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Benzotriazole corrosion inhibitors are frequently detected in rivers, lakes and groundwater and are not completely removed during wastewater treatment. Photochemical transformation may be a major degradation pathway in the environment. Presented here are kinetic studies and photochemical half-lives under natural conditions for substituted benzotriazoles and a structural series consisting of benzimidazole, indazole, and inole. Benzotriazole undergoes direct photodegradation and reacts rapidly with hydroxyl radicals, but is relatively unreactive towards singlet oxygen. Despite long photochemical half-lives, photochemical transformation may take over a prominent role because little removal by sorption to particles and slow microbial degradation processes are expected in surface water.

Aquatic photochemical kinetics of benzotriazole and structurally related compounds

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Abstract

Benzotriazole corrosion inhibitors are not completely removed during wastewater treatment and are frequently detected in surface waters. Here, the photochemical kinetics of benzotriazoles and structurally related compounds were assessed for natural aqueous environments. The direct photochemical half-lives during exposure to simulated sunlight ranged from 1.3 to 1.8 days for benzotriazole and its derivatives (4-methyl-, 5-methyl-, 4-hydroxy-substituted benzotriazoles). Benzotriazole is more resistant to direct photodegradation than indazole (0.28 days) and indole (0.09 days), while benzimidazole showed no significant decay. Hydroxyl radicals (1.6×10^{-16} M) and singlet oxygen (2.5×10^{-13} M) are formed during simulated sunlight exposure in the presence of dissolved organic matter (13 mg_C L^{-1}). All tested compounds reacted rapidly with hydroxyl radicals near the diffusion-controlled limit (8.3 to 12×10^{9} M^{-1} s^{-1}). Only 4-hydroxybenzotriazole and indole showed significant reactivity towards singlet oxygen and their photochemical half-lives in the presence of organic matter were shorter (0.1 days for both) than for benzotriazole and its methylated derivatives (1.4-1.5 days). The photochemical half-lives determined here are relatively long and support the persistence of benzotriazoles in the environment. At the same time, these results suggest that photochemical transformation can be supplementary to microbial degradation. While the presented study focused on environmental photodegradation kinetics, the relevance of transformation products remains to be investigated.

Keywords: benzimidazole, indazole, indole, organic matter, half-lives

Introduction

Quantifying and comparing environmental fate processes of organic pollutants is necessary to determine their persistence in the environment. In 2010, benzotriazole was identified as the fourth most common groundwater pollutant just after bisphenol A with concentrations as high as 100 ng L^{-1}, yet, its environmental persistence and fate processes are not completely understood.[1]

Benzotriazole and its methylated derivatives (4-methylbenzotriazole and 5-methylbenzotriazole) are widely used anticorrosion agents in airplane deicing fluids and automotive cooling applications.[2] Other benzotriazole derivatives have been used as ultraviolet light stabilizers in plastics, additives in dishwasher detergent, and chemical intermediates in dyes.[2, 3] Benzotriazole was first detected in the environment in subsurface waters beneath a North American airport.[4] Diffuse loss of significant amounts (often more than 20%) of deicing fluids after aircraft deicing operations occurs even when collection systems are in place, and these fluids contain approximately 0.05% of benzotriazole if undiluted.[5] Removal in wastewater treatment plants is incomplete and ranges from 13% to 62% and effluent concentrations are present in the low μM range (4.6 to 10 μM)[1, 6-10]. Consequently, benzotriazole has been detected in various lakes, rivers[3, 7, 8, 11, 12] and groundwater[1, 4, 13, 14], and its occurrence and analytic protocols have recently been reviewed by Herrero et al.[15] Benzotriazole has also been detected in tap water across Europe up to a concentration of 6.3 μg L^{-1}.[3, 13, 16] No specific toxicity of benzotriazole is known but it can cause acute and chronic effects in algae and bacteria and endocrine disrupting effects in fish (Chinese rare minnows) at low mM concentrations.[17-19] Thus, toxic effects may be most pronounced in the winter season when high quantities of deicing fluids are being used and aqueous concentrations increase locally.

Benzotriazoles are persistent in the aquatic environment because microbial degradation is slow and removal by sorption and sedimentation is not expected due to its low affinity to organic matter (log K_{ow} = 1.23, log K_{oc} = 2.85).[2, 14, 20, 21] Consequently, photochemical degradation may be a relevant natural fate process of benzotriazole in surface waters.

Many studies have examined the photochemistry of benzotriazole under enhanced UVC light conditions (254 nm), focusing on degradation mechanism and kinetics. Different photoproducts, such as aniline and phenazine, were identified and laser flash photolysis demonstrated that the five-member ring was broken from an N-N bond fission with high-energy irradiation.[22, 23] Several studies have confirmed that the photodegradation of benzotriazole is pH-dependent (pK_a around 8.6)[23-25] with faster decay at lower pH as the deprotonated species is much less photoreactive due to lower absorptivity.[24] During irradiation with UVC light (254 nm), the decay rates were slower in the presence of organic matter, which was assumed to be due to light screening and scavenging of hydroxyl radicals ($^{\bullet}OH$) by the organic matter.[25, 26] While these studies offer information for engineered systems such as advanced drinking water and wastewater treatment, they are not representative for fate processes under natural conditions in the environment. In the aquatic environment, organic matter acts as a photosensitizer due to production of excited organic matter itself and reactive oxygen species (e.g., singlet oxygen and hydroxyl radicals). In addition to transformation of benzotriazoles by direct photochemical processes indirect photochemical reactions with these organic matter-derived reactive species have yet to be quantified.

