Efficacy of Alum and Coal Combustion By-Products in Stabilizing Manure Phosphorus

Z. Dou,* G. Y. Zhang, W. L. Stout, J. D. Toth, and J. D. Ferguson

ABSTRACT

Animal manures contain large amounts of soluble phosphorus (P), which is prone to runoff losses when manure is surface-applied. Here we report the efficacy of alum and three coal combustion by-products in reducing P solubility when added to dairy, swine, or broiler litter manures in a laboratory incubation study. Compared with unamended controls, alum effectively reduced readily soluble P, determined in water extracts of moist manure samples with 1 h of shaking, for all three manures. The reduction ranged from 80 to 99% at treatment rates of 100 to 250 g alum kg^{-1} manure dry matter. The fluidized bed combustion fly ash (FBC) reduced readily soluble P by 50 to 60% at a rate of 400 g kg^{-1} for all three manures. Flue gas desulfurization by-product (FGD) reduced readily soluble P by nearly 80% when added to swine manure and broiler litter at 150 and 250 g kg^{-1}. Another by-product, anthracite refuse fly ash (ANT), was ineffective for all three manures. In all cases, reduction in readily soluble P is primarily associated with inorganic phosphorus (P$_i$) with little change in organic phosphorus (P$_o$). Sequential extraction results indicate that the by-product treatments shifted manure P from H$_2$O-P into a less vulnerable fraction, NaHCO$_3$–P, while the alum treatment shifted the P into even more stable forms, mostly NaOH-P. Such shifts in P fractions would have little influence on P availability for crops over the long term but would retard and reduce potential losses of P following manure applications.

IN MANY AREAS with intensive animal farming, long-term manure applications to agricultural land have resulted in soil P buildup to levels far exceeding agronomic optimum ranges (Sims, 2000). These high-P soils are often associated with elevated P losses in surface runoff, subsurface drainage, or erosion, as has been demonstrated repeatedly (Sims et al., 1998; Sharpley et al., 1994). As a result, increasing regulatory pressure is being placed on animal agriculture to improve management of N and P in animal manure to reduce nutrient loadings to the environment.

On animal farms under given conditions (soil characteristics, transport factors, etc.), freshly applied manure, especially if surface-spread without incorporation, may function as a major source for P enrichment in runoff waters. Preedy et al. (2001) reported a surge of P export in overland and subsurface drainage waters from grassland receiving dairy slurry or P fertilizer applications. Compared with the control, dairy slurry treatment of 29 kg P ha^{-1} resulted in a 37-fold increase in P loss within 32 h after the application. In a watershed-scale study, Sharpley et al. (2001) demonstrated that fields receiving manure or fertilizer within 3 wk before rainfall were much more vulnerable to P loss than fields receiving zero P application during the previous 6 mo. Where fertilizer or manure was applied within 3 wk of the simulated rainfall events, dissolved and total P in runoff was not related to Mehlich-3 soil P, but increased with increasing rates of P applications (Sharpley et al., 2001).

Phosphorus concentrations in animal manures typically are many times greater than in soils. For example, on a dry matter basis total P concentrations ranged from 4 to 7 g kg^{-1} in dairy manures and 7 to 30 g kg^{-1} in poultry manures (Barnett, 1994), compared with 0.3 to 2.4 g total P kg^{-1} in 23 surface soils (0–5 cm) receiving long-term manure applications (Sharpley, 1996). More critically, much of the P in manure is water soluble. Dou et al. (2000a,b; 2002) found that P concentrations in water extracts of manure samples with 1 h of shaking ranged from 2 to 11 g total phosphorus (P$_t$) kg^{-1} manure dry matter. In comparison, the 23 surface soils receiving long-term manure applications tested by Sharpley (1996) had labile P (extracted in bicarbonate solution) concentrations less than 0.5 g kg^{-1}. Clearly, it is imperative to carefully manage manures when surface-applied to prevent the large amount of soluble P contained in manures from being dissolved and carried to streams through runoff.

Perhaps, reducing the solubility of manure P *before* field application can provide an effective source control measure. A number of manure treatments based on chemistry principles have been investigated, one of which is alum (aluminum sulfate). Alum, when added to animal manure, stabilizes manure P through the formation of aluminum phosphate or other Al–P binding mechanisms (Moore and Miller, 1994; Cooke et al., 1986). Substantial reduction in water-soluble P has been reported when alum was added to poultry manure (Moore and Miller, 1994; Moore et al., 2000). Phosphorus in runoff water from field plots receiving alum-treated poultry litter was reduced by 87% compared with the control plots receiving untreated poultry litter (Shreve et al., 1995).

