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Nitrogen bound to manure fiber is increased by applications of simple phenolic acids



Jonathan J. Halvorson^{1*} , Scott L. Kronberg¹, Rachael G. Christensen¹, Ann E. Hagerman² and David W. Archer¹

Abstract

Background: Polyphenolic compounds like tannins can increase nitrogen (N) excreted in feces when consumed by ruminants but less often noted is increased N in fecal acid detergent fiber (ADF-N). Some simple phenolics are thought to facilitate binding interactions between nitrogenous compounds and soil. We hypothesized that contact with common phenolic acids, such as found in crops, could increase ADF-N, in excreted manure.

Methods: We performed two separate experiments to test our hypothesis. In the first experiment, we applied three solutions (i.e., 0.001, 0.01, 0.1 M) of sodium benzoate (B0), sodium 4-hydroxybenzoate (B1), 3,4-dihydroxybenzoic acid (B2), gallic acid (B3), ammonium benzoate (AB), and ammonium chloride (AC) to dried pulverized manure and measured ADF-N. In the second experiment we modified the methodology, by applying more compounds at a single concentration (0.001 M) and including an added nitrogen (NH₄Cl) treatment.

Results: We found a statistically significant interaction between treatment and concentration in the first experiment ($P < 0.0001$), but the main effects were inconsistent and there was no significant difference between the treatment means and the control mean (samples treated with water). Conversely, we observed a significant treatment effect in the second experiment ($P < 0.0001$), but no significant effect of the added N or interaction. Samples treated with water, B0, or B3 were similar and indistinguishable from untreated manure. The treatment with B1, caffeic acid, (CAF), or B2 increased ADF-N from 13.2 to 17.5% while +(-)catechin (CAT), and *p*-coumaric acid (*p*-COUM), increased it by 19.7 and 22.2% respectively. Epigallocatechin gallate (EGCG) and ferulic acid (FER) increased ADF-N by 32.6 and 34.1%, respectively.

Conclusions: The results support our hypothesis that N in manure can complex with manure ADF following exposure to benzoic acid and especially cinnamic acid derivatives. This resulted in greater amounts of N bound to relatively recalcitrant fibers in excreted manure. Thus, N mineralization may be impacted by increasing or decreasing the amount of N bound to manure fibers or other recalcitrant soil compounds such as lignin, but it is unclear whether such N would be less available to plants, or for volatilization, or leaching.

Keywords: Manure, Acid detergent fiber, Nitrogen, Phenolic acids, Hydroxybenzoic acids, Hydroxycinnamic acids, Polyphenol

Background

The phenolic class of secondary plant metabolites (PSMs) ranges from large complex tannins to simple phenolic acids. These compounds participate in many important plant functions including responses to herbivory, environmental stress, and competition (e.g., Kong et al. 2019; Kumar et al. 2020; Naikoo et al. 2019; Siqueira et al. 1991; Yang et al. 2018). In soils, PSMs participate in numerous

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reactions that affect biological, chemical, and physical phenomena, stimulate or inhibit soil microorganisms, and affect important biogeochemical processes such as organic matter formation and nutrient cycling (e.g., Chomel et al. 2016; Hättenschwiler and Vitousek 2000; Mallik 1997; Mandal et al. 2010; Marchiosi et al. 2020; McGivern et al. 2021; Schmidt et al. 2013; Siqueira et al. 1991). When consumed by ruminants such as cattle or goats, PSMs (especially tannins) can change nutrient use efficiency and can improve animal health and environmental services (e.g., Kelln et al. 2020; Ku-Vera et al. 2020; Maxin et al. 2020).

Large complex PSMs such as tannins are not usually associated with annual crops. Instead, relatively simple phenolic acids such as hydroxybenzoic acids and hydroxycinnamic acids are more common, especially in cereals (Gunia-Krzyżak et al. 2018; Naczka and Shahidi 2006; Otte et al. 2020; Stuper-Szablewska and Perkowski 2019). Simple phenolic compounds may enter soil as decomposition products, root exudates, or through the actions of microorganisms and may participate in important soil processes like nutrient cycling or the formation of protected or polymerized soil organic matter (Šmejkalová et al. 2006; Sokol et al. 2019). Tannins and phenolic acids are known to sorb to soil (Cecchi et al. 2004; Makino et al. 1996) and have been found to reduce N solubility when added to soil presumably through abiotic mechanisms that bind unspecified forms of N to soil organic matter or the inorganic soil matrix (Halvorson et al. 2013, 2016). Less often noted are changes in ruminant manure composition associated with consumption of phenolic compounds including increases in the amount of N recovered in fecal acid detergent fiber (ADF-N) (Halvorson et al. 2017; Powell et al. 2009).

Acid detergent fiber in forages and manure is composed of cellulose, lignin, and acid-insoluble ash (Van Soest et al. 1991). Forage ADF is typically composed of about 80% cellulose, with lignin ranging from about 11% in grasses to about 16% in alfalfa and 0.3–2.9% ash (Colburn and Evans 1967). Espinosa et al. (2017) reported that cereal straws (e.g., crop residues) are composed of 34–44% cellulose, 27–38% hemicellulose, 16–18% lignin and 6–9.5% ash. Any N that is sequestered in these plant cell wall fractions has low biological availability and tends to be recovered in ADF. Such N is a feature of fresh and stockpiled forages and has been attributed to the formation of complexes in the presence of tannins or to Maillard browning reactions caused by heating and drying (Licitra et al. 1996). In manure, lignin may directly or indirectly inhibit the decomposition of cellulose by competing for or releasing phenolic degradation products that inhibit hydrolytic enzyme activity. (Kim 2018; Liao et al. 2005). Lignin is considered to be insoluble (Naczka

and Shahidi 2006; Pérez et al. 2002) and decomposes relatively slowly in soil contributing to stocks of recalcitrant soil organic matter especially as it becomes depolymerized and associated with mineral constituents (Angst et al. 2021). Acid insoluble ash in ADF may originate from biogenic mineral fractions and contamination from soil and dust and contain silica (Crocker et al. 1998; Van Soest 1994).