The present study focuses on photochemical degradation kinetics of benzotriazole derivatives but also includes the structurally related compounds

benzimidazole, indazole and indole. The environmental fate of benzimidazole has not been studied in detail with the exception of carbendazim,[27-29] a benzimidazole derivative. Due to its presence in a wide range of pesticides and pharmaceuticals, benzimidazole is likely to be found in the aquatic environment.[28, 30] Monitoring the persistence of benzimidazole fungicides in surface waters is necessary, as they can cause toxic effects in aquatic microorganisms and invertebrates.[31]

Here, we identified photochemical transformation processes of benzotriazole and structurally related compounds to investigate their fate processes in the aquatic environment. We assessed the half-lives for direct photodegradation, the reactivity with reactive oxygen species (hydroxyl radicals, singlet oxygen), and the effects of organic matter on the transformation kinetics of these compounds during light exposure. We demonstrated that benzotriazole undergoes direct photodegradation by UVB irradiation and reacts rapidly with hydroxyl radicals, but is relatively unreactive towards singlet oxygen. Overall, our results suggest that the fate by photochemical processes is competitive with microbial degradation in surface waters.

Materials and Methods

Materials. All solutions were prepared with nanopure water (resistivity > 18 MΩ cm, Barnstead NANOpure System). Experiments at pH 7.5 were carried out in 10 mM phosphate buffer from sodium phosphate dibasic dihydrate (Sigma Aldrich, ≥ 99%) adjusted to 30 mM ionic strength with sodium chloride (Merck, ACD reagent grade). The following reagents were used as received: Indole (Sigma Aldrich, 99+%), indazole (Sigma Aldrich, 98%), benzimidazole (Sigma Aldrich, 98%), benzotriazole (TCI, >98.0%), 4-methylbenzotriazole (Fluka), 5-methylbenzotriazole (Acros organics), 4-hydroxybenzotriazole (Aldrich), 2-hydroxyterephthalic acid (Sigma

Aldrich, 97%); Rose Bengal (Sigma-Aldrich), p-nitroanisole (Aldrich), pyridine (Sigma), ammonium bicarbonate (Fluka), ammonium acetate (Prolabo®), formic acid (AnalaR NORMAPUR VWR, 99-100%), acetic acid (Fluka), and ethanol (Fluka); acetonitrile and methanol (Merck KGaA, ≥ 99.9). Furfuryl alcohol (Aldrich) was distilled prior to use. The terephthalic acid potassium salt (K_2TPA) was prepared from terephthalic acid (Sigma Aldrich, 98%) as described elsewhere.[32] Briefly, TPA (0.06 moles) and KOH (0.12 moles) were dissolved in nanopure water, placed on ice, and ethanol was added to precipitate a white powder. The precipitate (K_2TPA) was filtered and dried on a vacuum line for 90 minutes.

Stock solutions of the test compounds were prepared daily in nanopure water. Suwannee River Fulvic Acid II (SRFA II, 1S101F) and Waskish Peat organic matter (1R107H) were obtained from the International Humic Substances Society (IHSS) (St. Paul, MN, USA) and solutions were prepared by dissolving approximately 250 mg_{HA} L^{-1} in nanopure water at pH 10.0 by adding sodium hydroxide and sonicating the solutions until a stable pH was reached. DOM solutions were then adjusted to around pH 7 with hydrochloric acid, filter sterilized (0.2 µm, cellulose acetate membrane, VWR), and frozen until use. The total organic carbon content was determined (Shimadzu Corporation, TOC-L analyzer).

Photodegradation during light exposure

Solutions of test compounds (10 µM) were exposed to light from a Xe lamp (Newport, at 300 W, see Figure 1A for spectrum) simulating the solar light spectrum with and without dissolved organic matter (SRFA(II), 13 mg_C L^{-1}) present. For exposure to enhanced UVB or UVA light, a photoreactor (Rayonet; Southern New

England Ultraviolet Co, see supporting information (SI), **Figure S1** for spectra) with six RPR-3000 Å or eight RPR-3500 Å bulbs, respectively, was used.