Recent studies also tested coal combustion power plant by-products as manure amendments for reducing soluble P and decreasing its potential loss. Through laboratory incubations, Dao (1999) amended feedlot manure or composted manure with Class C fly ash materials and obtained an 85 to 93% decrease in water-soluble P compared with untreated manure samples. When the fly ash–treated manure was mixed with soils, soil extractable P was reduced substantially. In another study, El-rashidi et al. (1999) packed leaching columns with dairy

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manure atop fluidized bed combustion fly ash (FBC) material. Water was added and leachate was collected weekly for 10 wk. Phosphorus in the leachate was reduced by more than 80% compared with the control containing dairy manure alone. Presumably, reduction of soluble P in manure treated by FBC or similar fly ash may be attributed to chemical precipitation and surface retention.

Coal-burning power plant by-products have long been introduced into agricultural systems as soil amendments with demonstrated agronomic benefits such as reduced subsoil acidity and improved root growth and crop yields (Stout et al., 1979; Stehouwer et al., 1999). In a more recent study addressing environmental concerns, Stout et al. (1998) amended several high-P soils with FBC or flue gas desulfurization by-product (FGD). The by-products reduced water-soluble P in the amended soils by 45 to 72% compared with untreated soils. The reduction was attributed to the conversion of readily desorbable soil P, measured in water extracts, into less soluble forms.

Byproducts FBC and FGD are generated at coal-burning power plants where limestone ($CaCO_3$) is used to remove SO_2 from the flue gas. These by-products are often mixtures of coal ash, anhydrite, and limestone residues with alkaline components in the form of carbonates, hydroxides, and oxides (Stehouwer et al., 1999). Adoption of SO_2 removing methods is required by the USEPA to conform to the Clean Air Act and would generate more than 50 Tg of by-products on an annual basis (USEPA, 1988). This vast amount of by-products, if tested successfully, may be used as manure amendments for agronomic and environmental benefits.

The primary purpose of this study was to investigate the efficacy of alum and three by-products of coal combustion power plants for reducing P solubility when amended to dairy, swine, or broiler litter manures through laboratory incubation. Changes in P fraction distributions in manure resulting from the various treatments were also studied.

MATERIALS AND METHODS

Manure Samples and Treatments

Dairy manure was obtained from lactating cows at a commercial operation, and swine manure was from gilts at a university research facility. Freshly excreted dairy or swine manure, along with small amounts of sawdust or straw bedding, was scraped from the barn floor and grab samples were taken from the manure pile. Broiler litter manure was obtained from a local commercial operation at the end of a production cycle. Multiple grab samples, including crust and base sawdust bedding, were collected and composited. The composite broiler sample was sieved in the laboratory to pass a 4.75-mm screen to improve uniformity. All bulk manures were homogenized in the laboratory by stirring before splitting into subsamples for treatments. Manure dry matter content was determined on homogenized subsamples by drying in a convection oven at 60°C. Homogenized subsamples were also used to determine total P in microwave-assisted acid digests (Walter et al., 1997), analyzed by the phosphomolybdate blue method of Murphy and Riley (1962).

Table 1. Selected characteristics of chemical amendments and manure samples.

Characteristic	Alum	ANT†	FBC†	FGD†
pH‡	2.24	13.02	13.00	7.87
Dry matter, g kg^{-1}	986	999	997	779
		mg kg^{-1} dry matter		
Ca		50 300	160 800	272 100
K		33 800	1 700	6 500
Mg		400	13 700	900
P		510	660	540
B		46	691	61
Fe		900	9 800	400
Zn		1 200	1 800	1 300
Al		2 200	4 700	–
Ni		115.9	126.2	108.0
Mo		70.1	58.1	41.5
Cu		13.3	47.3	22.4
As		83.4	48.1	48.2
Cd		7.5	7.5	–
Mn		–	–	–
Pb		–	–	13.2
Se		80.9	177.6	218.4

† ANT, anthracite refuse fly ash; FBC, fluidized bed combustion fly ash; FGD, flue gas desulfurization by-product.
‡ Determined with 1:1 solid–water mixture.

Chemical amendments included technical-grade alum [$Al_2(SO_4)_3 \cdot 14H_2O$] and coal-combustion power plant by-products FBC, FGD, and anthracite refuse fly ash (ANT). Chemical and physical characteristics of the amendments are presented in Table 1. Preliminary trials were conducted using dairy manure to determine effective amendment rates and incubation time. A basic consideration for selecting the range of treatment rate was to achieve a sizable reduction in water-soluble P while avoiding excessive use of amendment. The final rates were set as following: alum at 25, 50, 100, and 250 g kg^{-1} manure (dry matter basis); FBC at 50, 100, 200, and 400 g kg^{-1}; and FGD at 50, 100, 150, and 250 g kg^{-1}. The ANT fly ash material was obtained at a later stage of the study, and its rates were arbitrarily set at 25, 50, 100, and 250 g kg^{-1} (same rates as alum). In terms of incubation time, Dao (1999) reported little difference in soluble P reduction when manure was amended with Class C fly ash and incubated for 1, 3, or 6 wk. We tested 3, 5, and 7 d of incubation and found little time difference in water-soluble P reduction. The full-scale investigation was performed with 3 d of incubation.

