Photodegradation of hydroxyfluorenes in ice and water: a comparison of kinetics, effects of water constituents, and phototransformation by-products

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ABSTRACT

The photochemical behavior of organic pollutants in ice is poorly studied in comparison to aqueous photochemistry. Here we report a detailed comparison of ice and aqueous photodegradation of two representative OH-PAHs, 2-hydroxyfluorene (2-OHFL) and 9-hydroxyfluorene (9-OHFL), which are newly recognized contaminantsthat are present in the wider environment including colder regions. Interestingly, their photodegradation kinetics were clearly influenced by whether they reside in ice or water. Under the same simulated solarirradiation ($\lambda > 290$ nm), OHFLs photodegraded faster in ice than in equivalent aqueous solutions and this was attributed to the specific concentration effects caused by freezing. Furthermore, the presence of dissolved constituents in ice also influenced photodegradation with 2-OHFL phototransforming the fastestin 'seawater' ice (k = xxxx) followed by 'pure water' ice (k = xxx) and 'freshwater' ice (k=xxxx),   Clearly the presence of dissolved water constituents (specifically Cl⁻, NO_3^- Fe(III) and humic acid (HA)) influences the

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phototransformation kinetics, either enhancing (e.g. Cl-, Fe(III)) or suppressing (HA) phototransformation, but this is based on the quantity of the constituent present in the ice, the specific OHFL isomer under investigation and the matrix type (e.g. ice or aqueous solution). Careful derivation of key photointermediates was undertaken in both ice and water samples using tandem mass spectrometry. Ice phototransformation of the OHFLs exhibited fewer by-products and 'simpler' pathways giving rise to a range of hydroxylated fluorenes and hydroxylated fluorenones in ice. These results are of importance when considering the fate of PAHs and OH-PAHs in cold regions and their presence in falling snow and the sunlit snowpack.

Keywords: Ice Photochemistry; Hydroxyfluorene; photodegradation kinetics; Effects of main water constituents; Intermediates; Implications for cold environments.

1. Introduction

The occurrence and relevance of organic contaminants in ice and snow, particularly in remote cold environments is receiving growing attention in the scientific literature, with snow/ice serving as a repository as well as a reactive surface for atmospherically deposited species (Na et al. 2011, Fuoco et al. 2012) (Pućko et al. 2015) (Cipro et al. 2017) (Lebedev et al. 2018). There are relatively fewer studies that have investigated pollutant photochemistry in ice or snow and yet this process may be important for determining chemical fate, with sunlit photochemical transformation serving as l an important sink or pathway for organic pollutants (Grannas 2016). Recent studies illustrate the significance of ice and snow as a reactive media for environmental photochemistry Weber et al., 2009(Rowland and Bausch 2011) (Kahan and Donaldson 2010). It has been shown that Arctic, Antarctic and subpolar ice/snow can play an important role in the photochemical transformation of anthropogenic organic contaminants, such as polycyclic aromatic

hydrocarbons (PAHs) (Ram and Anastasio 2009), hydroxy PAHs (OH-PAHs) (Ge et al. 2016a), and benzene (Kahan and Donaldson 2010). Furthermore, photoinduced production of a variety of reactive oxygen species (ROS) from key water constituents, such as dissolved organic matter and nitrate, and the following efficient oxidation of organic pollutants have been reported to occur in sunlit ice/snow (Grannas et al. 2014) (McFall et al. 2018) (Hullar et al. 2012).

Photochemical transformation of organic compounds in ice has been observed, although there are significantly fewer published studies regarding these processes compared with aquatic photochemistry. In surface waters, photochemical degradation is a key process in determining the fate of organic micropollutants, including persistent organic pollutants as well as pharmaceutical and personal care products(Fasnacht and Blough 2002) (Ge et al. 2016b) (Ge et al. 2010) (Yan and Song 2014). In contrast, ice photochemistry is not well documented. Only a few organic pollutants have been studied with regards to their photochemical alteration and fate in sunlit ice (Rowland and Bausch 2011) (Corrochano et al. 2017) (Grannas et al. 2014) (Hullar et al. 2018). Nevertheless, in several studies, differences in photochemical behavior were observed between ice and aqueous solutions.. For example, under the same light irradiation conditions, anthracene (Malley et al. 2017), phenanthrene (Xue et al. 2019), aldrin (Rowland and Bausch 2011), guaiacol (Hullar et al. 2020), methyl-parathion and fenitrothion (Weber et al. 2009) photodegraded more efficiently in ice than in equivalent aqueous solution. Furthermore, the photolysis mechanism of anthracene at ice surfaces appears to be different to that in aqueous solution, with kinetics changing from first-order in water to second-order at ice surfaces (Malley et al. 2017). Given this different behavior, ice photochemistry is interesting and needs to be investigated further as it likely affects the fate and longevity of organic chemicals associated with snow and ice and subsequently affects the quantity and type of chemical released to the wider environment

75 during melt water release.

