

Carl H. Bolster and Karamat R. Sistani
 USDA-ARS, Animal Waste Management Research Unit, Bowling Green, KY
 carl.bolster@ars.usda.gov

Abstract

To increase crop yields, phosphorus (P) is often applied to agricultural fields in the form of fertilizer or animal manure. The over application of P, however, can result in the increase in P loads to surface waters which often times leads to eutrophication. Considerable research has been undertaken to identify ways to prevent P loss from fields. Because P mobility in the environment is controlled to a large extent by its sorption to soil, sorption isotherms are often conducted to obtain P sorption parameters. In most studies P is added as an inorganic salt to a pre-defined background solution such as CaCl₂ or KCl. The limitation with this type of approach, however, is that the application of P to agricultural fields is often in the form of animal manures. Given that manure leachate differs significantly in ionic composition, organic matter content, and pH from a CaCl₂ or KCl solution, it is unclear whether sorption parameters obtained using ionic solutions will be representative of the sorption of manure-derived P in the environment. Therefore, the purpose of this study was to determine whether the sorption behavior of manure-P is similar to that of inorganic-P. Single-point P isotherms (PSI) were conducted on eight soils with the following solutions: KH₂PO₄-amended 0.01 M CaCl₂ solution, KH₂PO₄-amended 0.03 M KCl solution, water-extracted dairy manure, water-extracted poultry litter, and swine lagoon effluent. Results show that the sorption behavior of manure-P is different from that of inorganic-P and that the differences are dependent on soil texture and manure type. Our results should caution anyone from using results from CaCl₂- or KCl-P sorption studies to estimate manure-P fate and transport in the environment.

Significance and Motivation:

- The indiscriminate application of fertilizers and manures to crop and pasture lands often results in excess P being transported from agricultural fields to surface and ground waters.
- When P enriched waters reach surface waters, whether through surface or subsurface pathways, eutrophication is often the result.
- To reduce runoff losses a better understanding of the mechanisms controlling P sorption are required.
- A common approach for obtaining soil P sorption parameters is through the use of sorption isotherms.
- In most cases, P sorption isotherms are conducted with inorganic P salts dissolved in an inorganic ionic solution.
- However, in many cases P is added to soils in the form of animal manures.
- Therefore, in this study we compare the effect of P source (manure vs. KH₂PO₄) and solution matrix (manure extract, CaCl₂, or KCl) on the sorption behavior of P to eight different soils.



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Materials and Methods:

- Soil Collection and Characterization**
 - Surface soils (0 - 15 cm) were collected from seven locations in KY and one location in AL representing the following soil series:
 - Belknap, Collins, Hartsells, Lakin, Loring, Melvin, Pembroke, and Zanesville.
 - Soils were air dried, passed through a 2-mm sieve and characterized for the following:
 - Soil texture, pH, organic carbon, and oxalate and Mehlich-3 extractable P, Fe, and Al.
- Manure Collection and Characterization**
 - Three types of manures were used in this study: swine lagoon effluent, poultry litter extract, and dairy manure extract.
 - Extracts were obtained by mixing manure with distilled water at a 1:100 ratio for 24 hr.
 - All manure solutions were passed through a 0.45-µm filter prior to use.
- P sorption studies**
 - P sorption was evaluated using single-point P additions (40 ml solution mixed with 0.9 g soil)
 - PSI = S/log(C)
 - Five different solutions were compared:
 - 0.01 M CaCl₂ + KH₂PO₄, 0.03 M KCl + KH₂PO₄, swine effluent, poultry litter extract, dairy manure extract.
 - Initial DRP averaged 13.5 mg L⁻¹ for all five solutions.
 - Soil was equilibrated with each solution for 24 hr.
 - Organic matter sorption was quantified by measuring initial and final DOC concentrations in each solution.

Results: Soil and Manure Properties

- The pH, ionic composition, and DOC content varied noticeably between the different manure solutions (Table 1).
- DOC was highest for the dairy manure extract (310 mg L⁻¹) and lowest for the swine effluent (45 mg L⁻¹).
- pH was highest for the swine effluent (8.40) and lowest for the dairy manure (7.39).
- The dairy manure extract contained the highest or second highest concentrations of the major cations Ca, K, Mg, and Na yet had the lowest IS.
- DRP constituted 100% of the total P in the swine effluent whereas for the poultry litter and dairy manure extracts the percentages were 82 and 69, respectively.

Table 1. Selected properties of P solutions

Parameter	0.01 M CaCl ₂	0.03 M KCl	Dairy manure	Poultry litter	Swine effluent
pH	5.20	5.08	7.39	8.12	8.40
IS (mmol L ⁻¹)	30.5	30.5	5.6	23.5	24.1
DOC (mg L ⁻¹)	0	0	310	270	45
DRP (mg L ⁻¹)	13.9	14.0	13.2	13.4	13.2
TP (mg L ⁻¹)	14.1	ND	19.1	16.4	12.9
Al (mg L ⁻¹)	0	0	0.648	0.138	0.018
Ca (mg L ⁻¹)	400	0	38	5.9	53
Fe (mg L ⁻¹)	0	0	0.30	0.51	0.58
K (mg L ⁻¹)	17	1200	39	190	200
Mg (mg L ⁻¹)	0	0	21	11	35
Mn (mg L ⁻¹)	0	0	0.43	0.093	0.14
Na (mg L ⁻¹)	0	0	0.61	47	45

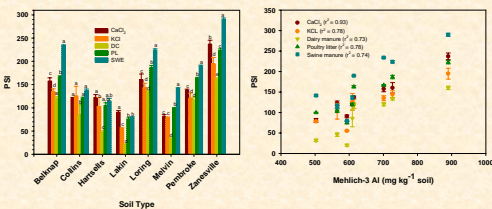
- A wide range in physical and chemical characteristics was observed for the eight soils used in our study (Table 2).
- Soil pH values ranged from 4.6 to nearly 7.
- Sand content ranged from 4 to 62%.
- Mehlich-3 extractable P ranged from 3.6 to 94.9 mg kg⁻¹ soil and total P ranged from 80 to nearly 460 mg kg⁻¹.
- Mehlich-3 extractable Al ranged from 503 to 900 mg kg⁻¹ and for Fe ranged from 33 to 163 mg kg⁻¹.
- Oxalate extractable Al ranged from 243 to 690 mg kg⁻¹ and for Fe ranged from 160 to 1274 mg kg⁻¹.

