Supplemental Information

Molecular characterization of organic matter mobilized from Bangladeshi aquifer sediment: tracking carbon compositional change during microbial utilization

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Contents:

Section 1: Calculation of organic carbon in sediment

Sediment Porewater Organic Carbon (DOC) = 0.33 ± 0.06 mg OC g-1 sediment
Sediment Organic Matter (LOI) = 6.5 ± 1.5 mg/g

Using van Bemmelan factor (Burt, 2011) (58% OM = OC) to estimate sediment OC:

6.5 mg/g * 0.58 = 3.77 mg OC/g sed

DOC in sediment porewater as percent of sediment OC:

0.33/3.77 * 100 = 8.75 %

Error for the above calculation:

Err,gy= 0.06/3.77=0.0159
Err,gt=0.33/(3.77^2)*(0.58*1.5)=0.0202
Err = sqrt[(0.06/3.77)^2+(0.33/(3.77^2)*(0.58*1.5))^2]
= 0.0257 mg OC/g sed
0.0257/3.77*100=0.68 %

DOC in sediment porewater represented 8.8 ± 0.7 % of OC in sediment.

Table S1. Dissolved organic carbon concentrations in initial waters (mg-C L^{-1})*

Initial Waters	Pond Recharge	Rice Field Recharge	Sediment Porewater
Rep 1	27.0	12.3	856
Rep 2	29.0	25.3	1103
Rep 3	33.1		1219

* Samples combined together during processing of FT-ICR-MS data are grouped together with thick lines.

Table S2. Dissolved organic carbon concentrations in incubation waters (mg-C L^{-1})*

		1.5 days	17 days	18 days	19 days	20 days	80 days	81 days	91 days	184 days
Pond Recharge, Sterilized Sediment	Rep 1	212.9	219.30		254.6			253.4	184.7	222.9
	Rep 2	202.7	230.68		238.4			240.5		
	Avg. (stdev)	207.8 (7.2)	235.8 (14.8)				226.2 (36.5)			
Rice Recharge, Sterilized Sediment	Rep 1	226.0	213.48			264.9		230.7	201.8	247.4
	Rep 2	369.3	220.73			216.0		245.5		
	Avg. (stdev)	297.7 (101.4)	228.8 (24.3)				226.0 (22.2)			
Pond Recharge, Native Sediment	Rep 1	145.0		162.9	153.8		50.9		40.0	
	Rep 2	147.0		161.6	155.6					
	Avg. (stdev)	146.0 (1.4)	158.5 (4.5)				45.5 (7.7)			
Rice Recharge, Native Sediment	Rep 1	135.5		145.0		148.6	37.3		26.67	20.75
	Rep 2	142.6		174.2		140.8	31.5			
	Avg. (stdev)	139.1 (5.0)	152.1 (15.1)				31.77 (5.3)			

* Samples combined together during processing of FT-ICR-MS data are grouped together with thick lines.

Table S3. Methane concentrations in incubation bottles (mg-C L^{-1})

