

SUPPLEMENTARY MATERIAL

Explicit microrelief-controlled decoupling of initial aerobic (in hummocks) and anaerobic (in hollows) decay in superficial layers of *Sphagnum*-dominated peatlands.

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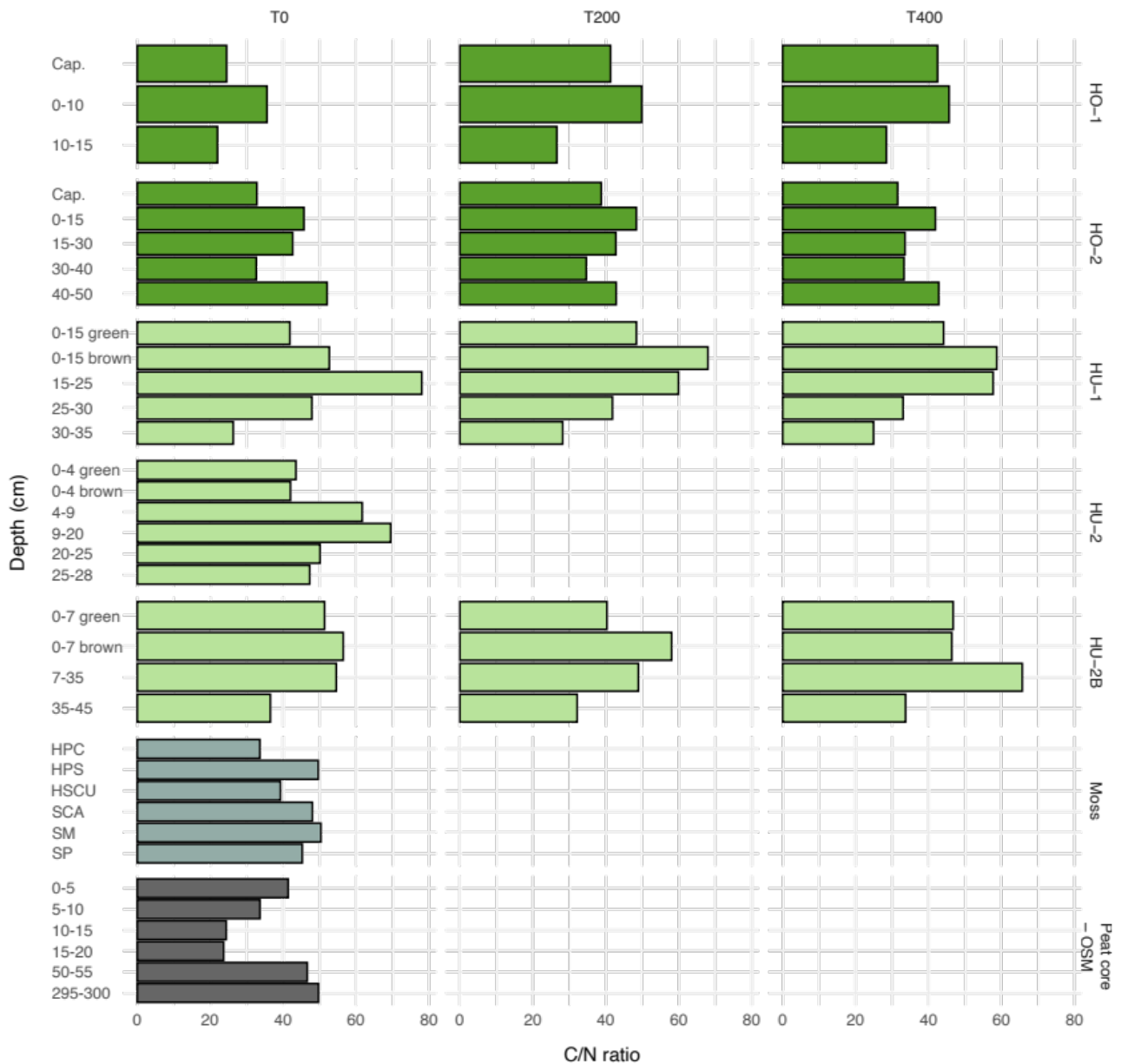


Figure SM 1: Carbon to nitrogen ratio of all the cores before incubation (T0, original sample) and after 200 and 400 days of incubation (T200 and T400, respectively). Hollow (HO) and hummock (HU) surface moss cores, fresh moss samples (Moss) and the long peat core (OSM). In the y axis the depths are shown in cm. Moss species are *Polytrichum commune* (HPC), *Polytrichum strictum* (HPS), *Sphagnum cuspidatum* (HSCU), *Sphagnum capillifolium* (SCA), *Sphagnum magellanicum* (SM), *Sphagnum papillosum* (SP).