The dairy and swine manures for amendment were freshly collected "as-is" samples. The much drier broiler litter was moistened with deionized water to enhance P-stabilizing reactions. The amended broiler litter samples had a moisture content of 42% after the adjustment, instead of 28% as in the original samples. Moore and Miller (1994) also increased the moisture content of poultry litter in their trial of alum treatments. In the present study, each treatment consisted of triplicate samples of 20 g dry matter equivalent manure per sample. The manures were weighed into plastic beakers, amendments were added and the mixtures stirred, and the beakers were then covered with plastic film to retard evaporation losses. During the 3-d incubation (at ambient temperature around 25°C), the content in the beakers was stirred manually twice daily. Untreated control manure samples were handled in the same manner.

Laboratory Analyses

At the completion of incubation, subsamples of treated and untreated moist samples were processed immediately for the determination of pH and readily soluble P. Moist samples of 2 g each were weighed into plastic tubes, capped, and shaken in 98 mL deionized H_2O for 1 h on a reciprocal shaker and

filtered through Whatman (Maidstone, UK) 42 paper. Aliquots of the filtrates were analyzed for pH using a glass electrode, inorganic phosphorus (P_i) by the phosphomolybdate blue method (Murphy and Riley, 1962), and P_t by inductively coupled plasma (ICP) spectrometry. Concentrations of organic phosphorus (P_o) in filtrates were calculated as the differences between P_t and P_i. Additionally, aliquots of filtrates were used to determine ammoniacal N concentrations using the indophenol blue method (Keeney and Nelson, 1982).

The remaining treated and untreated samples were oven-dried at 60°C and ground to pass a 2-mm sieve. Samples of selected treatments, including control, alum at 100 g kg^{-1}, FBC at 400 g kg^{-1}, and FGD at 250 g kg^{-1}, were tested for P fraction distributions. These samples were extracted through a rigorous sequential extraction procedure described by Dou et al. (2000a), which was adapted from a soil P fractionation scheme (Hedley et al., 1982). Briefly, this procedure involves extracting 0.30-g, dried, ground samples with deionized H_2O, 0.5 M NaHCO$_3$, 0.1 M NaOH, and 1 M HCl solutions, in that order. Repeated 1-h shaking and filtering is performed with each extractant (30 mL) until the P in the last filtrate is negligible before proceeding to the next extractant. Individual filtrates were analyzed for concentrations of P_i and P_t. The sums of P in the relevant extracting solutions are referred to as H_2O-P, NaHCO$_3$–P, NaOH-P, and HCl-P fractions, respectively. Phosphorus in residues at the completion of the sequential extractions was estimated by subtracting the sum of P in the four fractions from acid digest total P of the manure samples. It is apparent that P extracted in H_2O, NaHCO$_3$, NaOH, and HCl in that order is increasingly stable, or decreasingly susceptible to potential environmental loss.

Analysis of variance and mean separation by Duncan's New Multiple Range Test ($P = 0.05$) were performed using the General Linear Models procedure (SAS Institute, 1999). All results were reported as treatment means and based on manure dry matter after adjusting for the amount of amendment added. Where appropriate, standard errors were reported to illustrate variability about the means.

RESULTS AND DISCUSSION

Baseline Information on Untreated Manures

The raw manures contained dry matter of 155, 174, and 720 g kg^{-1} and acid digest total P of 7.86, 27.13, and 18.20 g kg^{-1} for the dairy, swine, and broiler litter manures, respectively. These data are comparable with relevant book values such as those listed in American Society of Agricultural Engineers (1993) and MidWest Plan Service (1993).

At the completion of incubation, the untreated control samples had readily soluble P concentrations averaging 3.06, 5.65, and 2.81 g P_t kg^{-1} for the dairy, swine, and broiler samples, respectively. These accounted for 39, 21, and 15% of the acid digest total P of the manures. Also, 85 to 91% of the readily soluble P was inorganic P. That water extracts of manure samples contain much higher P_i than P_o is consistent with our previous findings using manures from various sources (Dou et al., 2000a; 2002).

