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

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Text S1 Quality assurance and quality control

Before sampling, the canisters were repeatedly filled and evacuated pure nitrogen at least three times to remove the potential contaminants and then the evacuated canisters were placed in laboratory for 24 hours. After that, 10% evacuated canisters were selected randomly to be refilled with pure nitrogen and were analyzed in the same way as the samples. Only when no targeted VOCs were detected, the canisters were considered as clean ones and can be used for formal sampling.

Field blank canisters refilled with pure nitrogen were brought to sampling site and returned to laboratory (lab) for analysis in the same way as samples. The targeted VOCs were not detected or presented the level below the method detection limits (MDLs). During the period of lab analysis, lab blank (the canister filled with pure nitrogen) was analyzed firstly to check if any contaminants remained in the system of GC/MSD coupled with pre-concentrator. All VOCs detected in this work were identified based on their retention times (RTs) in GC and m/z obtained from MSD and were quantified by calibration curves. The VOCs without standards were identified by their match to the NIST library and were semi-quantified based on the species whose RTs were close to them or based on the species which have a similar chemical structure to them. The gas standards were prepared by dynamically diluting the Photochemical Assessment Monitoring Stations (PAMS) standard mixture and TO-15 standard mixture to 0.5, 1, 5, 15 and 30 ppb, respectively. The gas standards of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) were dynamically diluted to 0.1, 0.5, 1, 2 and 4 ppb, respectively. The calibration curves were obtained by running the five diluted standards in the same manner as the collected samples. Each day before the sample analysis, the system was checked by high pure nitrogen (99.999%) and calibrated with a one-point calibration (1ppb). If the relative percent difference from the initial calibration curve were > 15%, the recalibration is made.

Table S1. The VOC fluxes measured in A, B and C during the experiments ($\mu g\ m^{-2}\ h^{-1}$).

Species	A	B	C	Species	A	B	C
n-Butane	0.09±0.06	0.15±0.08	0.10±0.10	Toluene	0.17±0.24	1.01±0.39	1.59±0.52
2,3-Dimethylbutane	-0.05±0.08	0.14±0.21	-0.74±0.75	Ethylbenzene	0.21±0.09	0.31±0.10	0.45±0.11
Isopentane	0.03±0.05	0.24±0.1	0.05±0.10	m/p-Xylene	0.66±0.29	1.02±0.33	1.44±0.43
n-Pentane	0.15±0.10	0.22±0.1	0.24±0.09	o-Xylene	0.42±0.17	0.50±0.17	0.71±0.20
Cyclohexane	-0.35±0.17	0.05±0.02	0.17±0.13	Ethanol	-0.50±0.37	-0.28±0.59	-0.22±0.50
2-Methylpentane	0.28±0.18	0.41±0.38	0.31±0.40	Acetone	0.52±0.75	-0.81±0.82	0.57±1.97
3-Methylpentane	-0.13±0.14	0±0.05	-0.04±0.08	Methyl Acetate	-0.16	-0.35	-0.40
2,3,4-Trimethylpentane	0.11±0.06	0.4±0.26	0.39±0.25	Ethyl Acetate	-1.05±0.49	-0.56±0.84	-0.53±1.03
n-Hexane	0.16±0.10	0.14±0.13	0.03±0.30	Propyl Acetate	0.42	0.33	0.31
Cyclohexane	-0.01±0.04	0.01±0.02	0.01±0.01	Butyl Acetate	0.11±0.31	0.07±0.17	0.08±0.23
2-Methylhexane	-0.08±0.04	-0.11±0.11	0.03±0.02	2-Butanone	-0.05±0.31	0.53±0.85	0.05±0.33
3-Methylhexane	0.06±0.03	0.2±0.13	0.28±0.13	Isobutyl Acetate	0.01±0.25	-0.32±0.32	-0.85±0.35
2,4-Dimethylhexane	0.22±0.08	0.24±0.15	0.29±0.04	Tert Butanol	0.73±0.32	0.56±0.33	1.02±0.44
Methylcyclohexane	0.01	0.00	0.01	Allyl glycidyl ether	0.60	0.50	0.51
n-Heptane	0.05±0.04	0.05±0.03	0.09±0.04	3-Methylhexanol	0.64	0.29	0.46
2-Methylheptane	0.05±0.14	0.66±0.44	0.34±0.15	Dimethoxymethane	0.47±0.47	0.37±0.08	0.83±0.12
3-Methylheptane	2.29	0.53	2.03	Tetrahydrofuran	0.21±0.21	0.07±0.07	0.26±0.22
n-Decane	0.32±0.21	0.29±0.17	0.39±0.24	Isovaleraldehyde	0.15±0.09	-0.53±0.82	-0.87±0.81
n-Octane	0.2±0.06	0.25±0.02	0.27±0.06	2-Ethylhexanal	0.37	0.00	1.17
2-Butene	0.31±0.26	0.85±0.2	0.95±0.37	Chloromethane	-0.08±0.12	0.27±0.12	0.39±0.12
1-Pentene	-0.02±0.01	0.54±0.38	0.23±0.36	Chloroform	0.06±0.26	0.50±0.26	-0.17±0.56
1,3-Pentadiene	-0.01±0.09	0.09±0.19	-0.06±0.19	1,1-Dichloroethane	-0.03±0.05	0.05±0.03	0.04±0.02
1-Hexene	0.05±0.01	0.05±0.02	0.09±0.05	1,2-Dichloroethane	-0.04±0.12	0.12±0.13	-0.02±0.09

