Supporting information

Comparison of DET, DGT and conventional porewater extractions for determining nutrient profiles and cycling in stream sediments

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Figure S21. Photos of (a) Site 1 and (b) Site 2 taken at the time of sampling. The area in which cores were collected is in the foreground of each photo.

Preparation of agarose diffusive gel

Diffusive gels were prepared by dissolving 2.5% (w/v) ultrapure agarose (Life Technologies) in boiling water until completely dissolved. The solution was pipetted into molds, consisting of two acid washed glass plates clipped together and separated by a 0.125 cm thick spacer, respectively for different diffusive layer thicknesses, which were heated to 95°C to avoid premature setting of the gel. The gels were allowed to set for 45 minutes at room temperature and upon removal from the molds, washed 2-3 times in deionised water

Preparation of staining gel

Gel stock solution consists of 40% Acrylamide/bisacrylamide solution, mixed in a 1:1.66 ratio with chilled deionised water. For every 10 mL of gel stock solution, 70 μL of 10% (m/v) potassium persulfate solution (AR grade, Sigma) and 20 μL of N, N, N, N-tetramethylethylenediamine (TEMED; Sigma) was added. The solution was pippetted into molds consisting of two acid washed glass plates separated by a 0.75 mm thick plastic spacer and allow to polymerise at room temperature in a fume hood. Polymerised gels were transferred into an acid-washed plastic container filled with deionised water and the water was changed 3-4 times, with a few hours between changes, to remove any unreacted reagents from the gels. Prepared gels were stored in deionised water at 4 °C.

Nutrient concentrations determined by DGT and DET

The DGT-measured concentrations (C_{DGT}: ng mL^{-1}, converted to μg L^{-1}) of NH_4-N and NO_3-N in sediment pore waters were calculated from the accumulated analyte mass using the DGT equation (Eq 1) [1] :

$$C_{DGT} = M\Delta g/DAt \quad (1).$$

Where, M is the mass of analyte species bound to the binding phase (ng) determined by measuring the concentration of a known volume of the elutent or a dilution thereof, corrected using the elution factor [2], Δg is the diffusive layer thickness (0.09 cm), *D* is the diffusion coefficient of the analyte species through the diffusive layer (1.42×10^{-6} and 1.07×10^{-6} cm^2s^{-1} for NH_4-N at site 1 and 2 respectively, and 1.50×10^{-6} cm^2s^{-1} for NO_3-N) at experimental temperature (26°C), *t* is the deployment time (36000-43200 s, equal to 10-12 h) and *A* is the area of the probe exposed to the solution (1.8 cm^2).

The concentration of nutrients from the DET deployments (μg L^{-1}) were calculated from the dilution factor for the elution.

$$C_{DET} = Cs\ (V_e + V_g)/V_g \quad (2).$$

Where, *C*s is the concentration of NH_4-N/NO_3-N measured in the eluent, *V*e the eluent volume and *V*g the gel volume (0.1125 mL).

Table S1. Description, sediment characteristics, water quality measurements and water colu,mn nutrient concentrations at the two study sites. Values are the mean ± standard deviation (n = 3).

Site	**Site 1**	**Site 2**
Site description		
Depth (m)	0.67 ± 0.05	0.45 ± 0.06
Field light intensity (µmol m^{-2} s^{-1}), in air	2540	3040
Field light intensity (µmol m^{-2} s^{-1}), in water	1680	900
Background water physicochemistry and nutrient concentrations		
pH	8.0 ± 0.1	8.5 ± 0.2
Temperature (°C)	30.5 ± 0.1	31.4 ± 0.2
DO saturation (%)	81.6 ± 4.4	100.1 ± 7.3
Conductivity (µS cm^{-1})	1082.5 ± 14.8	495.5 ± 6.4
Turbidity (NTU)	2.1	17.5
Chlorophyll a (µg L^{-1})	0.33 ± 0.11	0.16 ± 0.05
NH_4-N (µmol L^{-1})	2.53 ± 0.24	1.56 ± 0.17
NO_3-N (µmol L^{-1})	0.43 ± 0.22	0.16 ± 0.22
PO_4-P (µmol L^{-1})	0.51 ± 0.02	0.42 ± 0.03
TDN (µmol L^{-1})	20.09 ± 1.61	33.27 ± 10.29
TDP (µmol L^{-1})	0.71 ± 0.02	0.65 ± 0.09
TN (µmol L^{-1})	23.81 ± 3.60	29.29 ± 4.46
TP (µmol L^{-1})	0.65 ± <0.01	0.86 ± 0.19
TC (mmol L^{-1})	1.48 ± 0.16	1.70 ± 0.17
TOC (mmol L^{-1})	0.34 ± 0.14	0.49 ± 0.15
Sediment characteristics		
Clay (0–2 µm) (%)	1.0 ± 0.18	1.5 ± 0.28
Silt (2–20 µm) (%)	11.3 ± 2.3	18.8 ± 2.5
Fine sand (20–200 µm) (%)	31.6 ± 1.6	27.75 ± 2.8
Coarse sand (200–2000 µm) (%)	52.8 ± 3.6	13.4 ± 3.6
Gravel (>2000 µm) (%)	3.3 ±2.1	38.3 ± 6.11
Sediment surface chlorophyll *a* (mg m^{-2})	255.6 ± 145.8	80.0 ± 66.73
Total nitrogen (%)	0.03 ± 0.01	0.05 ± 0.02
Total phosphorus (%)	0.02 ± <0.01	0.03 ± 0.01
Total organic carbon (%)	0.29 ± 0.11	0.62 ± 0.27
Gravimetric moisture content (%)	65.2 ± 34.6	47.3 ± 27.7
Bulk density (g cm^{-3})	1.10 ± 0.23	1.34 ± 0.32
Porosity (%)	58.5 ± 8.81	49.5 ± 12.3

Table S2. The average Fe (II) and PO_4-P concentrations determined by colourimetric DET techniques.

		Fe (II) (µmol L^{-1})	PO_4-P (µmol L^{-1})
Site 1	Light	29.5 ± 21.7	3.8 ± 2.7
	Dark	37.6 ± 26.1	5.3 ± 4.1
Site 2	Light	80.6 ± 78.7	16.5 ± 14.4
	Dark	127.2 ± 99.8	22.9 ± 18.6

Table S3. Ratio of C_{DGT}/C_{PW} and C_{DET}/C_{PW} for NH_4-N at site 1.

Site 1	Light		Dark	
Depth	C_{DGT}/C_{PW}	C_{DET}/C_{PW}	C_{DGT}/C_{PW}	C_{DET}/C_{PW}
-0.5	0.13	0.17	0.12	0.16
0.5	0.18	0.27	0.19	0.30
1.5	0.27	0.44	0.18	0.44
2.5	0.27	0.47	0.18	0.58
3.5	0.47	0.83	0.17	0.30
4.5	0.32	0.61	0.18	0.26
5.5	0.28	0.57	0.16	0.30
6.5	0.28	0.71	0.17	0.43
7.5	0.21	0.51	0.16	0.39
8.5	0.18	0.43	0.19	0.36

Table S4. Ratio of C_{DGT}/C_{PW} and C_{DET}/C_{PW} for NH_4-N at site 2.

Site 2	Light		Dark	
Depth	C_{DGT}/C_{PW}	C_{DET}/C_{PW}	C_{DGT}/C_{PW}	C_{DET}/C_{PW}
-0.5	0.53	2.03	0.10	0.14
0.5	0.19	0.50	0.16	0.37
1.5	0.20	0.57	0.20	0.59
2.5	0.23	0.67	0.15	0.52
3.5	0.29	0.55	0.39	0.79
4.5	0.27	0.46	0.19	0.76
5.5	0.25	0.52	0.22	0.69
6.5	0.22	0.71	0.17	0.84
7.5	0.27	1.01	0.20	0.88
8.5	0.25	0.85	0.21	0.95

Table S5. Ratio of C_{DGT}/C_{PW} and C_{DET}/C_{PW} for NO_3-N at site 1 and 2.

	Light		Dark	
	C_{DGT}/C_{PW}	**C_{DET}/C_{PW}**	**C_{DGT}/C_{PW}**	**C_{DET}/C_{PW}**
Site 1				
Core 1	-	-	0.81	-
Core 2	-	-	0.61	-
Core 3	-	-	0.60	-
Core 4	0.10	-	0.34	-
Core 5	-	-	-	-
Site 2				
Core 1	-	-	0.11	-
Core 2	-	-	0.37	-
Core 3	0.17	-	0.52	-
Core 4	-	-	0.54	-
Core 5	0.17	-	0.08	-

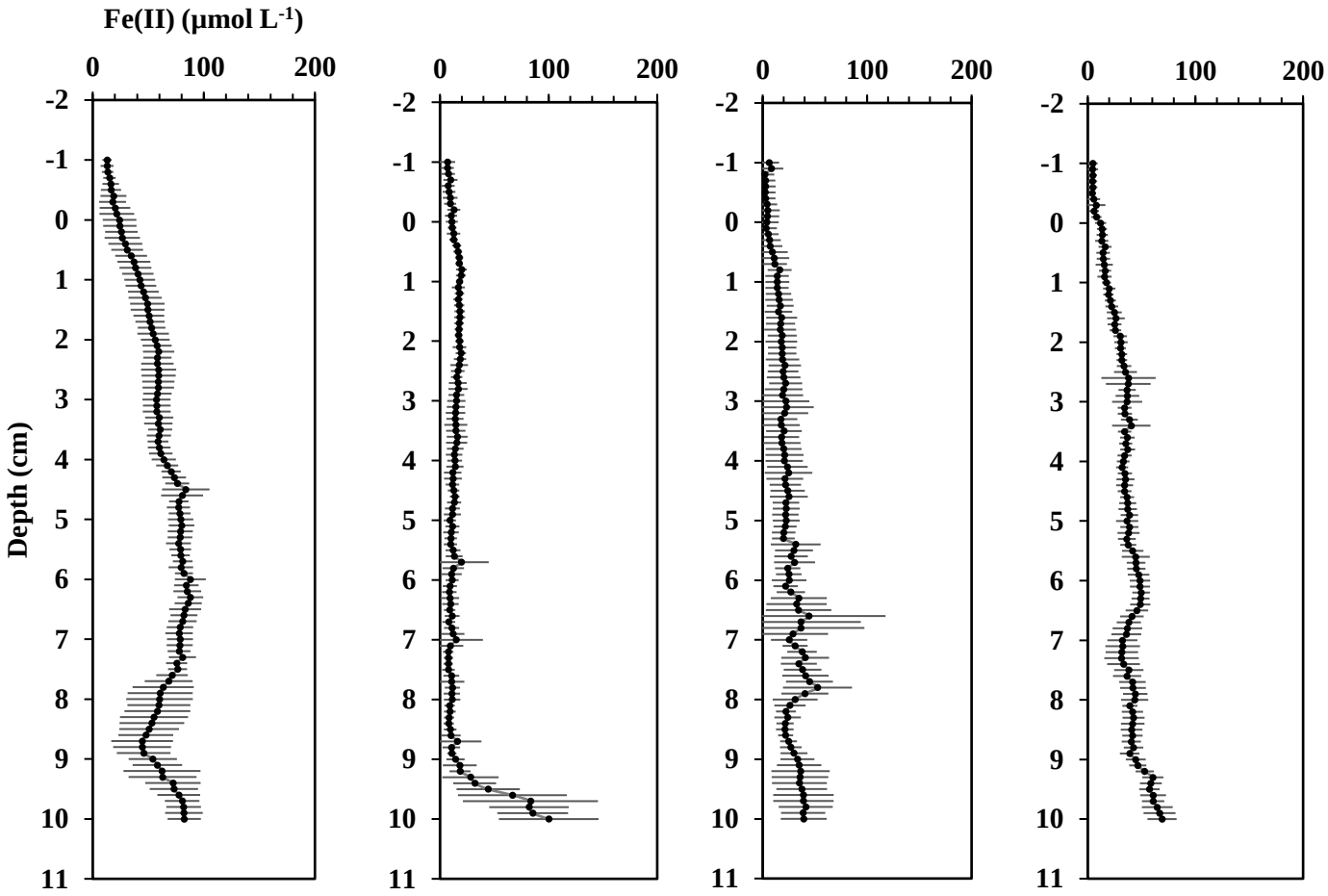

Figure S1. Pore water Fe (II) depth profiles determined by colourimetric DET for each sediment core (1, 3, 4 and 5) at site 1 during light incubations.