All test solutions contained furfuryl alcohol (40 μM) as a singlet oxygen probe molecule. Solutions (4 mL) were placed into borosilicate tubes (PYREX®, 7.5 cm, inner diameter 1.0 cm) in front of the Xe Lamp and stirred (400 rpm). The steady state hydroxyl radical concentration ($[^{\bullet}OH]_{ss}$) was quantified using TPA as a hydroxyl radical probe molecule for experiments in the sunlight simulator with organic matter (SRFA(II)). TPA reacts with hydroxyl radical to give a hydroxylated fluorescent product, hydroxyterephthalic acid (hTPA)[32]. To determine $[^{\bullet}OH]_{ss}$ a solution in an open borosilicate tube (PYREX®, 8.5 cm, inner diameter 1.5 cm) containing SRFA(II) (13 mg_C L^{-1}) and TPA potassium salt (10 μM) was irradiated under the same conditions as applied in the sunlight simulator experiments (Xe lamp, Newport, at 300 W). The $[^{\bullet}OH]_{ss}$ was calculated by monitoring the production of hTPA (**SI, Figure S2**). The production rate constant of hTPA was divided by (a) the average percent yield of 35% for hTPA produced by the reaction of TPA and hydroxyl radical,[32] (b) by the concentration of TPA (10 μM), and (b) by the second order reaction rate constant of TPA with hydroxyl radical (4.4×10^9 M^{-1} s^{-1}).[32] The $[^{\bullet}OH]_{ss}$ produced from SRFA(II) during sunlight simulator experiments was calculated as 1.6 $\pm 0.1 \times 10^{-16}$ M.

To calculate the quantum yields for direct photolysis, analogous experiments were performed in enhanced UVB light (Rayonet with eight RPR-3000 Å bulbs). The spectral overlap of the UVB light source and the absorption of the compounds were higher than for the Xe-lamp, which reduces the error in these calculations. A p-nitroanisole-pyridine actinometer was used[33]. Therefore, solutions of p-nitroanisole (8 μM) and pyridine (0.5 mM) in nanopure water were irradiated in quartz tubes.

Details on the degradation kinetics of p-nitroanisole and test compounds and the quantum yield calculation can be found in the SI (**Figure S3, Table S1-S2**).

Reaction rate constants with reactive oxygen species

Singlet oxygen. The reaction rate constant with singlet oxygen was measured in solutions containing sensitizer (Rose Bengal, 1-10 μM), furfuryl alcohol (40 μM) and the test compound (10 μM) at pH 7.5, irradiated by a Xe lamp (Newport, at 300 W, 455 nm low pass filter) while stirred in borosilicate tubes. Rose Bengal photobleached during extended light exposure. For the compounds that required longer exposure time because of their low reactivity, the concentration of Rose Bengal was quantified spectroscopically every 30 minutes and re-adjusted to maintain constant concentrations throughout the experiment. The steady-state singlet oxygen concentration, $[^1O_2]_{ss}$, was assessed by dividing the observed degradation rate constants (k_{obs}, s^{-1}) of furfuryl alcohol by its second order reaction rate constant of 8.3 ± 0.1 × 10^7 M^{-1} s^{-1}.[34] The second order reaction rate constant of the test compounds were then assessed by dividing their observed decay rate constants (k_{obs}, s^{-1}) by $[^1O_2]_{ss}$.

Hydroxyl radicals. The degradation rate constants from the reaction with hydroxyl radical were assessed by competitive kinetics studies with benzoic acid. Reaction solutions prepared in nanopure water consisted of benzoic acid (5 μM), test compound (5 μM), and 1 mM hydrogen peroxide (H_2O_2) to produce hydroxyl radical during exposure to UVA light. Solutions (4 mL) were placed into borosilicate tubes (PYREX®, 7.5 cm, inner diameter 1.0 cm) on a turntable inside a photoreactor (Rayonet; Southern New England Ultraviolet Co, eight RPR-3650 Å bulbs). None of the test compounds of interest absorb light at 365 nm and no degradation by direct photochemical reactions was observed. The second order reaction rate constants of

the test compounds with hydroxyl radical were determined by linear regression of the degradation of test compound (as $\ln[C/C_0]$) versus the degradation of benzoic acid (as $\ln[C/C_0]$) and the corresponding slope was multiplied by the reaction rate constant of benzoic acid with hydroxyl radical, 5.9×10^9 M^{-1} s^{-1}.[35]

Sample analysis

Samples were analyzed by Ultra Performance Liquid Chromatography (UPLC) on a C18 column (Waters Aquity, BEH130 C18, 1.7 µm, 2.1×150 mm) with injection volume of 5 µL. Furfuryl alcohol and all test compounds were analyzed using 75% sodium acetate buffer (pH 5.9, 15.6 mM) and 25% acetonitrile with 0.15 ml min^{-1} flow rate. Furfuryl alcohol was detected by absorbance at 219 nm. Benzotriazole, 4-methylbenzotriazole and 5-methylbenzotriazole were detected by absorbance at 275 nm and 4-hydroxybenzotriazole was detected by absorbance at 290 nm. Benzimidazole, indazole and indole were detected by fluorescence with excitation at 275 nm and emission at 320, 315, and 350 nm, respectively. The analysis of benzoic acid was performed on the same UPLC with a using formic acid (0.1%) and methanol (B) with the following gradient: 0-3 min, 85%A-15%B; 3-8 min, 50%A-50%B; 8-10 min, 0%A-100%B; 10-15 min 85%A-15%B followed by fluorescence detection with excitation at 225 nm and emission at 425 nm. For hydroxyterephthalate, an eluent composition of 70% formic acid (0.1%) and 30% methanol and fluorescence detection with excitation at 250 nm and emission at 410 nm was used. For p-nitroanisole, an eluent composition of 40% acetate buffer (pH 5.0, 15.6 mM) and 60% acetonitrile and absorbance detection at 316 nm was used.

