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 have metal complexing properties and are used as anticorrosive additives and flame retardants in aircraft de-icers and anti-ice fluids (ADAFs), in cooling and hydraulic fluids and for silver protection in dishwashing agents. The content of BTs in ADAFs varies between 0.2 and 1.7%. The content in dishwashing agents is reported with 0.09 mg per wash to 27.8 mg.

BTs are compounds with a low vapor pressure, high water solubility and a high polarity (logKow 1.44 for BT and 1.71 for TT, respectively). Moreover, they are quite persistent against biological and photochemical degradation processes in the aquatic environment. 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. In the urban water cycle they are ubiquitous present. This is the first investigation of benzotriazoles in the marine environment.

Material and Methods

Surface water samples (1000 mL) were taken on board the research vessels Ludwig Prandl and Heincke as well as from shore sampling stations distributed along the German bight and their feeder rivers (Rhine, Scheldt, Ems, Weser and Elbe) several times during 2010. 500-700 mL, filtered with GF-C, were acidified with HCl and spiked with 20 ng 1-H-benzotriazole as internal standard. The samples were extracted by OASIS HLB 500 mg, eluted were the cartridge’s by 15 mL methanol. The extracts were evaporated to 150 µL and analyzed by HPLC-ESI-MSMS.

Results and Discussion

Concentrations and mass fluxes in rivers

→ Concentrations in investigated rivers were detected for total benzotriazoles from 200 to 1500 ng/L
→ The total mass flux of benzotriazoles into the North Sea from the large Rivers was estimated with 78 t/a, dominated by the Rhine with 57 t/a

Study of dilution and persistence

To investigate if decreasing concentration are based on degradation or merely on dilution versus salinity was assessed with utilization of following Egs.

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DF = \frac{\text{salinity datapoint}}{\text{salinity seawater}}
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NC = \frac{c(\text{datapoint})}{c(\text{freshwater psu >1})}
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The mostly linear observed relationship indicates that the decrease of concentration occurs mainly due to dilution with seawater. A significant degradation is not observed.

Distribution in the German Bight

→ Benzotriazoles were detected in all samples above the MQL of 1 ng/L
→ The contamination close to the East Frisian Islands is mostly based on the riverinput of the Rhine and Scheldt
→ In close to the North Frisian Island the contaminated seawater mixed with the contamination of Weser and Elbe

Conclusion

• This study has shown that a high amount of benzotriazoles are discharged via the investigated rivers into the North Sea
• Benzotriazoles are poorly degradable polar organic pollutants which are present in the anthropogenic water cycle as well as in the North Sea.
• Benzotriazoles are persistent in the marine environment