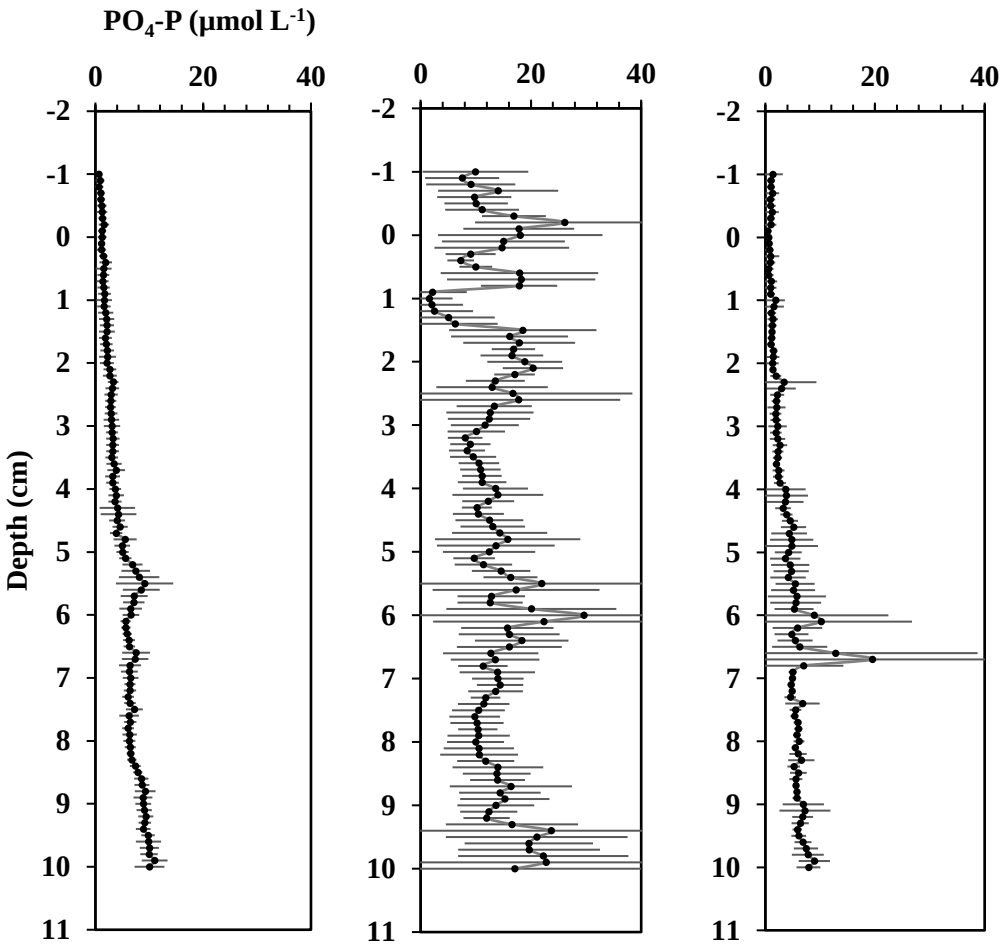

Figure S2. Pore water PO_4-P depth profiles determined by colourimetric DET for each sediment core (1, 2 and 5) at site 1 during light incubations.

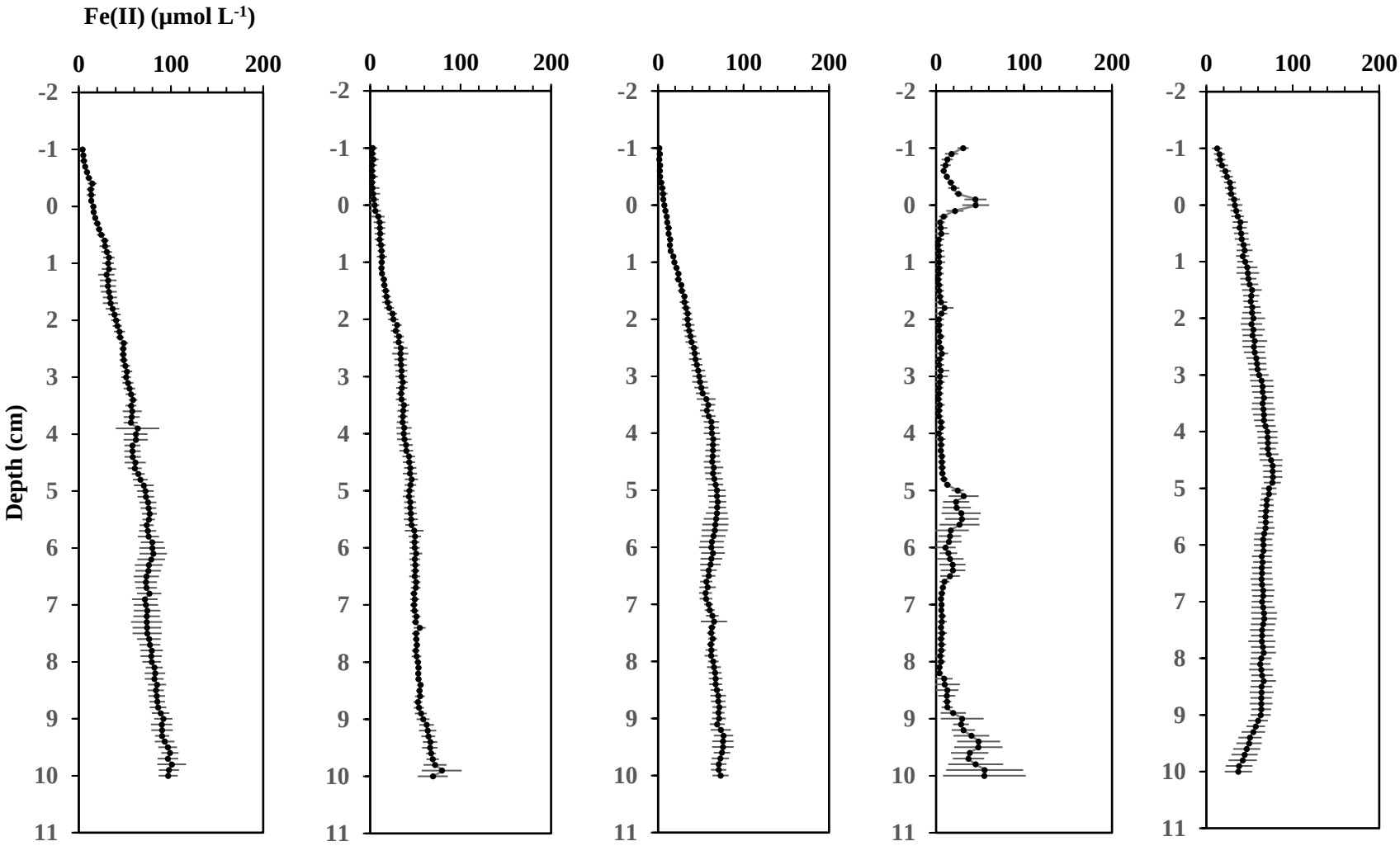

Figure S3. Pore water Fe (II) depth profiles determined by colourimetric DET for each sediment core (1 - 5) at site 1 during dark incubations.

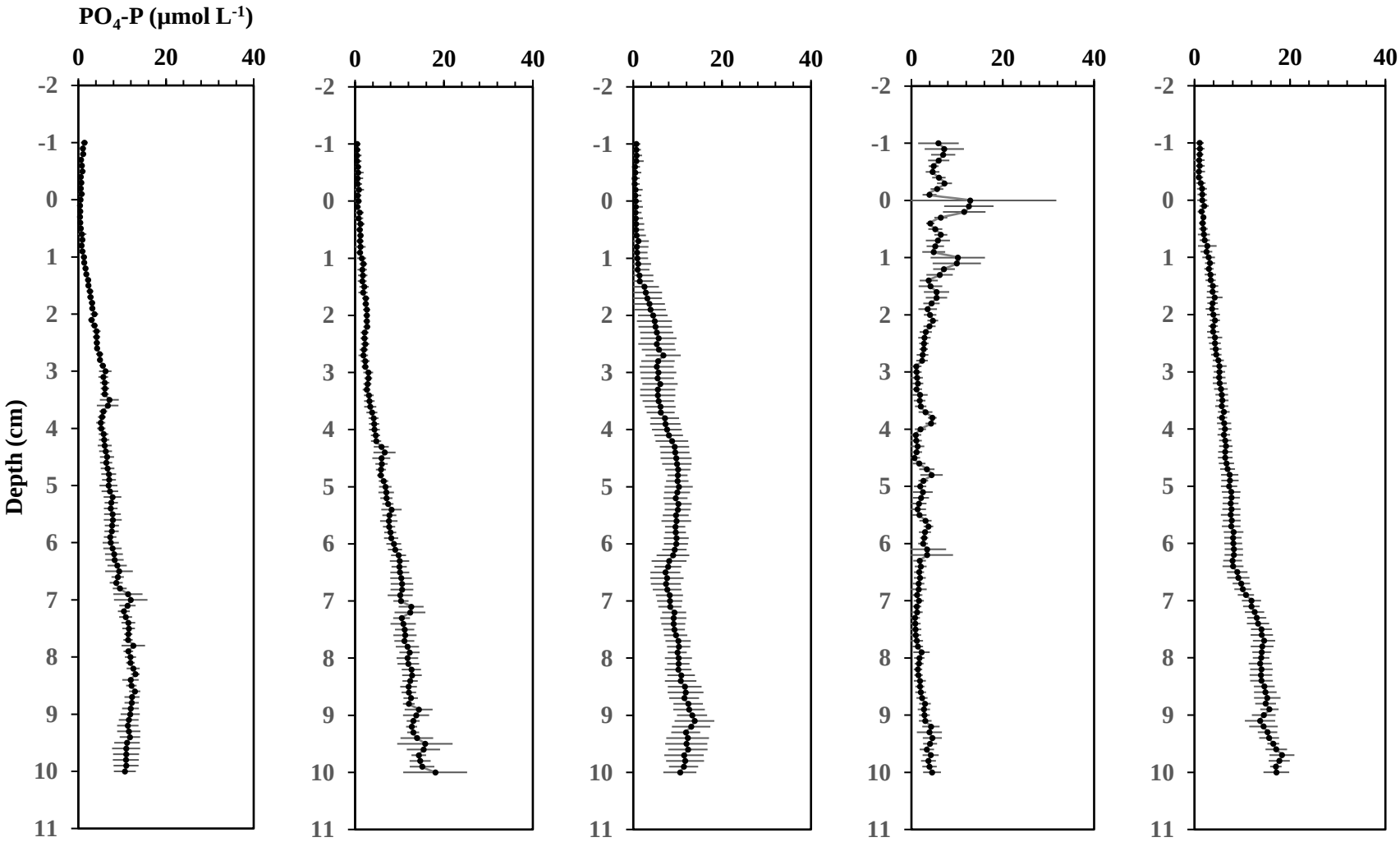

Figure S4. Pore water PO_4-P depth profiles determined by colourimetric DET for each sediment core (1 - 5) at site 1 during dark incubations.