Many studies have demonstrated that consumption of polyphenolic PSMs like tannins by cattle can increase N use efficiency, reduce enteric greenhouse gas emissions and shift the pattern of N excretion from urine to manure (Aboagye and Beauchemin 2019; Addisu 2016; Min et al. 2020; Orzuna-Orzuna et al. 2021; Waghorn and McNabb 2003). However, much less is known about potential effects of dietary simple PSMs, such as benzoic and cinnamic acid derivatives, on animal performance or manure quality. Manure contributions to soil fertility and organic matter are influenced by its composition, quantity, and patterns of distribution (Rayne and Aula 2020) and thus new information about the effects of simple PSMs on manure quality and quantity will be of great interest to producers seeking to benefit from combining crop and animal production (Archer et al. 2018; Sekaran et al. 2021). The direct and indirect linkages between consumption of PSMs and both animal and human health are increasingly appreciated and a focus of continuing research (Kumar and Goel 2019; Santana-Méridas et al. 2012; Tufarelli et al. 2017). Consequently there is growing consensus that an integrative approach for managing PSMs in agroecosystems is needed that will benefit humans, crops, livestock, and the soil (Clemensen et al. 2020; Iqbal et al. 2020).

While many studies have focused on the effects of dietary PSMs on animal health and productivity, fewer have addressed their effects on manure composition (Halvorson et al. 2017; Ingold et al. 2015; Powell et al. 2009) or decomposition (Hao et al. 2011; Ingold et al. 2018, 2021; Powell et al. 2011). Notably, there is dearth of information regarding interactions between nondietary PSMs and excreted manure. Manure, deposited on a field directly by animals or applied mechanically to soil, could encounter phenolic compounds, originating from plant residues or microbial activity, that might impact its composition, rate of mineralization, and subsequent nutrient availability to plants. The objective of this study was to uncover evidence of interactions between simple phenolic plant secondary compounds and excreted manure. Based in part on previous observations we hypothesized that topical applications of benzoic and cinnamic acid derivatives would increase sorption of soluble N in manure to the insoluble ADF fraction. Since such simple phenolic acids are common in plants and soil, they would

likely be encountered directly by grazing animals, as part of the diet, by deposited excreta and during composting (Cascant et al. 2016; Marchiosi et al. 2020; Salami et al. 2019; Strobel 2001).

Materials and methods

Feeding and manure collection

The manure used in this study originated from beef cattle in the resident herd at the Northern Great Plains Research Laboratory in Mandan, ND. Samples of manure were collected from individual Angus heifers (18-months old, ~385 kg) after a minimum 2-week adjustment period on the diet. The heifers were fed collectively, using a feed wagon, with a mixed daily ration calculated as 9.53 kg oat hay, 907 g of corn grain and 907 g of dry peas animal⁻¹ day⁻¹ (Table 1). The oat hay was locally sourced, near Almont, ND, and corn and peas were obtained from a feed mill in Harvey, ND. The ration contained 8.2% crude protein and was intended to represent a maintenance ration for beef heifers, providing 24.3 Mcal d⁻¹ allowing for 0.947 kg d⁻¹ gain calculated using the 2016 beef cattle model (National Academies of Sciences and Medicine 2016). The average ADF content of the mixed ration (32.6%) was comparable to other forages (Jung et al. 1997). Throughout the experiment, all animals had ad libitum access to trace mineralized salt (American Stockman Big 6) and tap water.

Manure sample collection occurred between 27 February and 13 March 2020. Cows were held individually in pens (~9.3 m²) overnight, and manure was collected off the pen floor using a shovel the following morning. The pens had impervious concrete floors; thus, manure was easily collected with minimal contamination with urine and other substances. The pens were cleaned after each day's collection. Daily collections of manure were composited by cow, dried to a constant weight at 55 °C and

ground in a Wiley mill with a 2 mm screen. The dry and ground samples were stored in double-bagged 1-gallon Ziplock plastic bags and frozen (-20 °C) until use. Representative samples of oat-hay, corn and peas used for the ration were procured and stored air-dry at room temperature until analysis.

Set-up of the experimental

We performed two separate experiments, hereafter referred to as Experiment 1 and 2 to test our hypothesis.

Experiment 1

Experiment 1 was designed as a randomized complete block. Twenty samples of manure (mass 13 ± 0.1 g) from five randomly selected heifers were weighed into 10 cm by 20 cm in-situ forage bags (ANKOM Technology, Macedon NY) and secured with two nylon zip ties. Randomly selected bags from each animal were assigned to receive one of the 20 treatment combinations (total n=100), which included handling only (Untreated), deionized water (H₂O) or one of the three concentrations (i.e., 0.001 M, 0.01 M or 0.1 M) of aqueous solutions of six compounds: sodium benzoate (B0), sodium 4-hydroxybenzoic acid (B1), 3,4-dihydroxybenzoic acid (B2), 3,4,5-trihydroxybenzoic acid monohydrate (B3, gallic acid), ammonium benzoate (AB), and ammonium chloride (AC) (Table 2). These compounds were selected to evaluate the effects of hydroxybenzoic acids with varying substituent configurations and to determine if additions of ammonia would impact ADF-N in the presence (AB) or absence (AC) of a benzene ring. Derivatives of both benzoic and cinnamic acids are naturally common and sometimes added to animal feed or silage to improve stability or inhibit pathogens (Del Olmo et al. 2017; Muck et al. 2018). The treatment solutions were prepared fresh on the day of use.

