

1997

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# ADSORPTION AND DESORPTION OF PHOSPHORUS AND NITROGEN BY IMMERSED STALKS

J. E. Gilley, B. Eghball, D. B. Marx

**ABSTRACT.** Adsorption and desorption of phosphorus (P) and nitrogen (N) by stalk residues may influence the concentrations of P and N in runoff. A laboratory study was conducted to measure the effects of P and N constituents in solution on adsorption and desorption of P and N by corn, soybean, and wheat stalk residues. Experimental variables included type of stalk material (corn, soybean, and wheat), inorganic nutrients in solution ( $PO_4\text{-P}$  and  $NO_3\text{-N}$ ;  $PO_4\text{-P}$  and  $NH_4\text{-N}$ ;  $NO_3\text{-N}$  and  $NH_4\text{-N}$ ; and  $PO_4\text{-P}$ ,  $NO_3\text{-N}$ , and  $NH_4\text{-N}$ ), solution concentration (0, 6, 12, and  $24\ \mu\text{g g}^{-1}$  residue), and stalk immersion period (25, 250, 2500, 25000, and 86400 s). The initial concentration of each of the P and N constituents in a particular test solution was the same (0, 6, 12 or  $24\ \mu\text{g mL}^{-1}$ ). Corn-stalk residues released  $PO_4\text{-P}$ ,  $NO_3\text{-N}$ , and  $NH_4\text{-N}$ . The quantity of  $PO_4\text{-P}$  released generally increased as the length of time the corn stalks were immersed became greater. The presence of P and N constituents in solution in general did not affect the quantity of  $NO_3\text{-N}$  released by corn-stalk residues. Soybean-stalk residues released  $PO_4\text{-P}$  and adsorbed relatively small amounts of  $NH_4\text{-N}$ . Wheat-stalk residues released  $PO_4\text{-P}$ , and adsorbed  $NO_3\text{-N}$  and  $NH_4\text{-N}$ . The presence of stalk residues, P or N solution concentration, and residue immersion period may influence P and N concentrations of overland flow. The amount of P and N adsorbed or desorbed by residue materials can be significantly different if more than one nutrient constituent is present in solution.

**Keywords.** Corn, Crop residue, Nitrogen movement, Nutrient losses, Overland flow, Phosphorus, Runoff, Soybean, Water quality, Wheat.

Environmental concerns can arise if runoff from agricultural areas contains substantial amounts of nutrients (Gilley et al., 2002). Inorganic fertilizer or manure can serve as a source of nutrients in overland flow (Eghball and Gilley, 1999). Denitrification, leaching, mineralization, nitrification, and volatilization can influence nitrogen (N) conversions following land application (Eghball, 2000; Eghball et al., 2002).

The nutrient content of runoff may be influenced by crop residue on the soil surface (Gilley et al., 2007). Cermak et al. (2004) conducted a laboratory study to measure adsorption and desorption of P and N by corn, soybean, and winter wheat residue collected from a farm in southeast Nebraska. At the time of collection, the soybean, corn, and winter wheat residue had been in the field following harvest for 16, 77, and 119 days, respectively. The crop residue materials were placed in solutions containing  $PO_4\text{-P}$ ,  $NO_3\text{-N}$ , or  $NH_4\text{-N}$ . An increase in solution concentration did not affect release of  $PO_4\text{-P}$  from corn and soybean residue. However, as residue immersion time became greater, the amount of  $PO_4\text{-P}$  re-

leased from corn and soybean residue consistently increased. In the present study, the effects of more than one P and N constituent in solution on adsorption and desorption of P and N by selected stalk residues was examined.

Crop residues subjected to rainfall were found to be a substantial source of soluble nutrients in agricultural runoff (Schreiber, 1985). The amounts and patterns of nitrogen mineralization from decomposing crop residues are affected by their initial chemical composition and condition and by climatic variables (Kumar and Goh, 2003; Rosolem et al., 2005).

Schreiber and McDowell (1985) determined concentrations, quantities, and kinetics of  $PO_4\text{-P}$ ,  $NO_3\text{-N}$ ,  $NH_4\text{-N}$ , and organic carbon released from wheat straw residue as functions of simulated rainfall intensity. For the given experimental conditions, less than 1% of the total N and 8% to 14% of the total P in the wheat residue was leached. Leaching losses were found to increase with greater amounts of wheat residue (Schreiber, 1985). Schreiber (1999) determined that less than 1.5% of the total N and 4.2% to 6.0% of the total P contained in corn residue was leached. Lower rainfall intensities and higher residue loading rates generally produced greater nutrient concentrations and losses.

Ginting et al. (1998) examined leaching of P from corn residue as affected by the length of time residue remained in water. Approximately 34% of the total P in residue was released over a 5 min immersion period, compared to 57% over a 20 h period. When the information reported by Ginting et al. (1998) is compared to other data available in the literature, it can be concluded that greater nutrient leaching results from immersing corn residue in water than from exposing corn residue to simulated rainfall.

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Submitted for review in May 2008 as manuscript number SW 7490; approved for publication by the Soil & Water Division of ASABE in March 2009.

This article is a contribution from the USDA-ARS in cooperation with the Agricultural Research Division, University of Nebraska, Lincoln.

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The solutions in which residue materials are submerged by overland flow may contain multiple nutrient constituents at varying solution concentrations. Thus, selected P and N constituents and solution concentrations were included as experimental variables in this study. Residue materials may be submerged for a relatively short time by overland flow or for extended periods in tile-drained areas or poorly drained terrace channels and basins. Therefore, the length of time stalks are immersed could influence surface water quality characteristics.

Adsorption and desorption of nutrients by crop residue materials could affect the concentrations of dissolved constituents in overland flow. If the conditions under which crop residues adsorb and desorb nutrients can be identified, it may be possible to adopt cropping and management practices that reduce nutrient concentrations in runoff without negatively impacting groundwater quality. Nutrients adsorbed or desorbed by crop residue materials could be maintained on-site and used by succeeding crops rather than transported in runoff, causing off-site surface water quality concerns. The objective of this laboratory study was to measure the effects of P and N constituents in solution on adsorption and desorption of N and P by corn, soybean, and wheat stalk residues.