All first-order degradation rate constants, k_{obs} (s^{-1}), were assessed by linear regression of normalized, log-transformed normalized concentrations ($\ln(C/C_0)$) versus irradiation time.

Results and Discussion

The photochemical degradation kinetics of benzotriazole derivatives and structurally related compounds are presented below. We first present the degradation kinetics and half-lives under simulated sunlight conditions for direct photochemical processes. Then we quantify the reaction rate constants with hydroxyl radicals and singlet oxygen. Finally, we show the effects of DOM and assess the contribution of indirect processes to the overall photochemical half-lives.

In addition to benzotriazole derivatives, we also investigated the structurally related compounds benzimidazole, indole, and indazole, which differ in the number and position of the N atoms in the 5-membered ring (see Figure 1B for structures). Some benzimidazole fungicides (e.g., 2-aminobenzimidazole and carbendazim) have been detected in secondary wastewater treatment plant effluent, emphasizing the stability of benzimidazole and its occurrence in surface water.[28, 36-38] However, indirect photochemical reactivity of benzimidazole in the presence of organic matter has not yet been studied. Indazoles are rare in nature but are often part of the structure of biologically active compounds.[39] Lastly, indole is the backbone of a wide variety of naturally occurring biomolecules, including tryptophan, an essential amino acid.[40] We studied these compounds to further investigate possible structural effects of nitrogen-heterocyclic compounds on photodegradation relative to benzotriazoles and to assess the connection between the photochemistry of benzotriazoles and the indole-containing amino acid tryptophan.[41]

Photodegradation and half-lives

Benzotriazoles and structurally related compounds undergo direct photochemical reactions because they absorb light in the UVB range of the solar spectrum, with the exception of benzimidazole (**Figure 1**). Benzimidazole was also one of the photoproducts identified for photodegradation of carbendazim[29] and is thus expected to be relatively photostable. Data in **Figure 2** show direct photochemical degradation of the tested compounds during exposure to simulated sunlight. Indole and indazole degrade significantly faster with half-lives of 0.1 and 0.3 days, respectively, compared to benzotriazole (1.8 days). The methylated and hydroxylated benzotriazole derivatives all decay at similar rates with half-lives ranging from 1.3 to 1.6 days (**Table 1**). To calculate quantum yields for direct photochemical degradation, analogous experiments were performed in enhanced UVB light (see SI for details). Benzotriazole shows similar molar absorptivity as indole and indazole, yet a lower quantum yield results in the slower observed degradation kinetics.

For benzotriazole, direct photochemical transformation may lead to opening of the five-member ring from a N-N bond fission as observed previously with high-energy irradiation.[22, 23] Future research should further investigate the identification and quantification of photoproducts of benzotriazole under sunlight conditions.

Effects of reactive oxygen species and organic matter. Dissolved organic matter can act as a sensitizer and thus enhance degradation of organic molecules by indirect photochemical processes. Here, we investigated the reactivity of all test compounds with hydroxyl radicals and singlet oxygen. The data show that these are the two prominent reactive oxygen species contributing to the indirect photodegradation of benzotriazole derivatives and structurally related compounds.

Hydroxyl radicals. The reaction rate constants of all test compounds have been assessed by competitive reaction of benzoic acid with hydroxyl radical, which was produced photochemically from hydrogen peroxide (for kinetic data see SI, **Figure S4 and Figure S5**). All compounds are reactive towards hydroxyl radical with reaction rate constants near the diffusion-controlled limit (**Table 1**). The reaction with hydroxyl radical is expected to include radical addition reactions resulting in hydroxylation of the benzene ring. Formation of 4-hydroxybenzotriazole was observed in analogous experiment with higher starting concentration of benzotriazole (50 μM, **Figure S6, Figure S7**). The yield of 4-hydroxybenzotriazole formation was relatively low (~ 4%). Methylated and hydroxylated benzotriazoles reacted slightly faster than unsubstituted benzotriazole, likely due to the increased the electron density in the benzene ring from the electron donating methyl and hydroxy substituents. Steady-state concentrations of hydroxyl radicals in surface waters are relatively low ranging from 10^{-15} to 10^{-17} M.[42, 43] Thus, despite the high reactivity, the reaction with hydroxyl radicals may cause only moderate transformation of benzotriazole derivatives in the environment.

