Influence of Antecedent Soil Moisture and Rainfall Rate on the Leaching of Nitrate and Phosphate from Intact Monoliths of Agricultural Soil

by

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A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree
Master of Science
in
Geography

Waterloo, Ontario, Canada, 2010

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

The export of nitrogen (N) and phosphorus (P) from agricultural catchments is a major problem worldwide. The export of these nutrients is largely driven by storm events, and the hydrologic response of catchments varies within and between storm events. Antecedent soil moisture and rainfall rates have both been shown to affect the discharge and nutrient export from agricultural catchments, but their relationship to nutrient export is not fully understood. Currently, there are no studies that examine the leaching of both nitrate (NO_3^-) and phosphate (PO_4^{3-}) from soil pools under the combined influence of differences in soil moisture and rainfall rates. The objectives of this study were to examine the combined effect of antecedent soil moisture and rainfall rates on the hydrologic response of soil and the export of NO_3^- and PO_4^{3-} from the soil. The approach used intact soil monoliths in two experiments to first characterize the hydrologic response of the soil, and secondly to assess how the hydrologic response of the soil affects the leaching of NO_3^- and PO_4^{3-} from soil pools.

Differences in antecedent soil moisture and rainfall rates influenced both the amount of discharge and the hydrologic flow paths in the soil. As was expected, antecedent soil moisture governed the depth of discharge, with more discharge (runoff ratios= 0.89 to 0.91) produced by wet soil and the least runoff produced by dry soil (runoff ratios= 0.08 to 0.14) although this was not affected by the rainfall rate. Instead, rainfall rates predominantly affected hydrologic flow paths in the soil, with preferential flow at the beginning of the leaching period under high intensity rainfall (especially in wet soil), and predominantly matrix flow occurring under low intensity rainfall. The rainfall intensity did not appear to affect discharge volume.

The mass of both NO_3^- and PO_4^{3-} exported was higher under low intensity rainfall, ranging from 11.2 to 60.1mg/m^2 and 77 to 4980µg/m^2, respectively and from 0.9 to 34.4mg/m^2 and 18.4 to 732µg/m^2, respectively under high intensity rainfall. Antecedent soil moisture was significantly positively correlated with the depth of discharge produced, which also had a significant positive relationship with the mass of NO_3^- and PO_4^{3-} exported (Spearman's ρ= 0.75 to 0.81, p= <0.001), with greater masses of both nutrients exported from wet soil than dry soil. Soil moisture had contrasting influences on the NO_3^- concentrations in leachate, where NO_3^- concentrations and soil moisture were negatively related under low intensity rainfall and positively related under high intensity rainfall. Concentrations of PO_4^{3-} in leachate were more variable, with no clear relationship to soil moisture, discharge, rainfall rate or soil PO_4^{3-} pools. Antecedent soil moisture and the rainfall rate have a combined influence on the concentration of NO_3^- in leachate and an influence on the mass of both

NO_3^- and PO_4^{3-} exported. Although different hydrologic flow paths (matrix, preferential) were observed under the variable antecedent conditions and rainfall rates, this did not appear to affect nutrient fluxes from soil. This may be related to available nutrient pools and distributions in the soil in the current study.

Understanding of the influence of flow types on the export of soil nutrient pools requires further study in a lab and a comparison of the breakthrough of NO_3^- and PO_4^{3-} from soil pools with that of a conservative tracer (Cl^-). Nutrient and tracer breakthrough could then be compared to the hydraulic conductivity of the soil and the progression of the wetting front to fully understand the flow paths occurring and their effect on nutrient leaching.

Acknowledgements

First and foremost, I am extremely grateful to my supervisor, Dr. Merrin Macrae for all her help and patience throughout the last two and a half years. Merrin has always been very approachable and easygoing, and always made me feel like I was a capable grad student. Merrin was always available when I needed to bounce ideas off her, needed help with equipment and just generally for moral support.

I would also like to thank Dr. Bill Quinton, my committee member, for all of his help and feedback and for helping me finally come up with a simple, reliable way to simulate rainfall.

Rick Bourbonniere was very helpful throughout the course of this thesis, helping with the installation of field equipment and even carrying heavy monoliths from the field site to my car when I was really tired. He was always a pleasure to work with and I really enjoyed his company during field days.

Margaret Reist, my research assistant, was a lifesaver on many occasions, helping me in the field and in the lab during some VERY long, boring days. I couldn't have asked for a more organized, hard-working RA! Margaret weighed out 10g of soil hundreds of times and performed numerous other mundane, repetitive tasks, and always did so with diligence, enthusiasm and without complaining. If Margaret had ten seconds free, she would find something productive and helpful to do! She was truly wonderful.

A thank you goes out to Lauren Cymbaly for her help in the field, and for being very capable in the identification of plants!

A big thank you goes out to John Mount, who has graciously allowed many researchers access to his farm for many, many years! John sadly passed away in December of 2008 and his presence is greatly missed at the field site. John was always greeted us upon arrival and was very glad to see us.

I would like to thank Mike Stone and Ian McKenzie for allowing me to take over their lab facilities for various periods of time, and for assisting me in the use of equipment. I am very grateful to Kathy Mulroy for showing me how to use Mike Stone's autoanalyzer.

A big thank you goes to John Debrone at the ENV woodshop, who was extremely helpful in helping me design and build my monolith stands, and everyone at the Engineering Machine Shop, who provided free PVC pipe and were extremely helpful in helping me figure out a design for my monoliths.

Another huge thank you goes to all my wonderful friends, who regularly provided me with great amounts of support, and fun and distraction on many, many Thursday nights! All of the loud talking, hilarious conversations, trivia, dance parties, love and support have been a very welcome distraction from the stress that research inevitably brings! I would also like to show my appreciation for the Grad House for being such welcoming hosts, with their friendly staff, delicious grad burgers and many delicious local beers.

Lastly, I would like to thank my parents for bringing me into this world, always being supportive of my every endeavor (financially and otherwise), always making me feel like I'm the most awesome person in the world, and listening patiently to many a stressed out phone call.

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Chapter 1

Introduction and Problem Statement

1.1 Study Rationale and Objectives

Nonpoint source pollution of surface and ground water with elevated concentrations of nitrogen (N) and phosphorus (P) exported from agricultural watersheds where fertilizer and manure are applied has been a major environmental concern worldwide for over 30 years (Sims et al., 1998; Carpenter et al., 1998; Gottschall et al., 2007). Nitrogen and phosphorus are commonly deficient in natural soils, warranting the use of fertilizer and manure in agriculture. Not all N and P added to the soil this way is used by plants (Gardiner and Miller, 2004), and fertilizer and manure are often added in excess of crop needs to account for losses of both nutrients (mainly N), and their immobility in the soil (specifically P), resulting in excess nutrients in agricultural soil, which are susceptible to leaching and export from agricultural basins (Carpenter et al., 1998; Sims et al., 1998).

Nitrogen and phosphorous differ in their mobility and ability to be exported from agricultural catchments; N is mobile and highly susceptible to leaching (Gardiner and Miller, 2004; Goehring et al., 1996), whereas P is very reactive and adsorbs to soil particles (Gardiner and Miller, 2004). It was traditionally thought that P was not susceptible to leaching because of these properties (Dils and Heathwaite, 1999; Sims et al., 1998), but P is susceptible to leaching when adsorption sites in the soil are full (*e.g.* Gardiner and Miller, 2004; Sims et al., 1998; Dils and Heathwaite, 1999) or under certain flow conditions such as preferential flow (Stamm et al., 1998). Soil nutrients in agricultural catchments can be present to varying degrees in recently surface-applied manure and granular fertilizer and can already be incorporated into the matrix of the soil. There are many interacting controls on the export of N and P from each of these pools in agricultural landscapes and as such, it is difficult to predict and quantify N and P loading from these diffuse sources (Carpenter et al., 1998).

Many studies show that nutrient loading from agricultural landscapes increases during storm events compared to baseflow conditions (Macrae et al., 2007, 2007b; Biron et al., 1999; Vanni et al., 2001; McHale et al., 2002; Sharpley et al., 2008) and that nutrient export varies between and within precipitation events (Macrae et al., 2007; Britton et al., 1993; Vanni et al., 2001). Snowmelt events also cause a great deal of nutrient export (Macrae et al., 2007, 2007b; Dils and Heathwaite, 1999). The influence of antecedent soil moisture and rainfall rates on nutrient export from agricultural basins is not well understood, and study findings differ on the influence of soil moisture and rainfall rates on nutrient export (Welsch et al., 2001; Vanni et al., 2001; Britton et al., 1993; Flury, 1996). Antecedent soil moisture and rainfall rate are thought to influence the hydrologic response of and flow types occurring in the catchment, and in turn may affect nutrient export (Macrae et al., 2007; Britton et al., 1993; Biron et al., 1999; Langlois and Mehuys, 2003). It is important to understand how the different flow types in the soil affect the export of both pools of nutrients (Kung et al., 2000b). In order to predict and model nutrient losses from agricultural landscapes and nutrient loading in surface and ground water, the effect of antecedent soil moisture and rainfall rates on flow types in the soil and the export of both pools of nutrients needs to be fully understood (Macrae et al., 2007, 2007b; de Rooij and Stagnitti, 2002; Gaynor and Findlay, 1995; Britton et al., 1993; Biron et al., 1999; Kung et al., 2000a, 2000b; Sims et al., 1998). Vertical leaching of nutrients is one of the pathways in which export of N and P from agricultural catchments occurs (Flury, 1996) and it is necessary to understand how antecedent soil moisture and rainfall rates influence the leaching of agricultural nutrients in the soil matrix in order to fully understand nutrient export from agricultural basins (Flury, 1996), even though export of nutrients occurs by other means (*e.g.* overland flow, lateral subsurface flow) and from other sources (recently surface-applied nutrients). It is necessary to perform leaching studies in a lab setting to control and isolate the variables that influence the flow paths in the soil and thus nutrient leaching. To date, there are no lab or field studies which examine the combined effects of antecedent soil moisture and rainfall rates on nutrient leaching. Therefore, the overall objective of this thesis is to examine the combined effects of antecedent soil moisture and rainfall rate on nutrient leaching from agricultural soil. Specific research questions are:

1) How is the hydrologic response of the soil affected by antecedent soil moisture, and rainfall rate?

2) How do each of these factors individually and together affect the leaching of soil nitrate and phosphate?

It was hypothesized that antecedent soil moisture would have a greater effect on nutrient export than rainfall rate. Soil moisture influences the amount of discharge from catchments by influencing the amount of water that goes into storage in the soil (de Rooij and Stagnitti, 2002; Flury, 1996; Welsch et al., 2001; Geohring et al., 2001) and therefore the amount of mobile water in the soil that is available to transport nutrients. Therefore, soil moisture has been shown to have a significant effect on nutrient flux (Flury, 1996; Welsch et al., 2001). It was also thought that the rainfall rate would largely drive the flow paths (*i.e.* matrix versus preferential flow) occurring in the soil, and that the flow paths would have different effects on NO_3^- and PO_4^{3-} leaching because of the differing mobility of these nutrients in the soil, with matrix flow producing higher NO_3^- concentrations in leachate, and macropore flow causing higher PO_4^{3-} concentrations. The following sections will outline the soil components of the nitrogen and phosphorus cycles, then outline current knowledge on how antecedent soil moisture and rainfall rate affect the hydrologic response of and nutrient export from the soil.

1.2 Literature Review

1.2.1 Nitrogen and Phosphorus Risks and Cycling

1.2.1.1 Problems and Risks Associated with Nitrogen and Phosphorus Export from Agricultural Catchments

Nitrogen and phosphorus are both plant macronutrients and are usually found in inadequate quantities in agricultural soils, necessitating the use of fertilizer (Gardiner and Miller, 2004). These nutrients each have different properties, and consequently different levels of mobility in the soil (Gardiner and Miller, 2004). Both nutrients are generally found in higher quantities in the top 10cm of soil (Gardiner and Miller, 2004).

Levels of P in surface water are usually low because of its low solubility (Gardiner and Miller, 2004), but excess P in surface water can cause eutrophication (Howarth et al., 1988, 1996; Carpenter et al., 1998; Simard et al., 2000; McHale et al., 2002) at concentrations as low as 5-30µg/L (Jiao et al., 2004; Simard et al., 2000; McDowell and Sharpley, 2001), causing problems for marine ecosystems, fishing industries, recreation and the use of freshwater for drinking (Carpenter et al., 1998). Eutrophication is one of the most important causes of poor water quality in freshwater and estuarine ecosystems because it can affect aquatic productivity and food web structure (Vanni et al, 2001). Elevated concentrations of N in some streams and lakes can cause eutrophication as well (Grimm et al., 2003), and nitrate (NO_3^-) in groundwater is a threat to drinking water quality (Jiao et al, 2004). Elevated concentrations of NO_3^- have become common in wells near heavily fertilized fields and feedlots (Gardiner and Miller, 2004). Just under 29% of the population of Ontario is reliant on groundwater for their primary drinking water (Anon, 1996), as are 30.3% of Canadians as a whole (Anon, 2004). The current guideline from Health Canada (Anon, 2007) and in most countries (Jiao et al., 2004) for acceptable NO_3^--N levels is 10mg/L. The main health risk from exposure to NO_3^- and nitrite (NO_2^-) is methaemobloginaemia ('blue-baby syndrome') in bottle-fed infants, which causes changes to the oxygen-transporting capacity of hemoglobin, thereby causing cyanosis and asphyxia (Carpenter et al., 1998; Czapar et al., 1994). Clean water is a crucial resource worldwide for many uses, including drinking, recreation, fishing, support of biodiversity and aesthetic enjoyment (Carpenter et al., 1998).

1.2.1.2 Nitrogen Forms and Cycling in Soils

Nitrogen exists in different forms and locations in the soil and is added to the soil either through fertilization (manure or granular fertilizer) or by natural means (nitrogen fixation). Inorganic forms include ammonium (NH_4^+), NO_3^- and nitrite (NO_2^-), and organic forms of N consist of amine groups, plant proteins and chlorophyll (Grainer and Miller, 2004; Madigan and Martinko, 2006). Nitrogen fixation is the primary source of soil N in natural ecosystems (Gardiner and Miller, 2004). Nitrogen gas is converted into useable forms by symbiotic or non-symbiotic microorganisms (Table 1). Nitrogen is added to the soil in natural ecosystems by the decomposition of organic residues (Madigan and Martinko, 2006). Decomposition occurs rapidly in warm, well-aerated, moist soils and is slower in clays and during cooler seasons (Powlson, 1993). It is the major source of N in unfertilized soils, but the amount of N produced from this process is inadequate for crop needs. Small inputs of NO_3^- and NH_4^+ occur due their presence in rainwater (Gardiner and Miller, 2004). Nitrogen is added to agricultural soil in granular fertilizer (as NH_4^+ or NO_3^-, depending on crop needs) and manure (mostly organic N; Powlson, 1993), which is decomposed and the organic forms of N converted into NH_4^+ in the process of mineralization (Figure 1; Gardiner and Miller, 2004; Madigan and Martinko, 2006). After NH_4^+ is mineralized or applied in granular fertilizer, most of it is rapidly nitrified to NO_3^- within a few days unless the soil is strongly acidic, cold or waterlogged (*i.e.* anoxic; Powlson, 1993). Nitrogen that was not recently applied will have been incorporated into the soil matrix (Gardiner and Miller, 2004) and will generally exist in inorganic forms (Powlson, 1993), whereas more recently applied nutrients will be concentrated on or near the soil surface (Gardiner and Miller, 2004) and may include organic forms (Powlson, 1993). All components of the N cycle are biologically mediated and thus occur at greater rates during higher temperatures (Powlson, 1993). Most crops only use between 40-70% of N applied in fertilizer and manure, resulting in excess N (mainly NO_3^-) in the soil (Gardiner and Miller, 2004), which is susceptible to losses through denitrification and leaching.

Process		Organism
Nitrification	$NH_4^+ \rightarrow NO_3^-$	*Nitrosomonas*
	(1) $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O +$ energy	
	(2) $2NO_2^- + O_2 \rightarrow 2NO_3^- +$ energy	*Nitrobacter*
Denitrification	$NO_3^- \rightarrow NO_2 \rightarrow NO \rightarrow N_2$	*Bacillus, Paracoccus, Pseudomonas*
N_2 fixation	$N_2 + 8H \rightarrow 2NH_3 + H_2$ Free-living: aerobic	*Azotobacter*, Cyanobacteria
	Free-living: anaerobic	*Clostridium*, purple and green bacteria
	Symbiotic	*Rhizobium, Bradyrhizobium, Frankia*
Mineralization	Organic N$\rightarrow$ NH_4^+	Many organisms
Anammox	$NO_2^- + NH_3 \rightarrow 2N_2$	*Brocadia*

Table 1- Reactions involved in the soil component of the nitrogen cycle.

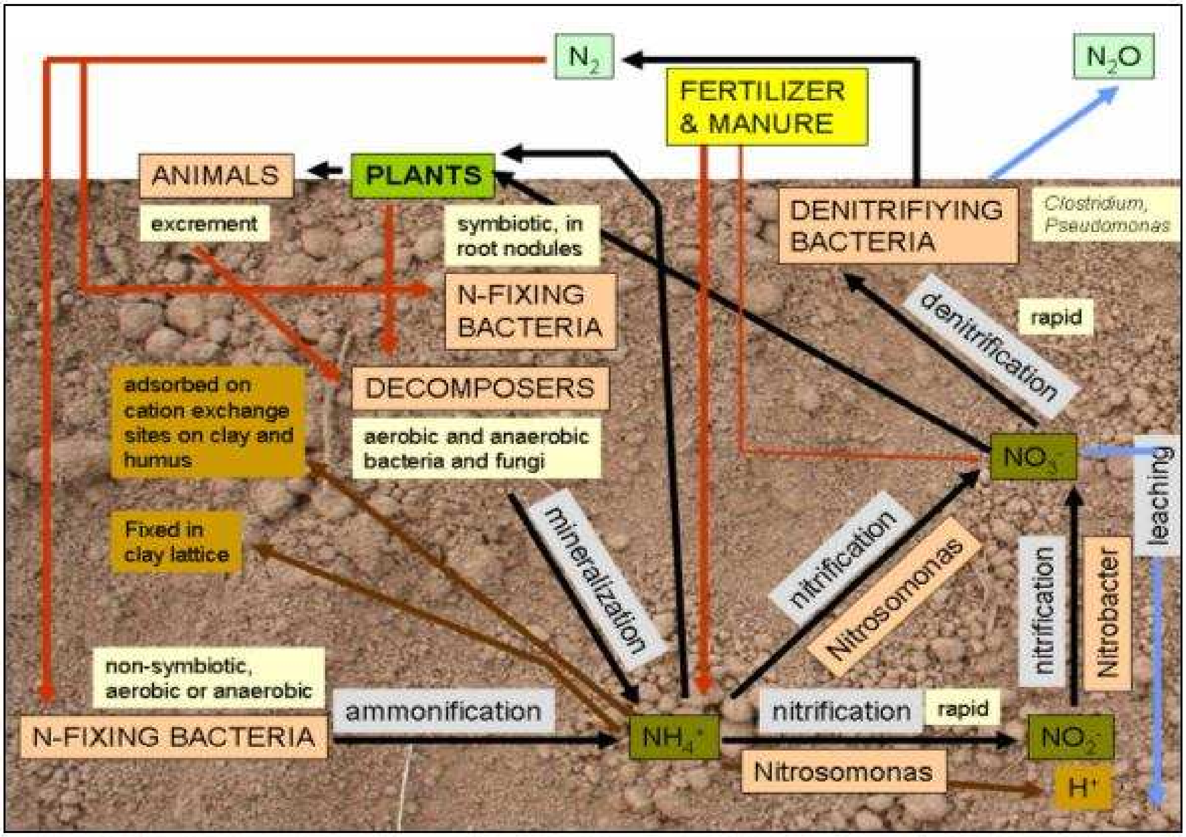


Figure 1- The soil components of the nitrogen cycle

(adapted from Gardiner and Miller. 2004 and Anon, 2005; soil background image from Anon, 2007).

Denitrification is one of the main pathways for N loss and is the main means by which gaseous N is formed biologically, primiarly as N_2 but also N_2O to a small extent (Table 1; Powlson, 1993). Denitfirication occurs in anoxic conditions, which can form when soil is waterlogged following heavy rains, and can occur rapidly (Madigan and Martinko, 2006), with extensive losses of NO_3^- in a short period of time (Gardiner and Miller, 2004). It is temperature dependant, since it is driven by microbial activity (Gottschall et al, 2007). Leaching of NO_3^- is another major method of N loss from agricultural landscapes and it occurs due to the mobility of NO_3^- in percolating water and its tendency not to adsorb to cation exchange sites on clay and humus particles in the soil (Gardiner and Miller, 2004; Powlson, 1993). Ammonium is not as susceptible to leaching as NO_3^- because of its tendency to adsorb to cation exchange sites. Less N is leached when a growing crop is present on the soil, because a lot of the NO_3^- and NH_4^+ is taken up by the crops and therefore not susceptible to leaching (Powlson, 1993).

1.2.1.3 Phosphorous Forms and Cycling in Soils

Phosphorus is also a key nutrient in plant growth and the second most deficient in agricultural soil, after N, warranting the use of manure and inorganic fertilizer (Gardiner and Miller, 2004). It is very reactive (Simard et al., 2000) and does not exist in elemental form in agricultural systems, but instead exists in organic and inorganic forms. Inorganic forms of P consist of orthophosphate

($H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-}) and phosphate that has combined with elements such as Ca, Al, Mg or Fe to form insoluble compounds (Gardiner and Miller, 2004; Busman et al., 1998). Organic phosphorus exists in nucleoproteins (DNA and RNA), ATP and ADP and has roles in cell division, plant growth processes and the development of bones and teeth in mammals. Phosphorus can be immobilized by adsorption into the soil matrix, on clay or humus particles (McDowell and Sharpley, 2001). Phosphate is able to adsorb to exchange sites on clay and humus particles because it combines with Ca^+, Mg^+, Al^+ or Fe^+ (Holtan et al, 1988). The P adsorption capacity of the soil increases with clay content and decreases with redox potential (Holtan et al, 1988) and also varies with the chemical and mineralogical composition of the soil (Akhtar et al., 2003). Phosphorus is not classified in terms of compounds like N, but instead based on different soil 'pools' of P, and based on its solubility and reactivity (Busman et al., 1998). Phosphorus is generally fairly immobile in the soil, but is still susceptible to losses by leaching (Gardiner and Miller; Jiao et al., 2004; Carpenter et al., 1998), especially if adsorption sites in the soil are saturated past a critical level of availability due to annual buildup of soil P from fertilizer and manure application (McDowell and Sharpley, 2001).

Phosphorus is generally available in three ‘pools’ within the soil; the soil solution pool, active pool and the fixed pool. Phosphorus in the soil solution pool is that which is available to plants, while the active pool consists of organic P and P adsorbed to soil particles that can be easily transferred to the solution pool. The fixed pool of P is generally not available to plants and consists of P that has formed insoluble compounds with various cations (Busman et al., 1998).

Phosphorus can also be classified in terms of its solubility and reactivity. Phosphorus exists in soluble or dissolved (<0.45μm in diameter) and particulate (>0.45μm) forms (Simard et al., 2000). Soluble P is either reactive and therefore biologically available (largely inorganic orthophosphate; PO_4^{3-}) or unreactive (organic P in plant and animal tissues). Reactivity is determined by whether P reacts with reagents designed to separate elemental P from chemical compounds (Simard et al., 2000). Particulate P is either P adsorbed to small clay or humus particles in the soil, or makes up part of large organic molecules. Total P is all forms of P (particulate, dissolved, reactive and unreactive; Carlson and Simpson, 2007).

Once added to the soil in manure or naturally present in decaying organic matter, organic P is mineralized by prokaryotes (Figure 2) and the rate of this reaction varies with temperature and soil moisture, becoming rapid when soils are warm, moist and well-drained (Busman et al., 1998; Gardiner and Miller, 2004). Phosphorus in fertilizer and manure is initially quite mobile and available to plants, but reactions begin quickly once it is added to the soil that makes it less soluble and available. The rates and products of these reactions depend on the moisture content, soil pH, temperature, soil properties and the minerals present in the soil (Busman et al, 1998). Phosphorus reacts readily with oxygen in the air to form PO_4^{3}, which then tends to combine with cations (Ca, Mg, Fe, Al) in the soil to form low-solubility substances that are generally not available to plants (fixed pool; Holtan et al, 1988) which helps to explain the low proportion of P added in manure and fertilizer (5-30%; Gardiner and Miller, 2004) that is used by plants (Anon, 2000), when compared to N, which is more mobile and diffuses throughout the soil after application (Gardiner and Miller, 2004). Continued application of P in excess of crop needs will increase the fertility of the soil to an extent, but much of the added P becomes fixed and unavailable and accumulates in the soil (Busman et al, 1998). Phosphate is the only form of P taken up from the soil by plants and converted into organic P (solution pool; Anon, 2006) and is the form that is bioavailable to algae in aquatic environments (McHale et al., 2002; Carlson and Simpson, 2007). Between 50 and 75% of P in most soils is in the inorganic form (Anon, 2001). When the plants die, or when animals that have consumed the plants produce waste, the organic P is then returned to the soil as organic residues (Busman et al, 1998).

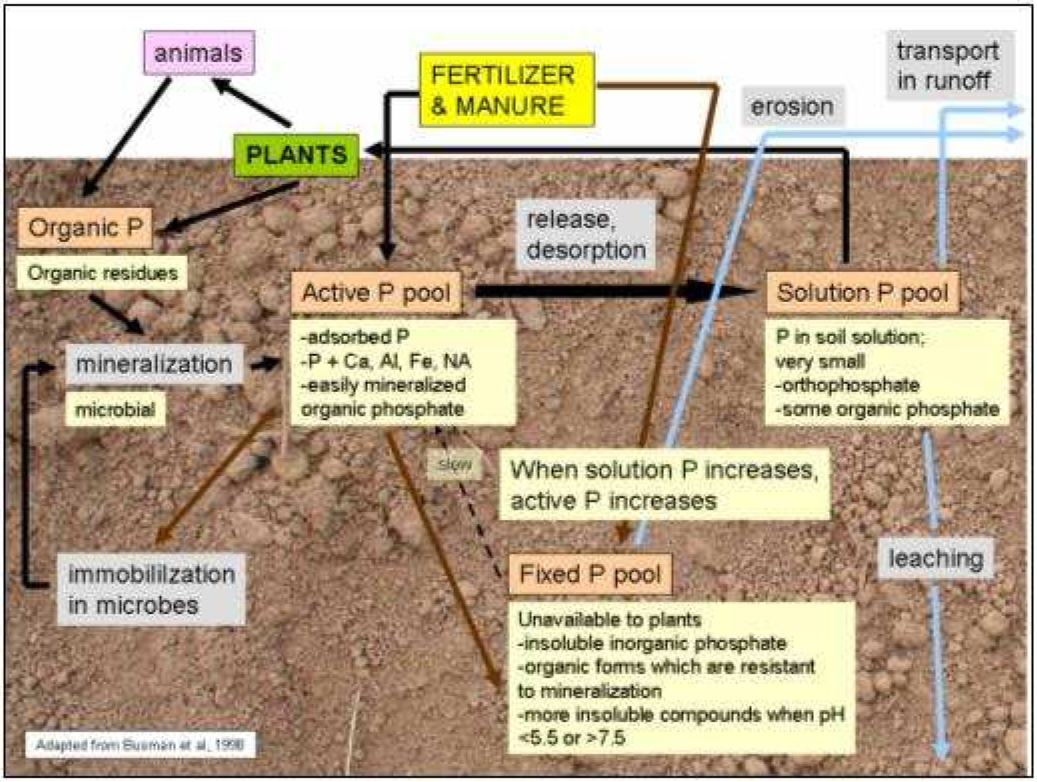


Figure 2- The soil components of the phosphorus cycle
(adapted from Busman et al, 1998).

Phosphorus adsorbed to soil particles can be lost via transport in surface runoff or to a lesser extent by leaching (Busman et al., 1998). If adsorption sites on the soil particles are full, then losses of P due to leaching are more likely (Sims et al., 1998). Some studies have found that dissolved organic P is mobile in the soil and that organic P (dissolved and particulate) may be susceptible to leaching (Chapman et al, 1997), and since it could mineralized to dissolved reactive P during leaching (Jiao et al, 2004), export of organic P from agricultural basins could also lead to eutrophication.

The amount of N and P exported to surface water depends on such factors as the timing of fertilizer and manure application in relation to rainfall, the rate, season, chemical form and amount of application, soil type, texture, and structure, the amount of P already in the soil, the amount and type of crop cover (Carpenter et al., 1998) and the hydrologic flow paths occurring in the soil (Kung et al., 2000a).

1.2.1.4 Diffusion of Soil Nutrients throughout Soil Water

Fick's law states that solutes will diffuse throughout the water naturally due to the random thermal motion of the solute molecules until an equilibrium concentration of the solute is reached in the entire volume of water (Smettem, 1986). The rate of diffusion is quite slow and is driven by the concentration gradient of the solute and the diffusion coefficient of that particular solute (Smettem, 1986). Nitrate, for example, diffuses at a rate of 5mm per day, and the NO_3^- movement initiated by a rainfall event of as small as 2mm can cause the same amount of NO_3^- transport (Smettem, 1986). Since the rate of the diffusion of solutes is so slow compared to the rate of water movement in soils, equilibrium can only be reached between the percolating water and soil water if the rate of water flow in the soil is lower than the rate of diffusion of the solute. Unsaturated hydraulic conductivity even in soil classified as a 'confining layer' exceeds the rate of NO_3^- diffusion in the soil so complete equilibrium of nutrients within the soil volume is unlikely to exist (Vidon and Hill, 2006).

1.2.1.5 Location of Agricultural Nutrients in Recently Surface-Applied Solutes versus Incorporated into Soil Matrix

Nutrients in agricultural soil are found in two sources in the soil; on or near the soil surface if fertilizer and manure have been recently applied and have not yet been incorporated into the soil (Sims et al., 1998; McDowell and Sharpley, 2001; Geohring et al., 2001), and in soil matrix pores when the nutrients were not recently applied and have subsequently been incorporated into the soil profile (Flury, 1996; Macrae et al., 2007a; Welsch et al., 2001). The longer the time between nutrient application and rainfall events, the more cycling of nutrients and use by plants that occurs, and the greater amount of incorporation of the nutrients into the soil matrix (McDowell and Sharpley, 2001; Gaynor and Findlay, 1995). The source of nutrients is important because different flow paths (matrix and preferential flow) have different effects on the transport of nutrients from each of these two sources. It is important to understand how the different nutrient sources and flow paths interact in order to understand the vertical leaching of nutrients through the soil and therefore bulk nutrient transport from agricultural catchments.

1.2.2 Influence of Antecedent Soil Moisture and Rainfall Rates on Discharge Depth from Vertical Leaching

The water content of the soil can affect the amount of discharge that is produced by the soil (de Rooij and Stagnitti, 2002), with more discharge produced sooner at higher rates by wetter soil (Flury, 1996; Welsch et al., 2001; Geohring et al., 2001). Hydraulic conductivity of unsaturated soil decreases with water content (Barraclough, 1989a) because water moves first into smaller pores in dry soil because of the difference in matric potential between large and small soil pores (Kung et al., 2000a; Munyankusi et al., 1994), and thus tends to go into storage in the matrix of the soil (Kung et al., 2000a, b; Brady and Weil, 1996) rather than be transported (Brady and Weil, 1996), even if the infiltration rate of the soil is exceeded (Barraclough, 1989a).

Some studies have found a positive relationship between the depth of rainfall and the amount of discharge produced (*e.g.* Sharpley et al., 2008; Edwards et al., 1988; Biron et al., 1999; Sharpley et al., 2008), but there are very few studies that examine the role of the rainfall rate on the amount of discharge produced by soil. Higher rainfall rates have been found to produce higher discharge rates (*e.g.* Wildenschild et al., 1994; Dils and Heathwaite, 1999; Sharpley et al., 2008), which are correlated with greater total amounts of discharge (de Rooij and Stagnitti, 2002). Many authors that study different natural rainfall events do not discuss differences in discharge between events, and simulated rainfall is often simulated either at unrealistically high rates or for unrealistically long periods of time.