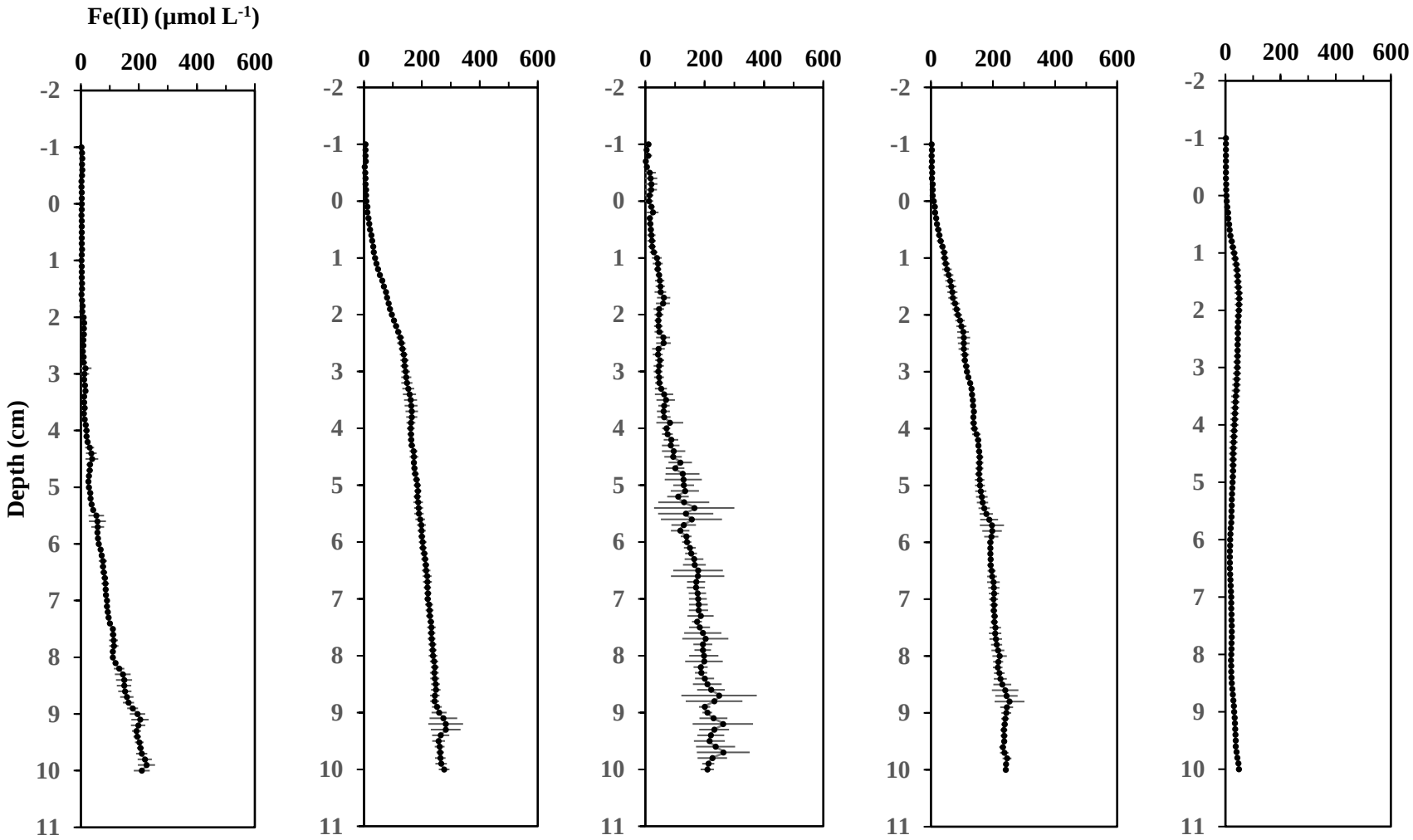

Figure S5. Pore water Fe (II) profile determined by colourimetric DET for each sediment core (1 - 5) at site 2 during light incubations.

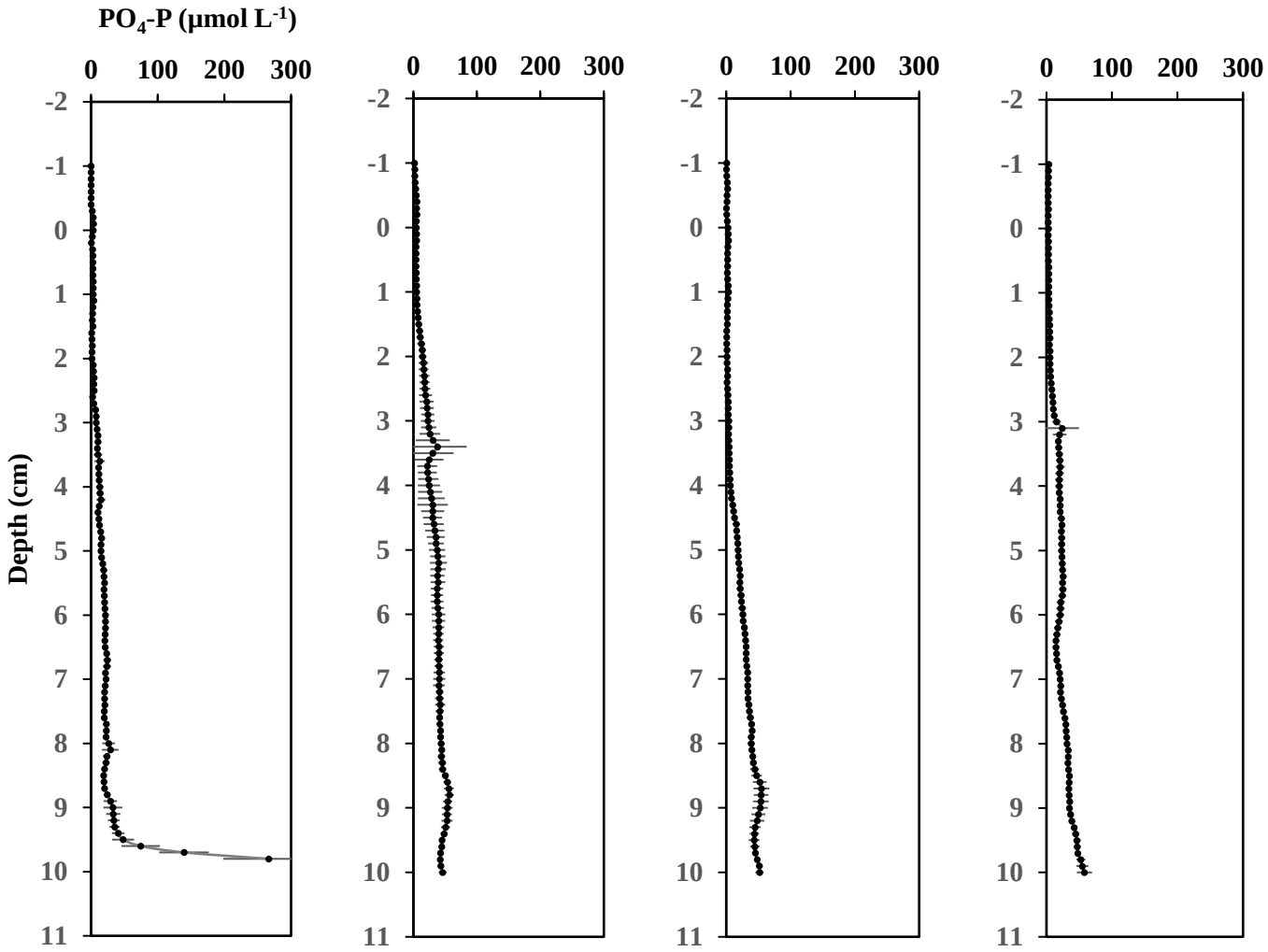

Figure S6. Pore water PO_4-P depth profiles determined by colourimetric DET for each sediment core (1, 2, 3, and 4) at site 2 during light incubations.