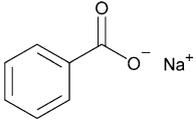
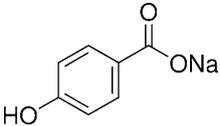
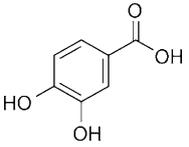
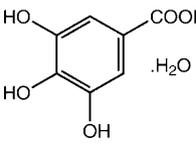
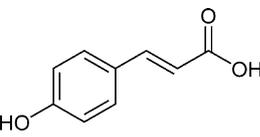
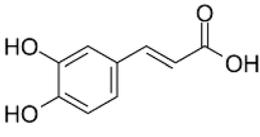
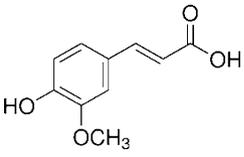
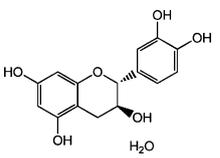
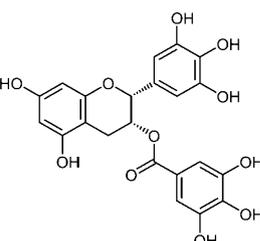
Table 1 Feed analysis^a for the oat hay-corn-pea mixed ration

Component ^b	CP	Fiber		TDN	NEm	NEg	Nel	Macrominerals						Micronutrients				
	%	ADF	NDF					Ca	P	K	Mg	Na	S	Cu	Fe	Mn	Mo	Zn
								Mcal cwt ⁻¹						ppm				
Oat hay	7.0	36.9	58.3	60.4	60.1	34.0	63.2	0.18	0.10	1.48	0.14	0.18	0.12	2.1	106	28	1.65	43.7
Corn	8.6	2.9	9.2	87.8	98.6	67.7	89.7	0.04	0.21	0.37	0.13	0.04	0.10	0.4	44	6	0.63	39.1
Peas	19.7	17.0	23.3	66.2	68.6	41.7	86.1	0.22	0.33	0.91	0.17	0.05	0.15	3.9	129	13	0.89	67.0
Ration Mix	8.2	32.6	51.6	63.0	63.8	37.3	67.1	0.17	0.13	1.35	0.14	0.16	0.12	2.1	103	25	1.51	45.2

^a CP: Crude Protein, (%); ADF: Acid Detergent Fiber, (%); NDF: Neutral Detergent Fiber, (%); TDN: Total Digestible Nutrients, (%); NEm: Net Energy Maint, (MCal/cwt); NEg: Net Energy Gain, (MCal/cwt); NEl: Net Energy Lact, (MCal/cwt); Ca: Calcium, (%); P: Phosphorus, (%); K: Potassium, (%); Mg: Magnesium, (%); Na: Sodium, (%); S: Sulfur, (%); Cu: Copper, (ppm); Fe: Iron, (ppm); Mn: Manganese, (ppm); Mo: Molybdenum, (ppm); Zn: Zinc (ppm). Dry matter values for oat hay, corn and peas were 88.6, 86.8 and 90.1% respectively. Data: from single mixed samples, are shown on a dry weight basis

^b Animals, fed collectively, were supplied with a total mixed ration providing 9.53 kg oat hay, 907 g of corn and 907 g of peas, animal⁻¹ day⁻¹

Table 2 Some properties of the treatment compounds and 0.001 M solutions

Treatment	Source	Structure	Anhydrous MW	$\text{pK}_{\text{a}1}^{\text{a}}$	$\text{K}_{\text{ow}}^{\text{b}}$	0.001 M Solution ^c Soluble-N (mg/L)	0.001 M Solution ^c pH
Sodium benzoate (B0, $\geq 99\%$)	Alfa Aesar, Haverhill, MA USA		144.1	4.2	1.87	0.08 (13.0)	5.33 (5.22)
Sodium 4-hydroxybenzoate (B1, $\geq 99\%$)	Alfa Aesar, Haverhill, MA USA		160.1	4.5	1.58	0.26 (14.9)	5.72 (5.58)
3,4-dihydroxybenzoic acid (B2, $\geq 99\%$)	Frontier Scientific, Logan, UT USA		154.1	4.3	0.86	0.25 (13.6)	3.90 (3.82)
Gallic acid monohydrate (B3, $\geq 98\%$)	Sigma-Aldrich, Inc., St Louis, MO USA		(170)	4.4	0.7	0.25 (16.2)	3.76 (3.76)
<i>p</i> -Coumeric acid (<i>p</i> -COUM, $\geq 98\%$)	Sigma-Aldrich, Inc., St Louis, MO USA		164.2	4.6	1.79	0.32 (17.8)	3.73 (3.75)
Caffeic acid (CAF, $\geq 98\%$) ^a	Sigma-Aldrich, Inc., St Louis, MO USA		180.2	4.5	1.15	0.43 (17.4)	3.77 (3.76)
<i>trans</i> -Ferrulic acid (FER, $\geq 99\%$)	Sigma-Aldrich, Inc., St Louis, MO., USA		194.2	4.4	1.51	0.30 (16.4)	3.76 (3.73)
(+)-Catechin hydrate (CAT, $\geq 98\%$)	Sigma-Aldrich, Inc., St Louis, MO USA		290.3	8.6	0.51	0.26 (16.9)	7.43 (6.67)
Epigallocatechin gallate (EGCG, $\geq 95\%$)	Biosynth International, Inc., San Diego, CA USA		458.4	7.7	1.2	0.29 (15.1)	6.30 (5.85)