## MATERIALS AND METHODS

### EXPERIMENTAL DESIGN

Once crop leaves disappear following harvest, stalks are the principal vegetative material found on the soil surface. Only a relatively small amount of vegetative material was used for the individual laboratory tests conducted in this study. It was critical that the crop residue materials used in the tests were relatively uniform. Therefore, only stalks that were not damaged during harvest were selected for testing.

The experimental variables used in this study included: three types of stalks (corn, soybean, and wheat), four solution concentrations (0, 6, 12, and 24  $\mu\text{g mL}^{-1}$ ), four solutions containing P and N constituents ( $\text{PO}_4\text{-P}$  and  $\text{NO}_3\text{-N}$ ;  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$ ;  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ ; and  $\text{PO}_4\text{-P}$ ,  $\text{NO}_3\text{-N}$ , and  $\text{NH}_4\text{-N}$ ), and five residue immersion times: 25 s (0.42 min), 250 s (4.2 min), 2500 s (42 min), 25,000 s (6.9 h), and 86,400 s (24 h). Each treatment was replicated four times. The initial concentration of each of the N and P constituents in a particular test solution was the same (0, 6, 12, or 24  $\mu\text{g mL}^{-1}$ ). In this article, the term adsorption is used in a general sense to describe the transfer of P and N from solution to the immersed stalks. Desorption, in turn, is used to characterize the transfer of P and N from the immersed stalks into solution.

### SITE DESCRIPTION AND STALK COLLECTION

The stalks were obtained from three fields at the University of Nebraska Roger's Memorial Farm located 18 km east of Lincoln, Nebraska, in Lancaster County. The silty clay loam soils at the site developed in loess under prairie vegetation. The farm was cropped using a corn, soybean, winter wheat rotation under a no-till management system. Anhydrous ammonia was applied to the corn acreage at a rate of 0.14 Mg N  $\text{ha}^{-1}$ , and ammonium nitrate was added to the wheat acreage at a rate of 0.14 Mg N  $\text{ha}^{-1}$ . Liquid ammonium polyphosphate fertilizer (10-34-0) was applied in the furrows of the corn and wheat fields at the time of planting at rates of 7.65 and 23.0 L  $\text{ha}^{-1}$ , respectively. No commercial fertilizer was added to the soybean acreage.

The fields that served as a source of wheat, soybean, and corn stalks were harvested on July 9, October 1, and October 3, 2001, respectively. At the time of collection, the corn (October 31, 2001), soybean (October 31, 2001), and wheat (August 9, 2001) stalks had been in the field following harvest for 28, 30, and 31 days, respectively. The adsorption and desorption measurements obtained in this study for the selected stalks are representative of conditions existing in a particular field at one point in time. Earlier studies showed that adsorption and desorption characteristics of crop residue changed with progressive decomposition of the residue materials (Harvis and Alberts, 1993).

The stalks were cut into sections approximately 11 cm long and placed in an oven maintained at a temperature of 60°C for 48 h. The dried stalks were then stored in plastic bags for later use in the laboratory tests. Since the stalks were oven dried, the same quantity of vegetative material was used in each of the laboratory tests conducted on a given type of crop residue.

### NUTRIENT CONCENTRATION OF SOLUTIONS

One-liter wide-mouth glass jars were used for the laboratory tests. The wheat, soybean, and corn stalks were added at rates of 25, 35, and 50 g per jar, respectively. This mass of material provided approximately the same residue volume for each of the stalk residues. In this investigation, stalk volume served as the parameter used for normalization. The selected stalk volume provided a sufficient amount of space above the vegetative materials to allow for complete immersion after the stalks absorbed water.

Initial nutrient solution concentrations of each of the  $\text{PO}_4\text{-P}$ ,  $\text{NO}_3\text{-N}$ , and  $\text{NH}_4\text{-N}$  constituents used in this study were 0, 6, 12, or 24  $\mu\text{g mL}^{-1}$ . These concentrations were selected after reviewing the results from a field runoff study reported by Nicolaisen et al. (2007). Nicolaisen et al. (2007) measured runoff nutrient contents from plots containing selected amounts of crop residue on which beef cattle or swine manure were added at rates required to meet annual corn N requirements.

Inorganic sources for  $\text{PO}_4\text{-P}$ ,  $\text{NO}_3\text{-N}$ , and  $\text{NH}_4\text{-N}$  were American Chemical Society certified  $\text{K}_2\text{HPO}_4$ ,  $\text{KNO}_3$ , and  $\text{NH}_4\text{Cl}$ . The inorganic salts were added to deionized-distilled water to obtain the desired nutrient concentrations, and samples of the solutions were analyzed for  $\text{PO}_4\text{-P}$ ,  $\text{NO}_3\text{-N}$ , and  $\text{NH}_4\text{-N}$ . The stalks were placed in each jar, and the nutrient solution was added until the stalks were completely immersed.

The laboratory experimental variables were selected to replicate conditions existing in the field when a unit volume of residue material (the normalizing parameter) is immersed by overland flow. The stalk diameter of selected corn, soybean, and wheat residue materials has been reported as 2.38, 0.60, and 0.29 cm, and their density is 168, 258, and 148  $\text{kg m}^3$ , respectively (Gilley et al., 1994). Thus, the volume provided by a unit mass of stalks varies among residue materials. In establishing the experimental procedures used in this investigation, the test volume was held constant (1 L). The amount of residue material required to fill the test volume was first determined (25, 35, and 50 g for wheat, soybean, and corn stalk residues, respectively). The quantity of water necessary to immerse the stalks was then identified (630 mL for corn, and 840 mL for soybean and wheat). Information provided by Gregory (1982) was used to extrapolate the volu-

**Table 1. Extractable nutrient content of the stalks (all values in  $\mu\text{g}$  of nutrient  $\text{g}^{-1}$  residue).**

Type of Stalk	PO <sub>4</sub> -P	NO <sub>3</sub> -N	NH <sub>4</sub> -N
Corn	620	168	405
Soybean	211	8	85
Wheat	178	35	49

metric data obtained under laboratory conditions to a unit area basis representative of field conditions.