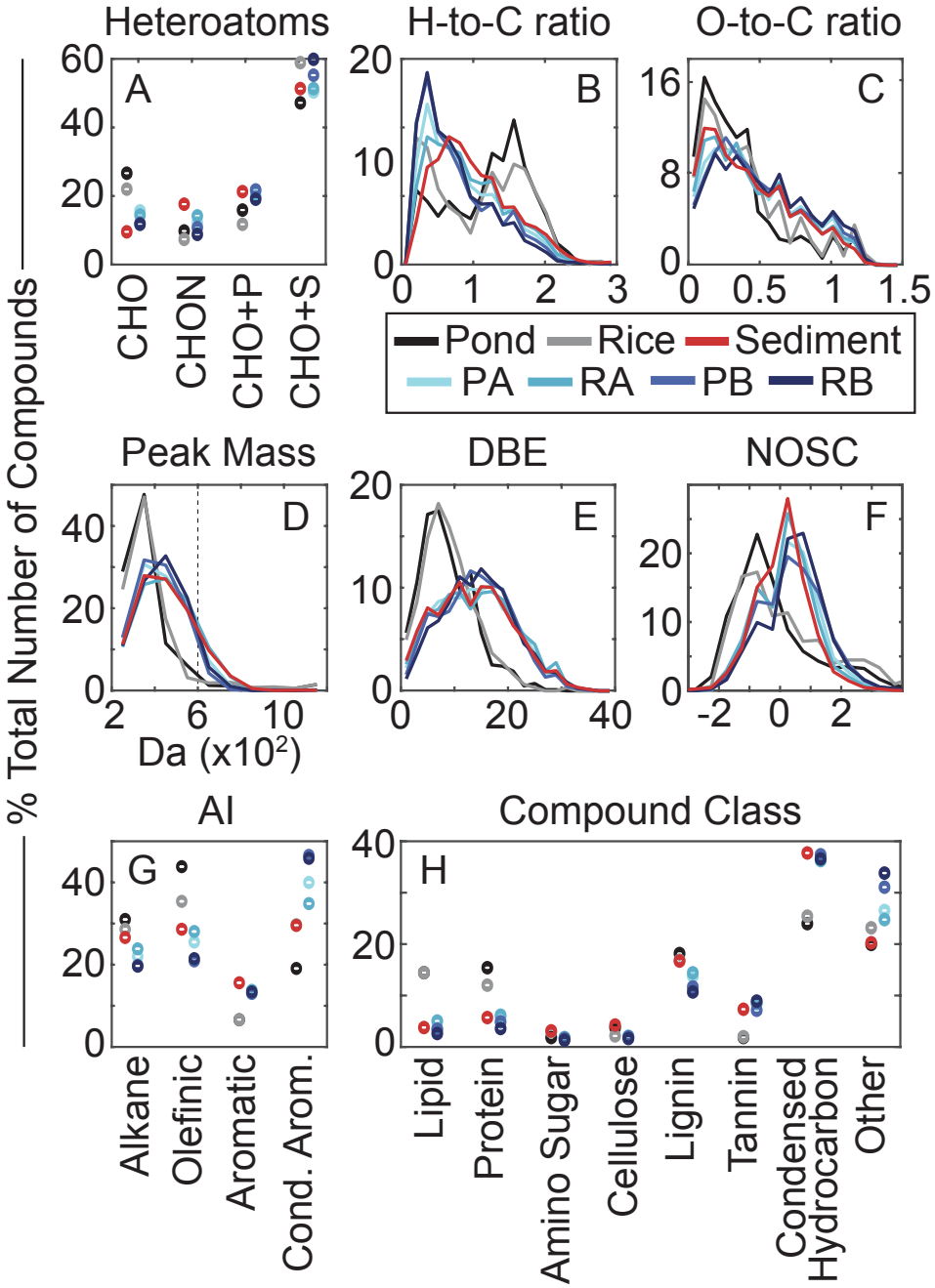
	18 days	273 days
Pond Recharge, Sterilized Sediment	Below detection	Below detection
Rice Recharge, Sterilized Sediment	Below detection	Below detection
Pond Recharge, Native Sediment	Below detection	198 ±46
Rice Recharge, Native Sediment	Below detection	368 ±45

Table S4. Compound Class Assignment

Compound Class	H-to-C ratio range	O-to-C ratio range
Lipid-like	1.5 – 2.3	0 – 0.2
Protein-like	1.5 – 2.2	0.2 – 0.5
Amino sugar-like	1.5 – 2.2	0.5 – 0.7
Carbohydrate-like	1.5 – 2.3	0.7 – 1.1
Lignin-like	0.8 – 1.5	0.25 – 0.67
Tannin-like	0.6 – 1.2	0.67 – 0.95
Condensed hydrocarbon-like	0.8 – 1.2 0 – 0.8	0 – 0.25 0 – 0.5