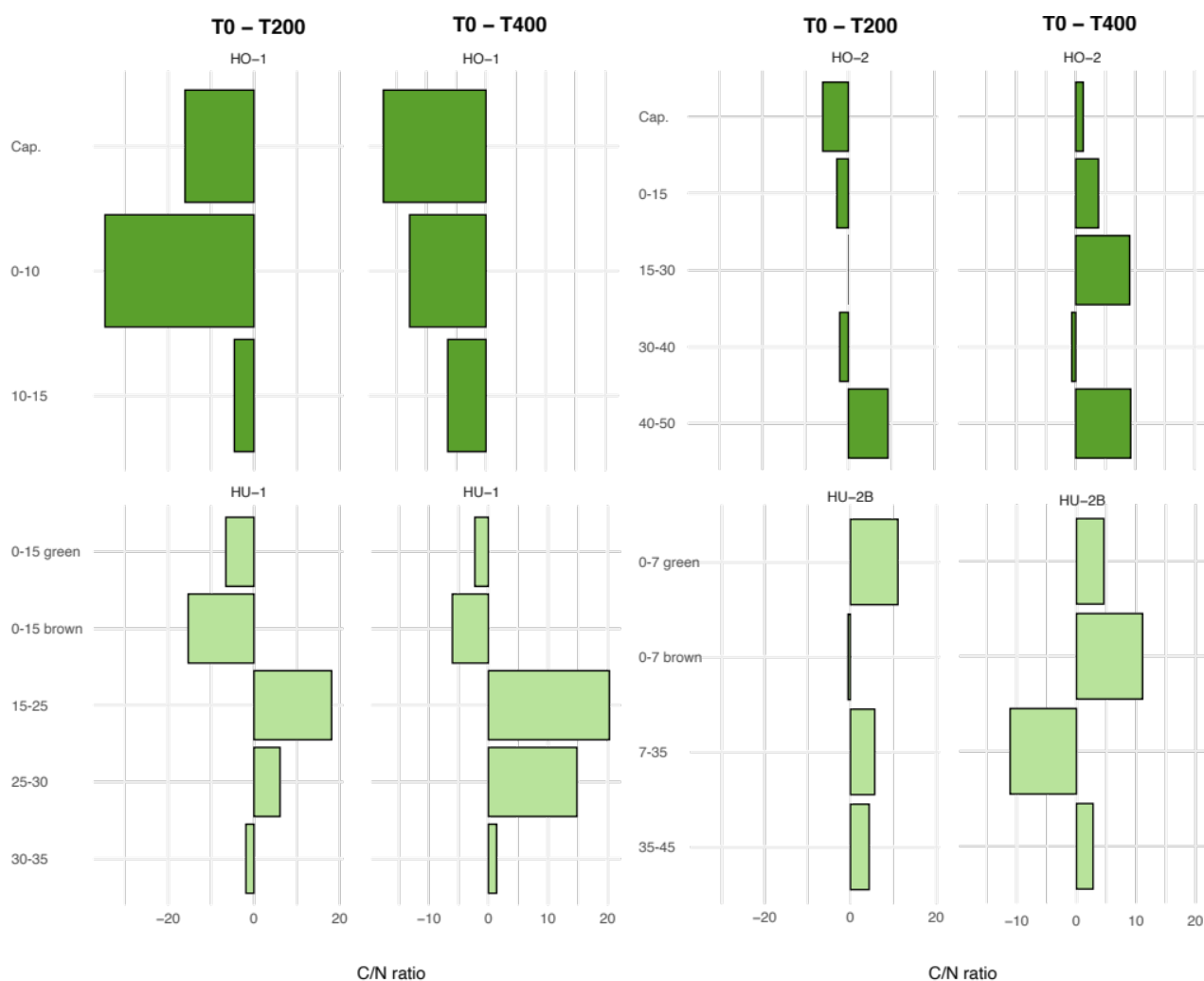


Figure SM 2: Differences in the carbon to nitrogen ratio (C/N) between the original sample (T0, i.e. before incubation) and after 200 and 400 days of incubation (T200 and T400, respectively) in surface moss cores samples studied by Py (HO-1, HO-2 and HU-1) and in a HU core collected in the vicinity of HU-2. In the y axis the depths are shown in cm.

