Litter decomposition enhances volatile organic compound emission from a freshwater wetland: insights from year-round in situ field experiments

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Abstract

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

Keywords: Biogenic volatile organic compounds; Fluxes; Litter decomposition; Freshwater wetland; Biosphere-atmosphere exchange
1. Introduction

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry of troposphere (Toro et al., 2006; Schnell et al., 2009; Chang et al., 2022). Once VOCs are emitted into real atmosphere, they can react with various oxidants (e.g., OH, HO\textsubscript{2} and RO\textsubscript{2}) to form ozone (O\textsubscript{3}) and secondary organic aerosols (SOA) (Kalashnikov et al., 2022), influencing regional air quality (Li et al., 2019) and climate change (Scott et al., 2014). Although anthropogenic contribution dominates the VOC mass in urban environments (Lamarque et al., 2010), ~90% of VOCs is actually from the biogenic source, namely biogenic VOCs (BVOCs), on a global scale (Otter et al., 2003). In addition to the contributions to O\textsubscript{3} and SOA, BVOCs have been revealed to significantly affect natural ecosystems (Fowler et al., 2009; Park et al., 2013). About 1,000 Tg/year of carbon was released into the atmosphere from ecosystems in the form of VOCs (Guenther et al., 2012). These BVOCs could change the specific biogeochemical processes within natural environments through stimulating or inhibiting the growth of plants and microbes (Peñuelas et al., 2014), modulating the cycling of carbon and nitrogen (Smolander et al., 2006; Gray et al., 2014).

Considering their great impacts on atmosphere and natural ecosystems, numerous studies on BVOCs have been conducted for decades (Duan et al., 2020). Most of these studies investigated living vegetation and have reported them as important contributors to atmospheric BVOCs. For example, terpenes, mainly isoprene, monoterpenes and sesquiterpenes, emitted by living terrestrial vegetations could account for over 40% of BVOC emissions (Navarro et al., 2014). Compared to living vegetation, studies on VOCs emitted by dead litters, particularly during their long-term decomposition, have been quite limited. Notably, in recent years a growing number of studies have found that the decomposition of dead litter could also release significant VOCs, changing seasonal profile of local or even regional VOCs (Leff and Fierer, 2008; White et al., 2009; Greenberg et al., 2012).

Furthermore, Gray et al. (2010) reported that the percentage of OVOCs such as methanol could reach 99% of emitted VOCs during litter decomposition (litter types: deciduous species, evergreen species and dead grass leaves). While Faiola et al. (2014) found that monoterpenes (80.3%) dominated the total VOCs released from leaf litters of coniferous forest. These
different research results reflected that the composition of VOCs emitted by litters varied significantly to litter types. In addition, temperature, sunlight, moisture and microbial metabolism have been identified as the key factors affecting uptake or release of VOCs during litter decomposition (Niiemets et al., 2004; Vickers et al., 2009; Zhang et al., 2021; Zeng et al., 2022). However, so far these studies focused on forest litter (Leff et al., 2008; Isidorov et al., 2010; Greenberg et al., 2012; Gray et al., 2014; Faiola et al., 2014; Svendsen et al., 2018) and terrestrial environments (Breider et al., 2015). VOCs emitted during the decomposition of litters from other natural environments are still largely unexplored, inducing the uncertainty of estimating BVOC budget by models (Tang et al., 2019).

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

Herein, we conducted in situ field experiments to measure VOC fluxes during year-round litter decomposition in a freshwater wetland. The entire observation consisted of 11 campaigns from January 9 to December 14, 2022. A total of 103 valid samples were obtained during the observation. To the best of knowledge, this is the first-ever result on VOC flux measurements in a freshwater wetland under long-term period of litter decomposition (across four seasons). The objectives of this work are (1) to explore whether the freshwater wetland acts as a potential sink or source of atmospheric VOCs and the effects of litter decomposition, (2) to investigate the seasonal pattern of VOC fluxes and (3) to analyze potential influencing factors.
factors modulating VOC fluxes during the litter decomposition. The insights gained from this study can serve as a reference for models or emission inventories to estimate global BVOC emissions and enhance our understanding of the role of freshwater wetlands in reactive VOC budget.