Sequential extraction results for the untreated control samples revealed some differences in P fraction distribution between manure types (Fig. 1). The H_2O-P fraction dominated the dairy samples with a distribution pattern of 70% H_2O-P, 16% NaHCO$_3$–P, 4% NaOH-P, and 3% HCl-P, plus 6% in residues. This pattern is consistent
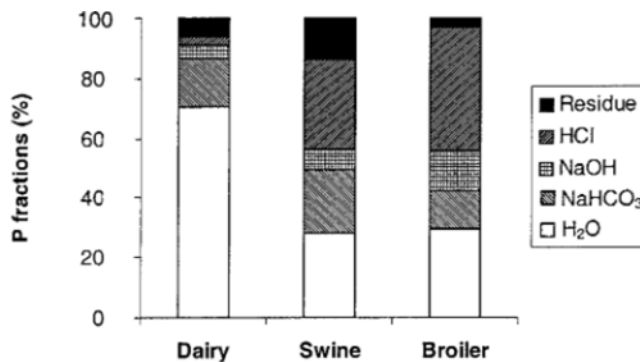

Fig. 1. Phosphorus fraction distributions in untreated dairy, swine, and broiler control samples.

with our previous findings using various manures (Dou et al., 2000a; 2002). However, for the swine and broiler samples, although the amount of cumulative water-extractable P was considerable (7.61 g P_t kg^{-1} for swine and 5.37 g P_t kg^{-1} for the broiler), H_2O-P as a fraction was no longer dominating. The fraction distribution was 28% H_2O-P, 21% NaHCO$_3$–P, 7% NaOH-P, and 30% HCl-P, plus 14% in residues for the swine, and 30, 13, 13, 41, and 3% for the broiler litter, respectively. Also, the NaOH-P and HCl-P fractions of the swine and broiler samples consisted of more P_o than P_i, which is contrary to the dairy samples (detailed data not presented).

Many factors can affect the solubility and fraction distribution of P in manures, such as animal species, growth stage, production level, and diet ingredients. A detailed discussion of the factors is beyond the scope of this study. Additionally, pH is an important factor affecting P solubility in general, and may have played a key role in the current study. Lower pH generally favors the dissolution of phosphate compounds (Lindsay, 1979). The untreated dairy manure had a pH of 6.01 while the swine and broiler samples had pH values of 8.07 and 8.74 (Table 2). This may partially explain why H_2O-P is the dominating fraction in the dairy but not in the swine and broiler samples.

Treatment Effects

Change in pH

Treatment effects on pH varied according to the type of manures and treatments (Table 2). For the dairy manure, alum lowered the pH whereas the three by-products raised pH. For the broiler samples, pH decreased steadily with increasing alum rates; FGD treatments decreased the pH slightly but consistently, whereas FBC and ANT had little effect. The swine manure appeared to have considerable buffering capacity with little pH change regardless of treatments. In general, pH changes were fairly small with the majority not exceeding one unit as compared with the untreated control samples.

Limited pH change may help explain why there seems to be a lack of, or inconsistent, treatment effects on the ammoniacal N concentrations measured in water extracts of moist samples with 1 h of shaking (Table 2).

Table 2. Treatment effect on pH and NH$_4$–N in water extracts of amended manures (moist sample, 1 h of shaking). Data presented are treatment means (g kg^{-1} manure dry matter).

Treatment†	Rate	Dairy		Swine		Broiler	
		pH	NH$_4$–N	pH	NH$_4$–N	pH	NH$_4$–N
	g kg^{-1}		g kg^{-1}		g kg^{-1}		g kg^{-1}
Alum	0	6.01a‡	0.71a	8.07a	14.0a	8.74a	4.32a
	25	6.71a	0.59b	8.02a	14.1a	8.32b	4.18a
	50	5.93a	0.63ab	8.21a	13.2a	7.85c	4.15a
	100	5.96a	0.81ab	8.12a	14.5a	7.18d	4.57a
	250	5.16b	0.85a	7.69a	16.5b	5.30e	5.92b
ANT	0	6.01a	0.71a	8.07a	14.0abc	8.74a	4.32a
	25	6.95b	0.47a	8.33a	13.7bc	8.68a	4.43a
	50	7.07b	0.56a	7.82a	15.0ab	8.65a	4.56a
	100	7.21b	0.54a	7.81a	15.3a	8.76a	4.34a
	250	7.01b	0.63a	8.00a	13.0c	8.62a	5.50b
FBC	0	6.01a	0.71a	8.07a	14.0a	8.74a	4.32a
	50	6.14a	0.76a	7.99a	14.0a	8.65ab	4.49a
	100	6.58ab	0.70a	8.05a	14.0a	8.68ab	4.73a
	200	7.31b	0.70a	8.27a	16.9b	8.55bc	4.84a
	400	7.05b	0.85a	8.46a	16.8b	8.40c	4.81a
FGD	0	6.01a	0.71a	8.07a	14.0a	8.74a	4.32a
	50	7.24b	0.60a	7.97a	16.2b	8.19b	4.73a
	100	7.04bc	0.61a	7.87a	14.6a	8.02b	4.63a
	150	6.85c	0.76a	6.80a	14.0a	7.70c	4.78a
	250	6.88c	0.75a	7.50a	18.1c	7.61c	5.55b

† ANT, anthracite refuse fly ash; FBC, fluidized bed combustion fly ash; FGD, flue gas desulfurization by-product.
‡ Different letters within the same manure type $\times$ amendment combination indicate significant differences (= 0.05) using Duncan's New Multiple Range Test.