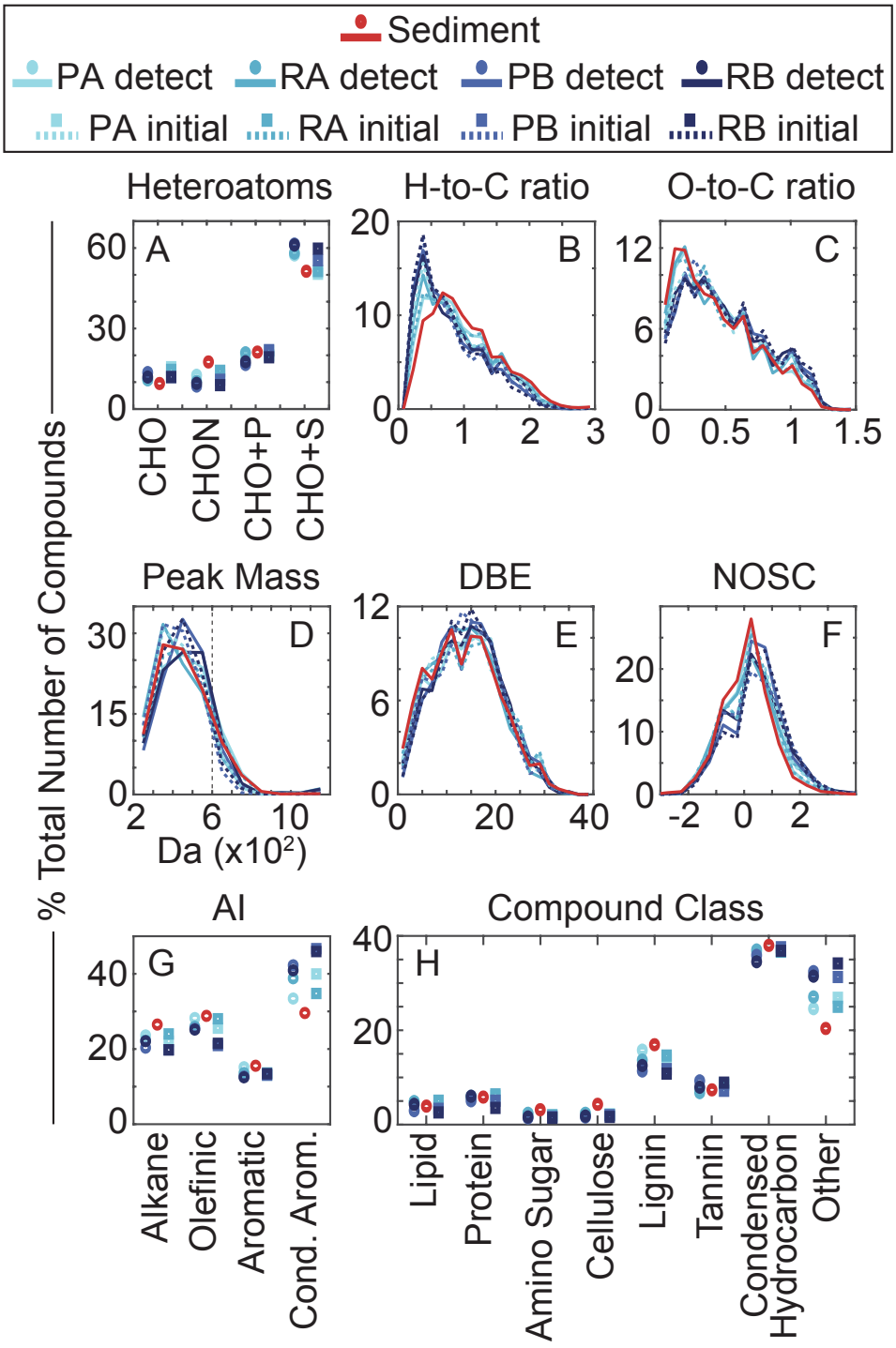
- Based on D'Andrilli et al. (2015).
- Compounds falling outside of designated ratios ranges were classified as 'other'