Tests were run to measure adsorption and desorption of stalks immersed in solutions containing P and N. When P and N were present, changes in the concentrations of P and N constituents in solution were measured following stalk immersion. Stalk adsorption and desorption tests were also made in solutions where P and N were not added.

Following residue immersion, the jars were covered to reduce evaporation and then left undisturbed at room temperature for the designated immersion time. The stalks were discarded once the designated immersion period had been reached. The nutrient solutions were filtered through a 0.45  $\mu\text{m}$  filter and stored in a cooler at 1 °C for later analysis. Each solution was analyzed for PO<sub>4</sub>-P (Murphy and Riley, 1962), NO<sub>3</sub>-N, and NH<sub>4</sub>-N (Lachat, Zellweger Analytics, Milwaukee, Wisc.). To normalize data, results were reported as the mass of P and N adsorbed or desorbed per unit mass of stalk material.

#### NUTRIENT CONCENTRATION OF STALKS

Procedures described by Harvis and Alberts (1993) were used to measure P and N concentrations of subsamples of the stalks. The stalks were dried at 60 °C for 2 h, and a 1 g sample was placed in a test tube containing 30 mL of deionized-distilled water and shaken for 2 h. After the liquid extraction process, the sample was centrifuged and filtered before P and N analysis was performed. The solutions were then analyzed for PO<sub>4</sub>-P (Murphy and Riley, 1962), NO<sub>3</sub>-N, and NH<sub>4</sub>-N

(Lachat, Zellweger Analytics, Milwaukee, Wisc.). The P and N concentrations of the stalks are shown in table 1.

#### STATISTICAL ANALYSES

Significant differences in P and N concentrations were found among experimental treatments using ANOVA (SAS, 2003). Hypothesis testing was employed to determine if the presence of P and N constituents in solution significantly affected adsorption and desorption of P and N by stalks. A probability level of 0.05 was considered significant. Regression analysis was used to develop predictive equations relating adsorption and desorption of P and N to stalk immersion time.

## RESULTS AND DISCUSSION

Both solution concentration and contact time significantly ( $p \leq 0.01$ ) impacted the nutrient content of solution for each of the nutrient constituents and stalks residues. Thus, solution concentration and contact time were examined independently when evaluating adsorption and desorption by the stalks residues. The values shown in parentheses in tables 2, 3, and 4 are used to determine if the presence of inorganic constituents in solution significantly affects adsorption and desorption of P and N by immersed stalks residues. If the reported p-value is <0.05, a significant difference in nutrient content exists between the respective solution and the treatment without inorganic constituents (0  $\mu\text{g mL}^{-1}$ ).

#### CORN-STALK RESIDUES

The corn-stalk residues contained an average of 620  $\mu\text{g}$  PO<sub>4</sub>-P  $\text{g}^{-1}$  residue (table 1). The presence of inorganic NO<sub>3</sub>-N and PO<sub>4</sub>-P in solution significantly reduced the quantity of PO<sub>4</sub>-P that was released by the corn-stalk residues (table 2). As residue immersion time increased from 2500 to 86400 s, the amount of PO<sub>4</sub>-P released from corn-stalk residues consistently increased. The corn-stalk residues

**Table 2. Change in nutrient content ( $\mu\text{g}$  nutrient in solution  $\text{g}^{-1}$  residue) of solution as affected by solution concentration and contact time with corn residue.<sup>[a]</sup>**

Inorganic nutrient source	Solution concentration ( $\mu\text{g/mL}$ ) <sup>[b]</sup>	Measured Nutrient Constituent								
		PO <sub>4</sub> -P			NO <sub>3</sub> -N			NH <sub>4</sub> -N		
		PO <sub>4</sub> -P, NO <sub>3</sub> -N	PO <sub>4</sub> -P, NH <sub>4</sub> -N	PO <sub>4</sub> -P, NO <sub>3</sub> -N, NH <sub>4</sub> -N	NO <sub>3</sub> -N, PO <sub>4</sub> -P	NO <sub>3</sub> -N, NH <sub>4</sub> -N	NO <sub>3</sub> -N, PO <sub>4</sub> -P, NH <sub>4</sub> -N	NH <sub>4</sub> -N, PO <sub>4</sub> -P	NH <sub>4</sub> -N, NO <sub>3</sub> -N	NH <sub>4</sub> -N, PO <sub>4</sub> -P, NO <sub>3</sub> -N
0	152	152	152	80.4	80.4	80.4	117	117	117	
6	135 (0.04)	154 (0.84)	144 (0.32)	60.5 (0.49)	102 (0.45)	3.58 (0.01)	75.2 (0.01)	102 (0.18)	95.9 (0.04)	
12	129 (0.01)	121 (0.01)	152 (0.96)	54.8 (0.37)	86.9 (0.82)	79.7 (0.98)	46.3 (0.01)	71.7 (0.01)	100 (0.12)	
24	116 (0.01)	163 (0.20)	119 (0.01)	27.0 (0.06)	77.2 (0.91)	69.3 (0.70)	47.7 (0.01)	73.1 (0.01)	97.2 (0.06)	
25	-5.63	6.38	3.86	15.9	18.7	-23.3	-4.49	-0.67	3.62	
250	-6.49	18.9	14.3	7.8	18.6	-27.2	-10.7	-9.23	-4.18	
2500	41.6	57.6	82.6	28.5	41.5	5.34	-3.33	3.69	8.48	
25000	233	244	228	116	192	169	86.2	99.3	132	
86400	404	410	410	110	163	168	290	362	374	

[a] The change in nutrient content was obtained by subtracting the final solution concentration from the initial concentration, multiplying the difference by the volume of solution, and dividing the result by the residue mass. Therefore, positive changes in nutrient content indicate release from the crop residue, while negative values represent adsorption.