Moore et al. (2000) reported significant decreases in ammonia volatilization loss (i.e., increases in ammoniacal N in manure) in alum-treated poultry litter; their findings were coupled with substantial decreases in pH with alum treatments. On the other hand, Dao (1999) recorded no treatment effect on total Kjeldahl nitrogen (TKN) when beef feedlot manure or manure compost was treated with alum or fly ash, despite considerable changes in pH (up to 3 units). Dao explained that the manure samples possibly contained little ammoniacal N to begin with, due to volatilization losses before sample collection, while manure organic N is relatively stable and would not be affected by the amendments or pH change. In the present study, the ammoniacal N of the untreated control samples appeared to be considerably lower than published book values (American Society of Agricultural Engineers, 1993). We do not know if substantial volatilization loss occurred during the time period from farm sample collection to post-incubation analyses. But for the dairy samples (control or treated) with very low ammoniacal N concentrations, substantial volatilization loss is unlikely given the low pH. It is possible that the dairy sample, collected fresh from the floor of a free stall barn, consisted of mainly fecal material with little urine. Nitrogen in dairy feces is primarily organic and relatively stable.

Reduction in Readily Soluble Phosphorus

There was a general trend of decreasing readily soluble P with increasing treatment rates (Fig. 2). Also illustrated in Fig. 2 is that decrease in readily soluble P is primarily associated with P$_i$, whereas changes in P$_o$ are small and inconsistent. The latter might be attributed to the low P$_o$ concentrations in water extracts, coupled with a relatively large variation since P$_o$ values were calculated (P$_t$ − P$_i$) instead of direct measurements.

Alum effectively reduced readily soluble P (mainly P$_i$) for all three manures (Fig. 2a). The dairy and broiler samples had almost identical responses to the increasing alum rates, whereas the swine manure was somewhat less responsive at the lower rates. This may be explained by the fact that the dairy and broiler samples contained similar amounts of readily soluble P$_i$ (2.79 g kg^{-1} in dairy and 2.42 g kg^{-1} in the broiler) while the swine sample contained almost twice as much readily soluble P$_i$ (4.81 g kg^{-1}). Apparently, decrease in soluble P was accentuated at an alum rate of 100 g kg^{-1} for the dairy and broiler and 250 g kg^{-1} for the swine samples. At these rates, readily soluble P$_i$ was reduced by 99, 86, and 80% as compared with the untreated manure samples.

At the accentuated rates, estimated molar ratios of Al to P were 1.33:1, 0.96:1, and 0.57:1 for dairy, swine, and broiler samples, respectively, based on the amount of Al added through alum and the acid digest total P concentration of the manure. If we use readily soluble P$_i$ instead of acid digest total P for the calculation, the ratios would be 3.7:1, 4.3:1, and 5.4:1, a range considerably narrower among the three manures. We argue that readily soluble P$_i$ is a better measurable parameter than acid digest total P for reflecting the relative magnitude of manure P that is most responsive to the treatments of this study.