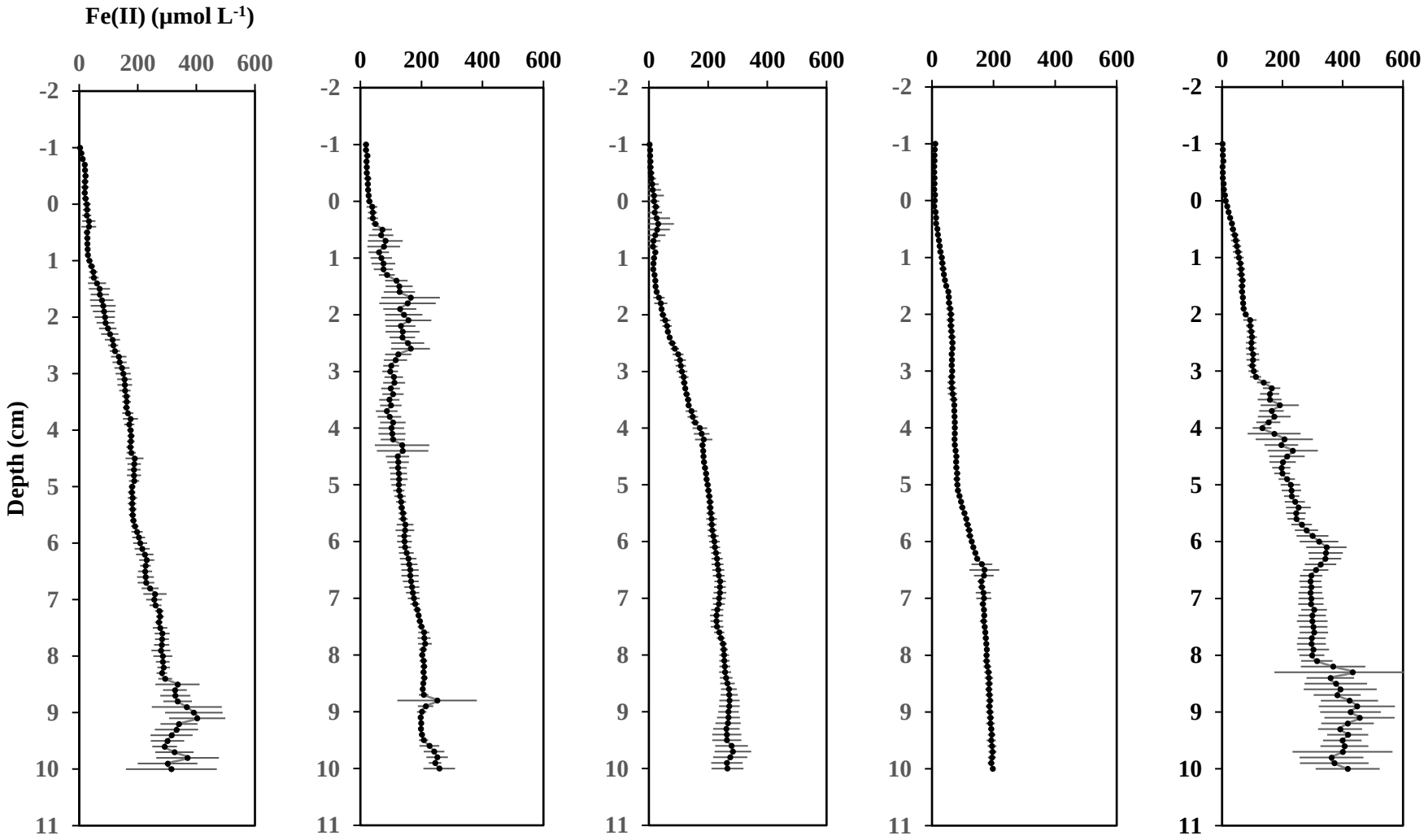

Figure S7. Pore water Fe (II) depth profiles determined by colourimetric DET for each sediment core (1 - 5) at site 2 during dark incubations.

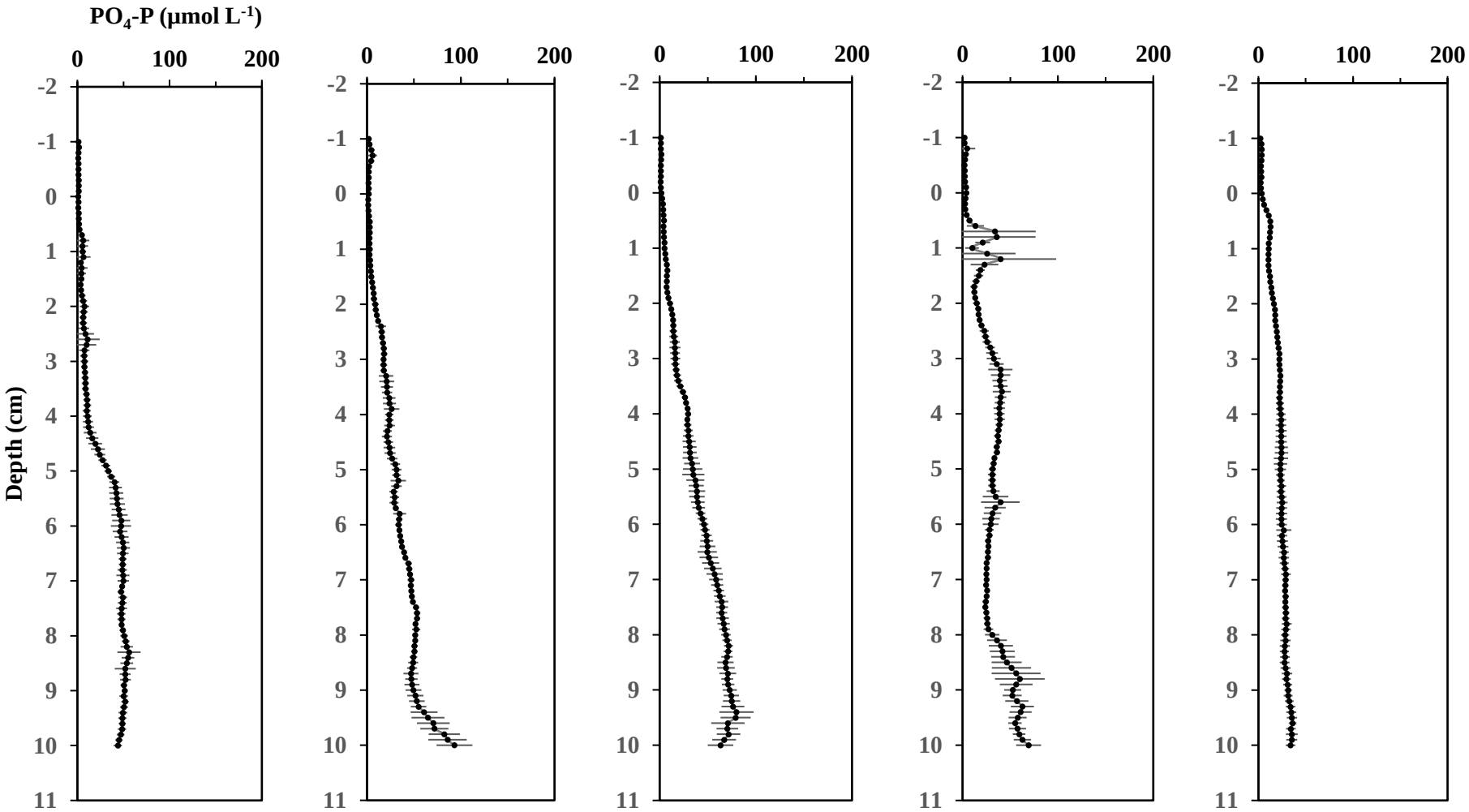

Figure S8. Pore water PO_4-P depth profiles determined by colourimetric DET for each sediment core (1 - 5) at site 2 during dark incubations.

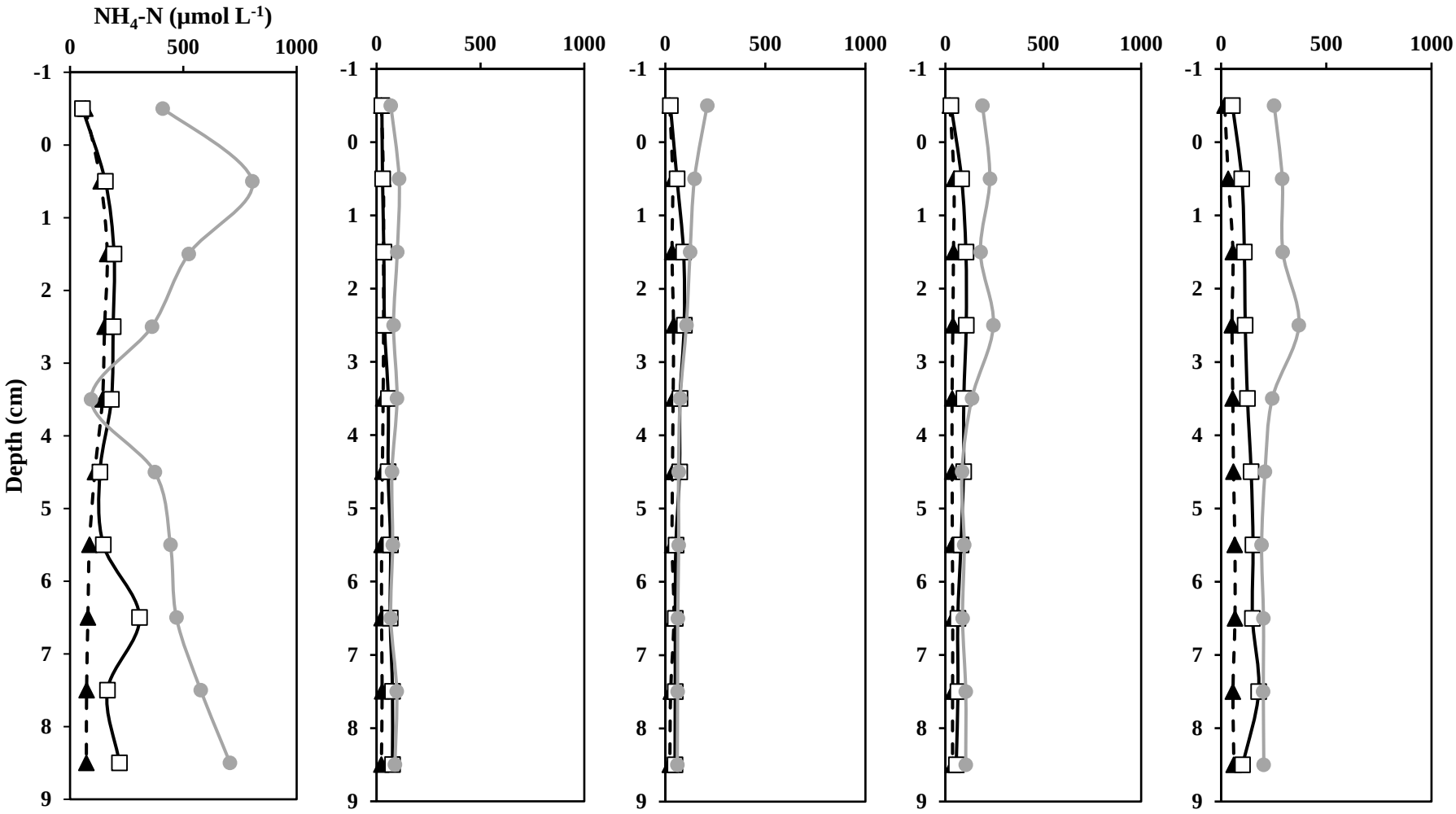

Figure S9. Pore water NH_4-N depth profiles determined by DGT (Black dash line with ▲), DET (Black solid line with □) and conventional extraction (Grey solid line with ●) for each sediment core (1 - 5) at site 1 under light incubation (1).