[b] The values in parentheses represent the  $P > |t|$ .

[c] The values provided for a given contact time are mean measurements obtained for all solution concentrations.

**Table 3. Change in nutrient content ( $\mu\text{g}$  nutrient in solution  $\text{g}^{-1}$  residue) of solution as affected by solution concentration and contact time with soybean residue.<sup>[a]</sup>**

Inorganic nutrient source		Measured Nutrient Constituent								
		PO <sub>4</sub> -P			NO <sub>3</sub> -N			NH <sub>4</sub> -N		
		PO <sub>4</sub> -P, NO <sub>3</sub> -N	PO <sub>4</sub> -P, NH <sub>4</sub> -N	PO <sub>4</sub> -P, NO <sub>3</sub> -N, NH <sub>4</sub> -N	NO <sub>3</sub> -N, PO <sub>4</sub> -P	NO <sub>3</sub> -N, NH <sub>4</sub> -N	NO <sub>3</sub> -N, PO <sub>4</sub> -P, NH <sub>4</sub> -N	NH <sub>4</sub> -N, PO <sub>4</sub> -P	NH <sub>4</sub> -N, NO <sub>3</sub> -N	NH <sub>4</sub> -N, PO <sub>4</sub> -P, NO <sub>3</sub> -N
Solution concentration ( $\mu\text{g}/\text{mL}$ ) <sup>[b]</sup>	0	67.4	67.4	67.4	0	0	0	27.9	27.9	27.9
	6	84.9 (0.04)	53.7 (0.11)	62.7 (0.58)	7.48 (0.79)	-15.1 (0.60)	-36.1 (0.21)	18.3 (0.37)	12.4 (0.15)	21.3 (0.54)
	12	25.9 (0.01)	54.5 (0.13)	78.3 (0.20)	-49.4 (0.09)	49.2 (0.09)	-22.6 (0.43)	-1.95 (0.01)	27.8 (0.99)	-7.19 (0.01)
	24	-16.4 (0.01)	121 (0.01)	48.7 (0.03)	-40.7 (0.16)	-31.3 (0.27)	22.1 (0.44)	-40.2 (0.01)	-31.6 (0.01)	-47.9 (0.01)
Contact time (s) <sup>[c]</sup>	25	-15.0	13.9	-4.2	-6.49	0.95	9.64	-4.70	-17.9	-31.9
	250	-1.35	29.4	8.63	-4.82	24.1	10.4	-28.5	-16.0	-44.8
	2500	11.0	40.1	27.3	-13.68	14.6	9.70	-15.3	-46.4	-57.4
	25000	116	131	129	1.39	14.0	0.44	-19.3	-16.4	3.79
	86400	92.1	157	161	-79.8	-50.2	-75.9	70.5	142	123

[a] The change in nutrient content was obtained by subtracting the final solution concentration from the initial concentration, multiplying the difference by the volume of solution, and dividing the result by the residue mass. Therefore, positive changes in nutrient content indicate release from the crop residue, while negative values represent adsorption.

[b] The values in parentheses represent the  $\text{Pr} > |t|$ .

[c] The values provided for a given contact time are mean measurements obtained for all solution concentrations.

placed in solutions containing inorganic NH<sub>4</sub>-N and PO<sub>4</sub>-P released 6 to 410  $\mu\text{g}$  PO<sub>4</sub>-P  $\text{g}^{-1}$  residue as residue immersion time increased from 25 to 86400 s. Potential release of PO<sub>4</sub>-P from corn-stalk residues can be estimated from the equation (fig. 1):

$$y = -8.00\text{E-}08x^2 + 0.0114x + 6.76 \quad (R^2 = 0.99) \quad (1)$$

where  $y$  is the amount ( $\mu\text{g}$   $\text{g}^{-1}$  residue) of PO<sub>4</sub>-P released, and  $x$  is residue immersion time (s).

Phosphorus is often the nutrient limiting the growth of vegetation in ponds and lakes. Increasing phosphorus con-

centration usually results in increased growth of aquatic vegetation. Results from this study indicate that release of PO<sub>4</sub>-P from corn-stalk residues may contribute to P transport in surface runoff.

Corn-stalk residues, which contained an average of 168  $\mu\text{g}$  NO<sub>3</sub>-N  $\text{g}^{-1}$  residue, released NO<sub>3</sub>-N (table 2). However, the amount of NO<sub>3</sub>-N released, in general, was not significantly affected by the concentration of P and N in solution. For the solutions containing inorganic NO<sub>3</sub>-N and NH<sub>4</sub>-N, corn-stalk residues released 19 to 192  $\mu\text{g}$  NO<sub>3</sub>-N  $\text{g}^{-1}$  residue as stalk immersion time varied from 25 to 25000 s. The follow-

**Table 4. Change in nutrient content ( $\mu\text{g}$  nutrient in solution  $\text{g}^{-1}$  residue) of solution as affected by solution concentration and contact time with wheat residue.<sup>[a]</sup>**

