

**FATE AND TRANSPORT OF AGRICULTURAL NUTRIENTS IN MACRO-POROUS  
SOILS**

A Thesis

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Master of Science

By

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## ABSTRACT

The major objective of this study is to address water quality problems associated with application of liquid manure to subsurface-drained agricultural lands. There are over 600 large and medium sized confined animal feeding operations (CAFOs) in New York, most of which utilize land application to manage this waste stream. Due to the regions shallow soil and humid weather, most fields have been equipped with tile drainage. The concern is that handling the manure in a liquefied state may enhance the likelihood of contamination of the tile drainage discharge and its potential impacts on downstream water quality. Laboratory studies were used to investigate how manure liquidity (percent solids) affects the transport of manure constituents through the soil. Soil columns were constructed, subjected to simulated rainfall. Effluent samples were analyzed for soluble reactive phosphorus (SRP). As expected, results show enhanced SRP transport through macropores with decreasing percent solids (i.e., more liquidy manure).

## BIOGRAPHICAL SKETCH

Alisa Royem was born in Southwestern Colorado, where she fostered an appreciation for rivers, mountains, and the outdoors. At a young age she fell in love with rivers and today is motivated to study the quality and quantity of water in the face of climate change. Alisa graduated from Fort Lewis College in 2006 with a liberal arts degree in Environmental Biology.

Alisa's experiences growing up motivated her to gain a more technical and formal education regarding water resources. As such, she worked as a water technician at the Institute of Arctic and Alpine Research (INSTAAR) at University of Colorado, Boulder where she was inspired to apply to graduate school.

Alisa moved away from her home state in 2009 to start a Master's of Science degree at Cornell University. While living in the water rich state of New York, she furthered her passion for water resources by learning to kayak. Today she can be found on rivers around the world where she spreads her knowledge and love for water resources and continues to study issues surrounding the quantity and quality of the world's waters.

## ACKNOWLEDGMENTS

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## TABLE OF CONTENTS

	TITLE	Page no.
	BIOGRAPHICAL SKETCH .....	iii
	ACKNOWLEDGMENTS .....	iv
	TABLE OF CONTENTS .....	v
	LIST OF FIGURES .....	vi
	LIST OF TABLES .....	vii
CHAPTER 1:	INTRODUCTION .....	1
CHAPTER 2:	EXPERIMENTAL METHODS .....	5
	<i>Column Preparation</i> .....	7
	<i>P-Application Treatments</i> .....	8
	<i>Experimental Set-Up</i> .....	8
CHAPTER 3:	RESULTS .....	9
	<i>Water Application and Collection Volumes</i> .....	11
	<i>SRP Loads and Concentrations</i> .....	13
CHAPTER 4:	DISCUSSION .....	24
CHAPTER 5:	CONCLUSIONS .....	27
REFERENCES:	.....	28
APPENDIX 1:	<i>Deviations from initial experiment design</i> <i>and sampling period.</i> .....	34
APPENDIX 2:	<i>Auxiliary Macropore Information</i> .....	37

## LIST OF FIGURES

### LIST OF FIGURES

Figure 1: Soil column design	p. 8
Figure 2: Cumulative sprinkler volume vs. Cumulative sample collection volume	p. 11
Figure 3: Total Water Effluent Collection by Macropore size class and Matrix vs Macropore Collection Site	p. 12
Figure 4: Total water collection by Macropore size and Topical Treatment	p. 13
Figure 5: Flow weighted mean of SRP by Macropore size class and Topical Treatment	p. 15
Figure 6: Mean Total P by Macropore size class and Topical Treatment	p. 16
Figure 7: Mean SRP Loads Macropore size class and Topical Treatment	p. 18
Figure 8: SRP Loads vs. Cumulative sample collection volume	p. 20
Figure 9: Phosphorus percent recovery by Macropore size class and Topical Treatment	p. 22
Figure 10: Phosphorus percent recovery by Macropore size class and Topical Treatment	p. 23

## LIST OF TABLES

Table 1: Available P through Morgan's analysis (mg/ Kg) by field soil horizon.	p. 6
Table 2: Available Morgan's Soil analysis of composite column samples (the top 70 cm were mixed).	p. 6



## CHAPTER 1

### INTRODUCTION

Phosphorus (P) is an essential element for plant growth but in many regions the continual application of fertilizers and manure has built-up soil P levels that often exceed crop needs (Sharpley et al., 1996). Elevated levels of P are usually the primary nutrient driving eutrophication in freshwater aquatic ecosystems and there are numerous examples of water-quality impairment associated with nonpoint source P pollution from animal operations and agricultural practices (Borsch et al., 2001; Carpenter et al. 1998; Daniel et al., 1994, 1998; Parry, 1998; USGS, 1999; Vollenweider, 1968). Shallow soils and tile drained fields, prevalent in the Upstate NY, make this an ever pressing concern as small farm operations are giving way to CAFOs and massive cattle lots (Nehring et al., 2009). Concern over agriculture's role in accelerating eutrophication of freshwaters and estuaries have prompted federal and state nutrient management regulations guiding land application of livestock manure (Sims and Kleinman, 2005). Excess P in association with eutrophication has been identified by the U.S. Environmental Protection Agency (EPA) as the greatest impediment to achieving water quality goals stated in the Clean Water Act (David and Gentry, 2000). Intensive livestock production has been identified as a primary source of P in surface waters (USGS, 1999). Vidon and Cuadra (2011) recently stated that, "Phosphorus is a contaminant of national importance and it is crucial to thoroughly understand the process regulation P transport." Dils and Heathwaite (1999) found that field drains were effective conduits for P export from agricultural catchments and henceforth, called for further study on surface and subsurface transport pathways in order to develop effective mitigation practices for P loss from diffuse agricultural sources.

Dairy farming is the largest agricultural industry in New York State (NYS), providing

over fifty percent of NY's agricultural income (DiNapoli, 2010). As of 2009, the state had around 5,500 dairy farms with almost 619,000 milking cows, making NY the third largest dairy state in America (NYS Department of Agriculture and Markets Division of Milk Control and Dairy Services, 2010). However, a better understanding of liquid manure flow processes to tile drains and how manure contaminants can be managed and controlled on the subsurface is essential to water quality management and not well understood. Several studies have focused on P contamination of surface waterways via surface runoff and erosion (Sharpley et al., 1994; Sharpley, 1995; Hawkins and Scholefield, 1996; Eghball and Gilley, 1999; Gburek et al., 2000), but a better understanding of subsurface P transport is needed to determine how controlled drainage may impact water quality risks and guide better manure application management decisions.

Flow through macropores has been shown to affect the chemical quality of effluent (Buttle and Leigh, 1996; Villholth et al., 1998; Shipitalo et al., 2000; Kohler et al., 2001, Geohring et al., 2001). There are several consequences of macropore flow including, but not limited to: 1) recharge of the ground water before the soil reaches field capacity; 2) movement of some of the chemicals applied at the soil surface to greater depth than predicted by Darcian flow; and 3) Leaching of applied chemicals from smaller pores to the surface of macropores (Cullum, 2009). Macroporous soils in tile drained fields are of great concern as research suggests that nutrients, pesticides, and bacteria transport from the soil surface to tile-drains via soil macropores is likely an important transfer mechanism in artificially drained soils (Shalit and Steenhuis, 1996; Kladvko et al., 1999; Geohring et al., 2001; Stone and Wilson, 2006).

Although macropores are a small proportion of soil volume, usually comprising less than

5% of the soil porosity, constructed biologically or artificially, they are significant pathways for water and solute movement (Stone and Wilson, 2006; Vidon and Cuadra, 2010). Surface water contributions to P in waterways have been extensively studied, however even though macropores are understood to be major pathways for P losses (e.g. German and Beven, 1985, 1986; Chen and Wagenet, 1992; Stammet al., 1998; Djodjic et al., 1999; Simard et al., 2000), most models and experiments have focused on the processes describing P losses via surface runoff and erosion. Only recently have researchers begun to directly quantify the relative importance of macropore flow verses matrix flow on tile drained fields of the Mid-west and none have been conducted on the fields of Upstate NY.

