Supporting Information

Energy and nutrient recovery from sewage sludge and manure via anaerobic digestion with hydrothermal pretreatment

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Total 13 pages
7 tables
4 figures

Table S1. Peak assignments for ^{13}C NMR spectra of sludge, manure, and their treatment samples.

Spectral domain	Chemical shift region (ppm)	Representative structure	Chemical shift (ppm)	Refs
Alkyl	0–50	mobile (CCH_3)	13	1
		methyl carbon ($-CH_3$)	23	1
		mobile methylene carbon ($-CH_2-$)	30, 31	1, 2
Methoxyl	50–60	$O-CH_3$	57, 56	1, 3
		lignin-like structures	56	2, 4
O/N-alkyl	60–110	amino acid	61.5	5
		CH_2OH	62	3
		crystalline components of C6 in hexose, or C5 in pentose	65	2, 4
		hydrocarbon	71.29	6
		-CHOH-	72	3
		C-O-C	73	1
		C2, C3, C5 from cellulose	72–74	4
		non-crystalline components of C4	83	4, 7
		crystalline components of C4	88	2, 4
		O-C-O	103.00	3
		deoxygenated anomeric C1 from cellulose	105	4
		anomeric carbon	105.00	2
		O-C-O	110	1
		anomeric carbon	102, 106, 111.50	5
Aromatic	110–160	aromatic C	129	1
		-C=C-	130	3
		syringyl-like systems	137	7
		phenolic carbon, aromatic ethers N-substitute aromatic C	152.7	5
Carboxyl, carbonyl	160–210	hydroxyls	168.86	6
		COO/N-C=O	172, 174	1, 2

Table S2. Significant analysis of biogas production (after seed blank correction). Different lowercase letters behind the same row groupings indicate significant differences at $P < 0.05$ among different samples according to a Tukey HSD test.

Sample	Total Gas (mL/g VS)	Total CH_4 (mL/g VS)	Total CO_2 (mL/g VS)	$\frac{CH_4\text{-}COD}{COD_{initial}}$ (%)
Sludge	308.7±2.1 ^{d}	283.6±1.2 ^{f}	99.2±1.7 ^{e}	42.0±0.2 ^{e}
S125	567.4±4.0 ^{c}	383.8±1.6 ^{e}	140.1±2.5 ^{d}	53.3±0.2 ^{c}
S225	551.9±5.4 ^{c}	404.9±2.5 ^{d}	103.2±3.3 ^{e}	37.7±0.1 ^{f}
Manure	742.2±28.2 ^{b}	490.1±2.3 ^{c}	226.9±2.6 ^{b}	79.0±0.3 ^{b}
M125	1152.0±10.1 ^{a}	738.9±5.2 ^{a}	366.3±5.8 ^{a}	86.8±0.3 ^{a}
M225	558.6±6.8 ^{c}	503.7±1.5 ^{b}	172.6±2.2 ^{c}	45.9±0.2 ^{d}

Table S3. Results of the batch ultimate digestibility test (after seed blank correction).

Sample	$COD_{initial}$ [a] (mg/L)	COD_{final} [b] (mg/L)	$COD_{destroyed}$ [c] (%)	CH_4 content (%)	$\frac{CH_4\text{-}COD}{COD_{initial}}$ (%)	$COD_{balance}$ [d] (%)
Sludge	1986±17	1228±18	38.2	74.1±0.2	42.0±0.2	-3.8
S125	1753±20	915±18	47.8	73.3±0.2	53.3±0.2	-5.5
S225	1663±3	992±17	40.3	79.7±0.3	37.7±0.1	2.6
Manure	2233±112	693±26	69.0	68.4±0.1	79.0±0.3	-10.0
M125	2159±82	621±53	71.3	66.9±0.2	86.8±0.3	-15.5
M225	1834±29	1281±15	30.1	79.8±0.3	45.9±0.2	-15.8

[a] $COD_{initial}$ is the mean value of parallel samples stored in 4 °C.

[b] COD_{final} is the mean value of repeated samples incubated in the dark at 35 °C.

[c] $COD_{destroyed}$ is calculated using the mean value of $COD_{initial}$ and COD_{final}, and the specific calculation formula is as follows:

$$COD_{destroyed}(\%) = \frac{COD_{initial} - COD_{final}}{COD_{initial}} \times 100$$

[d] $COD_{balance}$ is the difference between the mean value of $COD_{destroyed}$ (%) and $\frac{CH_4\text{-}COD}{COD_{initial}}$ (%).