Inorganic nutrient source		Measured Nutrient Constituent								
		PO <sub>4</sub> -P			NO <sub>3</sub> -N			NH <sub>4</sub> -N		
		PO <sub>4</sub> -P, NO <sub>3</sub> -N	PO <sub>4</sub> -P, NH <sub>4</sub> -N	PO <sub>4</sub> -P, NO <sub>3</sub> -N, NH <sub>4</sub> -N	NO <sub>3</sub> -N, PO <sub>4</sub> -P	NO <sub>3</sub> -N, NH <sub>4</sub> -N	NO <sub>3</sub> -N, PO <sub>4</sub> -P, NH <sub>4</sub> -N	NH <sub>4</sub> -N, PO <sub>4</sub> -P	NH <sub>4</sub> -N, NO <sub>3</sub> -N	NH <sub>4</sub> -N, PO <sub>4</sub> -P, NO <sub>3</sub> -N
Solution concentration ( $\mu\text{g}/\text{mL}$ ) <sup>[b]</sup>	0	64.9	64.9	64.9	10.8	10.8	10.8	39.0	39.0	39.0
	6	55.0 (0.25)	31.7 (0.01)	46.4 (0.03)	-11.2 (0.44)	45.7 (0.22)	-271 (0.01)	-18.4 (0.01)	-8.93 (0.01)	-43.6 (0.01)
	12	8.83 (0.01)	-22.6 (0.01)	32.2 (0.01)	31.3 (0.47)	26.5 (0.58)	-36.5 (0.10)	-82.6 (0.01)	-34.7 (0.01)	-43.6 (0.01)
	24	-56.7 (0.01)	119 (0.01)	95.9 (0.01)	-105 (0.01)	15.7 (0.86)	-77.3 (0.01)	-133 (0.01)	-158 (0.01)	-83.5 (0.01)
Contact time (s) <sup>[c]</sup>	25	-34.2	9.06	9.03	-13.9	4.55	-108	-56.8	-47.5	-48.8
	250	-15.6	31.3	31.6	-1.18	8.12	-83.8	-68.8	-75.5	-70.4
	2500	5.54	53.4	64.4	2.73	20.1	-80.4	-95.3	-113	-65.2
	25000	89.5	61.9	106	20.0	48.2	-77.0	-73.6	-70.0	-48.6
	86400	45.0	85.5	88.4	-101	42.7	-119	50.3	103	68.3

[a] The change in nutrient content was obtained by subtracting the final solution concentration from the initial concentration, multiplying the difference by the volume of solution, and dividing the result by the residue mass. Therefore, positive changes in nutrient content indicate release from the crop residue, while negative values represent adsorption.

[b] The values in parentheses represent the  $\text{Pr} > |t|$ .

[c] The values provided for a given contact time are mean measurements obtained for all solution concentrations.

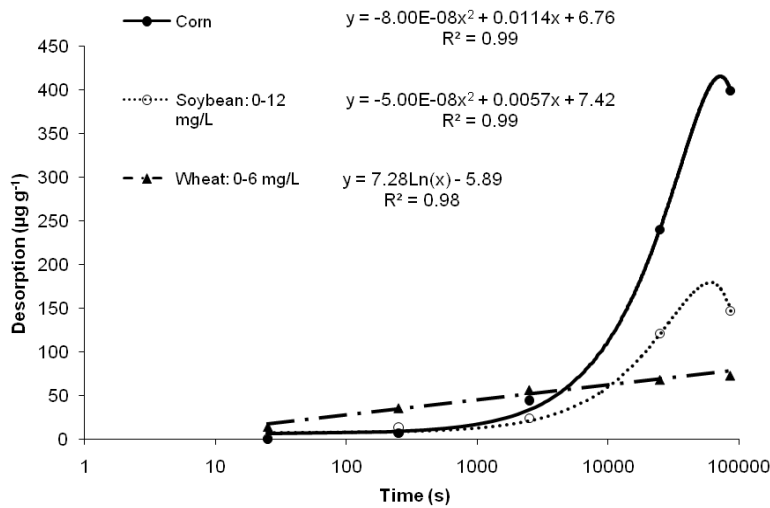


Figure 1. Release of  $\text{PO}_4\text{-P}$  by corn, soybean, and wheat stalks. Values shown for corn residue are mean measurements obtained for solution concentrations of 0, 6, 12, and 24  $\mu\text{g mL}^{-1}$ . For the soybean residue, mean values are reported for solution concentrations of 0, 6, and 12  $\mu\text{g mL}^{-1}$ . Mean values shown for wheat residue were obtained from solution concentrations of 0 and 6  $\mu\text{g mL}^{-1}$ .

ing equations can be used to estimate potential release of  $\text{NO}_3\text{-N}$  by corn-stalk residues (fig. 2):

$$y = -2.00\text{E-}08x^2 + 0.0032x + 37.0 \quad (R^2 = 0.92) \quad (0 \mu\text{g mL}^{-1}) \quad (2)$$

$$y = 23.2\text{Ln}(x) - 114 \quad (R^2 = 0.76) \quad (6 \text{ to } 24 \mu\text{g mL}^{-1}) \quad (3)$$

where  $y$  is the amount ( $\mu\text{g g}^{-1}$  residue) of  $\text{NO}_3\text{-N}$  released, and  $x$  is stalk immersion time (s). It was not possible to obtain a single regression equation with the desired degree of accuracy that could be used over all solution concentrations. Therefore, equations 2 and 3, which are applicable for selected concentrations, were derived from the experimental data.

Nitrate is the principal inorganic nitrogen form in waterbodies that are well aerated. Nitrate-N can be lost from surface waters due to denitrification when oxygen is depleted. Nitrogen loss in runoff can contribute to environmental degradation. Nitrate in runoff from fields receiving manure, compost, or fertilizer may be carried to rivers and lakes. The elevated nitrate level in the Gulf of Mexico may contribute

to the hypoxia condition, a zone depleted of oxygen and marine life (Burkart and James, 1999). Corn-stalk residues appear to have the potential to contribute to  $\text{NO}_3\text{-N}$  transport in surface runoff.

The quantity of  $\text{NO}_3\text{-N}$  released by corn-stalk residues did not consistently increase with residue immersion time (table 2). Wilhelm et al. (2005) found that the  $\text{NO}_3\text{-N}$  content of corn-stalk residues decreased linearly from the soil to the ear. Since the corn-stalk residues used in the experimental tests were obtained from different positions along the stalk, variations in the  $\text{NO}_3\text{-N}$  content of the residue materials would be expected among replicate tests. The variations in initial  $\text{NO}_3\text{-N}$  content among individual corn stalks elements may have caused differences in measurements among replicate treatments.