^a Acid dissociation constant for the first ionization ($\text{pK}_{\text{a}1}$)

^b Octanol-water partition coefficients (K_{ow}) from <https://pubchem.ncbi.nlm.nih.gov/>. Low values correspond to polar compounds while higher values are indicative of nonpolar ones

^c Values without parentheses are for a 0.01 M aqueous solution of the treatment compound. Values in parentheses are for a solution containing 0.01 M of the treatment compound + 0.01 M Ammonium chloride

The samples were placed into 1-quart Ziplock bags with 90 mL of the assigned treatment solution. Sealed Ziplock bags containing the sample and solution were agitated with an orbital shaker at 100 rpm for 4 h at room temperature. After 4 h, the excess solution was drained from the 1-quart plastic bag and the treated manure sample remaining in the in-situ bag was subjected to four vigorous rinses with deionized water alternating with firm squeezing (double-gloved hand) to remove excess liquid. After the final cycle, the washed manure sample, still contained by the Ankom in-situ bag was dried at 55 °C for a minimum of 36 h. Dried sample bags were stored frozen (−15 °C) until transport for analyses.

Experiment 2

Experiment 2 was also laid out in a randomized complete block design similar to Experiment 1. However, for Experiment 2, we doubled the number of manure sources, and assessed a broader range of treatment compounds including both hydroxybenzoic and hydroxycinnamic acids, common to crops, and several other polyphenolic compounds of interest. We examined only a single solution concentration but added a second treatment factor, inorganic N, to detect possible additive effects of the treatment compounds and additions of amino-containing compounds. We also increased the length of time that manure samples were incubated with treatment solutions, minimized subsequent sample handling, and increased post-treatment drying time.

Twenty-one samples of dried and ground manure from each of ten randomly selected heifers were prepared as described for Experiment 1. Manure samples from each animal were randomly selected to receive one of the treatment combinations, which included untreated manure, deionized water, or 0.001 M aqueous solutions of nine compounds, namely, sodium benzoate, sodium 4-hydroxybenzoate, 3,4-dihydroxybenzoic acid, gallic acid monohydrate, (+) catechin (CAT), epigallocatechin gallate (EGCG), ferulic acid (FER), *p*-coumaric acid (*p*-COUM), or caffeic acid (CAF) (Table 2). In addition to being a common phenolic acid, the GA treatment was of interest because it is a subcomponent of some hydrolysable tannins (e.g., 1,2,3,4,6-pentagalloylglucose) while CAT, a flavan-3-ol, was chosen because it is a building block of some condensed tannins. EGCG was included because it combines characteristics of both condensed (flavan-3-ol) and hydrolysable (galloyl group) tannins making it a useful model compound. Its low MW (relative to the usual definition for tannins) makes it easily soluble and it readily forms complexes with proteinaceous compounds (Hagerman 2012). A second set of 0.001 M solutions was prepared that contained both the treatment compound (or H₂O) and NH₄Cl added

as solids at the time of each solution preparation. Thus, the total number of samples for Experiment 2 was 210 (10 cows × 10 treatments (9 compounds + H₂O) × 2 N treatments + Untreated).

Treatment solutions were applied to manure subsamples in Ziplock bags, sealed, and agitated for 24 h at room temperature. After incubation, treated manure remaining in the in-situ bags was not rinsed as in Experiment 1 but instead, excess solution was removed by manual squeezing. The damp manure sample still contained by the in-situ bag was dried at 55 °C for 72 h. Dried sample bags were stored frozen (−15 °C) until transport for analyses. Aliquots of the treatment solutions were collected and stored frozen.

Chemical analyses of feed and manure

Chemical analyses were conducted on diet components and untreated manure samples by a commercial lab (Ward Laboratories Inc., Kearney, NE). Total C and N was determined by dry combustion using a LECO FP-2000 CN analyzer (LECO Corporation, St. Joseph, MI). Inorganic N was determined colorimetrically with a Lachat Quikchem 8500 (Hach Company, Loveland, Colorado) and organic N estimated as the difference between total and inorganic N. The concentrations of total P (P₂O₅), K (K₂O), S, Ca, Mg, Na, Zn, Fe, Mn, Cu, and B in feed and manure were determined by Inductively Coupled Plasma (ICP) spectrometry (iCAP 6500 Duo ICP instrument, Thermo Fisher Scientific Inc., Waltham, MA) and pH was measured by electrode.

The effects of treatment solutions on fiber-bound N in manure were determined by Ward Labs from the amount of N (LECO) retained in acid detergent fiber (ADF-N). Acid detergent fiber was measured by the Van Soest technique (Van Soest et al. 1991) following the Ankom method (Vogel et al. 1999), using a Fiber Analyzer 220 (ANKOM Technology, Macedon, NY), and using the customary acid detergent solution.