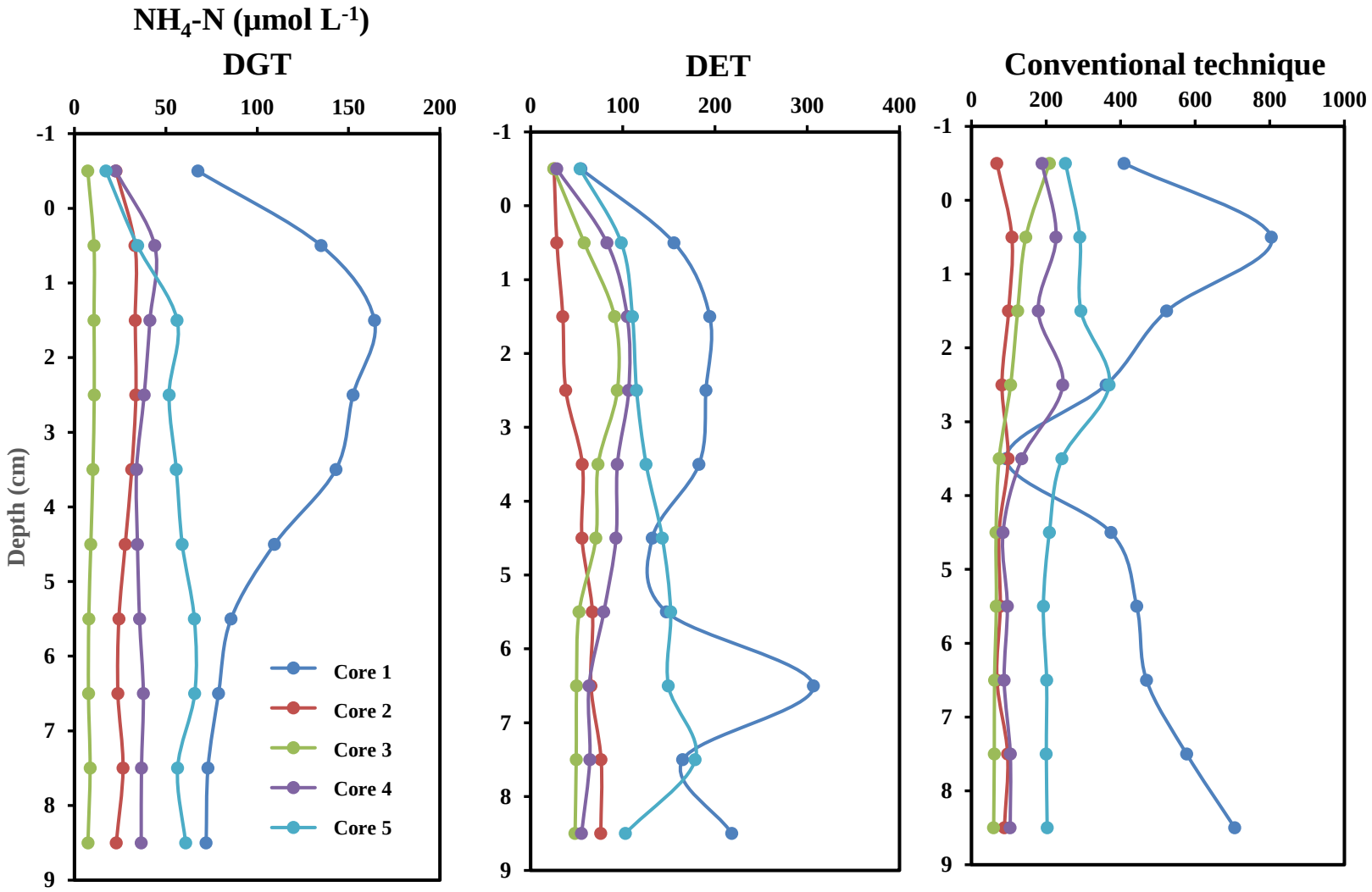

Figure S10. Pore water NH_4-N depth profiles determined by DGT, DET and conventional extraction for each sediment core (1 - 5) at site 1 during light incubations (2).

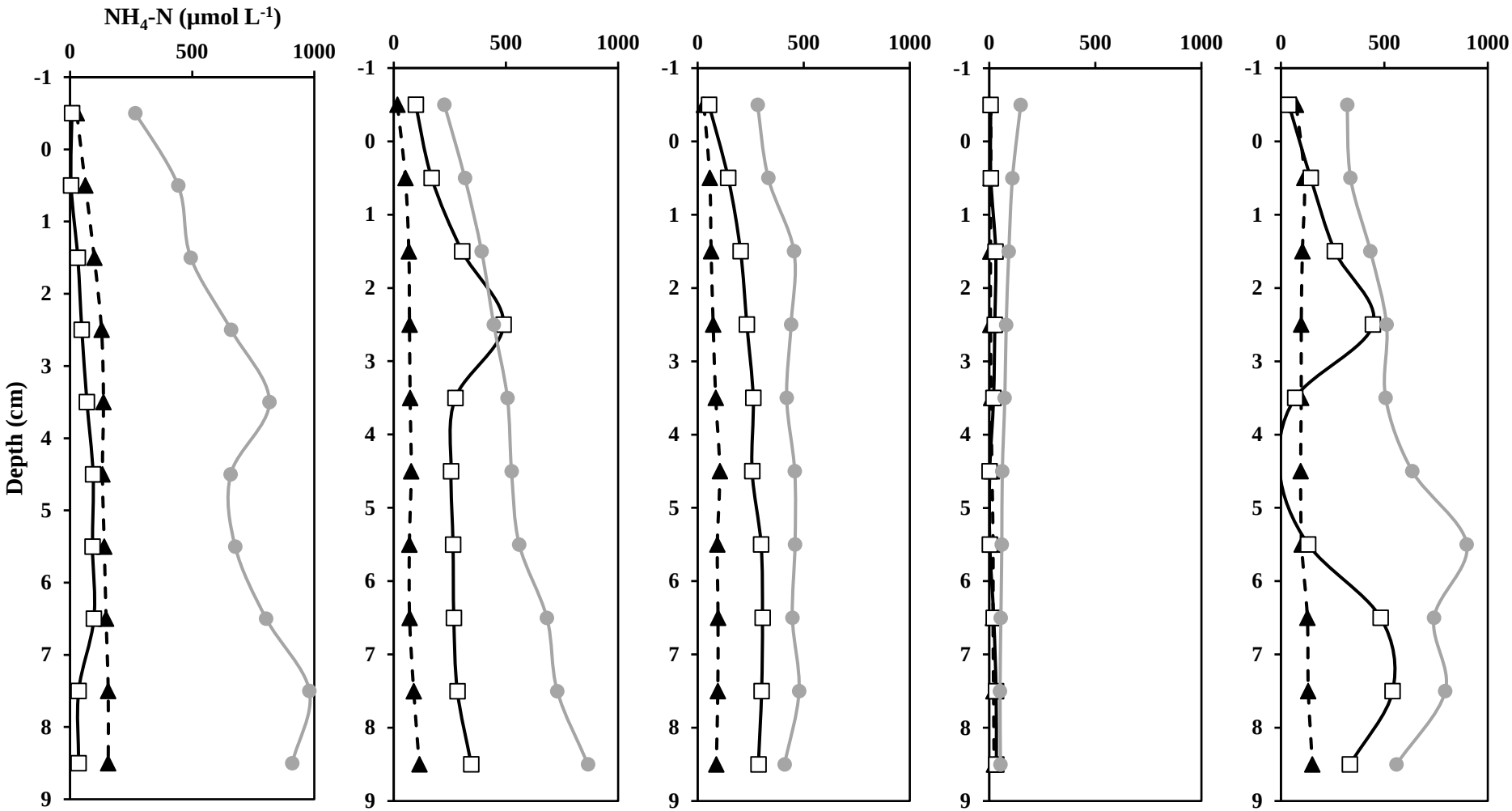

Figure S11. Pore water NH_4-N depth profiles determined by DGT (Black dash line with ▲), DET (Black solid line with □) and conventional extraction (Grey solid line with ●) for each sediment core (1 - 5) at site 1 during dark incubation (1).

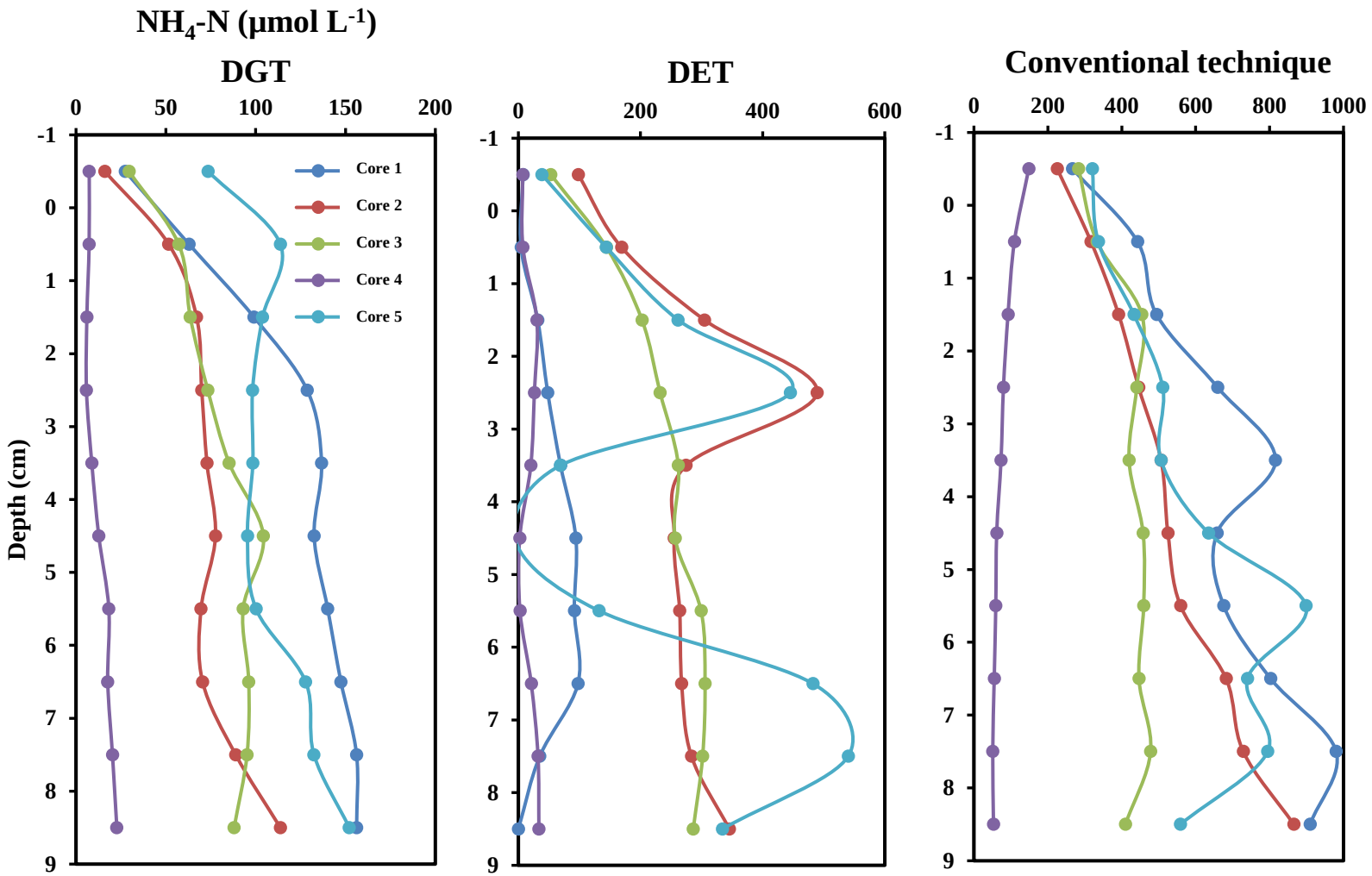

Figure S12. Pore water NH_4-N depth profiles determined by DGT, DET and conventional extraction for each sediment core (1 - 5) at site 1 during dark incubations (2).