α-Pinene	-0.10±0.02	0.01±0.05	0.14±0.10	1,2-Dichloropropane	-0.00±0.02	0.01±0.00	0.02±0.01
β-Pinene	0.03±0.07	0.25±0.13	0.15±0.1	Trichlorofluoromethane	0.07	0.04	0.04
2-Methyl-1-Butene	0.67	0.30	0.30	Trichloroethylene	0.00±0.03	0.01±0.01	0.04±0.06
2-Methyl-2-Butene	0.36	0.22	0.17	Tetrachloromethane	0.02±0.02	0.06±0.04	0.03±0.03
α-Octene	0.10±0.02	0.09±0.03	0.12±0.02	Tetrachloroethene	-0.23	0.14	0.13
2,4-Dimethyl-1-Heptene	0.06	0.12	0.17	Dimethyl sulfide	0.56±0.40	0.83±0.55	0.69±0.19
Cyclooctatetraene	0.56	0.63	0.43	Dimethyl Disulfide	0.04±0.01	0.11±0.05	0.42±0.20
Benzene	-0.01±0.04	0.18±0.08	0.07±0.03	Dimethyl Trisulfide	0.34	0.18	0.13

Table S2. VOC fluxes measured in previous studies and in this work (unit: $\mu g\ m^{-2}h^{-1}$).

Study sites		Flux	Main species	References
Subalpine forest floor		2.5-93.4	Isoprene	Hellen et al., 2020
Fen		1571 (Isoprene), 268 (Methanol)	Isoprene	Holst et al., 2010
Fen		298	Isoprene (1571) and methanol (268)	Seco et al., 2020
Fen		4773.6	methanol, acetaldehyde, acetone, DMS, isoprene, and monoterpenes	Vettikkat et al., 2023
Fen		0-250	Isoprene	Haapanala et al., 2006
Fen		166.3	Isoprene	Männistö et al., 2023
Bog		44.5	Isoprene	
Freshwater wetland	No litter addition	2.90±9.09		This study
	1.4 kg litter	5.93±10.40	Aromatics	
	2.8 kg litter	8.30±13.25		

Table S3. The relationship between the fluxes ($\mu g \ m^{-2} \ h^{-1}$) of CH_3Cl and total halocarbon and temperature (°C).

