Supplementary Material

1. Soil Texture

Table S1. Soil particle size distribution in three forest types in central Amazonia. The data represent the percentage composition of total sand, silt, and clay. Each sample is a composite sample from two nearby points in the field. AR = ancient river terrace forest, WS = white sand forest, UP = upland forest.

Soil Texture				
Forest type	samples	sand (%)	silt (%)	clay (%)
AR	TR1.1	45.449	37.801	16.75
AR	TR1.2	45.449	37.801	16.75
AR	TR1.3	47.639	30.061	22.30
AR	TR1.4	47.639	30.061	22.30
AR	TR1.5	12.38	56.22	31.40
AR	TR1.6	12.38	56.22	31.40
AR	TR2.1	41.543	34.457	24.00
AR	TR2.2	41.543	34.457	24.00
AR	TR2.3	42.078	35.422	22.50
AR	TR2.4	42.078	35.422	22.50
AR	TR2.5	47.17	28.68	24.15
AR	TR2.6	47.17	28.68	24.15
WS	CP1.1	46.15	52.35	1.50
WS	CP1.2	46.15	52.35	1.50
WS	CP1.3	50.07	47.68	2.25
WS	CP1.4	50.07	47.68	2.25
WS	CP1.5	74.398	24.252	1.35
WS	CP1.6	74.398	24.252	1.35
WS	CP2.1	76.599	22.301	1.10
WS	CP2.2	76.599	22.301	1.10
WS	CP2.3	24.134	74.616	1.25
WS	CP2.4	24.134	74.616	1.25
WS	CP2.5	73.883	24.517	1.60
WS	CP2.6	73.883	24.517	1.60
UP	TF1.1	23.011	26.139	50.85
UP	TF1.2	23.011	26.139	50.85
UP	TF1.3	12.595	30.255	57.15
UP	TF1.4	12.595	30.255	57.15
UP	TF1.5	12.698	38.602	48.70
UP	TF1.6	12.698	38.602	48.70
UP	TF2.1	11.892	40.858	47.25
UP	TF2.2	11.892	40.858	47.25
UP	TF2.3	10.194	32.506	57.30
UP	TF2.4	10.194	32.506	57.30
UP	TF2.5	9.587	35.413	55.00
UP	TF2.6	9.587	35.413	55.00

2. Calibration gas composition

Table S2. Multi-component calibration mixture in synthetic air, as used for the calibration of the PTR-QMS. Uncertainty is a conservative estimate of the combination of gravimetric preparation and analysis uncertainties.

Compound	CAS#	Concentration (ppb)	Uncertainty
Formaldehyde	50-0-0	992	5%
Acetaldehyde	75-07-0	426	5%
Methanol	67-56-1	521	5%
Ethanol	64-17-5	528	5%
Acetonitrile	75-05-8	523	5%
Acetone	67-64-1	497	5%
Isoprene	78-79-5	468	5%
DMS	75-18-3	487	5%
a-Pinene	80-56-8	488	5%
Camphene	79-92-5	504	5%
B-Pinene	18172-67-3	512	5%
a-Phellandrene	4221-98-1	432	5%
3-Carene	13466-78-9	458	5%
Limonene	5889-54-8	489	5%
o-Cymene	527-84-4	481	5%
y-Terpinene	99-85-4	476	5%
B-Caryophyllene	87-44-5	98.3	5%
a-Humulene	6753-98-6	95.2	5%

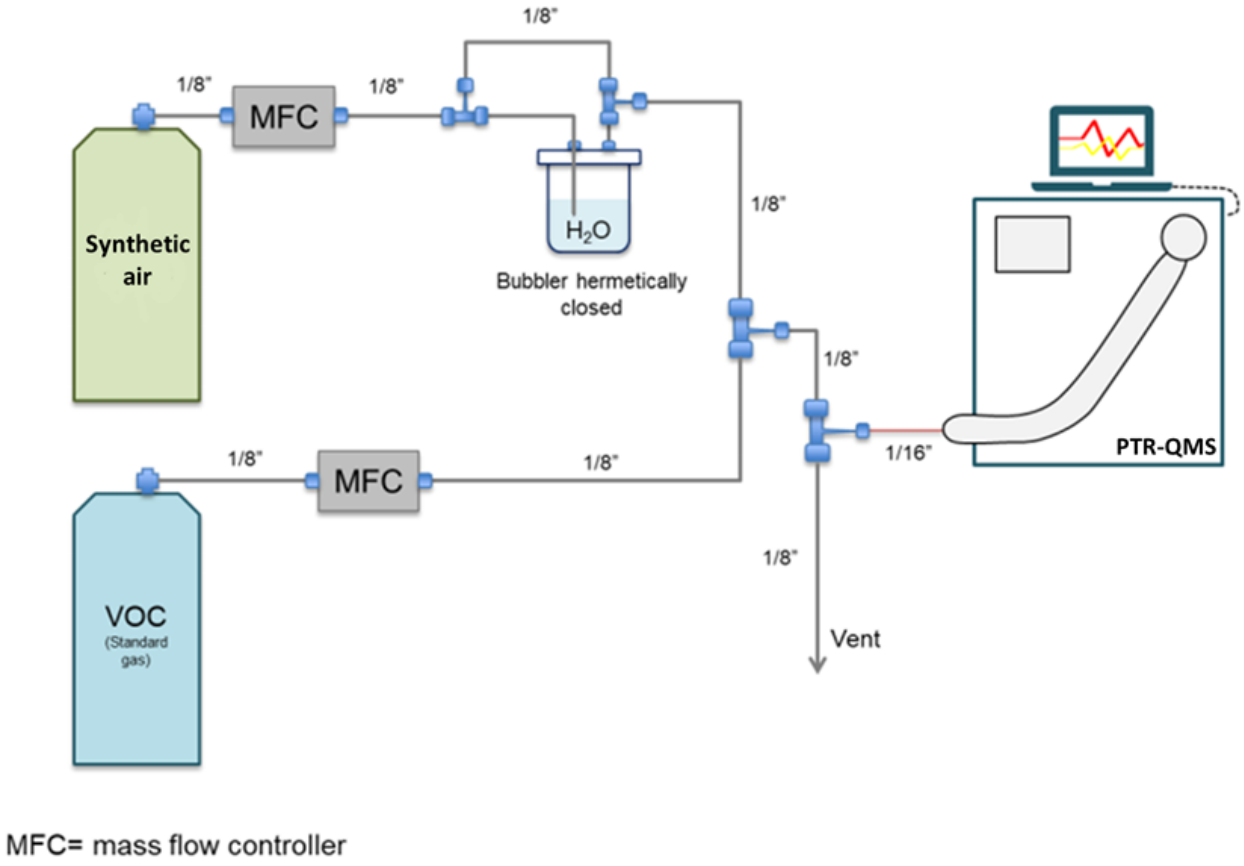

Figure S1. PTR-QMS calibration setup scheme, the VOC standard gas is as described in Table S2, adapted from Caetano (2022)

3. Gas Chromatography - Time of Flight Mass Spectrometer (GC-TOF-MS) analysis

3.1 GC-TOF-MS: Material & Methods

After determining gas mixing ratios on the PTR-QMS and the Los Gatos Analyzer, samples were collected onto cartridges (stainless steel tubes filled with Tenax TA and Carbograph 5 TD adsorbents, Markes International, UK) at a rate of 200 sccm for 10 min, which resulted in 2L air samples for compound identification and quantification analyses with the GC-TOFMS. The cartridges were stored in an air-conditioned room for up to six months until they were analyzed.