1.2.3 Vertical Hydrologic Flow Paths in Soil

Vertical water flow in unsaturated, heterogeneous soil is not uniform in space and time and may be complicated by preferential flow in macropores, complicating the use of Darcy’s Law or the Richard’s equation to describe and predict flow (Kung et al., 2000b; Armstrong et al., 1999). It is influenced instead by variations in soil structure and the varying water content and matric potential throughout the soil (Armstrong et al., 1999).

Darcy’s law as it applies to vertical flow in unsaturated soil is written as

$$qx = -K_h(\theta) \bullet \frac{d[z + \varphi(\theta)]}{dz} \qquad [1]$$

where dz/dz represents the gravitational potential energy gradient, which equals unity in unsaturated soil (-1 for downward flow and +1 for upward flow; Dingman, 2002), and thus the equation is properly expressed for vertical flow in unsaturated soil as

$$qx = -K_h(\theta) \bullet \left[1 + \frac{d\varphi(\theta)}{dz}\right] \qquad [2]$$

where $-K_h(\theta)$ is the hydraulic conductivity of the soil (K_h) as it varies with water content (θ), and $\frac{d\varphi(\theta)}{dz}$ represents the matric potential energy gradient as it varies with water content (θ). Darcy’s law states that water movement in unsaturated soil occurs in response to the hydraulic conductivity of the soil and the gradient of matric potential, both of which are influenced by the water content of the soil, with hydraulic conductivity increasing with soil moisture and matric potential decreasing (*i.e.* becoming less negative) with soil moisture (Kung et al., 2000a, b; Dingman, 2002). In natural soil, the matric potential and hydraulic conductivity of the soil also vary with the soil structure, specifically the grain and pore size distribution in the soil, so that both properties vary both with space and with time (Brusseau and Rao, 1990; Brady and Weil, 1996).

The Richard’s equation is also commonly used to describe and model water movement in unsaturated soil. It equation describes unsaturated water movement in successive layers of soil and in each layer, hydraulic conductivity, matric potential gradients and water contents are homogenous in space, although they may change with time (Dingman, 2002). The Richard’s equation is derived from Darcy’s law and the law of conservation of mass (Dingman, 2002).

Darcy’s law and the Richard’s equation do not consider that water incident on the soil surface would enter pores of a wide size spectrum (Kung et al., 2000b). Water flow in unsaturated soil can very generally be classified in one of two flow types; matrix and preferential flow through macropores . Matrix flow is characterized by water flowing slowly through small pores, where the water flows through a large proportion of the total volume and the rate of flow in different parts of the soil is very similar (Barraclough, 1999a). However, water that enters the soil surface does not necessarily flow through the entire soil matrix, and is sometimes routed quickly through large soil pores that are created by burrowing insects, vegetation stems, freeze-thaw cycles, segregated ice in the soil in the winter and interaggregate pore space and cracks (macropores) in the soil (Kung, 1990; Bower-Bowyer, 1993). Infiltrating water will enter larger soil pores when the moisture content is higher and many matrix pores are filled with water (Dingman, 2002) or when the rate of water application (*i.e.* rainfall) exceeds the maximum infiltration rate of the soil matrix (Dingman, 2002). Macropores tend to be more abundant in the upper layers of the soil (de Rooij and Stagnitti, 2002) and are more abundant in highly structured soils with a high clay content (Armstrong et al., 1999) because shrinkage cracks are created during dry periods (Simard et al., 2000). The distribution of macropores varies spatially (Czapar et al., 1994) and they are not continuous from or always visible on the surface of the soil (Czapar et al., 1994). Often, flow paths in the soil converge into macropores (de Rooij and Stagnitti, 2002). Macropores may be filled partially or totally with air, obstructing water flow and complicating water movement (Armstrong et al., 1999).

Rates of water movement in unsaturated soil in which preferential flow is occurring are rapid and exceed the saturated hydraulic conductivity of the soil (Kung et al., 2000a). Macropores account for a small amount of space but a large proportion of water flow through the soil (Richard and Steenhuis, 1988) because water flows quickly through them (Kung et al., 2000a; Trudgill et al., 1983a; Burt and Pinay, 2005). The faster rate of flow in macropores is due to their larger size, because in a larger soil pore, there is less soil surface area in contact with a given volume of flowing water, and thus the electrostatic attraction of the water to the soil and the surface tension of the water have less of an influence (Brady and Weil, 1996). Both this electrostatic attraction to the pore walls and the surface tension of the water cause capillarity, in which water will rise up a small tube due to the interaction of these two forces (Brady and Weil, 1996). The height of the rise in a capillary tube is proportional to 0.15 divided by the radius of the tube (Brady and Weil, 1996). These same two forces also influence the rate at which water flows in soil pores of different sizes, with the flow rate increasing non-linearly with increasing pore and crack size (Brady and Weil, 1996; Armstrong et al., 1999). The total flow rate in saturated soil pores is proportional to the fourth power of the radius of the space, causing larger (macropore) pore spaces to account for the most saturated water movement (Poiseuille’s law; Brady and Weil, 1996). When macropores exist as cracks in the soil, the rate of flow in them is proportional to the third power of the crack width (also Poiseuille's law; Armstrong et al., 1999).

Soil properties and heterogeneity, along with the water content of the soil and rainfall rate, all influence the flow type that will occur in the soil (Richard and Steenhuis, 1988). Both flow types can occur to varying extents simultaneously through the same soil (Richard and Steenhuis, 1988) and the dominance of a particular flow type can change with depth in the soil, due to differences in soil properties and water content (Trudgill et al., 1983b). The relative dominance of each flow type in the soil may be influenced (among other factors) by the rainfall intensity and the antecedent soil moisture at the time of rainfall, but these influences are not fully understood. Therefore, each rainfall event, because of the variation in rainfall intensity and antecedent soil moisture, may have a different effect on the leaching of solutes through the soil through preferential flow paths.

Many authors have shown that preferential flow can occur under a variety of conditions. There are two such conditions under which it occurs which are relevant to this study. In the first condition *(1)*, preferential flow occurs under high intensity rainfall if the rainfall rate exceeds the infiltration rate of the soil (Barraclough, 1989a; Armstrong et al., 1999), and this happens to a greater degree in wet soil (Barraclough, 1989a). Under high intensity rainfall, water will enter preferential flowpaths to a lesser extent in dry soil, because of the greater matric potential (Kung et al., 2000a), and when it does enter macropores, some will enter into the macropore wall due to higher matric potential in the macropore wall than in the macropore (Barraclough, 1989a), resulting in later and less discharge in dry soil (de Rooij and Stagnitti, 2002), even under high intensity rainfall. The second condition *(2)* under which preferential flow flow occurs is under lower intensity rainfall, once the soil has wet up (Armstrong et al., 1999). Kung et al (2000a) have shown that as the soil wets up under low to moderate rainfall rates (5.0 and 7.5mm/hour), the gradient of matric potential first favours water to enter the smallest matrix pores, and as the soil wets up and the matric potential decreases, water enters and travels through larger and larger pores, eventually flowing preferentially in progressively larger soil pores. Preferential flow will occur sooner after the start of rainfall in this scenario in wet soil because the matric potential gradient will be less due to the higher moisture content of the soil (Kung et al., 2000a).

1.2.3.1 Influence of Rainfall Rate on Vertical Flow Paths

High rates of rainfall are correlated with water movement through larger pores (Barraclough, 1989a) and with preferential flow (Akhtar et al., 2003; Armstrong et al., 1999). Matrix flow tends to dominate during low rainfall rates, regardless of the soil structure (Barraclough, 1989a). Rainfall occurring at lower rates does not exceed the infiltration rate of the soil, and as a result, water tends to enter smaller soil pores (Barraclough, 1989a). At higher rainfall intensities, the infiltration rate of smaller soil pores will be exceeded (Trudgill et al., 1983), causing more of the rainfall at the soil surface to be routed into successively larger soil pores with increasing rainfall intensity (Barraclough, 1989a).

1.2.3.2 Influence of Antecedent Soil Moisture on Vertical Flow Paths

The water content of the soil can affect whether or not and the extent to which preferential flow will occur (Kung et al., 2000a). Infiltrating water tends to go into storage in smaller soil pores when the soil is dry because of the gradient of matric potential (Kung et al., 2000a; Munyankusi et al., 1994). As a result, infiltrating water that enters large pores in dry soil will often move into the pore walls, rather than being transported through the soil (Barraclough et al., 1989a; de Rooij and Stagnitti, 2002). As this matric potential gradient diminishes, water will flow through larger and larger pores, some of which will constitute preferential flow paths (Kung et al., 2000a; Barraclough, 1989a; James and Roulet, 2007). More hydrologic pathways are active as the soil becomes wetter and the number and size of active preferential flowpaths can change (and increase) throughout an event as the water content of the soil increases (Kung et al., 2000b). Therefore, preferential flow is more likely to occur in wetter soils (Kung et al., 2000b; Barraclough, 1989a), but has been shown to occur in drier soils if the infiltration rate of the soil is exceeded (Barraclough, 1989a; Burt and Pinay, 2005). After rainfall stops, the larger soil pores empty of water first, with successively smaller soil pores emptying as the soil dries (Barraclough, 1989a) and the hydraulic conductivity of the soil decreasing accordingly (Barraclough, 1989a).

1.2.4 Influence of Hydrologic Flow Paths and Discharge Depth on Solute Transport

1.2.4.1 Influence of Discharge on Nutrient Transport

Many studies have found a positive correlation between discharge and nutrient concentrations (Britton et al., 1993; Macrae et al., 2007; Stieglitz et al., 2003) and the mass of nutrients exported (Owens et al., 2000; Kladivko et al., 1999; Macrae et al., 2007a; Jiao et al., 2004; Kung et al., 2000b), but this relationship is inconsistent and varies between events (Macrae et al., 2007a; Britton et al., 1993; Biron et al., 1999; Vanni et al., 2001) due to the influence of antecedent soil moisture on nutrient transport (Britton et al., 1993; Flury, 1996; Vanni et al., 2001; McHale et al., 2002). Since discharge is higher from wet soil (de Rooij and Stagnitti, 2002; Geohring et al., 2001), it is expected that nutrient flux will increase with discharge.

1.2.4.2 Influence of Hydrologic Flow Paths and Nutrient Sources on Nutrient Transport

The low rate of matrix flow allows for greater diffusion of mobile solutes such as NO_3^- from areas of high concentration to areas of low concentration, allowing for some equilibration of solute concentrations between the percolating water and the surrounding soil water (Barraclough, 1989a; Britton et al., 1993). However, immobile solutes such as PO_4^{3-} may be re-adsorbed within the soil profile because of the slow rate of matrix flow (Trudgill et al., 1983a; Kung et al., 2000a; Akhtar et al., 2003). If the slowly percolating water is low in solute concentrations and most nutrients are present in the soil matrix, then it will remove solutes such as NO_3^- from the soil (Armstrong et al., 1999; Kladivko et al., 2009), but will not remove immobile solutes such as PO_4^{3-} from the soil profile (Trudgill et al., 1983; Kung et al., 2000a). If the percolating water is high in solute concentrations because of recently applied fertilizer or manure, then it will deposit adsorbing solutes such as PO_4^{3-} in the soil more than soluble solutes such as NO_3^- (Armstrong et al., 1999) because the slow rate of matrix flow will allow for the adsorption of PO_4^{3-} by the soil matrix (Kung et al., 2000a; Geohring et al., 2001). During matrix flow, the concentrations of solutes in the leachate will be relatively constant with time (Kung et al., 2000a) because the low flow rate of water flow will allow for the equilibration of solute concentrations between soil and event water (Kung et al., 2000a). This will cause the leachate to be fairly uniform in composition throughout the soil volume and therefore uniform in composition when it leaves the soil (Kung et al., 2000a; Trudgill et al., 1983a).

The high velocity of preferential flow does not allow for much interaction between the percolating water and soil water in smaller soil pores (Armstrong et al., 1999; Trudgill et al., 1983a; Burt and Pinay, 2005), and thus renders solutes in soil water in small pores relatively immobile (Barraclough, 1989a; Chapman et al., 1997) and exports lesser quantities of nutrients in soil water than matrix flow (Jiao et al., 2004; Burt and Pinay, 2005). The leaching of PO_4^{3-} from the matrix of the soil is not well studied and is less well understood than the leaching of soil NO_3^-, but it is likely that both nutrients would be leached minimally when preferential flow is occurring because of the lack of contact with the soil matrix. Both non-adsorbing and adsorbing nutrients already present in the event water (*i.e.* recently surface-applied manure and granular fertilizer) will be transported more readily when preferential flow is occurring, as adsorbing solutes present in the event water will behave much like more conservative, non-adsorbing solutes and pass through the soil with minimal loss to soil water (Barraclough, 1989a; Akhtar et al., 2003; Kung et al., 2000b). Because of the higher rate of transport and tendency not to lose solutes in event water to the surrounding soil matrix, preferential flow can transport surface-applied solutes in event water to greater depths within the soil profile than matrix flow (Trudgill et al., 1983b).

The two scenarios under which preferential flow occurs that were discussed previously (1= infiltration excess preferential flow; 2= saturation preferential flow) have differing effects on the temporal changes in the concentration of non-adsorbing solutes such as NO_3^- and adsorbing solutes such as PO_4^{3-} when they are already present in the soil matrix. In scenario 1, the percolating water will firstly be dominated by event water, bypassing NO_3^- pools in the soil matrix, and causing concentrations of NO_3^- in leachate to start off low. Through time, matrix pores will become progressively more and more active in the transport of percolating water (Kung et al., 2000a), accessing more NO_3^- in the matrix of the soil. Concentrations of NO_3^- in leachate will begin to rise through time as matrix pores become more active in leaching (Kung et al., 2000a; Britton et al., 1993). In scenario 2, water will percolate firstly through matrix pores, accessing existing NO_3^- pools in the soil matrix and the concentration of NO_3^- in leachate will start off high. Through time, as larger and larger soil pores become active in transporting water, a higher proportion of percolating water will be moving quickly through the larger soil pores and therefore not accessing NO_3^- pools in the soil matrix, and NO_3^- concentrations in leachate will drop (Kung et al., 2000a; Britton et al., 1993). The opposite is true for PO_4^{3-} since it is an adsorbing solute. In scenario 1, PO_4^{3-} concentrations will start off higher due to the transport of PO_4^{3-} from the walls of large soil pores when preferential flow is active (Kladivko et al., 1991). When these nutrient sources run out and when matrix flow becomes more dominant, PO_4^{3-} concentrations in leachate will decrease because PO_4^{3-} is not transported nearly as much as NO_3^- in matrix flow because the slow rate of matrix flow allows for the re-adsorption of PO_4^{3-} to the soil matrix (Kung et al., 2000a; Akhtar et al., 2003). In scenario 2, PO_4^{3-} concentrations in leachate will be low when matrix flow is dominant, and will increase as preferential flow becomes more dominant.

These two scenarios also have different effects on the temporal changes in the concentration of surface-applied solutes. When solutes are surface-applied, adsorbing solutes behave like non-adsorbing solutes during preferential flow (Kung et al., 2000a; Armstrong et al., 1999). Therefore, in scenario 1, concentrations of both NO_3^- and PO_4^{3-} would start off high and decrease with time as matrix pores became more active (Kung et al., 2000a, b; Armstrong et al., 1999), with more NO_3^- than PO_4^{3-} transported when matrix pores are active (Kung et al., 2000a). In scenario 2, concentrations of both nutrients in leachate will increase as preferential flowpaths become more active (Kung et al., 2000a, b; Armstrong et al., 1999). Although the leaching of surface-applied solutes is not directly studied here, the results will still be discussed in terms of their potential impact on surface-applied solutes.

1.2.5 Relevance of Lab Leaching Studies to the Understanding of Nutrient Export from Agricultural Catchments

The leaching of nutrients through the soil is of particular concern in fields with drainage tiles, as this is the typical transport pathway for nutrients into drainage tiles (McDowell and Sharpley, 2001; Flury, 1996; Sims et al., 1998; Kladivko et al., 2009). Tiles are commonly installed in poorly drained soils such as clays, which are more susceptible to the creation of macropores through cracking (Gradiner and Miller, 2004). Drainage tiles provide a faster and more efficient conduit for all nutrients applied to agricultural soil to surface water because of the lack of direct contact between the water they contain and the soil (Davis et al., 2000; Dils and Heathwaite, 1999; Sims et al., 1998; Kladivko et al., 1991), especially when macropore flow is occurring (Macrae et al., 2007a; Simard et al., 2000). Tiles also circumvent nutrient management implements like buffer strips and riparian zones (Dils and Heathwaite, 1999). Tiles increase the drainage rate of soils and therefore the discharge from agricultural catchments considerably (Burt and Pinay, 2005).

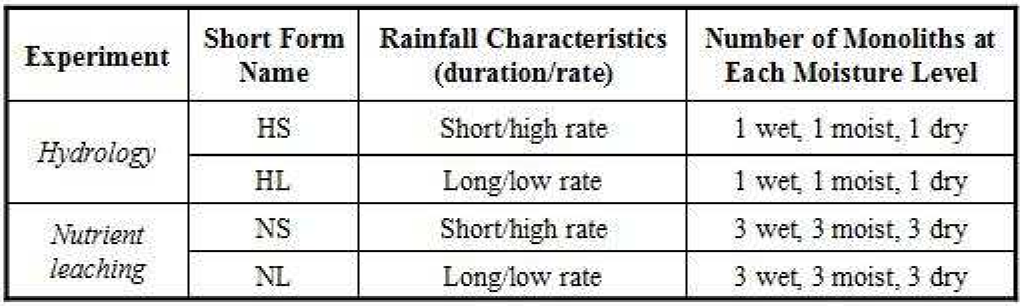
Although monoliths do not accurately represent all of the types of flow in an agricultural catchment (such as overland flow and lateral subsurface stormflow; Kung et al., 2000a, b; Flury, 1996), they are still a valid means of furthering the understanding of the influence of individual variables on vertical nutrient transport through the soil because of the importance of this transport pathway in the transport of nutrients to drainage tiles. Drainage tiles are the main pathway of nutrient transport to streams in some agricultural watersheds (*e.g.* Macrae et al., a, b; Sims et al., 1998; Kladivko et al., 1991, 2009; McDowell and Sharpley, 2001). The relationships between antecedent soil moisture and rainfall rates are not always clear from field studies, so these variables need to be isolated and studied in more detail in lab experiments, which allow for greater control over experimental variables (Hall et al., 1989; Rickson, 2001; Bower-Bowyer and Burt, 1989). Lab leaching studies in which realistic rainfall rates are used to study the leaching of soil nutrient pools, rather than surface-applied solutes or tracers, are also rare. Because nutrient export from existing soil pools due to natural rainfall events does occur (Macrae et al., 2007; Kung et al., 2000a; Kladivko et al., 2009; Welsch et al., 2001; Macrae et al., 2007), more realistic lab experiments are needed to understand leaching behavior under these circumstances. It is important to use intact soil columns when performing leaching experiments, because repacked columns do not retain natural soil structures (Akhtar et al., 2003; Belford, 1979; Persson and Bergström, 1991) and therefore do not accurately represent leaching in natural soil (Kung et al., 2000a, b). Therefore, the effects of antecedent soil moisture and the rainfall rate on the hydrologic response of the soil and nutrient transport will be isolated and studied using intact soil monoliths.

Chapter 2

Study Site and Methods

2.1 Experimental Design

In order to examine the effects of antecedent soil moisture and rainfall rates on the hydrologic response of agricultural soil and nutrient export in a controlled setting, two separate experiments were performed on intact soil monoliths in a lab. The objective of the first experiment was to assess the hydrologic response of the soil in terms of the amount of runoff produced and the dominant flow paths in the soil, as determined by temporal changes in soil moisture at different depths in the soil (referred to as the 'hydrology experiment'). The objective of the second experiment was to assess quantity and timing of nutrient (NO_3^- and PO_4^{3-}) export from the soil (referred to as the 'nutrient leaching experiment'). In both experiments, two different types of rainfall events were simulated; long duration with low intensity and short duration with high intensity (Table 2). Monolith soil was dried to three different levels of soil moisture (referred to as 'wet', 'moist', and 'dry') in both events in both experiments. Climatic and soil physical and chemical conditions were also monitored in the field for comparison to the hydroclimatic conditions created in the lab.



Experiment	Short Form Name	Rainfall Characteristics (duration/rate)	Number of Monoliths at Each Moisture Level
Hydrology	HS	Short/high rate	1 wet, 1 moist, 1 dry
	HL	Long/low rate	1 wet, 1 moist, 1 dry
Nutrient leaching	NS	Short/high rate	3 wet, 3 moist, 3 dry
	NL	Long/low rate	3 wet, 3 moist, 3 dry

Table 2- Nomenclature of rainfall treatments and number of monoliths in each experiment.

2.2 Study Site

The study site (John Mount Farm; JMF) is located in Flamborough, Ontario, Canada in the Flamborough Plain physiographic region, approximately 40km northwest of Hamilton (43° 22' N, 80° 07’ W, 265-270m asl) (Kaufman, 2005; Heagy, 1993) and adjacent to the Beverly Swamp. Monoliths were collected from the untilled interface between a naturally drained, conventionally tilled cultivated field and a treed riparian zone (Figure 3). The cropped field is under a corn-winter wheat-soybean-hay rotation, with winter wheat in production during 2008 when the monoliths were collected (Leach, 2009). The field was top-dressed with granular nitrogen fertilizer and a custom herbicide in the spring (April) of 2008, potash and P were applied in 2007 (field was cultivated with soybeans) and nitrogen and phosphorus were applied in granular fertilizer in 2006 (Leach, 2009). The field has been farmed for over 100 years with a similar crop rotation and application of a combination of manure, potash and chemical fertilizer depending on crop needs (Leach, 2009). Research has been undertaken in the adjacent riparian zone and swamp for many years (*e.g.* DeSimone, 2009; Leach, 2009; Cymbaly, 2009; Zhang, 2007; Kaufman et al., 2005; Galloway and Branfireun, 2004; Warren et al., 2001; Munro et al., 2000; Munro, 1989, 1987, 1982, 1979; Woo and Valverde, 1981).

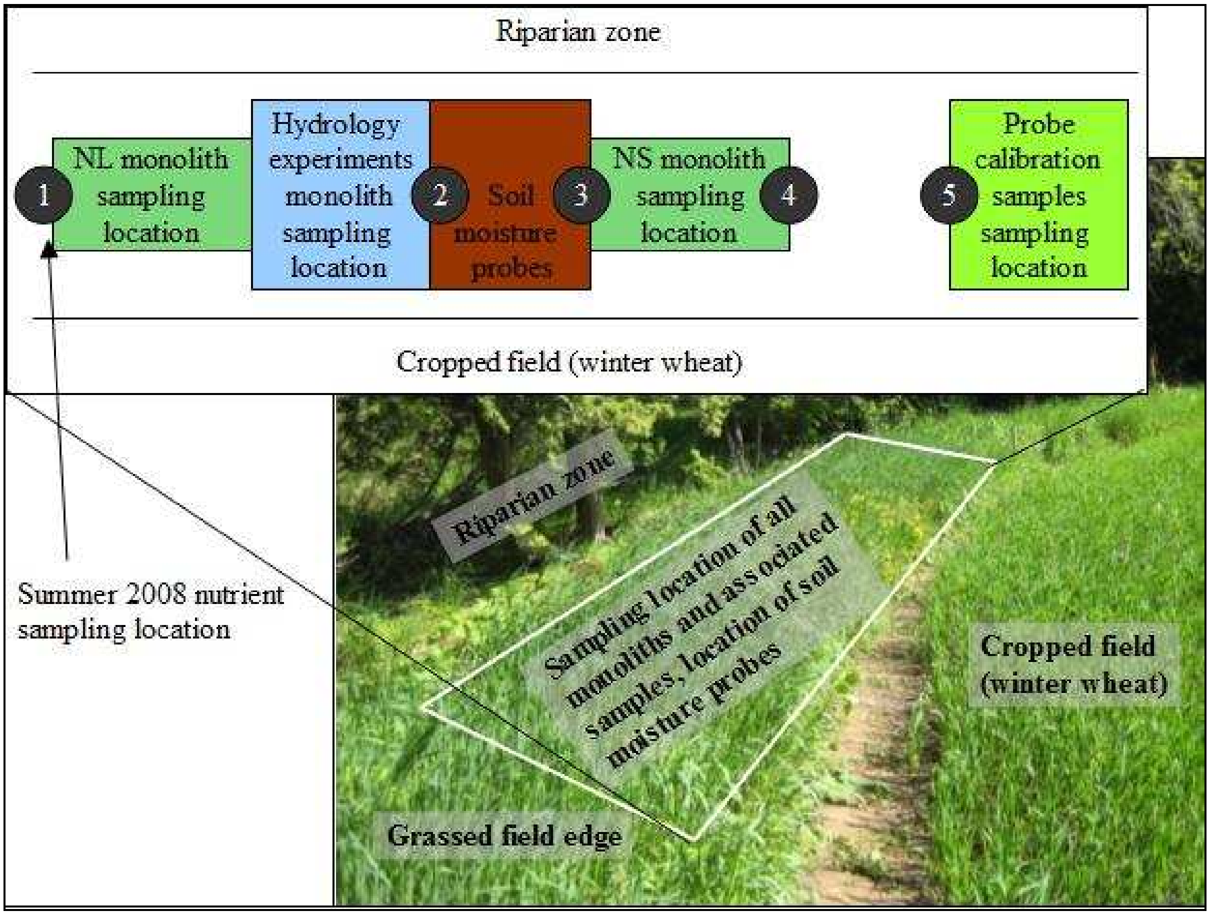


Figure 3- Photo of site of monolith and sample collection, with schematic diagram showing all sampling locations.

NL = long nutrient leaching experiment; NS = short nutrient leaching experiment; numbers are soil nutrient pool samples taken with an auger during the summer 2008 field season.

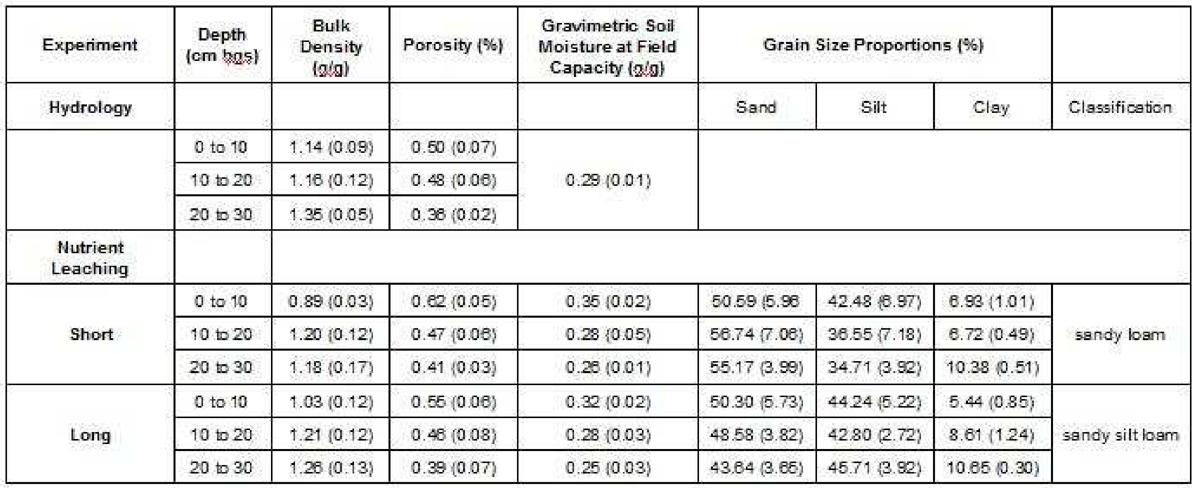
The climate at the site is classified as humid continental (Warren et al., 2001). The mean annual air temperature is 7.6°C and the average air temperature from May 1- October 31 is 16.0°C (Environment Canada, 2009). The 30-year (1971-2000) average annual rainfall at the site is 830.7mm, or 83% of the average annual precipitation 973mm (Environment Canada, 2009), with an average summer rainfall (May 1-October 31) of 480mm (Kaufman, 2005).

The study site lies within the Spencer Creek watershed. Spencer Creek is a second order stream that runs through the swamp, approximately 20 meters away from the sampling site (Galloway and Branfireun, 2004). Groundwater flow through the adjacent riparian zone is predominantly lateral, parallel to Spencer Creek (Zhang, 2007). A dam on Spencer Creek upstream of the swamp is released every fall and occasionally during other periods, flooding the riparian zone (Leach, 2009).

The soils at the study site are grey-brown luvisols and melanic brunisols according to the FAO classification system (cambisols; Pesant and Wicklund, 1971) and are well-drained and moderately stony Guelph loam according to the Canadian System of Soil Classification (Heagy, 1994). The soil is underlain by approximately 40 meters of shallow Guelph formation dolostone (Heagy, 1995), above which are layers of stony to sandy Wentworth till (1-6m), gravel, silt, sand and clay (Heagy, 1993; Galloway and Branfireun, 2004). The topography of the monolith collection site is flat, with a step down (approximately 1m) into the adjacent riparian zone that is the result of long-term soil erosion from the adjacent agricultural field (Leach, 2009). The adjacent field slopes towards the site and the riparian zone, which has an organic layer depth of 0.3-1.5m, underlain by marl (0.5-1m thick), then layers of sand, gravel and silty sand in sequence (Zhang, 2007).

Grain size varies only slightly by depth, with clay content increasing with depth. Soils at the NS event monolith collection site contain slightly more sand than those at the NL event monolith collection site. Sand is the most dominant sediment fraction by mass except for the 20-30cm depth at the NL event site, where silt is the most dominant fraction. The experimental soils are on the boundary between sandy loams and sandy silt loams, with slightly more sand at the NS event site.

The experimental soils have bulk densities of 1.16 ± 0.10g/cm^3 and porosities of 0.47 ± 0.06 (Table 3). In general, bulk density and porosity are comparable between the three sites where the monoliths were collected, although bulk density is slightly higher and porosity slightly lower at the hydrology experiment collection site. Bulk density increases with depth while porosity decreases at all sites. There are no visually distinct changes in soil character (structure, colour, grain size), other than obvious changes in bulk density from the soil surface (0 to 10cm) to lower depths (10 to 30cm).



Experiment	Depth (cm bgs)	Bulk Density (g/g)	Porosity (%)	Gravimetric Soil Moisture at Field Capacity (g/g)	Grain Size Proportions (%)			
Hydrology					Sand	Silt	Clay	Classification
	0 to 10	1.14 (0.09)	0.50 (0.07)	0.29 (0.01)				
	10 to 20	1.16 (0.12)	0.48 (0.06)					
	20 to 30	1.35 (0.05)	0.38 (0.02)					
Nutrient Leaching								
Short	0 to 10	0.89 (0.03)	0.62 (0.05)	0.35 (0.02)	50.59 (5.96	42.48 (6.97)	6.93 (1.01)	sandy loam
	10 to 20	1.20 (0.12)	0.47 (0.06)	0.28 (0.05)	56.74 (7.06)	36.55 (7.18)	6.72 (0.49)	
	20 to 30	1.18 (0.17)	0.41 (0.03)	0.26 (0.01)	55.17 (3.99)	34.71 (3.92)	10.38 (0.51)	
Long	0 to 10	1.03 (0.12)	0.55 (0.06)	0.32 (0.02)	50.30 (5.73)	44.24 (5.22)	5.44 (0.85)	sandy silt loam
	10 to 20	1.21 (0.12)	0.46 (0.08)	0.28 (0.03)	48.58 (3.82)	42.80 (2.72)	8.61 (1.24)	
	20 to 30	1.26 (0.13)	0.39 (0.07)	0.25 (0.03)	43.64 (3.65)	45.71 (3.92)	10.65 (0.30)	

Table 3- Soil bulk density, porosity, grain size ranges and soil type for each experimental site.