76   The present study selected two representative OH-PAHs, 2-hydroxyfluorene (2-OHFL) and

77 9-hydroxyfluorene (9-OHFL), to compare their photodegradation kinetics, the effects of key

78 constituents, and to determine transformation products formed in both ice and water.

79 OH-PAHs are newly recognized organic contaminants derived from the hydroxylation of

80 PAHs, through abiotic processes in the atmosphere and biological cellular transformation

81 reactions They have been found in a variety of environmental matrices, such as the

82 atmosphere, surface waters, and even Arctic biota (Barrado et al. 2012) (Itoh et al. 2006)

83 (Pojana and Marcomini 2007). OH-PAHs are commonly used as biomarkers of human

84 exposure to PAHs (Guo et al. 2013), and some of them demonstrate higher toxicity than their

85 parent PAHs (Cochran et al. 2012). Of the widely detected OH-PAHs, 2-OHFL and 9-OHFL

86 are abundant in the environment (Johnson-Restrepo et al. 2008), and 9-OHFL presents

87 photomodified toxicity to *V. fischeri* (Ge et al. 2016b). They are therefore suitable candidates

88 for ice photochemistry studies with the aim of this study to observe the nature of their

89 photodegradation in ice and compare this to ther aqueous behaviour.

90 **2. Materials and methods**

91 **2.1. Chemicals**

92   2-OHFL and 9-OHFL (both purity $\geq$ 98%, chemical structures in Table S1), as well as

93 humic acid sodium salt (HASS, CAS No. 68131-04-4), were obtained from Sigma-Aldrich,

94 Inc.   (Milwaukee,   WI,   USA).   The   derivatization   reagent

95 *N*,*O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) was provided by Agilent Technologies,

96 Inc. All organic solvents (HPLC grade) were purchased from Tedia Company, Inc. Other

97 reagents used were of guaranteed grade. Ultrapure water was prepared using a Milli-Q

98 Millipore system (Waters, USA). Local fresh water and seawater were sampled, filtered and

99 characterized as described in our previous study (Ge et al. 2010). Oasis HLB cartridges

100　(WAT106202) were purchased from Waters, USA.

2.2. Photochemical experiments

102　Aqueous OHFL solutions (C_0 = 0.5 μM) were prepared in MilliQ water with acetonitrile

103　(2% in volume) as a cosolvent, and by addition of water constituents (Cl^-, HASS, NO_3^-, and

104　Fe(III)) when needed. The solutions were divided to two aliquots. To carry out aqueous

105　photolytic reactions, one aliquot was sampled into quartz tubes (vol. 40 mL, dia. 23 mm),

106　placed in a merry-go-round apparatus, and irradiated using a Pyrex-well cooled and filtered

107　high-pressure mercury lamp (500 W) in a fume hood (25°C) (Fig. S1). Pyrex-filtered mercury

108　lamps were usually employed to simulate solar radiation ($λ > 290$ nm) (Dolinová et al. 2006,

109　Ziolli and Jardim 2003, Matykiewiczová et al. 2007). Samples from another aliquot were

110　pipetted into the same tubes, and frozen at -20 °C. The same apparatus and light source were

111　moved in a freezer [-(5 ± 1) °C] to perform ice photochemical experiments. The irradiated

112　samples were taken at predetermined intervals to investigate photolytic kinetics and

113　transformation products. Dark controls were carried out for each batch of the experiment. All

114　the experiments were conducted in triplicate.