Best Management Practices (BMP) were borne from the need to address water quality problems associated with agricultural nonpoint sources (NPS) pollution of streams, lakes, and estuaries (Loehr et al., 1979, Puckett, 1995; Ehkolm et al., 2000; Shrpley et al., 2001; Andraski and Bundy, 2003; DeLaune et al., 2004), where “best” implies improving water quality without decreasing productivity (Walter et al., 1979). Subsurface tile drains were established in an attempt to improve water quality by altering farm hydrology in order to reduce surface runoff through contaminant loading by attempting to control hydrologic processes (Scott, 1998). While the installation of tile drains may improve hydrologic conditions on the field, the installation of tile drains as a water quality BMP may not be advisable particularly where shallow soils result in decreased infiltration rates and potentially rapid contaminant delivery (Schoot, 1998).

In the past three decades there has been an increased awareness of the impact of land management activities on the quality of surface water and ground water resources. While, livestock and poultry manure can provide valuable organic material and nutrients for crop and

pasture growth, the nutrients can degrade environmental quality if they enter water bodies in excessive amounts. There is growing concern about the large amounts of manure-nutrients being generated by large animal feeding operations and the potential for some of the nutrients to enter water resources and impair water quality. There are over 600 large and medium sized confined animal feed operations (CAFO's) in NY, many of which apply their manure to tile drained fields. In light of this, the major objective of this research is to address water quality problems associated with application of liquid manure to subsurface drained lands associated with CAFOs.

This study attempts to better understand manure liquidity and its subsequent effluent SRP concentration in order to elucidate manure interactions in an attempt to better manage manure waste from CAFOs and large animal feed lots.

## CHAPTER 2

### EXPERIMENTAL METHODS

Soil column experiments were conducted to determine differences in effluent phosphorus (P) under three different P-application treatments (inorganic fertilizer ( $P_2O_5$ )), manure at 3.5% solids, and manure at 7% solids; control = tap water) and three degrees of macroporosity (3 mm macropore, 1 mm macropore, and no macropore). The macropore sizes were chosen based on research findings reported in the literature that suggested macropores 2 mm in diameter are a threshold for significant macropore flow (Kirkby, 1988; Digman, 1993); i.e., we chose macropore diameters slightly larger and slightly lower than this reported threshold. We also recognize that this threshold depends on the matrix soil particle or aggregate sizes. The soil used in this study was sieved to have a maximum size class of 5 mm and, depending on the assumed distribution of soil particles sizes, should have a minimum critical pore diameter on the order of 1 mm to allow matrix bypass flow according to Buttle and Leigh (1997).

**Column Preparation:** Experiments were conducted on dry-packed soil in twenty-four 30 cm high polyvinyl chloride (PVC) columns with a diameter of 10 cm. Three types of soil columns were constructed: two with macropores (1 mm and 3 mm diameter) and one with no macropore.

The soil used in these experiments was an Odessa silt loam, a Fine, illitic, mesic Aeric Endoaqualfs (5-10% sand, 50-60% silt, and 30-40% clay) obtained from the top 70 cm of a field on a cooperating farm 15 miles north of Union Springs, NY one week prior to the experiment. Topsoil was collected from site and dried using the soil dryer set to 100 degrees. The soils were analyzed at the Cornell Nutrient Analysis Lab for a variety of relevant constituents and

properties (Tables 1 and 2). A test of Morgan's Available P (mg/kg) by depth indicate a large decline of SRP by vertical distance in soils heavily fertilized with P. Levels by depth found in the literature have similar vertical profiles due high application rates of fertilizers and soil water mixing. A 2008 study done by Soldat and others, found that Morgan's level P in upstate NY ranged from 73, 40 and 15 mg P/ kg when averages by depth of 0-2 cm, 0-5 cm, and 0-15 cm respectively. We found similar average levels by depth, 83, 4 and 1.25 mg P/kg by depth of 0-8 cm, 8-30 cm, and 30-60 cm respectively, table 1.

Columns were prepared with 1500 kg of soil and 1500 kg of quartz sand and mixed together by hand and packed into columns to a bulk density of 1.2 g/cc. Column walls were roughened by sanding to diminish soil separating from the walls during shrinking. Duplicate soil columns were made to run experiments with 3, 1, 0 mm macropores for the two P-applications and tap water treatments.

Table 1. Available P through Morgan's analysis (mg/Kg) by field soil horizon.

<b>Field Soil Depth (cm)</b>	<b>Average P (mg/Kg)</b>
<b>0 - 8</b>	83
<b>8 - 30</b>	4
<b>30 - 60</b>	1.25

Table 2. Available Morgan's Soil analysis of composite column samples (the top 70 cm were mixed).

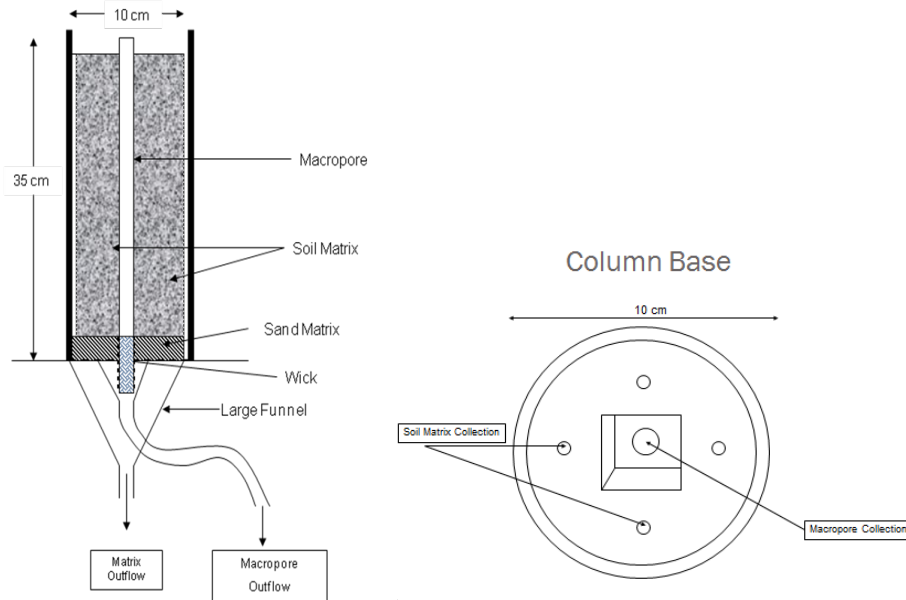
<b>Soils Sample</b>	<b>Available Morgan's P mg/Kg</b>	<b>Available Morgan's Fe mg/Kg</b>	<b>Available Morgan's Al mg/Kg</b>	<b>Available Morgan's Mn mg/Kg</b>	<b>Water pH</b>	<b>Organic Matter %</b>	<b>Total Carbon %</b>	<b>C/N Ratio</b>
A	3	1.5	9	6	7.3	2.8	1.62	10.8
B	3.5	1.5	9.5	5.5	7.4	2.7	1.64	10.9
C	3	2	10	8	7.4	2.7	1.63	10.9
Columns Average	<b>3.17</b>	<b>1.67</b>	<b>9.5</b>	<b>6.5</b>	<b>7.37</b>	<b>2.73</b>	<b>1.63</b>	<b>10.9</b>

Macropores were constructed by inserting 1 and 3 mm dowels into the columns while they were being filled and removing the dowels immediately before initiating the experiments.

The base of each column was fitted with a screen and filled 2 cm high with sand (0.8-0.12 mm). The base of the column was capped and drilled with four 8 mm diameter hole spaced equally around the periphery of the column in order to drain the matrix. A central hole was drilled as the macropore outlet and fitted with a fiberglass wick (15 mm diameter) to collect macropore effluent. The central hole was included in all columns even if there was no macropore in the soil. The fiberglass wicks were rinsed with distilled water to remove any potential P in the wicks (Seltzer, 1999).

A flexible plastic tube was fit snugly into the macropore center hole to collect the macropore sample. A funnel was taped to the bottom of the column and directed into a collection bottle to collect a matrix sample. Samples were collected when collection tubes reached 25 mL.

Soil columns were soaked in tap water for 24 hours. Wetting was from the bottom-up by placing them in plastic tubs and increasing the water depth 5 cm/hour. Columns were drained for 24 hours to emulate soil conditions at field capacity and preservation of macropore construction. The dowel used to create the macropore was removed; P-treatments were applied to the top of the columns.



