



# Study of the photodegradation of a fragrance ingredient for aquatic environmental fate assessment



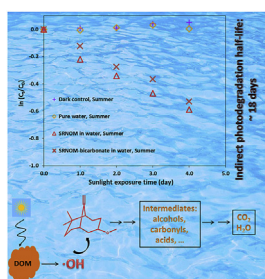
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## HIGHLIGHTS

- Indirect photodegradation of Pamplewood was estimated to be about 18 days.
- Reaction with hydroxyl radicals is the mechanism for the indirect photodegradation of Pamplewood.
- Indirect photodegradation of Pamplewood is expected to eventually lead to complete mineralization.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Photodegradation is an important abiotic degradation process to be taken into account for more accurate assessment of the fate of chemicals in the aquatic environment, especially those that are not readily biodegradable. Although the significant role of indirect photodegradation in the environmental fate of chemicals has been revealed in recent research, because of the many confounding factors affecting its kinetics, no straightforward approaches can be used to investigate this degradation process for environmental fate assessment. The indirect photodegradation of a fragrance ingredient named Pamplewood was studied in this work for its fate assessment. Indirect photodegradation rates under various indoor and outdoor conditions were measured by using an LC-MS method. Although the half-lives varied from 4 to 13 days, they collectively indicated that Pamplewood is intrinsically photolabile and can undergo rapid photodegradation. Results from quencher experiments revealed that  $\cdot\text{OH}$  was the main reactive intermediate responsible for indirect photodegradation, with a half-life of about 18 days in sunlit surface water, based on the experimentally determined second-order rate constant ( $8.48 \pm 0.19 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Photodegradation products of Pamplewood were also studied by GC-MS, LC-MS and total organic carbon content analyses. The results indicated that intermediates of Pamplewood photodegradation continued to photodegrade into smaller and more polar species. Complete mineralization of Pamplewood was observed when it was reacted with hydroxyl radicals in an aqueous solution. This novel approach can be applied for a more realistic environmental fate assessment of other non-readily biodegradable, hydrolysis-resistant, and non-sunlight-absorbing fragrance ingredients.

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## 1. Introduction

Chemicals discharged into surface water may degrade via biotic and abiotic (e.g., hydrolysis, oxidation, and photodegradation)

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processes. While abiotic processes such as photodegradation in water have been widely considered for plant protection products and pharmaceuticals (Sakkas et al., 2006; Zeng and Arnold, 2013; Challis et al., 2014; Remucal, 2014), such processes have been less often investigated for personal care products (Buerge et al., 2003; Sakkas et al., 2007; Canterino et al., 2008). This is also the case for fragrance ingredients, as investigations on their fate have mainly been focused on their biodegradability potential (Dick et al., 2016). Screening methods for ready biodegradability, both experimental and computational, have been developed and extensively applied to fragrance materials (Jenner et al., 2011; Boethling, 2014; Seyfried and Boschung, 2014; Seyfried et al., 2014, 2015). For non-readily biodegradable fragrance ingredients, which may end up in surface waters, abiotic processes—especially photodegradation—are likely to affect their fate in the aquatic environment.

Photodegradation may occur via direct and indirect mechanisms. In direct photodegradation, the absorption of a photon by the chemical results in bond cleavage or rearrangement to form new chemical species (Mill, 1999). Only those chemicals that have UV absorbance at wavelengths greater than 290 nm can undergo direct photodegradation. The rate constant is determined by the rate of photon absorption, quantum yield, and light screening (Leifer, 1988). During indirect photodegradation, dissolved organic matter (DOM) or other photosensitizers absorb light and produce a series of reactive species that can degrade a chemical. Reactive species include hydroxyl radicals ( $\cdot\text{OH}$ ), singlet oxygen ( $^1\text{O}_2$ ), carbonate radicals ( $\cdot\text{CO}_3^-$ ), triplet excited state DOM ( $^3\text{DOM}^*$ ), hydrated electrons, and many others (Challis et al., 2014).

Photodegradation of the monocyclic musk tibetene was studied by Canterino et al. (2008) to assess its environmental impact on aquatic ecosystems. They observed that tibetene photodegraded into three products mainly by direct photodegradation. Buerge et al. (2003) quantified the photodegradation processes that lead to the elimination of the non-readily biodegradable polycyclic musks galaxolide and tonalide in lakes. They concluded that galaxolide and tonalide were degraded primarily via direct photodegradation and that indirect photodegradation by reactive oxygen species was of minor importance. In contrast, Ward (2010) found that indirect photodegradation was also important for both compounds in natural water systems, where the half-life was shown to be decreased by an additional 40% for galaxolide and 60% for tonalide by taking into account indirect and direct photodegradation. The insignificance of indirect photodegradation observed by Buerge and co-workers was most likely due to a flaw in their photodegradation experiment, where the aqueous solutions contained 0.8–2.4 mg/L of methanol because the stock solutions were prepared with this solvent. The presence of an organic solvent carrier in the aqueous irradiation solutions could quench radical reactive species, which is detrimental to indirect photodegradation.