Singlet oxygen. Data in **Table 1** also show the reaction rate constants of singlet oxygen with all test compounds (further information in SI, **Table S3**). Among all test compounds, only 4-hydroxybenzotriazole and indole react at relatively fast rates with singlet oxygen (k = 1.31 ± 0.04 × 10^8 M^{-1} s^{-1} and k = 4.34 ± 0.01 × 10^7 M^{-1} s^{-1}, respectively). The reaction rate constant of 4-hydroxybenzotriazole represents the combined rate constants of the phenol and phenolate species (pK_a = 7.7, experimental pH = 7.5). The reaction of singlet oxygen with other benzotriazole derivatives are so slow (k < 6.0 × 10^5 M^{-1} s^{-1}) that the reaction is not expected to contribute significantly

to their fate in the environment, considering environmental steady-state concentrations of singlet oxygen of 10^{-12} to 10^{-13} M in surface waters.[44-46]

Comparing indole to indazole and benzimidazole, the additional nitrogen in the 5-membered ring may be the cause of lower reactivity of indazole and benzimidazole with singlet oxygen. Indoles are thought to react with singlet oxygen at the 2,3-C=C double bond and substitution with N atoms at the 2-position (indazole), 3-position (benzimidazole) or both positions (benzotriazole) disrupts this site of attack. It is notable that histidine carries the same imidazole ring structure as benzimidazole and reacts rapidly with singlet oxygen (k = 8.3 ± 1.1 × 10^7 M^{-1} s^{-1}).[47] Imidazoles react with singlet oxygen across the 2,4 (or 2,5) C atoms. This mode of reactivity is not favored for benzimidazole because it would lead to disruption of aromaticity in the adjoining ring.

Dissolved organic matter. Data in **Figure 3A** show that the decay of benzotriazole only increases slightly in the presence of 13 mg_C L^{-1} of Suwannee River Fulvic Acid (II) during exposure to simulated sunlight and after correcting for light screening effects (Student t-test, $p < 0.001$). The observed half-life was 1.4 days and represents transformation by direct and indirect photochemical processes. Enhanced degradation can be attributed to the reaction with hydroxyl radicals. We measured the steady-state concentration of hydroxyl radicals to be 1.6 × 10^{-16} M during exposure of DOM (SRFA(II), 13 mg_C L^{-1}) to simulated sunlight. The estimated half-life based on the reaction with this concentration of hydroxyl radicals was 5.8 days.

Previous studies reported a net inhibition effect of DOM on the degradation of benzotriazole.[25] Data in **Figure 3B** demonstrate that light screening is mostly responsible for these observations. The decay rate of benzotriazole progressively decreases with increasing concentration of DOM during exposure to enhanced UVB

light. The sensitizing effect of DOM increases with DOM (sensitizer) concentration and only becomes apparent after correcting for light screening (see SI **Table S4** for details).

Data in **Figure 4** summarize the reaction rate constants during exposure to simulated sunlight and data in **Table 1** shows the photochemical half-lives that were observed in the presence and absence of DOM. The last column in **Table 1** lists half-lives based on the reactions with hydroxyl radicals and singlet oxygen as estimated from the compound-specific reaction rate constants and the steady-state concentrations of the reactive oxygen species.

The presence of DOM had minimal effects on benzotriazole and its methylated derivatives. The observed indirect photochemical decay in the presence of DOM (**Figure 4**, dark grey bars) is well described by the sum of direct degradation rates and the estimated reaction rate with hydroxyl radical (stacked bars). This is also true for indazole and benzimidazole. In contrast, DOM significantly sensitized the degradation of 4-hydroxybenzotriazole, decreasing the photochemical half-life from 1.3 days ('no DOM') to 0.1 days ('with DOM'). However, the reaction with hydroxyl radical and singlet oxygen alone cannot explain the observed enhancement. We believe the discrepancy is due to reactivity with triplet-state DOM. Excited-state DOM can oxidize organic molecules by direct electron abstraction or via an energy transfer pathway[48, 49] and may be the reason for the enhanced reactivity of 4-hydroxybenzotriazole.

Indole degrades rapidly during irradiation with a half-life of 0.7 days and the reaction with singlet oxygen accounts for the majority of indirect photochemical degradation. The observed decay rate in the presence of DOM is 30% lower than the estimated decay rate based on direct transformation and the estimated reaction rate

constant with singlet oxygen and hydroxyl radicals. This difference can be explained by the fact that dissolved organic matter does not only sensitize but also slows down the photochemical decay of indole by repairing photodamage. Previous studies show that an indole radical cation is formed by direct photochemical reactions of indole and that in the case of tryptophan, this indole radical cation can be reduced back to indole by electron donors present in DOM.[41, 50] The fact that this non-screening inhibition behavior was not observed for benzotriazole derivatives suggests that they do not undergo photoionization as indole does, presumably due to their higher ionization energies.

Conclusions.

The presented data suggest that DOM is a net sensitizer in sunlit aqueous environments for the degradation of benzotriazole and structurally related compounds (with the exception of indole). Despite the structural similarity of benzotriazole to the highly photoreactive indole, it is much less photoreactive. In the top layer of sunlit surface waters, these benzotriazole derivatives are expected to naturally decay by direct photochemical processes. However, the photochemical half-lives are relatively long (1.3-1.8 days), supporting the persistence of benzotriazoles in the environment. Below the water surface where UV light is progressively screened, DOM still acts as a sensitizer and indirect phototransformation of benzotriazoles by reaction with hydroxyl radicals could become relatively more important. 4-Hydroxybenzotriazole is a product of photochemical and microbial transformation of benzotriazole.[10] The high photochemical reactivity of 4-hydroxybenzotriazole observed here suggests that it is not a stable end-product in the sunlit aquatic environment.