**Figure 1.** Soil Column Design

**P-APPLICATION TREATMENTS:** Liquid manure was collected from a local dairy farm lagoon and immediately analyzed for total Nitrogen (N), P, potassium (K), and percent solids content. The samples were refrigerated (4°C) until experiments commenced. Percent solids were 7%. Half of the manure was diluted with tap water for an application treatment of 3.5% solids. An inorganic-P ( $P_2O_5$ ) application treatment was prepared by dissolving 0.096 grams industrial fertilizer. Each treatment type was applied to the top of each column to represent an application rate of 5,000 gal/acre. A control treatment consisted of tap water with no additives.

**Experimental Set-Up:** The experiment was conducted in the Soil and Water Laboratory at Cornell University where the ambient temperature ranged from 20 to 30 °C.

All columns were positioned equidistant from a Pulsator APLT-2-20 sprinkler manufactured by Wade Rain within a circular radius of 2 meters (m). The sprinkler was adjusted



to deliver average rain intensity of 0.5 mm/hr representative of a low intensity storm event characteristic of the region events. Total average water applied to each column was 52 mm.

Leachate was collected in two 50 mL plastic Nalgene vials from each column: one was intended to collect macropore leachate and other matrix leachate. The same sample vials were used for the entirety of the experiment and rinsed after collection with tap water. Water volumes were recorded every hour for the first week of application, after which collection volumes were recorded at least two times per day and ultimately one time per day by the end of the experiment. Samples were collected for analysis when enough effluent was accumulated (at least 10 ml) or when the vial was full. Because of variability among columns' hydraulics, samples were collected at varying intervals depending upon the collection volume of effluent from columns. Samples were filtered within 24 hours of collection using vacuum filtration through a 0.45  $\mu\text{m}$  membrane filter. Samples were acidified for preservation by adding 200  $\mu\text{L}$  of concentrated HCl to each vial and tested with electronic pH recorded to assure pH below 2.0; samples were then refrigerated at 4°C until they could be analyzed for P.

When collection was unable to be supervised the sprinkler was turned off and the columns were covered with a plastic top to eliminate evaporation and loss of soil moisture. Over the sampling period of 21 days the columns were covered for 14 periods of 12 hours. Samples were analyzed for inorganic P, referred to here as soluble reactive phosphorus (SRP), using ascorbic-acid reduction on an OI Analytical FS-3000 flow injection autoanalyzer. Total P soluble was analyzed using Inductively-Coupled Plasma Mass Spectrometry (ICP). The detection limits for these were 0.023 ppm and 0.046 ppm, respectively. Dissolved organic P was calculated as the difference between total soluble P and SRP.

## CHAPTER 3

### RESULTS

#### WATER APPLICATION AND COLLECTION VOLUMES

Our study found that more total effluent water collection occurred through columns constructed with macropores; but there was not a significant difference between the amount of water collected from the columns without macropores and columns constructed with macropores (figure 3). Columns with 1 mm macropores on average produced more effluent than the other column types (figure 3). Inspection of columns indicated no visual collapse at the macropore surface, but these results possibly indicate an internal collapse of the 3 mm macropore structure within the column. Column water collection volumes by treatment type (figure 4) have no statistical differences, but possibly indicate a clogging of the macropore by the manure with higher percent solids. It is also possible that our sprinkler intensity was too low to initiate substantial flow through the macropores; i.e., maximum flow is obtained under ponding conditions with macropores connecting to the surface (Czapar, et al., 1992; Jacobsen et al., 1997). Under ponded conditions, more than 70% of the total water moving through soil is typically transmitted through these large pores that represent less than 1% of the soil volume (Watson and Luxmore, 1986).

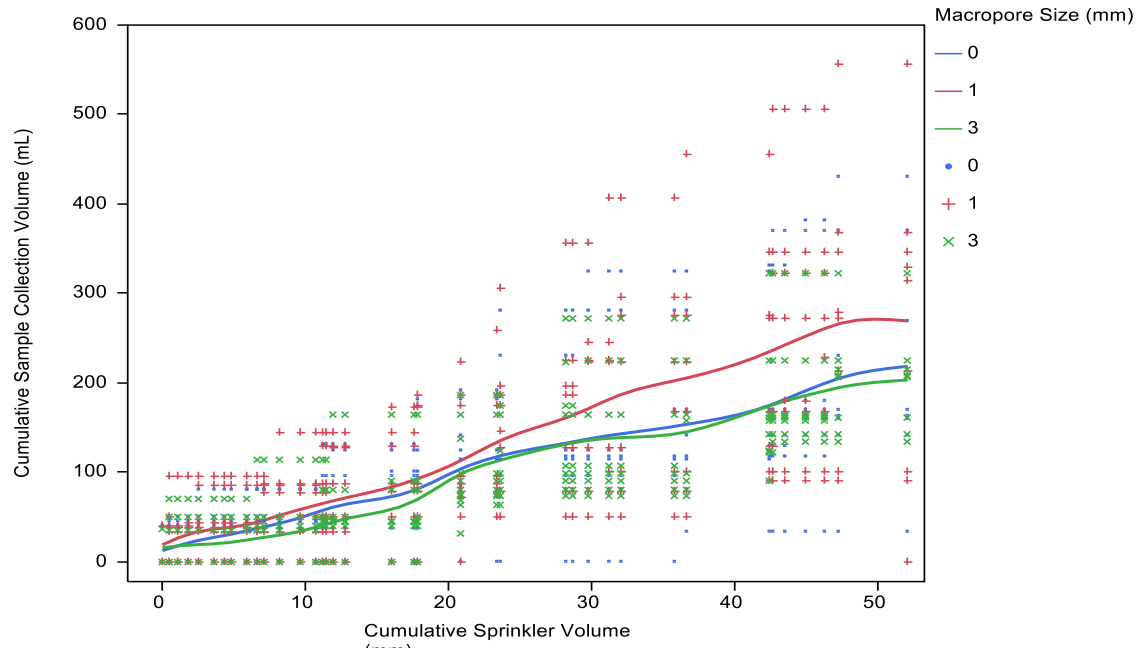


Figure 2. Cumulative water collected (mL) from each column as a function of cumulative sprinkler volume. Data points are cumulative data points for each column, lines are the averages for each column type. Blue dots represent discrete water collection samples from columns without macropores. Red crosses are representative to discrete water collection samples from columns constructed with one mm macropores. Green x's indicate the water collection samples from columns constructed with 3 mm macropores.

