



1 **Litter decomposition enhances volatile organic compound emission from a freshwater**

2 **wetland: insights from year-round in situ field experiments**

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15 **Abstract**

16 Plant litter could be a potential source of atmospheric volatile organic compounds (VOCs).
17 Previous studies are mostly restricted to forest litter, but VOC budget of wetlands, especially
18 freshwater wetlands, resulting from litter decomposition remains largely unexplored. Here we
19 performed in-situ VOC flux measurements in a freshwater wetland and three treatments
20 including A (no litter addition), B (1.4 kg litter) and C (2.8 kg litter) were designed to
21 investigate impacts of litter decomposition on wetland-atmosphere exchange of VOCs.
22 During year-round litter decomposition, average fluxes of net VOCs for B and C were
23 $5.93 \pm 3.13 \mu\text{g m}^{-2} \text{h}^{-1}$ and $8.30 \pm 4.00 \mu\text{g m}^{-2} \text{h}^{-1}$, respectively, significantly higher than that of A
24 ($2.90 \pm 2.74 \mu\text{g m}^{-2} \text{h}^{-1}$). These results suggested that freshwater wetland was a potential source
25 of atmospheric VOCs and litter decomposition enhanced VOC release. Net VOC flux showed
26 clear seasonal patterns and was highly correlated with ambient temperature ($p < 0.05$). In
27 general, higher positive VOC fluxes were observed in hot summer, while lower positive VOC
28 fluxes or negative VOC fluxes were observed in cold winter. Moreover, the release (positive
29 flux) or uptake (negative flux) of VOCs varied to chemical groups. Specifically, non-methane
30 hydrocarbons (NMHCs) including alkanes, alkenes and aromatics showed positive net fluxes,
31 and increased with added litter. Halocarbons showed a negative net flux in A, but positive net
32 fluxes in B and C. While oxygenated volatile organic compounds (OVOCs) showed negative
33 net fluxes in both A and B, and switched to a positive flux in C. Positive net fluxes of volatile
34 organic sulfide compounds (VOSCs) were observed in three treatments. According to flux
35 variations of specific VOC group, it has been suggested that temperature-driven biotic and
36 abiotic processes co-modulated VOC release or uptake occurring in the freshwater wetland.

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38 **Keywords:** Biogenic volatile organic compounds; Fluxes; Litter decomposition; Freshwater
39 wetland; Biosphere-atmosphere exchange

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45 **1. Introduction**

46 Volatile organic compounds (VOCs) play an important role in atmospheric chemistry of
47 troposphere (Toro et al., 2006; Schnell et al., 2009; Chang et al., 2022). Once VOCs are
48 emitted into real atmosphere, they can react with various oxidants (e.g., OH, HO₂ and RO₂) to
49 form ozone (O₃) and secondary organic aerosols (SOA) (Kalashnikov et al., 2022),
50 influencing regional air quality (Li et al., 2019) and climate change (Scott et al., 2014).
51 Although anthropogenic contribution dominates the VOC mass in urban environments
52 (Lamarque et al., 2010), ~ 90% of VOCs is actually from the biogenic source, namely
53 biogenic VOCs (BVOCs), on a global scale (Otter et al., 2003). In addition to the
54 contributions to O₃ and SOA, BVOCs have been revealed to significantly affect natural
55 ecosystems (Fowler et al., 2009; Park et al., 2013). About 1,000 Tg/year of carbon was
56 released into the atmosphere from ecosystems in the form of VOCs (Guenther et al., 2012).
57 These BVOCs could change the specific biogeochemical processes within natural
58 environments through stimulating or inhibiting the growth of plants and microbes (Peñuelas
59 et al., 2014), modulating the cycling of carbon and nitrogen (Smolander et al., 2006; Gray et
60 al., 2014).

61 Considering their great impacts on atmosphere and natural ecosystems, numerous studies on
62 BVOCs have been conducted for decades (Duan et al., 2020). Most of these studies
63 investigated living vegetation and have reported them as important contributors to
64 atmospheric BVOCs. For example, terpenes, mainly isoprene, monoterpenes and
65 sesquiterpenes, emitted by living terrestrial vegetations could account for over 40% of BVOC
66 emissions (Navarro et al., 2014). Compared to living vegetation, studies on VOCs emitted by
67 dead litters, particularly during their long-term decomposition, have been quite limited.
68 Notably, in recent years a growing number of studies have found that the decomposition of
69 dead litter could also release significant VOCs, changing seasonal profile of local or even
70 regional VOCs (Leff and Fierer, 2008; White et al., 2009; Greenberg et al., 2012).
71 Furthermore, Gray et al. (2010) reported that the percentage of OVOCs such as methanol
72 could reach 99% of emitted VOCs during litter decomposition (litter types: deciduous species,
73 evergreen species and dead grass leaves). While Faiola et al. (2014) found that monoterpenes
74 (80.3%) dominated the total VOCs released from leaf litters of coniferous forest. These



75 different research results reflected that the composition of VOCs emitted by litters varied
76 significantly to litter types. In addition, temperature, sunlight, moisture and microbial
77 metabolism have been identified as the key factors affecting uptake or release of VOCs during
78 litter decomposition (Niinemets et al., 2004; Vickers et al., 2009; Zhang et al., 2021; Zeng et
79 al., 2022). However, so far these studies focused on forest litter (Leff et al., 2008; Isidorov et
80 al., 2010; Greenberg et al., 2012; Gray et al., 2014; Faiola et al., 2014; Svendsen et al., 2018)
81 and terrestrial environments (Breider et al., 2015). VOCs emitted during the decomposition of
82 litters from other natural environments are still largely unexplored, inducing the uncertainty
83 of estimating BVOC budget by models (Tang et al., 2019).

