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Conserving Toxic Ammoniacal Nitrogen in Manure Using Natural Zeolite Tuff: A Comparative Study

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An accumulation of huge amount of animal solid and liquid waste poses serious problems to health of human beings and beasts alike and is the source of pollution of nearby streams and rivers. In addition, the large amount of undigested protein remaining in the excrement represents a valuable resource that for the most part is being wasted, due to our growing dependence on chemical fertilizers. To realize the magnitude of the problem, in the united states for example, approximately one billion metric tons of solid waste and nearly 400,000,000 tons of liquid waste are produced each year (Van Dyne and Gilbertson 1978).

Ammonical nitrogen can represent 40 to 60% of the total nitrogen in fresh livestock manure (Bouldin and Klauser 1981). Within hours after excretion N can be converted to free ammonia and then is subjected to loss and volatilization. During the early part of the twentyth century typical practice was to add gypsum, superphosphate, phosphoric acid and Kainite to freshly excreted manure or to apply these materials on the land at the time of manure application (Safley et. al. 1983). Benefit was realized from the increase of ammonia conservation.

The physical and chemical properties of many natural zeolites lend themselves to a wide variety of applications in the treatment of animal wastes, including the reduction of malodor and associated pollution, the creation of healthier environment for confined livestock, and control of viscosity and nutrient retentivity of the manure (Mumpton and Fishman, 1977; Miner 1984).

Febles et al., (1991) reported that natural zeolite mixed with bovine or swine waste reduced NH_4-N losses during composting and land application of zeolite treated-swine manure.

Andrew et al. (1993) reported that natural zeolite (clinoptilolite) can potentially capture ammonical nitrogen from mixed or liquid wastes, changing liquid-phase N to solid-phase N, thereby improving compost C:N ratios, and reducing ammonia losses and compost malodor.

Deposits of phillipsite zeolitic tuffs were discovered in Aritain area, northeast

Jordan by the author in 1984. These zeolitic tuffs were evaluated for their possible industrial uses and for ammonium heavy metals ions removal from wastewater (Dwairi 1992 and Dwairi 1993)

MATERIALS AND METHODS

A series of experiments were carried out to determine the effect of addition of chemicals and natural zeolite to manure in attempt to conserve ammonia. Jordanian natural phillipsitic tuff was used for this purpose, while, gypsum, superphosphate and phosphoric acid were chosen for the experiments to compare the results with the natural phillipsitic tuff.

The zeolitic tuff used were obtained from Aritain area, northeast Jordan. The mineralogy, chemical composition and other technical properties of this zeolitic tuff are discussed by the author elsewhere (Dwairi, 1987; Dwairi 1992;Dwairi 1993). The zeolitic tuff consists of phillipsite as the major zeolite mineral, calcite, olivine, and smectite clay. The zeolitic tuff samples were prepared by crushing and the samples to minus 2.0 mm, then washing the sample till free from Na, and other soluble salts. The sample were air died for 48 hours before use.

Gypsum used was certified grade of 99% pure

$CaH_4(PO_4)_3.H_2O$ purified grade of 99% pure

H_3PO_4 used is certified grade of 85.2% pure

The cation exchange capacity of the zeolitic tuff was determined according to Mercer and Ames (1978).

Dairy cattle manure was obtained in urine and feces components from lactating manure Holstein cows at the Nusair Dairy Farm Irbid, Jordan. The animals were being fed a typical corn silage-based ration.

A slurry was prepared by mixing the urine and feces collected at a feces \ urine weight ratio of 2.2 (ASAE 1982). Analysis of the mixture showed the following initial concentrations (wet basis)

Total Kjeldahl Nitrogen (TKN)	6890 mg/kg
Ammonia Nitrogen (NH_3^+-N)	2006 mg/kg
Total phosphorus (TP)	1050 mg/kg
Total Solids (TS)	14.7%

A randomized complete block experimental design with three replications was used. There were thirteen treatments (Table 1). One was a check that received no zeolitic tuff or chemical addition. The remaining nine were three treatments for each of the four zeolitic tuff and chemicals at levels of 100%, 150% and 200% of the cation exchange capacity of the zeolitic tuffs and the active ingredients of the chemicals needed to completely react with the ammonia present in the manure slurry. For the purpose of this experiment all the ammonia in the manure was considered to be in a free state (NH_3+NH_4^+). The Following equation was used to determine the amount of zeolitic tuff and chemical to be added to a given amount of manure.