Figure S1



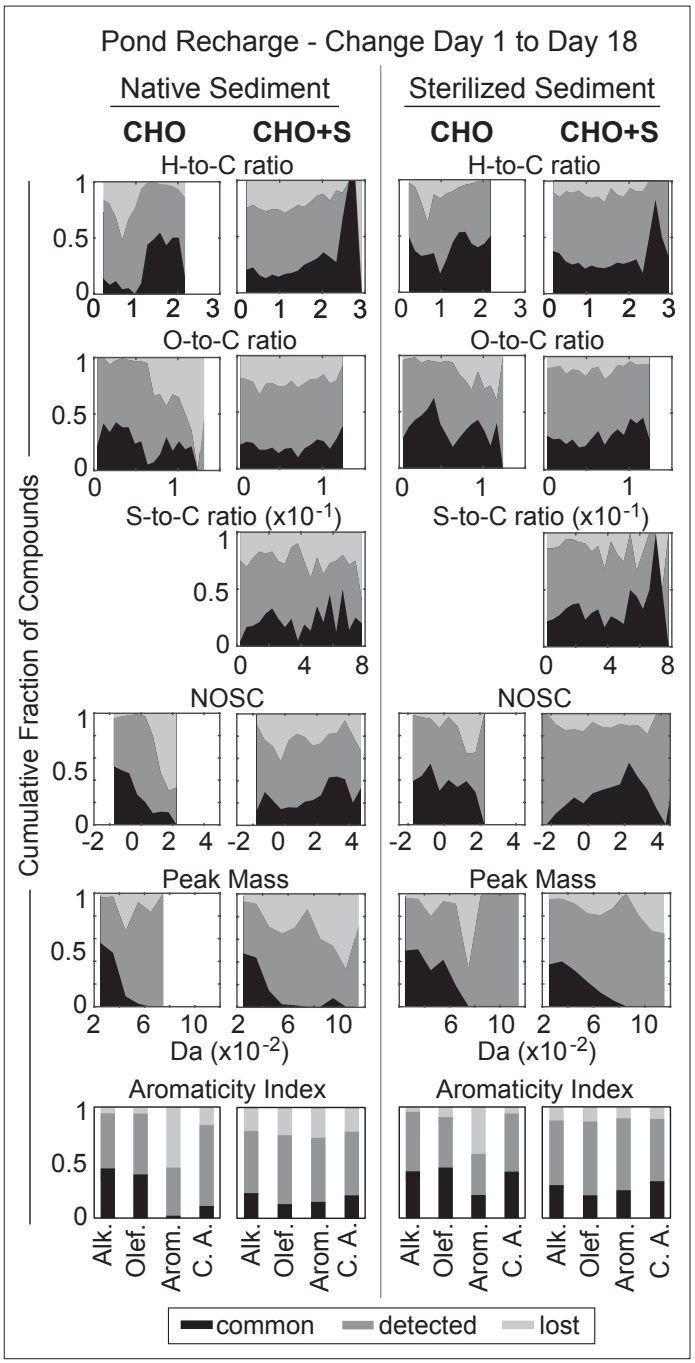
Chemical characteristics of (red) mobilized SOC, DOC in (black) pond and (grey) rice field recharge water, and (blues) DOC in incubation waters from day 1.5. PA = abiotic pond incubation; RA = abiotic rice field incubation; PB = biotic pond incubation; RB = biotic rice field incubation. **(a)** Percent of identified compounds in heteroatom groups. Proportional distributions of **(b)** H-to-C ratios, **(c)** O-to-C ratios, **(d)** peak mass, **(e)** double bond equivalents, and **(f)** nominal oxidation states of carbon. Percent of identified compounds in groupings based on **(g)** AI (alkanes, AI=0; olefinics, 0<AI≤0.5; aromatics, AI>0.5; condensed aromatics, AI≥0.67) and **(h)** compound classifications (Table S4).

Figure S2



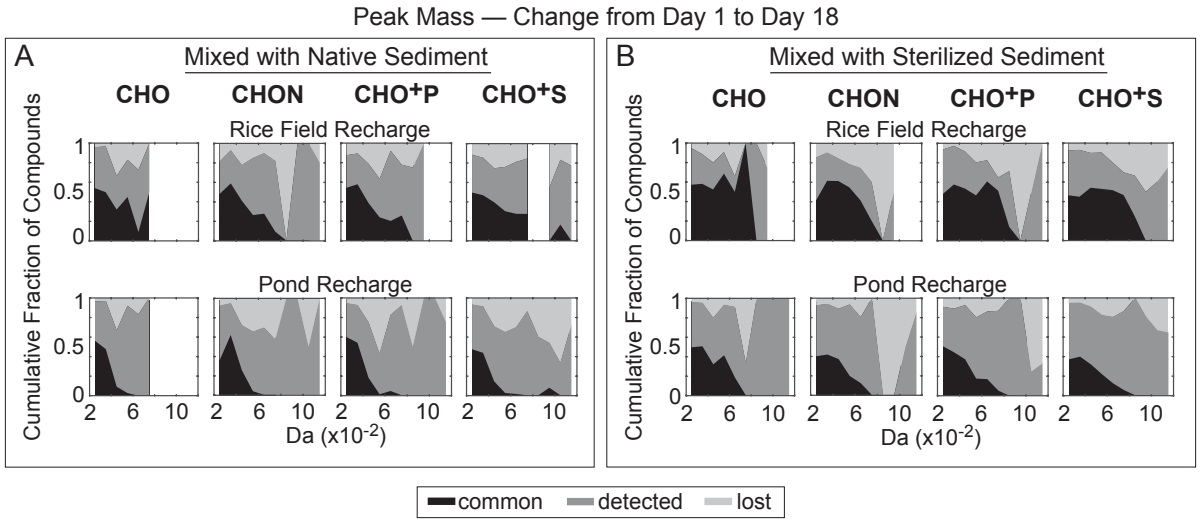
Chemical characteristics of (red) mobilized SOC, (dashed blues, squares) DOC in incubation waters from day 1.5, and (solid blues, circles) newly detected compounds on incubation day 18 that were not detected on incubation day 1.5. PA = abiotic pond incubation; RA = abiotic rice field incubation; PB = biotic pond incubation; RB = biotic rice field incubation. Panels as identified in Figure S1.