Values in parenthesis are standard deviation. Gravimetric soil moisture at field capacity for the hydrology experiment site was determined from monoliths (weighing), The value shown is the average from all three monoliths in both hydrology events.

The monolith collection site is vegetated predominantly with grasses (*e.g.* Smooth Brome Grass- *Bromis inermis*, Reedcanary Grass- *Phalaris arundinacea*) and some herbaceous species such as Wild Cucumber (*Dryopteris spinulosa*), Cow Parsnip (*Heracleum lanatum* Michx.), Canada Anemone (*Anemone canadensis*), Ostrich Fern (*Matteuccia struthiopteris*), Aster (*Aster* spp.) and Goldenrod (*Solidago* spp.). The adjacent riparian zone is dominated by deciduous trees such as Silver Maple (*Acer saccharinum L.*), Eastern White Cedar (*Thuja occidentalis* L.), White Elm (*Ulmus americana* L.) and Speckled Alder (*Alnus incana*) and subcanopy trees and shrubs such as Common Buckthorn (*Rhamnus cathartica* L.), Choke Cherry (*Prunus virginiana* L.), Sweet Viburnum (*Viburnum lentago* L.), and Elderberry (*Sambucus canadensis* L.; Cymbaly, 2009).

2.3 Methods

2.3.1 Field Methods

2.3.1.1 Collection of Monoliths

Monoliths were collected from the field on three occasions for the different experiments: (1) three monoliths for use in the hydrology experiment (August 19, 2008); (2) Nine monoliths for the short nutrient experiment (September 30, 2008); (3) 12 monoliths for the long nutrient experiment (October 23, 2008; sampling locations shown in Figure 3).

Monoliths were collected from areas at the field site that had not been walked on or used for any other sampling to ensure that soil sampled was as undisturbed as possible. Immediately before monolith extraction, existing vegetation on the collection site was cut to a height of 2cm or less, taking care not to walk directly on the area at which the monoliths were to be inserted. Monolith casings consisted of a 40cm length of 20cm diameter PVC pipe, sharpened at the bottom (Jensen et al., 1998). A drywall saw was used to cut into the soil before casing insertion, after which casings were hammered into the ground using a block of wood and sledgehammer (Figure 4) until approximately ten centimeters of the casing remained above the soil surface. No soil compaction was observed visually during the casing insertion process. When all casings had been inserted, a trench was dug beside the monoliths to a depth of approximately 40cm and a large metal spade was used to extract each monolith from the ground. Excess soil from the bottom of the monolith was cut off with a large bread knife, after which fiberglass window screening attached to the underside of each monolith with electrical tape. Monoliths were then placed on plywood to protect the bottom soil surface and transported to the lab.

Figure 4- Photos showing insertion of monolith casings into soil (a) and monolith removal (b).

2.3.1.2 Collection of Samples for the Determination of Soil Physical Properties

Additional samples were also collected using Shelby tubes (7.5cm ID, 8.5cm length, aluminum pipe) for the analysis of soil physical properties. These samples were taken at the time of monolith extraction, both for the hydrology experiment and separately for each of the events in the nutrient leaching experiment. Samples were collected at three depths in the soil (5cm, 15cm, 25cm), in triplicate beside each monolith. Samples were wrapped in tinfoil and placed in Ziploc bags and transported to the lab for processing. The volume of soil (Svol) in the Shelby tubes was determined by subtracting the amount of soil missing from the volume of the Shelby tube (63.8cm^3). The following parameters were determined using mass: gravimetric (Gm) and volumetric soil moisture content (Vm), porosity, bulk density (Bd), % saturation (%sat) and the gravimetric soil moisture at field capacity (Gfc). Field moist soils were weighed (Mf), then immersed in water for 24 hours to obtain a saturated weight (Ms), left to drain to field capacity for 12 hours (Mfc), then dried for 24 hours at 105°C to obtain a dry weight (Md). Soil physical characteristics are calculated as follows:

$$Bd(g/cm^3):\frac{Md}{Svol} \qquad [3]$$

$$Porosity(\%):\frac{(Ms-Md)}{Svol} \qquad [4]$$

$$Gm(g/g):\frac{(Mf-Md))}{Mf} \qquad [5]$$

$$Vm(cm^3/cm\ \ ):\frac{Gm}{Bd} \qquad [6]$$

$$\%sat:\frac{Vm}{porosity*} \qquad [7]$$

$$Gfc(g/g):\frac{(Mfc - Md))}{Mfc} \qquad [8]$$

*Porosity was determined for both Shelby tubes and monoliths. Shelby tubes were used to estimate soil moisture in monoliths during drying but monolith porosity was used in all subsequent calculations and the presentation of data in this thesis.

When monoliths and soil property samples were collected, care was taken to ensure there was minimal loss of soil, but regardless, small amounts of soil were sometimes lost from soil property samples and from monoliths. Because of the large surface area of each monolith, the elevation of the soil surface varied slightly, and this along with any loss of soil that occurred from the bottom of the monolith made obtaining an accurate estimation of soil volume difficult. Due to the challenges associated with obtaining a good estimate of soil volume, gravimetric moisture content is used throughout this thesis, rather than volumetric soil moisture, although volumetric soil moisture and % saturation are provided for context.

2.3.1.3 Monitoring Field Conditions for Comparison to Simulated Experimental Conditions

2.3.1.3.1 Determination of Soil Nutrient (NO_3^- and PO_4^{3-}) Pools, Summer 2008

Soil samples were also collected five times over the summer to determine the typical nutrient levels at the site, and for comparison to soil nutrient availability in the monoliths throughout the experiments. Soil samples were collected by inserting an auger into the soil vertically at three depths (0-10, 10-20, 20-30cm) at five different sites (15 samples in total) on Julian days (JD) 165, 184, 207, 227, and 247. Samples were placed in Ziploc bags and stored at 4°C in the dark until processing which occurred within 24 hours of collection. Soil samples were homogenized and two 10g subsamples were extracted with 50ml of deionized (DI) water and 50ml of 2M potassium chloride (KCl), respectively. Samples were then shaken for one hour, gravity filtered through Whatman 42 ashless filter paper, then filtered through 0.45µm cellulose acetate membrane filters paper. Soil extracts were frozen until analysis.

Samples which had been extracted with KCl were used to determine soil NO_3^- and NH_4^+ levels, and samples which had been extracted with DI water were used to determine soil PO_4^{3-} levels.

NO_3^- and NH_4^+ concentrations in extractants were determined using colorimetry (Bran+Luebbe Autoanalyzer (AAIII), University of Waterloo), where NO_3^- was reduced to nitrite and then reacted with sulphanilimide (detection limit 0.003mg N L^{-1}). PO_4^{3-} concentrations were determined using Ammmonium Molybdate-Stannous Chloride Reduction (Technicon AAII, University of Waterloo; detection limit 1 μg P L^{-1}). Soil nutrient pools are expressed as μg of N or P per g (dry weight) of soil.

2.3.1.3.2 Continuous Monitoring of Soil Moisture, Summer 2008

To assess the response of soil moisture to rainfall events in the field and compare this response to the results of the hydrology experiment, soil moisture was monitored at the field site throughout the summer 2008 field season (June 9-November 14) adjacent to where monoliths were collected (collection sites shown in Figure 3). Soil moisture was monitored at 15 minute intervals at 5, 17 and 30cm depth (S-SMA-M005, Onset Corporation) and recorded on a HOBO Weather station data logger. The probes were calibrated in the laboratory using soil samples collected from the monolith collection site.

2.3.1.3.3 Collection of Rainfall Data from John Mount Farm, 2008

Rainfall data at the study site was recorded at 15 minute intervals (0.2mm increments) using a tipping bucket rain gauge (Onset Computer Inc.) over the study season. The MET station containing the rain gauge was located approximately 200m away from the site of monolith collection. This data, as well as the data archive from this field site (March 2003- November 2008) were used to determine the quantity of rainfall to apply in the experiments and also to assess how closely the conditions simulated in both experiments matched those present at the field site, specifically the number and depth of rainfall events during the summer of 2008. Rainfall data was used in conjunction with soil moisture data to examine the response of soil at the field site to natural rainfall events.

2.3.2 Lab Setup and Procedures

2.3.2.1 Experimental Lab Setup

Monoliths were placed on stands, equipped with nested funnels to collect runoff or leachate during experiments. Monoliths rested on two large bolts (Figure 5) that contacted the bottom of the casing on opposite sides and nested funnels were held underneath each monolith, in contact with the bottom soil surface of the monolith. Leachate from the outer portion of the monolith adjacent to the casing was collected separately to examine the relative proportions of runoff coming from the inner portion of the monolith versus the soil adjacent to the monolith casing, to test whether or not preferential flow was occurring down the sides of the monoliths. Other authors (*e.g.* Barraclough, 1989a; Akhtar et al., 2003; de Rooij and Stagnitti, 2002; Trudgill et al., 1983a) have indicated the potential for preferential flow between the soil and casing walls due to natural pore spaces and the potential shrinkage of the soil as it dries. The soil within each monolith was not physically separated into inner and outer portions in any way; only the runoff collection was partitioned. The outer leachate collection area covered 20.8% of the total area of the bottom of the monolith (Figure 6). A strip of rubber tubing was glued to the top of the inner funnel to ensure contact between the bottom soil surface, and the inner funnel was deliberately positioned so that the weight of the monolith would press down on it and contact would be made with the bottom surface of the soil.

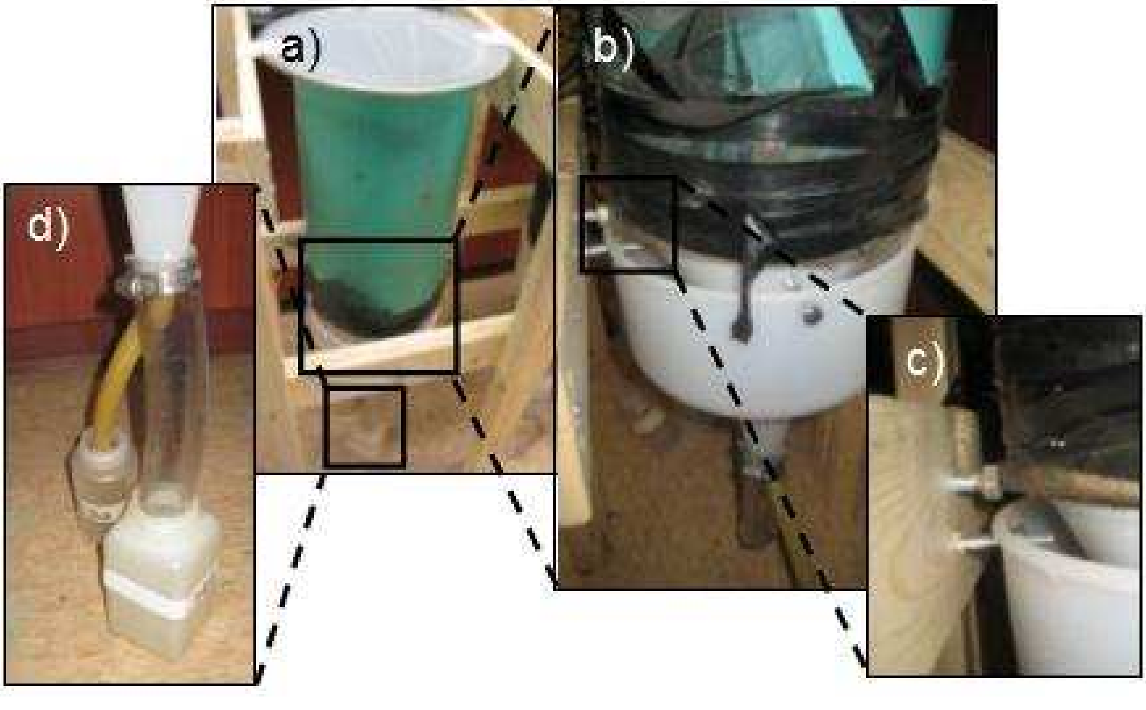


Figure 5- Laboratory monolith setup.

a) monolith (soil in turquoise PVC pipe) on stand overtop of discharge collection apparatus; bolts were passed through the upper horizontal supports and into the sides of the monolith casing to keep the monolith upright; b) bottom of monolith, showing window screening attached with electrical tape and discharge collection apparatus, showing nested funnels and bolts that support the monolith; c) bolts that

support monolith on stand- upper bolt rests underneath outer edge of monolith casing and lower bolt supports outer funnel; d) tubes leading to collection bottles; amber tube leads from inner funnel to collection bottle and large clear tube leads from outer funnel to collection bottle.

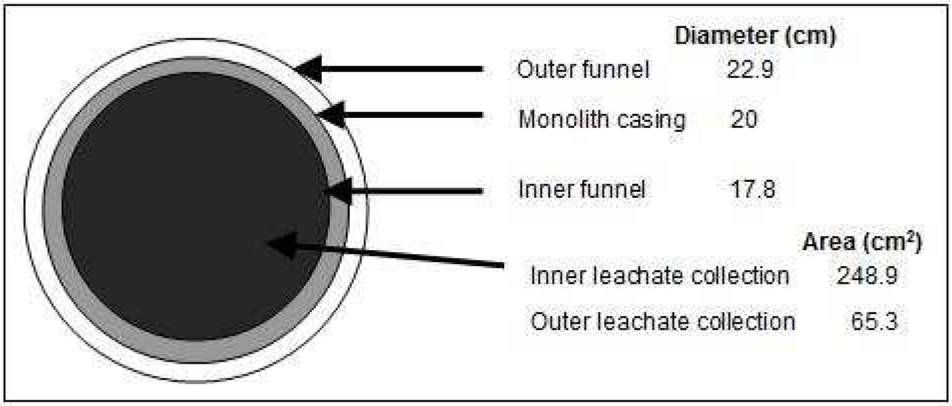


Figure 6- Relationship between diameter of outer funnel, monolith casing and inner funnel.

The inner funnel covers 79.2% of the area of the monolith, while the outer funnel covers the other 20.8%. The outer funnel collects discharge from the outer 1cm perimeter of the monolith. The wall of the monolith casing is 6.5mm thick.

2.3.2.2 Determination of Method and Duration of Rainfall Application

Before any of the experiments began, a series of preliminary trials were performed on three monoliths (the same ones used in the hydrology experiment) to determine how best to apply rainfall, and to determine the quantity of water to be applied to each monolith in order to produce runoff. The total depth of water applied to each monolith was calculated and it was estimated that a rainfall event of a depth of approximately 30mm or greater was needed to produce discharge from all monoliths. Rainfall data from 1998-2007 (collected at the University of Waterloo, (43° 28' 25.6"N, 80° 33' 27.5"W; Seglenieks, 2008) was also examined to determine the frequency of 30mm rainfall events, to ensure that a realistic rainfall quantity had been selected. Data from the University of Waterloo weather station was used instead of data from the Milgrove weather station (operated by Environment Canada; 43° 19.000'N, 79° 58.000'W, 268.2m asl; Environment Canada, 2009) because its 15 minute logging interval made it easier to delineate rainfall events than a 1 hour logging interval used by the Environment Canada Milgrove Weather station. Although the vast majority of days with rainfall have very little rain (5mm or less, Figure 7), there were 14 days in total over the 9 year period with rainfall of greater than 30mm, or at least one day on average within a given year with rainfall of more than 30mm. In some of these cases, a day with a large amount of rainfall was followed by another day with an appreciable amount of rainfall, which could result in an even higher rainfall total in a short period of time. Simulating a rainfall event of greater than 30mm therefore was realistic given observed natural rainfall patterns.

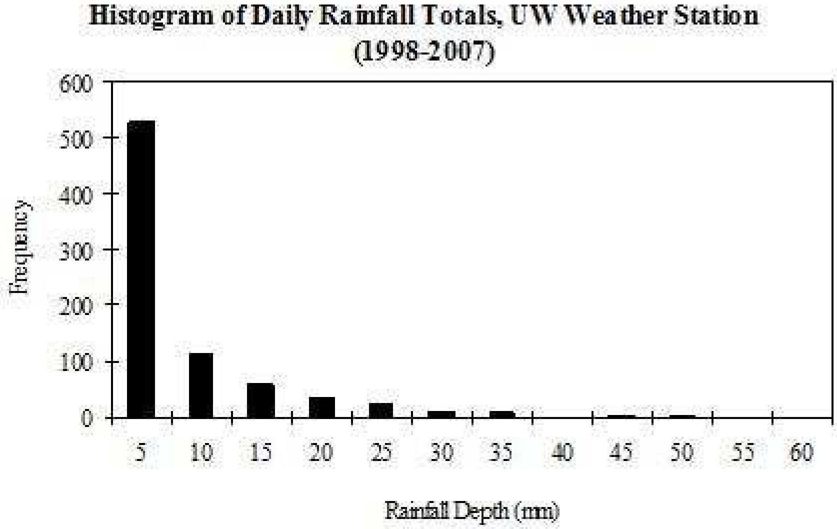


Figure 7- Histogram of daily rainfall data from the University of Waterloo weather station, 1998-2007.

Rainfall was applied to the surface of each monolith using a peristaltic pump, set to the lowest flow setting (2.8ml/s) applied to a mesh screen resting on top of the monolith casing, to break up water droplets. Because even the lowest pump speed produced very high rates of rainfall (0.9mm/10 seconds; 5.43mm/minute or 325.8mm/hour), rainfall could not be applied continuously. Rainfall was applied for ten seconds, followed by a longer period (0:02:30 in the short event and 0:22:00 in the long event) of no rainfall application. This pattern would be repeated at regular intervals but at the different frequencies stated above in each storm type in order to achieve a certain depth of rainfall application. A stopwatch was used to time rainfall application, and care was taken to ensure even coverage of the monolith surface with water. Two types of rainfall events were simulated in each experiment: one short event with a high rainfall rate (22.5mm/hour for 1.5 hours), and one long event with a low rainfall rate (2.5mm/hour for 12.5 hours in the hydrology experiment and 22.5 hours in the nutrient leaching experiment). The same depth of rainfall (30.8mm) was applied to the monoliths in each experiment, except for the long rainfall event in the nutrient leaching experiment, in which 56.1mm of rainfall was applied (discussed below in section 2.3.4).

2.3.3 Hydrology Experiment

As described above, two rainfall events were simulated in this experiment, and are referred to as HS (short event, high rainfall rate) and HL (long event, low rainfall rate). In each event, three individual monoliths were each dried to a different moisture level. In both events, rainfall application and discharge collection were timed and summarized in terms of the bulk discharge produced and the temporal changes in the runoff rate. Moisture probes (S-SMC-M005, Onset Corporation Inc.) were installed at approximately 5, 17 and 25cm depths in each monolith to track the progression of the wetting front but not to assess the moisture content of the monoliths during drying (determined by weighing). Probes were sealed with plumbing putty to prevent water from leaking from the side of the monolith. The moisture probes were calibrated in the laboratory using Shelby tubes. Briefly, samples were saturated with the probes in them, then weighed with probes intact. They were then left to drain to field capacity, weighed again, then left to air dry in the lab for several days, all while the probes logged moisture levels continuously. The mass of the probe and the Shelby tube was subtracted from the mass of each sample. The gravimetric moisture content from each weighing and the corresponding moisture content from each of the probes were regressed to develop one calibration equation for all moisture probes, which was used on all probe data (shown in 0; field and from the hydrology experiment). The probes were calibrated for the soil at the study site and to convert readings to gravimetric moisture content for comparison to moisture values obtained through weighing.

The same three monoliths were used for both the long and short hydrology events. Prior to each event, the three monoliths were saturated by immersing them in water to wick up from below for 24 hours. Monoliths were then taken out of the water and placed on the stands for 24 hours to drain to field capacity, at which point they were weighed. The moist and dry monoliths were then dried out under a fan in the laboratory (lab temperature was approximately 23°C), while a garbage bag was placed loosely overtop of the wet monolith (and eventually the moist monolith) to maintain its level of moisture. The dry monolith was dried under a fan for twice the length of time as the moist monolith in order to achieve contrasting moisture levels. After drying, the moist monolith was also capped loosely with a garbage bag. These different drying treatments were applied in order to get the monoliths to three different moisture levels, with each moisture level ideally separated by at least 0.02g/g. It was the intention to have the moisture level in the 'wet' monolith below field capacity by 0.2-0.5g/g, and the driest monolith at least 0.4-0.6g/g lower than this. It was determined from preliminary trials that monoliths at field capacity could be dried to different moisture levels during a two week period using the drying treatments described above. Monoliths were weighed periodically while they dried out to determine moisture content (Mf). Soil samples that were collected in Shelby tubes (8.5cm long, 7.5cm diameter) at the time of monolith collection were used for the rough determination of bulk density (equation 1) and porosity (equation 2) of the soil in the monoliths, in order to estimate the moisture level (gravimetric, volumetric and % saturation; equations 3-5, respectively) in the monoliths as they dried. Moisture levels simulated in the hydrology experiment were very consistent between events (Table 4), and ranged from 0.21g/g (dry) to 0.25g/g (wet), corresponding to a % saturation of 51-69%.

Experiment	Moisture Level	Gravimetric Moisture Content (g/g)			Volumetric Moisture Content (cm^3/cm^3)			% Saturation		
HS	*Wet*	0.25			0.38			68.8%		
	Moist	0.23			0.34			61.9%		
	Dry	0.21			0.29			50.5%		
HL	*Wet*	0.25			0.38			68.6%		
	Moist	0.23			0.35			63.6%		
	Dry	0.21			0.30			51.6%		
		min	median	max	min	median	max	min	median	max
NS	*Wet*	0.22	0.22	0.25	0.25	0.26	0.29	49.1%	50.3%	56.5%
	Moist	0.19	0.20	0.20	0.22	0.23	0.23	43.2%	44.4%	45.6%
	Dry	0.17	0.17	0.18	0.19	0.20	0.21	37.8%	39.1%	40.6%
NL	*Wet*	0.16	0.18	0.18	0.19	0.21	0.22	40.4%	45.5%	46.1%
	Moist	0.15	0.15	0.15	0.17	0.18	0.18	37.3%	38.3%	38.3%
	Dry	0.12	0.14	0.14	0.13	0.16	0.16	28.9%	34.8%	35.0%

Table 4- Moisture content of all monoliths at rainfall application in both experiments.

Notes: volumetric moisture content was calculated using the bulk density of the actual monolith and % saturation was calculated using the porosity from each individual monolith (determined by weighing at saturation). This difference in calculation was due to a lack of accurate smaller SP samples taken at this site. Values for the hydrology experiment represent the actual moisture level of each monolith, and the

minimum, median and maximum moisture levels in each group are shown for the nutrient leaching experiment (effectively representing the moisture level of each monolith).

Monoliths were weighed both at the beginning and end of the rainfall applications. Throughout and following rainfall application, runoff collection bottles were checked visually and switched (time recorded on bottle) when there was an appreciable (approximately >20mL) amount of runoff. Runoff volume in each bottle was determined gravimetrically. The runoff was weighed and mass was converted to a depth in mm. From this and the timing of runoff collection, the runoff rate in mm/hour was calculated. It should be noted that runoff probably stopped before the last runoff sample was taken, and that the total duration of runoff was, in reality, less than what is reported here.

After the completion of both short and long events, the soil was removed from each monolith and dried for 48 hours in an oven at 105°C. The dry mass of soil (Md) was then used to calculate the bulk density and porosity of each monolith, which were in turn used to calculate gravimetric and volumetric moisture content and % saturation respectively at each weighing.

2.3.4 Nutrient Leaching Experiment

Moisture levels simulated in the short nutrient leaching (NS) event (0.17-0.25g/g or 38-57%) were higher than those in the long nutrient leaching (NL) event (0.12-0.18 or 29-46%) and moisture levels were generally lower in the nutrient leaching experiment than they were in the hydrology experiment (Table 4). It was difficult to achieve the same moisture levels in the nutrient leaching experiment as in the hydrology experiment, because the monoliths were not wet up in the lab before they were dried out. Wetting up the monoliths in the nutrient leaching experiment would have flushed out and moved nutrient pools in the soil. Field conditions at the time of monolith collection therefore influenced the moisture contents simulated in the nutrient leaching experiment and the lesser amount of spread between moisture levels between groups in the nutrient leaching experiment.

Two events with the same rainfall rates as in the hydrology experiment were simulated in the nutrient leaching experiment (2.5mm/hour and 22.5mm/hour). The same depth of rainfall as in the hydrology experiment (30.8mm) was applied in the NS event, but more (56.2mm) had to be applied in the NL event because the monoliths were very dry when they were collected from the field. Nine monoliths were used in this experiment, divided into three groups, each of which was dried to a different moisture level ('wet', 'moist', 'dry'). Rainfall was simulated in the same manner as in the hydrology experiment. Leachate was collected in the same manner as in the hydrology experiment analyzed for the amount of leachate, and for the concentration and mass of NO_3^- and PO_4^{3-}. The flow-weighted mean nutrient concentration (FWMC) for each monolith was determined from the total mass of each nutrient exported (Tnm) and the volume of leachate from the monolith (Vl) using the following equation:

$$FWMC(mg/L) : \frac{Tnm}{Vl} \qquad [9]$$

Soil samples were taken for the determination of soil nutrient pools at a) the time of monolith collection, b) just before the start of rainfall application, and c) after the end of leaching in both nutrient leaching events. Samples adjacent to each monolith were taken in triplicate with an auger for the determination of soil nutrient (NO_3^- and PO_4^{3-}) pools at the time of monolith collection (a) in both events. To determine soil nutrient pools at time (b), a different approach was used in each event. In the NS event, soil samples were collected in Shelby tubes in triplicate at three depths (0-10, 10-20 and 20-30cm) adjacent to each monolith and were transported on ice to the lab. Samples were weighed, then dried in the lab in the same manner as the corresponding monolith in order to determine nutrient levels in the monoliths at the time of rainfall applications. In the NL event, four monoliths were collected for each group (wet, moist, dry) instead of three, and the extra monolith was used instead of Shelby samples, which dried out faster than the monoliths in the lab, to determine soil nutrient pools at the time of rainfall application. Soil samples were taken in triplicate at three depths (0-10, 10-20, 20-30cm) with an auger from one monolith from each group at the time of rainfall application to determine nutrient pools (b). To determine nutrient pools at time (c), soil samples were also taken with an auger in triplicate at three depths (0-10, 10-20 and 20-30cm) from each monolith after the end of leaching to determine the nutrient pools remaining after leaching.

2.3.4.1 Quality Control During Chemical Analysis

Whenever samples were run for chemical analysis, at least 5% of samples were run in duplicate. DI water and KCl blanks were taken during soil extractions and run to ensure there was no detectable NO_3^-, NH_4^+ and PO_4^{3-}. Blanks were also taken of the distilled water used as rainfall in both nutrient leaching experiments and were run for NO_3^- and PO_4^{3-}. When leachate was being run for $PO4_+^{3-}$ and NO_3^-, several DI water blanks were inserted into each run. In general, duplicate analyses demonstrated analytical precision within 5% of reported values.

Chapter 3

Results

3.1 Introduction

The following results chapter will examine the hydrologic response of monoliths in the hydrology and nutrient leaching experiments, followed by nutrient export during the nutrient leaching experiment. Unless noted otherwise, discussions about and figures showing discharge totals and nutrient export totals refer to that from the whole monolith (inner and outer leachate), where time series of discharge rates or nutrient export are just for inner leachate if not specified. In addition to experimental results, this chapter will also discuss conditions at the field site (rainfall, soil moisture and soil nutrient pools) and how they relate to those simulated in the experiments.

3.2 Hydrologic Response of Monolith Soil

3.2.1 Hydrology Experiment

3.2.1.1 Differences in Discharge Amount with Variable Antecedent Soil Moisture and Rainfall Rates

The three soil moisture levels used in the two hydrology events were 0.25, 0.23 and 0.21g/g, which corresponded with 69, 62-64 and 51-52% saturation (Table 4). Volumetric soil moisture and % saturation are provided for context. The depth of runoff increased with soil moisture (Figure 8, Figure 9) and ranged from 4-28mm in the short event and 2-27mm in the long event. Runoff depths were similar between monoliths of the same moisture level in each event. Runoff ratios were very high in wet soil (0.91 and 0.89 in the HS and HL events, respectively) and were much lower in moist (0.26, 0.25) and dry soil (0.14, 0.08). There was a significant correlation (Spearman's $\rho = 0.956$, $p = 0.003$) between gravimetric soil moisture and discharge when both events were examined together. The relationship between soil moisture and discharge was very similar between the two different rainfall intensities (Figure 15, part a). In this text, the term discharge refers not to the rate but to the bulk volume of leachate from each monolith and is equivalent to runoff, and thus the terms discharge rate and runoff rate refer to the rate of leaching.

3.2.1.2 Differences in Discharge Timing and Rate with Variable Antecedent Soil Moisture and Rainfall Rates

Timing of the onset of discharge, in general and relative to the advancement of the wetting front, varied with soil moisture and rainfall rates. In all cases in the HL event, discharge did not occur until the bottom soil probe had shown a response (Figure 9). The moisture level in all layers of the soil had wet up to points approaching field capacity (approximately 0.28-0.30g/g for the entire monolith; the gravimetric moisture content at field capacity would likely be above this for the top layer of soil and lower for the bottom layer of soil) before discharge was produced. However, in the HS event, discharge occurred before moisture changes were observed at all depths (Figure 8). In fact, in the wet monolith, discharge occurred before any soil moisture changes were observed at the bottom of the soil. The moist and dry monoliths produced discharge after the top two layers of soil showed a soil moisture response and as the deep probe was beginning to show a response.

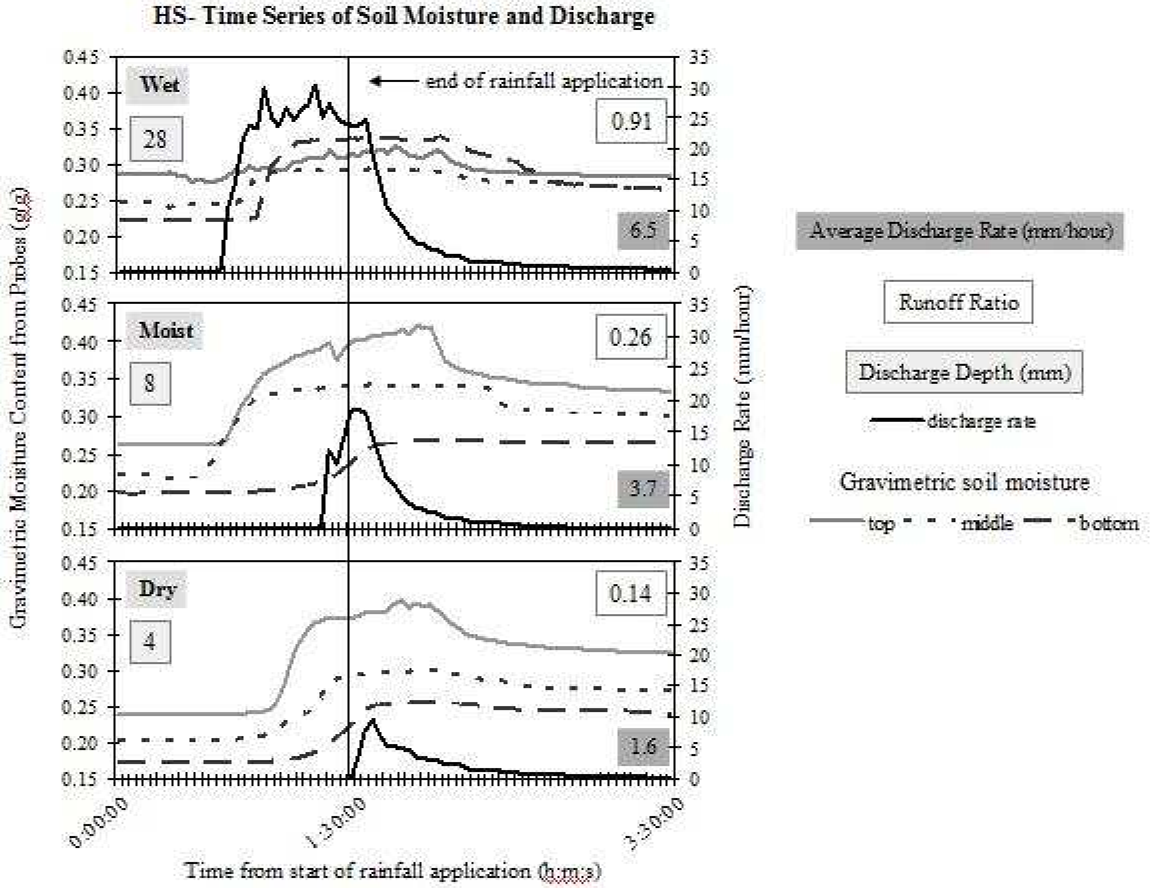


Figure 8- Temporal trends in discharge and soil moisture in the short hydrology event.