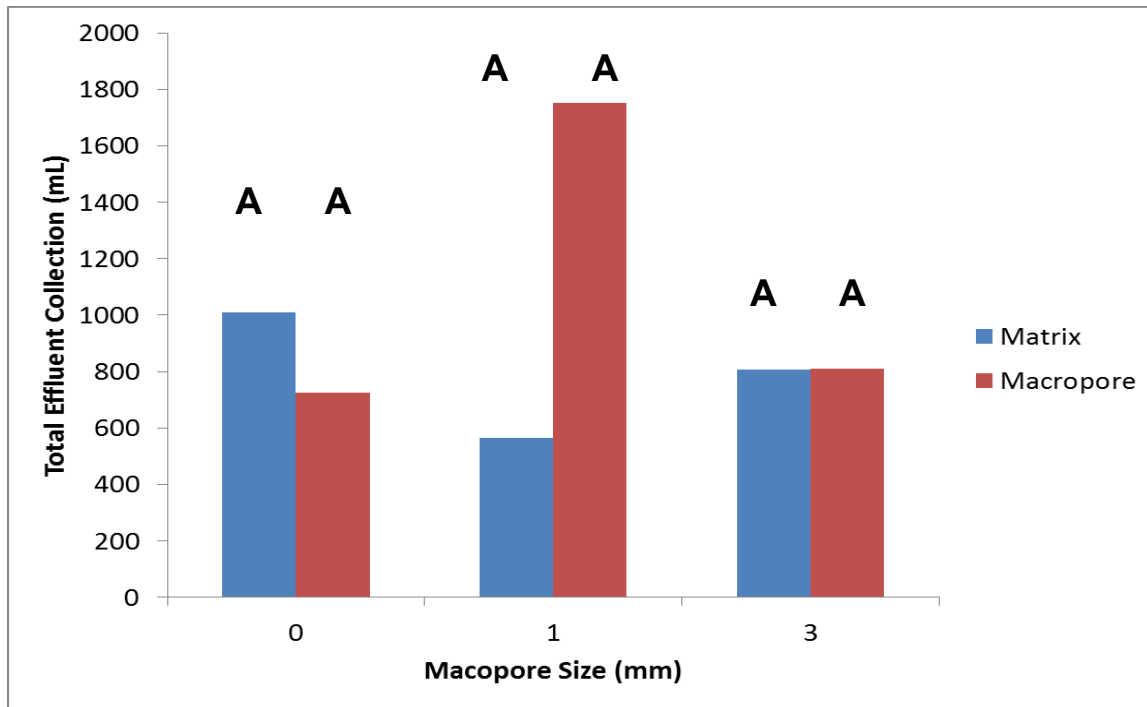


Figure 3. Total Water Collection (mL) from columns separated by macropore or matrix collection site. Blue Columns indicate matrix collection sites. Red columns indicate macopore collection site. Note that control columns, constructed without macropores, had a sample collection from the center of the collection tube. Total collection volume (mL) analyzed by macropore size and collection site through statistical ANOVAs. Levels not connected by the same letter are significantly different at the .05 level.

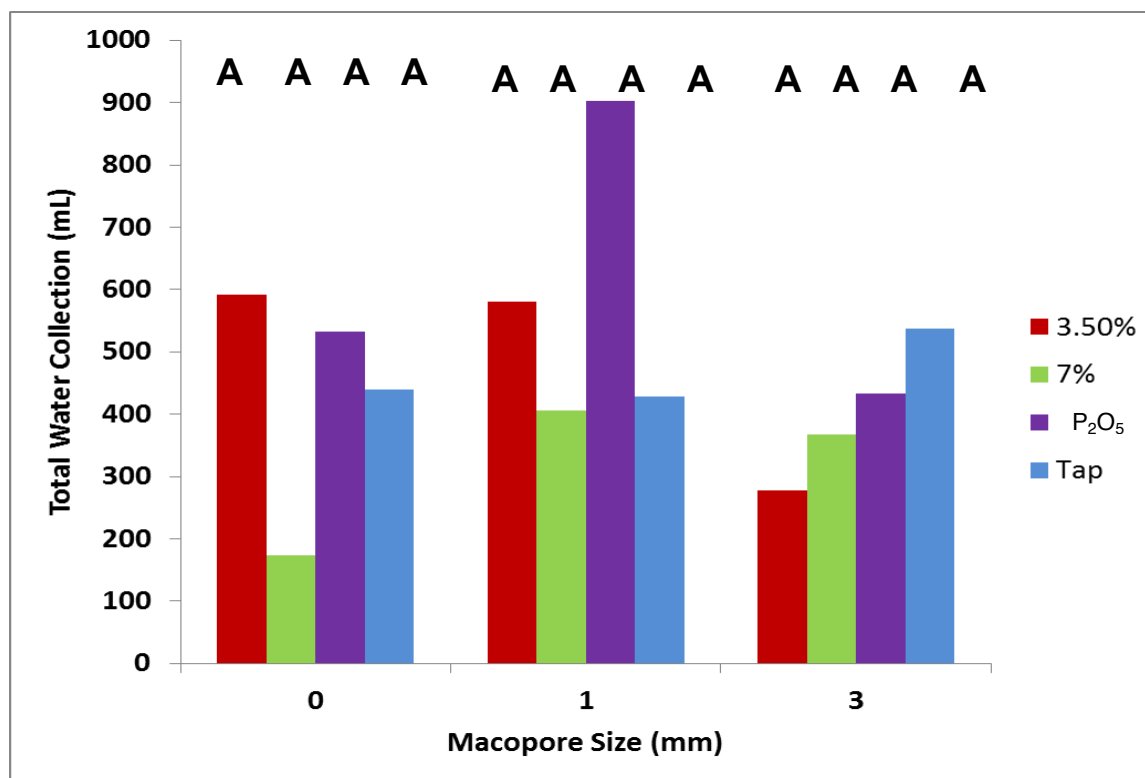


Figure 4. Bar graph of average total water accumulation (mL) from each column by macropore size classification and treatment type. Total collection volume (mL) analyzed by treatment type and macropore interaction through statistical ANOVAs. Letters represent columns grouped by macropore size class and analyzed by ANOVA's. Levels not connected by the same letter are significantly different at the .05 level defined by Least Squared Means Differences Tukey's analysis. Red bars represent the duplicate columns average of SRP loads (SRP (mg/L) by sample volume (mL)) treated with 3.5% solids manure broken apart by column macropore size class. Green bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with 7% solids manure analyzed by macropore size class. Purple bars represent the duplicate columns average of SRP loads (SRP (mg/L) by sample volume (mL) treated with P<sub>2</sub>O<sub>5</sub> inorganic treatment water broken apart by column macropore size class. Blue bars represent the duplicate columns average of SRP loads (SRP (mL) by sample volume (mL)) treated with tap water broken apart by column macropore size class.

## SRP LOADS AND CONCENTRATIONS

Comparison among the treatment types, by analysis of a Least Squared Means Differences Tukey's test show a statistical difference among columns with 3 mm macropores with higher concentrations for the 3.5% manure treatment relative to the 7% manure-solids and tap water; the  $P_2O_5$  treatment was notably higher than the 7% solids and tap water and similar to the 3.5% solids, but not significantly different than any of the treatments (Figure 4). We expected that the highest levels of P would be from columns treated with  $P_2O_5$ , due to its soluble form, but, although not statistically significant, the 3.5% solids had the highest average SRPP concentrations and a wider range of variance. As expected, the  $P_2O_5$  and 3.5% solids treatments consistently produced the highest average SRP effluent concentrations within each macropore-set, although there were no statistical differences observed. Indeed, there were no differences between any treatment types of columns with no macopores or 1 mm macropores regarding SRP concentrations.

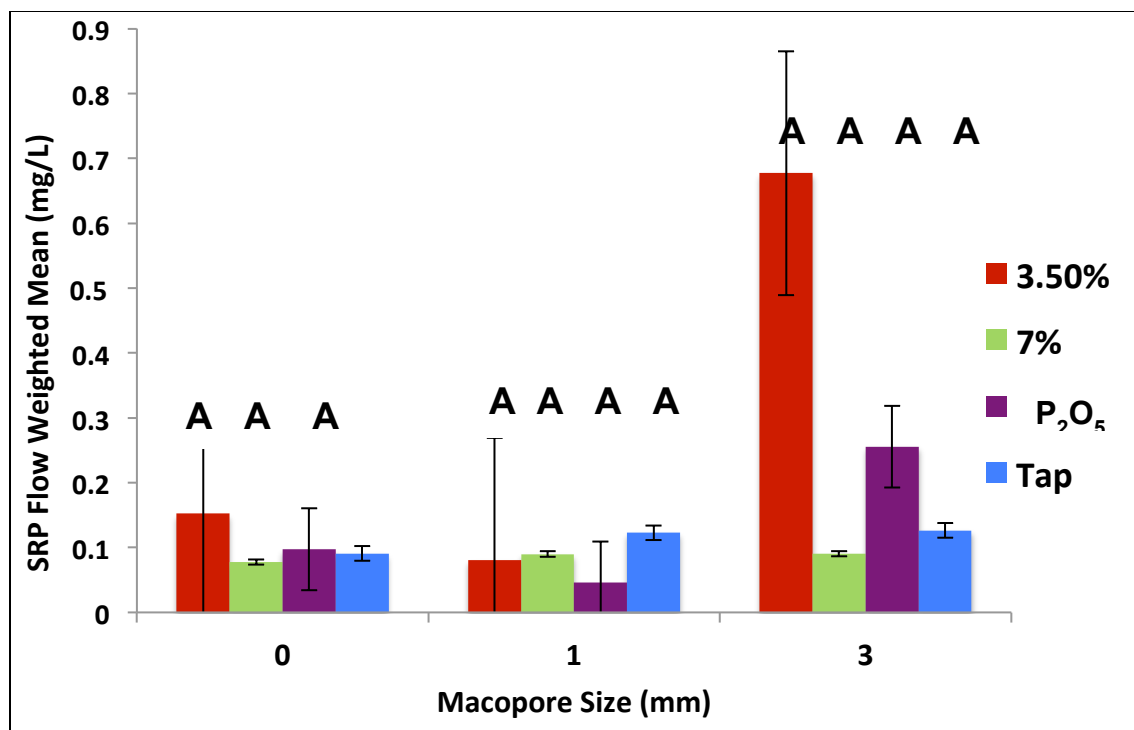


Figure 5. Flow weighted mean of SRP mg/L by duplicate column type. Log transformed SRP mg/L analyzed by treatment type and macropore interaction through statistical ANOVAs. Levels not connected by the same letter are significantly different at the .05 level defined by Least Squared Means Differences Tukey's analysis. Red bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with 3.5% solids manure broken apart by column macropore size class. Green bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with 7% solids manure analyzed by macropore size class. Purple bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with P<sub>2</sub>O<sub>5</sub> inorganic treatment water broken apart by column macropore size class. Blue bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with tap water broken apart by column macropore size class. All error bars are constructed using 1 standard error from the mean.