Figure S3=



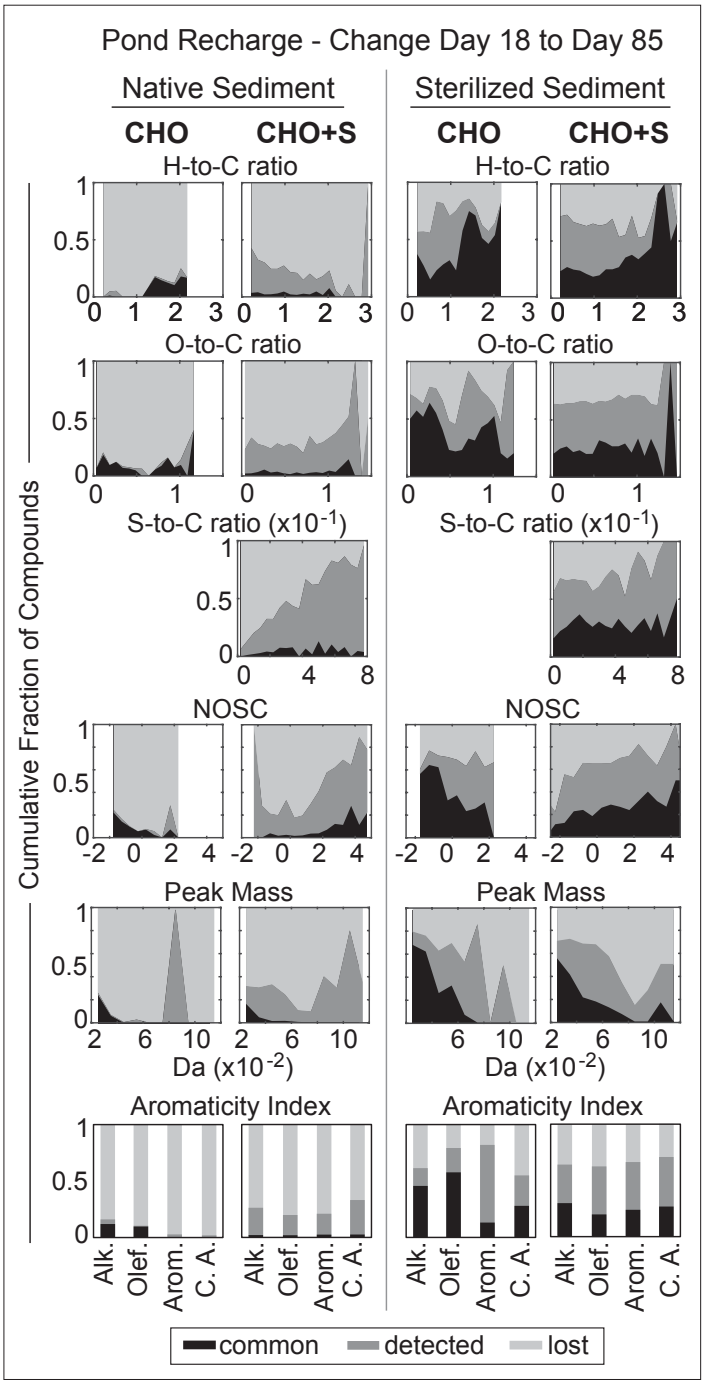
Relative change in chemical indices between day 1.5 and day 18 for pond recharge water incubated with native sediment and sterilized sediment. The cumulative fraction of compounds that were (black) identified at both time points, i.e., common, (dark grey) identified at the second time point but not at the first, i.e., newly detected, and (light grey) identified at the first time point but not at the second, i.e., lost, were separated by heteroatom groups (CHO and CHO+S are shown) and characterized based on H-to-C ratio, O-to-C ratio, S-to-C ratio, nominal oxidation state of carbon (NOSC), peak mass, and aromaticity index (alkanes, AI=0; olefinics, 0<AI≤0.5; aromatics, AI>0.5; condensed aromatics, AI≥0.67).