Samples were examined with a thermal-desorption gas chromatograph coupled to a time-of-flight mass spectrometer (TD-GC-TOF-MS; Bench TOF Tandem Ionisation, Markes International, UK). A complete description of the instrument, analytical procedure, and performance is available in Zannoni et al. (2020a, 2020b).

In the TD-GC-TOF-MS, the analytes are desorbed from the sampling tubes using two sequential stages, performed at 250°C for 10 minutes, then carried by a flow of He into the separating column in the gas chromatograph. The column is a dimethyl TBS β-cyclodextrin column (0.25µm, 0.25mm ID, 30 mL, from MEGA, Italy) which separates the analytes according to volatility and enantiomeric configuration. The separation method was specifically designed for the separation of chiral monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) and consisted of an initial 5 min when the oven temperature was held at 40°C, after which it was increased at a rate of 1.5 °C/min from 40°C to 150°C. Finally, the temperature was increased further at a rate of 30°C/min from 150°C to 200°C. Detection was performed by a Time-of-Flight Mass Spectrometer, which fragments the analytes through electron impact ionization at -70 eV for quantification and identification of the chemical species. Identification of the main chemical compounds was obtained by comparing the MS spectra with the MS library for the same ionization energy (NIST library), by injection of a calibration gas standard mixture (19 biogenic volatile organic compounds provided by Apel Riemer, USA), and by use of liquid standards. Chromatogram peak areas were integrated through TOF-DS software provided with the instrument (Markes International, UK). The standard gas used is a certified concentrated mixture (~100 ppbv) of 19 BVOCs, including among the other species four pairs of chiral terpenoids (α-pinene, β-pinene, limonene, linalool), isoprene, and one sesquiterpene (β-caryophyllene). The GC-TOF sensitivity was quantified by measuring the concentration of BVOCs in standard sorbent tubes filled with 2 L of gas standard diluted in a pure synthetic air flow with four dilution steps to achieve concentrations in the range of 0.05-1 ppb. Such calibrations were performed before or at the end of each sample batch. The obtained calibration factors were confirmed with standard cartridges containing a known BVOC concentration (~0.150 ppb) analyzed in a workflow, whereas for every ten samples analyzed, a standard cartridge was also measured. The standard cartridges analyzed in this way were used to determine the precision of the analysis (including any drift from the mass spectrometer), which was quantified as 22% (Zannoni *et al*. 2020a and Zannoni *et al.* 2020b).

3.2 GC-TOF-MS: Results

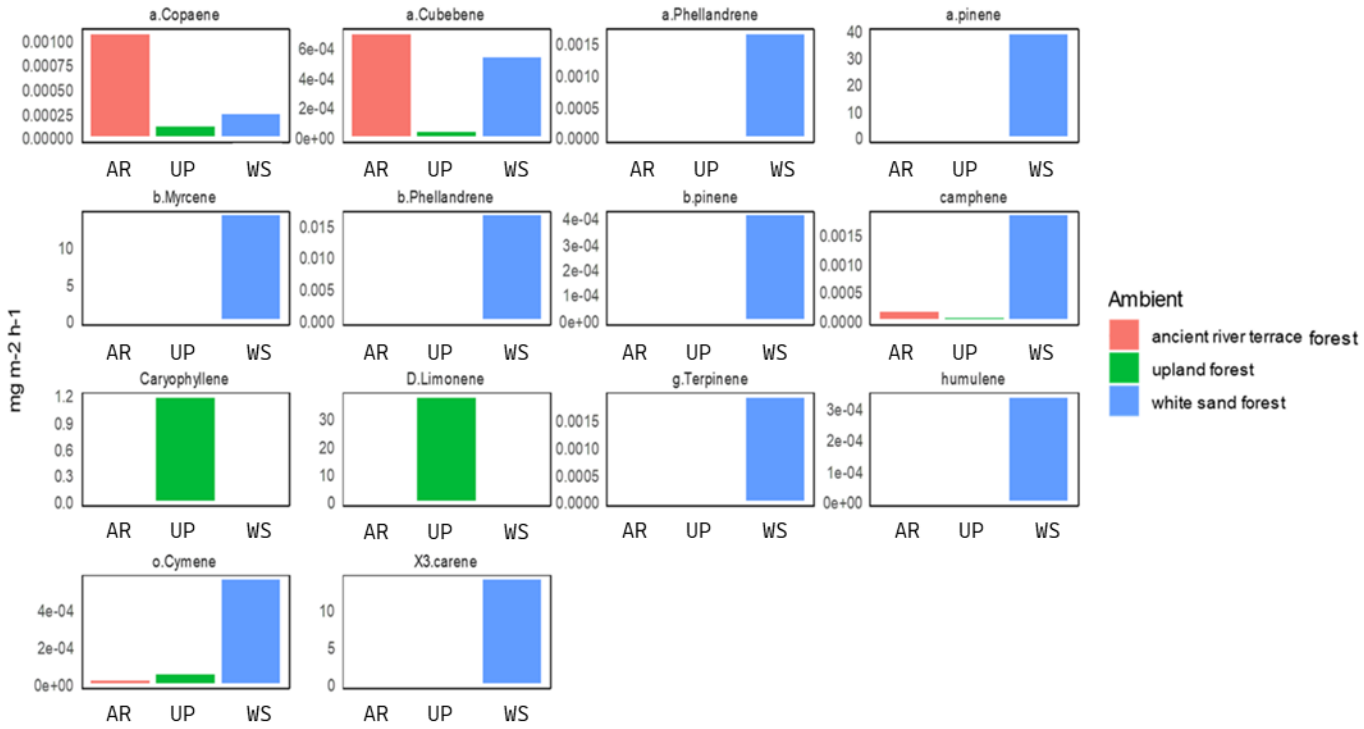

Figure S2. BVOC Fluxes from the soil and litter across the three forest types. Bar plot of the 12 samples from each environment.

4. Linear Models (LM)

4.1 White sand forest fluxes and its potential predictors

Firstly, we investigated the correlation between potential predictors of fluxes in the white sand forest. The Pearson correlations are shown in Figure S3a. Secondly, for the same ecosystem, we studied the correlation between potential predictors and the fluxes, for which the Pearson correlations are shown in Figure S3b.