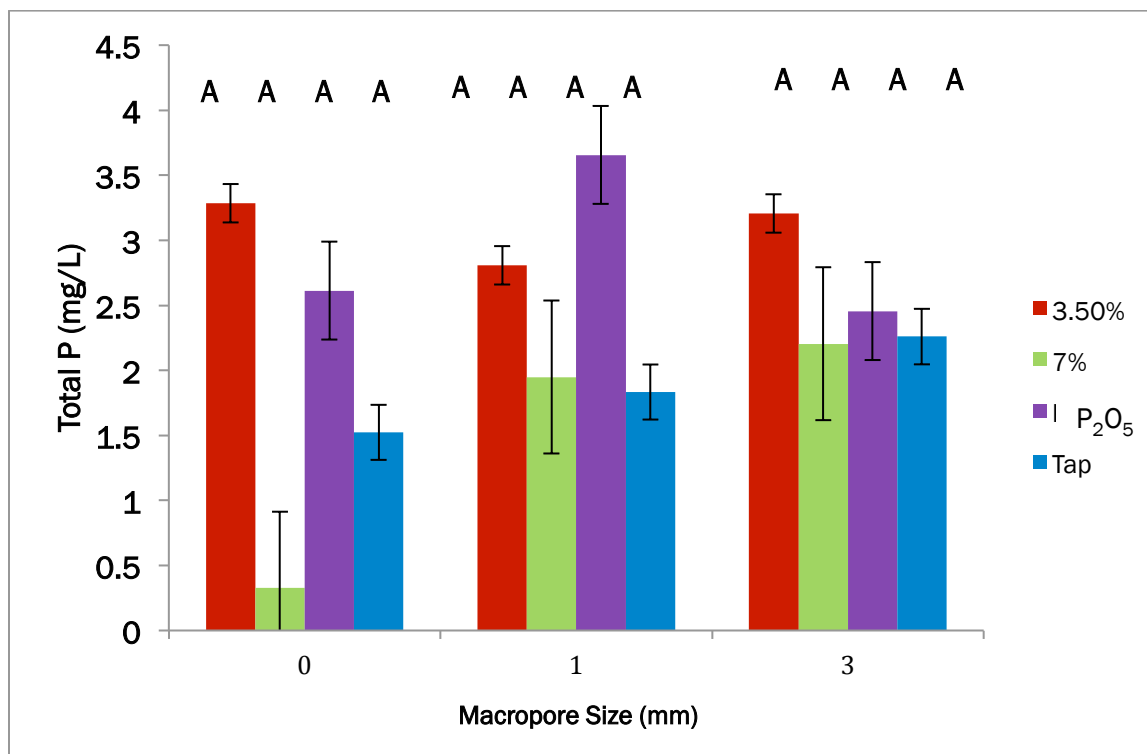


Figure 6. Total P concentration (mg/L) analyzed by macropore size column type (mm) and topical treatment type. Red bars represent the duplicate columns average of Total P loads ([Total P] by sample volume (mL)) treated with 3.5% solids manure broken apart by column macropore size class. Green bars represent the duplicate columns average of SRP loads ([Total P] by sample volume (mL)) treated with 7% solids manure analyzed by macropore size class. Purple bars represent the duplicate columns average of Total P loads ([Total P] by sample volume (mL)) treated with P<sub>2</sub>O<sub>5</sub> inorganic treatment water broken apart by column macropore size class. Blue bars represent the duplicate columns average of Total P loads ([Total P] by sample volume (mL)) treated with tap water broken apart by column macropore size class. Levels not connected by the same letter are significantly different at the .05 level defined by Least Squared Means Differences Tukey's analysis. All error bars are constructed using 1 standard error from the mean.



Although there are no national or state criteria established for P concentrations water, the EPA recommends, to control eutrophication, that total phosphate should not exceed 0.05 mg/L in a stream at a point where it enters a lake or a reservoir, and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs; similar levels are that required of sewage treatment plants (Muller and Helsel, 1999). Our concentrations were consistently higher than these recommended thresholds.

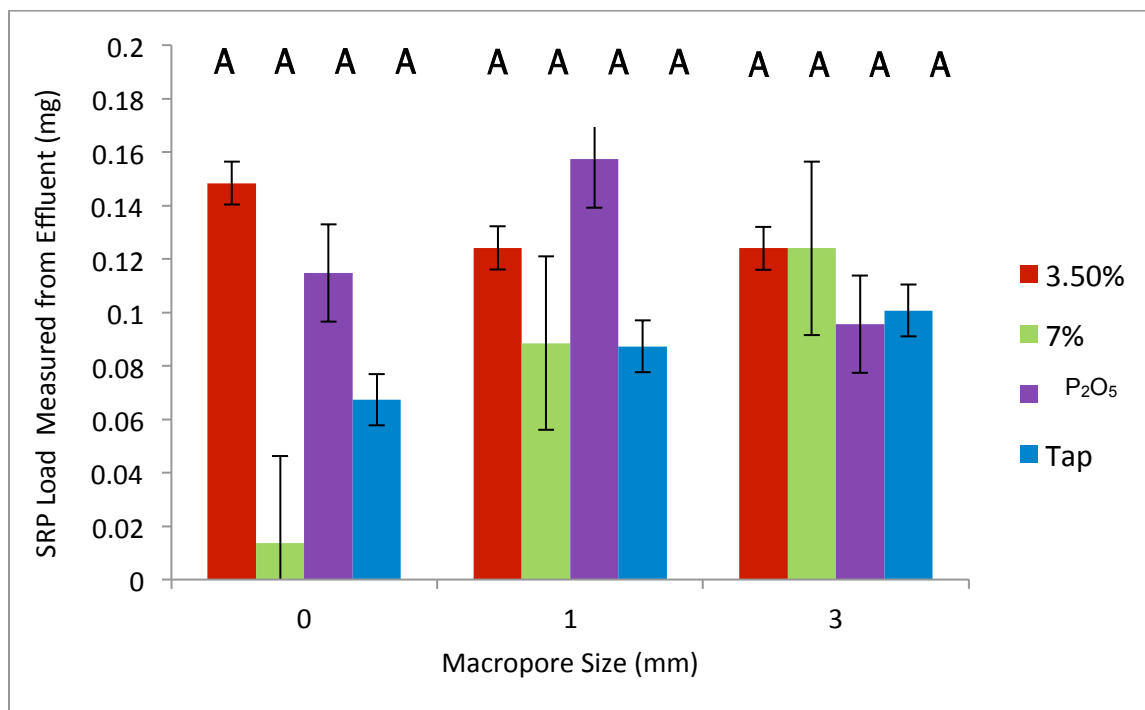


Figure 7. SRP averaged loads (mg) analyzed by macropore size column type (mm) and topical treatment type. Loads are [SRP] mg/L by effluent collection volume per sample (mL). Red bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with 3.5% solids manure broken apart by column macropore size class. Green bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with 7% solids manure analyzed by macropore size class. Purple bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with P<sub>2</sub>O<sub>5</sub> inorganic treatment water broken apart by column macropore size class. Blue bars represent the duplicate columns average of SRP loads ([SRP] by sample volume (mL)) treated with tap water broken apart by column macropore size class. Levels not connected by the same letter are significantly different at the .05 level defined by ANOVAs. All error bars are constructed using 1 standard error from the mean.