Cooke et al. (1986) proposed two different mechanisms responsible for P removal when alum is used for wastewater treatment: formation of AlPO$_4$ under acidic conditions (pH < 6) and sorption and entrapment of inorganic and organic P on Al(OH)$_3$ flocs at higher pH. Accordingly, the sorption–entrapment mechanism seems to play a major role in the reduction of readily soluble P in the current study because of favorable pH. Sorption–entrapment being the major mechanism also helps explain the high Al to P mole ratios estimated in this study (from 3.7:1 to 5.4:1 based on readily soluble P$_i$). Obviously, formation of AlPO$_4$ would have a 1:1
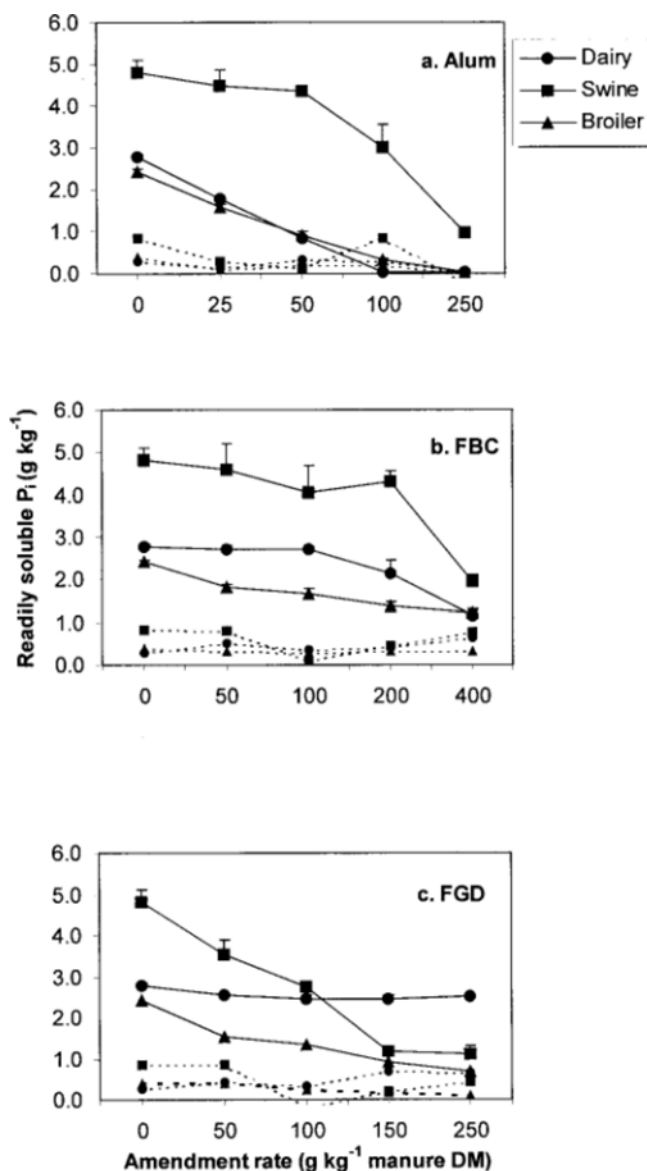
Fig. 2. Reduction of readily soluble P (solid lines for inorganic P and broken lines for organic P) in dairy, swine, and broiler manure samples treated with (a) alum, (b) fluidized bed combustion fly ash (FBC), and (c) flue gas desulfurization by-product (FGD). Readily soluble P was determined in filtrates of 2 g moist sample + 98 mL deionized water after 1 h of shaking. Error bars are means plus one standard deviation. DM, dry matter.

(Fig. 2c). At 150 g kg^{-1} for the swine and 250 g kg^{-1} for the broiler litter manure, decrease in readily soluble P_i was accentuated with approximately 80% reduction compared with the untreated control samples. The ANT treatments were generally ineffective for all three manures with less than 20% reduction in readily soluble P even at the highest rate (data not presented).

It appears that Ca and pH are the main factors affecting P solubility and its reduction in the by-product treatments. The dairy manure had a relatively low pH (6.01) and thus the effectiveness of the by-products depended on the increase of pH in addition to the increase in Ca. The FBC was effective only at the two highest rates (200 and 400 g kg^{-1}) when the pH was raised to above 7.0 (Table 2) coupled with considerable addition of Ca. The FGD was ineffective at all rates for the dairy manure because of limited addition of Ca at the lower rates and insufficient pH increase at the higher rates. In contrast, the swine and broiler manures had initial pH above 8.0, and thus the relative effectiveness of the by-products was largely driven by the amount of Ca added in the treatments. As illustrated in Fig. 2b and 2c, both swine and broiler samples exhibited a trend of steady decrease in readily soluble P_i with increasing rates of FBC or FGD. The ANT fly ash contained the smallest amount of Ca as compared with FBC and FGD (Table 1) and thus was ineffective for all three manures regardless of pH.

By rough estimates, pH above 7.0 and a Ca to P mole ratio (readily soluble P_i based) greater than 10:1 appeared to be the prime conditions for the coal combustion by-products to be effective with a 50% or more reduction in readily soluble P_i. Elrashidi et al. (1999) discussed possible mechanisms involved in reduction of soluble P for FBC treated dairy manure, including (i) precipitation of insoluble Ca–phosphate compounds, (ii) retention of soluble organic P on FBC mineral surfaces, (iii) sorption of soluble inorganic P by Al- and Fe-hydroxides, and (iv) coprecipitation and/or entrapment of P by newly formed carbonates due to carbonization. It is likely that most of these mechanisms would involve Ca–P binding with relatively less strength than the Al–P binding in alum treatments. Results from the sequential extractions, discussed next, seem to support this supposition.

Shift in Phosphorus Fractions

Sequential extraction results clearly demonstrate the shift of P from water-extractable to more stable fractions. Mostly, the alum treatment shifted P into NaOH-P while the by-product treatments shifted P into NaHCO$_3$–P (Fig. 3). The shifts involved primarily P_i, whereas concentrations of P_o in the relevant fractions remained unchanged except in the alum treatments. All three manures with the alum treatment had much higher P_o concentrations associated with the NaOH-P fraction, as compared with the untreated control samples (detailed data not presented). This perhaps reflects the sorption–entrapment of organic P on Al(OH)$_3$ flocs discussed earlier.

Al to P mole ratio, whereas the sorption–entrapment mechanism may be associated with a much higher ratio because Al–P bonding on the surface of Al(OH)$_3$ flocs can be space-restricted and thus less efficient.