Despite the long photochemical half-lives, photochemical transformation appears to be a significant degradation process in the aquatic environment because removal by sorption to particles and microbial degradation processes are slow. [2, 14, 20, 21] Measured biodegradation half-lives of benzotriazole and 5-methylbenzotriazole for the decay during wastewater treatment are 1.0 and 0.9 days, respectively[10]. In particular, 4-methylbenzotriazole is more stable in wastewater treatment (half-life of 8.5 days)[7, 51] Microbial degradation alone is not sufficient to remove benzotriazoles considering the relatively short residence times in a treatment plant (0.5-0.7 days)[10] and much lower microbial activity in surface waters. Once the benzotriazoles entered surface waters, photochemical degradation may take over a prominent role in their transformation. However, the photochemical half-lives are expressed as days of full sunlight exposure and have to be corrected for actual hours of sunlight and sunlight intensity of the date and location of interest, which likely increase reported photochemical half-lives by a factor of five to ten.

Despite long half-lives of microbial and photochemical degradation of benzotriazoles, these processes are believed to be the dominant transformation reactions of these otherwise persistent pollutants. With a better understanding of the phototransformation pathways and rates of benzotriazoles, future research should be directed to identify photoproducts and investigate their potential toxic effects relative to the parent compounds.

Associated content

Supporting Information. Detailed methodology, Tables S1-S4, and Figures S1-S8.

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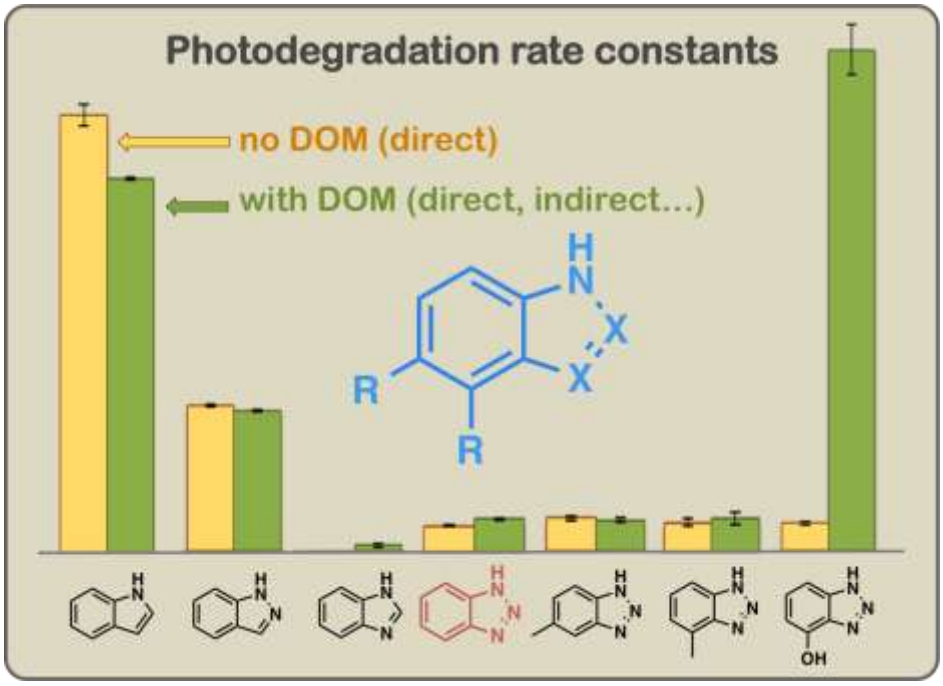

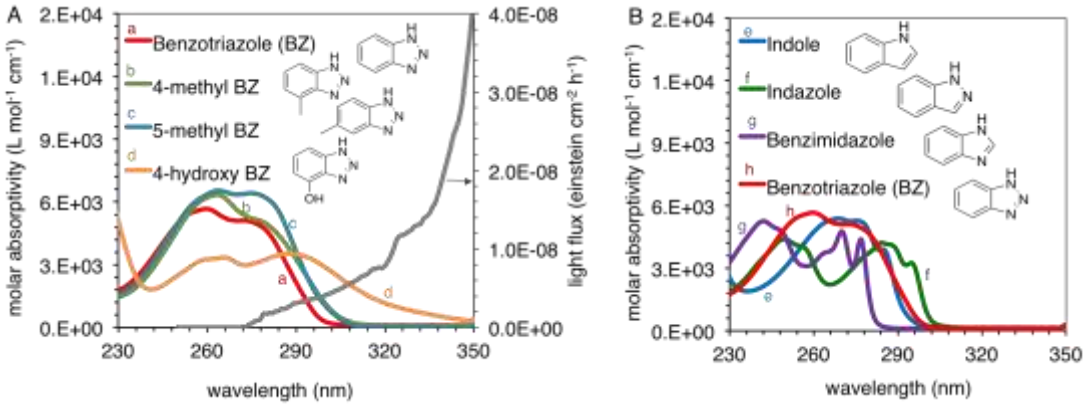

Figure 1. (A) Light flux of simulated sunlight (Xe-lamp, grey line) and molar absorptivities and chemical structures of benzotriazole derivatives and (B) of indole, indazole, benzimidazole and benzotriazole.