2.3. Analytical Determination

116　A Waters UPLC coupled with a BEH C18 column (50 mm × 2.1 mm, 1.7 μm) and a

117　fluorescence detector was employed for the separation and quantification of the OHFL

118　isomers (Ge et al. 2016b) (Ge et al. 2016a). The retention times were 2.76 min and 1.85 min

119　for 2-OHFL and 9-OHFL, respectively. To identify photodegradation products, the sampled

120　solutions (with a volume of 2) were extracted by solid phase extraction, and one half of the

121　extracted samples were derivatized with silylation reagents. The underivatized and derivatized

122　samples were analyzed by GC-MS/MS. The detailed descriptions of sample pretreatment and

123　analytical determination are provided in the Supplementary material.

3. Results and discussion

3.1. Comparison of photolytic kinetics in ices and waters

There was no significant loss of 2-OHFL and 9-OHFL in the dark controls. However, the two OHFLs were susceptible to photodegradation when exposed to the simulated solar irradiation ($\lambda > 290$ nm). The data conformed to exponential decay, indicating that the reaction was first order with respect to OHFL concentrations. The corresponding rate constants (k), half-lives ($t_{1/2}$) and correlation coefficients are provided in Table S2. The k values of 2-OHFL and 9-OHFL in pure-water ice were calculated to be $(8.7 \pm 0.4) \times 10^{-2}$ min^{-1} and $(9.2 \pm 0.7) \times 10^{-3}$ min^{-1}, respectively, indicative of the faster photodegradation of 2-OHFL. This is attributed to higher values of the light absorption coefficient (Fig. S1) and photolytic quantum yield of 2-OHFL than those of 9-OHFL (Ge et al. 2016a).