Statistically, comparisons among the SRP by loads are about the same as for concentrations, i.e., there were the same differences among treatments for the 3 mm macropore columns and the 3.5% solids and  $P_2O_5$  treatments were noticeably higher than any of the others for any of the macropore types (Figure 7).

It is interesting that the 7% solids and tap water treatments were similar to each other across all macropore sizes. We speculate that the high solid content may have resulted in clogging the macropores.

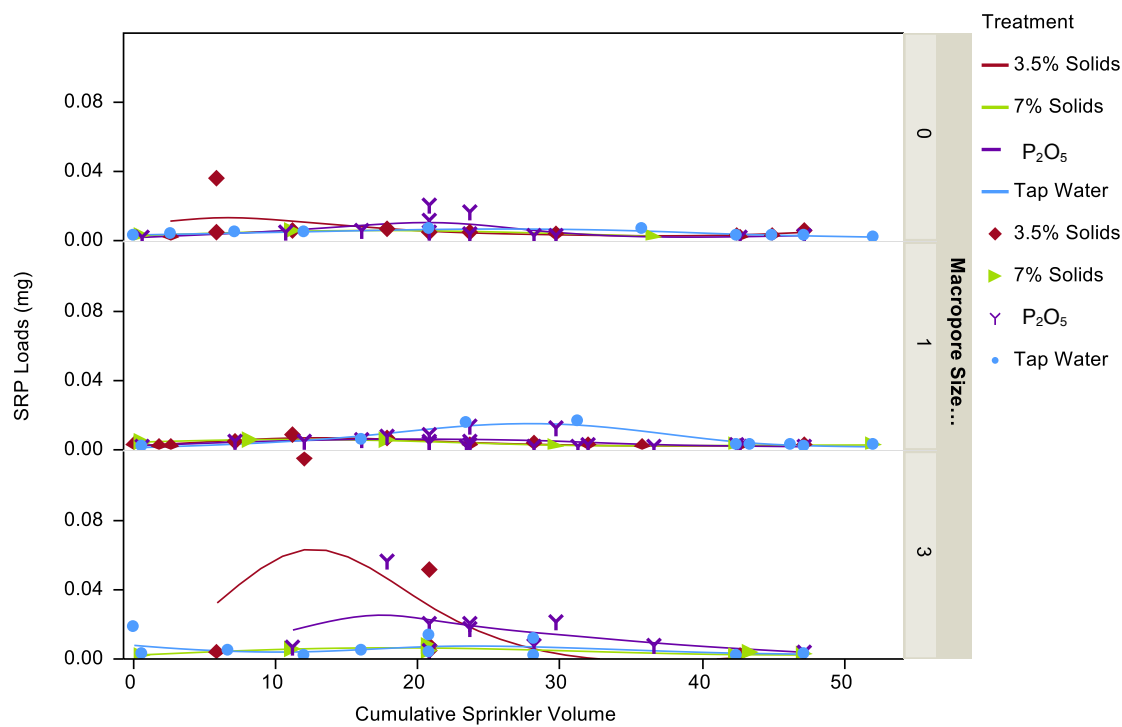


Figure 8. SRP loads (mg) by cumulative sprinkler volume (mm), macropore size classification (cm), and by treatment type. Loads were calculated by multiplying SRP concentrations (mg/L) by sample volume (mL). Lines are best average fits through data points. Red squares indicate discrete sample loads ([SRP] by sample volume (mL)) given a cumulative sprinkler volume (mm) from columns treated with 3.5% solids manure type. Red lines are the lines of best fit through the discrete collection samples of the 3.5% treatment type. Green arrows indicate sample loads ([SRP] by sample volume (mL)) of columns treated with 7% solids manure. Green lines are the lines of best fit through the discrete collection samples of the 7% treatment type. Purple “Y”s indicate discrete sample loads ([SRP] by sample volume (mL)) given a cumulative sprinkler volume (mm) from columns treated with  $P_2O_5$  inorganic treatment. Purple lines are the lines of best fit through the discrete collection samples of the  $P_2O_5$  inorganic treatment type. Blue circles indicate discrete sample loads ([SRP] by sample volume (mL)) given a cumulative sprinkler volume (mm) from columns treated with tap water. Red lines are the lines of best fit through the discrete collection samples of the columns treated with tap water.

As indicated by figure 8, SRP values analyzed through the duration of the experiment and separated by topical treatment, indicate a strong breakthrough of SRP around 11 mm of cumulative sprinkler application volume in the 3.5% manure application treatment type. Levels of SRP in the effluent collections of 7% solids,  $P_2O_5$ , and tap water have lower averages of SRP through time, thus, indicating a less pervasive source of P to water bodies.

SRP concentration peaks at 2.57 mg/L, produced from the 3mm macropore of the 3.5% solids manure application treatment type. The lowest found concentration of 0.03 mg/L was also found from the 3.5% manure application type in the 3 mm macropore size class column. Median SRP concentrations were 0.086 mg/L with upper and lower quantiles of 0.15 mg/L and 0.057 mg/L respectively. These results are consistent with other values presented in the literature (Pote et al., 1996; Scott et al., 1998; Vidon and Cuadra, 2011). SRP to Total P ratio have a median percentage of 24% with upper to lower quartiles of 50% to 15% respectively. These values are typical of SRP to TP ratios (Scott, et al., 1998; Schelde, et al., 2006; Smith, et al., 2007, Kato, et al., 2009).

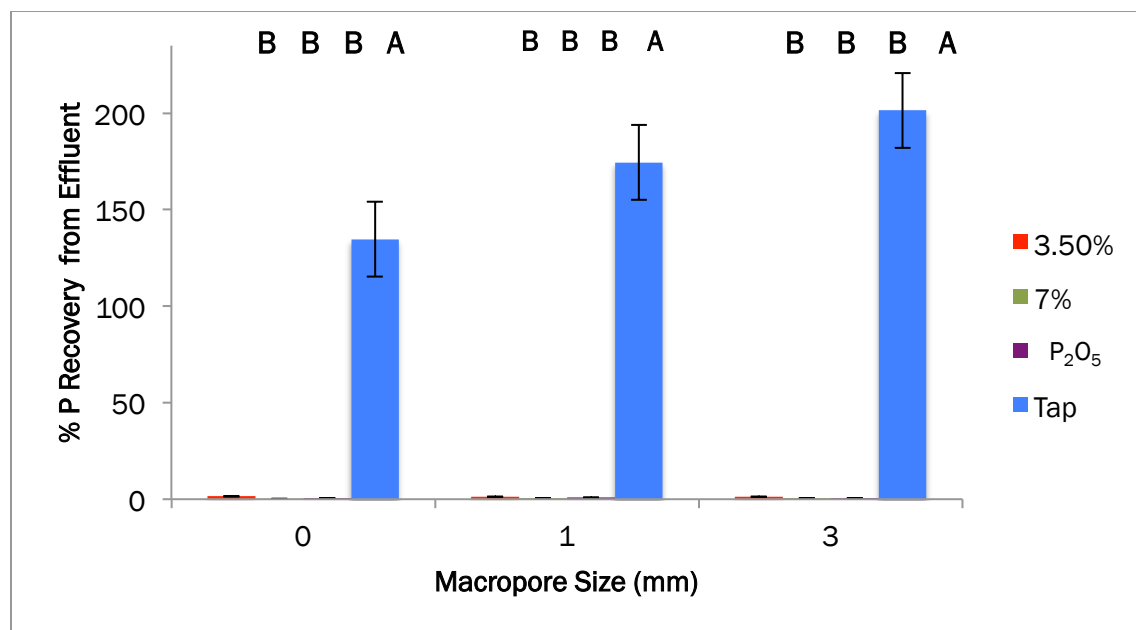


Figure 9. Percent recovery of P recovery analyzed by macropore size column type (mm) and topical treatment type. Percent recovery is calculated by total amount of P recovered (mg) by the total P applied (mg). Levels from the topical treatment of tap water are high due to small amount of initial topical P in water. Red bars represent the duplicate columns average of percent recovery of effluent given applied amount (mg P recovered in effluent by total mg P applied (mg)) treated with 3.5% solids manure broken apart by column macropore size class. Green bars represent the duplicate column average of percent recovery (mg P recovered in effluent by total mg P applied (mg)) treated with 7% solids manure analyzed by macropore size class. Purple bars represent the duplicate columns average of percent recovery (mg P recovered in effluent by total mg P applied (mg)) treated with P<sub>2</sub>O<sub>5</sub> inorganic treatment water broken apart by column macropore size class. Blue bars represent the duplicate columns average of percent recovery (mg P recovered in effluent by total mg P applied (mg)) treated with tap water broken apart by column macropore size class. Levels not connected by the same letter are significantly different at the .05 level defined by Least Squared Means Differences Tukey's analysis. All error bars are constructed using 1 standard error from the mean.