Guidelines for testing direct photodegradability of chemicals have been developed by the US EPA and the OECD (US EPA OPPTS 835.2210; OECD 316). Since the UV absorbance spectra of many fragrance ingredients do not overlap with the solar spectrum, studying their indirect photodegradability in sunlit surface water is especially important. However, it is difficult to develop standardized methods to test indirect photodegradation, since there are many confounding factors that may alter photodegradation mechanisms and pathways (Challis et al., 2014). The indirect photodegradation of pesticides (Zeng and Arnold, 2013), pharmaceuticals (Latch et al., 2003; Edlund et al., 2006), and amino acids (Boreen et al., 2008) has been investigated in terms of kinetics, mechanisms, and pathways. Substantial differences were observed in both the extent and the mechanisms of indirect photodegradation of diverse chemicals.

We aimed to explore the photodegradability of partially biodegradable fragrance ingredients to better understand their fate in the environment. An in-house fragrance ingredient, 3-methoxy-7,7-dimethyl-10-methylene-bicyclo[4.3.1]decane, internally named Pamplewood (Fig. 1), was used as the initial instance. Pamplewood was known to be poorly biodegradable from test results according to OECD Guidelines 301B and 301D. The ingredient was found to be hydrolysis-resistant and non-sunlight-absorbing on the basis of its structure and experimental measurements. We investigated the kinetics and mechanism underlying Pamplewood indirect photodegradation, as well as its photodegradation products and photomineralization. We demonstrated for the first time that knowledge gained from such investigations can be crucial for a more realistic aquatic environmental fate assessment of non-readily biodegradable, hydrolysis-resistant, and non-sunlight-absorbing fragrance ingredients.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Pamplewood, 3-methoxy-7,7-dimethyl-10-methylene-bicyclo[4.3.1]decane, CASRN 216970-21-7, purity (sum of two isomers) 97.7%, with a log  $k_{ow}$  of 4.66 and a water solubility of 7.07 mg/L, was produced and supplied by Firmenich. Isopropyl alcohol (IPA; anhydrous, 99.5%), *N,N*-dimethylaniline (DMA; 99%), and acetophenone (98%) were purchased from ACROS. Sorbic acid (SA; *trans,trans*-hexadienoic acid, 99%) and *L*-histidine (HIS; 98.5–101.0%) were purchased from MP Biomedicals.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Optima LC/MS<sup>®</sup> acetonitrile and methanol were purchased from Fisher Scientific. Humic acid and  $\text{H}_2\text{O}_2$  (30%) were purchased from Sigma-Aldrich. Suwannee River Natural Organic Matter (SRNOM; 2R101N) was purchased from the International Humic Substances Society. All stock solutions were prepared with ultrapure water (resistivity 18.2 M $\Omega$  cm, Millipore Corp.).

### 2.2. Preparation of solutions

The stock solution of SRNOM was prepared by dissolving 52.0 mg in 50 mL Millipore water at pH 10, with sonication, because the water solubility of SRNOM is higher under alkaline conditions. The resulting solution had a pH of 3.2, which was adjusted to pH 8.5 by using a 1 M NaOH solution. The stock solution of HIS was prepared by dissolving 194.0 mg in 50 mL Millipore water at pH 3. The pH of the resulting solution was readjusted to pH 7 with 1 M NaOH. The stock solution of SA was prepared by dissolving 71.9 mg in 50 mL Millipore water at pH 10. The pH of the resulting solution was readjusted to pH 7 with 1N  $\text{H}_2\text{SO}_4$ .

Aqueous stock solutions of Pamplewood were prepared by passive dosing (Smith et al., 2012; Butler et al., 2013), since it was challenging to introduce a hydrophobic chemical such as Pamplewood with a log  $k_{ow}$  of 4.6 into aqueous solution at realistically low

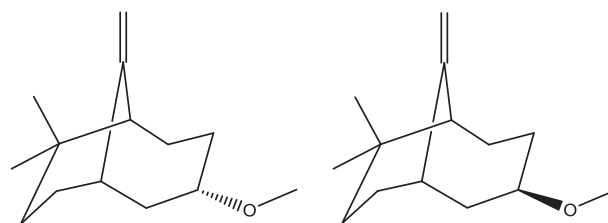


Fig. 1. Chemical structure of 3-methoxy-7,7-dimethyl-10-methylene-bicyclo[4.3.1]decane (Pamplewood).

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