2. Methodology

2.1 Study area

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

2.2 Experimental setup

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

### 2.3 Flux measurements

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

\[
 Flux = \frac{dC}{dt} \times \frac{V_c}{A_c} 
\]

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

### 2.4 Laboratory analysis

**VOCs**

The air samples were analyzed by a model 7200 pre-concentrator (Entech Instruments, California, USA) coupled to a gas chromatography and mass selective detector (GC/MSD, Shimadzu Corp, Tokyo, Japan). The analysis steps were described in detail elsewhere (Liu et al., 2021; Wang et al., 2023). Briefly, air samples were firstly drawn into a liquid-nitrogen cryogenic trap at -160 °C to be trapped and concentrated, then transferred to a secondary trap at -40 °C by pure helium. After these two steps, the H\(_2\)O and CO\(_2\) were mostly removed.
Subsequently, secondary trap was heated, and the VOCs were brought by helium to a third cry-focus trap at -170 °C. Once air samples were focused, the third trap was heated rapidly to be transferred into GC/MS system for further VOC analysis. The mixture was separated by a DB-1 capillary column (60 m × 0.32 mm × 1.0 μm, Agilent Technologies, USA) with helium as carrier gas. The initial oven temperature was set as 10 °C, kept 3 min, then increased to 120 °C at 5 °C min⁻¹, and then changed to 10 °C min⁻¹, finally reached at 250, held for 2 min. MSD was operated in SCAN model with electron impacting (EI, 70 eV) as the ionization method here. The Text S1 in supplement provided the information about quality assurance and quality control (QA/QC).