Gravimetric soil moisture at field capacity in the soil at the hydrology experiment site was 0.29g/g on average, and was 0.34, 0.28 and 0.26g/g at the 0-10, 10-20 and 20-30cm depths, respectively.

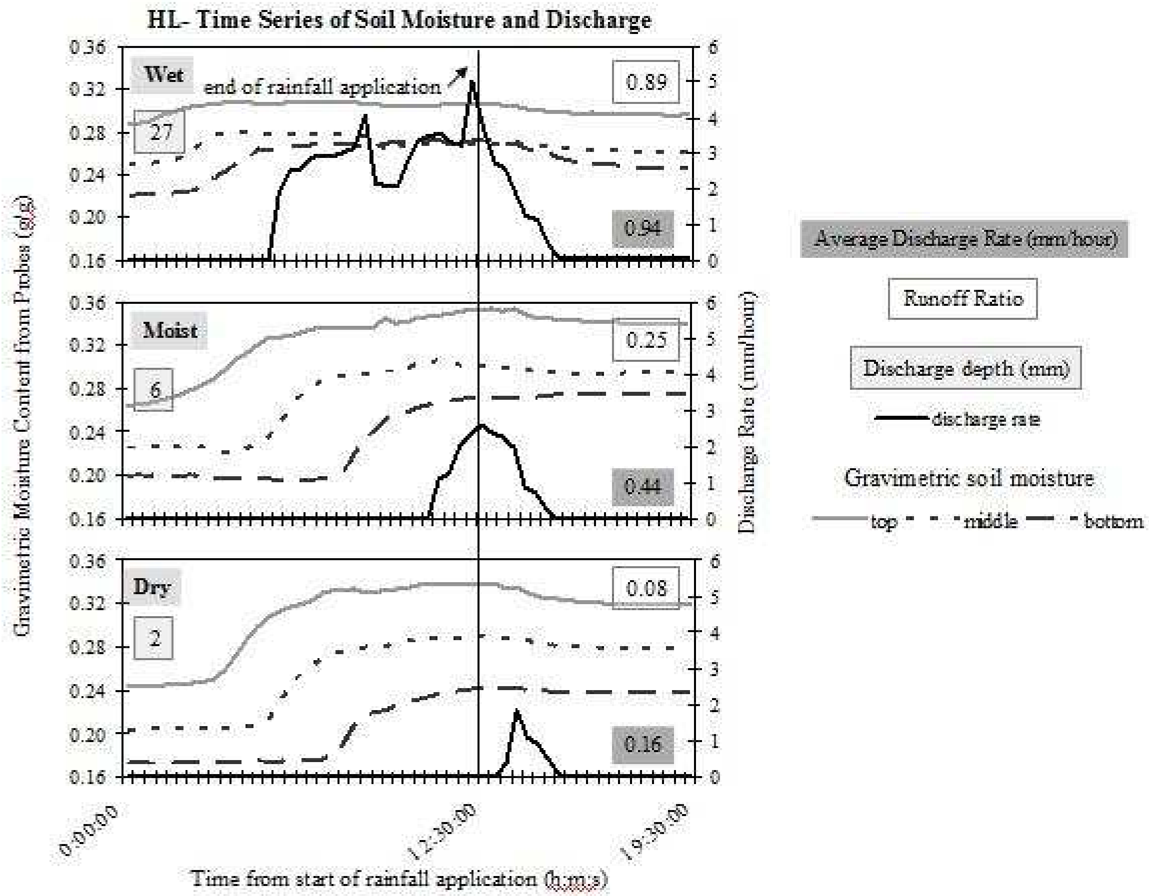
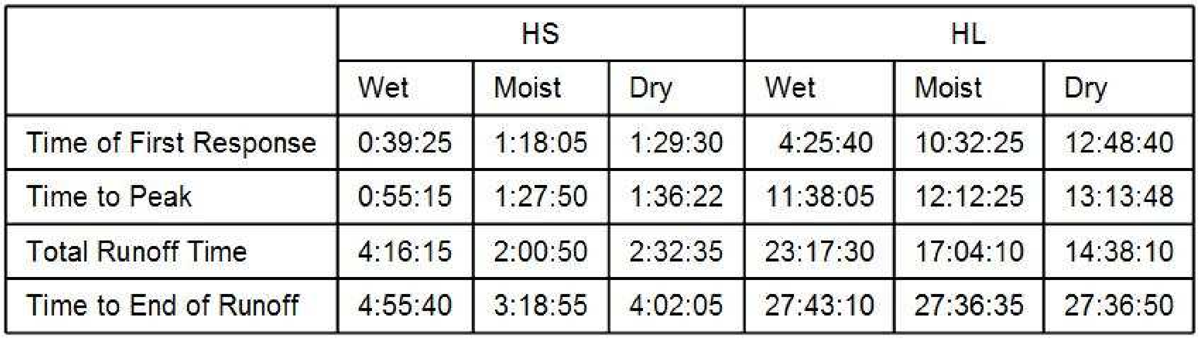


Figure 9- Temporal trends in discharge and soil moisture in the long hydrology event.

Gravimetric soil moisture at field capacity in the soil at the hydrology experiment site was 0.29g/g on average, and was 0.34, 0.28 and 0.26g/g at the 0-10, 10-20 and 20-30cm depths, respectively.

Discharge occurred first in the wet monoliths and last in the dry monoliths (Table 5). The duration of discharge, and also the lag to peak discharge (relative to the onset of discharge) were longest in the wet monoliths and shortest in the dry monoliths.



	HS			HL		
	Wet	Moist	Dry	Wet	Moist	Dry
Time of First Response	0:39:25	1:18:05	1:29:30	4:25:40	10:32:25	12:48:40
Time to Peak	0:55:15	1:27:50	1:36:22	11:38:05	12:12:25	13:13:48
Total Runoff Time	4:16:15	2:00:50	2:32:35	23:17:30	17:04:10	14:38:10
Time to End of Runoff	4:55:40	3:18:55	4:02:05	27:43:10	27:36:35	27:36:50

Table 5- Time to first response, peak, end of runoff and total runoff time for both events in the hydrology experiment.

Average discharge rates were highest from wet monoliths and lowest from dry monoliths in both events (short event shown in Figure 8, long event shown in Figure 9). There was no relationship between gravimetric soil moisture and the average discharge rate (data not shown; Spearman's ρ= 0.478, p= 0.338) or discharge and the average discharge rate (ρ= 0.714, p= 0.111) when all six monoliths were examined together. The slope of the points in the scatterplots of soil moisture and discharge rate (Figure 15, part b), and discharge and discharge rate (Figure 15, part c) is steeper in HS than HL. When discharge curves are plotted as a function of rainfall applied, similar trends are observed within moisture groups, where the onset of discharge occurred at similar times for each moisture level under the different rainfall rates (Figure 10). Maximum discharge rates are similar between events for each moisture level. However, discharge characteristics were slightly different as larger peaks were observed for both the wet and dry monoliths in the HL event and more tailing (i.e. longer gradual recession of hydrograph) is present on all curves in the HS event.

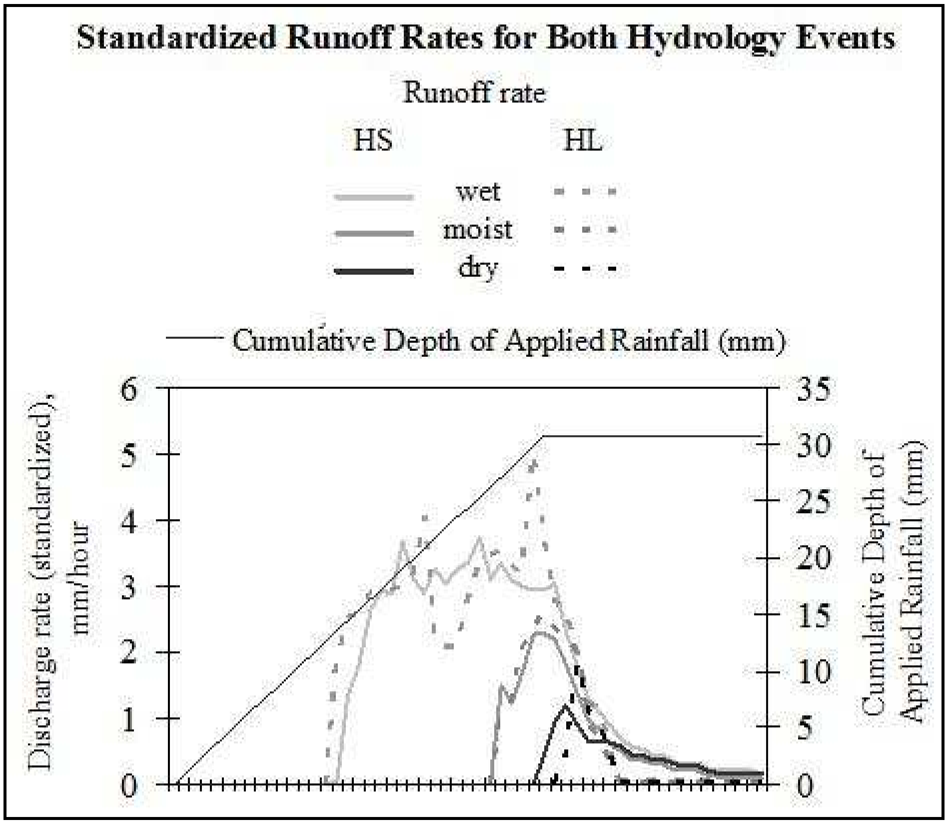


Figure 10- Discharge as a function of rainfall applied in both hydrology events.

3.2.2 Field Soil Moisture Response to Rainfall Events

Daily average soil moisture from each of the three probes installed in the field and daily rainfall totals from JMF were used to examine how soil moisture in the field responded to rainfall events for comparison to the lab results. There were two days with >30mm of rainfall in a 24 hour period (Figure 11), and several instances of successive days with appreciable depths of rainfall (>10mm). After approximately JD 281, the daily rainfall was generally lower in magnitude, but rainfall happened more frequently. These lower daily rainfall totals did not elicit as much of a response from the lower portion of soil (30cm) as the upper portion. Soil moisture responded (especially at 5cm and 17cm bgs) to almost all days with rainfall and changed more in response to rain events than moisture levels at 30cm. Low daily rainfall (<5mm) did not usually elicit a response in terms of soil moisture. Several days of medium depth rainfall (5-20mm) elicited a similar increase in soil moisture as one day with a high depth of rainfall (>30mm). Most rainfall events caused soil moisture levels to rise to or above field capacity, with the top 20cm of soil rising to field capacity more often than the soil at a depth of 20-30cm. Soil moisture levels did not reach saturation at all during the study period.

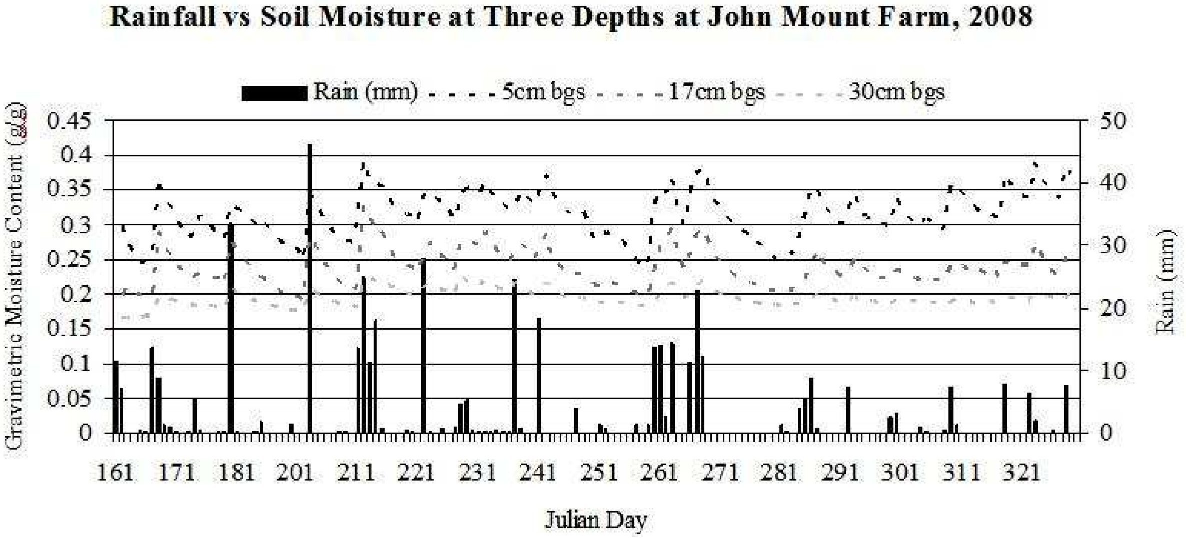


Figure 11- Temporal changes in daily average soil moisture from three probes and daily rainfall totals from the John Mount Farm, 2008.

Gravimetric soil moisture at field capacity was 0.34, 0.28 and 0.26g/g for the 0-10, 10-20 and 20-30cm depths, respectively. Porosity and thus the gravimetric soil moisture at saturation was 0.59, 0.47 and 0.40 for the 0-10, 10-20 and 20-30cm depths, respectively.

Days with rainfall totals of greater than 15mm were plotted up and examined individually to observe the fifteen-minute rainfall totals and changes in soil moisture in greater detail. Six rainfall events were chosen for discussion based on contrasting responses in soil moisture (fast increase at all depths and slow increase at all depths) and rainfall rates. The rainfall events on three of the days days were of higher intensity, with maximum rainfall rates of 28mm/hour, 10.8mm/hour, and 23.6mm/hour for JD 180, 213 and 237 respectively (Figure 12). In all of these events, the soil moisture increased and decreased quickly and almost simultaneously at all levels in the soil in response to the rainfall. The rainfall rate in the event on JD 213 was a lot lower than that of the other events but the soil response similar. The soil prior to this rainfall event was also wetter at 5 and 17cm bgs than in the other two high-intensity events.

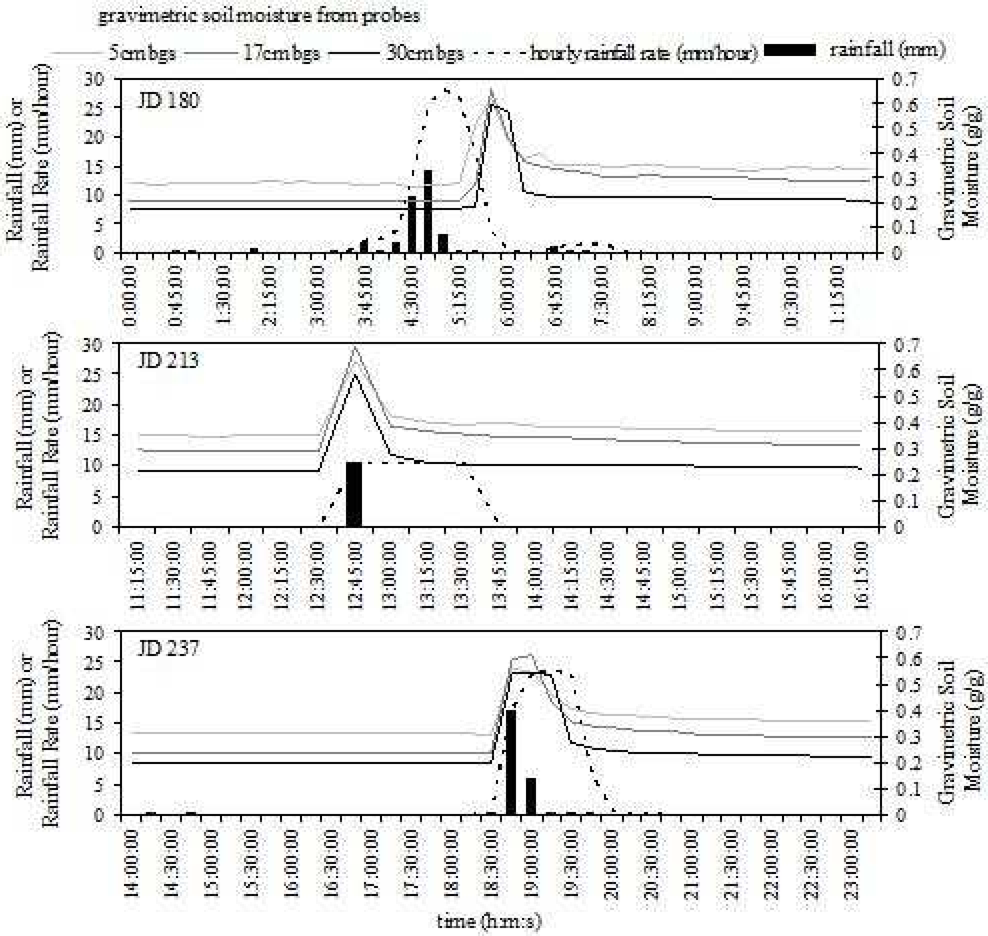


Figure 12- Temporal change in rainfall and soil moisture for three short, high-intensity rainfall events at the John Mount Farm.

Both sets of data are shown at 15-minute intervals. The two grey lines and solid black line represent the gravimetric soil moisture (g/g) from the three moisture probes, at 5, 17 and 30cm below ground surface. The solid black bars indicate the rainfall (mm) during each 15 minute period, and the dotted black line indicates the hourly rainfall rate (mm/hour). Rainfall from JD 180, 213 and 237 are represented.

The rainfall events on the three other days were of lower intensity, with maximum rainfall rates of 13.8mm/hour, 10.8mm/hour and 9.2mm/hour for JD 203, 211-212 and 267 respectively (Figure 13). In these three events, the moisture level at each depth in the soil rose much more slowly and in order from top to bottom instead of simultaneously like in the high-intensity events. Soil moisture also increased less in the deeper soil (30cm) than in shallower depths. On JD 203, moisture in the top layer of soil rose quickly, but moisture levels in the middle and bottom layers rose more slowly than that in the top layer. Soil moisture on JD 267 rose slowly in all layers. On JD 211-212, the first burst of rainfall only caused an increase in moisture in the top 5cm, while subsequent rainfall caused the soil moisture at 5 and 17cm to rise fairly quickly, while soil moisture at 30cm increased much more slowly, and only after the second burst of rainfall. In all of the events examined in detail, the soil moisture response reached a depth of 30cm.

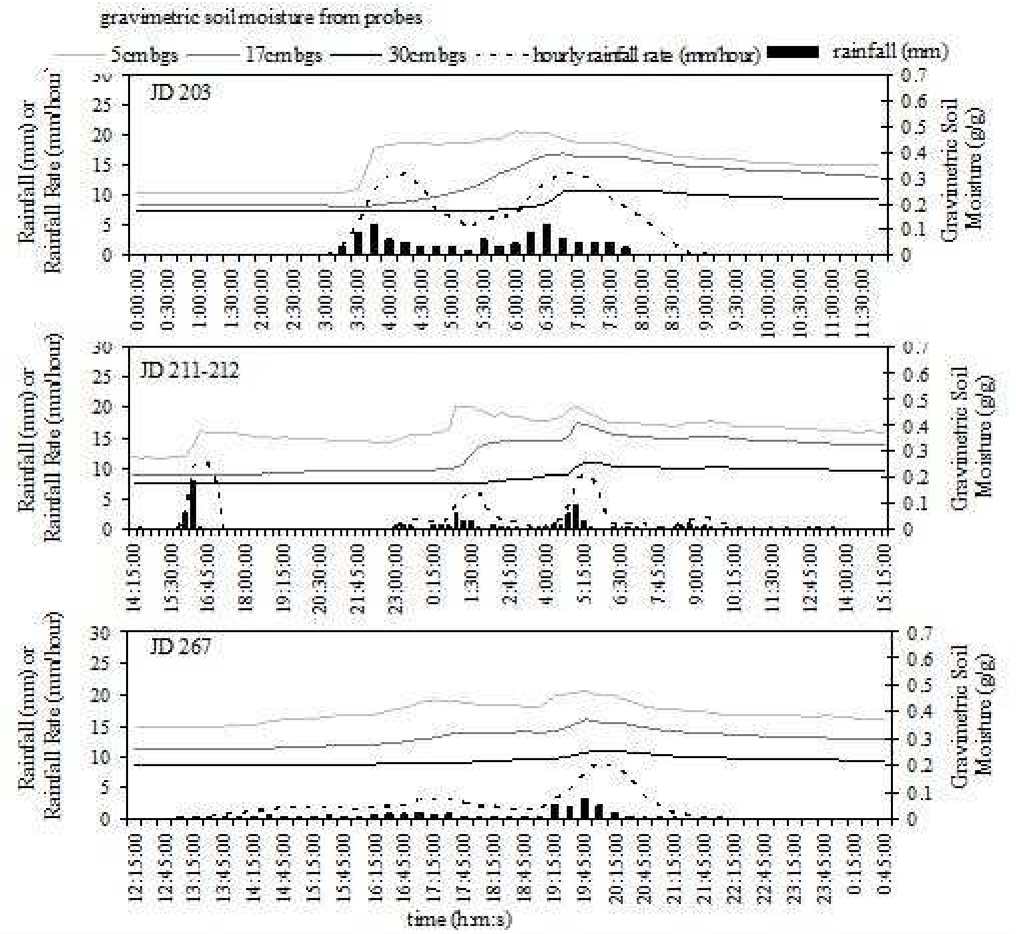


Figure 13- Temporal change in rainfall and soil moisture for three long, low-intensity rainfall events at the John Mount Farm.

Both sets of data are shown at 15-minute intervals. The two grey lines and solid black line represent the gravimetric soil moisture (g/g) from the three moisture probes, at 5, 17 and 30cm below ground surface. The solid black bars indicate the rainfall (mm) during each 15 minute period, and the dotted black line indicates the hourly rainfall rate (mm/hour). Rainfall from JD 203, 211-212 and 267 are represented.

3.2.3 Nutrient Leaching Experiment

3.2.3.1 Hydrologic Response of Soil Monoliths and Comparison with Results of Hydrology Experiment

The objective of the nutrient export experiment was not to characterize the hydrologic response of the soil; however, since a runoff volume is required to determine a nutrient flux, the results have been included here. Although simulated moisture levels were higher in the hydrology experiment than they were in the nutrient leaching experiment, and soil moisture was higher in the NS event than in the NL event, general comparison between events and experiments are still possible. The discharge depth was generally higher in the NL event than in the NS event. As was observed in the hydrology experiments, the wettest soil produced the greatest discharge depth (and highest runoff ratios) and the driest soil produced the lowest (Figure 14). This relationship was reinforced with a significant positive correlation between gravimetric soil moisture and discharge when each nutrient leaching event was examined separately ($\rho= 0.850$, $p= 0.004$ in NS and $\rho= 0.787$, $p= 0.012$ in NL; significant ρ values in Table 6) but not when they were examined together. When gravimetric soil moisture and the depth of discharge were plotted together on a scatterplot, the slope of the data points is similar between the NS and NL events, but the x-intercepts differ, reflecting the generally lower moisture levels in the NL event than in the NS event (Figure 15, part a). There was considerable within-group variation in the depth of discharge produced in wet and moist soil in the NL event, and moderate variation in wet soil in the NS event and dry soil in the NL event, with generally more within-group variation in the NL event. In the NS event, the monoliths within each group that had more discharge also had a disproportionately large amount of discharge from the outer portion of the monolith. However, this was not the case in the NL event.

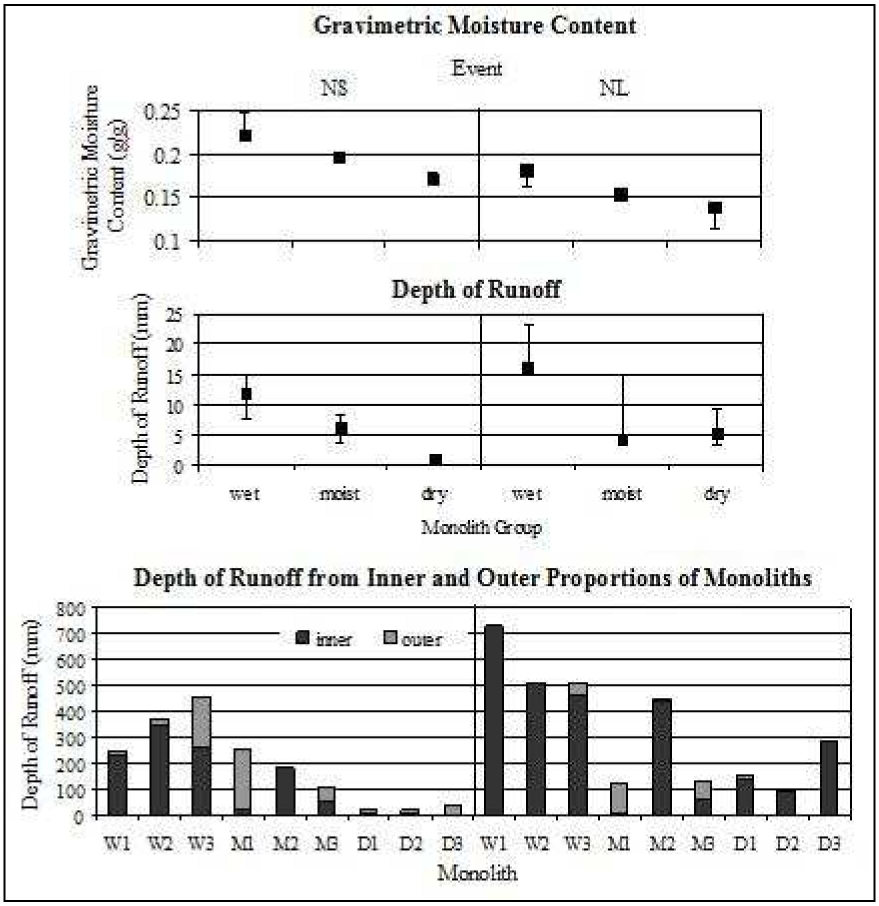


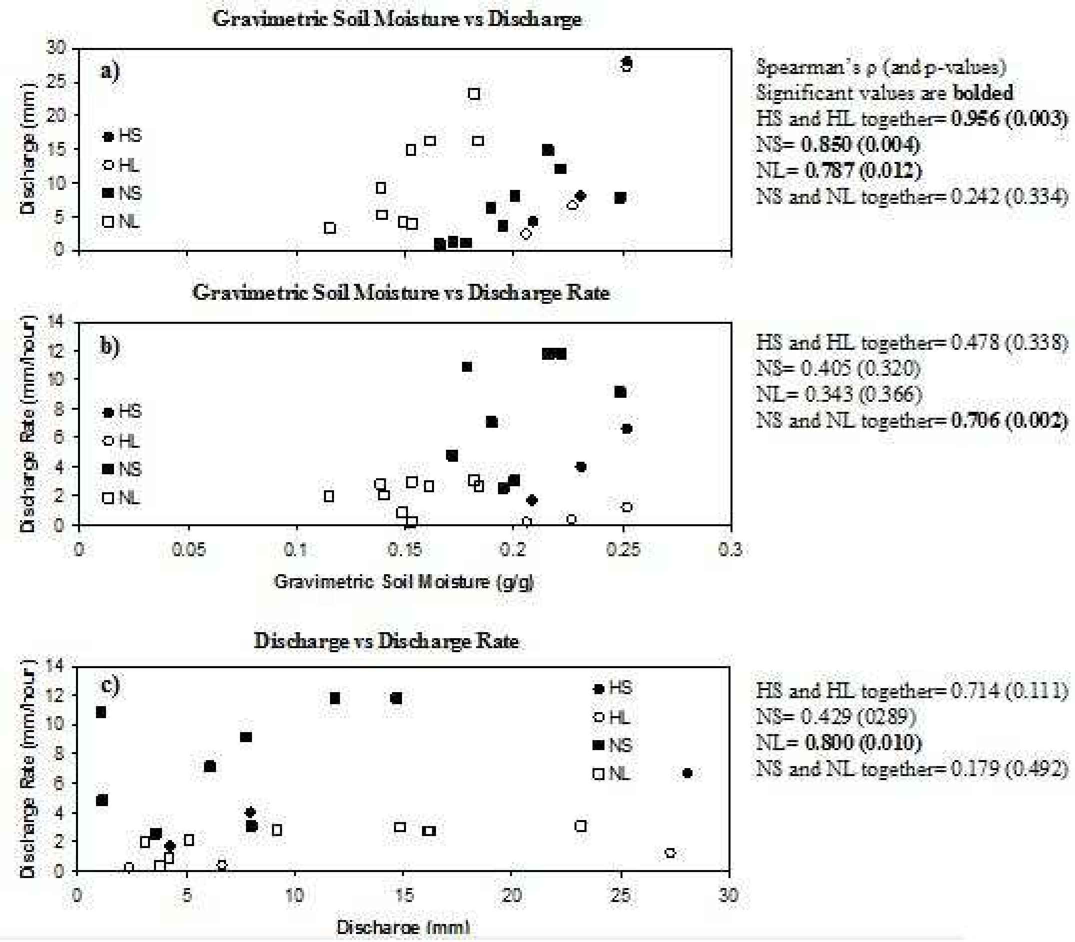
Figure 14- Gravimetric moisture content and discharge depth for groups of monoliths and proportions of discharge from inner and outer portions of the monoliths in the nutrient leaching experiment.

Boxes in the top two graphs represent the median value and error bars indicate the minimum and maximum of each variable within each group.

Significant Spearman Correlation Coefficients from Both Events Together		
Variable 1	*Variable 2*	*Spearman's ρ (p-value)*
Gravimetric Soil Moisture (g/g)	Average Discharge Rate (mm/hour)	0.706 (0.002)
Discharge (mm)	NO_3^- mass (mg)	0.806 (0.000)
	PO_4^{3-} mass (μg)	0.748 (0.000)
FWMC NO_3^- (mg/L)	NO_3^- mass (mg)	0.477 (0.045)
FWMC PO_4^{3-} (μg/L)	PO_4^{3-} mass (μg)	0.568 (0.016)
NO_3^- mass (mg)	PO_4^{3-} mass (μg)	0.647 (0.004)
Significant Spearman Correlation Coefficients from NS		
Gravimetric Soil Moisture (g/g)	Discharge (mm)	0.850 (0.004)
	FWMC NO_3^- (mg/L)	0.800 (0.010)
	NO_3^- mass (mg)	0.728 (0.026)
Discharge (mm)	Average Discharge Rate (mm/hour)	0.800 (0.010)
	PO_4^{3-} mass (μg)	0.750 (0.020)
Average Discharge Rate (mm/hour)	NO_3^- mass (mg)	0.733 (0.025)
Soil NO_3^- Pools (μg/g dry wt of soil)	FWMC NO_3^- (mg/L)	0.717 (0.030)
Significant Spearman Correlation Coefficients from NL		
Gravimetric Soil Moisture (g/g)	Discharge (mm)	0.787 (0.012)
	NO_3^- mass (mg)	0.686 (0.041)
Discharge (mm)	FWMC NO_3^- (mg/L)	-0.700 (0.036)
	NO_3^- mass (mg)	0.867 (0.002)
FWMC PO_4^{3-} (μg/L)	PO_4^{3-} Mass (μg)	0.683 (0.042)
NO_3^- mass (mg)	PO_4^{3-} mass (μg)	0.700 (0.036)

Table 6- Significant Spearman's ρ values (and p values) for all variables in the nutrient leaching experiment.

Values are significant to at least the 0.05 level.