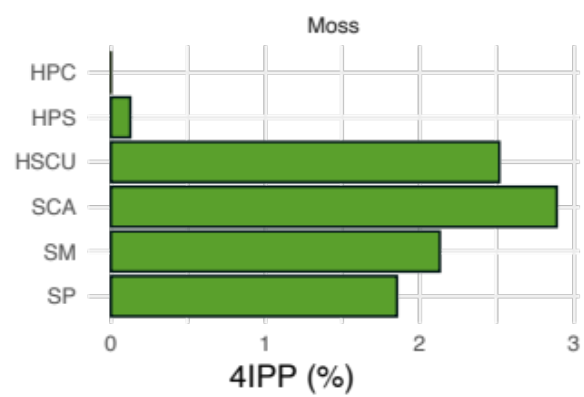


Figure SM 3: Proportion of 4-isopropenylphenol (4IPP) in fresh moss samples.

Scanning electron microscopy

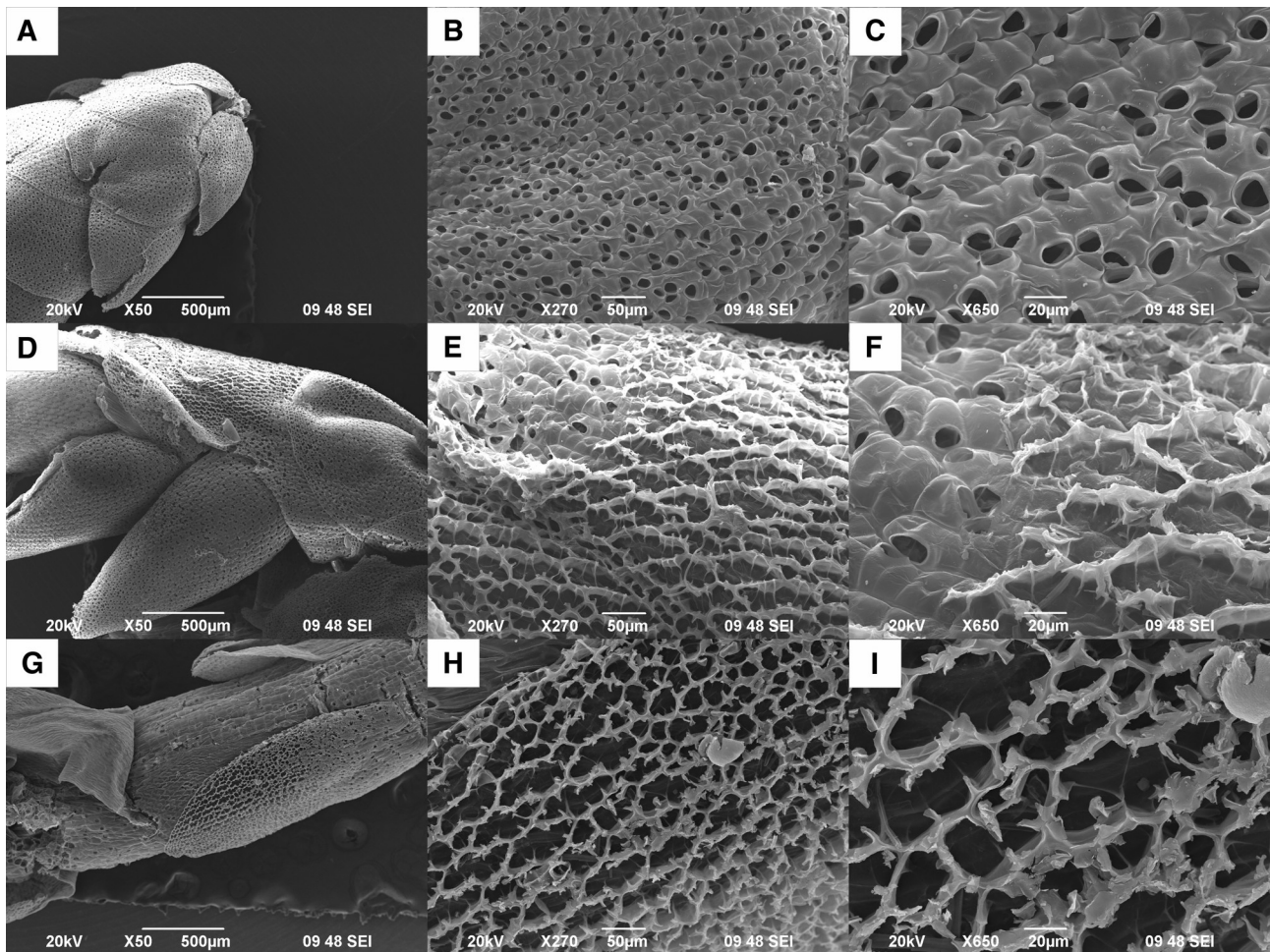


Figure SM 4: Scanning electron micrograph of *Sphagnum* spp. at different degradation states from core HO-2 (0-30 cm depth). Left columns are a general image of the sample; the middle and right-hand columns correspond to more detailed images of the same section of the sample. (A–C) Sample H0542 (photosynthetically active moss, 0-15cm, no-incubated). (B and C) detail of well-preserved hyaline cells and pores. (D – I) Sample H0543 (15-30 cm, no-incubated); coexistence of well preserved well-preserved hyaline cells (top left of photos E and F) with highly degraded hyaline cells where most of the cell content has been lost (bottom right E – F and H – I).