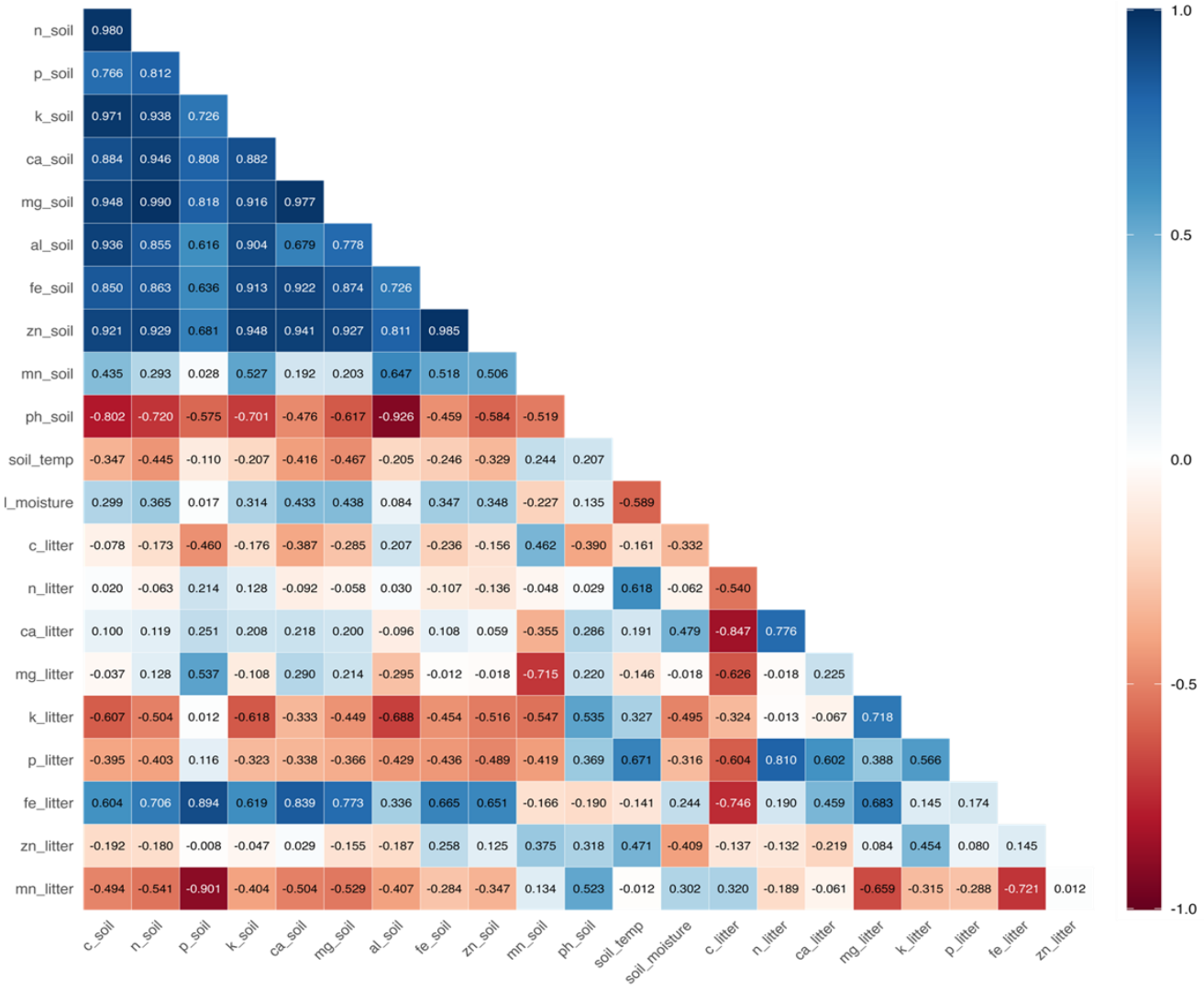

Figure S3a. Heatmap for the Pearson correlation coefficients for the potential predictors of fluxes in the white sand forest. N = 12.

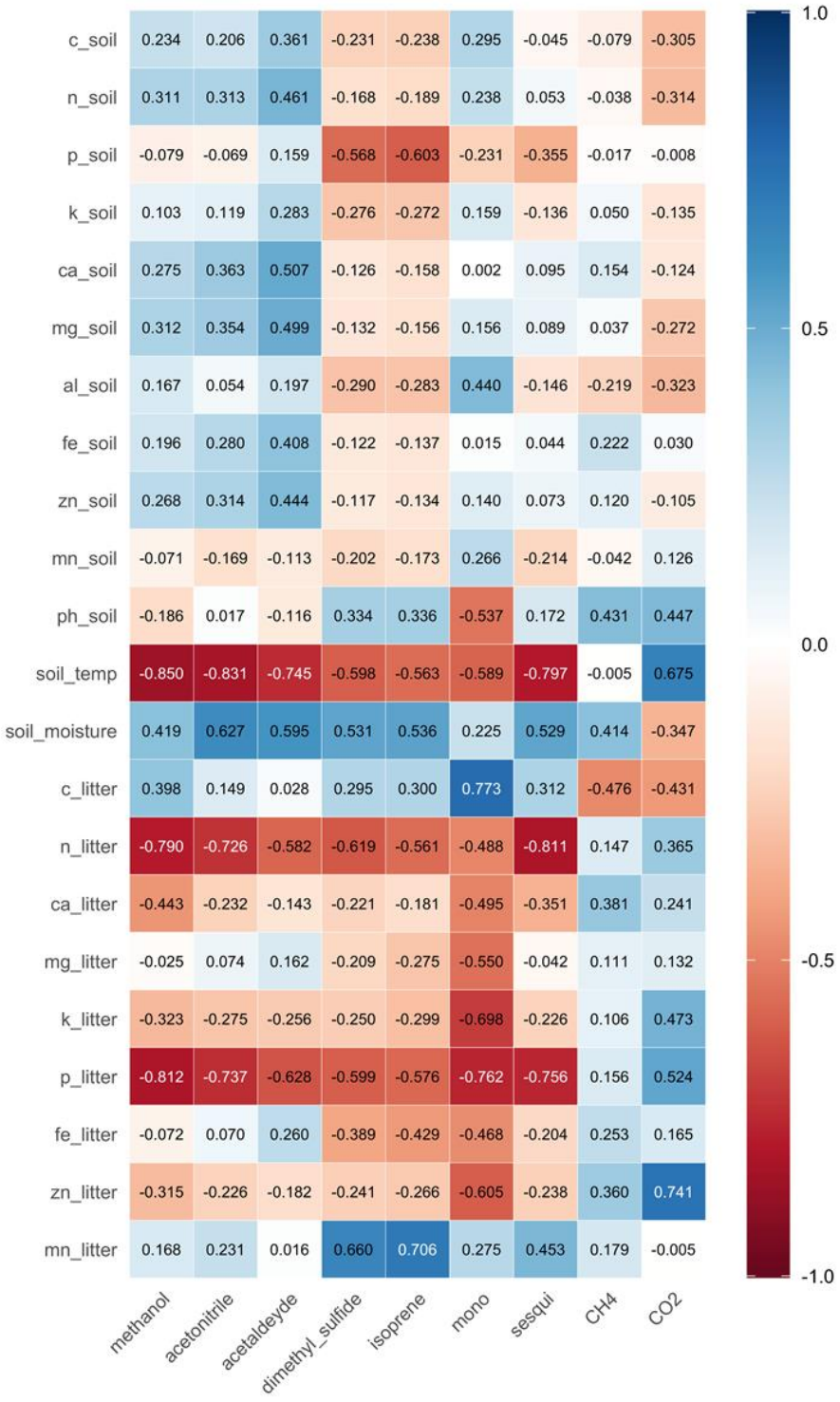

Figure S3 b. Heatmap for the Pearson correlation coefficients for the correlation between gas fluxes and its potential predictors in the white sand forest. N = 12.