Gravimetric Soil Moisture vs Discharge

Spearman's ρ (and p-values)
Significant values are **bolded**
HS and HL together= **0.956 (0.003)**
NS= **0.850 (0.004)**
NL= **0.787 (0.012)**
NS and NL together= 0.242 (0.334)

Gravimetric Soil Moisture vs Discharge Rate

HS and HL together= 0.478 (0.338)
NS= 0.405 (0.320)
NL= 0.343 (0.366)
NS and NL together= **0.706 (0.002)**

Discharge vs Discharge Rate

HS and HL together= 0.714 (0.111)
NS= 0.429 (0289)
NL= **0.800 (0.010)**
NS and NL together= 0.179 (0.492)

Figure 15- Scatterplots of a) soil moisture and discharge, b) soil moisture and average discharge rate, and c) discharge and discharge rate for all four events.

3.2.3.2 Difference in Depth and Timing of Runoff from Inner and Outer Leachate Collection

The inner and outer portions of the monolith account for 79.2% and 20.8% of the total monolith area, respectively. In several monoliths, the proportion of discharge from the outer area of the monolith was greater than the proportional area of the outer portion of the monolith (W3, M1, M3, D1-3 in the short event and M1 and M3 in the long event; Figure 14). However, in the case of all the dry monoliths in NS, very little (less than 1.2mm) discharge was produced in total for the monolith, so the proportion of discharge from the outer portion is misleading in terms of the actual volume of discharge it represents. Monolith dry 3 in the NS event only produced one sample of discharge, and it was from the outer portion of the monolith.

3.2.3.3 Relationship between Soil Moisture, Discharge Depth and Discharge Rate

There was a positive relationship between gravimetric soil moisture and the average discharge rate from each monolith when both events were examined together (values from significant correlations in Table 6; ρ= 0.706, p= 0.002), but not when they were examined separately (ρ= 0.405, p= 0.320 in NS and ρ= 0.343, p= 0.366 in NL). The scatterplot of these two variables in Figure 15, part b illustrates why there is no relationship between soil moisture and the discharge rate in each event, as there is no clear pattern or slope to the data points in either event and that the significant correlation between soil moisture and the discharge rate when both events are examined together is misleading. The discharge depth from each monolith was also significantly correlated with the discharge rate in the NL event (Table 6; ρ= 0.800, p= 0.010) but not in the NS event (ρ= 0.429, p= 0.289) or when both events were examined together (ρ= 0.179, p= 0.492). The slope of the data points is nearly horizontal in the scatterplot of discharge and the average discharge rate from the NL event (Figure 15, part c), indicating that there is not much of an increase in the discharge rate with increases in discharge in this event. The strength of the relationships between soil moisture and the average discharge rate and the depth of discharge and the average discharge rate was not as strong as that between soil moisture and the depth of discharge (Figure 15).

3.2.3.4 Temporal Changes in Discharge Rate for Monoliths in Nutrient Leaching Experiment

Discharge generally began later in dry soil and earlier in wet soil in both events (Figure 16). There was within-group variation in terms of the start of discharge production and peak discharge rate, especially in moist soil and dry soil in the NS event. Duration of discharge and the peak discharge rates were not perfectly related to soil moisture, as there were many instances (*e.g.* W1 in NS) where the wettest monolith began leaching last, or had the lowest peak discharge rate (*e.g.* M1 in NS), or that all monoliths had similar levels of soil moisture, but one had an anomalously high discharge rate (*e.g.* NL, M2). Discharge generally began later in all monoliths in the nutrient leaching experiment when compared to the hydrology experiment. The discharge rate was generally higher in the NL event, which also had more available water for transport (section 3.2.3.3). Generally, the rising limb of the hydrograph was steeper in the NL event than in the NS event. The discharge rate in all monoliths dropped right off after the end of rainfall application.

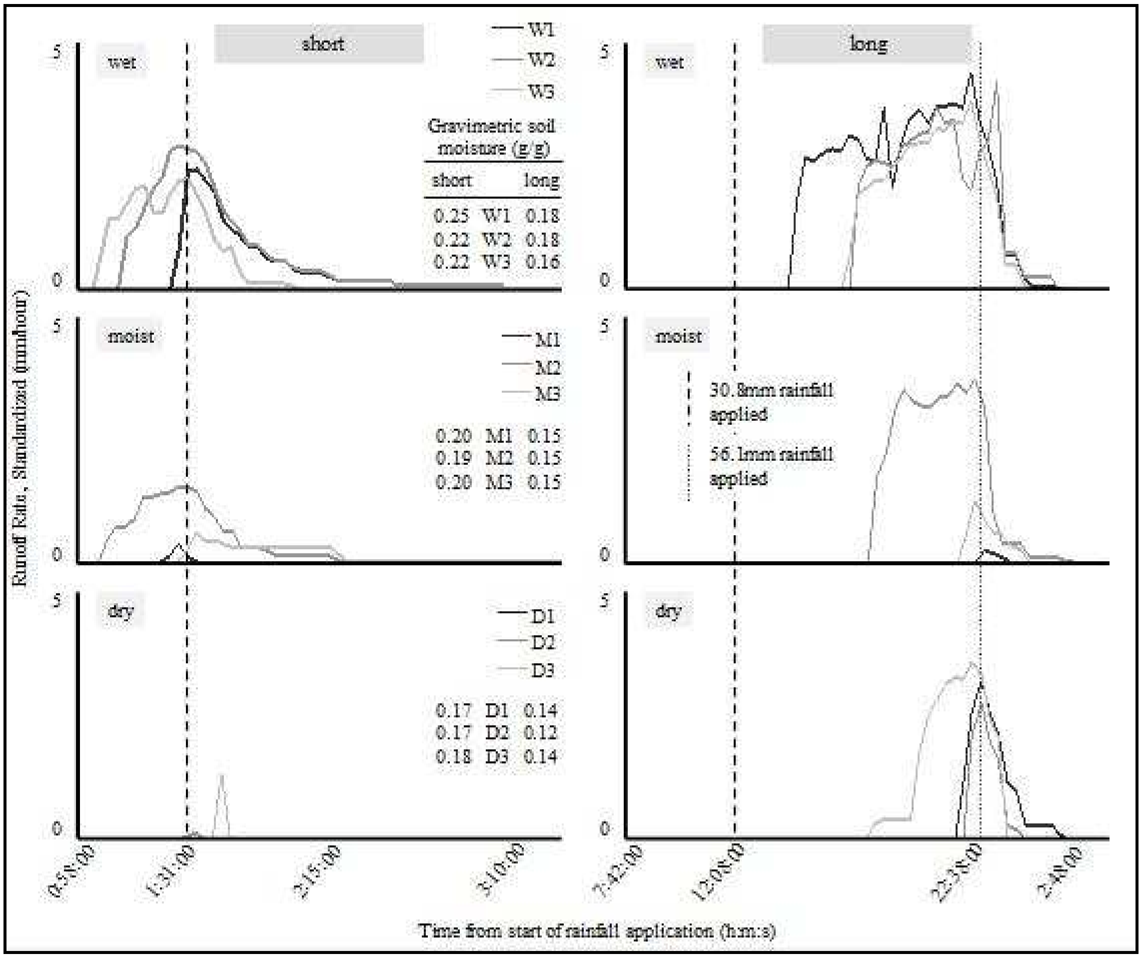
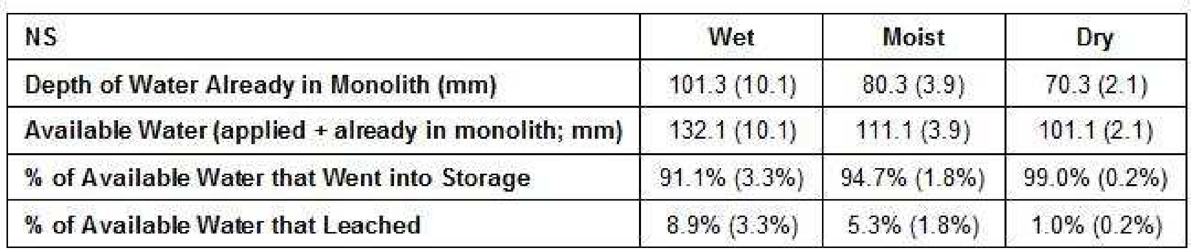


Figure 16- Temporal variability of the discharge rate for all monoliths in the nutrient leaching experiment, grouped by moisture level, with gravimetric moisture content of each monolith.

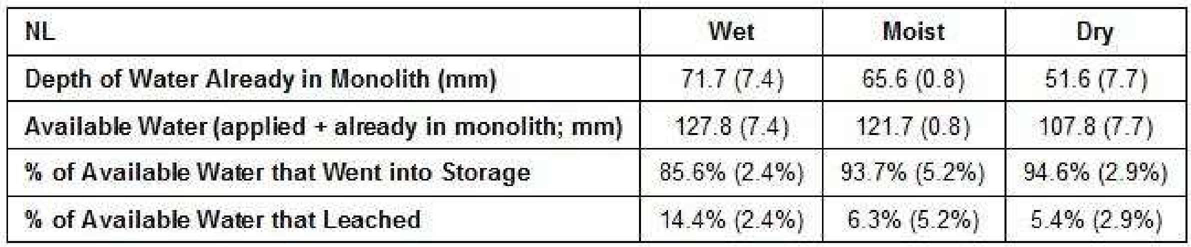
Hydrographs are from the leachate collected from the inner cylinder only. The discharge rates were normalized for the difference in time scales between the two experiments, but the actual time scale is plotted on each x axis.

3.2.3.5 Difference in Depth of Rainfall Applied between Nutrient Leaching Events

More rainfall was applied in the NL event (56.1mm) than in the NS event (30.8mm) due to the lower average moisture content of the monoliths prior to the NL event (0.15g/g in NL vs 0.20g/g in NS). The extra rainfall applied was close to the amount required to make up for the moisture deficit in the NL event (slightly less than required in wet soil, and more than required in moist and dry soil; Table 7). Therefore, there was a similar amount of total water in the soil in corresponding moisture levels in both events (wet= 132.1mm in NS, 127.8mm in NL; moist= 111.1, 121.7mm; dry= 101.1, 107.8mm). However, in general, more discharge was produced in the NL than in the NS event, indicating that more discharge was produced in proportion to the available water in the NL event.



NS	Wet	Moist	Dry
Depth of Water Already in Monolith (mm)	101.3 (10.1)	80.3 (3.9)	70.3 (2.1)
Available Water (applied + already in monolith; mm)	132.1 (10.1)	111.1 (3.9)	101.1 (2.1)
% of Available Water that Went into Storage	91.1% (3.3%)	94.7% (1.8%)	99.0% (0.2%)
% of Available Water that Leached	8.9% (3.3%)	5.3% (1.8%)	1.0% (0.2%)



NL	Wet	Moist	Dry
Depth of Water Already in Monolith (mm)	71.7 (7.4)	65.6 (0.8)	51.6 (7.7)
Available Water (applied + already in monolith; mm)	127.8 (7.4)	121.7 (0.8)	107.8 (7.7)
% of Available Water that Went into Storage	85.6% (2.4%)	93.7% (5.2%)	94.6% (2.9%)
% of Available Water that Leached	14.4% (2.4%)	6.3% (5.2%)	5.4% (2.9%)

Table 7- Amount of water applied, in storage and available for transport in groups of monoliths in the nutrient leaching experiment.

Mean values are shown with (stdev).

3.3 Leaching of Nutrients from Monoliths

3.3.1 Nitrate

3.3.1.1 Flow-Weighted Mean NO_3^- Concentration and Mass Exported

The relationship between the FWMC of NO_3^- and other variables (soil moisture, discharge, soil NO_3^- pools) varied between events. In the NS event, the FWMC of NO_3^- was related significantly to soil moisture (Table 6; ρ= 0.800, p= 0.010) but not to discharge (ρ= 0.617, p= 0.077; ρ values from all non-relationships in 0) and was highest in wet soil (which produced the most discharge; FWMC of NO_3^- in wet soil ranged from 23.4 to 40.0mg/L) and lowest in dry soil (11.5-18.1mg/L; Figure 17). When plotted on a scatterplot, it is evident that the relationship was stronger between soil moisture and the FWMC of NO_3^- than the relationship between discharge and the FWMC of NO_3^- in the NS event (Figure 18, parts b and c respectively). In the NL event, FWMC was highest in moist soil (26.9-

55.3mg/L) and lowest in wet soil (21.3-25.9mg/L) and there was a negative relationship between discharge and FWMC of NO_3^- (ρ= -0.700, p= 0.036), but no relationship between soil moisture and the FWMC of NO_3^- (ρ= -0.527, p= 0.145). The relationship between discharge and the FWMC of NO_3^- is not linear, but instead is concave, with the FWMC of NO_3^- decreasing more with increases in discharge at lower discharge rates (Figure 18, part d). The FWMC of NO_3^- was also significantly correlated with soil NO_3^- pools in the NS event (ρ= 0.717, p= 0.030). No correlation between soil NO_3^- pools and the FWMC or mass of NO_3^- exported was available because only average soil NO_3^- pools in each group were available, rather than soil NO_3^- pools for each monolith. The average FWMC of NO_3^- among all monoliths was higher in the NL event (31.7mg/L) than in the NS event (20.8mg/L).

The mass of NO_3^- exported was related to discharge and soil moisture in both events, with more NO_3^- exported from wet soil (9.0-10.8mg in NS and 10.9-18.9mg in NL) than in dry soil (0.29-0.62mg in NS and 3.5-6.9mg in NL; Figure 17). There was a significant correlation between discharge and the mass of NO_3^- exported when both events were examined together (ρ= 0.806, p= <0.001; Table 6) and in the NL event (ρ= 0.867, p= 0.002) but only a marginal relationship in the NS event (ρ= 0.636, p= 0.066; 0). There is more spread in the data points in the NS event than in the NL event when discharge and the mass of NO_3^- exported are plotted on a scatterplot (Figure 18, part a), reflecting the difference in the relationships between events. The relationship between discharge and the mass of NO_3^- exported is a reflection of the significant relationship between gravimetric soil moisture and discharge in each event and is reinforced by significant relationships between gravimetric soil moisture and the mass of NO_3^-exported in each event (ρ= 0.728, p= 0.026 in NS and ρ= 0.686, p= 0.041 in NL). The FWMC of NO_3^- in leachate was also related to the total mass of NO_3^- exported, with a significant relationship between these two variables when both events were examined together (ρ= 0.477, p= 0.045) but not when they were examined separately. The mass of NO_3^- exported was generally higher in the NL event (9.2mg on average) than in the NS event (5.1mg on average), as was the amount of discharge produced (10.7mm on average in NL vs 6.1mm in NS).

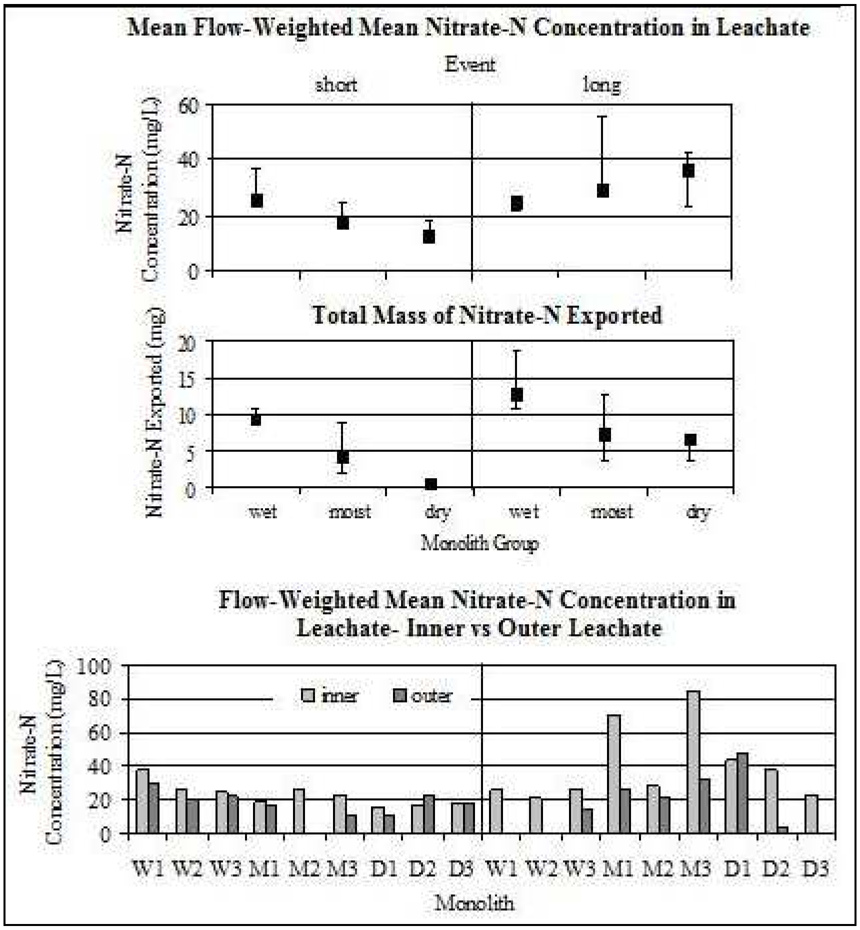
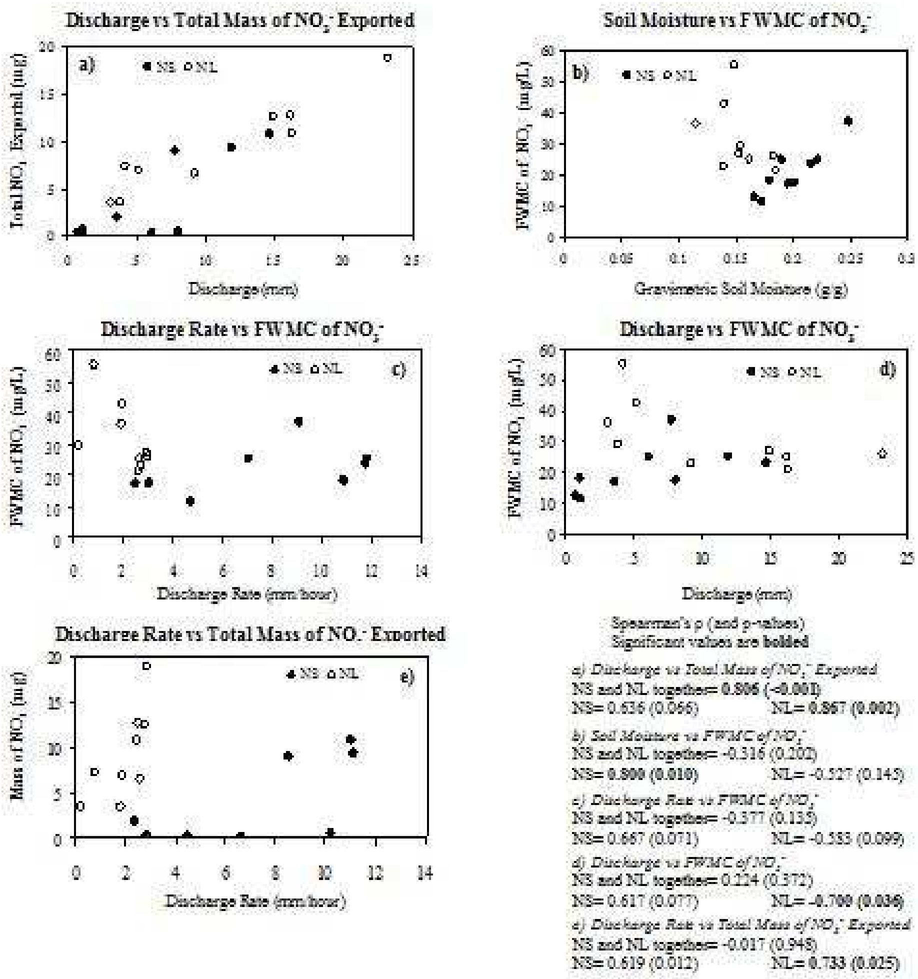


Figure 17- Flow-weighted mean (FWMC) NO_3^- concentration and total mass exported for groups of monoliths and the FWMC of NO_3^- in inner and outer leachate in all monoliths in the nutrient leaching experiment.

Error bars indicate the maximum and minimum of each variable within each group and boxes indicate the median value.



Spearman's ρ (and p-values)
Significant values are bolded

a) Discharge vs Total Mass of NO_3^- Exported
NS and NL together= **0.806 (<0.001)**
NS= 0.636 (0.066) NL= **0.867 (0.002)**

b) Soil Moisture vs FWMC of NO_3^-
NS and NL together= -0.316 (0.202)
NS= **0.800 (0.010)** NL= -0.527 (0.143)

c) Discharge Rate vs FWMC of NO_3^-
NS and NL together= -0.377 (0.135)
NS= 0.667 (0.071) NL= -0.583 (0.099)

d) Discharge vs FWMC of NO_3^-
NS and NL together= 0.224 (0.372)
NS= 0.617 (0.077) NL= **-0.700 (0.036)**

e) Discharge Rate vs Total Mass of NO_3^- Exported
NS and NL together= -0.017 (0.948)
NS= 0.619 (0.012) NL= **0.733 (0.025)**

Figure 18- Scatterplots of a) discharge and the total mass of NO_3^- exported, b) soil moisture and the FWMC of NO_3^-, c) the discharge rate and the FWMC of NO_3^-, d) discharge and the FWMC of NO_3^-, and e) the discharge rate and the mass of NO_3^- exported for the nutrient leaching experiment.

3.3.1.2 Comparing the Flow-Weighted Mean NO_3^- Concentration between Inner and Outer Leachate

The difference in the FWMC of NO_3^- between the inner and outer leachate was compared in order to examine if the outer leachate was dilute in terms of the FWMC of NO_3^- (Figure 17). This was the case in M1, M3 and D2 from the NL event, but otherwise the FWMC of NO_3^- was fairly similar between inner and outer leachate.

3.3.1.3 Relationship between Discharge Rate and NO_3^- Export

There were no relationships between the average discharge rate from each monolith and the FWMC of NO_3^- when both events were examined together (0; ρ= -0.377, p= 0.135) and separately (ρ= 0.667, p= 0.077 in the NS event and ρ= -0.583, p= 0.099 in the NL event). When the discharge rate and the FWMC of NO_3^- from each event were plotted on a scatterplot, there was a general positive trend to the scatter in the NS event and a general negative trend in the NL event, even though there was a great deal of spread in the scatter in both events. There was also no relationship between the average discharge rate and the mass of NO_3^- exported when both events were examined together (ρ= -0.017, p= 0.948) and in NS (ρ= 0.619, p= 0.102), while there was a significant correlation between these variables in the NL event (Table 6; ρ= 0.733, p= 0.025). In the NL event, the mass of NO_3^- exported increased more quickly than the discharge rate, as illustrated when the discharge rate and the mass of NO_3^- exported are plotted on a scatterplot (Figure 18, part e).

3.3.1.4 Temporal Changes in the NO_3^- Concentration in Leachate for Individual Monoliths

Nitrate-N concentrations in the NS event were fairly stable in time and ranged from 20-35mg/L, with the exception of D2, which had much lower NO_3^- concentrations. There were pulses of higher NO_3^- concentration in W1 and 3, and a decline when discharge rates dropped off in M1 and 2 (Figure 19). Nitrate concentrations were fairly stable with time after the initial pulse in wet soil, but were more variable in moist soil, varying through time in M2 and rising in M3. Only two leachate samples were collected from D2, one from D3 and none from the inner portion of D1, although one was collected from the outer portion of the monolith, shown in Figure 19. The mass of NO_3^- exported was closely related to the discharge rate in the NS event (data not shown) and was greater in monoliths with longer periods of high rates of discharge when only inner leachate is considered. The NO_3^--N concentration in leachate was more variable in time in the NL event, generally ranging from 20-50mg/L, with the exception of M1 and M3, which both had much higher NO_{3-}-N concentrations, ranging from 52-78 and 24-108mg/L respectively. There was a noticeable decline in the NO_3^- concentration with time in all three moist monoliths, at the end of the leaching period in the wet monoliths and in two of the three dry monoliths. The NO_3^- concentration started falling in M2 right at the beginning of leachate production, whereas the NO_3^- concentration fell in other monoliths after the end of rainfall application. The mass of NO_3^- exported varied with both the discharge rate and the NO_3^- concentration in leachate (data not shown).

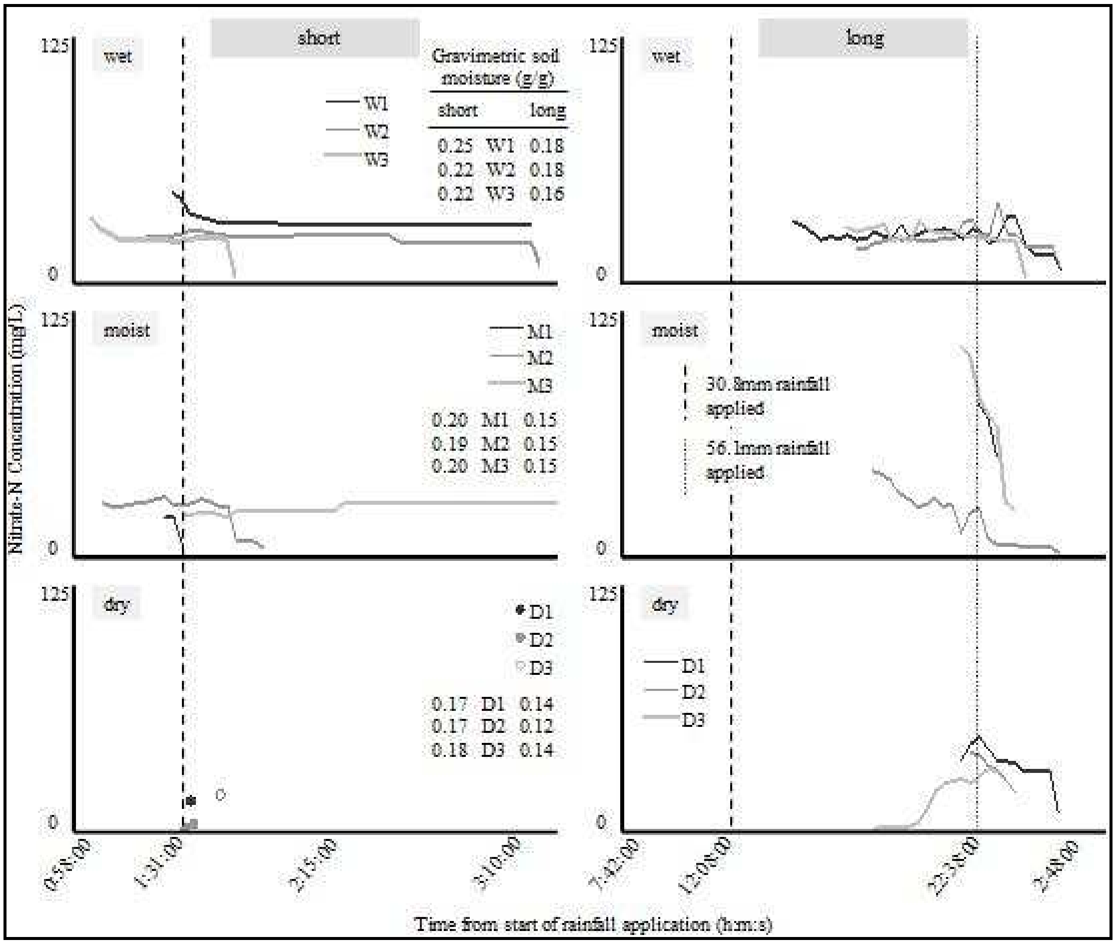


Figure 19- Temporal variability of NO_3^- concentration for all monoliths in the nutrient leaching experiment, grouped by moisture level with gravimetric moisture content of each monolith.

This figure shows concentrations in leachate collected from the inner cylinder only.

3.3.1.5 Soil NO_3^- and NH_4^+ Pools and Influence on Nutrient Export

Generally, NO_3^- increased between the time of monolith collection and rainfall application in each of the nutrient leaching events (short event shown in Figure 20, long event shown in Figure 21). There was within-group variation in NO_3^- at each time period, but no difference between soil NO_3^- levels between groups, indicating that nutrient pools were affected in the same way from each different drying treatment, and that there was no significant difference in the nutrient pools between groups of monoliths. There was more available soil NO_3^--N prior to rainfall application in the NS event (9.1-10μg/g) than in the NL event (6.6-7.5μg/g). This is in contrast to the FWMC and mass of NO_3^- leached, with higher FWMC and more NO_3^- exported in the NL event than in the NS event. Soil NH_4^+ was variable at the time of monolith collection and rainfall application, with no clear pattern in the change in soil NH_4^+ levels in either event between the time of monolith collection and rainfall application.

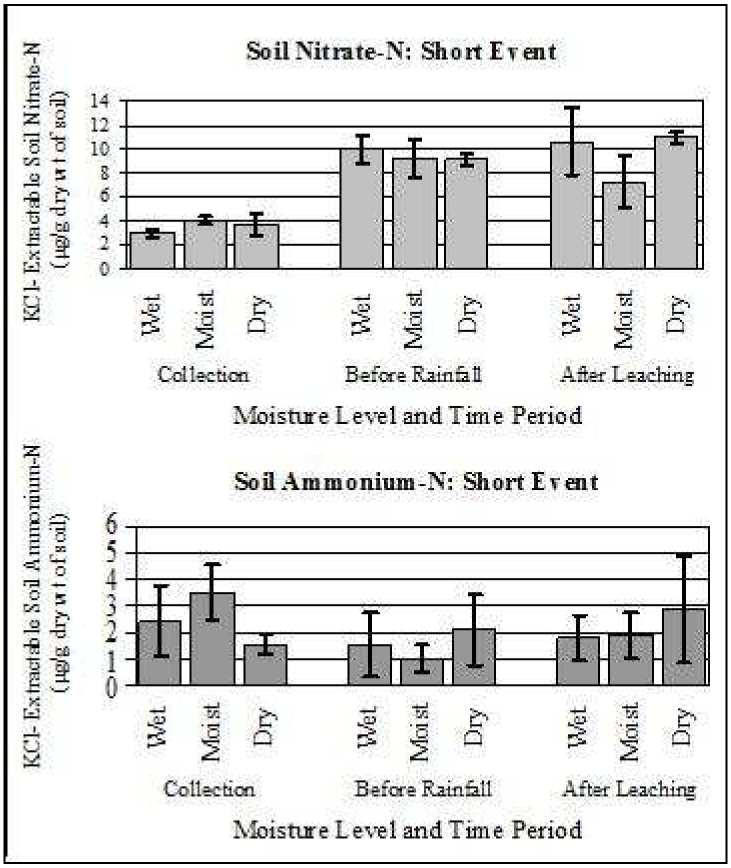


Figure 20- Soil KCl-extractable NO_3^- and NH_4^+ pools in the short nutrient leaching event at monolith collection, rainfall and after the end of leaching.

Error bars show standard deviation.

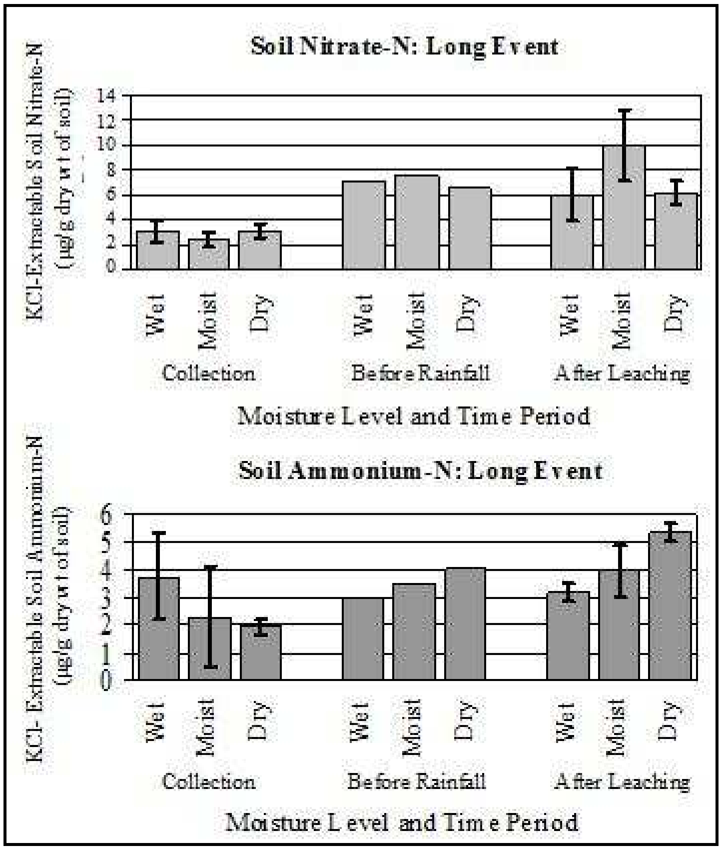


Figure 21- Soil KCl-extractable NO_3^- and NH_4^+ pools in the long nutrient leaching event at monolith collection, rainfall application and after the end of leaching.