Treatment solution pH was determined, and water-extractable N of thawed treatment solutions and untreated manure was determined using a Shimadzu TOC-LCSN analyzer equipped with a TNM-L module (Shimadzu Scientific Instruments, Columbia, MD). Samples of untreated manure (0.3 g), weighed into tared *Oak Ridge* centrifuge tubes (50 mL, nominal), were treated with 30 mL of room temperature (~23 °C) deionized water. After vortexing for 5 s and orbital shaking at 200 rpm for 1 h at room temperature, the samples were centrifuged for 8 min at 10,000 rpm (11,952 g), decanted through a Whatman #1 filter paper, and the liquid was analyzed for N content within 5 h.

Statistical analysis

Data analysis for these investigations was conducted using SAS/STAT software, version 9.4 of the SAS System for Windows (© 2002–2012 by SAS Institute Inc., Cary, NC, USA). Average basic composition of the oat hay-corn-pea diet and the manure subsequently produced by cows was determined arithmetically using PROC TABULATE.

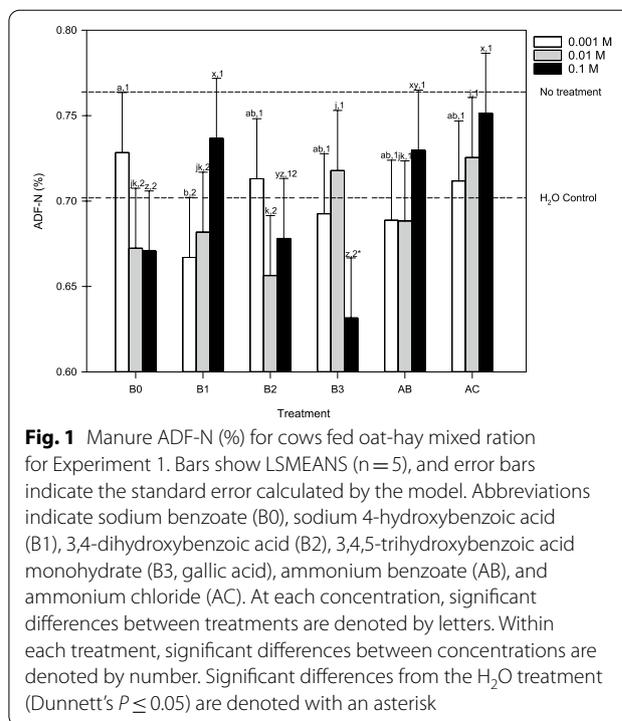
In Experiment 1, we tested whether the ADF-N in manure samples was increased by the 4-h exposure to solutions of treatment compounds (one of six compounds or just H₂O) applied at three concentrations; 0.001 M, 0.01 M and 0.1 M. We performed a linear mixed effects analysis by holding the treatment compounds and concentration as fixed effects and animals (n=5) to be a random effect. In Experiment 2, we tested whether the ADF-N in manure samples was increased by a 24-h exposure to a 0.001 M solution of treatment compounds applied with or without additional inorganic N in the form of NH₄Cl. We classified the treatment compounds and added N as fixed effects and considered animals (n=10) to be a random effect.

In both experiments, the effects of treatment combinations on manure ADF-N were tested using SAS PROC GLIMMIX (Gbur et al. 2012; SAS Intitute 2013). We considered ADF-N data as binomial and fit proportions of ADF-N to the model assuming a beta distribution with a logit link. LSMEANS from fitted models were used to test effects of treatment compound, concentration, and their interaction (Experiment 1) or the effects of treatment compound, added N, and their interaction (Experiment 2). Unless otherwise noted, post hoc multiple comparisons among treatment means were considered significant at $P \leq 0.05$ after adjustment with the Tukey–Kramer method. Additionally, Dunnett’s test was used to compare the proportion of ADF-N for each of the treatment combinations in each experiment to the proportion of ADF-N in H₂O-treatment used as the “control” in Experiment 1 or untreated manure in Experiment 2, to determine whether there had been a significant change in ADF-N from initial values in the manure. The LSMEANS (\pm standard error of the mean) produced by the mixed model analyses of ADF-N are expressed on an oven dry mass basis.

Results

Experiment 1

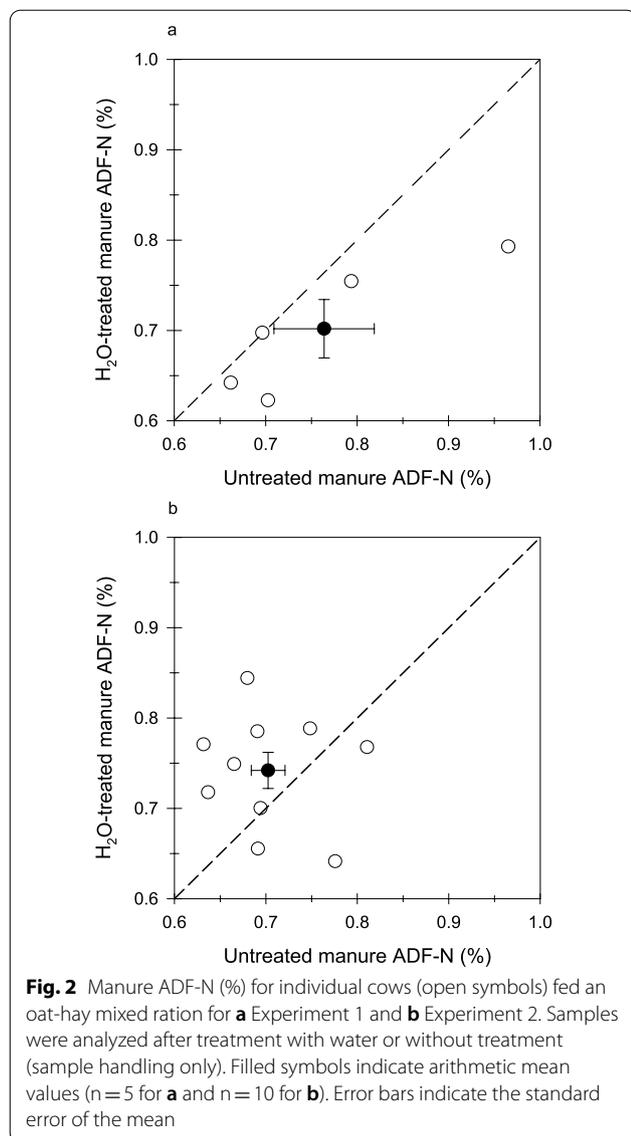
ADF-N demonstrated a significant ($P < 0.0001$) interaction between treatment and concentration. Main effects of treatment compound were observed at all concentrations (Fig. 1), but clear trends were not apparent across the different concentrations of each treatment. At the lowest treatment concentration (0.001 M), average



