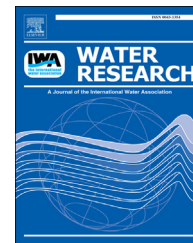




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Transformation of acesulfame in water under natural sunlight: Joint effect of photolysis and biodegradation

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ABSTRACT

The transformation of acesulfame in water under environmentally relevant conditions, including direct and indirect photolysis, biodegradation, and hydrolysis, was systematically evaluated. Under natural sunlight, both direct and indirect photolysis of acesulfame were negligible in sterilized systems at neutral or alkaline pH, whereas direct photolysis occurred at pH of 4 with a rate constant of 0.0355 d^{-1} in deionized water. No significant reduction in acesulfame contents was found in the dark controls or in the incubation experiments, indicating acesulfame was resistant to hydrolysis and biodegradation. In unsterilized systems, photolysis was substantially enhanced, implying that there was a joint effect of photolysis and biodegradation or that the sterilization process had the secondary effect of inactivating some photosensitizers. The near-surface summer half-life of acesulfame in the water from the Haihe River was 9 d. Specific experiments revealed the involvement of $^1\text{O}_2/^3\text{DOM}^*$ in acesulfame photolysis, whereas $\cdot\text{OH}$ exhibited only a slight contribution in the presence of DOM or bicarbonate. As indicated by the total organic carbon data, no significant mineralization occurred in both sterilized and unsterilized systems after acesulfame was irradiated under simulated sunlight for 7 d, suggesting the generation of persistent intermediates. Finally, major degradation intermediates were analyzed, and the degradation pathways of acesulfame under environmentally relevant conditions were proposed for the first time.

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1. Introduction

Recently, the environmental fate and toxicology of pharmaceuticals and personal care products (PPCPs), food additives, and other emerging chemicals have received increased attention due to their ubiquitous occurrence in the environment (la Farre et al., 2008; Caliman and Gavrilescu, 2009;

Brausch and Rand, 2011; Lange et al., 2012). Artificial sweeteners (ASs), which are used as sugar substitutes in foods, beverages, and PPCPs worldwide (Ferrer and Thurman, 2010; Buerge et al., 2011), are a group of emerging chemicals that have recently become a topic of concern (Kokotou et al., 2012; Lange et al., 2012). Similar to certain PPCPs, ASs ingested by humans are primarily excreted as the parent compound and discharged into the environment through treated and

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untreated domestic sewage (Caliman and Gavrilescu, 2009; Kokotou et al., 2012; Lange et al., 2012). Among the ASs, acetulfame (ACE) has caused greater concern due to its wide application, persistence and ubiquitous occurrence in the environment. ACE concentrations of up to 25, 34, and 46 $\mu\text{g/L}$ were reported in surface waters, groundwater, and wastewater treatment plants, respectively (Kokotou et al., 2012; Lange et al., 2012; Gan et al., 2013a). Therefore, the accumulation of ACE in the aquatic environment and its possible ecotoxicity and fate are cause for concern. However, information on the environmental fate of ACE is scarce and requires further study (Lange et al., 2012).

Once contaminants are discharged into natural water, they may undergo phase transfer (e.g., exchange between water and air, sorption/desorption) and transformation (e.g., biodegradation, hydrolysis, and photolysis) (Robinson et al., 2007; Wang et al., 2012). The high water solubility and low partition coefficient of ACE result in its partitioning to the water phase rather than into sediments or air (Lange et al., 2012). In addition, previous studies have confirmed that ACE is extremely resistant to biodegradation in wastewater treatment plants (Buerge et al., 2009; Mawhinney et al., 2011; Soh et al., 2011) and is generally resistant to hydrolysis (Lange et al., 2012). Regarding photolysis, only a few studies have documented that ACE could be degraded under UV irradiation (Coiffard et al., 1999; Soh et al., 2011; Sang et al., 2014). Sang et al. (2014) investigated the degradation kinetics of ACE under UV irradiation. However, no information regarding ACE's fate under environmentally relevant conditions could be found. A report from the U.S. National Library of Medicine Toxnet Data Network (<http://toxnet.nlm.nih.gov>) predicted that ACE may be susceptible to direct photolysis under sunlight irradiation. The prediction is based on the ability of the chromophores in the ACE structure to absorb at wavelengths $>290\text{ nm}$.