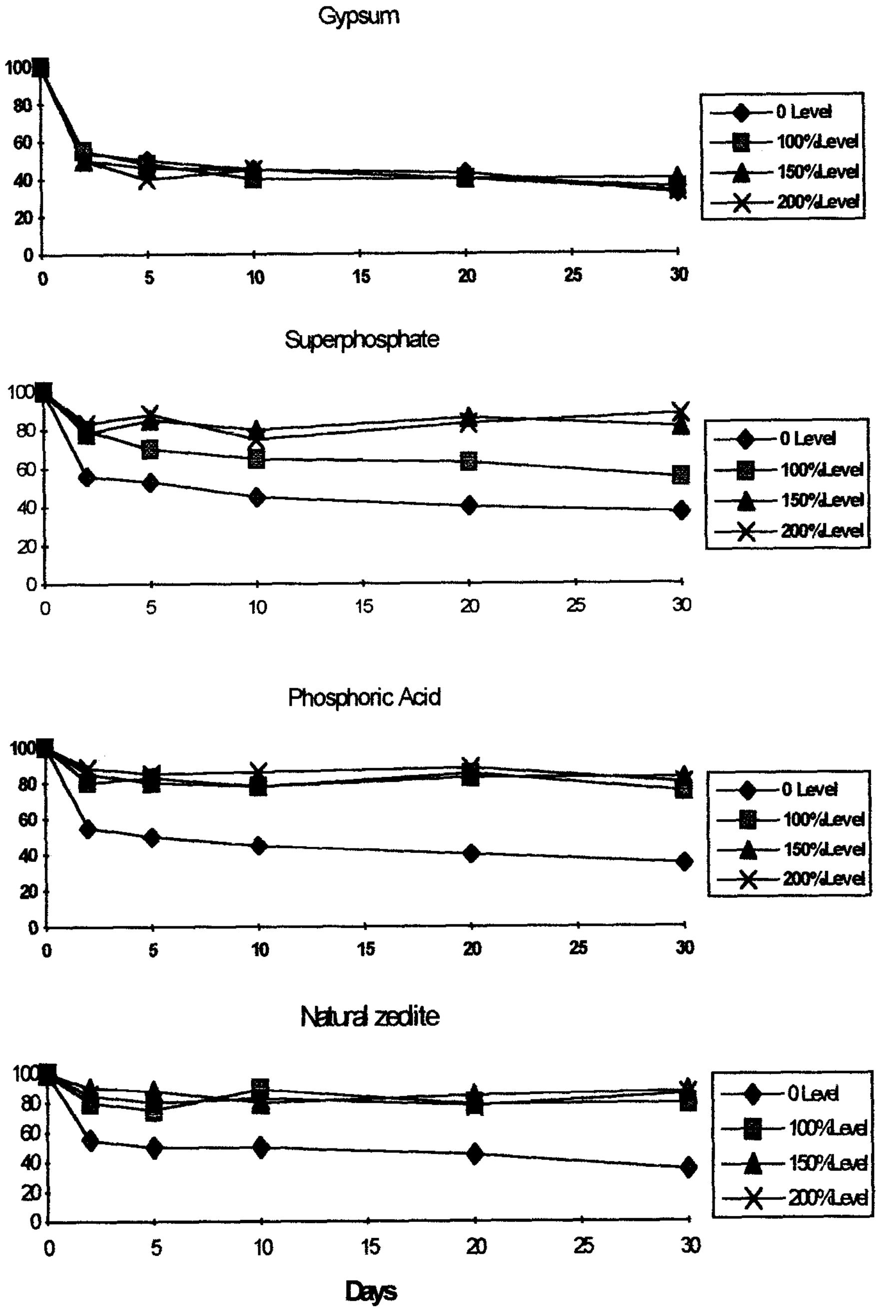
Amnt = M x NH_3-N x RATE X LEVEL/ PURITY
where
Amnt = amount of zeolitic tuff or chemical to add to manure mixture, g
M = a mount of manure, g
NH_3- = ammonia concentration, g NH_3-N/10^6g manure
RATE = rate of addition of zeolite or chemical to completely react with ammonia, g active ingredient/g NH_3-N, 100% level (Table 1)
LEVEL = proportion of zeolitic tuff or chemical added to what is theoretically needed (percentage)
PURITY = percentage of active ingredient in zeolitic tuff (taken form the percentage of zeolite minerals and their cation exchange capacity) or host chemical

The natural zeolite and chemicals were blended into 12 subsamples of fresh manure. Then small amounts of the resulting mixtures (50 to 150 g) were placed in 18 mm x 18 mm x 2 mm deep plastic trays. Eighteen trays for each of the ten treatments were prepared. The trays were then randomly placed in an open cabinet located under a fume hood and allowed to air dry simulating surface application. An elapsed times of 0,2,5,10,20, and 30 days were used, then three samples from each treatment were removed. The contents of the three trays of the same treatment were combined into a homogenous mixture and a subsample was then analyzed for TKN and NH_3-N (Safley 1983) using standard techniques (Standard Methods 1971). The total solids were also determined (Standard Methods 1971). The amount of TKN and NH_3-N remaining at each sample date were computed on dry weight basis.