Phototransformation kinetics of each OHFL in both ice and water were comparatively investigated using the same experimental light irradiation. The logarithmic decay of both chemicals is plotted in Fig. 1, illustrating that the OHFLs underwent faster photodegradation in ice than in the equivalent aqueous solutions under the same irradiation regime. The corresponding k values of 2-OHFL and 9-OHFL were 3.0 and 7.5 times faster, respectively, in pure-water ice than those in pure water (Table S2). This can be attributed to the specific concentration effect caused by freezing the aqueous solutions. Enhanced local concentrations of the OHFL molecules at the grain boundaries of the ice crystals would intensify light absorption and increase the probability of intermolecular reactions (Weber et al. 2009) (Ge et al. 2016b) (Werner et al. 2006). Thus, the overall apparent photolysis was accelerated in ice with the increased k values in pure-water ice compared with pure water. In previous studies, more efficient photodegradation of anthracene (Malley et al. 2017), phenanthrene (Xue et al. 2019), aldrin (Rowland and Bausch 2011), guaiacol (Hullar et al. 2020), methyl-parathion and fenitrothion (Weber et al. 2009) was also found in ice than in equivalent aqueous solutions.
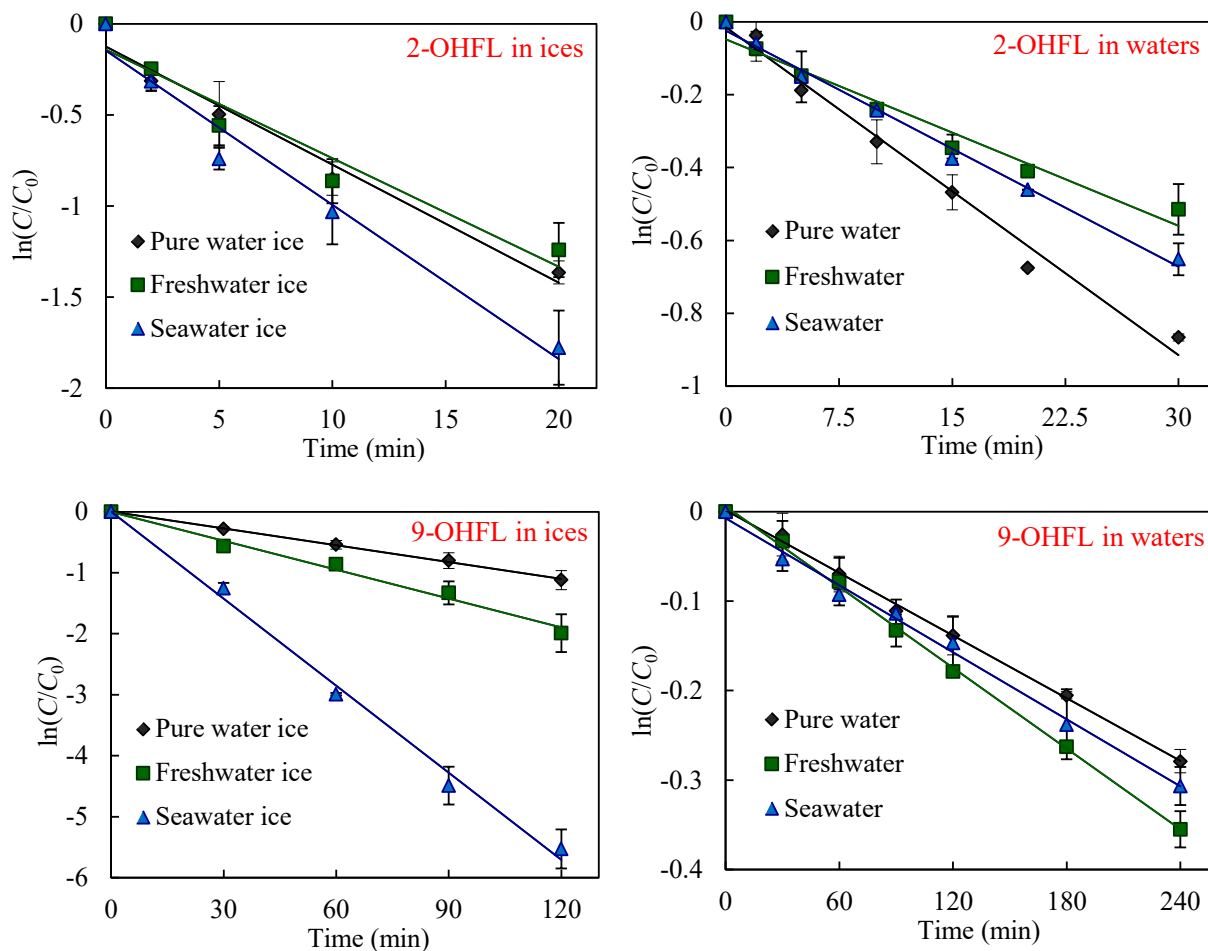
Fig. 1. Logarithmic decay for the photodegradation of 2-hydroxyfluorene (2-OHFL) and 9-hydroxyfluorene (9-OHFL) in ice and water under simulated solar irradiation ($\lambda > 290$ nm)