The corn-stalk residues contained an average of 405  $\mu\text{g NH}_4\text{-N g}^{-1}$  residue. When immersed in solutions containing inorganic  $\text{NH}_4\text{-N}$ , the corn-stalk residues released  $\text{NH}_4\text{-N}$  (table 2). The presence of inorganic  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  in solution significantly reduced the quantity of  $\text{NH}_4\text{-N}$  that was released from the corn stalks. For the solutions contain-

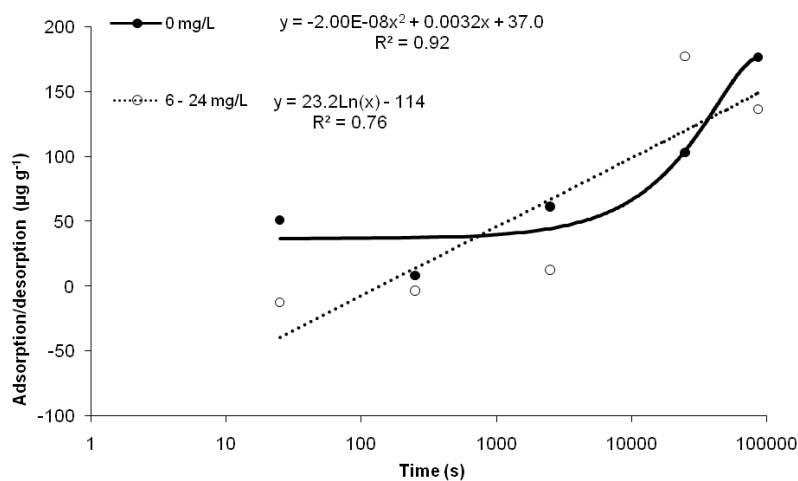
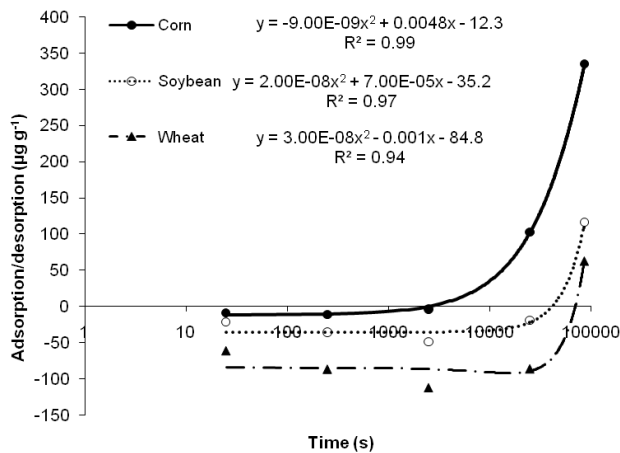


Figure 2. Adsorption and desorption of  $\text{NO}_3\text{-N}$  by corn stalks. Mean values are reported for solution concentrations of 0  $\mu\text{g mL}^{-1}$  and also 6, 12, and 24  $\mu\text{g mL}^{-1}$ .



**Figure 3.** Adsorption and desorption of  $\text{NH}_4\text{-N}$  by corn, soybean, and wheat stalks. Values shown are mean measurements obtained for solution concentrations of 0, 6, 12, and 24  $\mu\text{g mL}^{-1}$ .

ing inorganic  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ , the quantity of  $\text{NH}_4\text{-N}$  released from the corn stalks consistently increased from 4 to 362  $\mu\text{g g}^{-1}$  residue as stalk immersion time varied from 2500 to 86400 s. The following equation can be used to estimate potential adsorption and desorption of  $\text{NH}_4\text{-N}$  by corn-stalk residues (fig. 3):

$$y = -9.00\text{E-}09x^2 + 0.0048x - 12.3 \quad (R^2 = 0.99) \quad (4)$$

where  $y$  is the amount ( $\mu\text{g g}^{-1}$  residue) of  $\text{NH}_4\text{-N}$  released, and  $x$  is stalk immersion time (s).

Ammonium loss into surface waters can result in the poisoning of aquatic organisms if the concentration is  $>2.5 \text{ mg L}^{-1}$  (USEPA, 1986). In surface waters, ammonium may be converted to ammonia, which is also toxic to aquatic organisms. The rate at which ammonium is converted to ammonia is influenced by dissolved oxygen concentration, pH, and water temperature. Ammonium may also be converted to nitrate through the process of nitrification. Corn-stalk residues appear to have the potential to release substantial quantities of  $\text{NH}_4\text{-N}$ .

#### SOYBEAN-STALK RESIDUES

The soybean-stalk residues contained an average of 211  $\mu\text{g PO}_4\text{-P g}^{-1}$  residue. The mean quantity of  $\text{PO}_4\text{-P}$  released from the solutions containing inorganic  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  consistently increased from 14 to 157  $\mu\text{g PO}_4\text{-P g}^{-1}$  residue as stalk immersion time increased from 25 to 86400 s. Potential release of  $\text{PO}_4\text{-P}$  from soybean-stalk residues in solutions containing  $\text{PO}_4\text{-P}$  at concentrations varying from 0 to 12  $\mu\text{g mL}^{-1}$  can be estimated from the equation (fig. 1):

$$y = -5.00\text{E-}08x^2 + 0.0057x + 7.42 \quad (R^2 = 0.99) \quad (5)$$

where  $y$  is the amount ( $\mu\text{g g}^{-1}$  residue) of  $\text{PO}_4\text{-P}$  released, and  $x$  is stalk immersion time (s). Laboratory measurements obtained for  $\text{PO}_4\text{-P}$  concentrations of 24  $\mu\text{g mL}^{-1}$  were not included in equation 5 since a much better fit was provided if these data were omitted from the regression analyses. Including data from the largest concentration would have yielded a predictive equation covering a wider range of solution concentrations. However, the resulting equation did not provided the desired reliability.