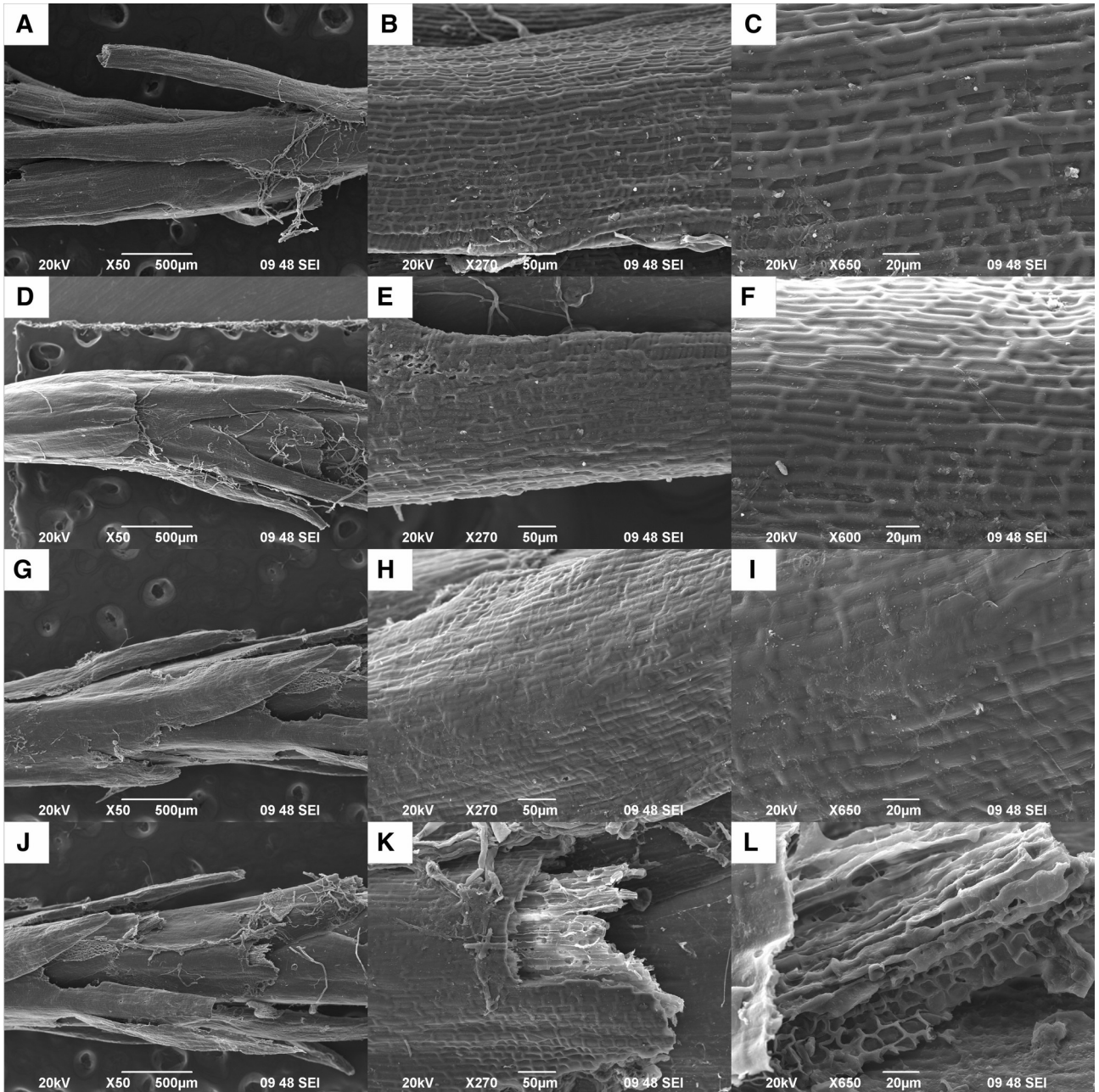


Figure SM 5: Scanning electron micrograph of Polytrichum spp. at different degradation states from core HU-1 (0-30 cm depth). Left columns are a general image of the sample; the middle and right-hand columns correspond to more detailed images of the same section of the sample. (A– C) Sample H0532 (0-15cm, no-incubated). (B and C) well-preserved cells showing a homogenous surface. (D – F) Sample H0533 (15-25 cm, no-incubated); limited change in the physical degradation of the moss material. (G – L) Sample H0534 (25-30 cm, no-incubated); coexistence of moss sections un-altered with more degraded sections (mainly at the edges of the shafts of fracture); the surface of the moss remains mostly physically unchanged.

Decay effects *Polytrichum* vs. *Sphagnum*

The lack of a decay effect of products that are enriched in *Polytrichum* – benzene, benzoic acid, hydroquinone, 5-hydroxymethyl-2-tetrahydrofuraldehyde-3-one, and an unidentified carbohydrate product (m/z 110 and 82) – shows that observed differences in sphagnum acid and H-type products indicate preferential loss from the *Sphagnum* tissues, not a vegetation effect. This might be reinforced by the incubation conditions, where part of the incubated sample remained underwater and the lack of a proper leaching effect. Scanning electron microscopy examination indicates that preferential loss of *Sphagnum* material compared to *Polytrichum* may also occur under field conditions, as greater change in *Sphagnum* compared to *Polytrichum* is observed with increasing depth (Figure SM1 and SM2)

Decay effects using THM-GC-MS

