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# A NOTE ON BENZOTRIAZOLE CONCENTRATIONS IN THE RECEIVING WATERS OF DIFFERENT SEWAGE TREATMENT PLANTS

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**ABSTRACT**

The concentrations of Benzotriazole (BTri), 4- and 5-methyl-benzotriazole (4-TTri, 5-TTri) were analyzed in the receiving river of a membrane bioreactor (MBR-MH), a conventional activated sludge (CAS-E) and a two-stage conventional activated sludge (CAS-M) sewage treatment plant (STP). All STPs were point sources for benzotriazoles in the aquatic environment as concentrations downstream the STPs were higher. Mean downstream concentrations ranged from 3.58 $\mu g L^{-1}$ (MBR-MH) to 1.1 $\mu g L^{-1}$ (CAS- M) and 0.64 $\mu g L^{-1}$ (CAS-E). CAS-E only slightly increased downstream concentrations as the receiving river was already contaminated with up to 0.49 $\mu g L^{-1}$ benzotriazoles from hydropower. 5-TTri was detected in lowest concentrations due to its good biodegradation, followed by BTri and 4-TTri. The latter two showed a potential to accumulate in the aquatic environment as they are only poorly biodegraded. Although the STPs were a point source for BTs into the aquatic environment, their impact strongly depended on the upstream water quality and the self-purification potential of the receiving river system..

**KEYWORDS**

4-tolyltriazole, 5-tolyltriazole, 1-H-benzotriazole, xenobiotic, micropollutants.

Sigma-Aldrich (Steinheim, Germany).

## 1. INTRODUCTION

Based on a study, benzotriazole (BTri), 4- and 5-tolyltriazole (4- TTri, 5-TTri), named here BTs, are polar, xenobiotic micropollutants used, among other applications, as corrosion inhibitors, for metal finishing, in cooling systems and in dishwashing detergents [1-3]. Study showed a production volume of approximately 9,000 tons per year in the US, their widespread usage, polar nature (logD 1.44 and 1.71 for BTri and TTri, respectively) and good water solubility, makes them almost omnipresent in all larger freshwater aquatic systems across Europe [4,5]. As concentrations above 0.97 mg L-1 for BTri and 0.40 mg L-1 for 5-TTri showed adverse effects in the aquatic organism Daphnia galeata, BTs are considered detrimental for aquatic systems [6]. According to a researcher, optimizing their removal during sewage treatment is implicitly needed as sewage treatment plants (STP) are often incapable to remove these compounds [7]. The findings in this study add extra information to deepen the understanding of BTs release into the receiving rivers of three different STPs.

## 2. MATERIALS AND METHODS

### 2.1 Chemicals

1-H-benzotriazole (99,8 % purity; CAS 95-14-7), 4-methyl-benzotriazole (CAS 29878-31-7) and 5- methyl-benzotriazole (CAS 136-85-6) were provided by Cimachem GmbH (Kirchheimbolanden, Germany). The surrogate standard 5, 6-dimethyl-benzotriazole (99% purity), sodium carbonate solution, toluol and all other chemicals werepurchased from

### 2.2 Chemical Analyses and Sampling Conditions

All river water samples were collected as 1 L grab samples in amber glass bottles. All samples were cooled until arrival, then frozen at -20°C and analyzed within 30 days. According to a researcher, preparation and determination of BTs concentrations in river samples was performed [8]. The samples were derivatized with acetic anhydride followed by analysis by GC/MS-MS with 5,6-dimethyl-benzotriazole as internal standard. Calibration was performed with 0.1, 1.0, 6.3, and 25.0 µg L-1. Limit of quantification was 0.01 µg L-1.

### 2.3 Receiving Rivers

The receiving rivers of three STPs with different treatment techniques being a membrane bioreactor (MBR-MH), a conventional activated sludge plant with intermittent nitrification/denitrification (CAS-E), and a two-stage (stage 1: high load stage; stage 2: low load stage for nitrification) activated sludge plant (CAS-M) were sampled for one year.

## 3. RESULTS AND DISCUSSION

BTs concentrations were analyzed in the receiving rivers to evaluate the effluence of the connected STPs (Figure 1). MBR-MH and CAS-M were one major point source for BTs into the aquatic environment as the detected BTs concentrations increased significantly downstream the STPs.