**CH₄ and CO₂:**

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

### 3. Results and discussion

#### 3.1 Overview of VOC fluxes

Throughout the entire in-situ observation, 62 VOCs including 19 alkanes, 11 alkenes, 5 aromatics, 15 OVOCs, 9 halocarbons and 3 VOSCs were detected and quantified in this study (Table S1). From the Table 1, regarding total net fluxes, three treatments all presented positive VOC fluxes, suggesting that the freshwater wetland could be a potential source of atmospheric VOCs. Obviously, as showed in Table 1, litter decomposition enhanced the VOC emissions from freshwater wetland. The average values of total net VOC fluxes measured in B and C were 5.93±3.13 μg m⁻² h⁻¹ and 8.30±4.00 μg m⁻² h⁻¹ (average ± standard error), respectively, ~2.04 times and ~2.86 times that of A (2.90±2.74 μg m⁻² h⁻¹). The effects of litter decomposition varied depending on VOC groups. For example, net fluxes of alkanes and alkenes measured in C were unexpectedly lower than in B. Moreover, the net flux of halocarbon measured in B was similar to that in C. These results reflected that besides the litter mass, other factors such as microbe activities (Lorah et al., 1999; Leff et al., 2008; Gray et al., 2014; Jiao et al., 2018; Svebdsen et al., 2018), which were discussed in detail in Section 3.3, might also affect the VOC fluxes measured in our experiments.
From the Table 1, both halocarbons and OVOCs showed net uptake into wetland in A. When inputting the litters, halocarbons shifted from net uptake into wetland to net positive efflux out of wetland. OVOC fluxes in A and B were both negative but showed a positive value in C, indicating that litter decomposition could be one of the crucial factors determining whether the freshwater wetland was a net source or a net sink of atmospheric OVOCs. As showed in Fig. 2, litter decomposition apparently affected the compositions of VOCs released from freshwater wetland. Notably, aromatic, a typical class of anthropogenic air pollutant, was the dominant VOC group released from freshwater wetland, accounting for 40.6%, 40.4% and 46.3% of total VOC emissions in A, B and C, respectively (Fig. 2). Recently, several studies gave the evidence of biogenic aromatic emission from living plants, straw, cyanobacteria and ocean phytoplankton (White et al., 2009; Rocco et al., 2021; Liu et al., 2021; Wohl et al., 2023; Wu et al., 2023). As Fig. S2 shows, during the year-round observation, the fluxes of VOC-driven carbon (C_{VOC}) in freshwater wetland averaged 2.47 ± 1.84, 4.69 ± 2.11 and 6.36 ± 2.78 μgC m⁻² h⁻¹ in A, B and C, respectively. The C_{VOC} accounted for < 0.05% of the carbon driven from CO₂ and CH₄. In comparison to CO₂ and CH₄, VOC emission was not a significant pathway for wetland-carbon transporting into atmosphere. However, given their relatively higher reactivities, these VOCs preferentially reacted with OH radicals once being released into atmosphere from freshwater wetland. This would prolong the atmospheric lifetime of CH₄, thus accelerating global warming. While global warming would in turn lead to greater release of VOC from the freshwater wetland as temperature was linearly correlated with VOC emission according to the discussion in Section 3.2. It is clear from Fig. S3 that these above-mentioned processes would develop a vicious circle. Previous studies also revealed that the wetland environment was a source of atmospheric VOCs, but what these studies mostly investigated were living plants and focused on the fens (Hellén et al., 2020; Seco et al., 2020; Vettikkat et al., 2023). As showed in Table S2, the net VOC fluxes measured in this study, representing the freshwater wetland, were lower than those obtained in fens. It could be realized that VOC emissions from fens were dominated by isoprene, with fluxes ranging from 2.5 μg m⁻² h⁻¹ to 4773.6 μg m⁻² h⁻¹. These were quite different from the results uncovered by our observation. The difference could be attributed to
the variety of sampling, analysis methods and detected VOC species among the studies on the one hand and to the wetland types on the other hand. In the present work, our experiments were carried out in flooded areas of the freshwater wetland and focused on dead litter decomposition, while earlier studies focused on relatively drier environments and living plants. Baggesen et al. (2022) pointed out that flooded condition would result in a negative net VOC flux and even overruled other effects. In addition, the GC/MSD technique used here failed to fully characterize higher molecular weight species, such as monoterpane, and lower molecular weight species, such as methanol, which have been reported to be released in significant amounts during the decomposition of litter (Gray et al., 2010; Faiola et al., 2014).

3.2 Seasonal patterns

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

In spring, as Fig. 3 shows, positive net VOC fluxes were showed in three treatments during the samplings conducted in March and April. However, the negative net VOC flux was found in A and the positive net VOC fluxes of B and C were also significantly lower observed in May than those measured in prior two samplings, which could be attributed to the sharp drop in temperature (-6.6 °C). As shown in Fig. 3, VOC emission enhanced by litter decomposition were much remarkable in hot summer. Considering that temperature was the key factor driving the seasonal patterns of VOC fluxes measured during the experiments, we further analyzed the relationships of net VOC fluxes with ambient temperature. As shown in Fig. 4, VOC fluxes presented significant positive correlations with temperature ($p < 0.05$) in three treatments. According to the linear fitting equations showed in Fig. 4, VOC uptake from air into wetland generally occurred at lower temperature ($< 10 ^\circ$C), and similar VOC uptake was found between B and C, both presenting less VOC uptake than A. In fact, lower temperature would limit microbial activities and was an unfavorable condition for decaying litters.
(Greenberg et al., 2012; Gray et al., 2014). Thus, higher VOC uptake measured in A could be mainly caused by abiotic process (Gray et al., 2014). Compared to A, the litter added in B and C covered the water surface, preventing VOC uptake from ambient air into wetland. Moreover, slow decaying of litter in B and C possibly also occurred even under low temperature. This process might release some VOCs into ambient air and offset part of VOC uptake, thus resulting in B and C lower net negative VOC fluxes than that showed in A. As displayed in Fig. 4, the slopes of linear fitting equation were 0.72 and 0.81 for B and C, respectively, higher than that of A (0.63). This further clarified that litter decomposition would stimulate VOC emission from freshwater wetland and suggested that the positive effect of litter decomposition was amplified by higher temperature.