4.2 Ancient river terrace forest fluxes and its potential predictors

Firstly, we investigated the correlation between potential predictors of fluxes in the ancient river terrace forest. The Pearson correlations are shown in Figure S4a. Secondly, for the same ecosystem, we studied the correlation between potential predictors and the fluxes, for which the Pearson correlations are shown in Figure S4b.

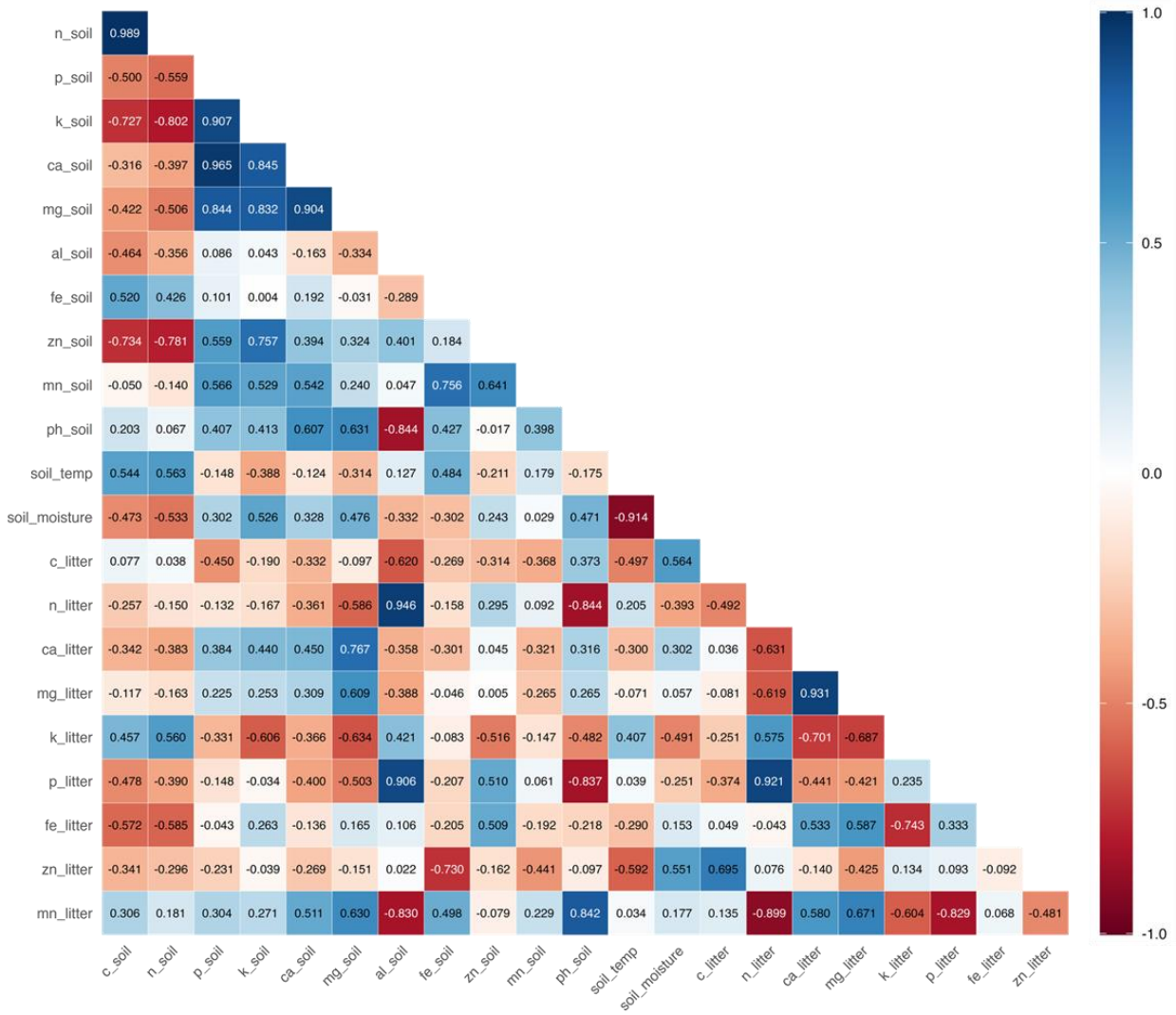

Figure S4a. Heatmap for the Pearson correlation coefficients for the potential predictors of gas fluxes ancient river terrace Forest. N = 12.