Error bars show standard deviation.

3.3.1.6 Change in Soil NO_3^- Levels Between the Start of Rainfall Application and End of Leaching

Soil NO_3^- pools were examined at three separate depths (0-10, 10-20 and 20-30cm) in the monoliths in the NS event just before rainfall application and after the end of leaching in order to determine if the soil NO_3^- levels throughout the soil profile changed due to leaching. This was not done for the monoliths in the NL event because soil NO_3^- pools were not available for each monolith at the time of rainfall application; only an average of soil NO_3^- pools at the time of rainfall application was available. The difference in soil NO_3^- levels between monoliths is evident, as is the difference in soil NO_3^- pools with depth. Generally, soil NO_3^- levels were highest in the top 10cm of soil prior to rainfall application (Figure 22). In every monolith, soil NO_3^- in the top 10cm fell between the start of rainfall application and the end of leaching, while soil NO_3^- levels rose in the bottom 20cm of soil.

The changes in soil NO_3^- pools at each level were different in every monolith. There was a greater change in soil NO_3^- levels in the bottom 20cm of the soil in the dry group, with the moist group having the greatest change in the top 10cm of the soil. In many monoliths (W3, M1, M2, D1, D2), soil NO_3^- levels were lower in the top 10cm of the soil after the end of leaching than they were in the bottom 20cm of soil.

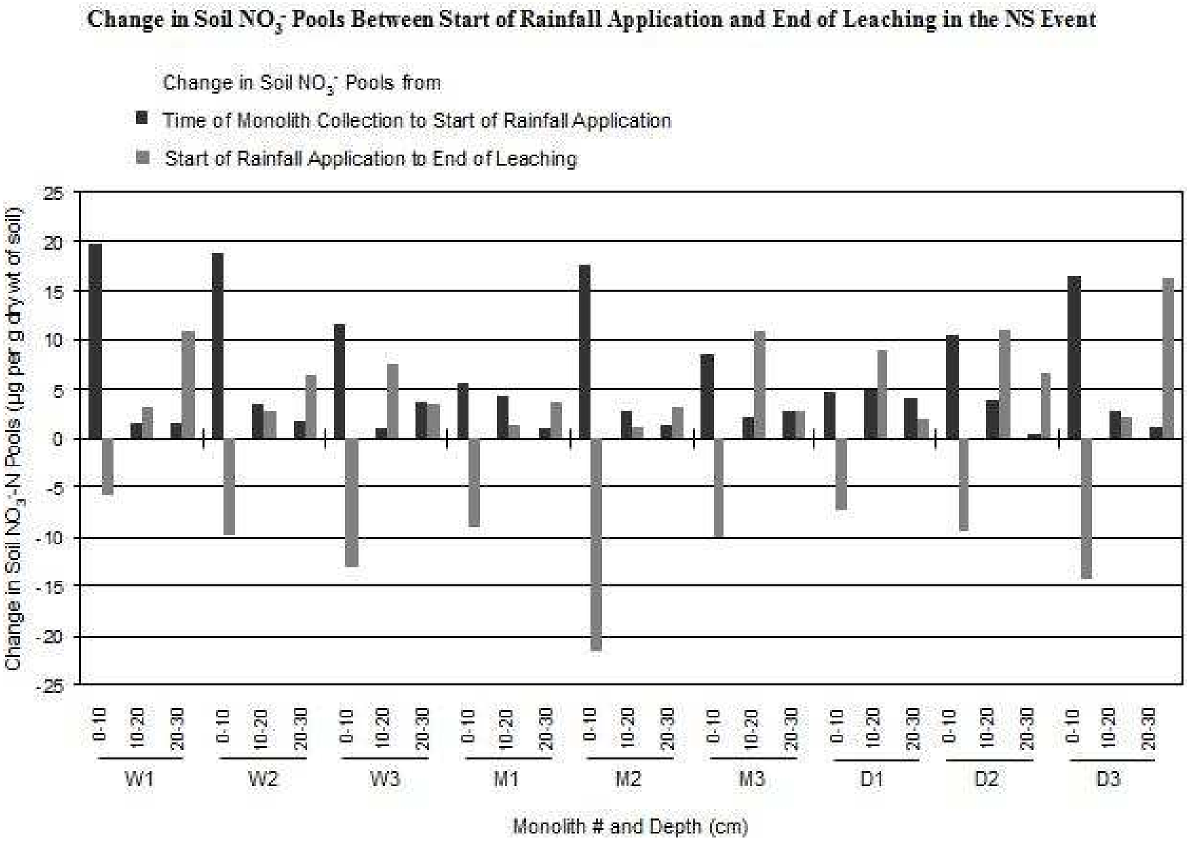


Figure 22- Change in KCl-extractable soil NO_3^- pools at three depths in the soil from the start of rainfall application to the end of leaching.

Bars represent the change in nutrient pools for the time periods described in the legend (between monolith collection and the start of rainfall application, and between the start of rainfall application and the end of leaching).

3.3.2 Phosphate

3.3.2.1 Flow-Weighted Mean PO_4^{3-} Concentration and Mass Exported

Generally, the FWMC of PO_4^{3-} in leachate was low and there were no significant differences in the FWMC of PO_4^{3-} between groups of monoliths (Figure 23). Neither soil moisture, discharge nor soil PO_4^{3-} pools had a significant relationship with the FWMC of PO_4^{3-}. It is evident when soil moisture and the FWMC of PO_4^{3-} and discharge and the FWMC of PO_4^{3-} are plotted on a scatterplot that there is a great deal of spread in the scatter for both events (Figure 24, parts b and c respectively) The FWMC of PO_4^{3-} among all monoliths was slightly higher in the NS event (12.5μg/L) than in the NL event (10.7μg/L) when the major outlier in the NL event (M3) is removed. Inclusion of this outlier drives the FWMC of PO_4^{3-} up to 133.64μg/L in the NL event. This outlier had a FWMC of PO_4^{3-} (116.9μg/L) that was almost two orders of magnitude greater than that of any other monolith in the experiment. The FWMC of NO_3^- from this monolith was the highest in this group, and in the experiment, but by less than an order of magnitude.

The average mass of PO_4^{3-} exported from monoliths only varied slightly between groups of monoliths in both events. Despite this, there was a significant relationship between the mass of PO_4^{3-} exported and discharge in the NS event (ρ= 0.750, p= 0.020; Table 6) and when both events were analyzed together (ρ= 0.748, p <0.001), but not in the NL event (ρ= 0.617, p= 0.077; 0). It is evident when discharge and the mass of PO_4^{3-} exported are plotted on a scatterplot that there is a positive relationship between these two variables in each event, and that in NL, the lack of a relationship between them is likely due to the outlier (M3, circled in black on Figure 24, part a), which exported almost two orders of magnitude more PO_4^{3-} (148.0μg) than any of the other monoliths in the experiment, but had a relatively low average discharge rate. The mass of NO_3^- exported from M3 in the NL event is the median of this group in comparison. The mass of PO_4^{3-} exported was also related to the FWMC of PO_4^{3-} in the NL event (ρ= 0.683, p= 0.042) and when both events are analyzed together (ρ= 0.558 (p= 0.016)), but not in the NS event (ρ= 0.350, p= 0.356). When the FWMC of PO_4^{3-} and the total mass exported are plotted on a scatterplot, there is more spread in the points from the NS event than those from the NL event (Figure 24, part e). The average mass of PO_4^{3-} exported from all monoliths was higher in the NL event (20.1μg with the outlier M3 and 4.2μg without) than it was in the NS event (1.7μg).

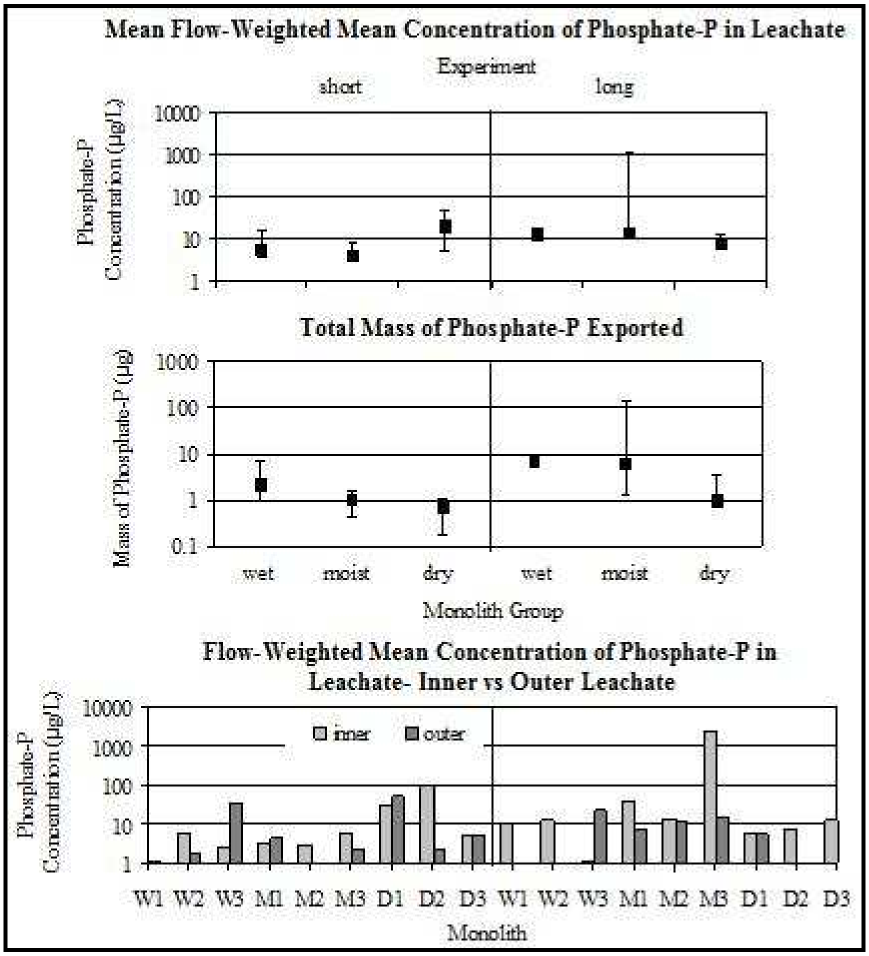
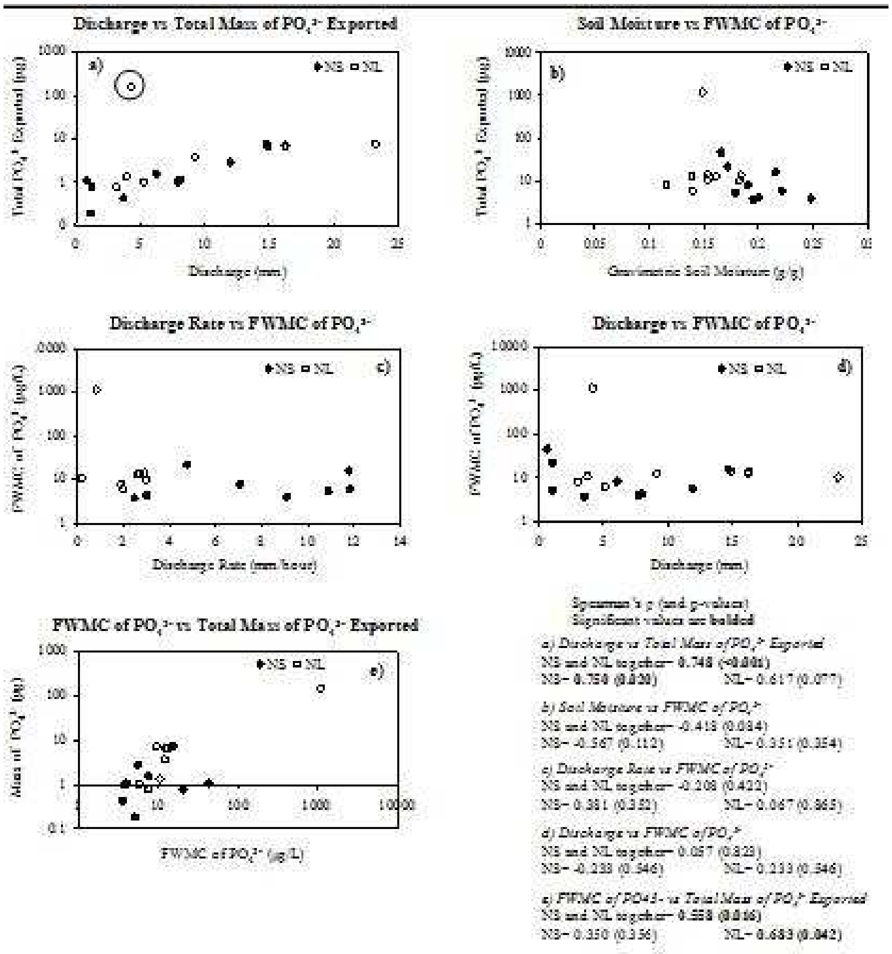


Figure 23- Flow-weighted mean PO_4^{3-} concentration, mass exported for groups of monoliths and the flow-weighted mean PO_4^{3-} concentration in inner and outer leaching in all monoliths in the nutrient leaching experiment.

Error bars represent standard deviation from each group of three monoliths and boxes represent the median value.



Spearman's ρ (and p-values)
Significant values are bolded

a) Discharge vs Total Mass of PO_4^{3-} Exported
NS and NL together– **0.748 (<0.001)**
NS– **0.750 (0.020)** NL– 0.617 (0.077)

b) Soil Moisture vs FWMC of PO_4^{3-}
NS and NL together– -0.415 (0.084)
NS– -0.567 (0.112) NL– 0.351 (0.354)

c) Discharge Rate vs FWMC of PO_4^{3-}
NS and NL together– -0.208 (0.422)
NS– 0.381 (0.352) NL– 0.067 (0.865)

d) Discharge vs FWMC of PO_4^{3-}
NS and NL together– 0.057 (0.823)
NS– -0.233 (0.546) NL– 0.233 (0.546)

e) FWMC of PO43- vs Total Mass of PO_4^{3-} Exported
NS and NL together– **0.558 (0.016)**
NS– 0.350 (0.356) NL– **0.683 (0.042)**

Figure 24- Scatterplots of a) discharge and the total mass of PO_4^{3-} exported, b) soil moisture and the FWMC of PO_4^{3-}, c) the discharge rate and the FWMC of PO_4^{3-}, and d) discharge and the FWMC of PO_4^{3-} for both nutrient leaching events.

3.3.2.2 Comparing the Flow-Weighted Mean PO_4^{3-} Concentration Between Inner and Outer Leachate

The difference in the FWMC of PO_4^{3-} between the inner and outer leachate was compared (Figure 23). In D2 in the NS event and M3 (the outlier) in the NL event, the FWMC of PO_4^{3-} was much higher in the inner leachate than in the outer leachate. In W3 from both events, the FWMC of PO_4^{3-} was much higher in the outer leachate than in the inner leachate.

3.3.2.3 Relationship between Discharge Rate and PO_4^{3-} Export

There were no relationships between the average discharge rate from each monolith and the FWMC of PO_4^{3-} when both events were examined together (0; ρ= -0.208, p= 0.422) and separately (ρ= 0.381, p= 0.352 in NS and ρ= -0.067, p= 0.865 in NL). When these variables are plotted on a scatterplot, there is a great deal of spread in the points, and the direction of the slope of the points in the NS event is fairly horizontal (Figure 24, part c). There was also no relationship with the average discharge rate and the mass of PO_4^{3-} exported when both events were examined together (ρ= -0.055, p= 0.833) and separately (ρ= 0.500, p= 0.207) in NS and ρ= 0.300, p= 0.433 in NL).

3.3.2.4 Temporal Changes in the PO_4^{3-} Concentration in Leachate for Individual Monoliths

Phosphate-P concentrations in the NS event were variable in time and ranged from 0.5-36.8µg/L in eight of the nine monoliths, with one monolith (D2) having a much higher PO_4^{3-}-P concentration in leachate (only one sample) of 101µg/L (Figure 25). There was no clear pattern to the variability in the PO_4^{3-} concentration in time in the wet or moist groups, except for M3, in which the PO_4^{3-} concentration rose towards the end of the leaching period. Only two leachate samples were collected from D2, one from D3 and none from the inner portion of D1, although one was collected from the outer portion of the monolith. The mass of PO_4^{3-} exported seemed to be related to both the variations in the discharge rate and in the concentration of PO_4^{3-} in the leachate (data not shown). The PO_4^{3-}-P concentration in leachate was more variable in time in the NL event, generally ranging from 2-30µg/L, with the exception of M3, which was anomalous in terms of the PO_4^{3-} concentration in leachate and the mass exported, which were both two orders of magnitude higher than those from any other monolith in the experiment. The concentration of PO_4^{3-} in leachate declined through time in the moist monoliths and in two of the three dry monoliths, but showed no clear pattern in the wet monoliths. The mass of PO_4^{3-} exported increased slightly at peak discharge rates and was related both to the discharge rate and concentration in leachate at all moisture levels (data not shown). The mass of PO_4^{3-} exported seemed to be somewhat related to the duration of high discharge rates.

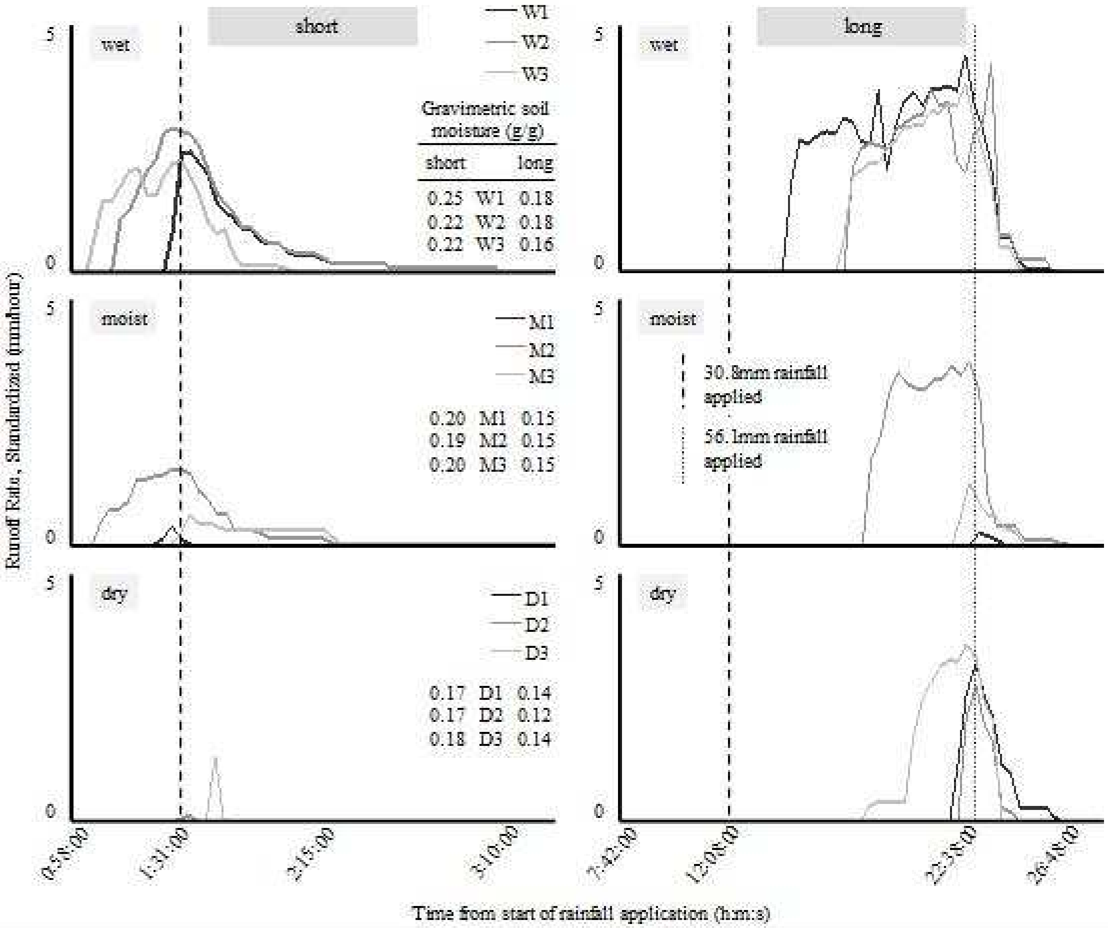


Figure 25-Temporal variability of phosphate concentration for all monoliths, grouped by moisture level with gravimetric moisture content of each monolith.

This figure shows concentrations in leachate collected from the inner cylinder only.

3.3.2.5 Soil PO_4^{3-} Pools and Influence on Nutrient Export

In both events, soil PO_4^{3-} levels were quite low compared to NO_3^- and did not differ between groups or between rainfall events. There was no significant difference in the PO_4^{3-} pools between groups of monoliths in either event, indicating that nutrient pools were affected in the same way from each different drying treatment. In the NS event, PO_4^{3-}-P pools ranged from 0.05-0.125µg/g at the start of rainfall application (Figure 26) and from 0.04-0.16µg/g at the start of rainfall application in the NL event. Studies in the adjacent riparian zone of groundwater nutrient levels also found PO_4^{3-} levels to be fairly low. Zhang (2007) found that SRP in groundwater (50, 100 and 150cm depths) ranged from

2-400µg/L, and SRP in riparian zone soil pools ranged from 0.4-4.6µg/g dry mass of soil. SRP was generally highest at the field edge and lowest near Spencer Creek (Zhang, 2007).

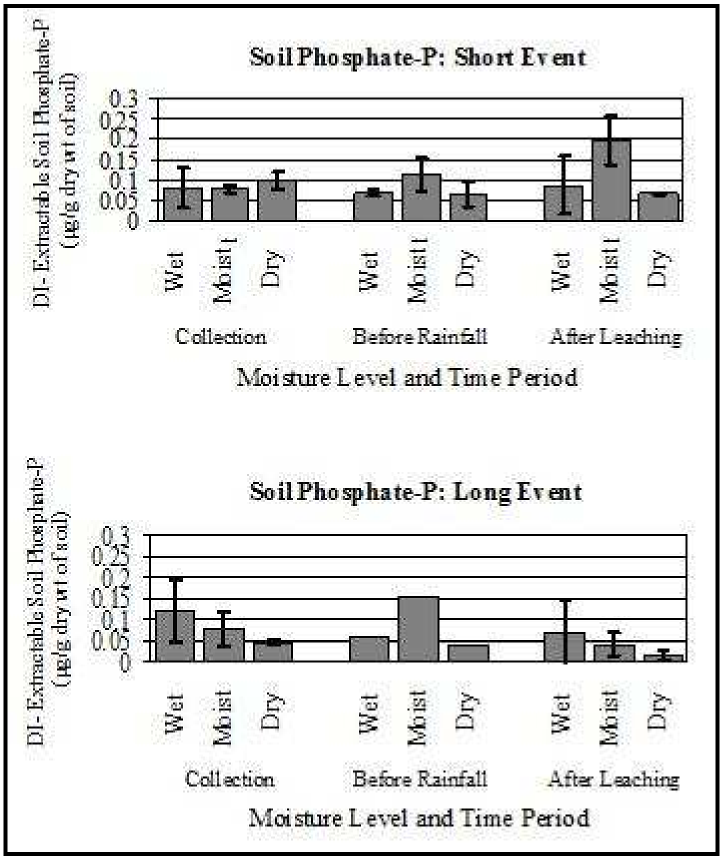


Figure 26- Soil DI-extractable PO_4^{3-} pools in both nutrient leaching events, at the time of monolith collection, the beginning of rainfall application and after the end of leaching.

Error bars indicate standard deviation.

3.3.2.6 Change in Soil PO_4^{3-} Levels Between the Start of Rainfall and the End of Leaching

Soil PO_4^{3-} pools did not change as consistently with depth between the start of rainfall application and the end of leaching as soil NO_3^- pools did (Figure 27). Soil PO_4^{3-} levels rose in the top 10cm of the soil in some monoliths and fell in others, while soil PO_4^{3-} rose in the bottom 20cm of the soil in some monoliths and fell in others.

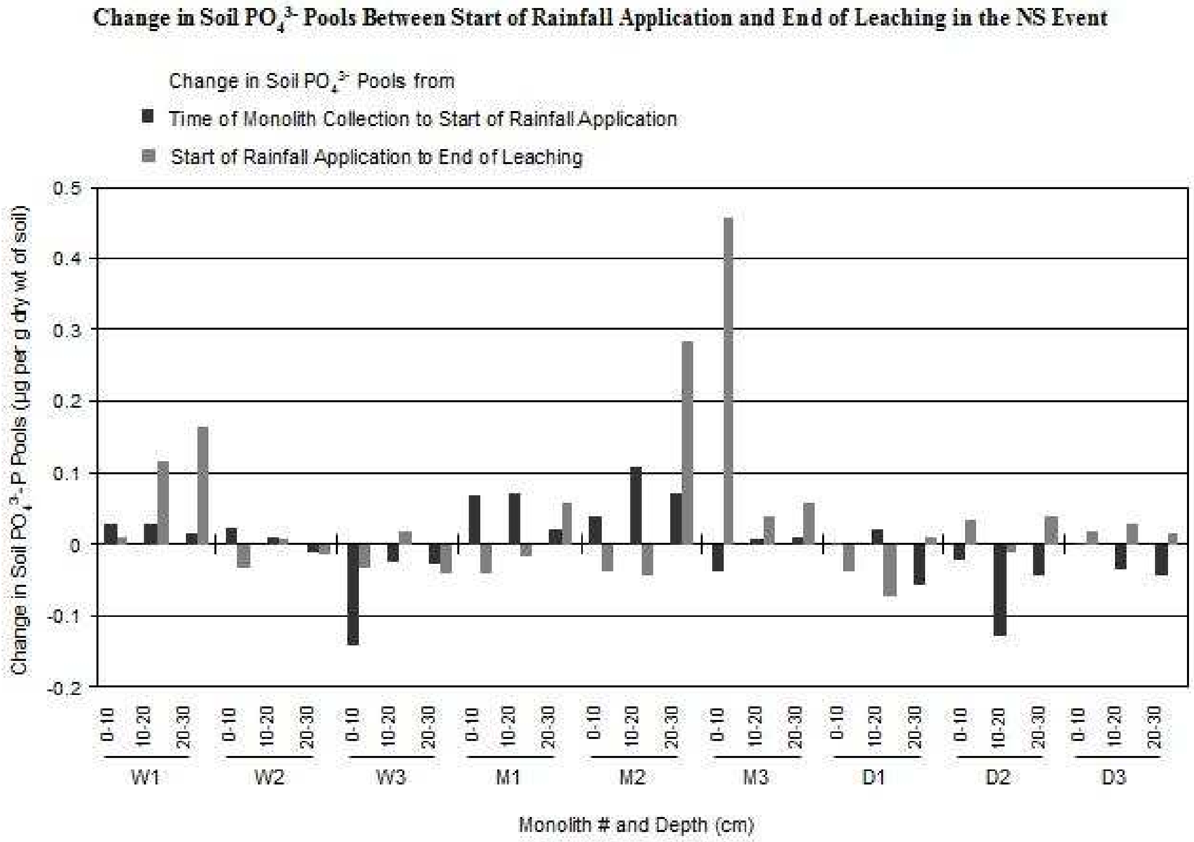
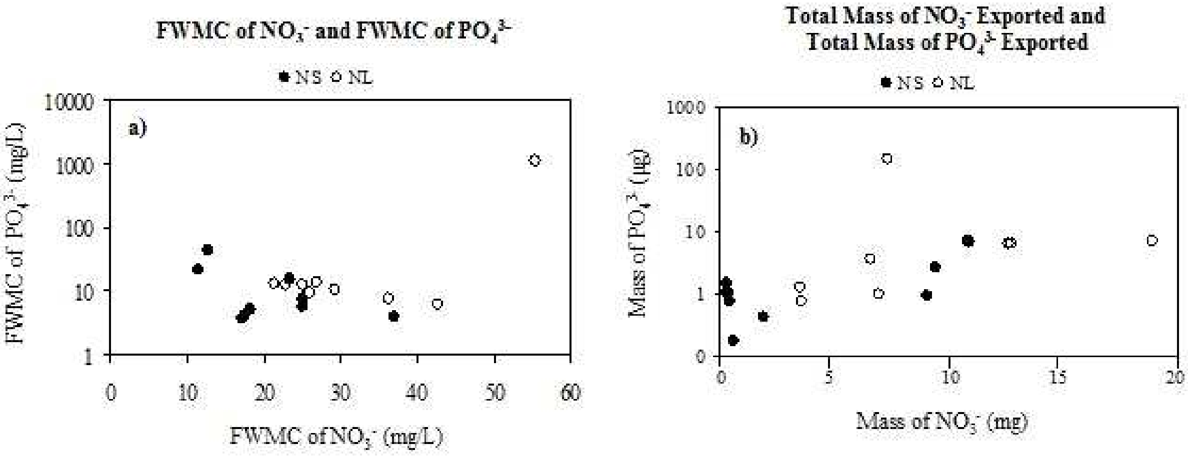


Figure 27- Change in DI-extractable soil PO_4^{3-} pools at three depths in the soil from the start of rainfall application to the end of leaching.

Bars represent the change in nutrient pools for the time periods described in the legend (between monolith collection and the start of rainfall application, and between the start of rainfall application and the end of leaching).

3.3.3 Relationship between the FWMC of NO_3^- and PO_4^{3-} and the Mass of NO_3^- and PO_4^{3-} Exported

There was no relationship between the FWMC of NO_3^- and PO_4^{3-} in either event (Figure 28; ρ= -0.367, p= 0.332 in NS and ρ= -0.183, p= 0.637 in NL) or when the events were examined together (ρ= -0.038, p= 0.880). There was a significant relationship between the mass of NO_3^- and PO_4^{3-} exported when both events were examined together (Table 6; ρ= 0.647, p= 0.004) and in the NL event (ρ= 0.700, p= 0.036) but not in the NS event (Figure 28; ρ= 0.218, p= 0.574). The scatterplot of these two variables illustrates how except for one outlier (M3 in NL), the mass of NO_3^- exported increases with the mass of PO_4^{3-} exported. The data points from NS are more clustered, with three monoliths that exported much more NO_3^- than the other monoliths. The relationship between the mass of NO_3^- and PO_4^{3-} exported is reflective of the strong relationship of both with the amount of discharge produced by the soil.



NS and NL together= -0.038 (0.880)
NS= -0.367 (0.332) NL= -0.183 (0.637)

NS and NL together= **0.647 (0.004)**
NS= 0.218 (0.574) NL= **0.700 (0.036)**

Spearman's ρ (and p-values)
Significant values are **bolded**

Figure 28- Scatterplots of a) the FWMC of NO_3^- and PO_4^{3-} and b) the total mass of NO_3^- and PO_4^{3-} exported for the nutrient leaching experiment.