ADF-N, observed in samples treated with B0, was significantly greater than the value recorded for B1. Otherwise, treatments could not be statistically distinguished from each other. The treatment with 0.01 M solutions of AC and B3 resulted in the highest values of ADF-N, both significantly greater than the lowest value for B2. The difference between treatment means was more apparent at the 0.1 M concentration. Samples treated with AC or B1 were significantly higher than samples treated with B0, B2, or B3.

The effects of concentration also varied with treatment. Average ADF-N increased significantly together with concentration for B1. Conversely, ADF-N decreased with treatment concentration for B0, B2, and for B3. Significant effects of concentration were not observed for AB or AC.

Average ADF-N in water-treated manure (0.70 \pm 0.03%) appeared consistently less than in untreated manure (0.76 \pm 0.03%) (Fig. 2a, Dunnett’s t-test $P \leq 0.05$) suggesting some N that was present in the fiber of untreated manure, was being solubilized and removed with the four vigorous rinses after each treatment period. We therefore considered values from the samples treated with H₂O as a more appropriate baseline to account for any systematic errors introduced by post-treatment sample handling. Consequently, although significant effects of additions of different hydroxybenzoic acids and solution concentrations were detected by our analysis, we found little



meaningful distinction between the treatment means and samples treated with water using Dunnett's test. Only the highest concentration of gallic acid resulted in significantly *less* ADF-N than the water control. This, together with the unexpectedly high amount of variability observed in untreated manure ADF-N among individual cows (ranging from 0.66 to 0.96%), indicated that a more robust experiment (Experiment 2, below), employing more animals, longer exposure to treatment solutions, and less post-treatment sample handling was needed to improve detection of treatment effects.

Experiment 2

Initial manure composition, containing an average C and N of 48.1 and 2.1%, respectively, demonstrated little

variation among individual animals and yielded a C:N ratio of 22.9 ± 0.4 (Table 3). Concentrations of inorganic N (ammonium and nitrate) were negligible compared to total N, averaging 93 ± 7 and 12 ± 1 mg kg⁻¹, respectively. Manure averaged $40.2 \pm 0.9\%$ ADF that contained an average concentration of $0.70 \pm 0.02\%$ N. Thus, N in the ADF fraction of manure accounted for an average $0.28 \pm 0.01\%$ of manure dry weight or about 13% of the total N content of the manure.

We observed a strong main effect of treatment on ADF-N ($P < 0.0001$) but no statistically significant differences due to the added NH₄Cl ($P \geq 0.96$) or evidence of a meaningful interaction ($P > 0.14$) (Fig. 3). The lowest concentrations of ADF-N were recorded in the samples treated with water, B0 and B3, but intermediate values were recorded in those treated with B1, CAF, B2, CAT and *p*-COUM. The highest concentrations of ADF-N were observed in samples treated with EGCG and FER.

Unlike experiment 1, average ADF-N in untreated samples ($0.70 \pm 0.02\%$) appeared more comparable to samples treated with water ($0.73 \pm 0.03\%$) (Fig. 2b, Dunnett's $P > 0.07$) and was therefore appropriate for use as a baseline. When compared to initial values in the untreated manure, ADF-N was not significantly affected by the H₂O, B0 and B3 treatments (Fig. 3) but was significantly increased by all other treatments. Percentage increases in ADF-N varied from 13.2 to 17.5% for the B1, CAF and B2 treatments, while the solutions of CAT and *p*-COUM increased ADF-N by 19.7 and 22.2%, respectively. Treatment with EGCG or FER resulted in the greatest increase of ADF-N, 32.6 and 34.1%, respectively. The changes in ADF-N did not appear correlated to compound properties like pKa or K_{ow} (Table 2, Fig. 3). For example, the pKa for B0 and B3 were similar to that FER but lower than EGCG. Additionally, while the K_{ow} for B0 was higher than either EGCG or FER, the K_{ow} for B3 was lower.

Discussion

The composition of manure produced by the mixed ration (Table 3), was within the typical range of values for cattle (Van Kessel and Reeves 2002; Ward, 2018) and contained comparable concentrations of N as manure produced by a diet of alfalfa hay with twice as much crude protein (Halvorson et al. 2020). The concentration of manure ADF was close to values collected in a feedlot by Ward et al. (1978) of 39.7% but lower than values for dairy cows (Pennington et al. 2009).

