

**Table S1.** Source and level of each HM in various AD substrates.

Substrate	Source	Heavy metals (mg/kg)						Reference
		Ni	Zn	Cu	Cd	Cr	As	
Food waste	-	-	64	65	8	-	-	[15]
Poultry manure	Feed supplements	-	203.37-394	19.78-94.73	0-0.60	0-65.10	0.75-4.59	[16]
Cattle manure	Feed supplements	-	33.82-224.12	14.08-58.78	0-3.60	0-3.60	0.73-4.65	
Swine manure	Feed supplements	-	332.47-901.82	266.83-1337.23	0-203.40	0-4.60	1.31-28.38	

Note) All references in this table can be found in the main text.

**Table S2.** Presence and outcome of HM on AD reported in previous studies included in this manuscript.

Heavy Metal	Substrate	Concentration	Outcome	Reference
Fe, Ni, Co, and Mo	Grass silage	75, 1.7, 0.75, and 0.5 mg/L	Advances COD, solubilization of SCFAs and higher methane turnout.	[22]
Co and Ni	Methanogenic biomass	0.05, 0.2 $\mu$ mol h <sup>-1</sup>  2 $\mu$ mol h <sup>-1</sup>	Higher methane yields  Inhibitory	[23]
Ni and Co  Mo	Maize silage	Total elimination from digester.  -	Methane production is reduced by 10 and 25 %.  Does not affect methane production.	[24]
Cd	Waste-activated sludge	0.1 mg/g VSS  10 mg/g VSS  Further increase	Augmented hydrolysis and acidification.  Inhibits hydrolysis, acidification, and methanogenesis.  Decreases enzyme activity and microbial diversity.	[25]
Ca, Fe, Ni, and Co	Simulated primary sludge (Dog food)	Not defined	Eradication of propionate at elevated VFA levels	[26]
Ni, Zn, and Cd	Potato waste	2.5-5.0 ppm range  At 2.5 ppm	Increase in biogas production rate (Cd>Ni>Zn).	[27]
Fe, Co, Mn, Ni,	Wastewater sludge	Not defined.		

Zn, and Mo		Deficiency.  Co-supplementation.	Under performance.  Acetate to methane conversion rate enhanced (9-50%)	[28]
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**Table S3.** Transformation of HM during AD reported in the previous literature included in this manuscript.

Heavy metal	Substrate	Fate of Heavy metals	Reference
Zn, Cu, and Mn	Pig slurry	HM has different distribution characteristics (Zn>Cu>Mn).  Concentration in residue depends on their inclusion in feed.	[34]
Zn, Cu, As, Cd, Pb, and Cr	Pig manure	Higher Zn, Cu, and As (931, 419, and 0.49 mg/kg)  Lower Cd, Pb, and Cr in biogas residue. (0.27, 1.66, 3.88 mg/kg)	[35]
Cu, Zn, Cd, As, Pb, Cr, and Mn	Co-digestion (Chicken manure and Corn stover)	Unequal speciation in biogas residue. (152.78, 1101, 0.32, 25.36, 5.32, 27.25, and 1234 mg/kg)	[36]
Zn, Cu, and As	Pig and dairy manure	HM in biogas residue remain higher than biogas slurry	[37]
Not defined	Chicken manure	In earliest stage acid generation causes VFA accumulation which dissolves HM. As a result, HM rise in biogas slurry	[38]
Zn, Cu, Ni, As, Pb, and Cd	Swine manure	HM transformed during the AD. The bioavailable fraction of Zn, Cu, Ni, Cd, As, and Pb were 9.71, -6.04, -19.24, 13.62, -16.48, and -7.22 %.	[39]
Zn, Cd, and Ca	Sediment sludge	pH drops when bought on ground, oxidation, and release of sulfides in soil	[40]

Note) All references in this table can be found in the main text.