Figure S4



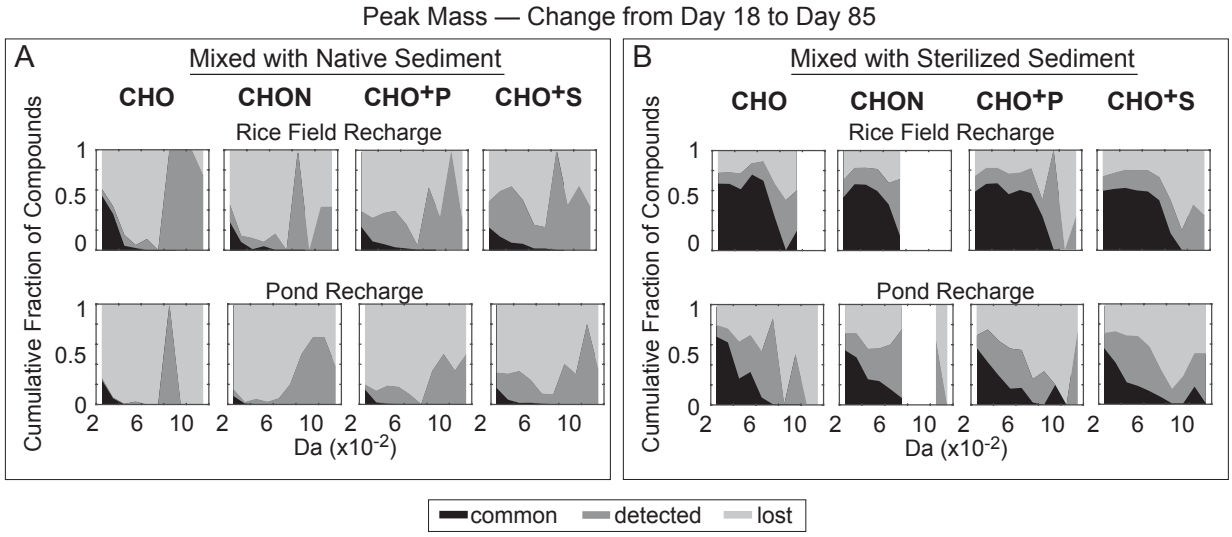
Relative change in peak mass between day 1.5 and day 18 for both rice field recharge water (top row) and pond recharge water (bottom row) incubated with **(a)** native sediment and **(b)** sterilized sediment. The cumulative fraction of compounds that were (black) identified at both time points, i.e., common, (dark grey) identified at the second time point but not at the first, i.e., newly detected, and (light grey) identified at the first time point but not at the second, i.e., lost, were separated by heteroatom groups.

Figure S5



Relative change in chemical indices between day 18 and day 85 for pond recharge water incubated with native sediment and sterilized sediment. The cumulative fraction of compounds that were (black) identified at both time points, i.e., common, (dark grey) identified at the second time point but not at the first, i.e., newly detected, and (light grey) identified at the first time point but not at the second, i.e., lost, were separated by heteroatom groups (CHO and CHO+S are shown) and characterized based on H-to-C ratio, O-to-C ratio, S-to-C ratio, nominal oxidation state of carbon (NOSC), peak mass, and aromaticity index (alkanes, AI=0; olefinics, 0<AI≤0.5; aromatics, AI>0.5; condensed aromatics, AI≥0.67).

Figure S6



Relative change in peak mass between day 18 and day 85 for both rice field recharge water (top row) and pond recharge water (bottom row) incubated with **(a)** native sediment and **(b)** sterilized sediment. The cumulative fraction of compounds that were (black) identified at both time points, i.e., common, (dark grey) identified at the second time point but not at the first, i.e., newly detected, and (light grey) identified at the first time point but not at the second, i.e., lost, were separated by heteroatom groups.

REFERENCES

Burt, R., Series Ed. *Soil Survey Laboratory Information Manual*; Soil Survey Investigations; 45, Version 2.0; United States Department of Agriculture, Natural Resources Conservation Service: National Soil Survey Center, Lincoln, Nebraska, 2011.

D'Andrilli, J., Cooper, W. T., Foreman, C. M. and Marshall, A. G.: An ultrahigh-resolution mass spectrometry index to estimate natural organic matter lability, Rapid Commun. Mass Spectrom., 29(24), 2385–2401, doi:10.1002/rcm.7400, 2015.