	CH₃Cl				Total halocarbons		
	A	B	C		A	B	C
r	0.24	0.17	-0.36		0.26	0.51	0.24
p	0.47	0.6	0.27		0.44	0.11	0.48

r is the Pearson correlation coefficient.

a. China
b. Yangtze River Delta
c. Wuhu

Kuihu Freshwater Wetland
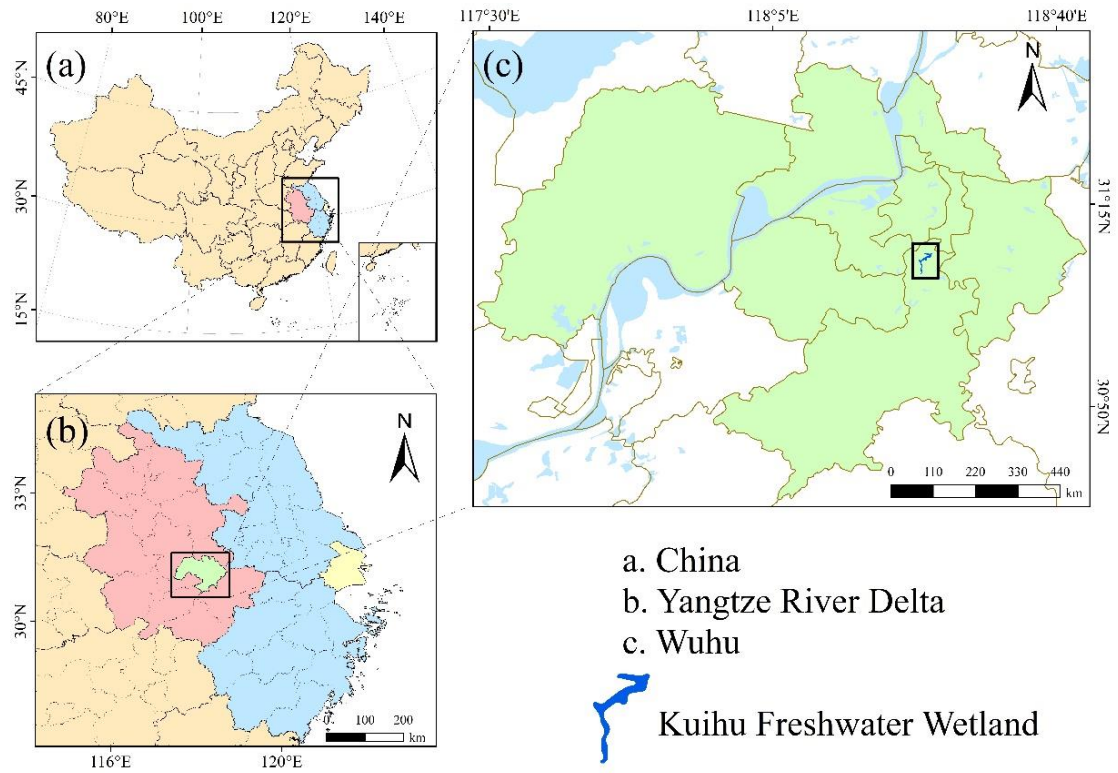
Fig. S1. The geographical location of Kuhui freshwater wetland.
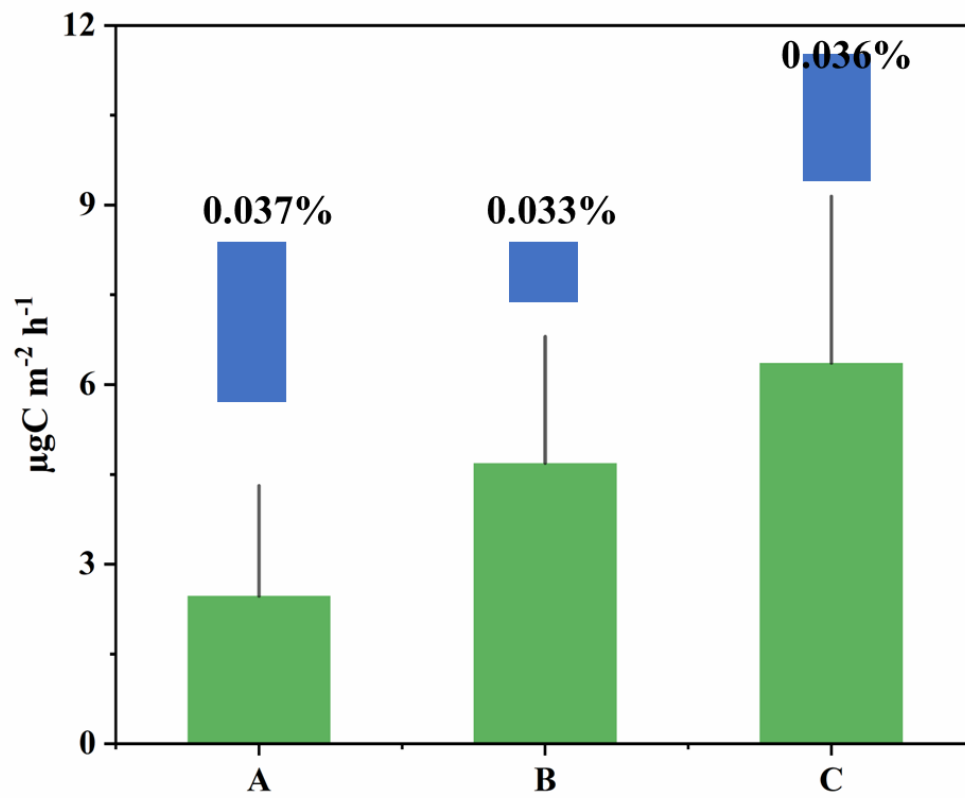