84 Wetlands cover only 5%-8% of the land surface but have a disproportionate impact on the
85 global carbon cycle (William et al., 2013; Davidson et al., 2018; Villa et al., 2019; Anderson
86 et al., 2020). Numerous studies concern wetlands mainly due to their well-known roles as the
87 sink of CO₂ and the source of CH₄ (Peng et al., 2022). As previously reported, the global net
88 carbon sequestration from wetlands was 830 Tg/year and meanwhile they also contributed
89 over 20% of global CH₄ emission (Whalen et al., 2005; Bergamaschi et al., 2007; Bloom et al.,
90 2010). However, far less work has been devoted to investigating uptake or release of VOCs in
91 these areas. Although some studies have recently reported VOC fluxes in peat, fen and forest
92 wetlands (Haapanala et al., 2006; Hellén et al., 2018; Jiao et al., 2018; Seco et al., 2020;
93 Männistö et al., 2023), the role of freshwater wetlands in VOC budget is still poorly
94 understood. Moreover, the decomposition of plant litters occurring in the freshwater wetland
95 is a very common natural phenomenon, but how this process affects the uptake or release of
96 VOCs remains unanswered.

97 Herein, we conducted in situ field experiments to measure VOC fluxes during year-round
98 litter decomposition in a freshwater wetland. The entire observation consisted of 11
99 campaigns from January 9 to December 14, 2022. A total of 103 valid samples were obtained
100 during the observation. To the best of knowledge, this is the first-ever result on VOC flux
101 measurements in a freshwater wetland under long-term period of litter decomposition (across
102 four seasons). The objectives of this work are (1) to explore whether the freshwater wetland
103 acts as a potential sink or source of atmospheric VOCs and the effects of litter decomposition,
104 (2) to investigate the seasonal pattern of VOC fluxes and (3) to analyze potential influencing



105 factors modulating VOC fluxes during the litter decomposition. The insights gained from this
106 study can serve as a reference for models or emission inventories to estimate global BVOC
107 emissions and enhance our understanding of the role of freshwater wetlands in reactive VOC
108 budget.

109 **2. Methodology**

110 **2.1 Study area**

111 In-situ field experiments were carried out at Kuihu (KH, 30.32°-31.57° N, 117.67°-118.73° E),
112 a typical freshwater wetland in southeastern Anhui Province (Fig. S1), about 20 km from the
113 city. The total area of KH is 5.05 km² and its wetland area is 4.46 km²
114 (<https://www.wuhu.gov.cn/openness/public/6596211/15236661.html>). Based on previous
115 statistical information, vegetation in local wetland is predominated by *Phragmites australis*
116 (the statistical document is available on request by writing to corresponding author). Here, we
117 thus used *Phragmites australis* litter as typical case to explore the VOC flux variations during
118 the litter decaying in the freshwater wetland.

119 **2.2 Experimental setup**

120 The aim of this study was to investigate that whether the freshwater wetland acts as the sink
121 or source of VOCs and the effects of litter decomposition, thus we selected sunny days and
122 avoid rainy/cloudy days, which could underestimate these VOC emissions (Li et al., 2023), to
123 conduct field measurements. The sampling time of 11 campaigns occurred at around
124 10:00-14:00. As showed in Fig. 1 (a), nine 1.1m × 1.1m × 1.1m (length × width × height)
125 stainless steel cuboidal boxes without the cover were installed in the flooded area of
126 freshwater wetland. The distance between the adjacent boxes was set as one meter. During the
127 experiments, three treatments, namely A, B and C, were designed and each of treatment
128 consisted of three parallel groups. For A, B and C, no plant litter addition, 1.4 kg litter
129 addition and 2.8 kg litter addition, respectively, were treated. Nine nylon mesh bags were
130 attached to each box, as shown in Fig. 1 (b). Each mesh bag in A, B and C contained 0 kg, ~
131 0.156 kg and ~ 0.311 kg litter. The *Phragmites australis* litters were collected directly from
132 Kuihu wetland and weighted by an electronic balance (HY-809B, ZHIZUN, China). Except
133 the litter mass, all settings of the three treatments were kept as constant as possible in our



134 experiments. Moreover, to avoid significant interference on the wetland ecosystem, only
135 *Phragmites australis* above the roots were cleared up and the roots remained in nine boxes as
136 showed in Fig. 1 (b).

137 2.3 Flux measurements

138 In situ static-chamber measurements for VOC fluxes were carried out in this study and more
139 detailed description about this method can be found in our previous studies (Wang et al., 2015;
140 Liu et al., 2021). The chamber (35cm × 35cm × 15cm) made of stainless-steel frames covered
141 with Teflon film was placed inside the cuboid box. The bottom of chamber was installed with
142 a urethane foam board, which allowed chamber to float on the water. Air samples inside the
143 chamber were collected by pre-evacuated 3.2-L silonite-treated stainless steel canisters
144 (Entech Instruments Inc., Simi Valley, CA, USA) at 0 min, 10min and 30min. A Teflon tube
145 extended into the center point of the chamber was used to draw air into the pre-evacuated
146 canister.

147 The calculation of net VOC fluxes was based on following equation:

$$148 \quad Flux = \frac{dC}{dt} \times \frac{V_c}{A_c}$$

149 where $\frac{dC}{dt}$ is the linear regression slope of the chamber headspace VOC concentration ($\mu\text{g m}^{-3}$)
150 versus time (min). V_c (m^3) is the volume of the chamber. A_c (m^2) is the base area of the
151 chamber that floated on the water. In fact, we found that VOC concentration in chamber
152 headspace has already leveled off at 30 min. Thus, here the first two points, which could
153 capture the initial fluxes, were used to calculate VOC fluxes (Zhang et al., 2021).