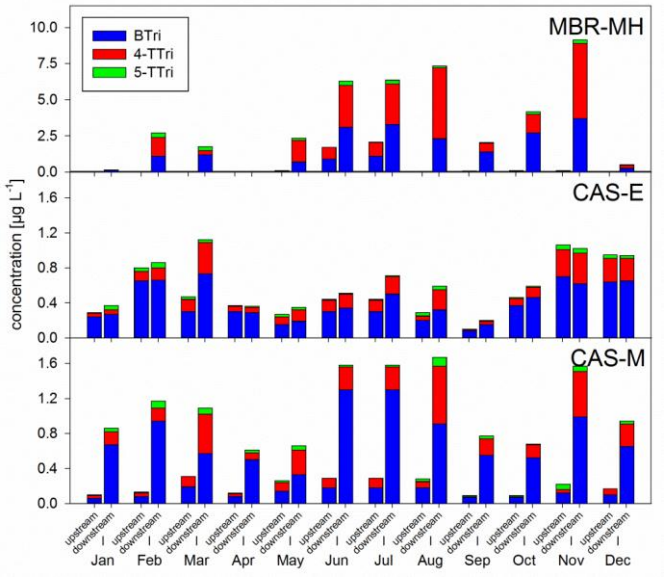


**Figure 1:** Concentrations of BTri, 4-TTri and 5-TTri upstream and downstream the WWTPs over one year. BTs impact on receiving waters for MBR-MH, CAS-E and CAS-M strongly depended on the biological removal capacity of the STP. CAS-E showed a high microbial BT biodegradation potential and thus the effluent concentrations were lower and the impact on the receiving river far less.

CAS-E showed no such effect as the receiving river was, in some months, higher contaminated with BTs (peak concentration of 1.06 µg L -1) than CAS-E effluents. MBR-MH showed the highest impact on the receiving water with BTs peak concentrations up to 10 µg L -1 and a strong fluctuation over the year as the receiving river is only a very small stream. MBR-MH effluents significantly increased the amount of BTri and 4-TTri, the two biologically very stable compounds. These compounds might accumulate and represent a potential threat for the ecosystem and drinking water supply as they are only slowly biodegraded. A similar impact pattern but with lower concentrations was found for the receiving river of CAS-M. This river exhibits similar seasonal fluctuations with low flow volumes during summer and high flow volumes in spring and winter. Again, BTri was found in highest concentrations up to 1.4 µg L-1 followed by 4-TTri with up to 0.6 µg L -1. CAS-E showed a lesser aquatic impact as the receiving river already contained relatively high BTs concentrations up to 1.0 µg L -1 from diffuse entry paths, e.g. hydropower plants. Therefore, the impact on the receiving river was far less as A) the river was already contaminated and B) CAS-E performed very well to remove BTs. Effluent concentrations were in some cases even lower than the upstream ones, thus reducing BTs concentrations downstream by dilution. Again, BTri with up to 0.7 µg L -1 and 4-TTri with up to 0.5 µg L -1 were again the dominant species. However, the STPs were not able to completely remove the BTs from the effluents and were considered point sources. Further removal processes like self-purification of the receiving rivers are required to finally prevent the accumulation of BTs in the receiving rivers.

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**REFERENCES**

[1] Finšgar, M., Milošev, I. 2010. Inhibition of copper corrosion by 1,2,3-benzotriazole: A review, Corrosion Science, 52, (9): 2737-2749.

[2] Jover, E., Matamoros, V., Bayona, J.M. 2009. Characterization of benzothiazoles, benzotriazoles and benzosulfonamides in aqueous matrixes by solid-phase extraction followed by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry, Journal of Chromatography, 1216, (18): 4013-4019.

[3] Vetter, W., Lorenz, J. 2013. Determination of benzotriazoles in dishwasher tabs from Germany and estimation of the discharge into German waters, Environmental Science and Pollution Research, 20, (7): 4435-4440.

[4] Reemtsma, T., Weiss, S., Mueller, J., Petrovic, M., Gonzalez, S., F. Ventura, B., Knepper, T.P. 2006. Polar Pollutants Entry into the Water Cycle by Municipal Wastewater: A European Perspective, Environmental Science and Technology, 40, (17): 5451-5458.

[5] Kiss, A., Fries, E. 2012. Seasonal source influence on river mass flows of benzotriazoles, Journal of Environmental Monitoring, 14, (2): 697-703.

[6] Seeland, A., Oetken, M., Kiss, A., Fries, E., Oehlmann, J. 2012. Acute and chronic toxicity of benzotriazoles to aquatic organisms, Environmental Science and Pollution Research, 19, (5): 1781-1790.

[7] Liu, Y.S., Ying, G.G., Shareef, A., Kookana, R.S. 2011. Biodegradation of three selected benzotriazoles under aerobic and anaerobic conditions, Water Research Journal, 45, (16): 5005-5014.

[8] Herzog, B., Lemmer, H., Huber, H., Horn, H., Müller, E. 2014. Xenobiotic benzotriazoles-biodegradation under meso-and oligotrophic conditions as well as denitrifying, sulfate- reducing, and anaerobic conditions, Environmental Science and Pollution Research, 21, (4): 2795-2804.