When comparing the photodegradation of each OHFL in different ice or water types, we found that glacial 2-OHFL photodegraded the fastest in seawater ice, followed by pure water ice and freshwater ice, whereas aqueous 2-OHFL underwent the fastest photodegradation in pure water, followed by seawater and freshwater (Fig. 1). For 9-OHFL, again the photodegradation rates varied markedly between ice and water, with the fastest photodegradation occurring in seawater ice (Fig. 1). From these observations, the photodegradation kinetics of the OHFLs appear to be dependent on the matrix (ice or water), as well as the aqueous constituents. In comparison with pure water, seawater and freshwater have varied water constituents, such as Cl$^-$ (the dominant seawater constituent), humic acid

(HA, main constituent in freshwater), NO_3^- and Fe(III), which are important photoreactive species in sunlit surface waters. Moreover, their photochemical reactivities will be altered when water freezes (Grannas et al. 2014, Fede and Grannas 2015) (Blaszczak-Boxe and Saiz-Lopez 2018). The roles of of these constituents on the OHFL photodegradation were comparatively investigated in both ice and water.

3.2. Effects of main water constituents in different phases

Under the same irradiation conditions the ice/aqueous photodegradation of the two OHFLs, as a function of Cl^-, HASS, NO_3^- and Fe(III) were studied, for which the results are presented in Fig. 2 and Table S2. Based on the profiles of Fig. 2, it was found that these individual constituents exhibited different effects on OHFL degradation in ice and   water. For 2-OHFL, Cl^- first enhanced and then suppressed the ice photolysis with a peak k value at a Cl^- concentration of 0.68 M, whereas the corresponding aqueous photolysis was   retarded by increasing concentrations of Cl^-. Conversely, increasing concentrations of HASS suppressed photodegradation in both ice and water whereas increasing concentrations of NO_3^- and Fe(III) accelerated the photoreaction of 2-OHFL in water and to a lesser extent in ice. For 9-OHFL, increasing concentrations of Cl^- displayed a similar accelerating effect on photolysis in ice but also in water, which for the latter is in contrast to 2-OHFL.   . Incremental increases in the concentrations of HASS and NO_3^- initially increased the rate of photolysis in ice but the highest concentrations of these species suppressed photolysis. The effect of varying concentrations in the aqueous solutions however had a negligible effect on aqueous photodegradation for 9-OHFL, in contrast to 2-OHFL.   . Interestingly, compared to Fe(III) in ice, that led to faster photodecay of 9-OHFL at lower Fe(III) concentrations, Fe(III) present in the aqueous solutions facilitated faster photodecay at increasingly higher concentrations, which was similar to the behavior of 2-OHFL.
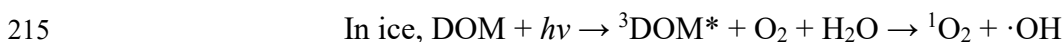
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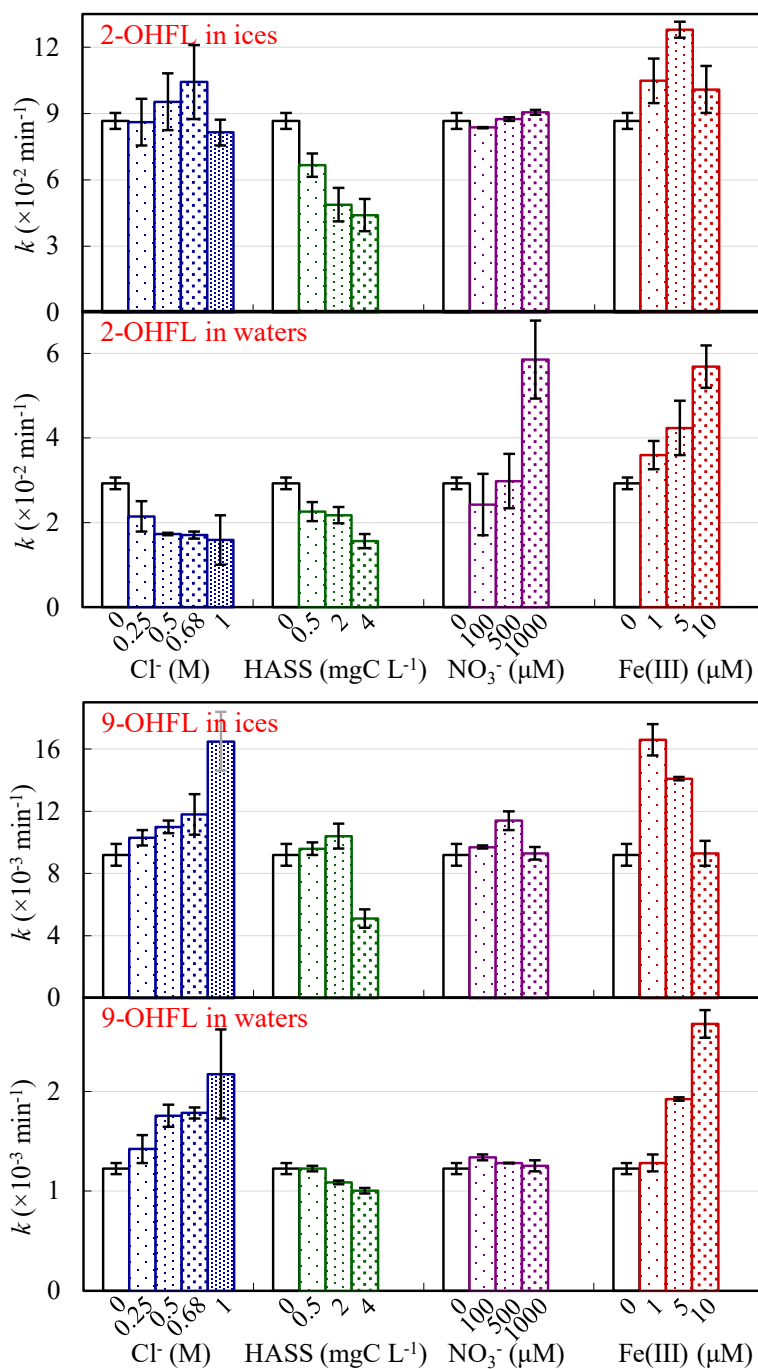
Fig. 2. Effects of aqueous constituents on photodegradation rate constants (k) of 2-hydroxyfluorene (2-OHFL) and 9-hydroxyfluorene (9-OHFL) under simulated sunlight ($\lambda > 290$ nm) irradiation. HASS represents humic acid sodium salt.