154 2.4 Laboratory analysis

155 VOCs

156 The air samples were analyzed by a model 7200 pre-concentrator (Entech Instruments,
157 California, USA) coupled to a gas chromatography and mass selective detector (GC/MSD,
158 Shimadzu Corp, Tokyo, Japan). The analysis steps were described in detail elsewhere (Liu et
159 al., 2021; Wang et al., 2023). Briefly, air samples were firstly drawn into a liquid-nitrogen
160 cryogenic trap at -160°C to be trapped and concentrated, then transferred to a secondary trap
161 at -40°C by pure helium. After these two steps, the H_2O and CO_2 were mostly removed.



162 Subsequently, secondary trap was heated, and the VOCs were brought by helium to a third
163 cry-focus trap at $-170\text{ }^{\circ}\text{C}$. Once air samples were focused, the third trap was heated rapidly to
164 be transferred into GC/MS system for further VOC analysis. The mixture was separated by a
165 DB-1 capillary column ($60\text{m} \times 0.32\text{mm} \times 1.0\text{ }\mu\text{m}$, Agilent Technologies, USA) with helium
166 as carrier gas. The initial oven temperature was set as $10\text{ }^{\circ}\text{C}$, kept 3 min, then increased to
167 $120\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C min}^{-1}$, and then changed to $10\text{ }^{\circ}\text{C min}^{-1}$, finally reached at 250, held for 2 min.
168 MSD was operated in SCAN model with electron impacting (EI, 70 eV) as the ionization
169 method here. The Text S1 in supplement provided the information about quality assurance
170 and quality control (QA/QC).

171 ***CH₄ and CO₂***

172 CH₄ and CO₂ were measured from canister air samples by gas chromatography (GC-2014,
173 Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID). CH₄ was directly
174 detected by FID. While CO₂ firstly was converted to CH₄ by flushed with H₂ through hot
175 nickel power catalyst, then detected by FID (Miao et al., 2022).

176 **3. Results and discussion**

177 **3.1 Overview of VOC fluxes**

178 Throughout the entire in-situ observation, 62 VOCs including 19 alkanes, 11 alkenes, 5
179 aromatics, 15 OVOCs, 9 halocarbons and 3 VOSCs were detected and quantified in this study
180 (Table S1). From the Table 1, regarding total net fluxes, three treatments all presented positive
181 VOC fluxes, suggesting that the freshwater wetland could be a potential source of
182 atmospheric VOCs. Obviously, as showed in Table 1, litter decomposition enhanced the VOC
183 emissions from freshwater wetland. The average values of total net VOC fluxes measured in
184 B and C were $5.93 \pm 3.13\text{ }\mu\text{g m}^{-2}\text{ h}^{-1}$ and $8.30 \pm 4.00\text{ }\mu\text{g m}^{-2}\text{ h}^{-1}$ (average \pm standard error),
185 respectively, ~ 2.04 times and ~ 2.86 times that of A ($2.90 \pm 2.74\text{ }\mu\text{g m}^{-2}\text{ h}^{-1}$). The effects of
186 litter decomposition varied depending on VOC groups. For example, net fluxes of alkanes and
187 alkenes measured in C were unexpectedly lower than in B. Moreover, the net flux of
188 halocarbon measured in B was similar to that in C. These results reflected that besides the
189 litter mass, other factors such as microbe activities (Lorah et al., 1999; Leff et al., 2008; Gray
190 et al., 2014; Jiao et al., 2018; Svebdsen et al., 2018), which were discussed in detail in *Section*
191 3.3, might also affect the VOC fluxes measured in our experiments.



192 From the Table 1, both halocarbons and OVOCs showed net uptake into wetland in A. When
193 inputting the litters, halocarbons shifted from net uptake into wetland to net positive efflux
194 out of wetland. OVOC fluxes in A and B were both negative but showed a positive value in C,
195 indicating that litter decomposition could be one of the crucial factors determining whether
196 the freshwater wetland was a net source or a net sink of atmospheric OVOCs. As showed in
197 Fig. 2, litter decomposition apparently affected the compositions of VOCs released from
198 freshwater wetland. Notably, aromatic, a typical class of anthropogenic air pollutant, was the
199 dominant VOC group released from freshwater wetland, accounting for 40.6%, 40.4% and
200 46.3% of total VOC emissions in A, B and C, respectively (Fig. 2). Recently, several studies
201 gave the evidence of biogenic aromatic emission from living plants, straw, cyanobacteria and
202 ocean phytoplankton (White et al., 2009; Rocco et al., 2021; Liu et al., 2021; Wohl et al.,
203 2023; Wu et al., 2023).

204 As Fig. S2 shows, during the year-round observation, the fluxes of VOC-driven carbon (C_{VOCs})
205 in freshwater wetland averaged 2.47 ± 1.84 , 4.69 ± 2.11 and 6.36 ± 2.78 $\mu\text{gC m}^{-2} \text{h}^{-1}$ in A, B and
206 C, respectively. The C_{VOCs} accounted for $< 0.05\%$ of the carbon driven from CO_2 and CH_4 . In
207 comparison to CO_2 and CH_4 , VOC emission was not a significant pathway for wetland-carbon
208 transporting into atmosphere. However, given their relatively higher reactivities, these VOCs
209 preferentially reacted with OH radicals once being released into atmosphere from freshwater
210 wetland. This would prolong the atmospheric lifetime of CH_4 , thus accelerating global
211 warming. While global warming would in turn lead to greater release of VOC from the
212 freshwater wetland as temperature was linearly correlated with VOC emission according to
213 the discussion in *Section 3.2*. It is clear from Fig. S3 that these above-mentioned processes
214 would develop a vicious circle.