Table S4. Percent contribution of carbon functional groups derived from ^{13}C solid-state NMR spectra of DI water (CK), sludge (S), and sludge hydrochars (S125 and S225) before (labeled as 0) and after (labeled as 63) anaerobic digestion [a].

Sample	Functional group (chemical shift)				
	Alkyl (0–50 ppm)	Methoxyl (50–60 ppm)	O/N-alkyl (60–110 ppm)	Aromatic (110–160 ppm)	Carboxyl and carbonyl (160–210 ppm)
CK-0	38.8	10.3	22.3	5.3	23.1
CK-63	37.5	9.4	15.8	5.2	32.1
S-0	44.4	9.5	19.4	0.5	26.1
S-63	38.7	8.2	10.8	4.5	37.7
S125-0	41.8	8.3	9.7	0.4	39.8
S125-63	38.7	5.9	4.1	3.9	47.4
S225-0	43.8	6.5	3.6	2.9	43.2
S225-63	44.5	7.9	13.2	6.5	27.8

[a] Data expressed as the relative percentage of peak area of each functional group divided by total peak area.

Table S5. Percent contribution of carbon functional groups derived from ^{13}C solid-state NMR spectra of DI water (CK), manure (M), and manure hydrochars (M125 and M225) before (labeled as 0) and after (labeled as 63) anaerobic digestion[a].

Samples	Functional group (chemical shift)				
	Alkyl (0–50 ppm)	**Methoxyl (50–60 ppm)**	**O/N-alkyl (60–110 ppm)**	**Aromatic (110–160 ppm)**	**Carboxyl and carbonyl (160–210 ppm)**
CK-0	38.8	10.3	22.3	5.3	23.1
CK-63	37.5	9.4	15.8	5.2	32.1
M-0	33.1	7.0	38.4	4.3	17.0
M-63	41.1	9.7	20.2	2.4	26.6
M125-0	32.7	8.3	36.3	4.9	17.5
M125-63	39.8	10.0	22.4	6.8	20.9
M225-0	58.4	6.8	9.8	8.2	16.8
M225-63	45.7	6.7	7.4	17.4	22.8

[a] Data expressed as the relative percentage of peak area of each functional group divided by total peak area.

Table S6. Characteristics of organic contents of sludge, manure, and their hydrochars before (0 day) and after (63 day) anaerobic digestion (after seed blank correction).

Sample	Reaction time	pH[a]	SCOD (g/L)	ΔTCOD[b] (g/L)	ΔSCOD[c] (g/L)	SCOD Contribution[d] (%)
Sludge	Day 0	7.52	0.51±0.02	0.76	0.99	131
	Day 63	7.32	-0.50±0.01			
S125	Day 0	7.45	0.52±0.02	0.84	0.51	61
	Day 63	7.30	0.00±0.04			
S225	Day 0	7.53	1.30±0.00	0.67	1.42	212
	Day 63	7.43	-0.13±0.01			
Manure	Day 0	7.49	1.45±0.01	1.54	1.84	120
	Day 63	7.11	-0.40±0.03			
M125	Day 0	7.43	0.54±0.01	1.54	0.85	55
	Day 63	7.09	-0.32±0.01			
M225	Day 0	7.44	0.54±0.02	0.55	-0.08	-14
	Day 63	7.34	0.61±0.02			

[a] pH was measured immediately after opening the bottles. The standard deviation are not shown because they are smaller than 0.02.

[b] $\Delta TCOD = \left| TCOD_{initial} \right| - \left| TCOD_{final} \right|$

[c] $\Delta SCOD = \left| SCOD_{initial} \right| - \left| SCOD_{final} \right|$

[d] SCOD contribution (%) = $\Delta SCOD / \Delta TCOD \times 100$

Table S7. Solution concentration of total P (liquid-TP), ammonia, and Mg, the percentage of liquid-TP to total P in both solid and solution phases (TP), solution pH, as well as the molar ratio of solution P, N, and Mg contents.