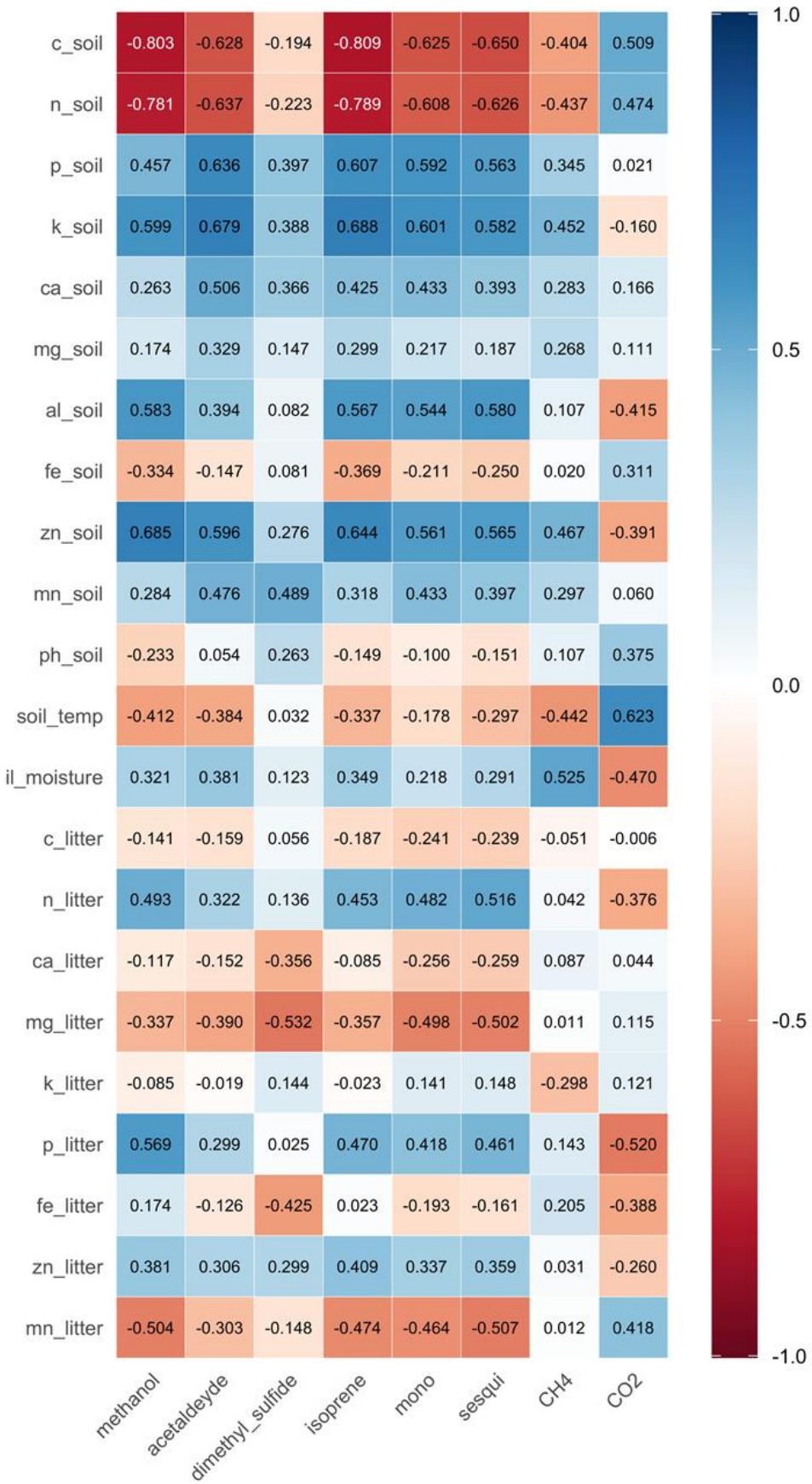
c_soil -0.803 -0.628 -0.194 -0.809 -0.625 -0.650 -0.404 0.509
n_soil -0.781 -0.637 -0.223 -0.789 -0.608 -0.626 -0.437 0.474
p_soil 0.457 0.636 0.397 0.607 0.592 0.563 0.345 0.021
k_soil 0.599 0.679 0.388 0.688 0.601 0.582 0.452 -0.160
ca_soil 0.263 0.506 0.366 0.425 0.433 0.393 0.283 0.166
mg_soil 0.174 0.329 0.147 0.299 0.217 0.187 0.268 0.111
al_soil 0.583 0.394 0.082 0.567 0.544 0.580 0.107 -0.415
fe_soil -0.334 -0.147 0.081 -0.369 -0.211 -0.250 0.020 0.311
zn_soil 0.685 0.596 0.276 0.644 0.561 0.565 0.467 -0.391
mn_soil 0.284 0.476 0.489 0.318 0.433 0.397 0.297 0.060
ph_soil -0.233 0.054 0.263 -0.149 -0.100 -0.151 0.107 0.375
soil_temp -0.412 -0.384 0.032 -0.337 -0.178 -0.297 -0.442 0.623
il_moisture 0.321 0.381 0.123 0.349 0.218 0.291 0.525 -0.470
c_litter -0.141 -0.159 0.056 -0.187 -0.241 -0.239 -0.051 -0.006
n_litter 0.493 0.322 0.136 0.453 0.482 0.516 0.042 -0.376
ca_litter -0.117 -0.152 -0.356 -0.085 -0.256 -0.259 0.087 0.044
mg_litter -0.337 -0.390 -0.532 -0.357 -0.498 -0.502 0.011 0.115
k_litter -0.085 -0.019 0.144 -0.023 0.141 0.148 -0.298 0.121
p_litter 0.569 0.299 0.025 0.470 0.418 0.461 0.143 -0.520
fe_litter 0.174 -0.126 -0.425 0.023 -0.193 -0.161 0.205 -0.388
zn_litter 0.381 0.306 0.299 0.409 0.337 0.359 0.031 -0.260
mn_litter -0.504 -0.303 -0.148 -0.474 -0.464 -0.507 0.012 0.418
methanol
acetaldeyde
dimethyl_sulfide
isoprene
mono
sesqui
CH4
CO2
1.0
0.5
0.0
-0.5
-1.0

Figure S4 b. Heatmap for the Pearson correlation coefficients for the correlation between gas fluxes and its potential predictors in the ancient river terrace forest. N = 12.

4.3 Upland forest fluxes and its potential predictors

Firstly, we investigated the correlation between potential predictors of fluxes in the upland forest. The Pearson correlations are shown in Figure S5a. Secondly, for the same ecosystem, we studied the correlation between potential predictors and the fluxes, for which the Pearson correlations are shown in Figure S5b.

