WATER RESEARCH 44 (2010) 3401–3409

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Solar photolysis kinetics of disinfection byproducts

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ARTICLE INFO

Article history:
Received 17 December 2009
Received in revised form
8 March 2010
Accepted 8 March 2010
Available online 17 March 2010

Keywords:
Photolysis
QSAR
DBP
NDMA
THM
HAA

ABSTRACT

Disinfection byproducts (DBPs) discharged from wastewater treatment plants may impair aquatic ecosystems and downstream drinking-water quality. Sunlight photolysis, as one process by which DBPs may dissipate in the receiving surface water, was investigated. Outdoor natural sunlight experiments were conducted in water for a series of carbonaceous DBPs (trihalomethanes, haloacetic acids, halopropanones, and haloacetaldehydes) and nitrogenous DBPs (nitrosamines, halonitromethanes, and haloacetonitriles). Their pseudo-first-order rate constants for photolytic degradation were then used to calibrate quantitative structure–activity relationship (QSAR) parameters, which, in return, predicted the photolysis potentials of other DBPs or related compounds. Nitrogenous DBPs were found to be more susceptible to solar irradiation than carbonaceous DBPs, with general rankings for the functional groups as follows: N-nitroso (N-NO) > nitro (NO_2) > nitrile (C≡N) > carbonyl (C═O) > carboxyl (COOH). Compounds containing a high degree of halogenation (e.g., three halogens) were usually less stable than less halogenated species (e.g., those with two halogens). Bromine- or iodine-substituted species were more photosensitive than chlorinated analogs. While most bromine- and chlorine-containing trihalomethanes and haloacetic acids persisted over the 6-h test, nearly complete removal (>99%) of nitrosamines occurred within 1 h of sunlight exposure. Indoor laboratory experiments using simulated sunlight demonstrated that the degradation of nitrosamines was ~50% slower when organic matter was present, and ~11% slower in non-filtered water than in filtered water.

1. Introduction

In addition to water recycling and reclamation programs, unintentional reuse of treated wastewater has occurred over the past few decades and will likely increase in the future as upstream wastewater treatment plants (WWTPs) discharge effluents into rivers or lakes that serve as downstream drinking-water resources. Drought and competing in-stream demands may result in substantial contribution of treated wastewater in water bodies (Krasner et al., 2008). Attention

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doi:10.1016/j.watres.2010.03.014

has been drawn to the impact of WWTP discharges as a source of multiple contaminants, such as pharmaceuticals, to aquatic life and downstream drinking-water sources.

Due to the common disinfection practice at U.S. WWTPs of adding chlorine, disinfection byproducts (DBPs) are likely to be present in WWTP discharges. Wastewater-derived DBPs may pose risks to downstream aquatic organisms (Mizgireuv et al., 2004) and human health. In a U.S. survey, for WWTPs that achieved breakpoint chlorination (i.e., free chlorine residual), the median concentrations of trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and trihalogenated acetaldehydes were 57, 70, 16, and 16 μg/L, respectively (Krasner et al., 2009). For WWTPs without breakpoint chlorination (i.e., chloramine residual), a median of 11 ng/L (75th percentile = 24 ng/L) of N-nitrosodimethylamine (NDMA) was detected (Krasner et al., 2009). Chlorination of effluent organic matter (EfOM) in an earlier study also resulted in the formation of chloral hydrate (i.e., trichloroacetaldehyde) and dichloroacetonitrile (Trehy et al., 1986). As WWTP effluents contain relatively high levels of bromide and iodide due to anthropogenic activities (Krasner et al., 2008), certain brominated and potentially iodinated DBPs may form too.

Some nitrogenous DBPs (including certain HANs, halonitromethanes [HNMs]) are more cytotoxic and genotoxic than the regulated carbonaceous DBPs (i.e., THMs, HAAs), and their toxicity was impacted by halogen substitution type: iodine > bromine > chlorine (Plewa and Wagner, 2009). The U.S. Environmental Protection Agency's (USEPA's) Integrated Risk Information System (IRIS) database indicates for NDMA and seven other nitrosamines that concentrations of low ng/L level in water are associated with a 10^{-6} lifetime cancer risk. Therefore, the treatment, fate, and transport of wastewater-derived DBPs in water resources require study.