Sample	Liquid-TP (mmol/L)		Liquid-TP/TP (%)		Ammonia (mmol/L)		Mg (mmol/L)		pH *	P:N:Mg
	Day 0	*Day 63*	*Day 0*	*Day 63*	*Day 0*	*Day 63*	*Day 0*	*Day 63*	*Day 63*	*Day 63*
CK	4.95 ±0.01	5.13 ±0.02	86.7 ±0.2	90.0 ±0.3	14.66 ±0.02	16.22 ±0.01	0.0584 ±0.004	0.232 ±0.003	8.11	1:3.16:0.05
S (Sludge)	5.20 ±0.01	5.36 ±0.00	68.8 ±0.1	69.7 ±0.0	15.55 ±0.08	18.19 ±0.13	0.0567 ±0.0014	0.229 ±0.005	8.07	1: 3.39: 0.04
S125	5.13 ±0.02	5.78 ±0.07	70.5 ±0.2	74.6 ±0.9	16.76 ±0.03	21.18 ±0.15	0.0944 ±0.0023	0.258 ±0.006	7.87	1: 3.66: 0.04
S225	5.25 ±0.01	4.49 ±0.01	67.4 ±0.1	60.4 ±0.2	17.92 ±0.03	16.89 ±0.16	0.0868 ±0.0021	0.214 ±0.004	8.22	1: 3.76: 0.05
M (Manure)	5.25 ±0.00	4.69 ±0.02	77.4 ±0.0	77.6 ±0.4	17.19 ±0.02	17.48 ±0.06	0.126 ±0.003	0.450 ±0.011	8.04	1: 3.73: 0.10
M125	4.93 ±0.04	4.97 ±0.05	73.9 ±0.5	76.7 ±0.8	17.04 ±0.13	18.03 ±0.10	0.0935 ±0.0022	0.258 ±0.006	8.23	1: 3.63: 0.05
M225	3.69 ±0.01	5.09 ±0.06	60.8 ±0.2	73.4 ±0.9	12.21 ±0.07	16.65 ±0.15	0.125 ±0.003	0.190 ±0.004	8.19	1: 3.27: 0.04

*pH value of liquid supernantant of samples, which was measured after opening the bottles and solid-liquid separation. Standard deviations are not shown because they are smaller than 0.02.

