Characterization of Organic Matter in Beef Feedyard Manure by UV-Visible and Fourier-transform Infrared Spectroscopies

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INTRODUCTION

Manure (a mixture of feces and urine) from beef cattle feedyards is a valuable source of nutrients for crops and assists with maintaining soil quality. However, humification and decomposition processes occurring during feedyard manure's on-farm life cycle influence the forms, concentrations, and availability of carbon (C) and nutrients, such as nitrogen (N) and phosphorus (P). An increased understanding of manure organic matter (OM) will improve estimates of fertilizer value of manure from different feedyard sources (e.g. manure accumulated in pens, stockpiled manure after pen scraping, settling basin and retention pond sediments). This will also assist with identifying factors related to nutrient loss and environmental degradation via volatilization of ammonia (NH_3) and nitrous oxide, and nitrate (NO_3^-) leaching. Fourier-transform infrared (FT-IR) and Ultraviolet-visible (UV-vis) spectroscopies are useful tools for characterizing structural and functional properties of OM and water-extractable OM (WEOM) from soil, livestock manure, and other organic amendments. Quantitative and qualitative information on specific functional groups in manure can be obtained based on FT-IR band heights, while ratios of UV-vis absorbance at specific wavelengths can characterize WEOM in regard to molecular weight, polarity and degree of humification.

OBJECTIVES: Use ***FT-IR*** and ***UV-vis*** spectroscopies and chemical analyses to evaluate the structural and functional properties of OM and WEOM in manures obtained from different sources (unconsolidated **surface manure**, **manure pack**, **settling basin** and **retention pond** sediments).

MATERIALS AND METHODS

- Triplicate samples of (1) unconsolidated surface manure from feedyard pens, (2) manure pack, (3) settling basin sediment (depth to 25 cm), and (4) retention pond sediment (depth to 12 cm) were collected from a commercial feedyard in Deaf Smith County, Texas (***Fig. 1***). Selected sample properties are presented in ***Table 1.***
- Manure WEOM was obtained by extracting samples with deionized water [1:100 (wt:vol) ratio manure to water] for 16 h at 250 rpm. The WEOM was analyzed for dissolved organic carbon (DOC) and dissolved nitrogen (DN) (***Table 2***).
- ***UV-visible*** spectral characteristics were evaluated on WEOM that was diluted 1:13 (vol:vol) with deionized water, and spectral data recorded between the wavelengths of 200 and 700 nm (***Fig. 2***).
- Ratios of E2/E3 (molecular weight), E2/E4 (lignin content), E2/E6 (proportion of humified to non-humified material), and E4/E6 (degree of humification, molecular weight, aromaticity) were calculated based on UV-vis absorbance of WEOM at 254, 280, 365, 472, and 664 nm (***Table 2***).
- The ***FT-IR*** spectra of OM and freeze-dried WEOM were obtained from potassium bromide (KBr) disks (1.0 mg sample + 100 mg KBr). Each sample was scanned 24 times with a resolution of 2.0 cm^{-1} and spectra were recorded from wavenumber 450 to 4000 cm^{-1}. All spectra were normalized (***Fig. 3, Table 3***).
- All analyses were conducted in triplicate and significance determined by single factor analysis of variance (ANOVA).