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In previous studies, the effects of dissolved constituents on photodegradation of many chemicals are generally reported for one phase only (ice/snow or water) (Li et al. 2018) (Ge et al. 2009) (Ge et al. 2010) (Ge et al. 2014) (Xue et al. 2019). For example, in our group, Ge et

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196   al. examined the effects of key water constituents on the aquatic photochemistry of antibiotics,

197   as well as on ice photodegradation of 9-OHFL (Ge et al. 2010) (Ge et al. 2009) (Ge et al.

198   2014) (Ge et al. 2019). However, in this current study the effects of dissolved constituents on

199   photodegradation in both ice and water have been conducted together, which allows direct

200   comparisons in chemical behavior in a reproducible approach (see Figure 2) and provides

201   confidence that subtle, yet statistically significant differences in the phototransformation rates

202   do occur between ice and liquid aqueous phases.

203   The following interpretation is provided to account for the effects observed by some of the

204   dissolved constituents. Humic acid (HA) impacts the aquatic photochemical behavior of

205   organic chemicals by three processes: competitive photoabsorption; reactive oxygen species

206   (ROS) scavenging; and, sensitization effects. The competitive absorption and sensitization

207   effects could also be caused by NO_3^-, and Fe(III) or Fe(III)-aquo complexes near the light

208   wavelength of 290 nm (Mack and Bolton 1999, Neamtu et al. 2009), although the

209   solar-wavelength cutoff is 295 nm at the Earth's surface. When ice forms from freezing water,

210   these species will be enriched at the grain boundaries of the ice crystals, and their effects may

211   be enhanced in ice compared to aqueous solutions. This process of solute enrichment and

212   effect enhancement for DOM and NO_3^- during freezing has been previously demonstrated

213   (Grannas et al. 2014, Fede and Grannas 2015, Blaszczak-Boxe and Saiz-Lopez 2018), and the

214   relevant reactions are as follows,

215   $$\text{In ice, DOM} + h\nu \rightarrow {}^3\text{DOM*} + O_2 + H_2O \rightarrow {}^1O_2 + \cdot OH$$

216   $$\text{In ice, } NO_3^- + H_2O + h\nu \rightarrow NO_2\cdot + \cdot OH + OH^-$$

217   Chloride ion (Cl$^-$) would have the ·OH scavenging and sensitization effects (Liu et al. 2009,

218   Chiron et al. 2006),

219   $$Cl^- + \cdot OH \rightarrow ClHO^{\cdot-}, ClHO^{\cdot-} + H^+ \rightarrow Cl\cdot + H_2O, Cl\cdot + Cl^- \leftrightarrow Cl_2^{\cdot-},$$

220   where ·OH can be photogenerated in the self-sensitized photooxidation process of OHFLs

221   (Ge et al. 2016b). Chlorine free radicals might be more reactive toward OHFLs than ·OH

222   (Hua et al. 2019), and the effects of Cl^- might also be altered by the freezing process.

223   Besides the above four aqueous constituents, there are many less abundant and photoreactive

224   dissolved species (Table S3). While these minor constituents may also affect the

225   photodegradation kinetics of the OHFLs, it is the major constituents of Cl^-、HA、NO_3^- and

226   Fe(III), (Table S3), that are expected to account for most of the matrix-(ice, water) dependent

227   effects. The stimulatory effect of Cl^- (2.43×10^4 mg L^{-1} ≈ 0.68 mol L^{-1}, Table S3) and Fe(III)

228   on ice photodegradation of the OHFLs may account for the faster photodegradation observed

229   in simulated sea water ice compared with freshwater and pure water ice types However,

230   slower photodegradation of 2-OHFL in simulated natural waters compared to pure water is

231   due to the likely suppressive effects of aqueous Cl^- and HA, although the relative abundance

232   of these constituents may determine whether photodegradation is promoted or suppressed.