In conjunction with sorption, biodegradation, volatilization, hydrolysis, and other biogeochemical processes, sunlight photolysis may reduce DBP concentrations to varying degrees in surface waters (Table 1). For example, dichloroacetonitrile spiked into drinking water was photodegradable (Lekkas and Nikolaou, 2004), and chloropicrin (i.e., trichloronitromethane [TCNM]) in the atmosphere was degraded under sunlight conditions (Allston et al., 1978). HAAs underwent varying levels of photolysis (Lifongo et al., 2004), and nitrosamines exhibited substantial photolytic losses under simulated sunlight conditions (Megan and Reinhard, 2007). However, the experimental conditions in these studies were different, which makes a comparison of the photolysis degradation of different groups of DBPs difficult.

Quantitative structure–activity relationship (QSAR) analysis is an empirical chemical property estimation method that can predict the behaviors of one chemical from other structurally similar chemicals. The method was developed by Hammett (1935), explored by Hansch et al. (1995), and widely applied in many areas, including the prediction of toxicity testing and pharmaceutical behavior (Hansch et al., 1995), the photolysis of polycyclic aromatic hydrocarbons (Chen et al., 2001) and haloaromatics (Peijnenburg et al., 1993), and the hydrolysis of trihaloacetic acids (Zhang and Minear, 2002). The QSAR application is based upon a key assumption that chemicals with similar structures behave similarly and their activity differences are attributed only to the type, number, steric, and electronic effect of their functional group(s). Because DBPs in one group share similar chemical structures, the QSAR technique should be applicable to DBP photolysis.

The purpose of this paper was to investigate the photolysis of several groups of DBPs and related compounds under uniform solar irradiation conditions. The pseudo-first-order degradation rate constants were obtained from experiments and subsequently used to calibrate the QSAR models. In turn, the calibrated QSAR models were used to predict the photolytic degradation of other DBPs or related compounds, such as iodinated DBPs, which have not been studied experimentally. Although the reactive mechanism and pathway of each DBP is uncertain and many other factors, such as receiving waterbody geometry (width, depth of the photic zone), flowrate, compound sensitivity, microbial activity, solar light spectra, and meteorological conditions are also critical in understanding the photolytic degradation of DBPs (Chen et al., 2008), the outcome of this study may serve as a basis for further and more thorough exploration of the role of photolysis in DBP removal.

2. Materials and methods

2.1. *Natural sunlight (outdoor) experiment*

Sunlight photolysis of DBPs was evaluated in 9-mL quartz test tubes (outside diameter = 13 mm). Concentrated DBP solutions were spiked into 200 mL of pH-buffered organic-pure water (pH ~7.2; phosphate buffer) in volumetric flasks to result in concentrations of ~500–1000 μg/L of each halogenated DBP and ~10,000 ng/L of each nitrosamine and were distributed evenly to multiple test tubes. Sample vials were capped to minimize volatilization or evaporation, and placed on an inclined platform on top of the laboratory roof in Tempe, Arizona, USA (33°25′12.35″N, 111°55′55.11″W). Samples were partially air cooled during the tests by a fan, as the surrounding air temperature was ~30 °C (Arizona Meteorological Network, http://ag.arizona.edu/azmet). Energy intensities were monitored on-site by a photometer (IL 1700, International Light Technologies, Inc., Massachusetts, USA). The solar spectrum was also extracted from a model named SPCTRAL2 (http://rredc.nrel.gov/solar/models/spectral/SPCTRAL2). The irradiation intensities appeared similar and remained constant in the range of 1150–1300 W/m^2 between 11 am and 3 pm (<10% difference).

Halogenated DBP and nitrosamine samples were exposed for 0, 0.5, 1.5, 3, and 6 h from 11 am to 5 pm on May 20, 2005 for the first run of the experiment. On July 25, 2005, nitrosamine photolysis experiments were repeated but for a shorter exposure time (i.e., 0, 1, 3, 5, 10, 20, 30, and 60 min). On August 10, 2005, a second run was conducted for up to 8 h for the THMs and HANs. A 6- or 8-h time period was chosen in order to have a nearly constant solar irradiation for each experiment. The total solar radiations of the three dates were recorded as 696, 681, and 405.7 langleys for May 20, July 25, and August 10, 2005, respectively, by Arizona Meteorological Network Mesa Station (http://ag.arizona.edu/azmet). The average air temperatures of the three dates however were similar, being 31.7, 33.3, and 33.9 °C, respectively.