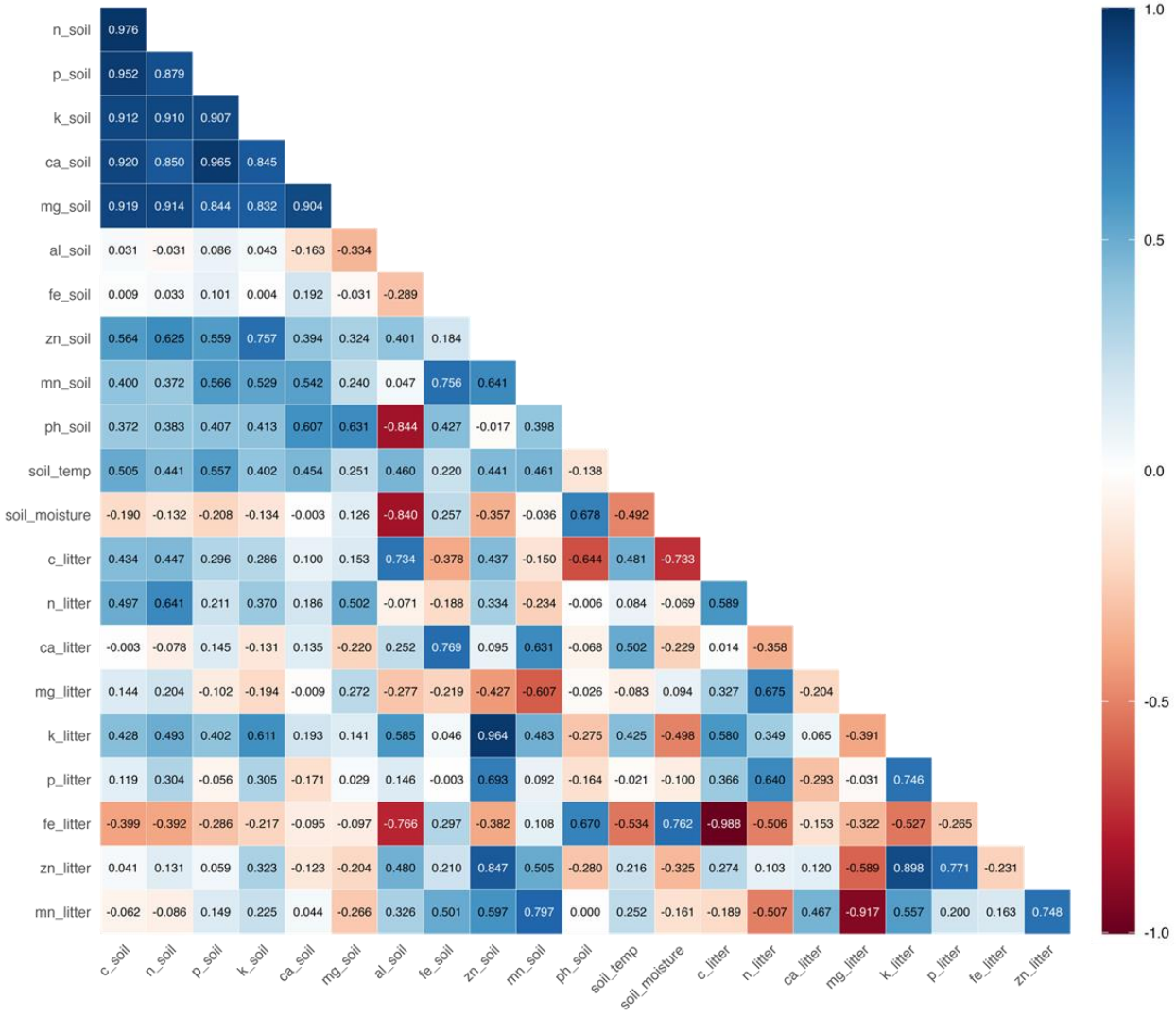

Figure S5a. Heatmap for the Pearson correlation coefficients for the potential predictors of gas fluxes in the upland forest. N = 12.

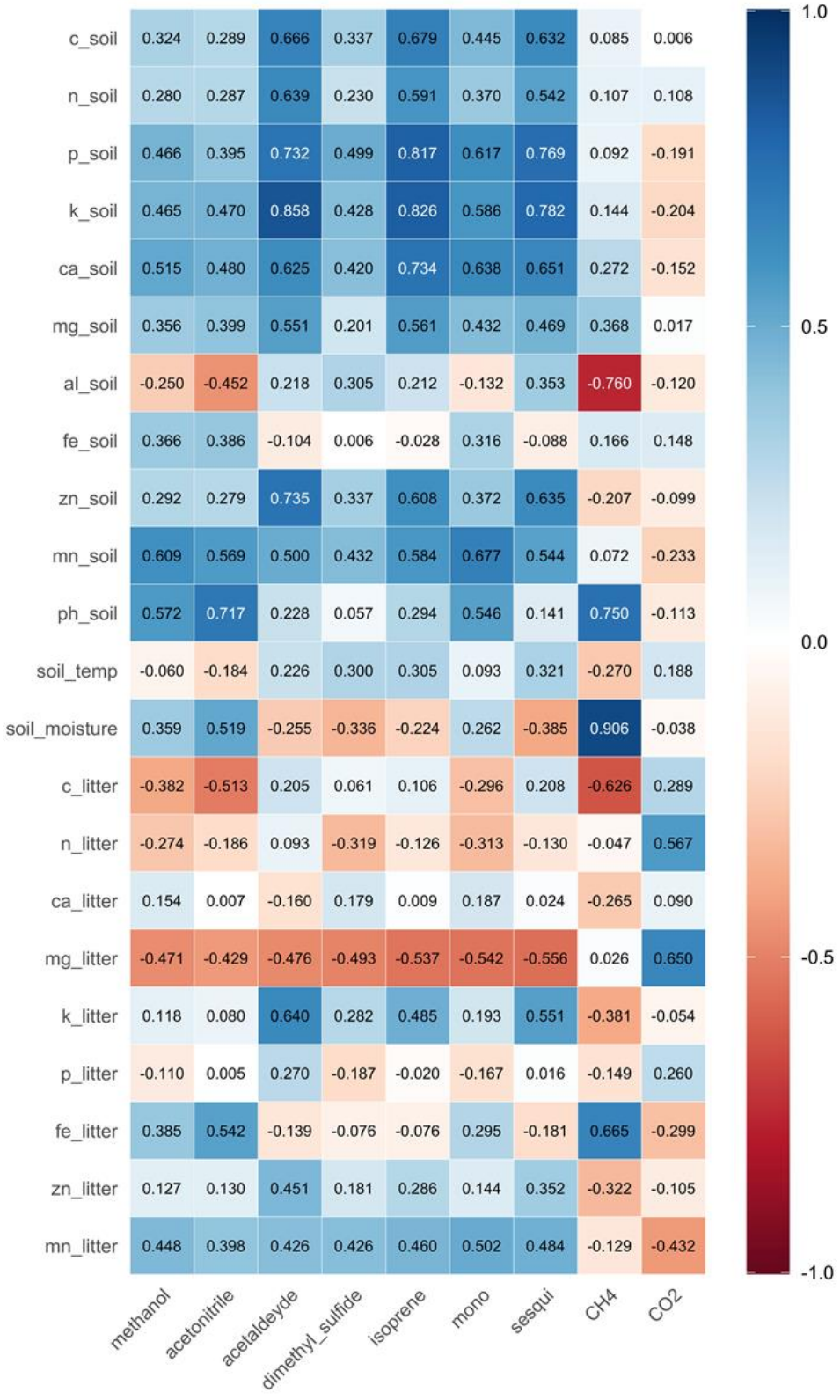

Figure S5b. Heatmap for the Pearson correlation coefficients for the correlation between gas fluxes and its potential predictors in the upland forest. N = 12.