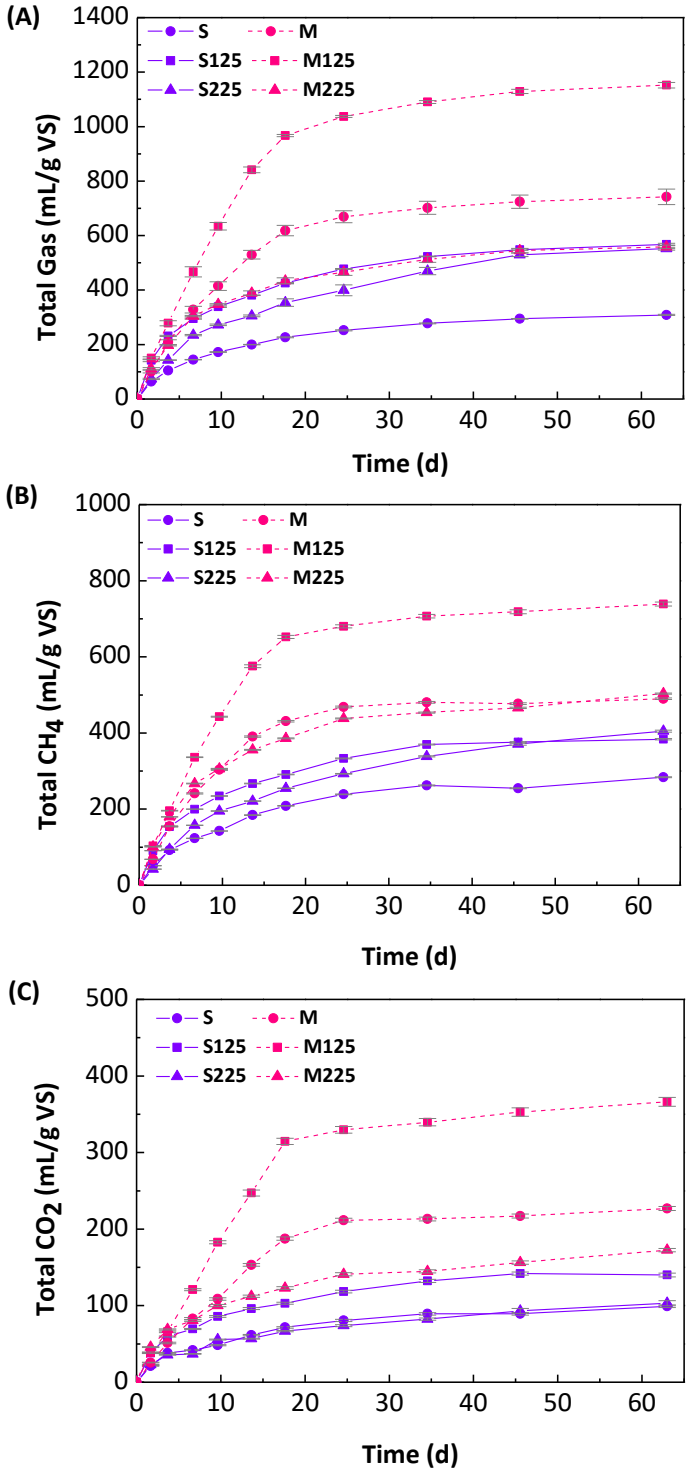

Figure S1. Cumulative total gas (A), methane (B), and carbon dioxide (C) production during the 63-day incubation period. Gas data obtained at 35 °C and 1 atm with seed blank correction. Error bars represent mean values ± one standard deviation (n = 3).

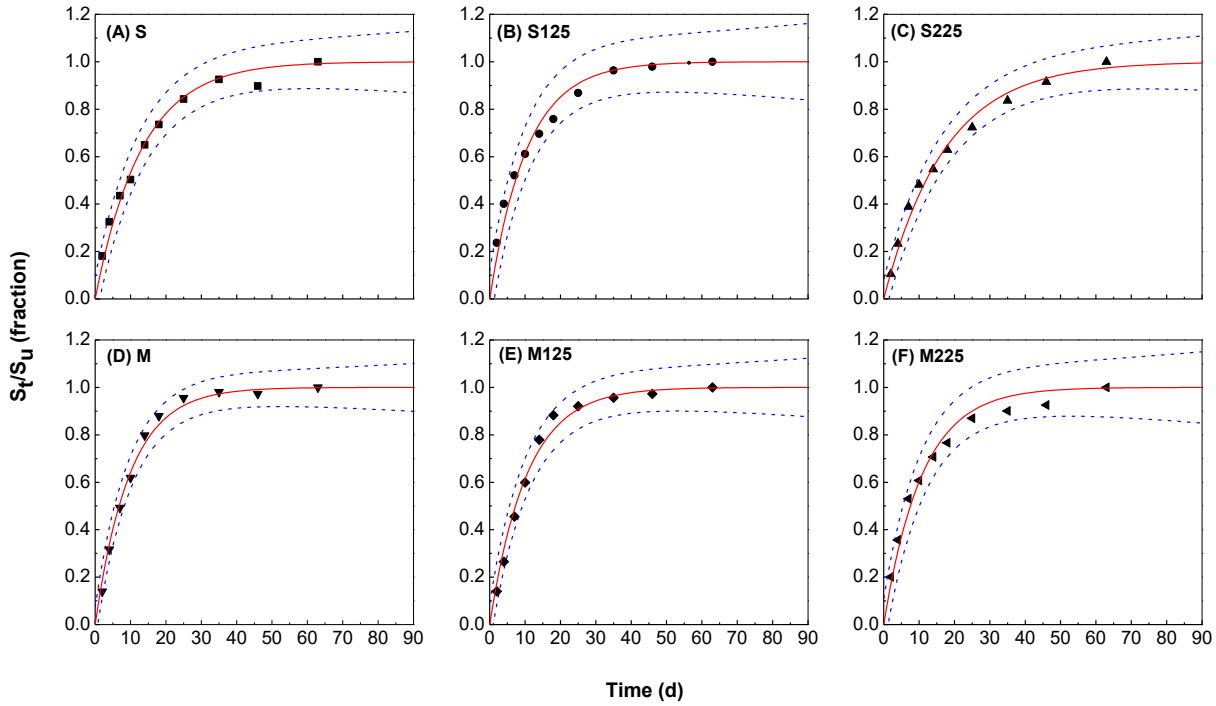

Figure S2. Normalized methane COD production from S (A), S125 (B), S225 (C), M (D), M125 (E), and M225 (F) over the incubation period. Solid lines are non-linear fits of the experimental data. Dashed lines are 95% confidence region.

