Transformation of carbamazepine in the presence of zero valent iron and adapted biology

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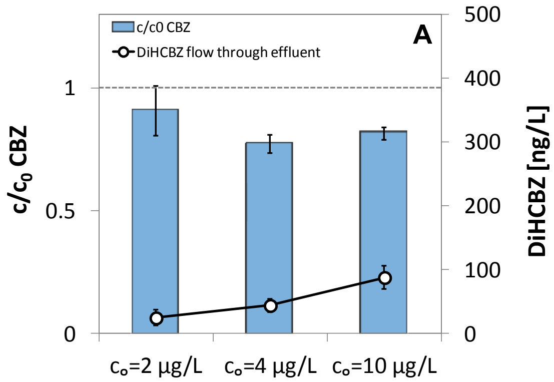
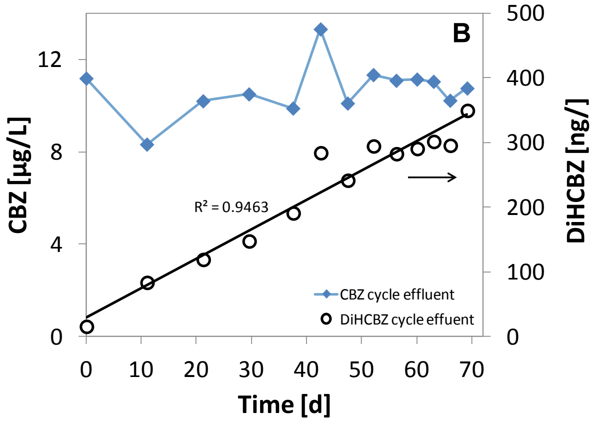
The antiepilepticum carbamazepine (CBZ) is suggested as an indicator substance for the anthropogenic influence on the water cycle [1]. It is known to be persistent since hardly biological, chemical or physical elimination in the natural water bodies was determined so far [2]. Nevertheless, in several studies evidences for a removal of CBZ under anaerobic redox conditions in the subsoil during bank filtration were found [3]. Therefore, more research regarding the behavior of CBZ in a strongly environment need to be done. This study investigates the transformation of CBZ under reductive conditions in column experiments.

The column test set up consists of a glass column (length:0,7 m, Ø=0,1 m, flux: 0,7 L/d) filled with iron sponge material and pea gravel (50:50). Zero valent iron (ZVI) induces hydrogen corrosion and lowers the redox potential. The anoxic raw water originates from a bank filtration site in Berlin (Germany). The CBZ influent concentration c_0 was varied from 2 to 10 µg/L CBZ. To investigate the influence of the residence time in a reductive environment, two operation modi were implemented (c_0=10 µg/L): (A) The flow-through mode with a residence time of 3.4 days and (B) a circular mode with a residence time of 69 days. The redox voltage of the column effluent was in the range of -0.5 V. The presence of methane in the system indicated adapted biology. With catalytic hydrogenation experiments eight possible transformation products of CBZ (m/z: 239; 241; 243; 245; 247; 249; 251; 253) were identified previously [4]. One of them, namely dihydro-carbamazepine (DiHCBZ, m/z 239) could be quantified.

The flow through column experiments show that after a run-in period of at least 120 days for each c_0 variation the c/c_0-ratio of CBZ in the effluent remained constant (Figure A). Higher influent concentrations of CBZ resulted in higher amounts of DiHCBZ in the effluent. Thus, five percent of the CBZ decrease can be attributed to DiHCBZ formation. High-resolution mass spectrometry also identified two more reduced transformation products with m/z-ratios of 243 and 245. The main part of the CBZ decrease can be explained by adsorption onto the ZVI.





Recycling the effluent of the column resulted in an enrichment of DiHCBZ (Figure B). Thus, 350 ng/L DiHCBZ were measured after 70 days of operation. After one cycle the CBZ content decreased to 80% of c_0 which can be explained by adsorption as it was the case in the flow through mode. The ensuing cycles showed constant effluent concentrations of CBZ in the range of c_0. The reason for this are probably desorption processes due to an increasing pH (up to pH=10.1). The data enable the calculation of transformation rates of DiHCBZ. Besides an abiotic reduction due to ZVI also the biotic impact on the CBZ transformation is conceivable since the column test is biologically active. This aspect is even more important since abiotic tests with an eletrochemical cell at the given redox voltage showed no transformation of CBZ at all [4].

The experiments indicate that carbamazepine can be transformed under reductive conditions at a redox voltage in the range of -0.5 V. If this strongly reductive environment appears within the subsoil due to biological or chemical processes the available amount of CBZ might be transformed to the products found in this study. This should be noted when the substance is proposed as an anthropogenic marker.

Literature: **[1]** Jekel, M. et al. (2015). Chemosphere 125: 155–167; **[2]** Clara, M., et al. (2004). Water Research 38(4): 947; **[3]** Schmidt, C. et al. (2005). ISBN 3-00-015478-7. (BMBF); **[4]** König, A. et al. (2015). Wasser 2015. conference proceedings: 517-521.