 2003). The content of Benzotriazoles in Dishwashing agents is reported with 0.09 mg per wash to 27.8 mg (Janna et al., 2011).

BTs are compounds with a low vapour pressure, high water solubility and a high polarity ($\log K_{ow}$ 1.44 for BT and 1.71 for TT, respectively) (US EPA, 2010). Moreover, they are quite persistent against biological and photochemical degradation processes in the aquatic environment (Hart et al., 2004). Thus, they can be characterized as mobile in aquatic environment. They are classified as toxic to aquatic organisms as they can cause adverse long-term effects on the aquatic environments (Cancilla et al., 1998, 2003; Pillard et al., 2001; Hem et al., 2003).

In the environment benzotriazoles were firstly reported in subsurface water close to airports as potential source in concentrations of 128 mg/L for BT, 17 mg/L for 4-TT and 198 mg/L for total TT (Cancilla et al., 1998). Because of the broad applications, BT and TT have high loads in waste waters treatment plants (WWTPs). The mean concentrations in untreated wastewaters of WWTPs of Berlin were 12 $\mu\text{g/L}$,

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1.3 $\mu\text{g/L}$ and 2.1 $\mu\text{g/L}$ for BT, 4-TT and 5-TT, respectively (Weiss et al., 2006). The elimination efficiency in WWTPs shows wide variations. In a study of 24 WWTPs of the Glatt Valley, Switzerland elimination rates were reported between 13 and 62% for BT and between 23 and 74% for the TT-isomers (Voutsas et al., 2006) while Weiss et al. (2006) determined removals of 37% for BT and 11% for 5-TT but no significant removal for the 4-TT-isomer. In sewage effluents of the UK were concentrations up to 3.6 $\mu\text{g/L}$ for BT and 5.7 $\mu\text{g/L}$ determined (Janna et al., 2011). Several studies showed that the BT and TT are widely distributed in surface waters (Giger et al., 2006; Reemtsma et al., 2006, 2010; Voutsas et al., 2006). Loos et al. (2009) detected BT and TT in 94% and 81% of 122 river water samples distributed over the European Union (EU) with mean concentrations of 493 ng/L and 617 ng/L for BT and TT, respectively. In an EU-wide study on groundwater, BT and TT were detected in mean concentrations of 1 and 4 ng/L, respectively (Loos et al., 2010a). Only one flux calculation is available for the river Danube into the Black Sea (Loos et al., 2010b). However, there are no data about concentration and distribution of BTs in the marine environment.

The objective of the present study was to investigate the occurrence and distribution of benzotriazoles in the German Bight and its major affluxes with respect to their spatial distribution as well as seasonal variations. Furthermore, the mass flux of BTs from the main rivers as sources of BTs into the North Sea was investigated. This study presents the first data on BTs in the marine environment and improves the understanding of the fate and the ecosystem risk assessment of BTs.

2. Experimental

2.1. Chemicals

1-H-benzotriazole (BT; 99%), 5-methyl-benzotriazole (5-tolyltriazole, 5-TT; 98%) and the deuterated 1H-Benzotriazole-d4 solution were purchased from Sigma–Aldrich (Steinheim, Germany). A tolyltriazole-isomer mixture was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Acetone (Nanograde) and methanol (Picograde) were purchased from LGC Promochem (Wesel, Germany). Formic acid and hydrochloric acid were purchased from Merck (Darmstadt, Germany). Pure water was obtained from a Milli-Q system (Millipore, Billerica, MA, USA).

2.2. Sample collection

Surface water samples (water depth <0.5 m) were taken by stainless steel bucket in pre-cleaned 1 L glass bottles on board of the research vessel *Ludwig Prandtl* along the rivers Elbe and Weser during four campaigns in March, May, August and October 2010 with sampling intervals of 10 km. In addition, 15 spot samples were taken from the shore of the rivers Elbe, Weser, Ems, the Rhine–Meuse delta and the river Scheldt in August 2010. North Sea samples were taken on board of the research vessel *Heincke* during three campaigns in March, July and September 2010. The sampling stations are shown in Fig. 1. Additional information on sampling are included in the Supplementary material.

2.3. Sample preparation

Solid phase extraction (SPE) was used for compound extraction and enrichment from the water samples. The unique river samples were filtered through glass fibre filters (GF-C, Whatman) while seawater samples were not filtered. SPE was performed with a self-designed glass based setup to prevent contaminations from plastic tubings. 500–700 mL surface water were acidified with hydrochloric acid to pH 2 and spiked with 20 ng of the internal standard 1-H-benzotriazole-d4. Oasis HLB cartridges (500 mg, 60 μm , Waters, Milfort, USA) were conditioned with 15 mL acetone, followed by 15 mL methanol and 5 mL acidified Milli-Q-Water. The water samples were passed through the pre-conditioned cartridges at a flow rate of 1–2 mL min^{-1} and afterwards washed with 5 mL acidified Milli-Q-Water. The cartridges were dried under vacuum for 5 min. The analytes were eluted with 15 mL methanol. The extracts were Roti-evaporated to 5 mL and further concentrated to a volume of 150 μL under a gentle stream of preheated nitrogen. The particulate phase on the filters was extracted by ultrasonic with 20 mL methanol two times for 15 min. The evaporation procedures were the same as described for the cartridges.

2.4. Instrumental analysis

The extracts were analyzed using high performance liquid chromatography-tandem mass-spectrometry (HPLC-MS/MS) in electrospray positive ionization mode. A HP 1100 HPLC by Agilent Technologies was used for separation equipped with a Phenomenex Synergi Hydro RP 80A column and a suitable guard column (Phenomenex Synergi 2 l Hydro RP Mercury 20 2 mm). The injection volume was 10 μL . The mobile phases were 1% formic acid as ionization aid in Millipore water and methanol, respectively. The operating flow was 200 $\mu\text{L}/\text{min}$ in gradient mode, starting with 90% of water as mobile phase



Fig. 1 – Map showing the sampling positions in the investigated rivers and the North Sea.

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