233   **3.3. Photochemical transformation products**

234   The model compound 9-OHFL was selected to investigate ice/aqueous phototransformation

235   byproducts and compare the main transformation pathways within ice or water based on the

236   unique GC-MS/MS analysis for both underivatized and derivatized samples. As shown in the

237   total ion chromatograms (Figs. 3 and S2), there are 9 significant transformation products

238   (TP180 ~ TP228), of which the corresponding MS and MS^2 mass spectra after sample

239   underivatization or derivatization are displayed in Fig. S3. Referring to the NIST mass

240   spectral library and the analytical approaches in previous studies (Ukpebor and Halsall 2012)

241   (Ge et al. 2016b) (Ge et al. 2016a) (Lehner et al. 2019), chemical structures were proposed

242   and tentative phototransformation pathways for ice or aqueous 9-OHFL are presented in Fig.

243   3.

244   There are similarities and also differences between the ice photochemical transformation

245   pathways and the water photodegradation pathways (Fig. 3). Under the same irradiation

246 conditions (λ > 290 nm), 9-OHFL transformed via two important initial photoreactions:

247 dehydrogenation and isomerization, both in ice and in water. Keto fluorene (TP180), and

248 single hydroxyl fluorenes (TP182, TP182' and TP182") occurred through the two reactions,

249 respectively. In water (aqueous solutions), these intermediates underwent further

250 photoreactions through multiple hydroxylations, forming double (TP212) and triple

251 hydroxylated fluorenones (TP228) in a stepwise process. In ice, however, these

252 hydroxylated by-products were not detected.

253 Based on photochemical mechanisms proposed for other chemicals in ice and water

254 (Sanches et al. 2011, Kahan and Donaldson 2007) (Klanova et al. 2003) (Ram and Anastasio

255 2009) and the ion chromatograms generated in this study proposed phototransformation

256 pathways are presented in Figure 3. In comparison with aqueous photodegradation of

257 9-OHFL, ice phototransformation exhibited fewer byproducts and simpler pathways,

258 which may be attributed to lower mobility of the chemical molecules in ice. The organic

259 chemicals in the frozen matrix tend to be segregated from the ice phase and are dispersed at

260 the ice grain boundaries or interstitial pores. Thus, their reactivity might be limited and

261 dependent on the interactions between the host water molecules and any constituent

262 substances also present at the ice grain boundaries. (Klanova et al. 2003). This interaction

263 between H_2O and photoexcited 9-OHFL molecules may generate •OH radicals (Ge et al.

264 2016b), however compared with a liquid aqueous phase e, the ice phase might not facilitate

265 the generation of sufficient •OH to induce the multiple hydroxylations observed here. For

266 other chemicals, photochemistry in ice can result in diverse photodegradation

267 intermediates and their corresponding transformation pathways have been reported for

268 monochlorophenols (Klanova et al. 2003) (Bláha et al. 2004) and *m*-cresol (Peng et al. 2012).

269 For example, these relatively smaller monoaromatic molecules, concentrated at ice grain

270 boundaries, appear to be susceptible to photopolymerization reactions (Klanova et al. 2003)

271 (Peng et al. 2012). However, given its relatively larger molecular size, polymerized products