For THM-GC-MS, the difference analyses (t -test) of the eight pairs for which t_0 , t_{200} , and t_{400} data are available, showed that the incubation causes an increase in a series of carbohydrate products (1,4-DMB, 1,2,4-DMB, dimethyl-methoxyfuranone), unspecific methoxybenzenes (G1, S1, tetramethoxybenzene), C15 FAME and iso/anteiso-C15 FAME increase, probably reflecting an increase in microbial OM, and strong decreases in H-type products (P12), the butenoic-acid-substituted sphagnum acid-derived methoxybenzenes (all 3 compounds) and other FAMEs (C14, C20-C30, and three cutin-derived FAMEs). The sum of cutin and sphagnum acid products also decreased significantly, as does the H/(G+S) ratio. Therefore, perhaps due to higher sensitivity than Py-GC-MS, THM does pick up the expected decay signal of *Sphagnum*-derived phenols. In the HU, the loss of sphagnum acid during incubation is larger for the superficial than deeper samples (0-15 cm = 3.2 %, 15-25 = 2.0 %, >30 cm = 0.4 %), probably because of the smaller sphagnum acid pools in the older materials. To the contrary, for the HO, the loss of sphagnum acid at the surface (capitulum) is 0.2 %, increasing to 0.5 % at 0-15 cm, 3.0 % at 30-40 cm and 3.1 % at 40-50 cm. The increase in sphagnum acid loss with depth on HO have to be interpreted with caution as the increased observability of carbohydrates in older materials may imply a dilution of the sphagnum acid visibility (closed data), but an effect of slow anaerobic cell rupture as a precondition on sphagnum acid release from hollows cannot be discarded. Again, differences are much bigger between t_0 and t_{200} than between t_{200} and t_{400} . In fact, depletion of sphagnum acid products is not significant for the t_{200} – t_{400} difference values.