5. Tangled Influences of Soil Moisture and Temperature on BVOC and CH_4 Fluxes

5.1 Relation between soil moisture and soil temperature (all forest types)

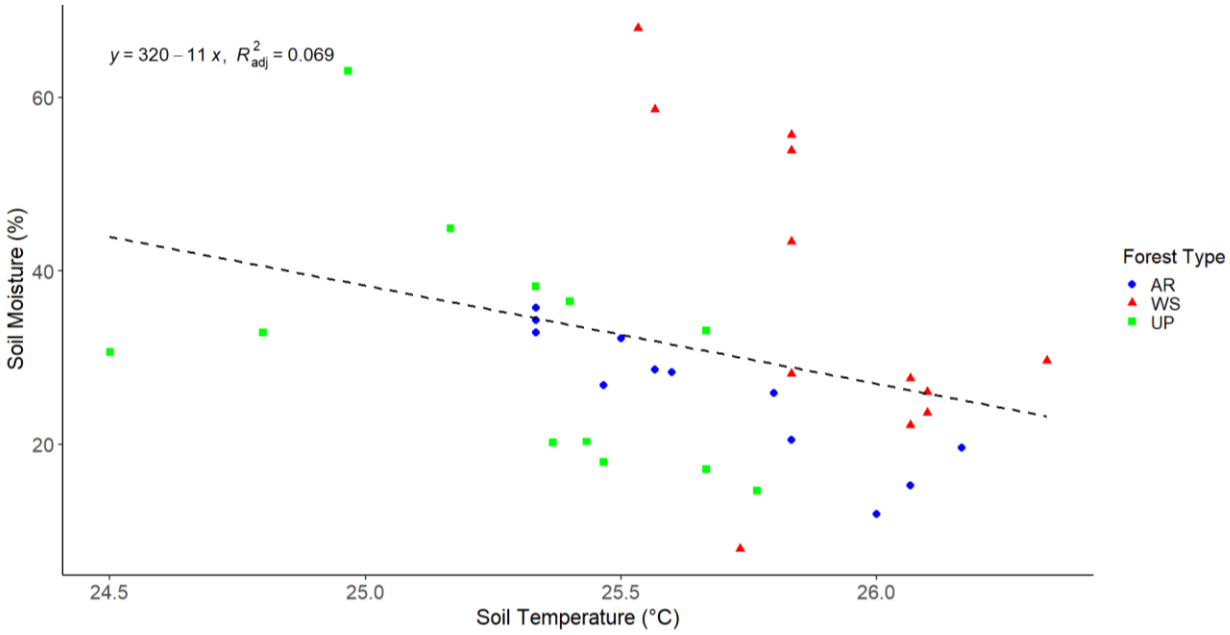

Figure S6. Relation between soil moisture and soil temperature in all forest types (AR, WS and UP), average of five measurements taken in the topsoil. The dashed line represents the linear regression fitted to the data, indicating the general trend of the relationship between soil moisture with soil temperature. This regression model was built based on 36 observations.

5.2Relation between soil temperature, soil moisture and CH_4 fluxes (all forest types)

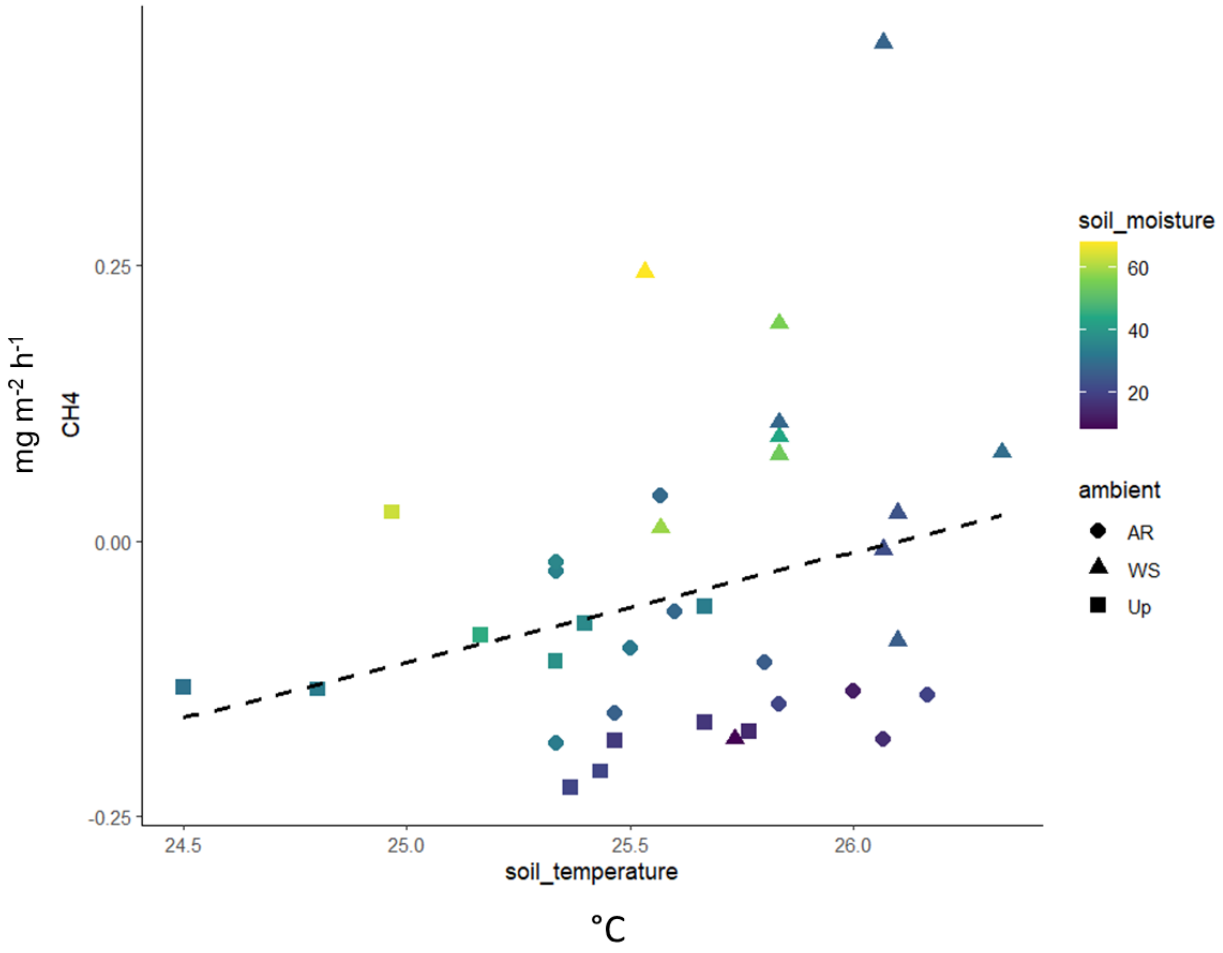

Figure S7. CH_4 flux from the soil and litter in the different forest types. The figure shows the relationship between soil moisture (colorbar) and soil temperature (x-axes), both an average of five measurements taken in the topsoil, with the flux of CH_4 (mg m^{-2} h^{-1}). The dashed line represents the linear regression fitted to the data, indicating the general trend of the relationship between soil moisture with CH_4 fluxes. This regression model was built based on 36 observations.

6. Spatial variability

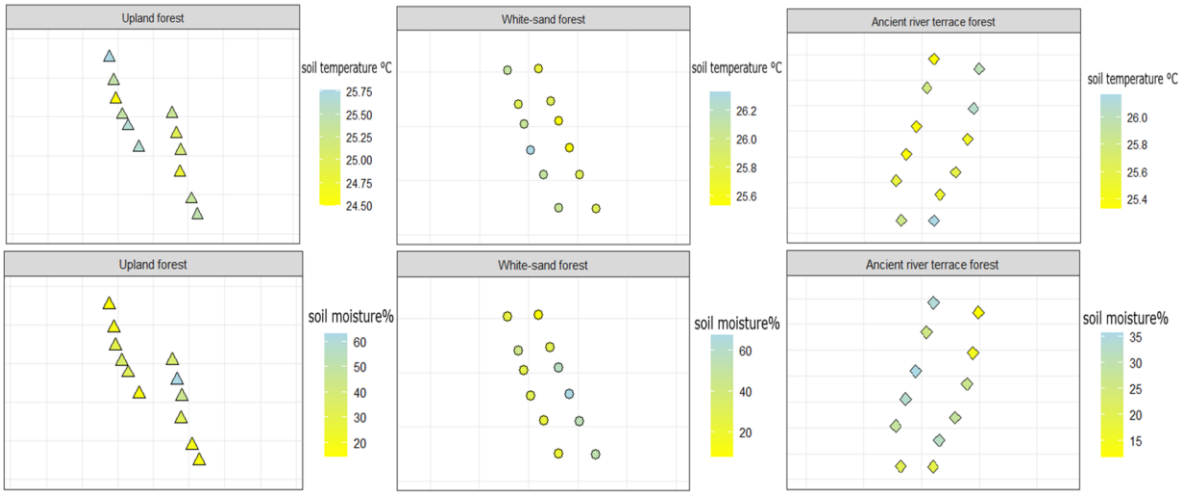

Figure S8. Map showing the two transects in each of the three forest types: UP, WS and AR, where chambers were installed. Each transect contains six sampling points, totaling 12 measurement points per forest type. The soil moisture data are expressed in % and soil temperature in °C.