272 were not detected for 9-OHFL in ice.
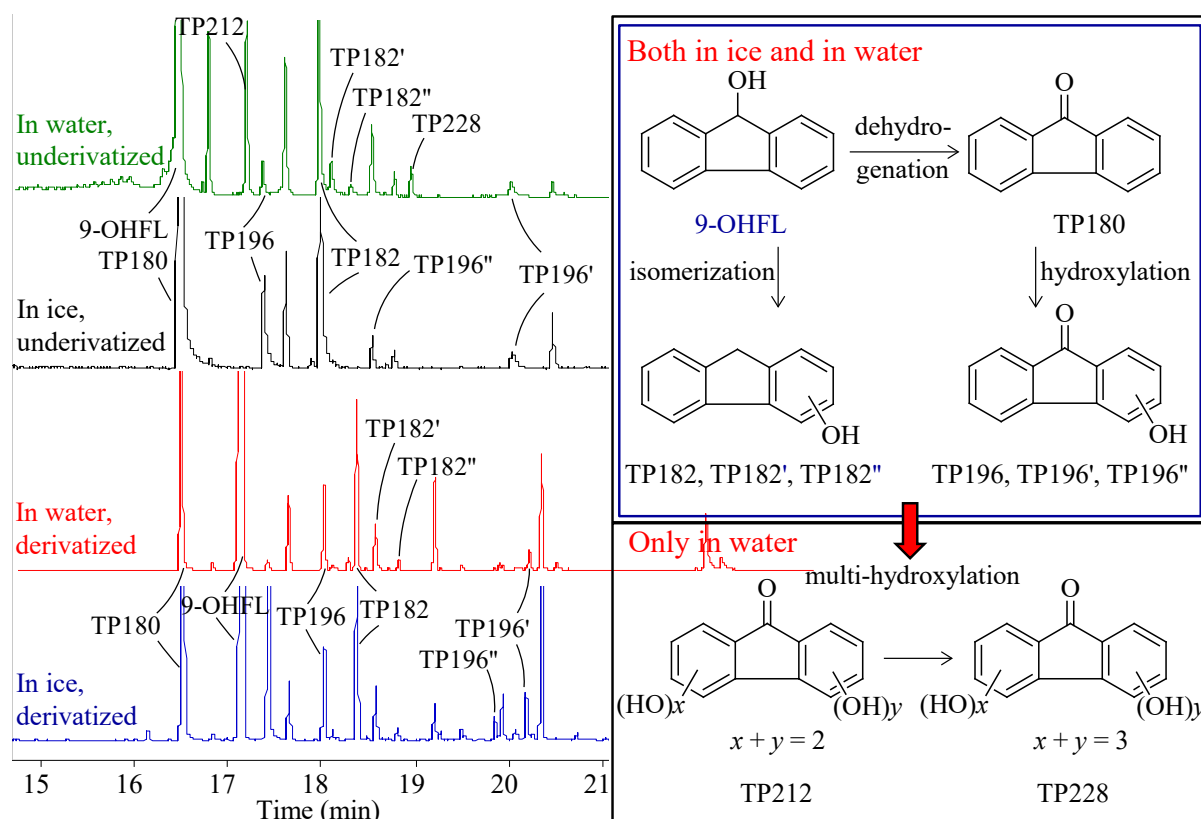
274 Fig. 3. Total ion chromatograms for underivatized and derivatized samples of 9-OHFL in ice and in water

275 after irradiation (λ > 290 nm), as well as the corresponding phototransformation pathways. The

276 transformation products are labeled "TPn", with n standing for the molecular weight.

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278 **4. Conclusion and environmental implications**

279   This study provides a detailed comparison of the ice and aqueous photochemical behavior of

280 widely detected hydroxy PAHs (two hydroxyfluorenes, 2-OHFL and 9-OHFL), and shows

281 that both their photodegradation kinetics and pathways can be greatly influenced by whether

282 they reside in ice or water. The more efficient photodegradation of OHFLs in ice than in

283 equivalent aqueous solutions, is probably attributable to the specific concentration effect

284 where molecules accumulate at ice-crystal boundaries during the freezing process. .

285 Interestingly,   2-OHFL photodegraded the fastest in seawater ice, followed by pure water ice

and freshwater ice, whereas aqueous 2-OHFL underwent the fastest photodegradation in pure water, followed by seawater and freshwater. Different rates of photochemical degradation between water and ice were also apparent for 9-OHFL as well. The experimental design and data analysis demonstrate , like water, the presence of dissolved constituents in ice (Cl^-, HASS, NO_3^- and $Fe(III)$) also appear to play a significant role in the phototransformation of OHFLs. Moreover, compared with aqueous photodegradation, phototransformation in ice exhibited fewer by-products and hence a 'simpler' transformation pathway, which may be attributed to lower mobility of the chemical molecules in ice.

Exposure to simulated sunlight facilitates the photodecay of OH-PAHs particularly in ice. Therefore, environmental photodegradation in cold environments, where ice and snow predominate, is likely to be an important sink, although photochemical half-lives will be dependent on latitude and season (Boreen et al. 2004) (Andreozzi et al. 2004). In high altitude regions at temperate latitudes (e.g. the north Qinling Mountains in China (Huai River region (32°~34° N)) or the European Alps (~46 oN) which are relatively close to anthropogenic PAH sources), then photochemical transformation in snowfall may be an important sink relative to rainfall/surface waters in adjacent low lying regions. It is plausible that photochemical decay in snow and ice is the predominant sink compared to biodegradation and other removal processes in colder regions. Importantly, many of the primary photo byproducts of the OHFLs retaine the core chemical structure of the parent OHFLs, suggesting that these compounds may present similar ecotoxicity and biological activity as the parent chemicals (Ge et al. 2014) (Ge et al. 2019) (Apell et al. 2020).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016.

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