3.4 Field Conditions in 2008

3.4.1 Soil Nutrient Levels 2008

For both NO_3^- and PO_4^{3-}, soil nutrient pools in both nutrient leaching events were within the typical range of soil nutrient pools found at JMF during the summer of 2008. When averaged for all depths and sampling locations, soil NO_3^--N ranged from 1.2-3.2μg/g dry weight of soil and PO_4^{3-}-P ranged from 0.03-0.07μg/g dry weight of soil in the field throughout the summer (Figure 29). Nitrate pools were much higher than soil PO_4^{3-} pools. Soil NO_3^- levels at JMF in 2008 got higher from JD 165-227, while soil NH_4^+-N levels fell slightly during this period, suggesting some conversion of NH_4^+ to NO_3^-. Nitrate and phosphate were generally more plentiful in the top 20cm of soil than in 20-30cm depths, with a few exceptions (JD 165 and 247 for NO_3^- and JD 184 for PO_4^{3-}). There was some between-site variability in terms of nutrient pools, but no consistent pattern between sites in terms of which had the highest level of nutrients.

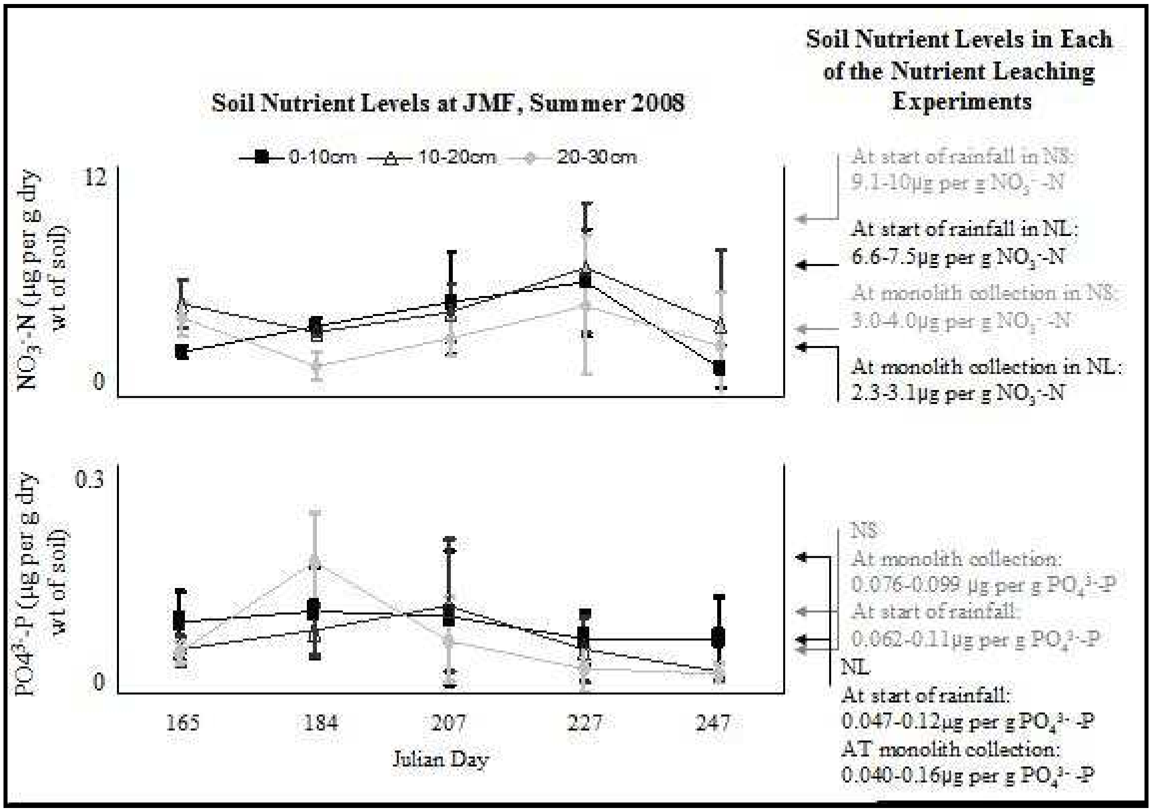
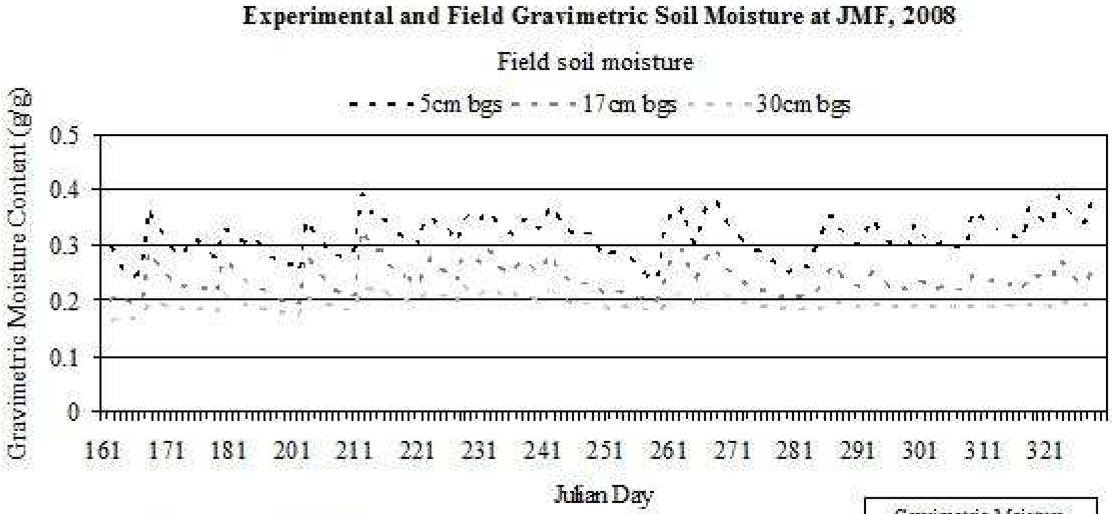


Figure 29- Soil KCl-extractable soil NO_3^--N and DI-extractable PO_4^{3-}-N pools throughout the summer of 2008 for each depth, averaged by sampling locations.

Error bars show standard deviation at each depth between sample collection sites. The line graph represents the soil nutrient levels throughout the summer of 2008 at JMF, and the arrows and values to the right represent nutrient levels simulated in each of the nutrient leaching events.

3.4.2 Soil Moisture Trends at John Mount Farm

The range of daily average gravimetric soil moisture from the soil moisture probes installed at JMF throughout the 2008 field season was 0.16-0.37g/g (Figure 30). The moisture levels simulated in each experiment were generally lower than those found naturally in the field, especially moisture levels simulated in the NL event, and moisture levels simulated in the nutrient leaching experiment were lower than those in the hydrology experiment.



Experimental Soil Moisture

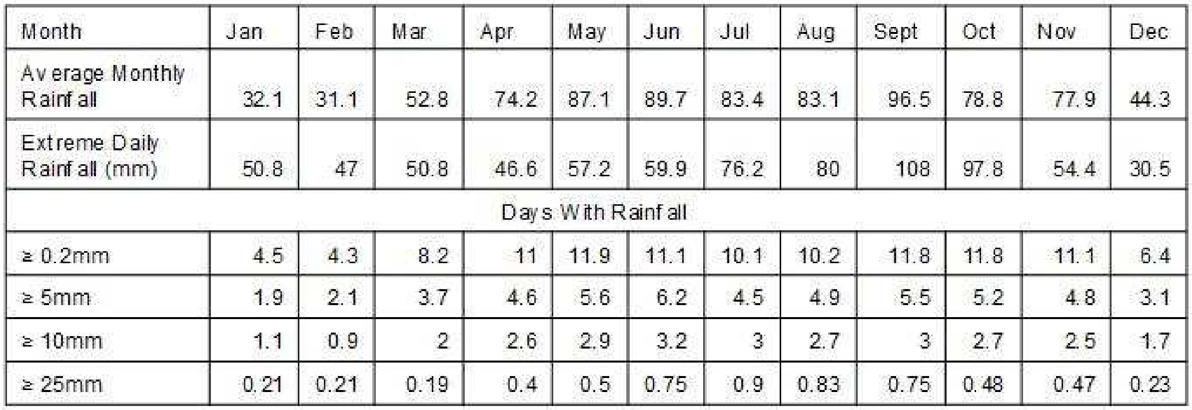
Event	Moisture Level	Gravimetric Moisture Content (g/g)	Event	Moisture Level	Gravimetric Moisture Content (g/g) min	median	max
HS	Wet	**0.25**	NS	Wet	0.22	0.22	**0.25**
	Moist	0.23		Moist	0.19	0.20	0.20
	Dry	**0.21**		Dry	**0.17**	0.17	0.18
HL	Wet	**0.25**	NL	Wet	0.16	0.18	**0.18**
	Moist	0.23		Moist	0.15	0.15	0.15
	Dry	**0.21**		Dry	**0.12**	0.14	0.14

Figure 30- Average daily gravimetric soil moisture at the John Mount Farm from probes at three depths and range of gravimetric moisture contents simulated in each experiment.

Bolded values in the table indicate the maximum and minimum values for each event.

3.4.3 Rainfall Trends at John Mount Farm

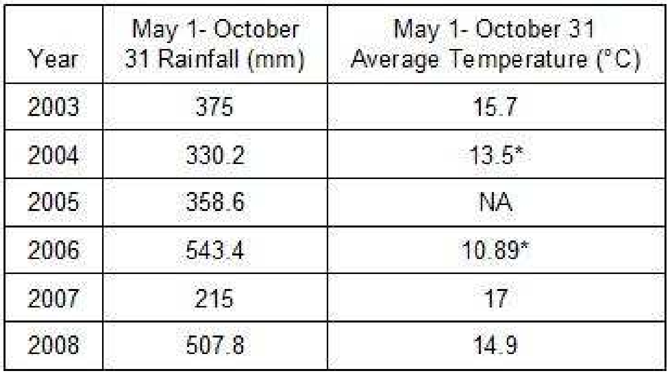
Rainfall trends at JMF were examined in order to assess the frequency of occurrence of the conditions simulated in the experiments at the field site. Thirty year climate normals from Environment Canada from the Milgrove weather station (closest Environment Canada weather station to study site) were used to examine monthly and daily rainfall totals, and the likelihood within any given month of rainfall exceeding certain amounts (Environment Canada, 2009). The highest average monthly rainfall occurs during the summer months (Table 8), as do the days with the highest extreme daily rainfall. The highest daily rainfall was 108mm, which fell in September. Each month (with the exception of December) had an extreme daily rainfall above 31mm and all months from May-October had an extreme daily rainfall above 56.2mm, indicating that the conditions simulated in the experiment have occurred in all these months of the year during the 30 year period. The likelihood of a day with a large rainfall event (≥25mm) is greatest in the summer months and highest specifically in July, with an average of just under one day per month with this magnitude of rainfall event.



Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Average Monthly Rainfall	32.1	31.1	52.8	74.2	87.1	89.7	83.4	83.1	96.5	78.8	77.9	44.3
Extreme Daily Rainfall (mm)	50.8	47	50.8	46.6	57.2	59.9	76.2	80	108	97.8	54.4	30.5
Days With Rainfall												
≥ 0.2mm	4.5	4.3	8.2	11	11.9	11.1	10.1	10.2	11.8	11.8	11.1	6.4
≥ 5mm	1.9	2.1	3.7	4.6	5.6	6.2	4.5	4.9	5.5	5.2	4.8	3.1
≥ 10mm	1.1	0.9	2	2.6	2.9	3.2	3	2.7	3	2.7	2.5	1.7
≥ 25mm	0.21	0.21	0.19	0.4	0.5	0.75	0.9	0.83	0.75	0.48	0.47	0.23

Table 8- Rainfall totals for Millgrove weather station based on averages from 1971-2000 (43° 19.000'N, 79° 58.000'W, 268.2m asl; Environment Canada, 2009).

Rainfall totals from May 1 to October 31 from the MET station 200m away from the study site at JMF from 2003-2008 were calculated in order to compare rainfall in this period in 2008 to previous years at the study site. Rainfall totals from only May to October were calculated to eliminate the possibility of snowfall complicating rainfall totals. The May-October rainfall totals ranged from 215mm in 2007 to 543.4mm in 2006, with 507.8mm of rainfall during this period in 2008, which was the second wettest year in this period (Table 9). The 30-year normal rainfall total for May- October is 518.6mm (Environment Canada, 2009), so 2008 was fairly average in terms of rainfall during this period. The rainfall totals for this seven year period illustrate the variability in rainfall during the warmer months at this site.



Year	May 1- October 31 Rainfall (mm)	May 1- October 31 Average Temperature (°C)
2003	375	15.7
2004	330.2	13.5*
2005	358.6	NA
2006	543.4	10.89*
2007	215	17
2008	507.8	14.9

Table 9- Total rainfall at the John Mount Farm from May 1-October 31 in 2003- 2008.

Intensity-duration frequency curves (Appendix A) were obtained for Cambridge (1980-1992; 43 20’ N, 80 19’ W; 268m asl; Environment Canada, 1992) and Hamilton (1971-2003; 43° 10’ N, 79° 56’ W; 238m asl; Environment Canada, 2003) in order to assess the frequency of occurrence of the three events simulated in the two experiments. The short event in both experiments (22.5mm/h for 0:01:32) has a return period of two years for both stations and the long events (2.5mm/h for 12:32:00 in the hydrology experiment and 22:38:00 in the nutrient leaching experiment) have a return period of less than one year and one year, respectively. Therefore, a long, low-intensity event such as the one simulated is approximately twice as likely to occur as a short, high-intensity event.

Daily rainfall totals were strongly left-skewed, as were event totals (data not shown), with the vast majority of days at JMF with rainfall having low rainfall depths (Figure 31). Fifty-one percent of days had rainfall totals of ≤ 2mm and 90% of days had rainfall totals of ≤ 16mm. There were twelve days out of the five year period with daily rainfall totals of > 30mm (or 2.8% of days with rainfall).

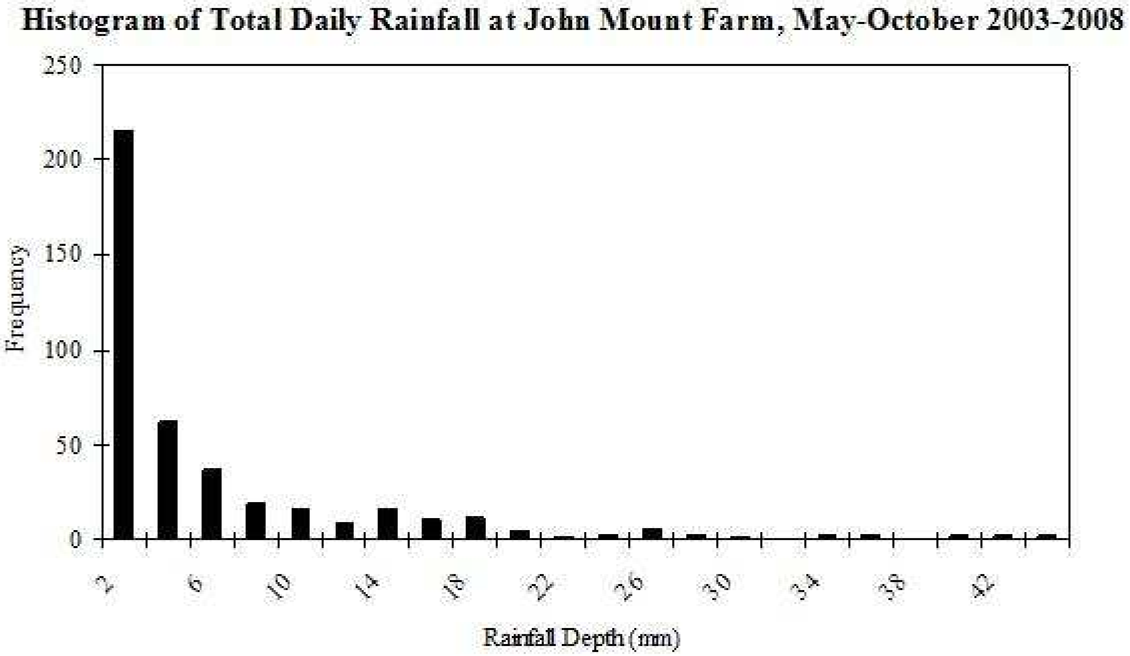


Figure 31- Histogram of daily rainfall depth at the John Mount Farm from May 1-October 31, from 2003-2008.

Event length followed a similar pattern to event depth, with many short events and few very long events (Figure 32). Only 3% of events were > 20 hours in length, while 89% of events were ≤ 5 hours in length.

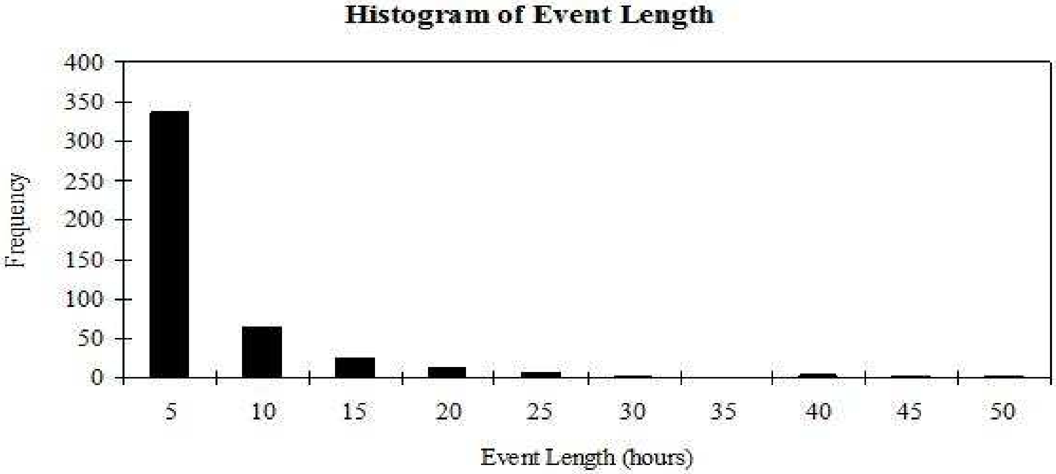


Figure 32- Histogram showing rainfall event length at the John Mount Farm for May 1-October 31, from 2003-2008.

Rainfall rates were low in the majority of events (Figure 33). Events with rainfall rates of ≥2.5mm/hour made up 23% of all events, while only one event had a rainfall rate of greater than 22.5mm/hour (0.3% of events).

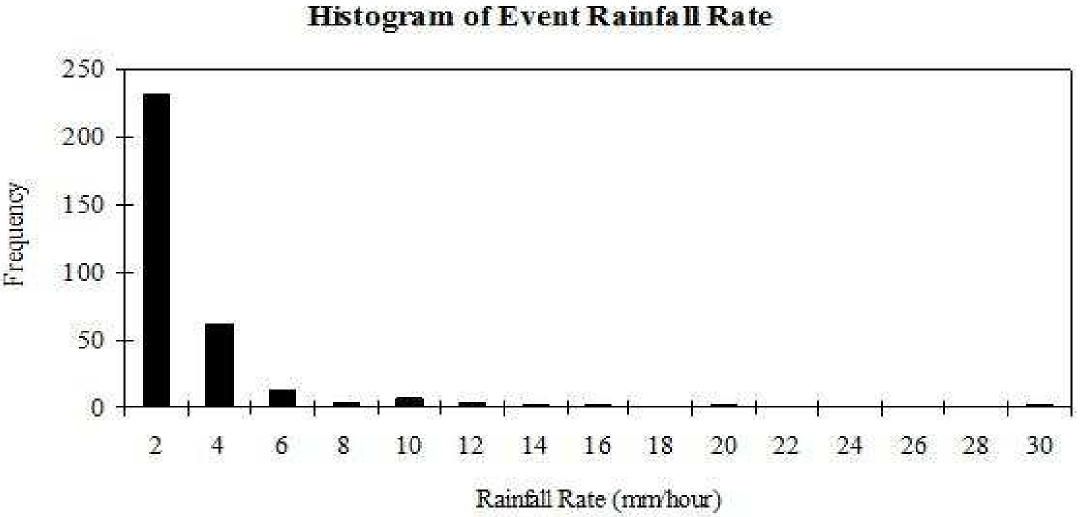
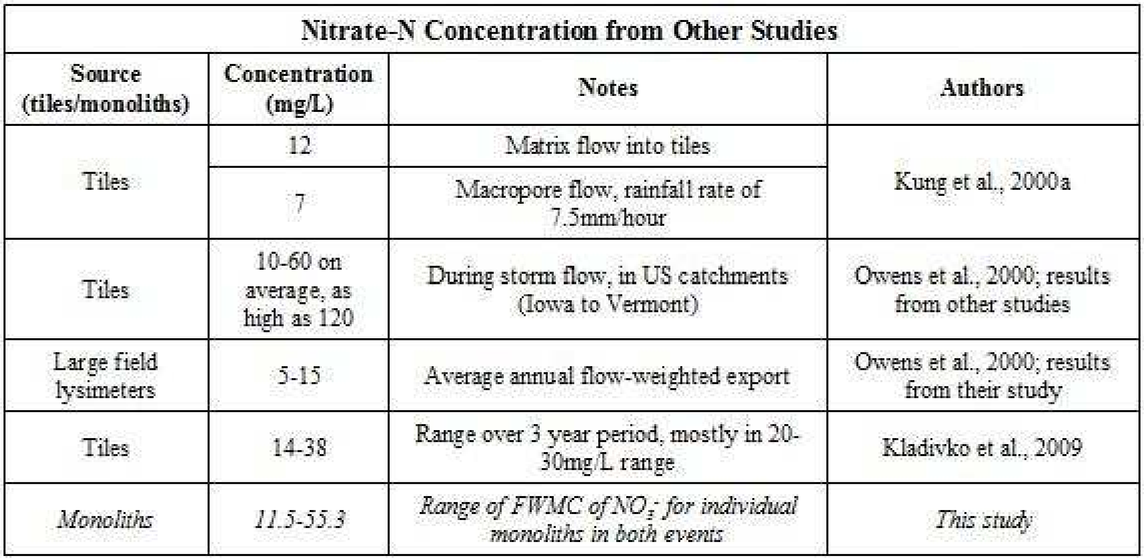


Figure 33- Histogram showing event rainfall rate at the John Mount Farm for May 1-October 31, from 2003-2008.

3.5 Nutrient Levels in Leachate and Tile Effluent in the Literature

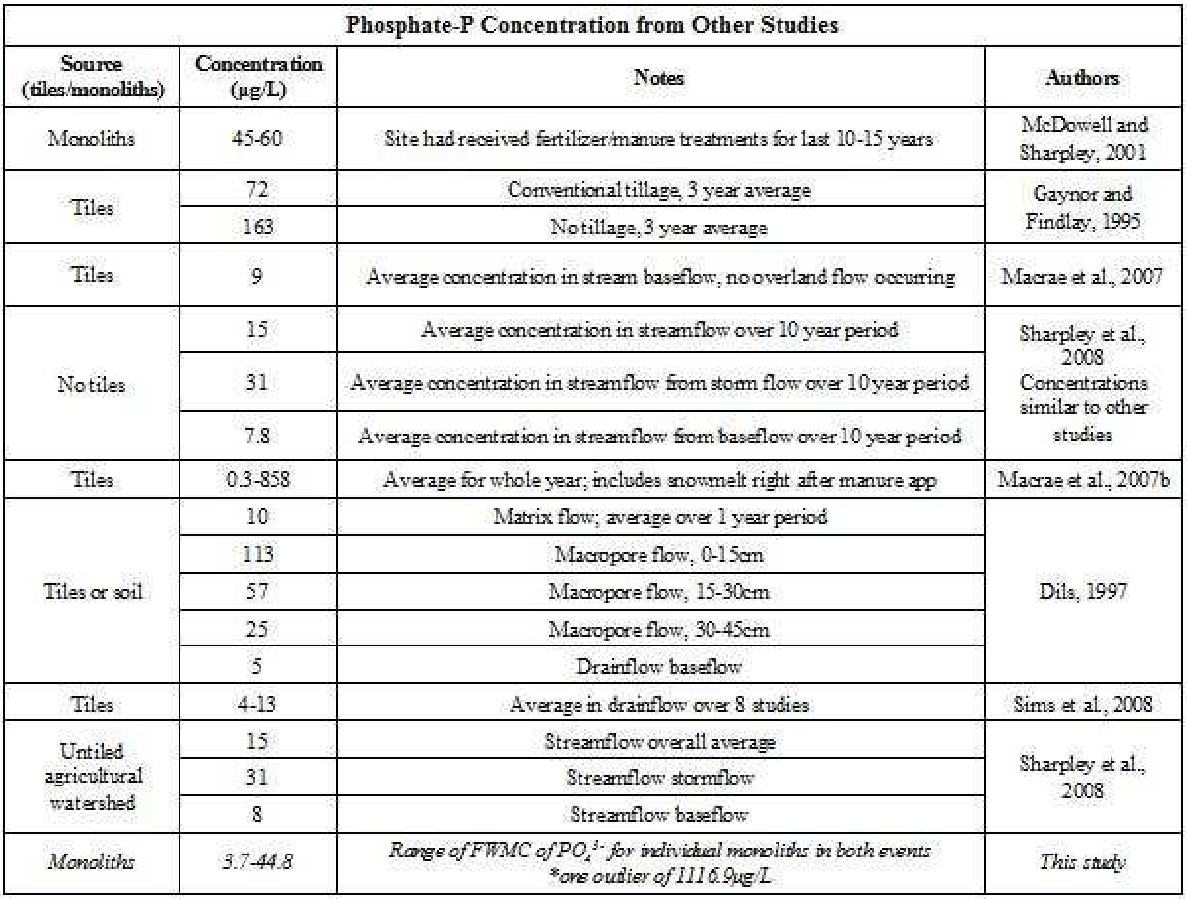
The average FWMC of NO_3^--N in leachate from each of the events in the nutrient leaching experiment (20.8mg/L and 30.7mg/L for the NS event and the NL event, respectively) is well within the range observed in other studies from both drainage tile effluent and large field lysimeters, as is the FWMC of NO_3^- from each individual monolith (FWMC of NO_3^- from individual monoliths shown in Figure 17, NO_3^- concentrations from the literature shown in Table 10). The average FWMC of PO_4^{3-}-P in leachate from each of the events in the nutrient leaching experiment (12.4 and 10.7µg/L for NS and NL, respectively) is generally on the lower end of the range of PO_4^{3-} concentrations seen in the literature, except for M3 in the NL event (seen as the upper error bar in the moist group of monoliths in the NL event in), which had a FWMC of PO_4^{3-} that was much higher than all of the concentrations seen in the literature (PO_4^{3-} concentrations from the literature shown in Table 11).



Nitrate-N Concentration from Other Studies

Source (tiles/monoliths)	Concentration (mg/L)	Notes	Authors
Tiles	12	Matrix flow into tiles	Kung et al., 2000a
	7	Macropore flow, rainfall rate of 7.5mm/hour	
Tiles	10-60 on average, as high as 120	During storm flow, in US catchments (Iowa to Vermont)	Owens et al., 2000; results from other studies
Large field lysimeters	5-15	Average annual flow-weighted export	Owens et al., 2000; results from their study
Tiles	14-38	Range over 3 year period, mostly in 20-30mg/L range	Kladivko et al., 2009
Monoliths	*11.5-55.3*	*Range of FWMC of* NO_3^- *for individual monoliths in both events*	*This study*

Table 10- Nitrate-N concentration in tile effluent and leachate from other studies.



Phosphate-P Concentration from Other Studies			
Source (tiles/monoliths)	**Concentration (µg/L)**	**Notes**	**Authors**
Monoliths	45-60	Site had received fertilizer/manure treatments for last 10-15 years	McDowell and Sharpley, 2001
Tiles	72	Conventional tillage, 3 year average	Gaynor and Findlay, 1995
	163	No tillage, 3 year average	
Tiles	9	Average concentration in stream baseflow, no overland flow occuring	Macrae et al., 2007
No tiles	15	Average concentration in streamflow over 10 year period	Sharpley et al., 2008 Concentrations similar to other studies
	31	Average concentration in streamflow from storm flow over 10 year period	
	7.8	Average concentration in streamflow from baseflow over 10 year period	
Tiles	0.3-858	Average for whole year; includes snowmelt right after manure app	Macrae et al., 2007b
Tiles or soil	10	Matrix flow; average over 1 year period	Dils, 1997
	113	Macropore flow, 0-15cm	
	57	Macropore flow, 15-30cm	
	25	Macropore flow, 30-45cm	
	5	Drainflow baseflow	
Tiles	4-13	Average in drainflow over 8 studies	Sims et al., 2008
Untiled agricultural watershed	15	Streamflow overall average	Sharpley et al., 2008
	31	Streamflow stormflow	
	8	Streamflow baseflow	
Monoliths	*3.7-44.8*	*Range of FWMC of PO_4^{3-} for individual monoliths in both events* **one outlier of 1116.9µg/L*	*This study*

Table 11- Phosphate-P concentration in tile effluent and leachate from the literature.

Chapter 4

Discussion

4.1 Influence of Antecedent Soil Moisture and Rainfall Rates on Discharge Depth and the Hydrologic Flow Paths in the Soil

4.1.1 Influence of Antecedent Soil Moisture and Rainfall Rates on Discharge Depth, Timing and Rates

Soil moisture had a greater influence than rainfall rate on the amount of discharge produced and the timing of discharge production, and had a lesser effect on the flow type that occurred. In both the hydrology and nutrient leaching experiments, more discharge was produced by wet soil than dry soil, this was reinforced by significant correlations between gravimetric soil moisture and discharge when both hydrology events were examined together, and in each nutrient leaching event. This is because the gradient of matrix potential between large and small soil pores favours water to enter into the matrix of the soil in dry soil (Kung et al., 2000a), so more water goes into storage in dry soil than in wet soil, and less discharge is produced. This happens even if the maximum infiltration of the soil is exceeded (Barraclough, 1989a). The rainfall rate did not have an effect on the depth of discharge produced, as discharge depths were the same between monoliths at the same moisture level in the hydrology events.

There was more discharge in general in the hydrology experiment, likely because some of the fines had been washed out of the monoliths during the preliminary trials prior to this experiment, in which discharge was produced, or when the monoliths were saturated and left to drain to field capacity. The runoff ratios from wet soil in the hydrology experiment were extremely high (0.91 in HS and 0.89 in HL) compared to those in other studies (*e.g.* 0.3-0.4 in Sharpley et al., 2008; 0.002-0.62 in a relatively steep, forested catchment in James and Roulet, 2007). However, comparisons between runoff ratios must be made with caution, as variations in soil type and structure between sites would cause a great deal of variation in runoff ratios. Some of the within-group variability in the relationship between soil moisture and discharge in the nutrient leaching experiment coincided with a greater amount of discharge from the outer portion of each monolith. The variation within each group could be simply due to the heterogeneity of the soil pore structure (Gaynor and Findlay, 1995).

At both high and low rainfall rates, discharge began earliest in wet soil and last in dry soil because less of the applied water went into storage in wet soil and therefore water percolated through the soil and exited earlier. In dry soil, the gradient of matric potential favours water to enter small pores first and go into storage (Kung et al., 2000a), and water is not transported through the soil until this gradient diminishes and water enters slightly larger soil pores. Because discharge is produced earlier in wet soil, peak discharge rates are achieved earlier and maintained for a longer period of time and the total duration of discharge is longer. This same relationship between discharge timing and discharge rates has been found in other studies (de Rooij and Stagnitti, 2002; Kung et al., 2000a, b).

There was a relationship between discharge and the average discharge rate under low intensity rainfall but not under high intensity rainfall. Other authors have found a relationship between discharge and the average discharge rate (*e.g.* de Rooij and Stagnitti, 2002; Kung 2000a, b; Barraclough, 1989a). There was no relationship between soil moisture and the average discharge rate (this was clear from the scatterplot even though there was a significant Spearman correlation), even though other authors have found a relationship between soil moisture and the discharge rate (*e.g.* de Rooij and Stagnitti, 2002; Kung et al., 2000a, b; Barraclough, 1989a). Therefore, the relationship between the discharge rate and discharge or soil moisture was not as good as that with the depth of discharge and soil moisture. This was illustrated where monoliths in the nutrient leaching experiment that had similar levels of soil moisture had very different peak discharge rates in some cases (*e.g.* moist monoliths in both events). Natural soil heterogeneity and the difference in the physical properties and pore structure of the soil between monoliths may have affected the flow paths and therefore the discharge rate between monoliths. The presence and activity of preferential flowpaths is associated with higher discharge rates (de Rooij and Stagnitti, 2002), so monoliths with more macropores may have higher discharge rates. The presence of macropores varies spatially in the soil (Armstrong et al., 1999; de Rooij and Stagnitti, 2002), so some monoliths may have more macropores than others.