215 Previous studies also revealed that the wetland environment was a source of atmospheric
216 VOCs, but what these studies mostly investigated were living plants and focused on the fens
217 (Hellén et al., 2020; Seco et al., 2020; Vettikkat et al., 2023). As showed in Table S2, the net
218 VOC fluxes measured in this study, representing the freshwater wetland, were lower than
219 those obtained in fens. It could be realized that VOC emissions from fens were dominated by
220 isoprene, with fluxes ranging from 2.5 $\mu\text{g m}^{-2} \text{h}^{-1}$ to 4773.6 $\mu\text{g m}^{-2} \text{h}^{-1}$. These were quite
221 different from the results uncovered by our observation. The difference could be attributed to



222 the variety of sampling, analysis methods and detected VOC species among the studies on the
223 one hand and to the wetland types on the other hand. In the present work, our experiments
224 were carried out in flooded areas of the freshwater wetland and focused on dead litter
225 decomposition, while earlier studies focused on relatively drier environments and living
226 plants. Baggesen et al. (2022) pointed out that flooded condition would result in a negative
227 net VOC flux and even overruled other effects. In addition, the GC/MSD technique used here
228 failed to fully characterize higher molecular weight species, such as monoterpene, and lower
229 molecular weight species, such as methanol, which have been reported to be released in
230 significant amounts during the decomposition of litter (Gray et al., 2010; Faiola et al., 2014).

231 **3.2 Seasonal patterns**

232 As shown in Fig. S4, the net VOC fluxes measured in three treatments all demonstrated
233 significant seasonal variations. VOC uptake from air to wetland generally occurred in cold
234 winter while net VOC emissions were found in warm and hot seasons. The highest VOC
235 emission was found in hot summer, followed by spring and fall. The overall seasonal pattern
236 of VOC fluxes observed here was similar with the previous studies conducted in wetland
237 environments (Hardacre et al., 2013; Seco et al., 2020).

238 In spring, as Fig. 3 shows, positive net VOC fluxes were showed in three treatments during
239 the samplings conducted in March and April. However, the negative net VOC flux was found
240 in A and the positive net VOC fluxes of B and C were also significantly lower observed in
241 May than those measured in prior two samplings, which could be attributed to the sharp drop
242 in temperature (-6.6 °C). As shown in Fig. 3, VOC emission enhanced by litter decomposition
243 were much remarkable in hot summer. Considering that temperature was the key factor
244 driving the seasonal patterns of VOC fluxes measured during the experiments, we further
245 analyzed the relationships of net VOC fluxes with ambient temperature. As shown in Fig. 4,
246 VOC fluxes presented significant positive correlations with temperature ($p < 0.05$) in three
247 treatments. According to the linear fitting equations showed in Fig. 4, VOC uptake from air
248 into wetland generally occurred at lower temperature (< 10 °C), and similar VOC uptake was
249 found between B and C, both presenting less VOC uptake than A. In fact, lower temperature
250 would limit microbial activities and was an unfavorable condition for decaying litters



251 (Greenberg et al., 2012; Gray et al., 2014). Thus, higher VOC uptake measured in A could be
252 mainly caused by abiotic process (Gray et al., 2014). Compared to A, the litter added in B and
253 C covered the water surface, preventing VOC uptake from ambient air into wetland.
254 Moreover, slow decaying of litter in B and C possibly also occurred even under low
255 temperature. This process might release some VOCs into ambient air and offset part of VOC
256 uptake, thus resulting in B and C lower net negative VOC fluxes than that showed in A. As
257 displayed in Fig. 4, the slopes of linear fitting equation were 0.72 and 0.81 for B and C,
258 respectively, higher than that of A (0.63). This further clarified that litter decomposition would
259 stimulate VOC emission from freshwater wetland and suggested that the positive effect of
260 litter decomposition was amplified by higher temperature.

261 In fall, it was worth noting that the negative VOC flux was measured in September (25.9 °C),
262 while positive VOC flux was found in October despite of its relatively lower temperature
263 (16.1 °C). This reflected that in addition to ambient temperature, the uptake or release of
264 VOCs could be influenced to some extent by other factors, thus seasonal variations of the net
265 VOC fluxes could be the combined results of these complicated factors.

266 **3.3 The flux variations of specific VOC groups**

267 As mentioned in *Section 3.1*, uptake or release of VOCs varied to their chemical groups. Here,
268 the measured fluxes of different VOC groups were analyzed in detail to explore the potential
269 factors determining their release or uptake.

270 **3.3.1 Alkanes**

271 Overall, freshwater wetland was the potential source of atmospheric alkane, as positive net
272 fluxes were measured in three treatments during the year-round observation (Table 1). For A,
273 B and C, alkanes accounted for 23.3%, 20.4% and 13.8% of total VOC emissions,
274 respectively (Fig. 2), which were comparable to that previously reported in decomposition of
275 tree leaf (~ 20%) (Svendsen et al., 2018; Viros et al., 2020). The emission percentage of
276 alkane showed a decreasing trend with litter addition, suggesting that alkane might not be the
277 dominant VOC composition emitted during litter decomposition in freshwater wetland. In
278 general, higher temperature would stimulate microbe activities and accelerate litter decaying,
279 further leading to more VOC release (Isidorov et al., 2002; Jiao et al., 2018; Svendsen et al.,
280 2018). However, from the Fig. 5, it was interesting that B and C presented higher alkane



281 emissions than A during the period with relatively lower temperature, while nearly equal
282 amounts of alkane emissions were observed in three treatments in hot July. This result
283 suggested that higher alkane emission in July might not be mainly resulting from litter
284 decomposition. Previous studies have revealed that alkanes can be stored in the upper cuticle
285 layer of vascular species (Bondada et al., 1996; Barik et al., 2004). Thus, during the initial
286 period of litter decomposition (lower temperature), higher emission fluxes of alkane measured
287 in B and C might be mainly due to the material composition of the litter itself rather than
288 resulting from the litter decomposition. Notably, in subsequent experiments such as those
289 conducted in March, June and July, relatively higher alkane emission was measured in A,
290 even comparable to that in B and C. This suggested that litter decomposition might not be
291 main source of alkanes and that other alkane-emitted sources might also exist in freshwater
292 wetland. In fact, earlier studies have found that root-emitted VOCs could act as chemical
293 signals belowground and be transported from the source (Delory et al., 2016). Root exudation
294 in the rhizosphere contained numerous chemicals like lower-molecular-weight organic acids,
295 which were reported to be the precursors of biogenic alkanes (Maffei, 1994; Viros et al.,
296 2020). Considering that the roots of *Phragmites australis* were not removed in our
297 experiments (Fig. 1), root emission might be an alkane source, which needed more
298 investigations in future to explore and confirm this.