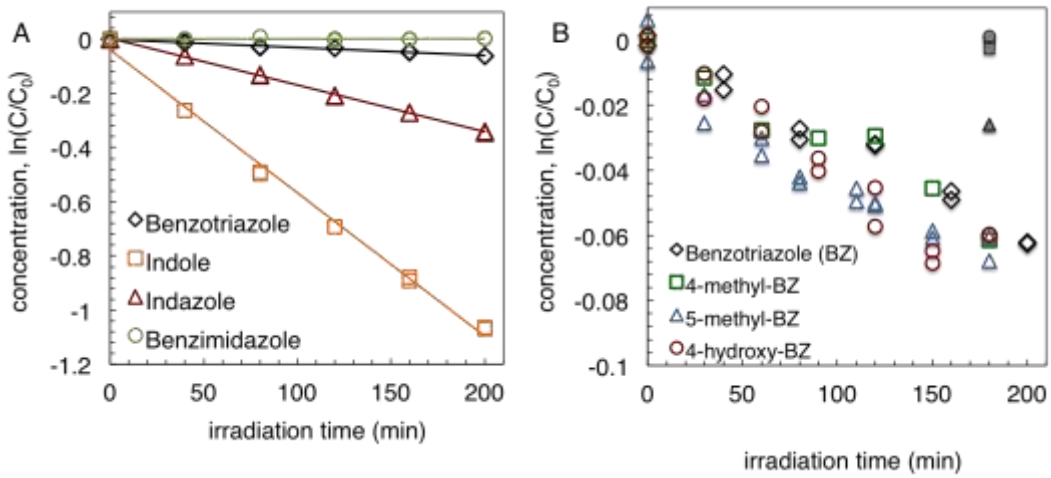

Figure 2. Degradation during exposure to simulated sunlight for (A) benzimidazole (green circles), benzotriazole (black diamonds), indazole (red triangles), and indole (orange squares) and (B) the benzotriazole derivatives 4-methylbenzotriazole (green squares), 5-methylbenzotriazole (blue triangles) and 4-hydroxybenzotriazole (red circles) and dark control samples (grey symbols). Measurements were performed in duplicate.

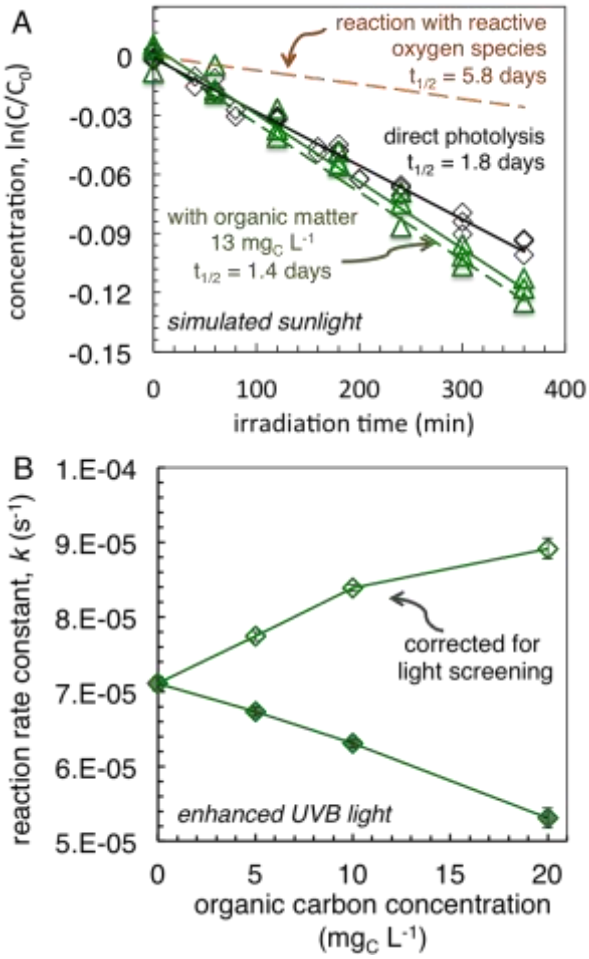

Figure 3. (A) Degradation of benzotriazole during exposure to simulated sunlight (black diamonds) and in the presence of organic matter (green triangles, SRFA(II), 13 mg_C L^{-1}), solid lines represented linear regression of measured data, dashed lines represent estimated degradation for the reaction with hydroxyl radical and singlet oxygen (orange dashed line) and the sum of direct and indirect reactions in the presence of organic matter (green dashed line). Data is corrected for light screening effects. (B) Reaction rate constants of benzotriazole during exposure to enhanced UVB light relative to organic matter concentration (Waskish Peat organic matter) as observed (green filled diamonds) and corrected for light screening effects by the organic matter (green open diamonds), lines connect data points. Measurements were performed in duplicates (without SRFA) and triplicates (with SRFA).