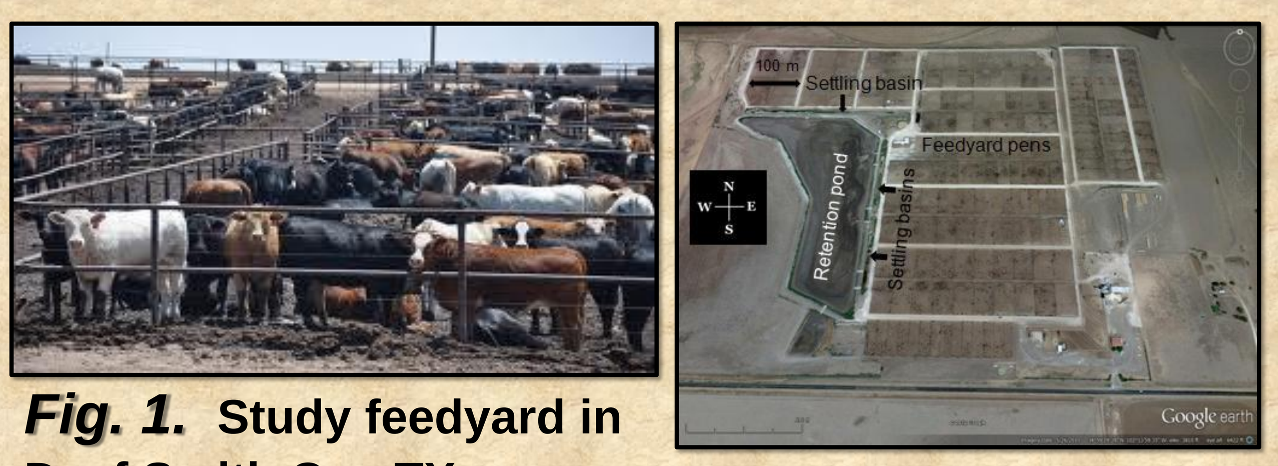

Fig. 1. **Study feedyard in Deaf Smith Co., TX.**

TABLE 1. **Selected properties of samples collected from different feedyard sources.** *Highest total N and NO_3^- concentrations were in settling basin sediment. Manure pack contained 92% and 43% less Total Ammoniacal N (TAN, NH_3+ NH_4^+) and OM, respectively, than surface manure, indicating NH_3 volatilization and OM decomposition.*

	DM†	TKN	Org. N	TAN	NO_3-N	P	K	OM	C:N ratio
	%	----------	----------	----------	%DM	----------	----------	----------	
Surface manure	94.2^{d}	2.6^{a}	2.5^{a}	0.259^{b}	0.003^{a}	0.88^{a}	1.78^{b}	79.9^{d}	15^{b}
Manure pack	85.9^{c}	2.6^{a}	2.5^{a}	0.022^{a}	0.022^{a}	1.41^{b}	1.97^{b}	45.5^{c}	11^{a}
Settling basin	16.9^{a}	3.6^{b}	3.4^{b}	0.003^{a}	0.118^{b}	1.82^{c}	1.07^{a}	27.5^{a}	11^{a}
Retention pond	51.6^{b}	2.7^{a}	2.7^{a}	0.040^{a}	0.029^{a}	1.56^{bc}	1.72^{b}	34.8^{b}	10^{a}

†DM, dry matter; TKN, Total Kjeldahl N; Org. N, Organic N; TAN, Total Ammoniacal N; P, Total P; K, Total K; OM, organic matter.