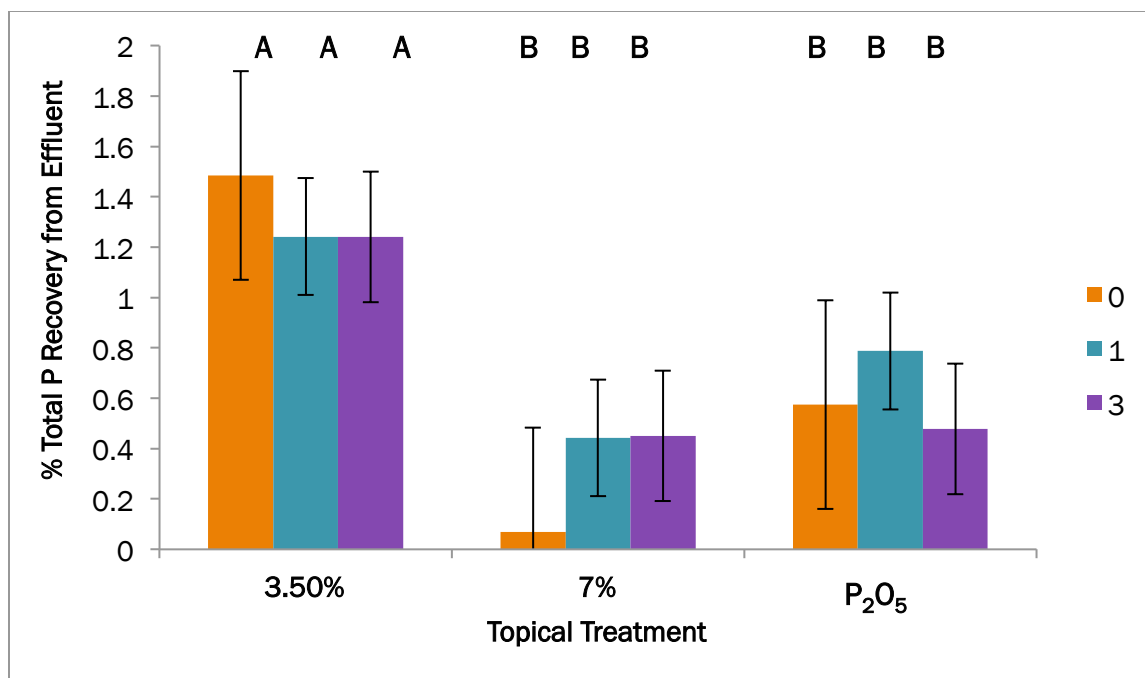


Figure 10. Percent recovery of P recovery analyzed by topical treatment type and macropore size column type (mm). Percent recovery is calculated by dividing the total amount of P recovered (mg) by the total amount applied (mg). Figure excludes tap water due to high return rate. Yellow bars represent the duplicate column average of percent recovery treated with 0 mm macropore size grouped by topical treatment type. Teal bars represent the duplicate column average of percent recovery treated with 1 mm macropore size grouped by topical treatment type. Purple bars represent the duplicate column average of percent recovery treated with 0 mm macropore size grouped by topical treatment type. Levels not connected by the same letter are significantly different at the .05 level defined by Least Squared Means Differences Tukey's analysis. All error bars are constructed using 1 standard error from the mean.

## CHAPTER 4

### DISCUSSION

Although there were few statistical differences of note, this study suggests that the 2 mm macropore diameter threshold (e.g., Kirkby, 1988; Dingman, 1993) may be applicable to P transport (Figures 3 and 4); i.e., we observed substantially higher amounts and concentrations of SRP for the  $P_2O_5$  and 3.5% solids treatments for the 3 mm macropore columns than for the 1 mm. Our results are also consistent with Cullum (2009) who found that macropore did not contribute the majority of the water moving to tile drains, even during the early stages of the drain flow hydrographs, it contributed a disproportionately large amount of solute ( $Br^-$  tracer). In our study, the presence of a macropore varied greatly in effluent produced, with no statistical or obviously discernible differences among column types, but columns with macropores produced the majority of SRP to the effluent.

One explanation for the lack of statistical differences among treatments is that the soil itself was likely a major source of SRP, which may have masked differences among treatments and macropore sizes. Indeed, table 1 indicates very high Morgan's P levels near the soil surface. Although our columns were constructed from a mixture of the top 70 cm, there was good potential for large variation in soil P content among columns. This would help explain our large variance in effluent P contents. Additional factors such as soil organic matter, pH, and texture can affect P concentrations from different soil types with similar soil P values (Sharpley et al., 1996) and heterogeneities remaining after we mixed the soil may have included some of these.

A large fraction of P retained in soil is bound to iron III (ferric iron) in the presence of oxygen and is released under anaerobic conditions concomitantly with reduced iron II (ferrous iron) (e.g., Morimer, 1941; Patrick and Khali,d 1974). The available Al, Fe, and Mn in the soils



used here (Table 2) may have been associated with the readily mobilized P observed for the tap water treatments. Note the total elemental Fe (from ICP analysis, data ranges median value= 0.36 mg/L,  $\bar{x}$  = 0.51 mg/L, high value = 3.7 mg/L) is high in this soil, so its reduction could lead to further desorption of P.

Schelde and colleges reported in 2006 that when compared against field studies, laboratory column experiments had a higher runoff/irrigation ratio of P particles than in the field due to (1) tile drains collected a lower ratio of irrigated water than the column study, leading to a dilution effect (2) filtering effects in the subsoil (Kretzschmar et al., 1999) of the field most likely reduced the number of mobilized colloids that effectively transported to the depth of the drains and (3) the laboratory experiments applied a much lower irrigation rate allowing more time for diffusive exchange of colloids between the matrix and the flowing water compared with flow conditions in the filed plots. In our present study, field measures produced similar comparisons ranging between 0.3 mg/L and 1.9 mg/L. Jacobsen et al. (1997), Geohring et al. (1998), Schelde et al. (2002), and de Jonge et al. (2004) observed high concentrations of particles right after breakthrough, followed by a decrease to a constant low level. Our study corroborates these findings with highest levels of SRP found directly after effluent breakthrough (2.57 mg/L).

Many studies have looked at the accumulation of P in soil and the subsequent soil-P increase with increasing manure application rates for beef, dairy, poultry, and swine wastes (Perkins et al., 1964; Herron and Erhart, 1965; Olsen et al., 1970; Murphy et al., 1972; Vitosh et al., 1973; Sutton et al., 1974; Cummings et al., 1975; Shortall and Leibhardt, 1975; Collins et al., 1978;), but no research can be found on the effect of manure dilution on soil-P accumulation or

subsequent P loads to waterways. The findings from this project suggest that the next step in this project is to address these issues.

## CHAPTER 5

### CONCLUSION

This study found that liquefying dairy manure significantly increased the concentrations and loads of SRP leached from soils with macropores of 3 mm. To date the strategies developed for nutrient management to address nonpoint source P pollution of surface waters have included (e.g., Sharpley et al., 2003): agronomic soil test P recommendations, environmental soil test P thresholds, and a P index to rank fields according to their vulnerability to potential P loss. Additional management recommendations have been broadened to include changing the time of applied manure (Sharpley et al., 2003; Geohring et al., 2001), riparian buffer establishment (Marjerison et al., 2011), and reduced feed P ration (Sharpley et al., 2003). The effectiveness of such management strategies is uncertain when applied to liquid manures. One additional recommendation may be to avoid diluting dairy manure before applying it to tile-drained fields, at least until research is conducted to assess the capacity of current practices to control P transport to surface waters.