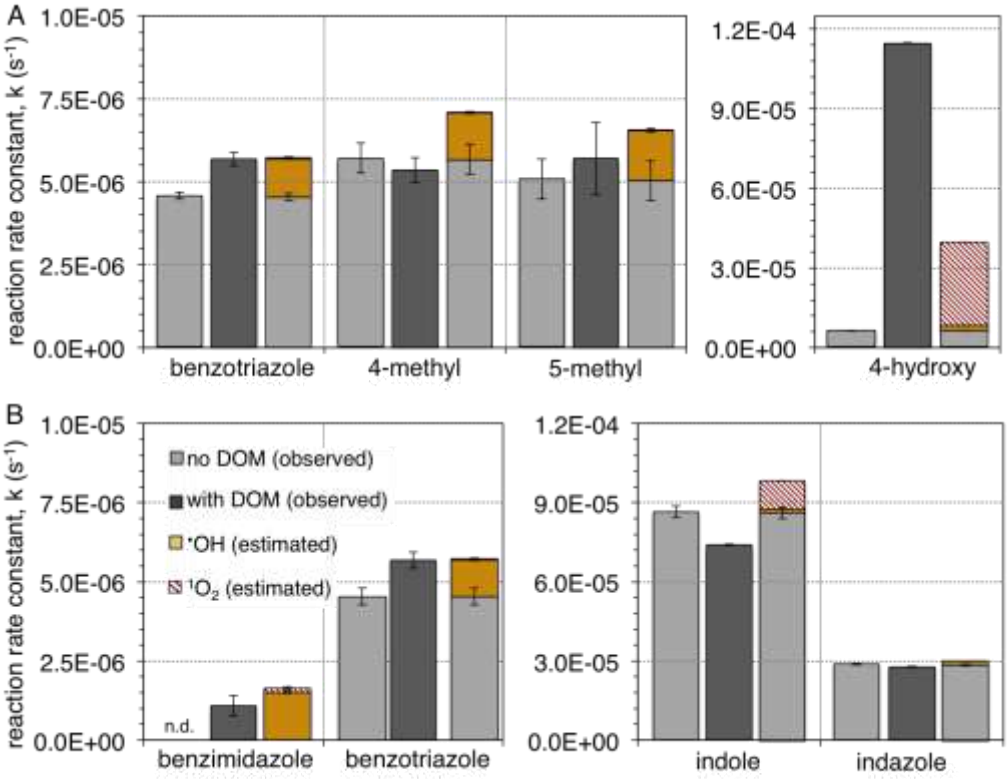

Figure 4. Degradation rate constants, k (s^{-1}), for (A) benzotriazole derivatives and (B) structurally related compounds under simulated sunlight conditions observed for direct photochemical degradation without dissolved organic matter ('no DOM', light grey bars) and in the presence of DOM ('with DOM', dark grey bars, corrected for light screening by SRFA(II), 13 mg_C L^{-1}). Third stacked bars represent the expected degradation in the presence of DOM as the sum of direct and indirect photochemical processes. Indirect photochemical processes were estimated for the reaction with hydroxyl radical (yellow bars) and singlet oxygen (red striped bars) as the product of the compound specific reaction rate constants and steady-state concentrations of these reactive oxygen species. No degradation has been detected: n.d. Error bars represent one standard deviation.

Table 1. Reaction rate constants with singlet oxygen and hydroxyl radicals and direct and indirect photochemical half-lives during exposure to simulated sunlight and in the presence of dissolved organic matter (DOM) for benzotriazole derivatives and structurally related compounds.

Compound	Reaction rate constant k (M^{-1} s^{-1})		Photochemical half-life $t_{1/2}$ (days) simulated sunlight		
	hydroxyl radical ($^{\bullet}OH$)	singlet oxygen ($^1O_2$)	*without DOM*	*with DOM* [a]	$^{\bullet}OH + {}^1O_2$ [b]
Benzotriazole (BZ)	8.31 ± 0.13 × 10^9	< 2.0 × 10^5	1.8	1.4	6.7
5-methyl BZ	8.81 ± 0.22 × 10^9	< 6.2 × 10^4	1.4	1.5	5.6
4-methyl BZ	9.41 ± 0.34 × 10^9	< 4.0 × 10^4	1.6	1.4	5.3
4-hydroxy BZ	12.20 ± 0.15 × 10^9	1.31 ± 0.04 × 10^8	1.3	0.1	0.2
Indole	8.94 ± 0.25 × 10^9	4.34 ± 0.01 × 10^7	0.1	0.1	0.7
Indazole	9.32 ± 0.16 × 10^9	< 3.0 × 10^5	0.3	0.3	5.1
Benzimidazole	9.38 ± 0.17 × 10^9	< 6.0 × 10^5	n.d.	7.4	4.9

[a] Suwannee River Fulvic Acid (II), 13 mg_C L^{-1}, [b] half-lives as the sum of the reaction with singlet oxygen and hydroxyl radical, estimated from the compound-specific reaction rate constant and steady-state concentrations for singlet oxygen (2.5 × 10^{-13} M) and hydroxyl radical (1.6 × 10^{-16} M).