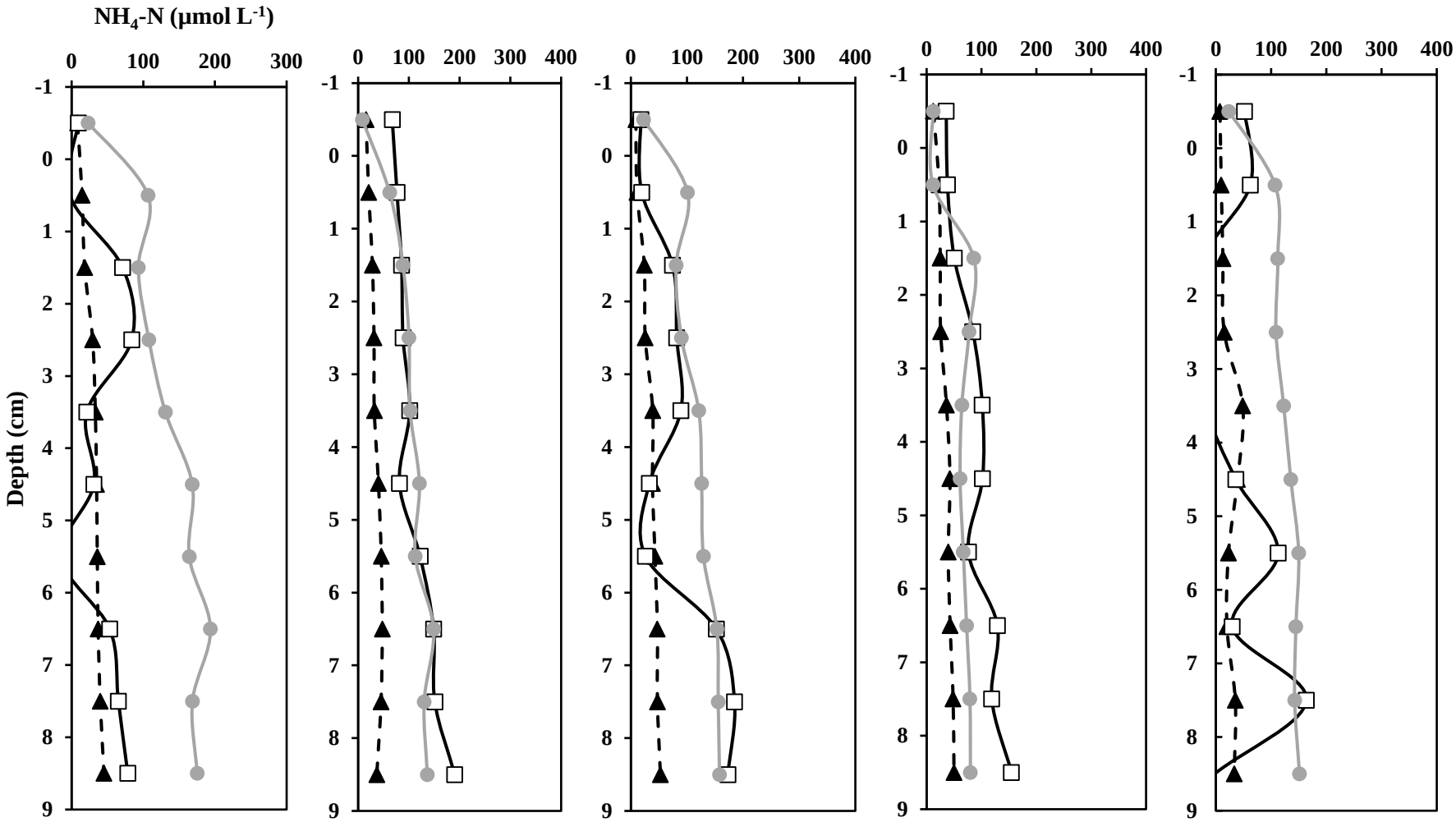

Figure S13. Pore water NH_4-N depth profiles determined by DGT (Black dash line with ▲), DET (Black solid line with □) and conventional extraction (Grey solid line with ●) for each sediment core (1 - 5) at site 2 during dark incubations (1).

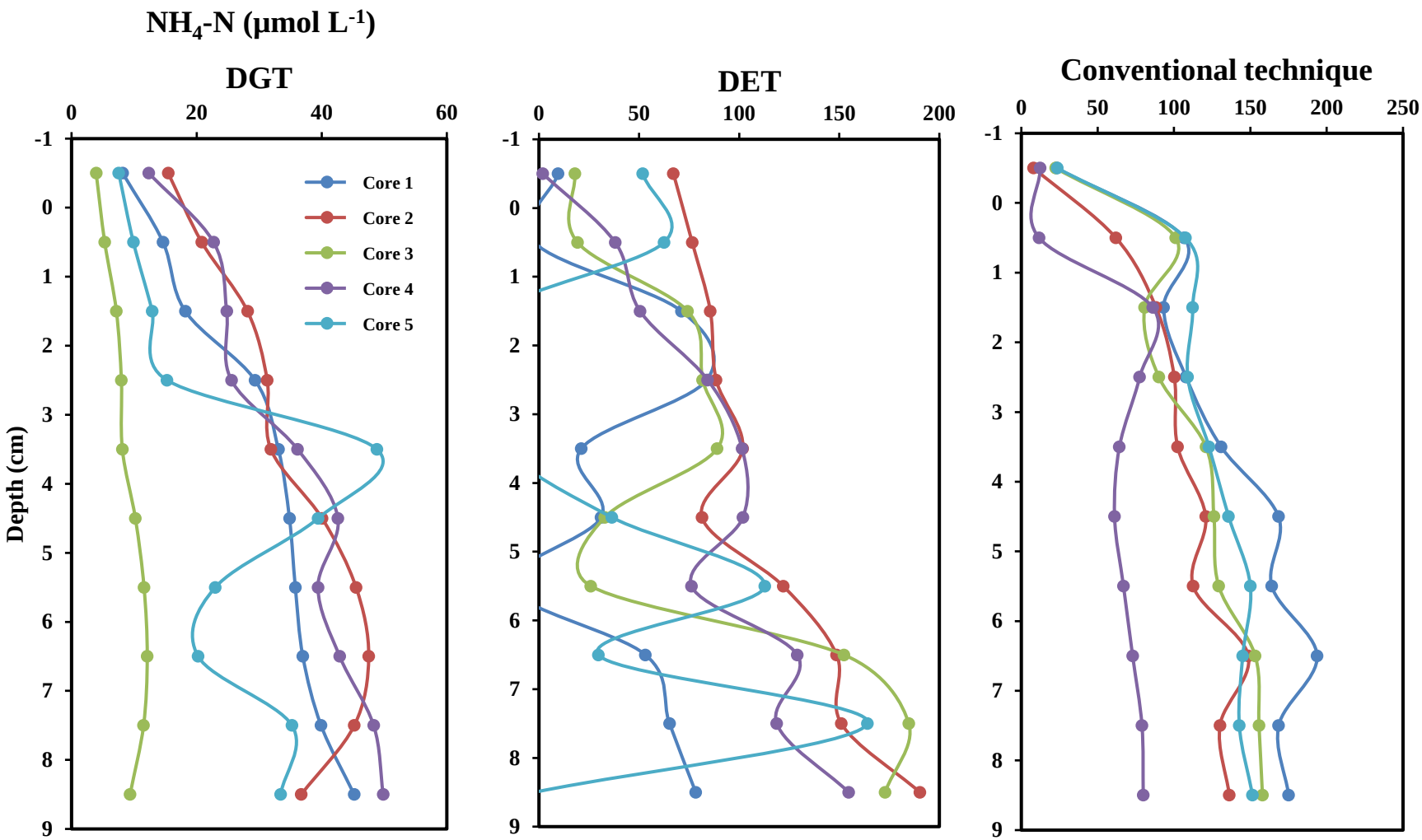

Figure S14. Pore water NH_4-N depth profiles determined by DGT, DET and conventional extraction for each sediment core (1 - 5) at site 2 during light incubations (2).

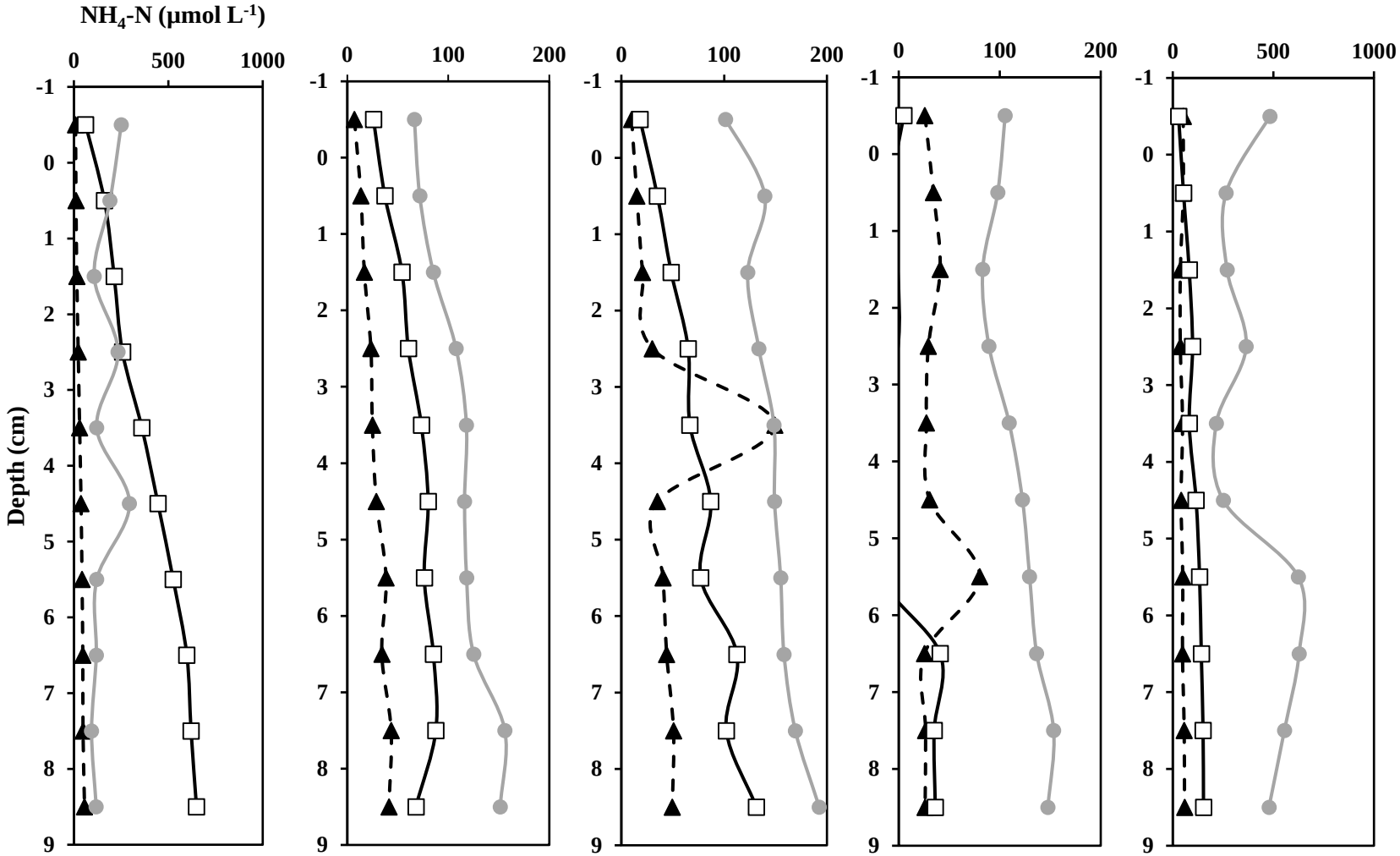

Figure S15. Pore water NH_4-N depth profiles determined by DGT (Black dash line with ▲), DET (Black solid line with □) and conventional extraction (Grey solid line with ●) for each sediment core (1 - 5) at site 2 during light incubations (1).