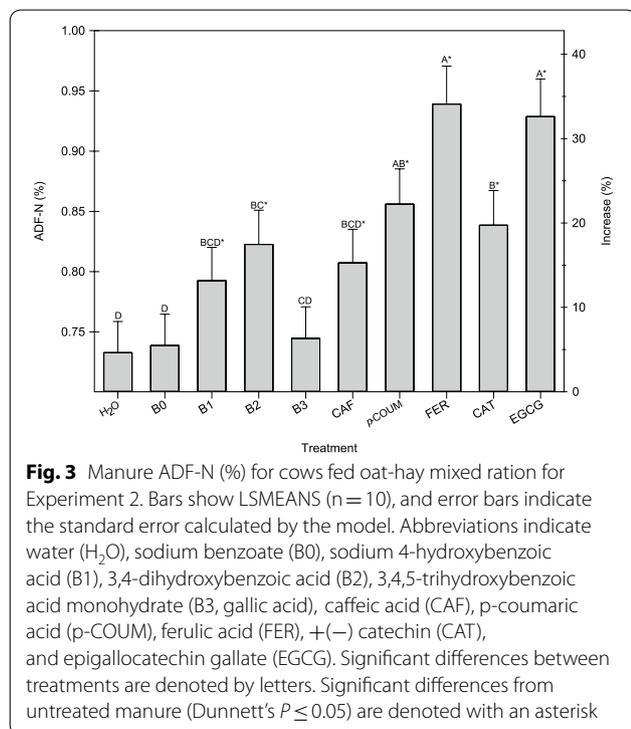
Although significant effects of additions of different hydroxybenzoic acids and solution concentrations were detected in Experiment 1, these results did not entirely support our hypothesis that solutions of benzoic and cinnamic acid derivatives would increase sorption of soluble N in manure to the insoluble ADF fraction.

Table 3 Manure composition^a from a mixed oat hay ration^b

Cow	pH _w	C _{tot} %	N _{tot}	N _{H2O}	ADF	ADF-N	N _{adf}	P ₂ O ₅	K ₂ O	S	Ca	Mg	Na	Zn mg kg ⁻¹	Fe	Mn	Cu	B
1	8.4	48.7	2.12	0.52	38.7	0.69	0.27	0.88	1.93	0.26	0.46	0.41	0.51	89.8	812.3	92.3	13.29	9.89
2	8.6	47.8	1.93	0.40	42.2	0.63	0.27	0.98	2.37	0.24	0.46	0.33	0.57	96.8	611.3	84.6	13.29	8.79
3	9.0	46.4	2.16	0.44	40.1	0.75	0.30	0.81	2.88	0.32	0.45	0.44	0.78	91.6	1178.2	107.6	14.50	12.31
4	6.1	48.6	2.24	0.36	33.0	0.78	0.26	1.18	1.33	0.23	0.47	0.45	0.21	90.0	515.1	89.9	13.73	7.14
5	7.8	48.7	2.13	0.44	39.4	0.69	0.27	0.75	1.29	0.24	0.51	0.41	0.37	69.7	906.4	105.5	12.64	8.79
6	8.1	49.1	2.04	0.43	41.9	0.68	0.29	0.58	0.88	0.22	0.39	0.37	0.51	142.2	706.0	119.1	16.70	7.69
7	8.3	47.4	2.08	0.52	39.9	0.69	0.28	0.91	1.65	0.26	0.40	0.42	0.78	113.8	715.5	103.2	14.94	10.22
8	8.3	48.9	2.10	0.53	41.9	0.67	0.28	0.80	1.47	0.24	0.48	0.41	0.46	67.4	476.6	88.7	12.53	8.90
9	8.8	46.4	2.26	0.56	41.5	0.81	0.34	0.55	1.82	0.23	0.39	0.33	0.45	82.0	1693.1	100.1	11.21	9.45
10	7.8	48.8	1.98	0.46	43.4	0.64	0.28	0.69	1.35	0.20	0.35	0.32	0.15	71.1	347.6	73.2	10.22	6.92
Avg.	8.1	48.08	2.11	0.47	40.2	0.70	0.28	0.81	1.70	0.25	0.44	0.39	0.48	91.4	796.2	96.4	13.3	9.00
SEM	0.3	0.3	0.03	0.02	0.9	0.02	0.01	0.06	0.18	0.01	0.02	0.02	0.07	7.2	124.5	4.2	0.6	0.51
CV%	10.0	2.1	5.0	13.6	7.3	8.3	8.1	23.0	34.4	13.2	11.9	12.2	43.0	24.9	49.3	13.7	13.9	17.7

^a pH_w: manure pH determined with H₂O; C_{tot}: Total C, (%); N_{tot}: Total N, (%); N_{H2O}: Water-extractable N (%); ADF: Acid detergent fiber (%); ADF-N: the concentration of nitrogen in ADF (%); N_{adf}: the product of ADF and ADF-N (%); P₂O₅: Phosphorus, (% P₂O₅); K₂O: Potassium, (% K₂O); S: Sulfur, (%); Ca: Calcium, (%); Mg: Magnesium, (%); Na: Sodium, (%); Zn: Zinc (ppm); Fe: Iron, (ppm); Mn: Manganese, (ppm); Cu: Copper, (ppm); B: Boron, (ppm). Values are corrected to a dry weight basis for manure dried at 55 °C for 72 h (9% moisture content). Mean and standard errors (SEM) are arithmetic

^b Animals (n = 10), fed collectively, were supplied with a mixed daily ration composed of 9.53 kg oat hay, 907 g of corn, and 907 g of peas, animal⁻¹ day⁻¹



Unexpectedly, the results revealed considerable variability in the concentration of manure ADF-N, even among animals fed the same ration. However, they also indicated manure ADF-N could be readily affected by some of the treatments.