299 3.3.2 Alkenes

300 From the Table 1, freshwater wetland was the source of atmospheric alkenes and litter
301 decomposition positively stimulated alkene release from the wetland. In contrast to alkanes,
302 relatively lower alkene emission, as displayed in Fig. 5, was observed in the initial stage of
303 litter decomposition, and meanwhile the effect of litter decomposition was not significant.
304 However, in hot July, alkene emission was much higher in B and C than that in A, suggesting
305 that alkene emission arising from litter decomposition was reinforced by higher temperature.
306 It was worth noting that similar alkene emissions were found between B and C in hot July,
307 suggesting that besides litter mass, alkene flux was also subject to other factors such as
308 microbial activities (Svendsen et al., 2018). Additionally, alkene flux measured in A was
309 similar from March to July except April when the temperature dropped sharply. It has been
310 previously reported that alkenes are the fatty acid derivatives in natural environments (Maffei,



311 1994; Viros et al., 2020), and thus root exudates and wetland microbes which were likely to
312 produce fatty acid might also contribute to the alkenes.

313 **3.3.3 Aromatics**

314 Traditionally, aromatic hydrocarbons (AHs) have been regarded as anthropogenic air
315 pollutants (Barletta et al., 2005; Kansal et al., 2009; Lamarque et al., 2010). However,
316 biogenic emission of AHs has attracted attention from atmospheric science community and
317 has been reported in recent studies (White et al., 2009; Misztal et al., 2015). During the
318 experiments, we also detected six AHs and found that they were even the largest VOC species
319 released from the freshwater wetland. From the Fig. 2, the percentage of AHs increased with
320 litter addition. Moreover, throughout the entire observation, AH fluxes measured in B and C
321 were higher than that in A (Table 1). These results reflected that litter decomposition could
322 enhance AH release from the freshwater wetland. In terms of individual AH species, as
323 showed in Fig. S5, we found that m/p-xylene was the largest AH species in A, while toluene
324 ranked No.1 contributor to total AH emission in B and C. This suggested that litter
325 decomposition could release more toluene than other detected AH species. Biogenic AH
326 emissions, particularly for toluene, have been observed in terrestrial, aquatic and marine
327 ecosystems (Liu et al., 2021; Rocco et al., 2021; Wohl et al., 2023; Wu et al., 2023). Previous
328 studies reported that AHs were emitted during the decomposition of tree leaf, but only
329 accounted for < 10% of total VOC emission (Faiola et al., 2014), quite different from our
330 results (> 40%, Fig. 2). Two explanations could be that, on the one hand, AH emission could
331 vary depending on litter types (Gray et al., 2010) and, on the other hand, that previous studies
332 investigated litter decomposition in aerobic environments, while our experiments were
333 conducted in flooded, relatively low-oxygen circumstances. A recent study measured VOC
334 emission during straw decomposition and found that AH emission could reach over 3 times
335 higher under flooded conditions than under non-flooded conditions (Wu et al., 2023).
336 Additionally, earlier studies revealed that biogenic toluene is preferentially produced under
337 anaerobic conditions (Jüttner and Henatsch, 1986; Mcrowiec et al., 2005; Moe et al., 2018).
338 Therefore, in our experiments, the low-oxygen environment could be favorable for biogenic
339 AH production.

340 **3.3.4 Halocarbons**



341 Overall, net halocarbon emission was relatively lower, accounting for 7.2% and 5.9% of total
342 VOC emission in B and C, respectively (Table 1). A negative flux was measured in A,
343 suggesting that the freshwater wetland could be the net sink of halocarbon. Undoubtedly, litter
344 decomposition enhanced the halocarbon emission, especially in hot July and August, but the
345 emission did not fully follow the seasonal patterns. As showed in Fig. 5, both B and C still
346 presented significant halocarbon emissions in October, and even in November, when the
347 ambient temperature was below 10 °C, halocarbon emission in C was comparable to that
348 measured in hot July. These results suggested that halocarbon emission was not majorly
349 controlled by temperature. Natural emissions of halocarbons have been previously reported in
350 marine (Philip et al., 1985), soil (Albers et al., 2017) and forest wetland (Jiao et al., 2018).
351 Typical halocarbon species emitted from natural source such as methyl chloride (CH₃Cl) and
352 chloroform (CHCl₃) were also detected in our experiments. Both CH₃Cl and CHCl₃ have been
353 reported to be formed through biotic (enzymatic reactions) (Rhew et al., 2003) and abiotic
354 processes (nonenzymatic Fenton-like reactions) (Huber et al., 2009). Jiao et al. (2018)
355 revealed that abiotic factor dominated the CHCl₃ emission in forest wetland, while microbial
356 activities controlled the CHCl₃ production in Antarctica tundra soils (Zhang et al., 2021).
357 These conflicting results reported by earlier studies reflected that biogeochemical process of
358 natural halocarbon were very complicated and varied to natural environments. During our
359 experiments, the CH₃Cl fluxes in A, B and C were -0.08±0.12, 0.27±0.12 and 0.39±0.12 μg
360 m⁻²h⁻¹, respectively, but CHCl₃ was undetectable in many measurements. Both the net total
361 halocarbon fluxes and CH₃Cl did not show significant correlations with ambient temperature
362 (Table S3), which was in line with the consequence reported by Jiao et al. (2018). This
363 suggested that halocarbon emission from freshwater wetland might be predominantly
364 controlled by abiotic process rather than temperature-dependent microbial activities (Gray et
365 al., 2014).