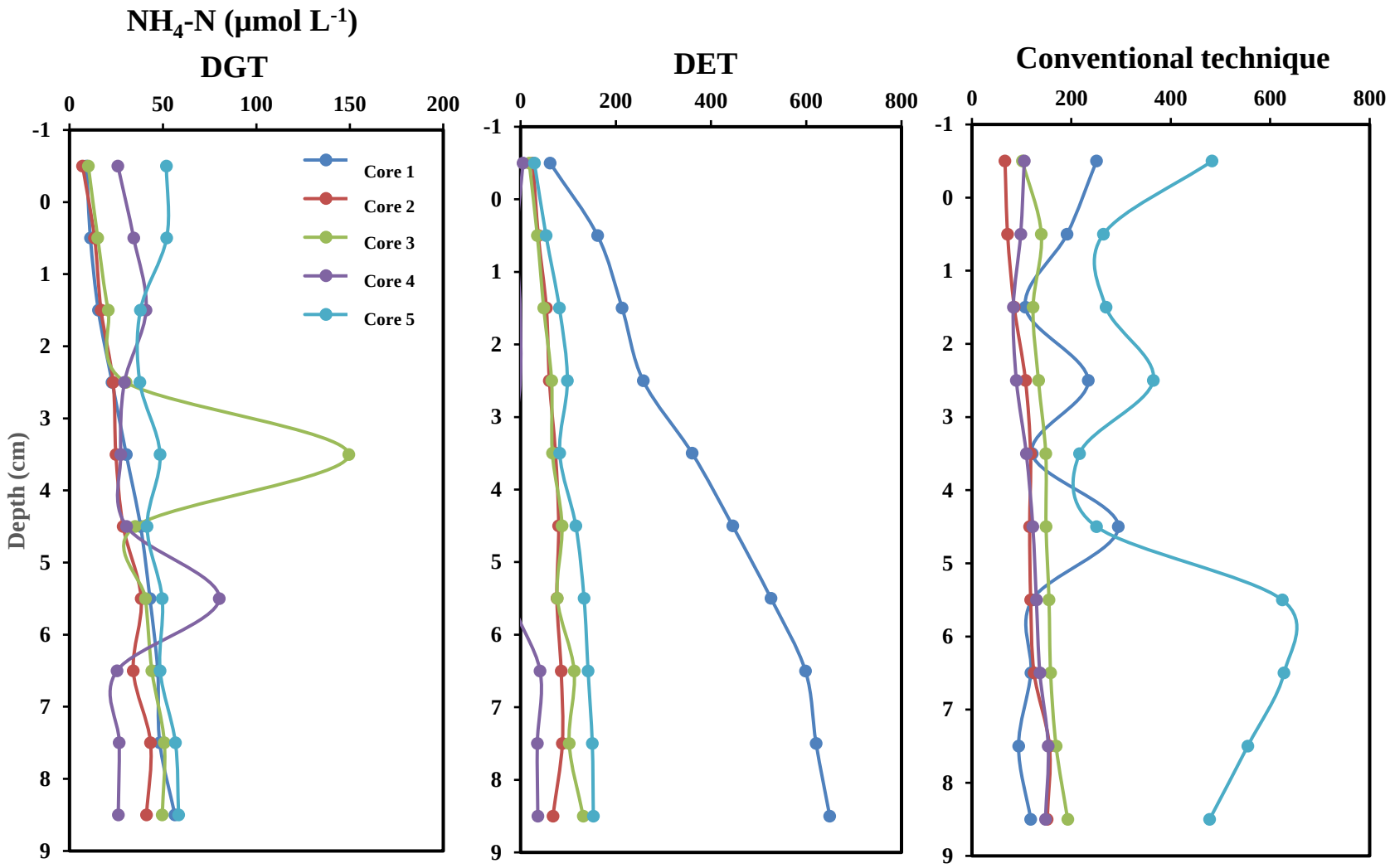

Figure S16. Pore water NH_4-N depth profiles determined by DGT, DET and conventional extraction for each sediment core (1 - 5) at site 2 during dark incubations (2).

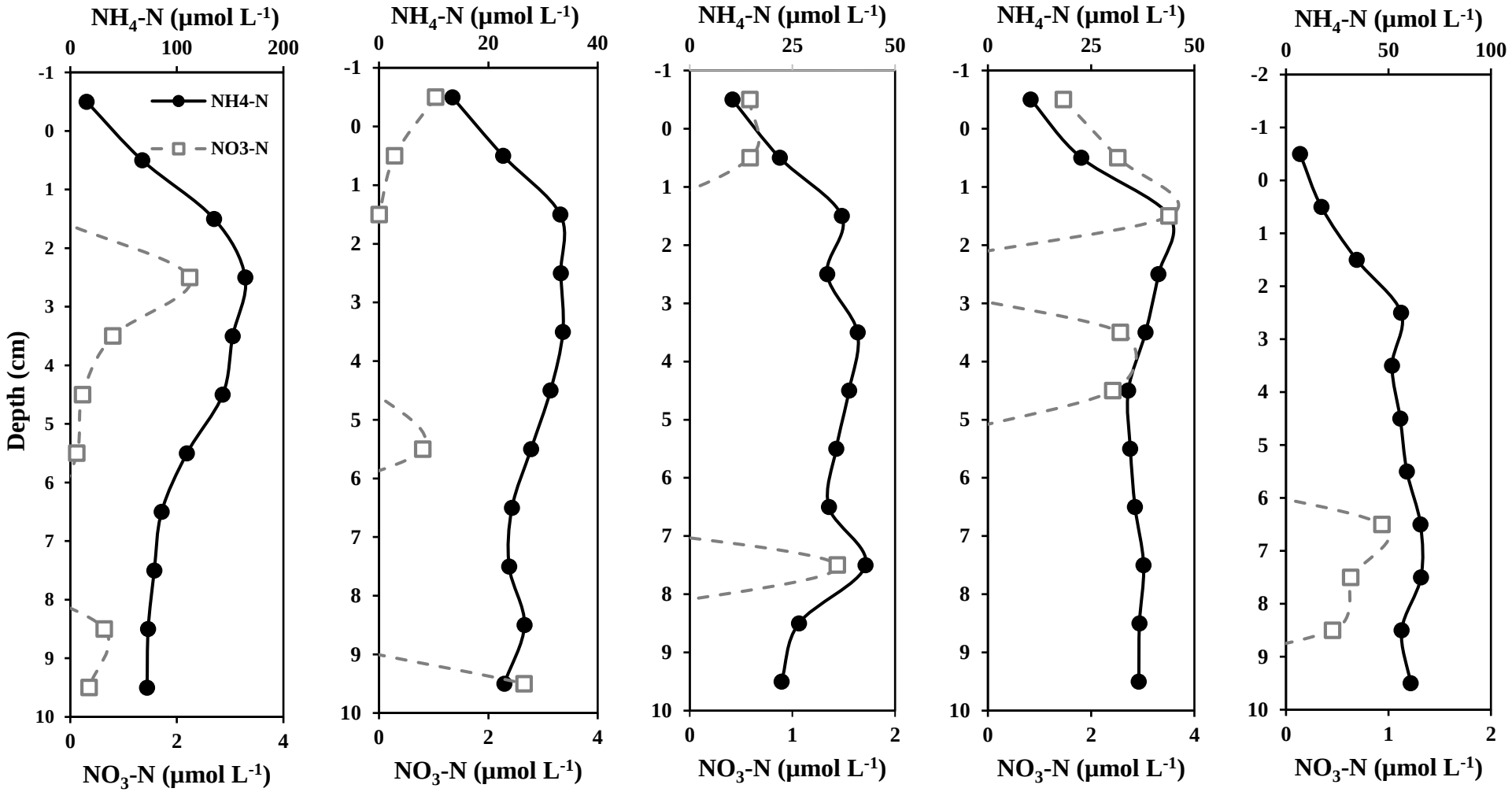

Figure S17. Pore water NH_4-N (Black solid line with ●) and NO_3-N (Grey dash line with □) depth profiles determined by DGT for each sediment core (1 - 5) at site 1 during light incubations.