RESULTS AND DISCUSSION

Fig 1 shows the amount of TKN remaining with time using zeolitic tuff, gypsum, superphophate and phosphoric acid at the three levels tested compared to the treatment receiving no addition, Fig (2) shows similar information for NH_3^+-N. From these figures it is evident that gypsum has the least effect in conservation of ammonia in the manure, while natural zeolite has the highest effect followed by superphosphate and phosphoric acid. Accordingly, natural zeolite, phosphoric acid and superphospate are beneficial in reducing nitrogen loss from manure. It is important to mention that ammonia could be generated with time in the manure by decomposition of the organic matter, and that the mean solids content of the manure in all experiments carried out on day 30 was 91%. Therefore, the remaining nitrogen had been greatly concentrated in these treatments.

The results of the this experiment showed that 95.3% of the ammonia was lost from the manure after 30 days in the control tests (no zeolite or chemicals were added). Similar results for ammonia loss from cattle manure was reported by



Gypsum

Superphosphate

Phosphoric Acid

Natural zeolite

Figure 1. Nitrogen conservation in manure after addition of natural zeolite and chemicals.

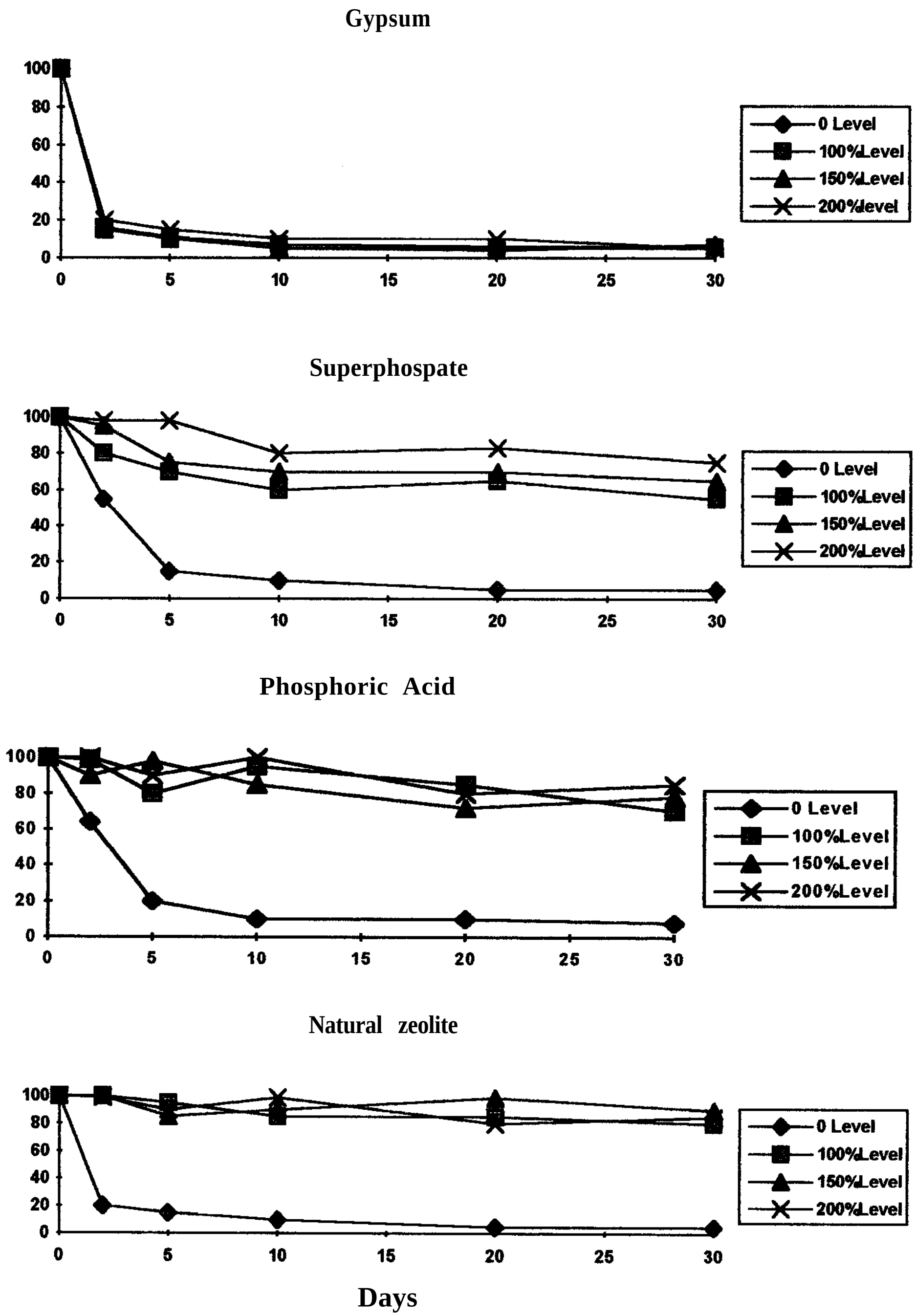


Figure 2. Ammonia conservation in manure after addition of natural zeolite and chemicals

Table 1. Manure/Chemical or natural zeolite treatments used

Treatmee no.	Material Added	Rate added % of that needed to theoretically react with NH4+ (%)	Gram active ingredient /g NH_3-N in manure
1	None	---	--
2	Gypsum[1]	100	2.5
3	Gypsum	150	3.8
4	Gypsum	200	5.1
5	Superphosphate[2]	100	14.8
6	Superphosphate	150	22.2
7	Superphosphate	200	29.6
8	Phosphoric acid[3]	100	5.8
9	phosphoric acid	150	8.6
10	phosphoric acid	200	11.5
11	Natural zeolite[4]	100	33
12	Natural zeolite	150	49.5
13	Natural zeolite	200	66

1 = $CaSO_4.2H_2O$ - Certified grade (99% pure). 2 = $CaH_4(PO_4)2.H_2O$ - Purified grade(99% pure). 3 = H_3PO_4- Certified grade (85.2% pure). 4 = Natural phillipsitic tuff collected from Aritain Area, Jordan

Table 2. Nitrogen recovery from chemicals and natural zeolite additions to manure

Treatment No.	Material added	Level added (%)	TKN remaining after 30 days (%)	Value of * TKN remaining ($/t)	Cost of**materials used ($/t)	Net value ($/t)
1	none	Non	40.3	2.02	-	2.02