366 3.3.5 Oxygenated volatile organic compounds

367 Unlike other VOCs, OVOCs presented uptake in most flux measurements conducted in the
368 freshwater wetland (Fig. 5). This was quite different from previous studies on the
369 decomposition of tree leaf litter, which released large amounts of OVOCs. For example, Gray
370 et al. (2010) reported that OVOCs accounted for over 99% of total VOC emissions during



371 plant litter decomposition. However, the litter decomposition investigated in these previous
372 studies generally took place in dry terrestrial environments or in laboratory incubations, while
373 our experiments were conducted in freshwater wetland under flooded conditions. As we know,
374 most OVOCs were polar organic molecules including alcohols, carbonyls and organic acids,
375 which are water soluble (Baggesen et al., 2022). Bourtsoukidis et al. (2018) reported that soil
376 could shift between methanol release when dry and methanol uptake when wet. OVOC
377 deposition was also found in early morning due to dew (Schallhart et al., 2016). Moreover,
378 previous studies reported OVOC uptake in ocean and lake environments (Seco et al., 2020;
379 Liu et al., 2021). Even in hot July, OVOCs such as acetone and acetaldehyde showed negative
380 net fluxes in the field observation of freshwater (Seco et al., 2020). Thus, even if OVOCs
381 could be produced during our field experiments, they were likely to dissolve in the water.
382 From the Fig. 5, three treatments all displayed OVOC uptake at initial stage (January) of litter
383 decomposition. On January 9th, the highest and lowest OVOC uptake was observed in A and
384 C, respectively, while completely opposite results were observed on January 21st. As known,
385 OVOCs can be consumed by microbes (Männistö et al., 2023). For B and C, litter
386 decomposition over time could provide a carbon source for microbes (Albers et al., 2018) and
387 increase their amounts and activities, further enhancing OVOC consumption by microbes.
388 This could result in increasing uptake of airborne OVOCs into freshwater wetland. It was
389 worth noting that in hot July, three treatments all presented positive flux values of OVOCs,
390 indicating that OVOCs actually could be produced in freshwater wetland. However, this
391 production might be hidden by its sink such as dissolution in water, microbial uptake and
392 abiotic deposition due to the concentration gradient between wetland and atmosphere
393 (Niinemets et al., 2014; Alber et al., 2017; Rinnan et al., 2020). Further, litter decomposition
394 enhanced OVOC emission in hot July. Although higher temperature could accelerate
395 microbial decomposition of litter and release more OVOCs, considering their water solubility,
396 higher OVOC emission fluxes were likely the outcome of strong evaporation, a typical abiotic
397 process (Leff and Fierer, 2008), in hot July.

398 **3.3.6 VOSCs**

399 In this study, we detected three VOSC species including dimethyl sulfide (DMS), dimethyl
400 disulfide (DMDS) and dimethyl trisulfide (DMTS), which were widely measured in aquatic



401 ecosystems (Liu et al., 2021). During the entire observed period, VOSC release from
402 freshwater wetland were found in three treatments (Table 1) and DMS dominated the VOSC
403 emission, accounting for $78.8 \pm 2.9\%$ (Fig. 6). Overall, litter addition enhanced VOSC
404 emissions from the freshwater wetland. However, as Fig. 5 shows, an abnormal phenomenon
405 was observed in August, which presented highest VOSC emission in B, followed by A and C.
406 As previously reported, VOSCs were generated from microbial metabolism of methionine and
407 cysteine (Achyuthan et al., 2017). Thus, all of these could produce methionine and cysteine
408 such as organics dissolved in water were probably responsible for higher VOSC emission in B
409 in August. As Fig. 5 shows, significant VOSC emission was still found in October ($T=16.1^\circ\text{C}$)
410 solely under the B and C, similar to that of AHs, halocarbons and OVOCs. This could be
411 attributed to the consequence of litter decomposition by microbes.

412 **4. Conclusions and limitations**

413 In this study, in situ flux measurements of VOCs were conducted in a freshwater wetland
414 during year-round litter decomposition. Three treatments including A (no litter addition), B
415 (1.4 kg litter) and C (2.8 kg litter) were designed to investigate the impacts of litter
416 decomposition on VOC fluxes measured during the field experiments. As a result, the net
417 TVOC fluxes measured in A, B and C were 2.90 ± 2.74 , 5.93 ± 3.13 and $8.30 \pm 4.00 \mu\text{g m}^{-2} \text{h}^{-1}$,
418 respectively, suggesting that the freshwater wetland was a potential source of atmospheric
419 VOCs and litter decomposition could enhance its net VOC release. Although revealed as the
420 source of VOCs in terms of net total flux, uptake or release of VOCs observed in freshwater
421 wetland varied depending on the specific VOC chemical groups. NMHCs and VOSCs both
422 showed positive net fluxes in three treatments. Halocarbons presented a negative net flux in A
423 and shifted to positive fluxes in B and C. Due to their water solubility, OVOCs measured here
424 mostly presented uptake in the wetland, and their fluxes were found to be negative in A and B,
425 but turn to be positive in C. This reflected that litter decomposition could result in freshwater
426 wetland becoming a source of atmospheric OVOCs. In line with previous studies on BVOC
427 emissions, net TVOC flux showed significant seasonal patterns. In three treatments, the
428 highest positive fluxes were observed in hot summer, followed by spring and fall, while the
429 negative net VOC fluxes were generally found in cold winter. Moreover, VOC emission
430 increasement resulting from litter decomposition exhibited monotonically increasing with



431 litter mass in the seasons except for fall, of which the highest flux presented in B, followed by
432 C and A. In three treatments, net VOC fluxes were significantly correlated with ambient
433 temperature ($p < 0.05$). Based on detailed analysis for flux variations of different VOC groups,
434 biotic and abiotic processes driven by temperature co-modulated VOC fluxes measured in
435 freshwater wetland.