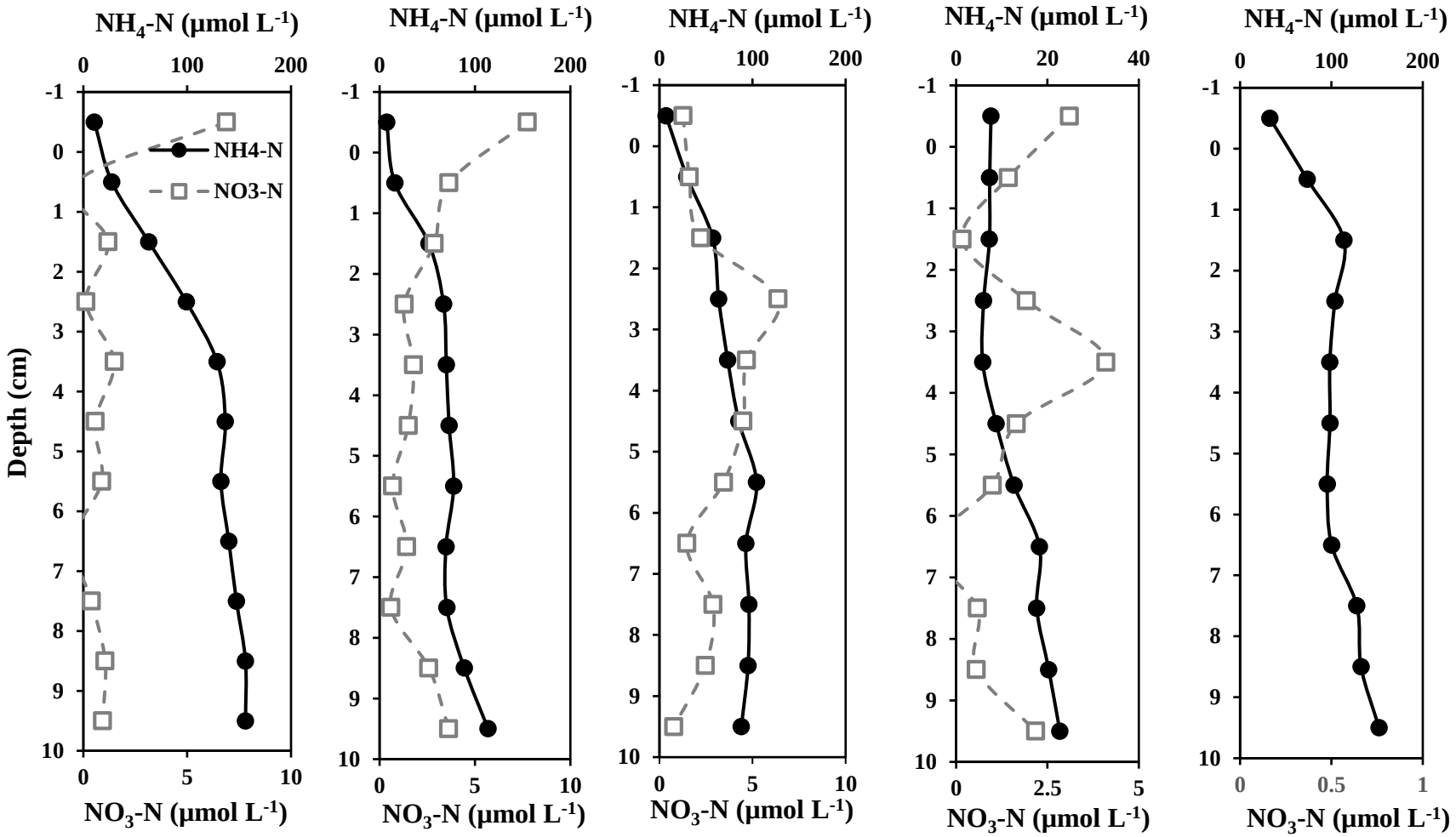

Figure S18. Pore water NH_4-N (Black solid line with ●) and NO_3-N (Grey dash line with □) depth profiles determined by DGT for each sediment core (1 - 5) at site 1 during dark incubations.

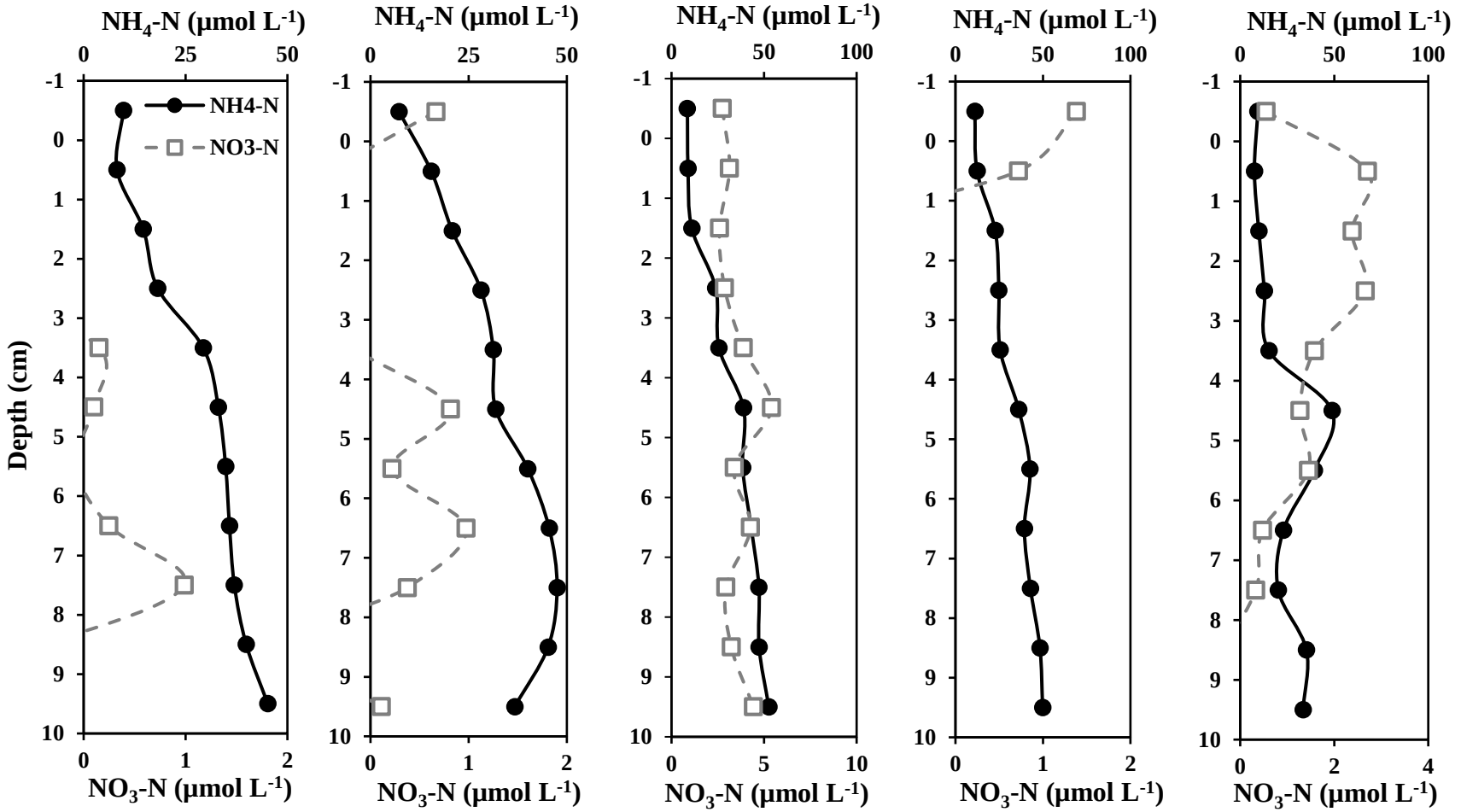

Figure S19. Pore water NH_4-N (Black solid line with ●) and NO_3-N (Grey dash line with □) depth profiles determined by DGT for each sediment core (1 - 5) at site 2 during light incubations.

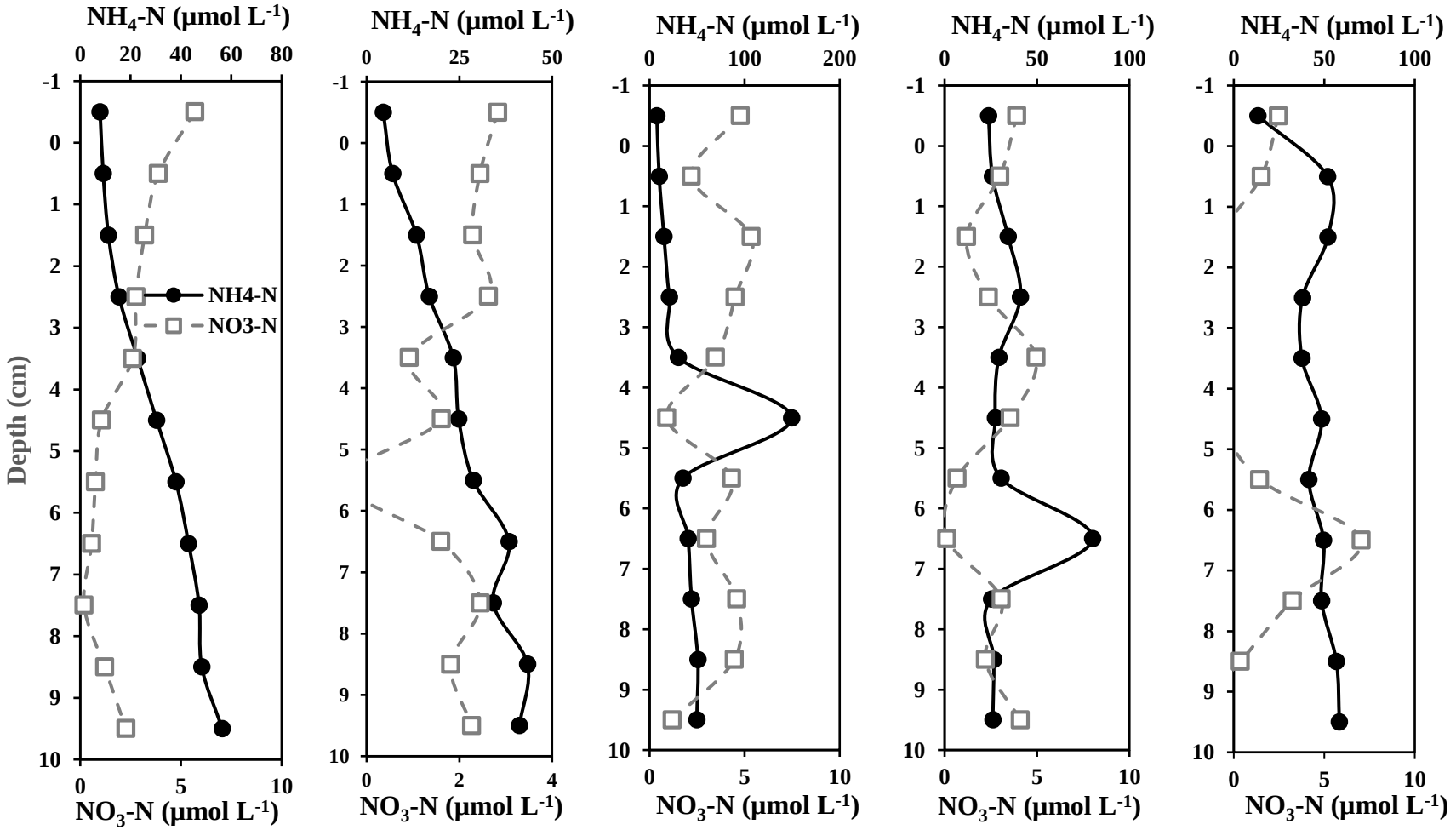

Figure S20. Pore water NH_4-N (Black solid line with ●) and NO_3-N (Grey dash line with □) profile profiles determined by DGT for each sediment core (1 - 5) at site 2 during dark incubations.

Figure S21. Photos of (a) Site 1 and (b) Site 2 taken at the time of sampling. The area in which cores were collected is in the foreground of each photo.

References

1. Zhang, H.; Davison, W., In situ speciation measurements of trace components in natural-waters using thin-film gels. *Nature* **1994,** *367*, (6463), 546–548.
2. Zhang, H.; Davison, W., Performance Characteristics of Diffusion Gradients in Thin Films for the In Situ Measurement of Trace Metals in Aqueous Solution. *Anal. Chem.* **1995,** *69*, (19), 3391-3400.