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

### 3.3 The flux variations of specific VOC groups

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

#### 3.3.1 Alkanes

Overall, freshwater wetland was the potential source of atmospheric alkane, as positive net fluxes were measured in three treatments during the year-round observation (Table 1). For A, B and C, alkanes accounted for 23.3%, 20.4% and 13.8% of total VOC emissions, respectively (Fig. 2), which were comparable to that previously reported in decomposition of tree leaf (~ 20%) (Svendsen et al., 2018; Viros et al., 2020). The emission percentage of alkane showed a decreasing trend with litter addition, suggesting that alkane might not be the dominant VOC composition emitted during litter decomposition in freshwater wetland. In general, higher temperature would stimulate microbe activities and accelerate litter decaying, further leading to more VOC release (Isidorov et al., 2002; Jiao et al., 2018; Svendsen et al., 2018). However, from the Fig. 5, it was interesting that B and C presented higher alkane...
emissions than A during the period with relatively lower temperature, while nearly equal amounts of alkane emissions were observed in three treatments in hot July. This result suggested that higher alkane emission in July might not be mainly resulting from litter decomposition. Previous studies have revealed that alkanes can be stored in the upper cuticle layer of vascular species (Bondada et al., 1996; Barik et al., 2004). Thus, during the initial period of litter decomposition (lower temperature), higher emission fluxes of alkane measured in B and C might be mainly due to the material composition of the litter itself rather than resulting from the litter decomposition. Notably, in subsequent experiments such as those conducted in March, June and July, relatively higher alkane emission was measured in A, even comparable to that in B and C. This suggested that litter decomposition might not be main source of alkanes and that other alkane-emitted sources might also exist in freshwater wetland. In fact, earlier studies have found that root-emitted VOCs could act as chemical signals belowground and be transported from the source (Delory et al., 2016). Root exudation in the rhizosphere contained numerous chemicals like lower-molecular-weight organic acids, which were reported to be the precursors of biogenic alkanes (Maffei, 1994; Viros et al., 2020). Considering that the roots of Phragmites australis were not removed in our experiments (Fig. 1), root emission might be an alkane source, which needed more investigations in future to explore and confirm this.

3.3.2 Alkenes

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

### 3.3.3 Aromatics

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

### 3.3.4 Halocarbons
Overall, net halocarbon emission was relatively lower, accounting for 7.2% and 5.9% of total VOC emission in B and C, respectively (Table 1). A negative flux was measured in A, suggesting that the freshwater wetland could be the net sink of halocarbon. Undoubtedly, litter decomposition enhanced the halocarbon emission, especially in hot July and August, but the emission did not fully follow the seasonal patterns. As showed in Fig. 5, both B and C still presented significant halocarbon emissions in October, and even in November, when the ambient temperature was below 10 °C, halocarbon emission in C was comparable to that measured in hot July. These results suggested that halocarbon emission was not majorly controlled by temperature. Natural emissions of halocarbons have been previously reported in marine (Philip et al., 1985), soil (Albers et al., 2017) and forest wetland (Jiao et al., 2018). Typical halocarbon species emitted from natural source such as methyl chloride (CH$_3$Cl) and chloroform (CHCl$_3$) were also detected in our experiments. Both CH$_3$Cl and CHCl$_3$ have been reported to be formed through biotic (enzymatic reactions) (Rhew et al., 2003) and abiotic processes (nonenzymatic Fenton-like reactions) (Huber et al., 2009). Jiao et al. (2018) revealed that abiotic factor dominated the CHCl$_3$ emission in forest wetland, while microbial activities controlled the CHCl$_3$ production in Antarctica tundra soils (Zhang et al., 2021). These conflicting results reported by earlier studies reflected that biogeochemical process of natural halocarbon were very complicated and varied to natural environments. During our experiments, the CH$_3$Cl fluxes in A, B and C were -0.08±0.12, 0.27±0.12 and 0.39±0.12 μg m$^{-2}$h$^{-1}$, respectively, but CHCl$_3$ was undetectable in many measurements. Both the net total halocarbon fluxes and CH$_3$Cl did not show significant correlations with ambient temperature (Table S3), which was in line with the consequence reported by Jiao et al. (2018). This suggested that halocarbon emission from freshwater wetland might be predominantly controlled by abiotic process rather than temperature-dependent microbial activities (Gray et al., 2014).