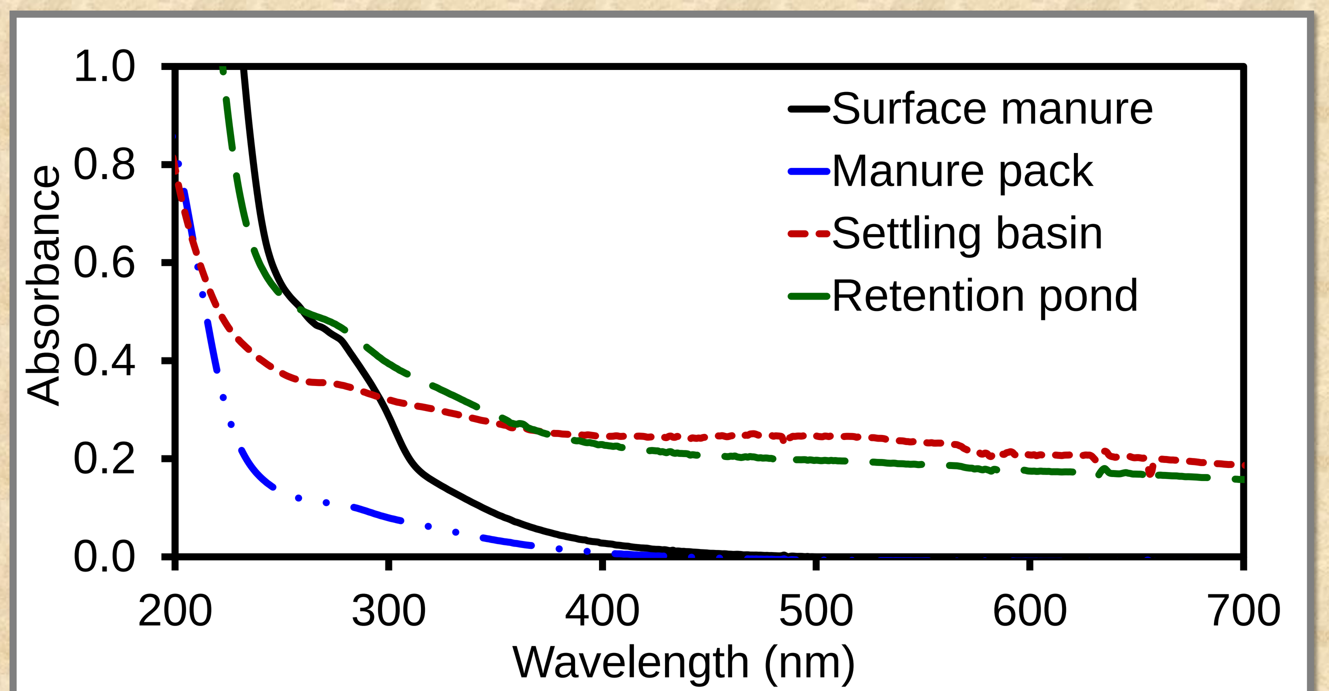

Fig. 2. **The UV-visible spectra of WEOM from feedyard manures from different sources.** *The shoulder around 280 nm is attributed to aromatic and phenolic compounds and was more prominent in surface manure, indicating decomposition of OM in other samples. Increases in absorbance at wavelengths >300 nm provide evidence of polymerization and condensation associated with humification.*

TABLE 2. **Chemical properties and UV-vis absorbance ratios of WEOM.** *Surface manure had up to 98% and 95% more DOC and DN, respectively, than other samples. The WEOM from settling basin sediment had a low C:N ratio. Specific absorbance ratios of E2/E3 (molecular weight), E2/E4 (lignin content), E2/E6 (proportion of humified OM), E4/E6 (degree of humification, molecular weight, aromatic groups) show that OM in manure becomes more humified, increases in molecular weight, and decreases in lignin content as it moves through the feedyard.*

	Chemical properties			UV-vis absorbance ratios			
	DOC†	DN	C:N	E2/E3 (A_{254}/A_{365})	E2/E4 (A_{280}/A_{472})	E2/E6 (A_{280}/A_{664})	E4/E6 (A_{472}/A_{664})
	----mg g^{-1}----						
Surface manure	45.2^{d}	9.73^{d}	4.6^{c}	7.24^{b}	30.5^{c}	103.0^{c}	3.34^{a}
Manure pack	8.70^{c}	2.12^{c}	4.1^{bc}	3.58^{a}	14.6^{b}	76.6^{b}	5.26^{b}
Settling basin	1.13^{a}	0.72^{b}	1.6^{a}	3.55^{a}	11.3^{a}	37.1^{a}	3.26^{a}
Retention pond	2.11^{b}	0.51^{a}	4.1^{b}	3.50^{a}	13.7^{b}	84.9^{b}	6.18^{b}