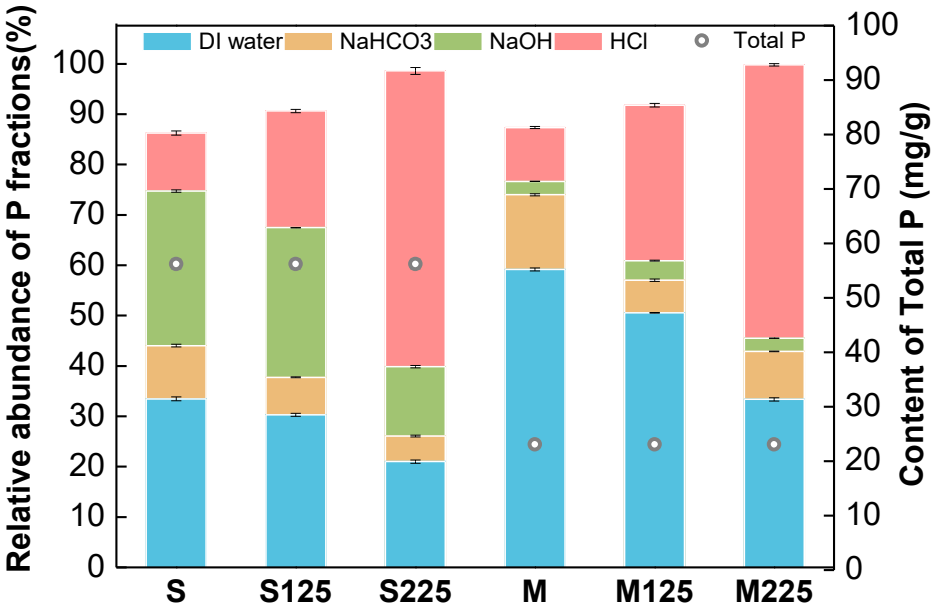

Figure S3. Relative percentage of P species in each sequential extraction step (color bars) and the total P content (open symbol) in sludge, manure, and their hydrothermally treated samples. Error bar represent results from two replicate extraction experiments.

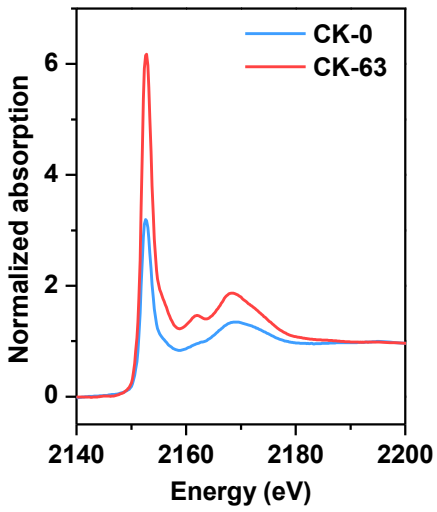

Figure S4. Normalized P XANES spectra of DI water sample (CK) at day 0 (labeled as 0) and day 63 (labeled as 63) of anaerobic digestion.

References

1. Wang, L.; Li, A.; Chang, Y., Relationship between enhanced dewaterability and structural properties of hydrothermal sludge after hydrothermal treatment of excess sludge. *Water Res* **2017,** *112*, 72-82.

2. Cimo, G.; Kucerik, J.; Berns, A. E.; Schaumann, G. E.; Alonzo, G.; Conte, P., Effect of heating time and temperature on the chemical characteristics of biochar from poultry manure. *J Agric Food Chem* **2014,** *62*, (8), 1912-8.

3. Cao, X.; Ro, K. S.; Chappell, M.; Li, Y.; Mao, J., Chemical Structures of Swine-Manure Chars Produced under Different Carbonization Conditions Investigated by Advanced Solid-State13C Nuclear Magnetic Resonance (NMR) Spectroscopy. *Energy & Fuels* **2011,** *25*, (1), 388-397.

4. Gomez, X.; Diaz, M. C.; Cooper, M.; Blanco, D.; Moran, A.; Snape, C. E., Study of biological stabilization processes of cattle and poultry manure by thermogravimetric analysis and ^{13}C NMR. *Chemosphere* **2007,** *68*, (10), 1889-97.

5. Amir, S.; Hafidi, M.; Merlina, G.; Hamdi, H.; Revel, J.-C., Elemental analysis, FTIR and ^{13}C-NMR of humic acids from sewage sludge composting. *Agronomie* **2004,** *24*, (1), 13-18.

6. Jouraiphy, A.; Amir, S.; Winterton, P.; El Gharous, M.; Revel, J. C.; Hafidi, M., Structural study of the fulvic fraction during composting of activated sludge-plant matter: elemental analysis, FTIR and ^{13}C NMR. *Bioresour Technol* **2008,** *99*, (5), 1066-72.

7. Conte, P.; De Pasquale, C.; Novotny, E. H.; Caponetto, G.; Laudicina, V. A.; Ciofalo, M.; Panno, M.; Palazzolo, E.; Badalucco, L.; Alonzo, G., CPMAS 13C NMR characterization of leaves and litters from the reafforestated area of Mustigarufi in Sicily (Italy). *Open Magnetic Resonance Journal* **2010,** *3*, 89-95.