Table 2. Selected soil chemical and physical properties

Soil Series	pH	Bulk Density	Total C %	Total P (mg kg ⁻¹)	Sand/Silt/Clay %	Oxalate-extractable P			Mehlich-3 Extractable P			
						Al	Fe	Ca	Al	Fe	Ca	
Belknap	4.61	2.25	1.03	394	19 / 69 / 12	155	404	1274	34.1	701	142	479
Collins	6.40	2.05	1.50	459	4 / 81 / 15	181	500	841	62.1	609	80.6	1432
Hartsells	5.68	1.71	0.614	80.1	60 / 30 / 10	15.6	385	160	3.92	565	32.7	379
Lakin	6.96	2.36	0.928	450	62 / 28 / 10	204	509	824	94.9	593	107	1759
Loring	5.34	1.93	1.35	252	8 / 80 / 12	49.4	429	1191	3.61	727	104	889
Melvin	5.49	2.28	0.932	249	12 / 67 / 21	91.2	243	1151	17.8	503	163	1355
Pembroke	5.70	1.31	1.30	350	8 / 70 / 22	114	690	908	27.1	613	33.1	1193
Zanesville	5.34	1.93	1.40	251	7 / 74 / 19	35.3	601	1148	2.72	900	106	991

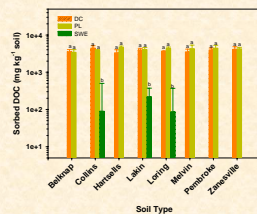
Results: P Single-point Isotherm (PSI)

- P sorption, as measured by the single-point P index (PSI), was a function of both soil and solution type. Specifically:
 - For all soils the PSI values for the dairy manure extract were significantly lower ($P < 0.05$) than the CaCl₂, poultry litter extract, and swine lagoon effluent solutions and were significantly lower than the KCl solution for six of the eight soils.
 - PSI values for the swine effluent were significantly higher than the other four solutions in five of the eight soils tested.
 - P sorption in the CaCl₂ solution was significantly higher in six soils and not significantly different in two soils than the KCl solution.
- Although PSI values varied significantly between solution types, the strongest single predictor of PSI for all solution types was the Mehlich-3 aluminum content of the soil.
 - Surprisingly, the slopes of the regression lines between PSI and Mehlich-3 Al were not statistically different between the five different solution treatments ($P < 0.05$).



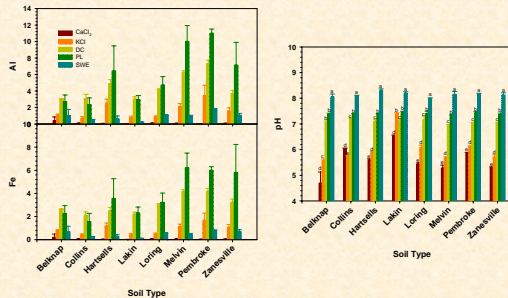
Results: DOC Sorption

- The amount of organic matter (as measured by DOC) sorbed to the soils was similar between the dairy and poultry manure extracts for all soils.
- Little or no organic matter sorption occurred with the swine effluent.
- The large amount of sorption of OM in the dairy manure solution may explain why P sorption was much lower in this solution compared to the CaCl₂ and KCl solutions.



Results: pH, Al, and Fe Changes Following Equilibration

- For the dairy and poultry manure solutions, large increases in Al and Fe concentrations were observed following the 24-hr equilibration period. On the other hand, little or no release of Al and Fe was observed for the swine effluent.
- The release of Al and Fe may be due to the dissolution of metal oxides by organic matter. (Note that little OM sorption was observed with the swine effluent.)
- Dissolution of metal oxides can affect P sorption to soils and may partially explain our results.
- For the poultry, CaCl₂, and KCl solutions, noticeable changes in pH occurred following the 24-hr equilibration period.
- P precipitation can occur at elevated pH and may explain, in part, the elevated P sorption observed for the swine effluent solution.



Conclusions

- Our results show that the sorption of phosphorus in manure solutions differs significantly from that of KH₂PO₄-amended CaCl₂ and KCl solutions and that the difference depends on manure and soil type.
- Our results suggest that the reduced P sorption observed in the dairy manure solution was likely due to the dissolution of metal oxides by organic matter.
- The enhanced P sorption in the swine effluent solution was likely a result of calcium phosphate precipitation due to high pH values. P sorption in the poultry litter solution was likely a combination of these processes.
- Saturation indices based on sorption parameters obtained using KH₂PO₄-amended CaCl₂ or KCl solutions may result in erroneous predictions of P loss from agricultural fields when P is applied in the form of animal manure.
- Therefore, our findings support the conclusions of others who have cautioned against basing manure application rates on sorption data collected from inorganic P salt experiments (e.g. Marshall and Laboski 2006; Robinson and Sharpley 1996; Siddique and Robinson 2003).
- Given the variability we observed in PSI values for the different manure solutions and soil types, predictions of manure-P sorption should be based on sorption studies using the specific manure and soil type of interest.
- Additional studies are needed to better understand how the various components in animal manures affect P sorption to soils.