3.3.5 Oxygenated volatile organic compounds

Unlike other VOCs, OVOCs presented uptake in most flux measurements conducted in the freshwater wetland (Fig. 5). This was quite different from previous studies on the decomposition of tree leaf litter, which released large amounts of OVOCs. For example, Gray et al. (2010) reported that OVOCs accounted for over 99% of total VOC emissions during
plant litter decomposition. However, the litter decomposition investigated in these previous studies generally took place in dry terrestrial environments or in laboratory incubations, while our experiments were conducted in freshwater wetland under flooded conditions. As we know, most OVOCs were polar organic molecules including alcohols, carbonyls and organic acids, which are water soluble (Baggesen et al., 2022). Bourtsoukidis et al. (2018) reported that soil could shift between methanol release when dry and methanol uptake when wet. OVOC deposition was also found in early morning due to dew (Schallhart et al., 2016). Moreover, previous studies reported OVOC uptake in ocean and lake environments (Seco et al., 2020; Liu et al., 2021). Even in hot July, OVOCs such as acetone and acetaldehyde showed negative net fluxes in the field observation of freshwater (Seco et al., 2020). Thus, even if OVOCs could be produced during our field experiments, they were likely to dissolve in the water. From the Fig. 5, three treatments all displayed OVOC uptake at initial stage (January) of litter decomposition. On January 9th, the highest and lowest OVOC uptake was observed in A and C, respectively, while completely opposite results were observed on January 21st. As known, OVOCs can be consumed by microbes (Männistö et al., 2023). For B and C, litter decomposition over time could provide a carbon source for microbes (Albers et al., 2018) and increase their amounts and activities, further enhancing OVOC consumption by microbes. This could result in increasing uptake of airborne OVOCs into freshwater wetland. It was worth noting that in hot July, three treatments all presented positive flux values of OVOCs, indicating that OVOCs actually could be produced in freshwater wetland. However, this production might be hidden by its sink such as dissolution in water, microbial uptake and abiotic deposition due to the concentration gradient between wetland and atmosphere (Niinemets et al., 2014; Alber et al., 2017; Rinnan et al., 2020). Further, litter decomposition enhanced OVOC emission in hot July. Although higher temperature could accelerate microbial decomposition of litter and release more OVOCs, considering their water solubility, higher OVOC emission fluxes were likely the outcome of strong evaporation, a typical abiotic process (Leff and Fierer, 2008), in hot July.

3.3.6 VOSCs

In this study, we detected three VOSC species including dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS), which were widely measured in aquatic
ecosystems (Liu et al., 2021). During the entire observed period, VOSC release from freshwater wetland were found in three treatments (Table 1) and DMS dominated the VOSC emission, accounting for 78.8±2.9% (Fig. 6). Overall, litter addition enhanced VOSC emissions from the freshwater wetland. However, as Fig. 5 shows, an abnormal phenomenon was observed in August, which presented highest VOSC emission in B, followed by A and C. As previously reported, VOSCs were generated from microbial metabolism of methionine and cysteine (Achyuthan et al., 2017). Thus, all of these could produce methionine and cysteine such as organics dissolved in water were probably responsible for higher VOSC emission in B in August. As Fig. 5 shows, significant VOSC emission was still found in October (T=16.1°C) solely under the B and C, similar to that of AHs, halocarbons and OVOCs. This could be attributed to the consequence of litter decomposition by microbes.