Fertilizer is not usually applied to areas planted to soybean, so soil residual P is typically not a concern on soybean

acreage. However,  $\text{PO}_4\text{-P}$  released from soybean-stalk residues may contribute to P transport in runoff.

The 8  $\mu\text{g g}^{-1}$  residue of extractable  $\text{NO}_3\text{-N}$  contained in the soybean-stalk residues was substantially less than the other residue materials (table 1). The soybean-stalk residues immersed in solutions containing P and N either adsorbed or desorbed  $\text{NO}_3\text{-N}$  depending on initial solution concentration and contact time (table 3). Initial solution concentration did not significantly affect adsorption or desorption of  $\text{NO}_3\text{-N}$  by the soybean-stalk residues.

Since soybean is a legume, soil N in general is not needed to support plant growth. The quantity of  $\text{NO}_3\text{-N}$  that is accumulated in the soybean residue is minimal. Therefore, the presence of soybean-stalk residues is expected to have a minimal impact on  $\text{NO}_3\text{-N}$  transport in runoff.

The soybean-stalk residues, which contained an average of 85  $\mu\text{g NH}_4\text{-N g}^{-1}$  residue, either adsorbed or desorbed  $\text{NH}_4\text{-N}$  depending on solution concentration and stalk immersion time (table 3). Soybean-stalk residues placed in solutions containing inorganic  $\text{NH}_4\text{-N}$  adsorbed  $\text{NH}_4\text{-N}$  at stalk immersion times varying from 25 to 2500 s. The following equation can be used to estimate potential adsorption and desorption of  $\text{NH}_4\text{-N}$  by soybean-stalk residues (fig. 3):

$$y = 2.00\text{E-}08x^2 + 7.00\text{E-}05x - 35.2 \quad (R^2 = 0.97) \quad (6)$$

where  $y$  is the amount ( $\mu\text{g g}^{-1}$  residue) of  $\text{NH}_4\text{-N}$  released, and  $x$  is stalk immersion time (s). Soybean-stalk residues appear to have the potential to adsorb relatively small amounts of  $\text{NH}_4\text{-N}$  transported in runoff.

#### WHEAT-STALK RESIDUES

Wheat-stalk residues contained an average of 178  $\mu\text{g PO}_4\text{-P g}^{-1}$  residue (table 1). The quantity of  $\text{PO}_4\text{-P}$  adsorbed by wheat-stalk residues was generally minimal (table 4). Wheat-stalk residues immersed in solutions containing  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  released 9 to 86  $\mu\text{g PO}_4\text{-P g}^{-1}$  residue as stalk immersion time increased from 25 to 86400 s. The following equation can be used to estimate potential release of  $\text{PO}_4\text{-P}$  from wheat-stalk residues in solutions containing nutrient concentrations varying from 0 to 6  $\mu\text{g mL}^{-1}$  (fig. 1):

$$y = 7.28 \text{Ln}(x) - 5.89 \quad (R^2 = 0.98) \quad (7)$$

where  $y$  is the amount ( $\mu\text{g g}^{-1}$  residue) of  $\text{PO}_4\text{-P}$  released, and  $x$  is stalk immersion time (s). Measurements from the other solution concentrations were omitted from the final regression analyses. It was not possible to obtain a reliable predictive equation using data from the larger solution concentrations because of the relatively large scatter in the experimental data. Following harvest, areas planted to wheat appear to have the potential to contribute to P transport by runoff.

The wheat-stalk residues used in this study contained 35  $\mu\text{g g}^{-1}$  residue of extractable  $\text{NO}_3\text{-N}$ , which is relatively small. The type of inorganic constituent in solution, solution concentration, and contact time influenced the quantity of  $\text{NO}_3\text{-N}$  adsorbed or desorbed by wheat-stalk residues (table 4). For solutions containing inorganic  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ , the quantity of  $\text{NO}_3\text{-N}$  that was released from the wheat-stalk residues consistently increased from 5 to 48  $\mu\text{g g}^{-1}$  residue as stalk immersion time varied from 25 to 86400 s.

The potential for wheat-stalk residues to increase the  $\text{NO}_3\text{-N}$  content of runoff is minimal because of the relatively

small amount of  $\text{NO}_3\text{-N}$  contained in the wheat-stalk residues. However, wheat-stalk residues appear to have the ability to adsorb  $\text{NO}_3\text{-N}$  transported in runoff.

The wheat-stalk residues contained an average of  $49 \mu\text{g NH}_4\text{-N g}^{-1}$  residue. When immersed in solutions containing inorganic  $\text{NH}_4\text{-N}$ , wheat-stalk residues adsorbed significant amounts of  $\text{NH}_4\text{-N}$  (table 4). The quantity of  $\text{NH}_4\text{-N}$  that was adsorbed generally increased as the concentration of inorganic  $\text{NH}_4\text{-N}$  in solution became greater. As an example, for the solutions containing inorganic  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$ , wheat-stalk residues adsorbed 9 to  $158 \mu\text{g g}^{-1}$  residue as initial solution concentration varied from 6 to  $24 \mu\text{g mL}^{-1}$ . The following equation can be used to estimate potential adsorption and desorption of  $\text{NH}_4\text{-N}$  by wheat-stalk residues (fig. 3):

$$y = 3.00\text{E-}08x^2 - 0.001x - 84.8 \quad (r^2 = 0.94) \quad (8)$$

where  $y$  is the amount ( $\mu\text{g g}^{-1}$  residue) of  $\text{NH}_4\text{-N}$  adsorbed or desorbed, and  $x$  is stalk immersion time (s).

Wheat could be planted as a buffer strip at the bottom of a hillslope to adsorb  $\text{NH}_4\text{-N}$  transported in runoff, much as a permeable reactive barrier (PRB) is used to treat groundwater (Roehl et al., 2005). A PRB is an emplacement of reactive media in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation goals down gradient of the barrier. One of the reactive processes that occurs within a PRB to remediate inorganic contaminants from groundwater is sorption or ion exchange (Naftz et al., 2002).