Fig. S2. The carbon fluxes contributed by VOCs in three treatments. The error bar was the standard error. Blue column represents the percentage of VOC-driven carbon in total calculated carbon (VOCs, CO_2 and CH_4).
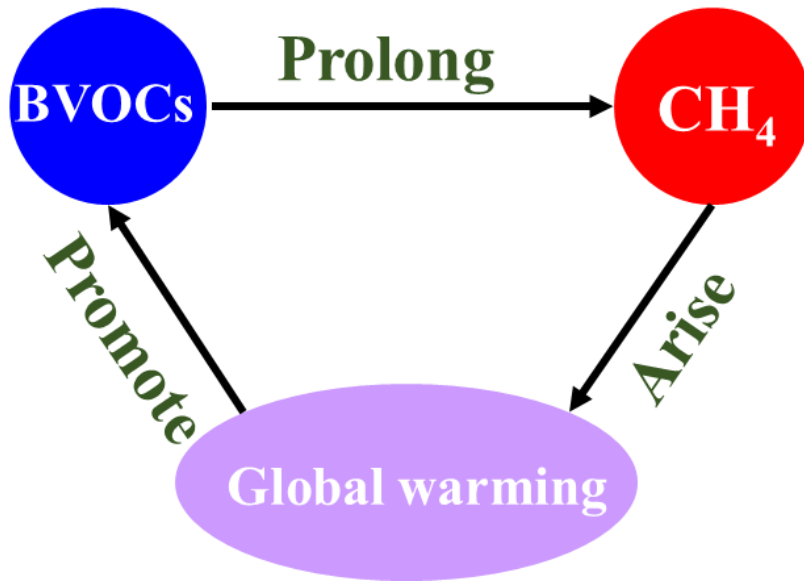
Fig. S3. The schematic plot of positive feedback loops among the BVOCs, CH_4 and global warming.