436 Overall, our study provides some new insights into the role of freshwater wetland in reactive
437 VOC budget. The results gained from this work could be indicative for current models
438 simulating BVOC emission as well as for biogeochemical process of reactive VOCs. Of
439 course, there are some limitations in this work that should be pointed out. First, our
440 measurements were all performed in daytime using off-line canister sampling. In future,
441 online observations considering both daytime and nighttime VOC fluxes are needed to
442 elucidate the role of the freshwater wetland in VOC budget more comprehensively. In
443 addition, we did not directly link the measured VOC fluxes to specific microbes in this study.
444 The next step should focus on the key microbes related to the release or uptake of VOCs and
445 uncover more detailed biogeochemical mechanisms of VOCs in freshwater wetlands.

446



447 **Data availability**

448 All raw data can be provided by the corresponding author upon request.

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454 **Competing interests**

455 The contact author has declared that none of the authors has any competing interests.

456 **Author contributions**

457 H.F., S.M., F.Z., J.Z., Z.Y., H.X., Y.H. conducted the field experiments and collected the
458 samples. H.F., S.M., Q.J., J.Z. analyzed the samples. H.F., S.M., T.W., F.Z., J.Z. designed the
459 experiments. H.F., T.W. provided the funding supports. H.F. wrote the paper. T.W., and X.W.
460 revised the paper.

461



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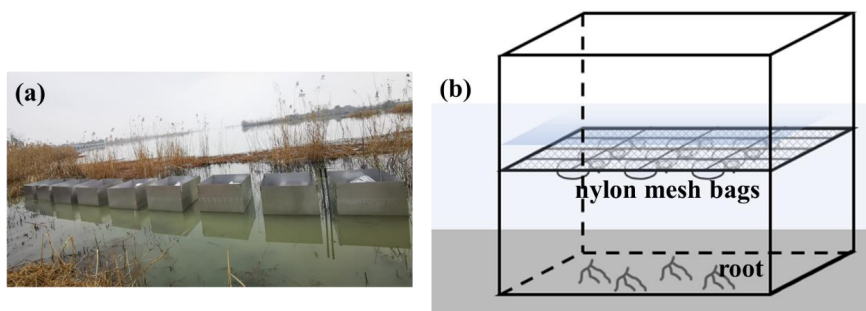
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734 **Table 1.** The net fluxes (mean \pm standard error) of different VOC groups under A, B and C
735 treatments (unit: $\mu\text{g m}^{-2} \text{h}^{-1}$) based on 11 campaigns during one-year litter decomposition.
736 Each treatment consists of three parallel groups. The number of measured compounds is
737 given in parentheses.

	A (No litter addition)	B (1.4 kg litters)	C (2.8 kg litters)
Alkanes (19)	0.76 \pm 0.35	1.45 \pm 0.48	1.20 \pm 0.64
Alkenes (11)	0.55 \pm 0.29	1.40 \pm 0.37	1.28 \pm 0.41
Aromatics (5)	1.33 \pm 0.68	2.86 \pm 0.84	4.02 \pm 1.04
Halocarbons (15)	-0.09 \pm 0.18	0.51 \pm 0.17	0.43 \pm 0.20
OVOCs (9)	-0.02 \pm 1.65	-0.07 \pm 1.73	0.64 \pm 2.48
VOSCs (3)	0.64 \pm 0.40	0.88 \pm 0.50	1.03 \pm 0.22
Σ	2.90 \pm 2.74	5.93 \pm 3.13	8.30 \pm 4.00

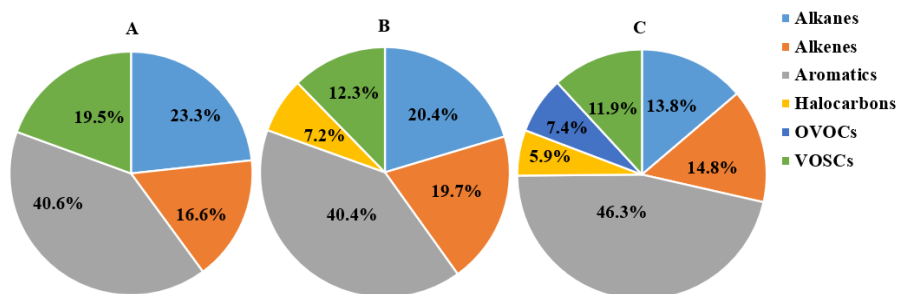
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740 **Figure 1.** Nine stainless steel cuboidal boxes without the cover in freshwater wetland (a). The
741 schematic diagram of cuboidal box was displayed in (b). Each treatment, namely A, B and C,
742 consists of three parallel groups.

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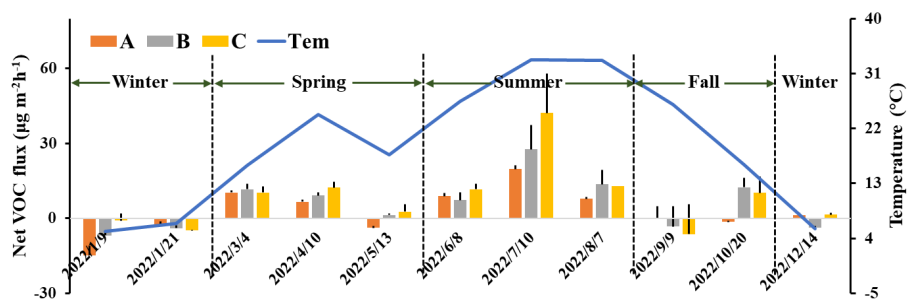


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745 **Figure. 2** Chemical compositions (mass percentage) of net VOC emissions under A, B and C

746 treatments.