Therefore, the goal of the present study was to investigate the transformation of ACE in natural water under environmentally relevant conditions, including direct and indirect photolysis, biotransformation and hydrolysis. The removal kinetics of ACE was studied using outdoor and indoor experiments under natural and simulated sunlight in sterilized and unsterilized laboratory solutions and in river water, and the influence of several parameters (i.e., pH, dissolved oxygen (DO), dissolved organic matter (DOM), nitrate, and bicarbonate) were investigated. The effects of singlet oxygen ($^1\text{O}_2$), hydroxyl radical ($\cdot\text{OH}$), and dissolved organic matter triplet states ($^3\text{DOM}^*$) on ACE photolysis were evaluated by specific experiments. Finally, major degradation intermediates were deduced, and degradation pathways were proposed. To our knowledge, this is the first report on the transformation of ACE under environmentally relevant conditions in the aquatic environment, which is important for understanding the fate and eco-risk of ACE.

2. Materials and methods

2.1. Chemicals and reagents

ACE, p-nitroacetophenone (PNAP), and pyridine (PYR) were purchased from Sigma–Aldrich (St. Louis, MO, USA).

Acetulfame-d4 (ACE-d4), which was used as an internal standard (IS), was obtained from TRC (North York, ON, Canada). HPLC grade methanol and acetonitrile were purchased from CNW (CNW Technologies GmbH, Germany). The DOM solutions were prepared from commercially available humic acid from Sigma–Aldrich (St. Louis, MO, USA). Deionized water (DIW) was used throughout the study. All of the other solvents and reagents were of HPLC or analytical grade.

2.2. Sampling campaign

Grab samples of river water were collected from the Haihe River in Tianjin, China, on August 5, 2013. The water was analyzed for parameters including pH, DO, total organic carbon (TOC), Cl^- , NO_3^- , NO_2^- , and HCO_3^- . The results are given in Table S1 in the Supplementary Materials (SM).

2.3. Photolysis experiments

The outdoor experiments were performed on the roof of a building at Nankai University in Tianjin, China (latitude: 39.13°N , longitude: 117.15°E) under natural sunlight beginning on August 8, 2013. Photolysis experiments were conducted using 100 $\mu\text{g/L}$ ACE in DIW, non-filtered Haihe River water (NF-HRW), and 0.45 μm filtered HRW (F-HRW), either sterilized (STE) or unsterilized (UNS). Sterilization was performed by autoclaving the water at 121°C for 30 min. The results in STE-DIW were recognized as arising from direct photolysis, whereas those acquired in STE-HRW were thought to result from both direct (negligible, *vide infra*) and indirect photolysis considering that HRW contained many photoactive species. The experiments were conducted in quartz tubes (o.d. = 2.8 cm, i.d. = 2.6 cm, $V = 50\text{ mL}$) that were sealed with quartz lids. The tubes were placed in a rack that positioned them at an angle of approximately 30° to the horizon with the upper end pointing due north (EPA, 1998). Direct photolysis was observed in the DIW (both STE and UNS) at pH values of 4, 7, 8, and 9. According to recommendations by the U.S. EPA (1998), pH values other than 8, which is the pH of the HRW (Table S1), were selected because the pK_a of ACE is 2.0 (Lange et al., 2012). The pH of the solutions was adjusted using 1 M sodium hydroxide or hydrochloric acid prior to irradiation (Falcyn et al., 2012; Wang and Lin, 2012). Each set of experiments was performed in triplicate. Dark controls (both STE and UNS) were prepared in the same manner as the samples for the irradiation experiments but wrapped tightly with aluminum foil. The duration of the experiments was 30 d, and the total irradiation time was approximately 21 d, excluding cloudy and rainy days. The PNAP/PYR system was used as chemical actinometer, and the quantum yields in natural sunlight were determined using the method developed by Dulin and Mill (1982).

To further elucidate the influencing factors on ACE photolysis, indoor experiments were conducted in a sunlight simulator (XPA-7, Nanjing Xujiang Motor Factory, China) equipped with a 1 kW xenon lamp and special UV filters, which could remove light below 290 nm. The indoor experiments were conducted in DIW (both STE and UNS) at pH values of 4, 7, and 9. To elucidate the effect of DO, deoxygenated and oxygenated samples were obtained by bubbling

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