The treatment effects on manure ADF-N observed were complex, and influenced by treatment compound, and concentration. The oat-hay ration resulted in manure in which ADF-N concentration was negatively related to the number of functional groups on hydroxybenzoic acids (compare B1-B3 in Fig. 1), but this pattern was observed only at the highest treatment concentration. At the lower concentrations, the relationship between ADF-N and OH functional groups did not show clear trends. Losses of some N from ADF with post treatment sample-handling suggests that it was not covalently held on the fiber but more likely linked by easily disrupted electrostatic interactions, hydrogen bonds or hydrophobic forces.

In Experiment 2, concentrations of ADF-N were significantly increased by all treatments except B0 and B3 indicating that most of the compounds immobilized some organic N species on manure fibers or perhaps acid insoluble ash. The lack of statistically significant change due to additions of ammonium chloride was somewhat surprising but in retrospect, the amount of N added to manure samples as NH₄Cl was very small (about 100 mg kg⁻¹ manure) compared to the relatively high concentration of N already present in the manure (2.11%, Table 3) and probably unlikely to be detected.

Mechanisms responsible for increased ADF-N due to solutions of phenolic compounds need further elucidation. No simple relationships were apparent between changes in ADF-N and compound pK_a or K_{ow} suggesting that N in manure does not form complexes with manure ADF by simple electrostatic or hydrophobic interactions.

We speculate that our observations might reasonably involve potential redox or binding effects associated with phenolic chemistry. Possible mechanisms could include ligand exchange, Coulombic forces, van der Waals forces, hydrophobic forces, hydrogen bonding, cation bridging, and chelation (Gmach et al. 2019; Philippe and Schumann 2014). Complexation and retention of dissolved organic matter is likely to be favored by the formation of bidentate complexes between two organic ligands in *ortho* position of an aromatic ring and a 2+ charge metal such as magnesium and calcium at the surface of oxides and hydroxides. Both are found lignocellulose-derived hydrophobic fractions and a feature of manure (Kaiser and Guggenberger 2000; Table 3; Philippe and Schumann 2014; Slabbert 1992).

Sorption of organic N by ADF constituents, observed in experiment 2, could have been partially induced by the relatively low pH of some of the treatment solutions and their effects on the degree of ionization of soluble amino-containing compounds in manure. Organic N accounted for the vast majority of the total N in manure and contains many amino-containing compounds (de Moura Zanine and de Jesus Ferreira 2015). The relatively low pH (<4) of B2, B3 *p*-COUM, CAF and FER treatment solutions could favor a protonated state for some amino groups on organic N and facilitate their sorption on the negatively charged sites. The surface charge of cellulose and lignin would be expected to be negative in an aqueous medium due to their characteristic carboxyl and hydroxyl groups (Ribitsch et al. 1996). However, the impact of a low treatment solution pH needed to induce a protonated state for amino acids may have been nullified by the pH of the manure that averaged 8.1 (Table 3). Further, solution pH cannot be invoked to explain the significant increases in ADF-N observed for the B1 and CAT or EGCG, treatments with relatively high solution pH. Of those only EGCG, a tannin, would be expected to form complexes with proteins or other nitrogenous compounds (Adamczyk et al. 2011; Hagerman 2012) that might sorb to ADF.

Experiment 2 supports a hypothesis that organic N in excreted manure can complex with the cellulose, lignin or ash that comprises ADF upon exposure to benzoic and especially cinnamic acid derivatives. However, the exact nature of these complexes will be influenced by the concentration and composition of nitrogen in the manure and the phenolic compounds themselves, the reaction conditions such as temperature or pH, and characteristics of the ADF that might vary with diet or with the individual animal. Similarly, crop residues or organic matter may interact directly with simple phenolic compounds in the soil and undergo reactions that could influence nutrient cycling. Mineralization kinetics of manure nutrients

may be impacted by increasing or decreasing the amount of N bound to manure fibers. Therefore, we recommend further studies to learn if such complexed N is, at least temporarily, sequestered and thus less available to plants, for microbial mineralization, volatilization or leaching.

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Authors' contributions

JJH initiated and conducted the experiment, analyzed the data, and took the lead on drafting the manuscript. SLK made substantial contributions to animal care, acquisition and handling of manure samples, and interpretation of the data. RGC provided expertise and analysis of phenolic compound effects on ruminant physiology and contributed to manuscript architecture. AEH provided key contributions to experimental conceptualization and design and interpretation of phenolic acid chemistry. DWA provided overall project leadership, logistical support, and interpretation of agroecosystem implications of the data. All authors made substantive contributions to initial drafts, subsequently revised later versions of the manuscript, and approved the submitted version. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets during and/or analyzed during the current study available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Manure used in this study originated from beef cattle in the resident herd at the Northern Great Plains Research Laboratory in Mandan, ND. The protocols for animal care and procurement of manure were approved by the animal care and use committee of the Northern Great Plains Research Laboratory in Mandan, North Dakota following procedures for management of livestock being bred, conditioned or held at the Northern Great Plains Research Laboratory but not used in research. Standards in the Federation of Animal Science Societies' Guide (3rd edition) for the Care and Use of Agricultural Animals in Research and Teaching were followed.

Consent for publication

Not Applicable.

Competing interests

The authors declare that they have no competing interests.

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