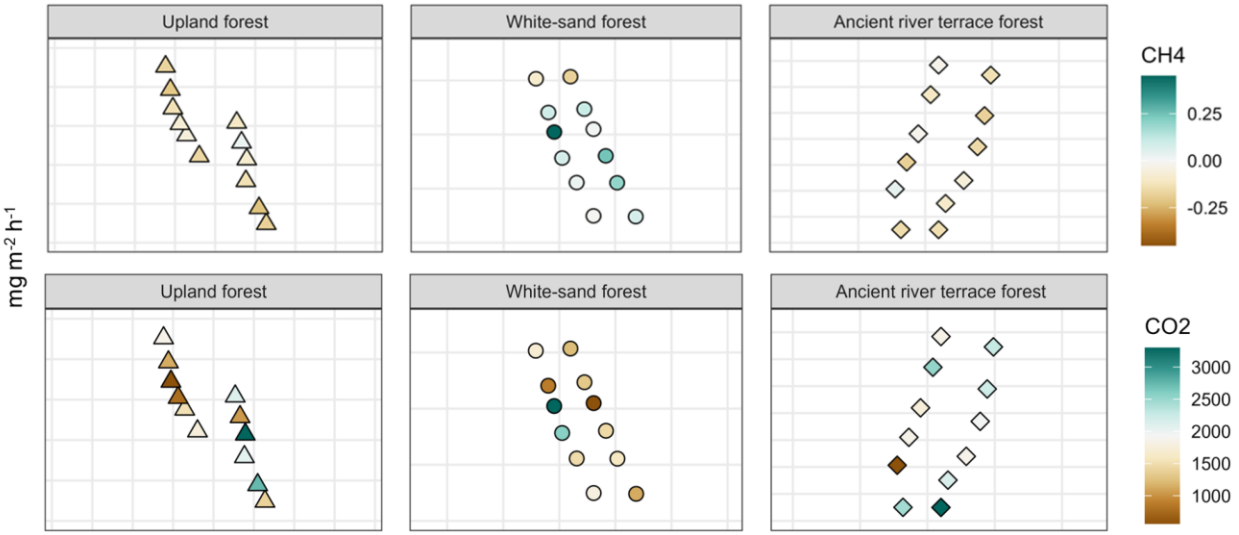

Figure S9. Map of the points collected showing the flux of GHG - methane and CO_2 in each of the three forest types: UP, WS, and AR, where flux measurements were conducted. Each transect contains six sampling points, totaling 12 measurement points per forest type. The gas flux data are expressed in mg m^{-2} h^{-1}.

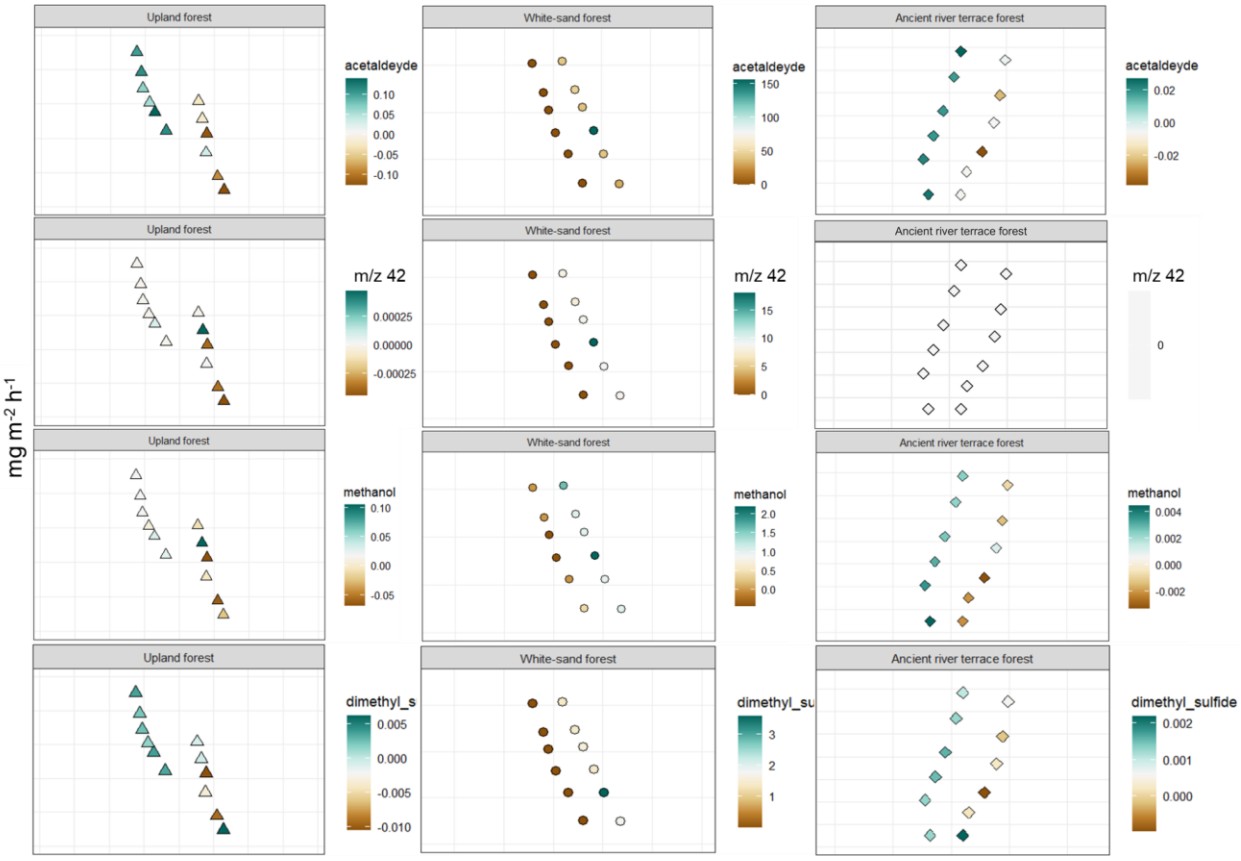

Figure S10. Map of the points collected showing the flux of BVOC in each of the three forest types: UP, WS, and AR, where flux measurements were conducted. Each transect contains six sampling points, totaling 12 measurement points per forest type. The gas flux data are expressed in mg m^{-2} h^{-1}.