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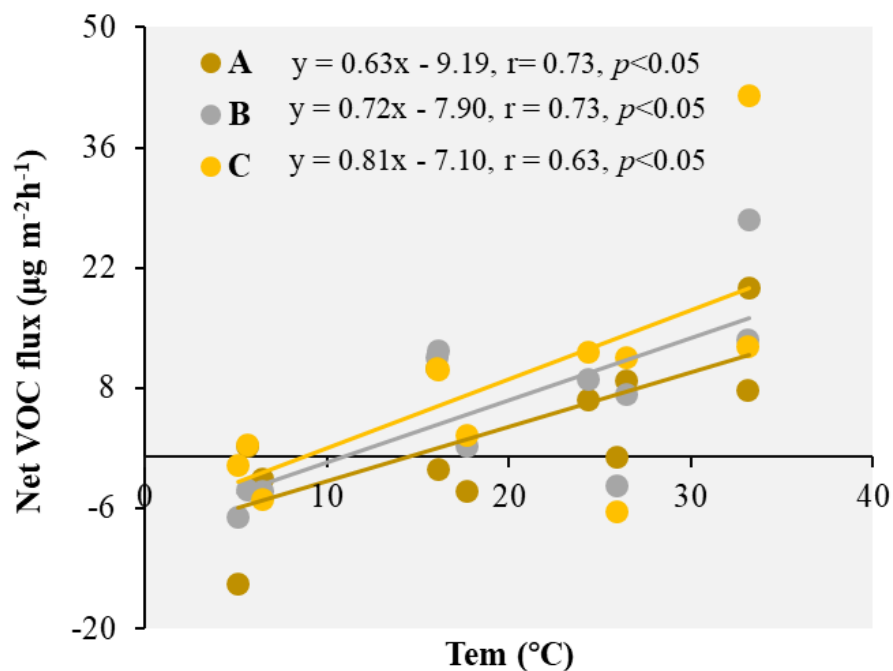
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Figure 3. Seasonal variations of net VOC fluxes under three treatments. The error bar (if

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more than two values) represents standard error of three parallel samples.

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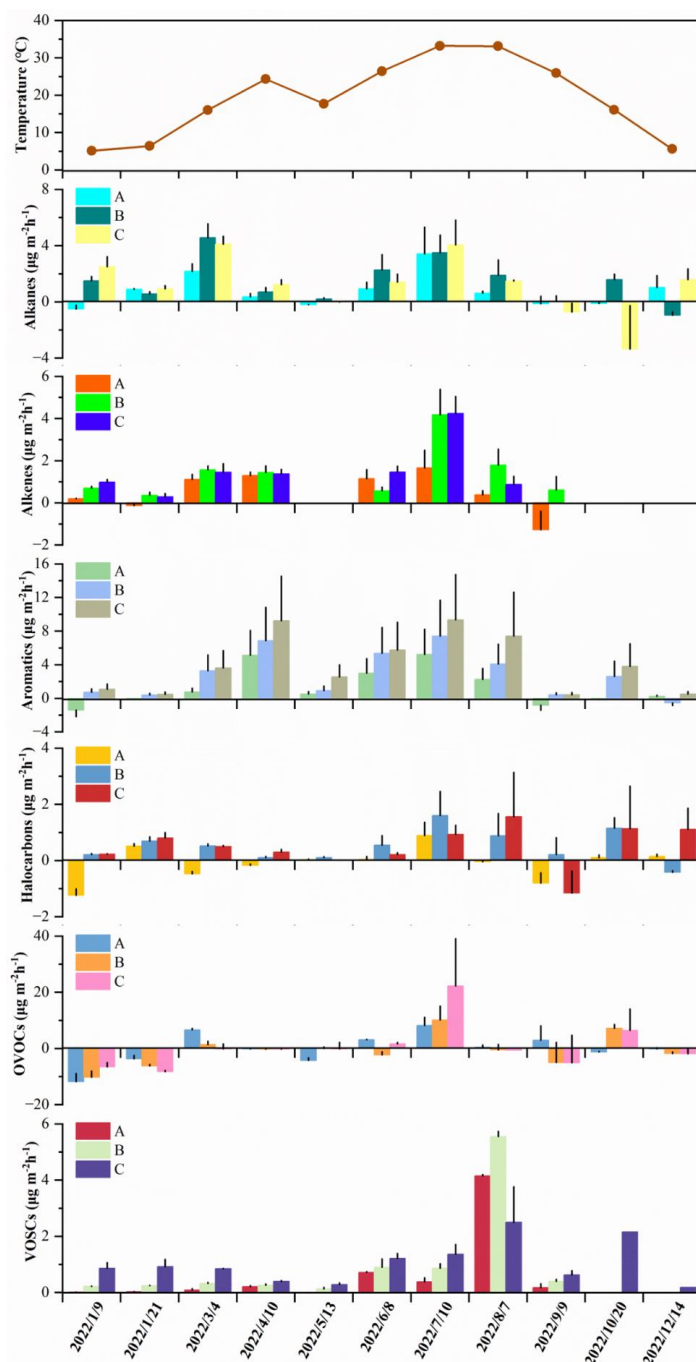


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753 **Figure 4.** The relationships of net VOC fluxes with ambient air temperature (Tem) during

754 one-year litter decomposition.

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Figure 5. The time series of air temperature and fluxes of different VOC groups. The error bar (if more than two values) represents standard error of three parallel samples.