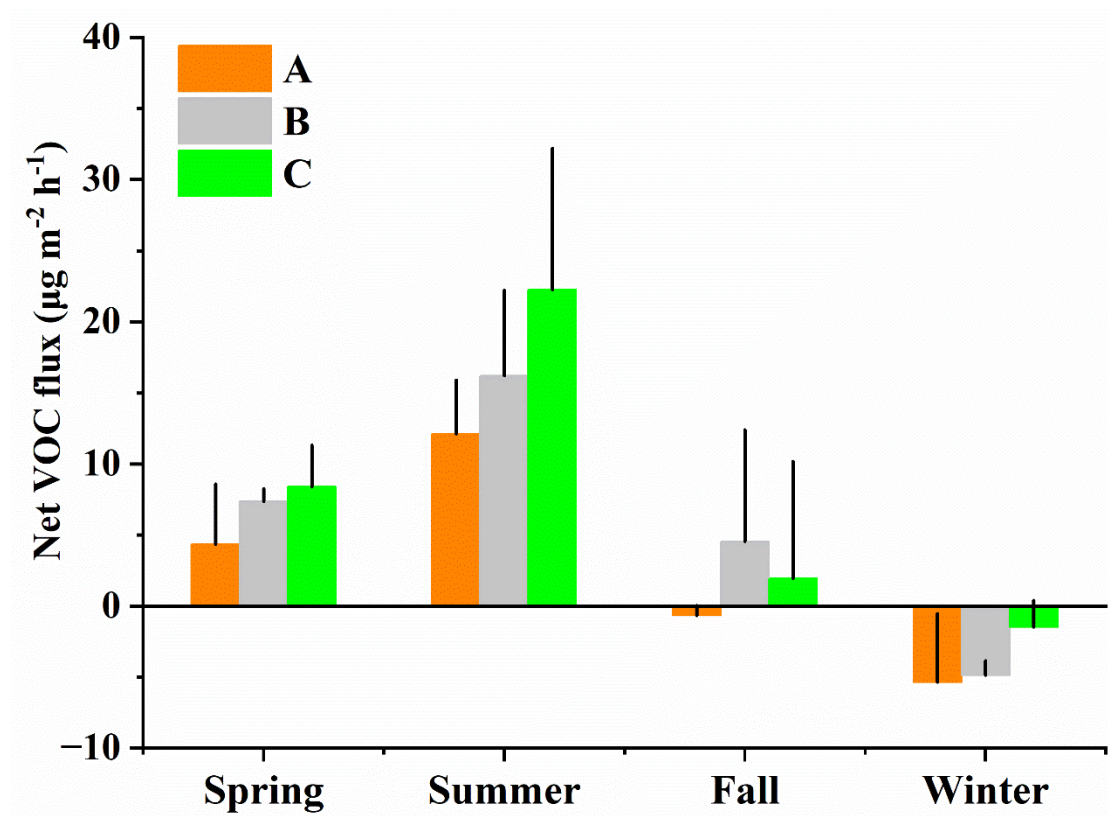
Fig. S4. The net VOC fluxes measured in three treatments in four seasons. The error bar is the standard error.
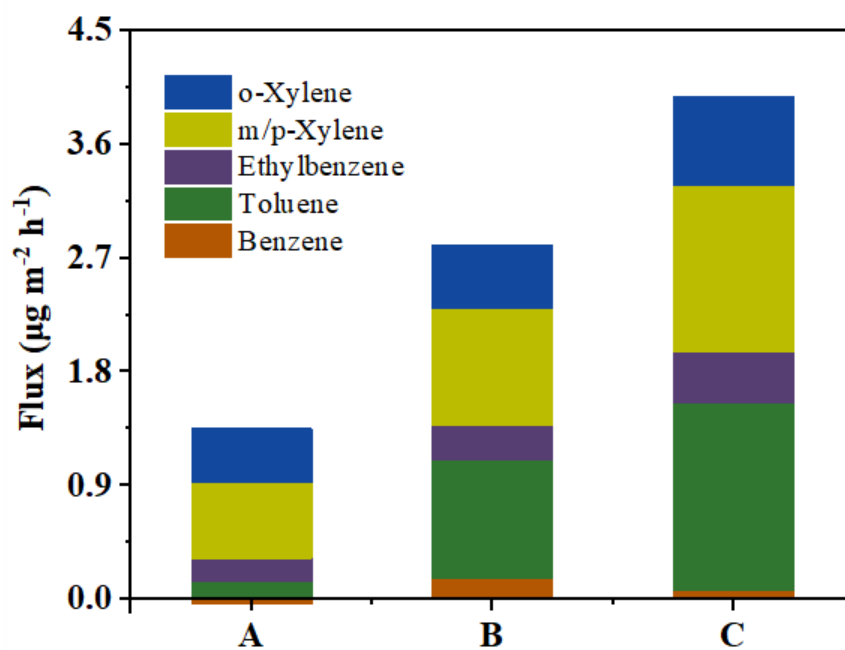
Fig. S5. The fluxes of individual AH species measured in three treatments during the observation.

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