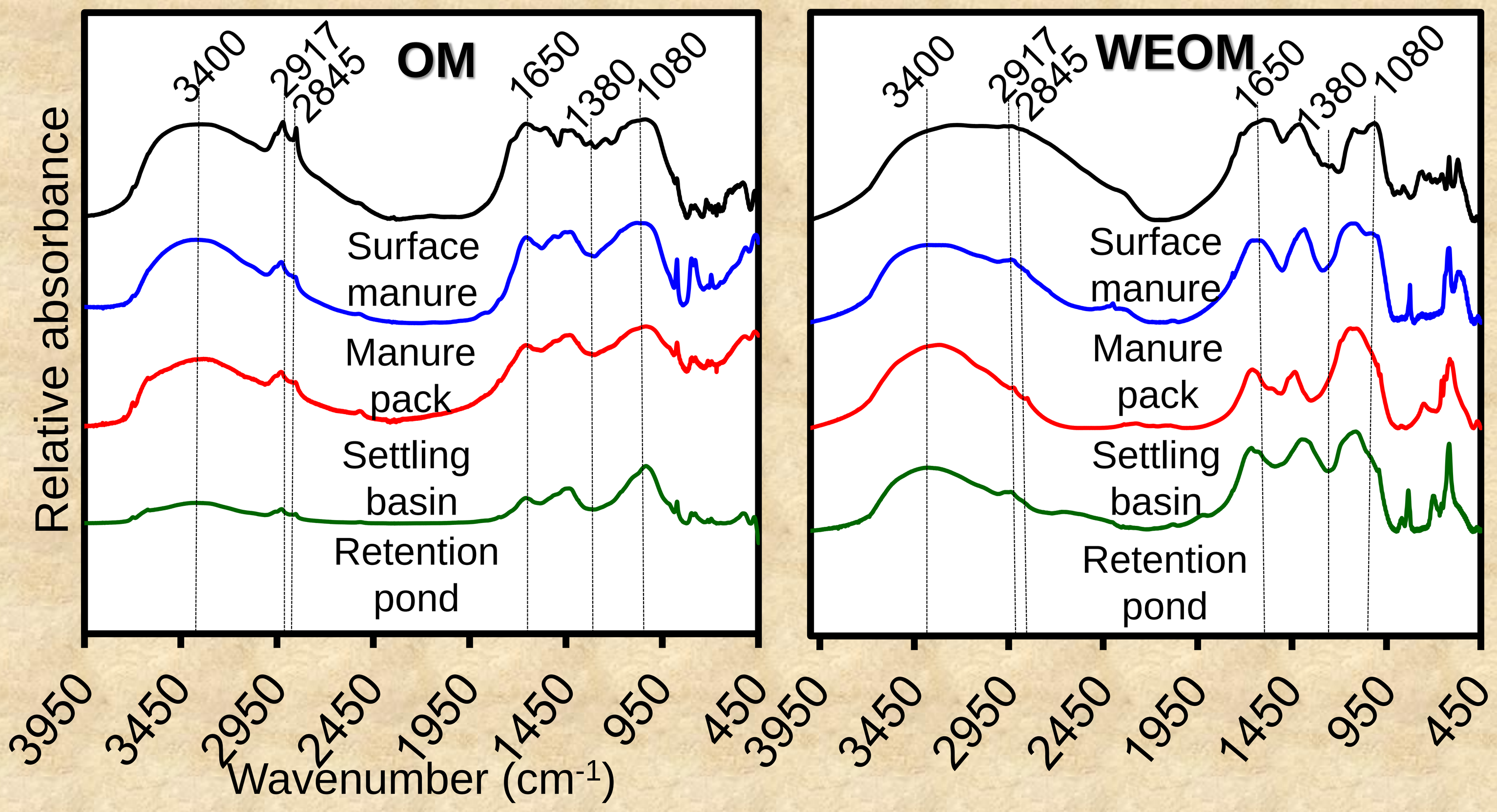

Fig. 3. **The FT-IR spectra and key spectral regions of OM and WEOM from samples taken from different feedyard sources.** *Band patterns were typical for manue OM and compositional changes were similar to that observed during manure composting (Hsu, J.H., and S.L. Lo. 1999. Environ. Pollut. 104:189-196). Absorbances at (1) 3400 cm^{-1} were attributed to O-H and N-H stretching), (2) 2917 and 2845 cm^{-1} were attributed to aliphatic C-H stretching of fats and lipids) (3) 1650 cm^{-1} were attributed to aromatics, COO^-, ketones, and/or N-H (Amide I), (4) 1380 cm^{-1} were attributed to nitrates, and (5)1150-1010 cm^{-1} were attributed to alcohols, polysaccharides, and/or phosphates.*

TABLE 3. **The FT-IR band heights of OM collected from different feedyard sources.** *Greater absorbance at 2917 and 2845 cm^{-1} by surface manure is attributed to a higher proportion of fats and lipids than in samples from other sources.*

	Approximate wavenumber (cm^{-1})					
	3400	2917	2845	1650	1380	1080
	----------	----------	Absorbance (a. u.)	----------	----------	----------
Surface manure	0.774^{c}	0.178^{c}	0.193^{c}	0.699^{c}	0.449^{c}	0.668
Manure pack	0.612^{c}	0.096^{b}	0.072^{b}	0.509^{bc}	0.365^{c}	0.631
Settling basin	0.457^{b}	0.089^{b}	0.080^{b}	0.334^{b}	0.178^{b}	0.381
Retention pond	0.087^{a}	0.082^{a}	0.023^{a}	0.099^{a}	0.059^{a}	0.283

CONCLUSIONS

- The composition and content of OM and nutrients in beef cattle manure differ depending upon source, with higher concentrations of available nutrients in more recently excreted materials (***Table 1***).
- As manure completes it's on-farm life cycle, concentrations of dissolved C and N decrease by 98% and 95%, respectively (***Table 2***).
- The UV-visible analysis revealed large differences in molecular weight, lignin content, and proportion of humified OM between manures from different sources (***Fig. 2, Table 2***).
- The FT-IR spectra of OM and WEOM indicated preferential decomposition of fats, lipids, and proteins over aromatic polysaccharides, such as lignin (***Fig. 3, Table 3***).
- Further work is warranted to evaluate how application of manure from different sources on a feedyard will influence soil quality and fertility.