The FBC treatments reduced readily soluble P (mainly P_i) at rates of 200 and 400 g kg^{-1} for the dairy, 400 g kg^{-1} for the swine, and at all rates (50, 100, 200, and 400 g kg^{-1}) for the broiler sample (Fig. 2b). At a rate of 400 g kg^{-1}, where the most reduction occurred for all three manures, readily soluble P_i decreased by 50 to 60% compared with the untreated control samples. The FGD treatments were ineffective for the dairy but effective for the swine and broiler manures with steady decreases in readily soluble P_i as the rate increased

Soil P fractions using Hedley's sequential extraction procedure (Hedley et al., 1982) are typically associated with certain chemical forms or physico–chemical associations. For example, the NaOH-P fraction is considered to be amorphous and crystalline Al and Fe phosphates plus chemically and physically protected organic forms, and the HCl-P fraction is stable Ca-bound phosphate (Hedley et al., 1982; Sharpley, 1996; Tiessen and Moir, 1993). For manure samples, we know little about the chemical or physico–chemical forms of the various P fractions. Nevertheless, given the chemical characteristics of the extractants and the rigorous, sequential extraction procedure, we can state with confidence that P associated with H_2O, $NaHCO_3$, NaOH, and HCl fractions have a decreasing vulnerability, or increasing stability, in that order regarding potential environmental loss. Therefore, for all three manures, by-product treatments reduced water-extractable P by converting it into less susceptible forms such as $NaHCO_3$–P; alum treatments reduced water-extractable P by converting it into even more stable forms such as NaOH-P. Such shifts in P fractions may have little effect on P availability for crop uptake over the long term but would retard and reduce potential losses of P following manure applications.

Implications

Surface-spreading manure onto no-till or pasture fields is a common practice on many animal operations. Also, manure applications occur both in and out of the growing season because of limited storage capacity as well as seasonal labor constraints. Phosphorus contained in manures surface-applied during the nongrowing season is particularly prone to runoff losses. Treating manure with alum or coal-burning power plant by-products before field application to stabilize soluble P can be a management option to address the special needs. This would be an addition to the traditionally recommended best management practices emphasizing in-the-field tactics such as application rate, time, and method.

However, addition of Al to soils through the use of alum-treated manures might be a concern. A cursory estimate was made to calculate the relative magnitude of Al addition. Assuming the swine manure in this study is to be applied at 30 kg total P ha^{-1} yr^{-1}, the equivalent manure dry matter applied would be 1106 kg ha^{-1} yr^{-1}. If the manure is treated with 250 g alum kg^{-1} dry matter before field application, the amount of Al added would be 25 kg ha^{-1} yr^{-1}. The consequent Al loading would be about 0.0125 g kg^{-1} yr^{-1} assuming the treated manure is mixed to a 15-cm depth with a soil bulk density of 1.33 g cm^{-3}. The estimated Al loading is negligibly small compared with Al contained in typical agricultural soils (14–40 g Al kg^{-1} soil; Stout et al., 1988). Periodic tillage is desirable to prevent Al and P from accumulating near the soil surface.

For the by-products, we estimated heavy metal loading rates assuming the swine manure treated with FBC at 400 g kg^{-1} in the current study is to be applied at 30 kg total P ha^{-1} yr^{-1}. The results suggest that the FBC-
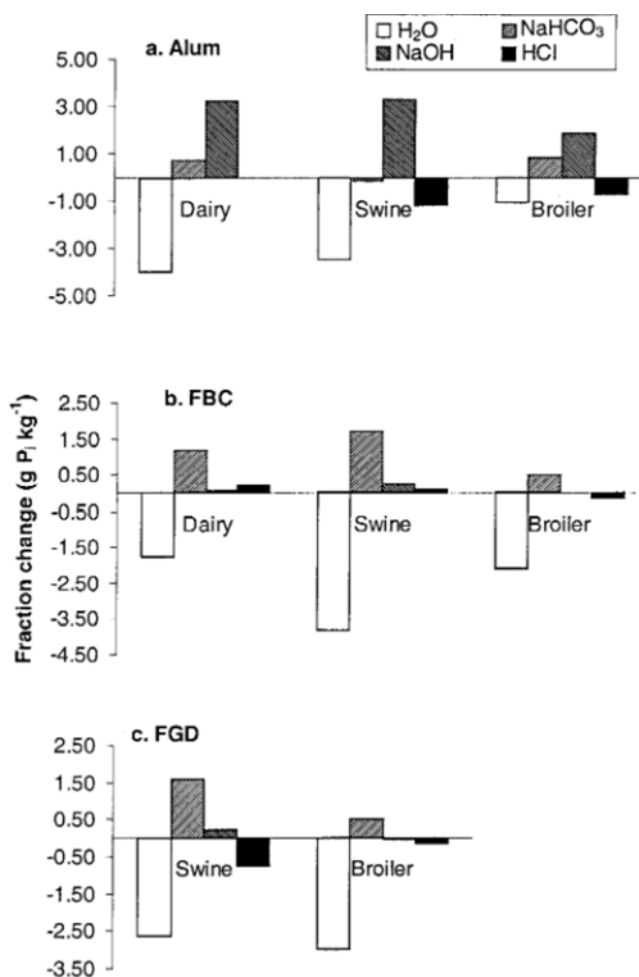