2	Gypsum	100	49.5	2.48	0.19	2.29
3	Gypsum	150	48.4	2.42	0.28	2.14
4	Gypsum	200	47.3	2.37	0.38	1.99
5	Superphosphate	100	52.2	2.61	14.38	-11.77
6	Superphosphate	150	61.3	3.07	21.57	-18.50
7	Superphosphate	200	67.3	3.37	28.76	-25.40
8	Phosphoric acid	100	57.9	2.90	6.43	-3.53
9	Phosphoric acid	150	62.5	3.13	9.64	-6.51
10	Phosphoric acid	200	64.3	3.22	12.86	-9.64
11	Natural zeolite	100	57.8	2.89	2.16	0.73
12	Natural zeolite	150	61.3	3.07	3.24	-0.17
13	Natural zeolite	200	65..7	3.29	4.32	-1.03

* Value of TKN remaining based on fresh manure TKN concentration. $0.71/Kg of N as $NH_4N\ O_3$ _ * * 1992 Prices for chemicals and natural zeolite

	Gypsum	Triplsuperphospate	phosphoric acid	Natural zeolite
Price ($1kg)	0.03	0.2781	0.2830	0.031
Purity (%)	85	60	53	55

other workers. A 92.7% of ammonia loss was obtained by Midgley and Weiser (1937) and a loss of 93.7% was reported by Safley et. al. (1983).

The results of ammonia conservation (remaining) in the manure using phosphoric acid and superphosphate at 100% rate and after 30 days was 62% and 43% respectively. These results are comparable to results (57.0% and 31%) obtained by Safley et. al. (1983). In comparison, natural zeolite conserved 61% of ammonia at the same rate and period of treatment. This indicates that Jordanian phillipsitic tuff natural material is as effective in ammonia conservation in the manure as phosphoric acid and better agent than superphosphate. The ability of this natural zeolite to conserve ammonia in the manure at different rates of 150% and 200% gave nearly similar results to phosphoric acid addition (Fig. 2).

One of the major consideration on adding chemicals or natural zeolite to manure to conserve nitrogen is cost. Table (2) lists and compares the relative amount of NH_3-N conserved, the cost of the materials added and the value of the nitrogen remained in the manure.

Based on the results of this study the addition of phosphoric and superphosphate is not cost effective, while the addition of natural zeolite especially at 100% level proved to be cost effective in conservation of ammonia in the manure. In addition, natural zeolite is able to work as a slow release for ammonia in the soil for a longer time (Miner 1984 and Dwairi 1997). This advantage would increase the value of the manure treated with natural zeolite.

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