# EMERGING POLLUTANTS: HOW HIGH RESOLUTION MASS SPECTROMETRY HELPS TO KEEP A TRACK ON THEM

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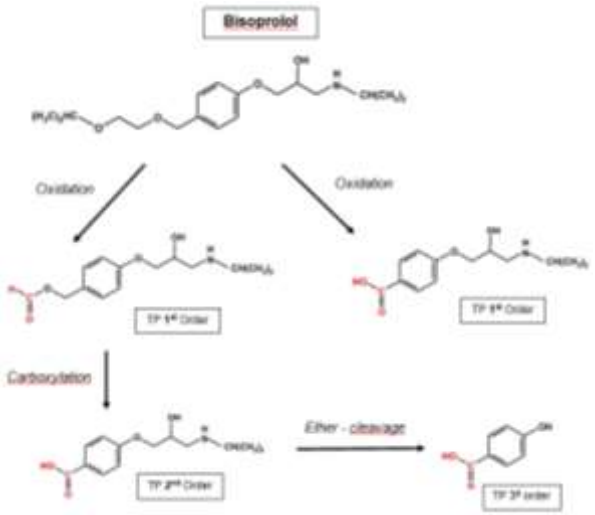
The intensive use of chemical substances such as pesticides, drugs, food additives and industrial chemicals has lead to the subsequent detection of these compounds in many countries. With the improper disposal, they enter the aquatic environment primarily by reaching the wastewater systems. About the residues of pharmaceuticals in the environment, especially in water, is being repeatedly reported since several years. Whether drugs and their metabolites are found in the aquatic environment, depends mainly on their consumption amount and biological degradability [1].

In the wastewater treatment plants, which are operated by the state of today's technology, biological degradation and transformation by the microorganisms in activated sludge are two of the most important micropollutant elimination processes. This may achieve biological mineralization, but is mostly limited to compound transformation [2]. That results to the formation of intermediate by-products generated by bacteria of the wastewater biocoenosis. These compounds have only hardly been investigated so far and therefore are predominantly unknown [3].

The rate of identification of new and emerging contaminants in the aquatic environment has been limited heretofore by reliance on targeted analytical techniques, which depend on compound-by-compound verification using authentic standards. Recent advancements in high-resolution mass spectrometry (HR-MS) and its application to the field of environmental chemistry has for the first time made possible identification of emerging contaminants in complex environmental mixtures without *a priori* knowledge of contaminant identity or occurrence [4-6].

**Table 1:** Transformation paths of Bisoprolol during biological treatment (lab scale)




Investigation focus of this study is the identification of the biotransformation products of three β-blockers in environmental aquatic samples and the results of the compound Bisoprolol are

presented for the first time. For this purpose the high performance liquid chromatography coupled with high-resolution mass spectrometry (HPLC-(HR)$MS^n$) was used. The applied Ion trap, *Orbitrap*, is a Fourier-transformation - mass spectrometer, with which it is possible to determine the exact mass of a molecule. According to this, a list of potential structure proposals is given. For more complex structures, a selected and targeted fragmentation of the molecules can be carried out in the orbitrap. Molecules break and fragment, often at characteristic points. From the measured mass of the fragments, their structural formula is determined and then from these individual modules the structural formula of the parent compound can gradually be assembled (Table 1).

Moreover the parent compound (Bisoprolol) was examined with regard on its toxicological significance via established ecotoxicological tests, e.g Daphnia Magna (Table 2). On the top of that, the mixture toxicity of it and its bio-products was estimated based on the knowledge of the mode of action in humans compared to the one in aquatic organisms.

**Table 2:**

| compound | $EC_{50}$ [mg/L] Daphnia magna | |
|---|---|---|
| | bio-test (observed) | ECOSAR (predicted) |
| | | |
| Atenolol | 440,8 | 79,9 |
| Bisoprolol | 132,8 | 8,9 |
| Metoprolol | 81,4 | 7,2 |
| | | |
| | 10-100 | 1-10 |
| | "harmful" | "toxic" |
| | | |

**Keywords**: wastewater, β-blockers , biotransformation products, Orbitrap, mixture toxicity

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