Winter wheat is harvested several months before corn and soybeans. Therefore, a buffer strip containing recently harvested wheat-stalk residues could potentially adsorb  $\text{NH}_4\text{-N}$  transported in runoff from upslope cropland areas. Nutrients adsorbed by the buffer strip should be utilized by the succeeding crop and removed during harvest to prevent excess accumulation of P and N.

#### COMPARISON TO FIELD CONDITIONS

Eghball and Gilley (1999) conducted a rainfall simulation study on a no-till site near Lincoln, Nebraska, that had a wheat residue cover of 65%. A wheat residue mass of approximately  $2.1 \times 10^3 \text{ kg ha}^{-1}$  was estimated for the study site using equations presented by Gregory (1982). Wheat residue was able to adsorb an average of  $71 \mu\text{g PO}_4\text{-P g}^{-1}$  residue over a 4 min period in the present study. Therefore, approximately  $0.15 \text{ kg ha}^{-1}$  of  $\text{PO}_4\text{-P}$  could be adsorbed over a 4 min period on a site with a wheat residue cover of 65%. During the second rainfall simulation run, Eghball et al. (2000) measured a total  $\text{PO}_4\text{-P}$  load of  $0.31 \text{ kg ha}^{-1}$  over a 60 min period on plots without a grass hedge where beef cattle manure had been applied at a rate required to meet corn N requirements. Thus, using values obtained in this investigation, wheat stalks appear to have the potential to adsorb approximately half of the  $\text{PO}_4\text{-P}$  transported in runoff over a 60 min period from a site on which beef cattle manure was recently added. The total adsorption capacity of wheat residue is not known.

Under field conditions, crop residue materials can adsorb or desorb P and N because of the interaction with rainfall (either neutral or acid) or surface runoff. Overland flow is a mixture of both liquid and solid phases. In this laboratory study, only the conditions relating to the liquid phase of surface runoff were examined.

Gilley and Kottwitz (1994) conducted a study to identify maximum surface storage provided by crop residue. They found that the cumulative volume of water stored in small ponds created by crop residue could be substantial. As an example, 2.67 cm residue elements (the approximate size of corn stalks) covering 10% to 30% of a surface with a 1% slope could provide a surface storage depth greater than 2 cm.

#### COMPARISON WITH PREVIOUS RESULTS

Adsorption and desorption of N and P from corn, soybean, and winter wheat stalk residues placed in solutions containing a single P or N constituent were examined by Cermak et al. (2004). Cermak et al. (2004) reported that corn and soybean stalks residues consistently released more  $\text{PO}_4\text{-P}$  as stalk immersion time became greater, and similar results were obtained in this study for solutions containing inorganic  $\text{PO}_4\text{-P}$  and one or more N constituents. Cermak et al. (2004) also found that the wheat-stalk residues used in their study adsorbed an average of  $35 \mu\text{g NH}_4\text{-N g}^{-1}$  residue for immersion times varying from 25 to 2500 s. In our investigation, wheat-stalk residues immersed in solutions containing both inorganic  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  adsorbed  $79 \mu\text{g NH}_4\text{-N g}^{-1}$  residue for the same three residue immersion periods.

#### CONCLUSIONS

This study shows that residue immersion in temporary ponds can influence adsorption and desorption of P and N transported in runoff. Corn-stalk residues released  $\text{PO}_4\text{-P}$ , and the quantity of  $\text{PO}_4\text{-P}$  released consistently increased as stalk immersion time increased from 2500 to 86400 s. The presence of inorganic  $\text{NO}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  in solution significantly reduced the quantity of  $\text{PO}_4\text{-P}$  that was released from the corn-stalk residues. However, the amount of  $\text{PO}_4\text{-P}$  released was generally not significantly influenced by the presence of  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$ , or  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ , and  $\text{PO}_4\text{-P}$  in solution. Corn-stalk residues released  $\text{NO}_3\text{-N}$ , but the amount of  $\text{NO}_3\text{-N}$  that was released, in general, was not significantly affected by the concentration of P and N in solution. The quantity of  $\text{NH}_4\text{-N}$  released from immersed corn-stalk residues was significantly affected by the presence of  $\text{NO}_3\text{-N}$  and  $\text{PO}_4\text{-P}$  in solution.

The mean quantity of  $\text{PO}_4\text{-P}$  released by soybean-stalk residues placed in solutions containing inorganic  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  consistently increased from 14 to  $157 \mu\text{g PO}_4\text{-P g}^{-1}$  residue as stalk immersion time increased from 25 to 86400 s. Initial solution concentration did not significantly affect adsorption or desorption of  $\text{NO}_3\text{-N}$  by the soybean-stalk residues. Soybean-stalk residues placed in solutions containing inorganic  $\text{NH}_4\text{-N}$  adsorbed  $\text{NH}_4\text{-N}$  at stalk immersion times varying from 25 to 2500 s.

Wheat-stalk residues placed in solutions containing  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  released 9 to  $86 \mu\text{g PO}_4\text{-P g}^{-1}$  residue as stalk immersion time increased from 25 to 86400 s. The type of inorganic constituent in solution, solution concentration, and contact time influenced the quantity of  $\text{NO}_3\text{-N}$  adsorbed or desorbed by wheat-stalk residues. Wheat-stalk residues adsorbed significant amounts of  $\text{NH}_4\text{-N}$ , and the quantity that was adsorbed generally increased as the concentration of inorganic  $\text{NH}_4\text{-N}$  in solution became greater.

Solution concentration and residue immersion time can affect P and N concentrations of solutions in which stalks are



immersed. Residue adsorption and desorption characteristics can be significantly different if more than one nutrient constituent is present in solution. Cropping and management practices should be adopted that reduce nutrient concentrations in runoff without negatively impacting groundwater quality.

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