**Table S4.** Typical studies regarding the impact of HM on AD process included in this manuscript.

Phase	Substrate	Heavy Metal	Impact	Reference
Hydrolysis	Poultry and animal manure	Cu	Interacts with cellulase and heavily alters hydrolysis	[46]
	Agricultural waste	Cu (150 mg/kg)	Cellulase activity spiked by 16.33 %. Microbial activity maintained. Stimulates enzymatic reactions.	[50]
	Agricultural waste	Cu (300 mg/kg)	Cellulase activity curtailed by 5.86 %. Complete disruption of microbial community.	[51]
	Pig manure	Cu (5000 mg/kg)  Higher Cu levels	Worked in favor of hydrolysis. Toxic to microorganisms. Forbids deterioration of composite organic macromolecules.	[51]
	<i>Phragmites</i> straw and cow dung	Ni (0.2, 0.8 and 2.0 mg/L)	Promoted biogas production.  Further Ni addition halted biogas production.	[52]
Acidogenesis/Acetogenesis phase	Sewage sludge	Cd, Cu, Cr, Zn, Pb, and Ni	Cd and Cu were most toxic to VFA diminishing microorganisms. Pb and Ni were least toxic.	[47]
	Dairy waste	Cr and Cd	Cd less than 20	[53]

			mg/L improved acidogenesis. Cd higher than 20 mg/L halted acidogenesis. Cr (5 mg/L) decreased VFA production.	
	Food waste	Cu	Cu (100 mg/L) stimulates VFA destruction. Smaller concentration can augment VFA-degrading organisms. More than 100 mg/L hindered acidogenesis.	[54]
Methanogenesis phase	Bamboo wastewater	Cu	5 mg/L had positive impact on methanogens. 300 mg/kg suppressed methanogens	[58]
	<i>Phragmites</i> straw and cow dung	Cu	Cu (30 & 100 mg/L) hiked biogas production by 43.62, 20.77 %.  Cu (500 mg/L) biogas production was reduced by 69.47 %.	[56]
	Anaerobic granular sludge	Ni (30 mg/L)	Ni less than 30 mg/L facilitated methanogenic activity.  Over 30 mg/L impeded methanogenic activity.  Supplement rate of 4 mg/L caused	[59]

			25 % higher biogas production.	
	<i>Phragmites australis</i> straw and Cow dung	Ni (0.8 mg/L)	18 % higher biogas production than without Ni addition.	[52]
	Organic fraction of MSW	Ca, K, Cr, Ni, Zn, Co, and Mo	Dosage of 0.06, 0.6, 3, and 6 mg/L improved cumulative biogas yield by 4.71, 15.29, 14.71, and 14.12 %, respectively.	[60]
	Swine manure	Ni	Crucial for coenzyme F430 of methanogenic microorganisms.	[8]
	Manure and industrial waste	Fe	Fe cuts down sulfide intermeddling.  Improving cellulase activity.	[61]
	Maize straw	Fe	0-4000 mg/L substantially improved biogas production.  Highest production at 1000 mg/L.	[61]
	Dairy manure	Fe	Below 12000 mg/L, there was no impact on methane production.  At 20000 mg/L methane production completely	[63]

			stopped.	
	-	Traces of Fe	Important for proteolytic enzymes.  Triggering cytochrome and ferredoxin evolution.	[64]
	Anaerobic granular sludge	Cd	Highest toxicity towards methanogens.  1 mg/L can affect methanogenic activity.	[59]
	Potato waste	Cd (0, 2.5 and 5 ppm)	Biogas generation rate was 2360, 5960, and 5040 ml respectively.	[26]
	Lactoserum	Cd (0.1-0.3 mg/L)	Enhances biogas production rate.  Act as cofactor and energizes enzymatic activity.	[65]
	Anaerobic granular sludge	Zn	2 mg/L promotes methanogenic activity. If exceeds 3 mg/L, the methanogenic activity declines.	[59]
	MSW	Zn	5 mg/L spiked biogas production by 4.44 %.  Dropped by 11.11 and 33.33 % when Zn concentration	[60]

			was 50 and 100 mg/L.	
	-	Zn	Zn concentration of 5 mg/L is required for methanogens to retain cell catabolism of methanogenic microorganisms.	[65]

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