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Evaluating the environmental impact of artificial sweeteners: A study of their distributions, photodegradation and toxicities

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ABSTRACT

While having a long tradition as safe food additives, artificial sweeteners are a newly recognized class of environmental contaminants due to their extreme persistence and ubiquitous occurrence in various aquatic ecosystems. Resistant to wastewater treatment processes, they are continuously introduced into the water environments. To date however, their environmental behavior, fate as well as long term ecotoxicological contributions in our water resources still remain largely unknown. As a first step in the comprehensive study of artificial sweeteners, this work elucidates the geographical/seasonal/hydrological interactions of acesulfame, cyclamate, saccharin and sucralose in an open coast system at an estuarine/marine junction. Higher occurrence of acesulfame (seasonal average: 0.22 μg L^{-1}) and sucralose (0.05 μg L^{-1}) was found in summer while saccharin (0.11 μg L^{-1}) and cyclamate (0.10 μg L^{-1}) were predominantly detected in winter. Seasonal observations of the four sweeteners suggest strong connections with the variable chemical resistance among different sweeteners. Our photodegradation investigation further projected the potential impact of persistent acesulfame and sucralose compounds under prolonged exposure to intensive solar irradiation. Real-time observation by UPLC–ESI/MS of the degradation profile in both sweeteners illustrated that formation of new photo by-products under prolonged UV irradiation is highly viable. Interestingly, two groups of kinetically behaved photodegradates were identified for acesulfame, one of which was at least six times more persistent than the parent compound. For the first time, acute toxicity for the degradates of both sweeteners were arbitrarily measured, revealing photo-enhancement factors of 575 and 17.1 for acesulfame and sucralose, respectively. Direct comparison of photodegradation results suggests that the phototoxicity of acesulfame degradation products may impact aquatic ecosystems. In an attempt to neutralize this prolonged environmental threat, the feasibility of UV/TiO_2 as an effective mineralization process in wastewater treatment was evaluated for both sweeteners. Under an environmental and technical relevant condition, a >84% removal rate recorded within 30 min and complete photomineralization was achieved within 2 h and delivering the best cost efficiency comparing to existing removal methods. A compilation of distribution, degradation,

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toxicity and attenuation results presented in this paper will go through critical discussions to explore some current issues and to pinpoint solutions for a better control in the emergent contamination of artificial sweeteners.

1. Introduction

Artificial sweeteners are being used as sugar substitutes in considerable and increasing amounts in food and beverages, especially for those who are diabetic and/or obese. They have also been used in other personal care and pharmaceutical products (Zygler et al., 2009) such as toothpastes. Although, from the beginning of their use, there has been controversies over their risk as potential carcinogens (Weihrauch and Diehl, 2004), these sweetener compounds are generally considered to be safe for use in foodstuffs (Kroger et al., 2006; Ahmed and Thomas, 1992; Cohen et al., 2008). Some of the low-calorie sweeteners currently approved by different international authorities as direct food additives include acesulfame, aspartame, cyclamate, saccharin and sucralose (US FDA, 2006; EU, 2003). Other flavorings are continually being developed and are increasingly commonly used in foodstuffs, especially because they confer longer shelf-life. Just as these compounds are metabolically inert in the human body, so scientists are finding, they are also inert in the environment. Concern is shifting from health concerns to ecosystem concerns. In terms of environmental degradation, among the five most commonly used artificial sweeteners named above, only aspartame decomposes under normal usage conditions, and safety clearance was given to the intake of even its breakdown derivatives (US FDA, 1983). Outstanding chemical stability in these sweeteners means they are passed out mainly unchanged into the domestic wastewater treatment system, with the intact compounds enter the aquatic environment almost directly.

Of the variety of artificial sweeteners being used, only acesulfame, cyclamate, saccharin and sucralose have been identified in wastewater effluents (Lange et al., 2012). Comparison with the sweetener content of influent shows substantial but variable resistance of these compounds to breakdown by wastewater treatment. Common mechanical and secondary microbial digestion can only partially mineralize and remove sweetener pollutants. Acesulfame and sucralose have been reported as the most persistent sweeteners with removal rates as low as 40% and 20%, respectively (Scheurer et al., 2009). Ironically, chemical and biological recalcitrance in compounds has been valued as an ideal marker property for tracing the influence of wastewater in the environment (Buerge et al., 2009). Now, that attitude is shifting, as concern for the long-term ecological effects are considered. Of the four most widely allowed safe artificial sweeteners, acesulfame, cyclamate, saccharin and sucralose are currently not considered in any existing effluent quality code, and no connection has been established between their pervasive presence and any environmental impact, until recently.

Widespread occurrence of acesulfame, cyclamate, saccharin and sucralose have been recorded from nano- to microgram levels in various rivers and lakes of European countries (i.e. Switzerland, Germany, Austria, Sweden, Serbia, Spain, UK, Belgium, Netherland, France, Italy and Norway) and North America (Loos et al., 2009; Mead et al., 2009; Torres et al., 2011). Sweeteners have also made their way into groundwater networks through surface water infiltration and percolation in soil aquifers, bringing levels to 34 $\mu g\ L^{-1}$ for acesulfame and 24 $\mu g\ L^{-1}$ for sucralose (Van Stempvoort et al., 2011). In contrast, lower concentrations of cyclamate and saccharin were measured in these same waters. These differences are probably due to subsurface attenuation processes variably experienced among the sweetener species. To date, the availability of occurrence data is confined to inland waters; very little is known about their fate in open coastal environment, where complex distribution forces are driven by the interplay of estuarine and oceanic hydrology and where a much larger scale dispersion of pollutants becomes likely. Especially, the behaviors of artificial sweeteners entering macro-hydrological system climatically sensitive to temperature, radiation, chemical and biological parameters, remain limitedly explored.

While artificial sweeteners are marketed as metabolically inert sugar substitutes, studies have revealed that they are not entirely inert in the environment. One study has found a potential xenobiotic interference in the normal biological functions in ecosystem (e.g. photosynthesis and feeding behaviors in zooplanktons) when and because these compounds invoke organisms' biological response to natural sugar (Kessler, 2009). For this newly emergent class of environmental contaminants, the long-term consequences of their ubiquitous distribution and those potentiated by possible chemical transformation over an extended pollution episode are uncharacterized.

Artificial sweeteners degrade at varying rates under different environmental conditions. Incubated in aerobic soils for a period of 1–3 months, acesulfame and sucralose showed signs of slow degradation, suggesting even the most persistent sweeteners are not necessarily inert to microbial actions (Buerge et al., 2011). In addition, positive observation of photo-induced decomposition and initial by-product identification in sucralose (Calza et al., 2013), indicating another probable course of natural elimination after prolonged exposure to sunlight. These findings significantly highlight another critical issue: namely, the formation and accumulation of potentially more deleterious by-products from natural degradation of artificial sweeteners. Indeed, there have been well-documented examples involving various other persistent organic pollutants including polyaromatic hydrocarbons (PAHs), pharmaceuticals, pesticides and personal-care products, in which the enhancement in degradation toxicity, especially phototoxicity, has clearly implied unforeseen environmental consequences over the long term (Petersen