4. Conclusions and limitations

In this study, in situ flux measurements of VOCs were conducted in a freshwater wetland during year-round litter decomposition. Three treatments including A (no litter addition), B (1.4 kg litter) and C (2.8 kg litter) were designed to investigate the impacts of litter decomposition on VOC fluxes measured during the field experiments. As a result, the net TVOC fluxes measured in A, B and C were 2.90±2.74, 5.93±3.13 and 8.30±4.00 μg m⁻² h⁻¹, respectively, suggesting that the freshwater wetland was a potential source of atmospheric VOCs and litter decomposition could enhance its net VOC release. Although revealed as the source of VOCs in terms of net total flux, uptake or release of VOCs observed in freshwater wetland varied depending on the specific VOC chemical groups. NMHCs and VOSCs both showed positive net fluxes in three treatments. Halocarbons presented a negative net flux in A and shifted to positive fluxes in B and C. Due to their water solubility, OVOCs measured here mostly presented uptake in the wetland, and their fluxes were found to be negative in A and B, but turn to be positive in C. This reflected that litter decomposition could result in freshwater wetland becoming a source of atmospheric OVOCs. In line with previous studies on BVOC emissions, net TVOC flux showed significant seasonal patterns. In three treatments, the highest positive fluxes were observed in hot summer, followed by spring and fall, while the negative net VOC fluxes were generally found in cold winter. Moreover, VOC emission increasement resulting from litter decomposition exhibited monotonically increasing with...
litter mass in the seasons except for fall, of which the highest flux presented in B, followed by C and A. In three treatments, net VOC fluxes were significantly correlated with ambient temperature (p < 0.05). Based on detailed analysis for flux variations of different VOC groups, biotic and abiotic processes driven by temperature co-modulated VOC fluxes measured in freshwater wetland.

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

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

Author contributions
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Table 1. The net fluxes (mean ± standard error) of different VOC groups under A, B and C treatments (unit: μg m⁻² h⁻¹) based on 11 campaigns during one-year litter decomposition. Each treatment consists of three parallel groups. The number of measured compounds is given in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>A (No litter addition)</th>
<th>B (1.4 kg litters)</th>
<th>C (2.8 kg litters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes (19)</td>
<td>0.76±0.35</td>
<td>1.45±0.48</td>
<td>1.20±0.64</td>
</tr>
<tr>
<td>Alkenes (11)</td>
<td>0.55±0.29</td>
<td>1.40±0.37</td>
<td>1.28±0.41</td>
</tr>
<tr>
<td>Aromatics (5)</td>
<td>1.33±0.68</td>
<td>2.86±0.84</td>
<td>4.02±1.04</td>
</tr>
<tr>
<td>Halocarbons (15)</td>
<td>-0.09±0.18</td>
<td>0.51±0.17</td>
<td>0.43±0.20</td>
</tr>
<tr>
<td>OVOCs (9)</td>
<td>-0.02±1.65</td>
<td>-0.07±1.73</td>
<td>0.64±2.48</td>
</tr>
<tr>
<td>VOSCs (3)</td>
<td>0.64±0.40</td>
<td>0.88±0.50</td>
<td>1.03±0.22</td>
</tr>
<tr>
<td>Σ</td>
<td>2.90±2.74</td>
<td>5.93±3.13</td>
<td>8.30±4.00</td>
</tr>
</tbody>
</table>
Figure 1. Nine stainless steel cuboidal boxes without the cover in freshwater wetland (a). The schematic diagram of cuboidal box was displayed in (b). Each treatment, namely A, B and C, consists of three parallel groups.
Figure 2 Chemical compositions (mass percentage) of net VOC emissions under A, B and C treatments.
Figure 3. Seasonal variations of net VOC fluxes under three treatments. The error bar (if more than two values) represents standard error of three parallel samples.
Figure 4. The relationships of net VOC fluxes with ambient air temperature (Tem) during one-year litter decomposition.
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.