



Phototransformation of three selected pharmaceuticals, naproxen, 17 α -Ethinylestradiol and tetracycline in water: Identification of photoproducts and transformation pathways

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ABSTRACT

Transformation products (TPs) may be formed during various processes, however, it was proved that one of the main mechanisms responsible for degradation of pharmaceuticals in natural waters is photolysis. Three compounds were selected, tetracycline (TC), 17- α -ethinylestradiol (EE2) and naproxen (NAP), for degradation experiments which were performed using a xenon lamp emitting light with a spectrum closely approximating that of natural sunlight. Identification of photodegradation products was achieved via liquid chromatography coupled with high resolution quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) providing accurate mass measurements and MS/MS experiments for structural elucidation. Results indicate that degradation of compounds under the study follows pseudo-first-order kinetics. Photolysis rate constants (k) were determined and half-lives ($t_{1/2}$) calculated to be 11, 120, and 13 min for TC, EE2 and NAP, respectively. Xenon lamp irradiation led to the formation of several photoproducts. Many of them have been identified for the first time. LC-QTOF-MS analysis allowed for the identification of seven, four, and eight TPs of TC, EE2 and NAP, respectively. Finally, the presence of parent compounds and identified TPs was investigated in various real-world water samples. Only three degradation products of 17- α -ethinylestradiol and naproxen were detected in wastewater effluent and treated water samples. Quantitative structure-activity relationship (QSAR) approach was applied in order to estimate physical-chemical properties of selected pharmaceuticals and their TPs. This allowed predicting the fate of all analytes in the aqueous environment.

1. Introduction

Pharmacologically active compounds (PhACs) are discharged into the aquatic environment in their unchanged or transformed forms due to inefficient elimination of such chemicals during the wastewater and water treatment processes [1]. Once they reach the environment, PhACs can undergo various processes in natural waters, including biodegradation or photodegradation resulting in a formation of new compounds which can be less or more toxic than the parent compounds. It is believed that the main mechanism responsible for elimination of pharmaceuticals from natural waters is photolysis [2]. The efficiency of this process depends on many factors e.g. depth and turbidity of water column, weather conditions, season and geographical location. The photolysis can be direct, where molecule absorb the radiation, or indirect, where active molecules, e.g., $\cdot\text{OH}$, $^1\text{O}_2$, $\text{ROO}\cdot$, excited triplet state dissolved organic matter ($^3\text{DOM}^*$), and e_{aq} are involved [3,4].

Furthermore, UV light is also applied during the drinking water and wastewater treatment processes [5]. Different PhACs are characteristically prone or resistant to photolysis which affects the effectiveness of their photodegradation. Therefore, it is important to expand our knowledge with regard to photoinduced transformation of different PhACs by examination of their environmental fate and further characterization of the risk posed by chronic exposure of aquatic organisms to low doses of degradation products.

Compounds selected for tracking their environmental phototransformation are widely used pharmaceuticals, tetracycline - a common antibiotic used in aquaculture and live stocking [6], naproxen - one of the most often applied non-steroidal anti-inflammatory drug (NSAID) [7], and 17- α -ethinylestradiol - a commonly used oral contraceptive [8]. Currently, there are many researches confirming their presence in environmental waters, e.g. wastewater [9,10] or surface water [9,11,12]. The presence of such pharmaceuticals in the aqueous

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