1 Supplementary information

2 **1. Possibility of desorption**

3 It has been suggested that CH₄ release from plant materials might result from CH₄ desorption in
4 low-CH₄ environments, e.g., after flushing with CH₄ free air (Kirschbaum et al., 2007).

5 It has previously been shown by Kirschbaum and Walcroft (2008) that desorption does not play 6 a significant role under ambient conditions of moisture, temperature and CH₄ concentrations 7 (Kirschbaum and Walcroft, 2008). However, whereas Kirschbaum and Walcroft used ambient 8 CH₄ levels for adsorption and investigated the desorption at ambient temperatures under low 9 CH₄ conditions, we also investigated adsorption to peat at much higher CH₄ concentrations of 10 12,500 ppm, 100 ppm and 10 ppm and its desorption at 50 °C. For each concentration level 6 11 vials were prepared and left to rest at room temperature for 3 days to allow the CH_4 to adsorb to 12 the peat surfaces. The samples were then divided into two groups, one being lyophilised 13 overnight, then flushed with CH₄ free air, while one was only flushed with CH₄ free air. A third 14 group of three peat samples, which contained no additional CH₄ but were also lyophilised and 15 flushed with CH₄ free air, served as control. Finally, all three groups were supplemented with 16 water and incubated at 50 °C for 17 h.

17 The objective of this experiment was to determine whether the observed CH_4 emissions were 18 indeed formed during the incubations or were due to an artefact caused by desorption of CH_4 , 19 possibly arising from microbial origin, from the material under higher than ambient CH_4 levels 20 in the soil or peat. Moreover, this experiment also enables us to determine if any of the adsorbed 21 CH_4 following the lyophilisation process could account for some of the CH_4 observed in our 22 measurements.

The peat samples treated with the highest CH₄ levels (12,500 ppm) showed an increased CH₄ release in both CH₄ supplemented groups ($2.2 \pm 0.9 \text{ ng g}^{-1}$ (dw) h⁻¹ and $3.3 \pm 0.3 \text{ ng g}^{-1}$ (dw) h⁻¹ for samples with and without lyophilisation, respectively) compared to the untreated control group ($0.4 \pm 0.1 \text{ ng g}^{-1}$ (dw) h⁻¹). However, the samples treated with 100 and 10 ppm CH₄ showed no significant increase, both with and without lyophilisation. Furthermore, samples of kaolinite and sea sand were tested for their adsorption potential of CH_4 using 10 ppm CH_4 but again no adsorption/desorption was detected.

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31 **2.** Exclusion of methane oxidation by methane consuming bacteria

Several experiments from the water dependence study were repeated to investigate the possible 32 33 influence of methanotrophic bacteria on CH_4 emissions. For the dry samples and those with a 34 sample to water ratio of 2:1, 1:1 and 1:2 the experiment was repeated at 40 °C with the addition of 20 µl diflouromethane (DFM) per vial. DFM was added to inhibit CH₄ oxidation by any 35 methanotrophic bacteria (Miller et al., 1998) possibly present in the non-sterile samples. No 36 37 significant effect was observed on the emission rates after adding DFM, leading to the conclusion that there were no methanotrophic bacteria active in the lyophilised samples. 38 Measured CH₄ emissions were 0.8 ± 0.2 ng g⁻¹ (dw) h⁻¹ without DFM and 0.4 ± 0.02 ng g⁻¹ (dw) 39 h^{-1} with DFM for the dry samples. The wetted samples showed emissions ranging from 1.6 ± 0.1 40 to 1.9 ± 0.1 ng g⁻¹ (dw) h⁻¹ with and without added DFM. 41

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43 **3. Arrhenius plots**



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We used the experimental data from samples SL, SG and PH to draw Arrhenius plots for CH₄ formation (Fig. S1). For all samples the results were found to follow a linear relationship at temperatures ranging from 30 to 90 °C. The activation energies (E_a) for CH₄ formation for each sample, calculated from the slope of the line, yielded values of 50.1 kJ mol⁻¹, 101.3 kJ mol⁻¹ and 79.2 kJ mol⁻¹ for SL, SG and PH, respectively. Again, this is strong supportive evidence of an abiotic underlying process as reactions with activation energies higher than 50 kJ mol⁻¹ are considered to be abiotic (Schönknecht et al., 2008).

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55 **References**

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