Fig. 3. Changes in inorganic P concentrations in four P fractions as affected by treatments: (a) alum at 100 g kg^{-1}, (b) fluidized bed combustion fly ash (FBC) at 400 g kg^{-1}, and (c) flue gas desulfurization by-product (FGD) at 250 g kg^{-1}, as compared with untreated controls.

treated manure may be applied for many years without exceeding the USEPA's heavy metal loading limits (Table 3). Also, levels of heavy metals contained in nine samples of FBC tested by Stout et al. (1988) are within ranges usually found in soils; these elements are mostly within the maximum tolerable dietary levels for dairy cattle (Table 3).

Clearly, treating manures with alum or coal combustion by-products for reducing soluble P and its loss into the environment needs to be balanced with other considerations such as the potential effect on soil and crop quality. Any enhancement of Al or heavy metals in soils receiving repeated applications of treated manures, and in crops, particularly pasture grasses, must be carefully monitored through appropriate soil and forage testing. Furthermore, the long-term success of any remediation measure depends on the adoption of sound nutrient management programs. Such programs should address both manure management at the end of the process and feeding management at the beginning of the process through an integrated approach. An integrated, whole-farm management program would be most effective in

Table 3. Annual heavy metal loadings to soils, estimated assuming fluidized bed combustion fly ash (FBC)–treated swine manure in present study is to be applied, as compared with loading limits established by the USEPA for sewage sludge land application. Heavy metals contained in nine FBC samples are within the range for soils and the maximum tolerable levels for dairy diets.

Metal	Loading from treated manure†	USEPA limits‡			FBC§		Soils§		Dairy diets¶
		Annual loading	Cumulative loading	Ceiling concentration	Mean	Range	Mean	Range	
	——— kg ha⁻¹ yr⁻¹ ———		kg ha⁻¹		——————————— mg kg⁻¹ ———————————				
As	0.21	2.0	41	75	–	–			50
Cd	0.003	1.9	39	85	0.5	–	0.5	0.01–0.70	0.5
Cr	–	150	3000	3000	15	9–23	200	5–1000	–
Cu	0.02	75	1500	4300	15	12–19	20	2–100	–
Pb	–	15	300	840	3.2	1.5–7.5	10	2–200	30
Hg	–	0.85	17	57	–	–	–	–	2
Mo	0.026	–	–	75	0.19	0.12–0.28	2	0.2–5	10
Ni	0.056	21	420	420	21	13–29	40	5–500	50
Se	0.078	5.0	100	100	0.29	0.16–0.58	–	0.1–2	–
Zn	0.80	140	2800	7500	55	29–105	50	10–300	–

† Calculated based on the heavy metal concentrations of FBC used in present study (Table 1) multiplied by the amount of FBC needed (400 g kg⁻¹ manure dry matter) to treat the swine manure (1106 kg dry matter) that is to provide 30 kg P kg⁻¹ ha⁻¹ as crop uptake.
‡ USEPA (1995).
§ Adapted from Stout et al. (1988).
¶ Adapted from National Research Council (1989).

The units for loading columns are $kg\ ha^{-1}\ yr^{-1}$, for cumulative loading $kg\ ha^{-1}$, and for the concentration columns $mg\ kg^{-1}$.

helping producers improve nutrient efficiency, enhance productivity, and minimize adverse environmental consequences.

CONCLUSIONS

There was a general trend of decreasing readily soluble P with increasing treatment rates of alum or coal combustion by-products for all three manures (dairy, swine, and broiler litter). Alum was most effective and reduced readily soluble P by up to 99%; by-products FBC and FGD decreased readily soluble P by 50 to 80% at the most effective rates tested. These amendments stabilize manure P by shifting it from water-extractable to less vulnerable and more stable fractions, mostly $NaHCO_3$–P with by-product treatments and NaOH-P with alum treatment. The P shifts are desirable and beneficial because P availability for crops would be similar over the long term, whereas P runoff potential can be substantially retarded and reduced. Treating manures with alum or coal-burning power plant by-products before field application can be a management tactic particularly useful on farms where manure surface spreading during the nongrowing season is practiced and is difficult to avoid due to various constraints. Loadings of Al or heavy metals to soils from treated manures are estimated to be well below the natural levels and within government regulated limits but should be carefully monitored through proper testing.

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