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## **APPENDIX 1: Deviations from the initial experimental design and sampling period**

Initially the experiment was run for a total of seven weeks. Analysis of the data indicated high levels of P after three weeks of data collection, possibly indicating microbial biological activity from prolonged saturation and manure content interaction. The inability to have a constant and consistent rain pattern on the soil columns may have significantly increased the availability of the soluble P as researchers have found that hydraulic variability such as flooding and drying of soils has subsequently lead to high P values in laboratory studies (Banach et al. 2009; Turner and Haygarth 2001). Specifically, Turner and Haywarth (2001) found that the process of drying and rapidly rewetting soil increased the amount of water-soluble phosphorus present after having released from the soil microbial biomass. They attributed this effect to direct release of phosphorus from the soil microbial biomass, because microbes can be killed by osmotic shock and cell rupture when rapid rehydration follows a period of drying.

Recently researchers have begun to acknowledge the importance of biological processes in P desorption or solubilization. Stutter et al. (2009) found that saturated areas near streams often become P sources and suggest that this could be caused by increased microbial and plant activity liberating soil-bound P. It was found by Quang and Dufey (1995) that a 10°C increase in temperature greatly increased the P-sorption capacity of soil iron and concluded that it was due to microbial activity lowering the redox potential at the higher temperature. An implication under field conditions is the high available P in the surface layers along with the desorbable P and any additional surface applied P can be mobilized by rainwater (with a low P content) and rapidly transported through the natural soil structure cracks and macropores.

A researcher should only run collection for a period of time that mimics the rainfall rate and pattern of the historical site of the soil and landscape under consideration to avoid this happening in the future.

Inconsistencies of the data could be from the following experimental set up and execution of the experiment.

- prolonged saturation
- inconsistent rain patterns of rain intensity.
- high initial values of P within the soil
- uncertainty of our collection scheme disassociating flow paths.

The composite soil blend placed into the columns may have not been thoroughly mixed, causing some localized pockets of the surface soil with high Morgan's available P concentrations.

Initial Calcium (Ca) concentrations are low so there was likely very little  $\text{CaPO}_4$  rapid dissolution. However, the Morgan's available P (which is actually an analytical approach to determining the amount of soluble P that is readily available to plant roots) would be readily leachable upon saturating the columns and adding tap water. Indicative of high P levels found in soil columns only treated with tap water.

Additionally, since the manure adds dissolved organic carbon (DOC) and the high biochemical oxygen demand (BOD) of it also facilitates reduction, the 3.5% dilution may easily move through the pores because of the fewer solids, having more opportunity to accentuate all the above processes. Increasingly study is investigating the mobilization and transport of colloids in natural soils as preferential flow phenomena may be largely responsible for the observed

leaching patterns of strongly sorbing contaminants (Heathwaite and Dils, 2000). Translocation of colloids depends on the prevailing conditions for transport, such as colloid stability in the soil solution, soil water content, and the pore size and geometry of the water- conducting pore system (Schelde et al., 2006). There is insufficient information at this time regarding the intrinsic and dynamic properties of the soil controlling the mobilization and transport of colloids in natural soils to make accurate predictions considering contaminant colloid leaching, but filtering effects in the subsoil probably reduce the number of mobilized colloids that were effectively transported to the effluent (Kjaergaard et al., 2004).

## **Appendix 2: Auxiliary Macropore Information**

Numerous studies have focused on the origins and distributions of macropores and their effects on infiltration and storm-runoff generation (Baven and Germann, 1982; Kirkby, 1988; Villholth et al., 1998; Vidon and Cuadra, 2011). Preferential flow through macroporous soils is one the most prominent known forms of subsurface flow and has been under intense study since the 1970's (Thomas and Phillips, 1979; Bouma, 1981; Beven and Germann, 1982; Cullum, 2009). However, it is generally difficult to assess the importance of macropores or to simulate their effects on water transportation because their number, orientation, size, and interconnectedness are highly dependent on local geology, soils, vegetation, and fauna (Dingman, 2002). Broadly defined, macropores are structural pore systems that provide pathways for relatively rapid transport of water and dissolved or suspended constituents through a porous medium (Villhoth et al., 1998). Attention to the transport of P to tile drains through macropores has been cited in the literature and has been found to effect the concentration of flow which would otherwise occur as natural subsurface flow (Scott et al., 1998; Geohring et al., 2001). Macropore formations in the environment is predominately created through worm holes, root holes, and voids within soil structural units and are ubiquitous in most natural soils (Baven & Germann, 1982). Macropores introduce preferential flow paths into natural soil systems, and hence invalidate homogeneous flow theory (Richards and Steenhuis, 1988).

The relationship between hydraulic conductivity, infiltration rates, and moisture content under conditions of preferential flow is extremely complex given our current understanding of flow processes and water transport through subsurface soils. Richards and Steenhuis (1988) defined three broad categories of exceptions to uniform homogeneous flow: (1) soils with cracks,

often due to swelling and shrinking clays (Blake et al., 1973; Bouma, 1981); (2) soils containing biologically created channels through floral and faunal activity (Gaiser, 1952; Aubertin, 1971, Ehlers, 1975; Hole, 1981); and (3) soils in which a fine textured layer overlies a coarse more permeable layer, which then promote wetting front instabilities or “finger flow” (Hill and Parlange, 1972). The first two categories, cracks and biologically induced channels, are commonly referred to as macropores (Luxmoore, 1981; Skopp, 1981). In a detailed study in a New Hampshire forest, Stresky (1991) found that more than 60% of the macropore were located in the upper 0.15 m of the soil. Macropores are typically on the order of 3 to 100 mm in diameter and are interconnected to vary degrees; thus they appear to allow water to bypass the soil matrix and move rapidly to the saturated zone or downslope at speeds much greater than predicted by Darcy’s Law (Kirkby, 1988). However, in Baven and Germann’s 1981 study they exposed the idea of delimiting macropores by size as arbitrary, given that macropores are often related more to details of experimental technique than to considerations of flow processes. Part of the difficulty understanding macropore transport processes is that they make up only a small percentage of the total pore space, on the order of 0.5% to 5% in many agricultural soils, yet they can account for the majority of water movement under certain conditions (Germann and Beven, 1981; Kneale, 1985). Nutrient and water transport through macropores of a size class below 3 mm is needed to address the transport characteristics of flow through macropores below their defined size.

A conceptual soil matrix is assumed to behave as a homogeneous substrate without macropores, describable by classical water flow equations based on Darcy’s law (Chen and Wagner, 1992). Macropore behavior is described in a variety of ways, but is usually historically

assumed to be a separate domain from the matrix, which interacts with macroporosity as a function of macropore geometry, pore size range and number, pore volume, and according to the shape of soil structural units (Bouma and Wosten, 1979; Beven and Germann, 1982). In the field, macropore geometry is much too complicated to be deterministically qualified; furthermore, it is difficult to measure macropore sizes, to determine the number of each size, and to know the number of observed macropores that are conductive. These difficulties suggest a need for a laboratory study that addresses these concerns in a controlled atmosphere. Laboratory studies with artificially constructed macropores have been used repeatedly (e.g. Bouma and Anderson, 1977; Czapar et al., 1992; Stehouwer et al., 1994; Buttle and Leigh, 1997; Geohring et al., 2001) to standardize soil conditions and hence permit the study of the effect of individual macropore properties of soil physicochemical behavior (Bouma and Anderson, 1977).

Chen and Wagenet (1992) concluded that three control situations of infiltration are recognized: macropore control, application control and matrix control. In this study, holding all other aspects constant, macropores were defined by different radii as differing topical treatments were applied to columns in duplicate. This study attempts to better understand macropore interaction with manure liquidity and its subsequent effluent SRP concentration in order to elucidate macropore size classes at scales historically ignored in the literature. It is important to understand macropore and manure interactions in an attempt to better manage manure waste from CAFOs and large animal feed lots.