The rainfall intensity affected the discharge rate, because the discharge rate was a product of the rate at which rainfall was applied. In proportion to the rate of rainfall application, discharge rates were very similar between the two rainfall rates.

4.1.2 Influence of Antecedent Soil Moisture and Rainfall Rates on the Hydrologic Flow Paths in the Soil

Although rainfall rates did not have an effect on the depth of discharge produced by the soil, they had an influence on the dominant flow paths in the soil at the beginning of leaching. Soil moisture affected the extent to which certain flow paths occurred, but only under high intensity rainfall. In wet soil under high rainfall rates, discharge was produced before the bottom soil moisture probe had shown any increase in soil moisture. This indicates that the percolating water that produced the first discharge in wet soil had likely bypassed the bulk of the soil matrix and was traveling quickly through a small portion of the soil volume (preferential flow; de Rooij and Stagnitti, 2002). If the entire matrix of the soil had been wet up prior to discharge production, then the probe would have indicated an increase in soil moisture. In moist and dry soil, the soil at the bottom of the monolith had begun to wet up but not reached its maximum level of soil moisture when discharge was produced. This indicates that the water was percolating slightly more slowly through the soil, but had reached the bottom of the soil profile before the entire matrix of the soil had wet up. This indicates that preferential flow was occurring in moist and dry soil, but the flow rate was lower, indicating that smaller soil pores were active in transporting water (Kung et al., 2000a, b).

The maximum discharge rate was achieved early on in wet soil and this rate was maintained until after the end of rainfall application, when it dropped off. Since the discharge rate was fairly constant, it is likely that soil pores of a similar size were active throughout the discharge period (de Rooij and Stagnitti, 2002; Kung et al., 2000a, b), indicating that preferential flow was occurring for the duration of the maximum rate, until just after rainfall application stopped and the discharge rate dropped. The falling discharge rate is indicative of progressively smaller soil pores contributing to discharge (Kung et al., 2000a, b), until the point when the matric forces in the soil dominate and no more discharge is produced (de Rooij and Stagnitti, 2002). In moist soil, the maximum discharge rate was lower than it was in wet soil, indicating that the macropores producing the discharge may have been fewer or smaller in size (Kung et al., 2000a, b). Preferential flow only occurred in dry soil for a shorter period of time and the maximum discharge rate was lower than in moist soil, which may indicate that the macropores that were active were smaller than those which were active in moist soil.

The dominant flow paths through the soil at the beginning of leaching were likely much different under low intensity rainfall than they were under high intensity rainfall and did not differ much between moisture levels like they did under high intensity rainfall. In all monoliths, discharge was produced well after the soil at the bottom of the monolith had reached the maximum level of moisture. This indicates that the bulk of the soil matrix was at its maximum level of moisture (likely near field capacity) before discharge was produced, and therefore that small soil pores were contributing to discharge (de Rooij and Stagnitti, 2002). If larger pores had been contributing to discharge, then discharge would have been produced before the entire matrix of the soil had wet up. The rainfall rate in this case was low enough such that the maximum possible infiltration rate of the soil was not exceeded and the rainfall entered smaller soil pores.

The same flow types were observed in response to natural rainfall events. High rainfall rates caused a rapid increase and decline in soil moisture, indicating faster water flow in larger soil pores (de Rooij and Stagnitti, 2002). Lower rainfall rates caused a slower increase in soil moisture and a delay in the moisture increase in each level of the soil, indicating slower water movement in smaller soil pores.

There was a clear difference in the dominant flow paths at the beginning of leaching under different rainfall rates, but no conclusions can be made about the flow paths in the soil throughout the rest of the leaching period. As was discussed in the literature review, there are two scenarios under which preferential flow can occur: when the rainfall rate exceeds the infiltration rate of soil matrix (de Rooij and Stagnitti, 2002) and after the soil wets up during a rainfall event and progressively larger soil pores become active in leaching (Kung et al., 2000a, b). This study can only identify preferential flow that occurs in the first scenario. Identification of preferential flow in the second scenario would require the use of a conservative surface-applied tracer such as Cl^-. When increasing amounts preferential flow occur as the soil wets up, the discharge rate increases along with a decline in the concentration of the tracer in discharge (Kung et al., 2000a, b). In future work, it would be helpful to perform a similar experiment using soil moisture probes and a conservative tracer to gain an understanding of the flow paths throughout the entire leaching period.

4.2 Influence of Antecedent Soil Moisture and Rainfall Rates on Nutrient Export

4.2.1 Influence of Antecedent Soil Moisture and Rainfall Rates on the Flow-Weighted Mean Nutrient Concentration and Bulk Nutrient Export

Antecedent soil moisture had a significant influence on the amount of discharge produced, which had significant relationships with the total mass of both NO_3^- and PO_4^{3-} exported under both high and low rainfall rates. Both nutrients were exported in greater quantities from wet soil than from dry soil. In dry soil, more of the infiltrating water goes into storage and enters the matrix of the soil because the matric potential of dry soil is greater than that of wet soil (Kung et al., 2000a). As a result, more water is available for leaching in wet soil than in dry soil (Kung et al., 2000a, b) and more soil pores are hydraulically active (Kung et al., 2000a) and therefore more water is moving through the soil and available to transport nutrients (de Rooij and Stagnitti, 2002) leading to higher total masses of nutrients exported. Other authors (*e.g.* Vanni et al., 2001; Sharpley et al., 2008; Stamm et al., 1998; McDowell and Sharpley, 2002) have reported positive relationships between discharge and the mass of nutrients exported.

There was a significant relationship between soil moisture and the FWMC of NO_3^- under high intensity rainfall but not under low intensity rainfall. There was a marginal relationship between the depth of discharge and the FWMC of NO_3^- and the average discharge rate and the FWMC of NO_3^- under high intensity rainfall. Therefore, soil moisture, which is the main driver of the amount of discharge and the discharge rate (under low intensity rainfall) has an influence on the concentration of NO_3^- in leachate under high intensity rainfall. The positive relationship between discharge and the FWMC of NO_3^- is contrary to what was expected, as more discharge and higher discharge rates are generally correlated with flow in larger soil pores (de Rooij and Stagnitti, 2002; Kung et al., 2000a, b), which cause lower NO_3^- concentrations in leachate (Kung et al., 2000a, b; Biron et al., 1999; Kladivko et al., 2009). This positive relationship between discharge and NO_3^- concentrations may indicate that preferential flow was minor and matrix flow was more dominant under high intensity rainfall in the nutrient leaching experiment (Kung et al., 2000a, b; Vanni et al., 2001; Kladivko et al., 2009). This is contrary to the findings of the hydrology experiment, where preferential flow was occurring at the beginning of the leaching period in wet soil in particular, and to a lesser extent in moist and dry soil.

Under low intensity rainfall, the FWMC of NO_3^- in leachate was inversely related to discharge and the average discharge rate, resulting in higher FWMC of NO_3^- in dry soil and lower FWMC of NO_3^- in wet soil. Other authors (*e.g.* Biron et al., 1999; Kladivko et al., 2009; Kung et al., 2000a, b) have found this same relationship. In dry soil under low rainfall rates, water will first enter the smallest matrix pores because of the gradient of matric potential (Kung et al., 2000a), thereby accessing a greater amount of NO_3^- in soil pools in dry soil than in wet soil, in which water would enter slightly larger pores first (Kung et al., 2000a), missing a large portion of the total soil NO_3^- pools. The leachate produced from dry soil under low intensity rainfall would have been in contact with more of the soil NO_3^- pools than that produced by wetter soil, so any leachate produced would be more concentrated in terms of NO_3^-. Because more water goes into storage in dry soil, as was shown in the results of this experiment, less leachate is produced and discharge rates are lower (de Rooij and Stagnitti, 2002). This explains the inverse relationship between both the depth of discharge and discharge rate and the FWMC of NO_3^-. The total mass of NO_3^- exported was still positively related to discharge under low intensity rainfall simply due to the greater volume of discharge produced.

There was no clear relationship between the FWMC of PO_4^{3-} in either event with soil moisture, the depth of discharge or the average discharge rate. There was a significant correlation between the FWMC of PO_4^{3-} and the mass of PO_4^{3-} exported under low intensity rainfall. Therefore, there is a clear need for more research into what affects concentrations of PO_4^{3-} in leachate because they affect the mass of PO_4^{3-} exported in some circumstances. Many studies (*e.g.* Gächter et al., 1998; Sharpley et al., 2008; Macrae et al., 2007b; McDowell and Sharpley, 2002; Stamm et al., 1998) found a positive correlation between the concentration of PO_4^{3-} in leachate and the depth of discharge and discharge rates. The lack of a correlation of the FWMC of PO_4^{3-} in this study may have been related to the low levels of PO_4^{3-} in the soil, which resulted in very little PO_4^{3-} exported and export patterns that were not as clear as those for NO_3^-.

4.2.2 Influence of Flow Paths on Nutrient Export

There was no conclusive evidence of preferential flow at the beginning of the leaching period in the nutrient leaching experiment when the temporal changes in nutrient concentrations were examined. Preferential flow occurred in the hydrology experiment at the beginning of the leaching period under high intensity rainfall in wet soil, and less so in moist and dry soil. Based on these results, some degree of preferential flow would be expected during this period in the NS event, especially in wet soil. The moisture content of the wet monolith in the HS event and the wet monoliths in the NS event was similar but a bit lower in the NS event, especially in monoliths W2 and 3. Therefore, preferential flow would be expected in the wet monoliths of NS because of similarity in moisture levels. Preferential flow bypasses solute in small soil pores (Kung et al., 2000a), so it would be expected that preferential flow would result in lower FWMC of NO_3^- in leachate than matrix flow (Kung et al., 2000a; de Rooij and Stagnitti, 2002; Britton et al., 1993). In contrast, preferential flow may result in higher PO_4^{3-} concentrations in leachate than matrix flow if the surface soil was saturated in terms of P (Geohring et al., 2001; Gächter et al., 1998; Stamm et al., 1998; Akhtar et al., 2003). Soil PO_4^{3-} levels in the nutrient leaching experiment and at JMF were low and suggest that the soil was not saturated in terms of PO_4^{3-}. In W1 in the NS event, there was a pulse of higher NO_3^- concentrations in leachate at the beginning of the leaching period. A pulse of higher NO_3^- and PO_4^{3-} concentrations in leachate was also observed in W3, with a pulse in PO_4^{3-} at the start of leaching in M2 and in the outer leachate from M1 from the NS event. It is possible that preferential flow was occurring in W1 and W3 from the NS event, but instead of causing more dilute NO_3^- concentrations at the beginning of leaching, NO_3^- pools from the surface soil (Macrae et al., 2007b) or the walls of the macropores was exported at the beginning of leaching (Kladivko et al., 1991), resulting in higher concentrations of NO_3^-. Nitrate concentrations dropped after this initial pulse, which may have indicated that the supply of NO_3^- from these pools ran out. Soil pools in W1 and W3 from the NS event indicated higher levels of NO_3^- in the top 10cm of soil than in the other monoliths in this event, so NO_3^- from the surface of the soil may have been transported quickly through the monoliths at the beginning of leaching. This was not the case for soil PO_4^{3-} pools in W3, M1 and M2, where soil PO_4^{3-} levels in the top 10cm of soil were similar to those of the other monoliths. Alternatively, this pulse in nutrient export could also have been caused by the flushing of nutrients from pores near the bottom of each monolith (Britton et al., 1993). This may have been the case for M1 and M2, which both had higher PO_4^{3-} levels in the bottom 10cm of soil than the other monoliths.

Temporal changes of the NO_3^- concentration in leachate were minor in most monoliths under high intensity rainfall, and may be due to changes in contributing areas of the soil, which would have likely varied slightly in NO_3^- pools. The spatial variability in soil NO_3^- pools was evident when soil NO_3^- pools at different depths in the soil in the NS event and the variability in soil NO_3^- pools between sampling locations at JMF in 2008. This lack of obvious preferential flow at the beginning of leaching could have been due to slightly lower moisture levels at the time of rainfall application, or differences in soil structure between sampling sites (*i.e.* fewer macropores at the NS collection site). Additionally, since the monoliths in the HS event had already been wet up to saturation and produced discharge twice before (in the preliminary experiments and in HL), it is possible that some of the fines were washed out of the soil profile, unblocking or enlarging large soil pores, and causing a higher degree of preferential flow. Macropores generally take longer than one year to develop (McDowell and Sharpley, 2001), so macropores destroyed during the process of hammering in the monolith casings may have been reopened prior to the hydrology experiments due to pre-wetting them, but not in the nutrient leaching experiment, because monoliths were not pre-wetted prior to rainfall application.

The results of the hydrology experiment showed that matrix flow was dominant at the beginning of the leaching period under low intensity rainfall. Some authors (*e.g.* Kung et al., 2000a,) have shown that preferential flow can occur under relatively low rainfall intensities once the soil wets up because the percolating water travels through progressively larger and larger soil pores at higher rates. There was no clear evidence of this type of preferential flow in either nutrient leaching event. Nitrate concentrations in leachate were fairly constant through time in all monoliths under high intensity rainfall and there was no clear dilution of NO_3^- in leachate later on in the leaching period. The NO_3^- concentration in leachate in all of the moist monoliths and two of the dry monoliths in the NL event dropped with time. This may have been due to the contribution of progressively larger soil pores to leaching (preferential flow), which would have resulted in lower NO_3^- concentrations, or because of NO_3^- supply limitation in the soil (Dils and Heathwaite, 1999). Since the wet monoliths in the NL event did not show any evidence of lower NO_3^- concentrations due to macropore flow, it is unlikely that even drier soil would exhibit this behavior, as it would likely take drier soil longer to wet up to the point that preferential flow would activate.

Under low intensity rainfall, the concentration of PO_4^{3-} in leachate followed a very similar pattern to that of NO_3^-, where concentrations were variable in wet soil, declined with time in moist soil and either increased or decreased with time in dry soil. This indicates that under low rainfall rates, the concentration of both NO_{3-} and PO_4^{3-} behaved similarly relative to changes in the discharge rate. Despite this relationship, it is difficult to draw conclusions about the behavior of PO_4^{3-} relative to

NO_3^- because of the low levels of PO_4^{3-} exported relative to NO_3^- and the lack of patterns in the bulk export and FWMC of PO_4^{3-} when groups of monoliths are examined. The temporal changes in the mass of NO_3^- and PO_4^{3-} exported with time were also similar in NL. The similarity in the temporal changes in the mass of nutrients exported was probably related to the significant relationship of discharge with the total mass of both nutrients exported. The clay content of the soil at this study site ranged from 5 to 11%, so the low clay content could have limited the ability of the soil to re-adsorb PO_4^{3-}, causing the changes in the concentration of PO_4^{3-} through time and the mass exported to behave similarly to NO_3^-.

4.3 Influence of Soil Nutrient Pools on Nutrient Export

Soil NO_3^- pools in the NS event were related to the FWMC of NO_3^- in leachate but not the total mass of NO_3^- exported. Soil PO_4^{3-} pools did not have a significant effect on either the FWMC or mass of PO_4^{3-} exported. Other studies (*e.g.* Gaynor and Findlay, 1995; Carpenter et al., 1998; McDowell and Sharpley, 2001) have found that the concentration of NO_3^- and PO_4^{3-} in leachate was positively related to soil pools and that NO_3^- export is increased following periods of drought or closely following fertilizer application (Macrae et al., 2007; Biron et al., 1999) due to a buildup of NO_3^- in the soil. There was an increase in soil NO_3^- pools between the time of monolith collection and rainfall application while monoliths were drying in both nutrient leaching events. This increase in soil NO_3^- pools resulted in soil NO_3^- at the start of rainfall application that was reasonably high compared to soil NO_3^- pools found throughout the summer of 2008 at JMF.

There was more soil NO_3^- available in the NS event than in the NL event, but the average mass of NO_3^- exported and the FWMC of NO_3^- from each monolith was higher in the NL event, indicating that NO_3^- may have been exported more efficiently under low intensity rainfall. Regardless of the recognized influence of nutrient availability on nutrient export from agricultural catchments, many such studies do not determine nutrient availability in their catchment, making it difficult to fully understand the temporal and spatial variability in nutrient export.

Many studies indicate that P exported from soil pools is related to the available P in the soil, but that P is exported only if the soil P pools are considerable and if a critical level of P-saturation in the soil is reached (*e.g.* McDowell and Sharpley, 2001; McDowell and Sharpley, 2001; Gächter et al., 1998; Carpenter et al., 1998). Above this threshold value, P is more easily released from the soil solution and be transported in leachate. The lack of correlation between soil PO_4^{3-} pools and the amount exported in this study could have been due to the low availability of PO_4^{3-} for transport. It would be beneficial to perform similar experiments in soil with different and higher clay contents and in those that are known to have soil PO_4^{3-} pools greater than the adsorption capacity of the soil to make trends in PO_4^{3-} export with different flow types more apparent.

When the change in soil NO_3^- pools with time was examined in the NS event, it was evident that NO_3^- was moved down through the soil profile from the top 10cm of soil to the lower 20cm of soil, with many monoliths having higher soil NO_3^- levels after the end of leaching in the 10-20 and/or 20-30cm depths than the 0-10cm depth after the end of leaching. Soil NO_3^- levels varied with depth in each monolith before rainfall application and after leaching, and the change in soil NO_3^- levels differed between different depths and between different monoliths. This illustrates differences in NO_3^- availability with depth and the differences in the extent to which it was transported in each monolith. The differences in the extent of NO_3^- transport illustrates how the flow paths and rates may vary between individual monoliths, and that they vary greatly in space in natural landscapes, illustrating the spatial variability in the transport of agricultural nutrients and the need for replicates of large monoliths when nutrient leaching is studied in a lab setting.

Changes in soil PO_4^{3-} pools between the start of rainfall application and the end of leaching in the NS event at different depths between monoliths were more variable than the changes in soil NO_3^- pools. Soil PO_4^{3-} levels in the 0-10cm layer of soil went up in some monoliths and down in others, with no obvious pattern to the changes. A drop in PO_4^{3-} levels in the 0-10cm layer usually corresponded with an increase in PO_4^{3-} levels deeper in the soil, but not always. Soil PO_4^{3-} levels were so low in both events that these variable changes may have not been significant.

4.4 Limitations of Lab-Based Studies

4.4.1 Simulation of Natural Conditions

It is very difficult to control nutrient concentrations in soil without adding fertilizer and manure to agricultural soil well before leaching experiments are performed so that it is completely incorporated into soil pores when rainfall is applied. Because of this, it is extremely difficult to simulate the same nutrient levels in the soil in separate experiments and in monolith replicates within one experiment.

There was some within and between group variability in soil nutrient pools (although not all of this is statistically significant) at the start of rainfall application in each experiment, and different nutrient levels in the soil between experiments. In this experiment, simulated soil NO_3^- pools were slightly high in comparison to those found in the field during the 2008 field season, illustrating the difficulty in simulating conditions in the lab that occur frequently in a natural setting. At this field site, there was little soil PO_4^{3-} likely because the fertilizer applied in the spring of the study year (2008) did not include phosphorus, and because the monoliths were not taken from the cropped field, so they may not have had as high of nutrient levels as the cropped area. The general immobility of phosphorus (Gardiner and Miller, 2004) may have resulted in little transport of phosphorus beyond the cropped area.

Soil moisture conditions simulated in the lab experiments were generally drier than those found naturally in the field during the 2008 field season, especially in the nutrient leaching experiment, in which the monoliths were not saturated prior to drying. When lab based leaching studies are to be performed on soil monoliths that cannot be wetted to a given moisture level, the experimenters are at the mercy of the field moisture levels at the time the monoliths are collected. Wetting the monoliths in the lab would have flushed some nutrients down through the soil and potentially out of the monolith if leachate was accidentally produced, potentially leading to inaccurate results in the actual leaching experiment. In the hydrology experiment, the simulated moisture levels of the monoliths were closer to those that occurred naturally during the field season, probably because the monoliths were first saturated, then left to dry in the lab. In the nutrient leaching experiment, the monoliths were collected from the field and dried for the same amount of time in the lab as the monoliths in the hydrology experiment. Conditions were even drier than natural conditions in the nutrient leaching experiment, with moisture levels in the NL event lower than those in the NS event. Even the ‘wet’ monoliths in both events dried out in the lab between the time of collection and the time of rainfall application.

There is no long-term soil moisture data available for the site, but the rainfall during the 2008 field season was typical of the period from 2003-2008. The soil moisture levels simulated in the nutrient leaching experiment were lower than those observed at JMF in 2008. Given that the rainfall during this period was fairly typical, the conditions simulated are likely more similar to those that occur during drier years where less rain falls.

Based on Environment Canada 30-year climate normals, intensity-duration frequency curves and rainfall data from the site, it is plausible that the simulated events would occur at least bi-annually, with the HL event more likely to occur than the HS/NS and NL events. The likelihood of daily or 24-hour rainfall of a similar magnitude as the simulated events is greater than the likelihood of the same depth of rainfall occurring in one separate event. The NL event, which was approximately 22.5 hours long, with a rainfall depth of 56mm, is less likely to occur than the other two event types, with a return period of greater than two years. Also, the rainfall rates simulated in this study were held constant through time, which is not typical of natural rainstorms.

4.4.2 Applicability to Catchment Studies

Some authors question the applicability of lysimeter studies to field conditions (*e.g.* Kung et al., 2000a) and while in situ measurement of solute behavior at a field scale is essential, lab leaching experiments on undisturbed soil monoliths are worthwhile (Mallants et al., 1996). There are several particular limitations of monolith studies related to the heterogeneity of field soils. The spatial variability in macropore distribution affects the representativeness of each monolith, because some may have been collected in an area of many macropores, while others may miss macropores altogether (Kung et al., 2000a). For this reason, large monoliths are better (Richard and Steenhuis, 1988), as are replicates of monoliths for each treatment (Kung et al., 2000a; Flury, 1996). This was illustrated in this study, where there was a great deal of within-group variation in the hydrologic response and nutrient export from the monoliths in the nutrient leaching experiment. Soil in intact monoliths does not resemble field soils exactly (Webster et al., 1993) because other processes occur at larger scales (overland flow, lateral subsurface flow, evapotranspiration, crop growth) in catchments (*e.g.* Belford, 1979; Biron et al., 1999; Langlois and Mehuys, 2003; Macrae et al., 2007; Flury, 1996; Welsch et al., 2001; Stieglitz et al., 2003). Therefore, studies such as this one with intact soil monoliths are most relevant to the understanding of the vertical transport of solutes through the top 30cm of soil to drainage tiles or to shallow groundwater and the results cannot be used to predict total nutrient export from catchments.

Additionally, several studies (Zhang, 2007; Leach, 2009 and DeSimone, 2009) have been undertaken at the study site to understand nutrient dynamics in the adjacent riparian zone. Leach (2009) found that the agricultural field contributed NO_3^- to the riparian zone during large rainfall events, and when high soil moisture corresponded with the Spencer Creek dam release, although NO_3^- inputs to the stream were generally low. It may be important to understand the interaction of upland hydrology and nutrient export in this particular catchment in order to understand nutrient inputs to Spencer Creek during periods of riparian zone flooding due to large rain events.

4.4.3 Limitations of Experimental Design

4.4.3.1 Relative Contribution of Inner and Outer Portions of Monolith to Discharge and Nutrient Export

The proportion of discharge when compared to the proportional area contributing to the inner and outer discharge collection varied among monoliths in the nutrient leaching experiment. Many monoliths (W3, M1, M3, D1-3 in NS and M1, M3 in NL) had proportions of discharge from the outer portion of the monolith that were higher than the proportion of the contributing area that the outer portion of the monolith represents. However, soil pores are not perfectly vertical (Munyankusi et al., 1994) and it is possible that pores that started out in more central parts of the monolith eventually emptied out closer to the edge and vice-versa. Also, many of these monoliths (D1-3 in NS) did not produce much discharge at all (0.73-3.6mm), which makes this high proportion of discharge from the outer portion misleading.

A few monoliths had discharge from the outer portion of the monolith (M3 and D1 from NS and M1 and M3 from NL in particular) that had a lower average NO_3^- concentration than the inner discharge. This indicates that there is a possibility of preferential flow down the monolith casing (Kung et al., 2000a, b; Biron et al., 1999; Kladivko et al., 2009). Monolith D1 from the NS event also had higher PO_4^{3-} concentrations from the outer portion of the monolith than the inner portion, further indicating the possibility of preferential flow down the inside of the monolith casing (Geohring et al., 2001; Gächter et al., 1998; Stamm et al., 1998; Akhtar et al., 2003).

4.4.3.2 Limitations of Type of Rainfall Simulation Used

Even at the lowest flow rate of the peristaltic pump that was used for rainfall simulation, rainfall could not be applied continuously to the monoliths because the rate of rainfall application would have been unrealistically high. As a result, rainfall had to be applied intermittently with different lengths of time between 10 second rainfall applications. Parkin et al. (1995) also used a rainfall simulator in which rainfall had to be applied intermittently in order to achieve the desired rainfall application rates. They indicated that this type of intermittent rainfall application may have produced unrealistic infiltration patterns because of the potential of the brief ponding of water on the soil surface due to the high application rate, followed by the funneling of surface water into topographic lows could have initiated macropore flow even thought he average rainfall rate was lower than the infiltration rate of the soil. It was not determined if these processes were at play in this study, but future studies of flow types in soil may benefit from the use of a more realistic rainfall simulator, the construction and testing of which is very time-consuming and expensive, and was outside of scope of this study.

4.4.3.3 Limitations Associated with the Method of Estimating Soil Nutrient Pools

In both the NS and NL events, there was an apparent increase in both soil NO_3^- and PO_4^{3-} levels in some cases between the start of rainfall application and the end of leaching, which may have been due to the source of soil samples for nutrient analysis at these times. Samples taken adjacent to the monoliths were used to determine nutrient levels at the time of rainfall application, whereas nutrient levels after the end of leaching were taken from the monoliths themselves. Soil nutrient pools are highly spatially variable (Welsch et al., 2001; Macrae et al., 2006), so this ‘increase’ in nutrient levels in the soil could actually be an underestimate of the nutrient levels at the time of rainfall application due to the natural spatial variability in soil nutrient pools.

Chapter 5

Conclusions

The export of nitrogen (N) and phosphorus (P) from agricultural catchments is a major problem worldwide. The export of these nutrients is largely driven by storm events, and the hydrologic response of catchments varies within and between storm events. Antecedent soil moisture and rainfall rate both have an effect on the hydrologic response of and nutrient export from agricultural catchments, but their relationship to nutrient export is not fully understood. Differences in soil moisture and rainfall rates are thought to cause different hydrologic flow paths in the soil (preferential flow and matrix flow), which may have different effects on the transport of soil nitrate (NO_3^-) and phosphate (PO_4^{3-}) pools. A thorough understanding of how hydrologic flow paths affect the export of NO_3^- and PO_4^{3-} is important to understand how the bulk export of nutrients from agricultural fields varies in time and space. The coupled influence of antecedent soil moisture and rainfall rates on the different flow paths in the soil and their effect on nutrient export has received relatively little attention in the literature, necessitating the investigation of the influence of both of these variables in a controlled laboratory setting. To increase our understanding of these processes, two lab studies were performed, firstly to examine the influence of antecedent soil moisture and rainfall rates on the flow paths in the soil, and secondly to examine their influence on the export of NO_3^- and PO_4^{3-} from soil pools.

Findings from this experiment indicated that antecedent soil moisture affects the discharge volume, where higher levels of soil moisture resulted in less of the infiltrating water going into storage in the soil, causing more discharge production. The rainfall rate did not affect the discharge volume but did affect the flow paths that the percolating water took in the soil, with macropore flow occurring at the beginning of the leaching period under high intensity rainfall. Preferential flow occurred to a greater extent in wet soil under high intensity rainfall than in dry soil, illustrating the combined influence of soil moisture and rainfall rates on the hydrologic flow paths in the soil. The rainfall rate ultimately did not affect the timing of discharge production, as the discharge rate was the same relative to the cumulative depth of rainfall application.

It was hypothesized that matrix flow would cause higher concentrations of NO_3^- than PO_4^{3-} in leachate, and that preferential flow would cause higher concentrations of PO_4^{3-} in leachate. However, this was not the case, and there was no clear evidence of preferential flow under either rainfall intensity when temporal changes in nutrient concentrations were examined. Further study is required to identify different flow types and how they affect the leaching of soil NO_3^- and PO_4^{3-} pools.

Antecedent soil moisture had the most significant effect on the mass of NO_3^- and PO_4^{3-} exported by affecting the amount of discharge produced by the soil. Higher levels of soil moisture resulted in more discharge, which resulted in more NO_3^- and PO_4^{3-} exported under both rainfall intensities. Soil moisture also had an effect on the concentration of NO_3^- in leachate, but its effect differed with the rainfall rate. At high rainfall rates, NO_3^- concentrations in leachate were highest from wet soil, whereas NO_3^- concentrations in leachate were highest in dry soil under low rainfall rates. Therefore, the concentration of NO_3^- in leachate was affected by both soil moisture and the rainfall rate. There were no clear patterns in or influences on the concentration of PO_4^{3-} in leachate.

The rainfall rate also had an influence on the mass of each nutrient exported. The average mass of NO_3^- exported and the average concentration of NO_3^- in leachate was higher under low rainfall rates, despite lower levels of NO_3^- in the soil, indicating that NO_3^- may have been exported more efficiently under low rainfall rates. This greater efficiency in nutrient export is likely due to the increased contact time with the soil and the greater area of soil in contact with the percolating water that would occur with under low rainfall rates due to the slower rate of water movement through the soil. The average mass of PO_4^{3-} exported was also higher under low rainfall rates, potentially for this same reason, although the mass of PO_4^{3-} exported in this study was quite low, making conclusions about PO_4^{3-} leaching behavior difficult.

Chapter 6

Recommendations

In this study, there were difficulties in identifying preferential flow in the monoliths of the nutrient leaching experiment. Therefore, future studies would benefit from more emphasis on identifying and quantifying preferential flow in monoliths. If larger monoliths were used, then soil moisture probes could be used in conjunction with a conservative tracer (Cl^- or Br^-) to identify preferential flow based on the progression of the wetting front and arrival time and concentration of the tracer. Isotopes could be used to distinguish between 'new' and 'old' water to identify how much export of existing soil pools occurs during different flow types. Obtaining saturated hydraulic conductivity measurements for each individual soil monolith after leaching experiments would aid in comparison of breakthrough times and leaching rates of conservative tracers under different flow types to those during saturated conditions, which would also aid in identifying preferential flow. It was difficult to draw conclusions on the effect of sorptivity on nutrient export, partially because of the low PO_4^{3-} levels in the soil. It would have been useful to have data on other phosphorus species (total phosphorus, particulate phosphorus) in order to examine how less mobile phosphorus fractions were affected by rainfall rate and soil moisture and to perform similar studies on soil with known high soil PO_4^{3-} levels. Authors (*e.g.* Sharpley et al., 2008 Dils and Heathwaite, 1999) have identified a need for research on the thresholds of operation of different hydrologic pathways and how soil moisture, rainfall rate and other factors, along with the variability in P sources in the soil, interact to transport it vertically through the soil, as P export is often episodic in nature (Macrae et al., 2007).

Since not all the processes that contribute to nutrient export can be easily studied in a lab, a complete understanding of how antecedent soil moisture and rainfall rate affect nutrient export requires studies of nutrient export at the field scale. Drainage tiles can allow an agricultural field to behave like a large lysimeter (Czapar et al., 1994; Richard and Steenhuis, 1988), so similar nutrient leaching experiments could be performed at the field scale. The following would be helpful additions to routine monitoring of drainage tile effluent and streamflow for nutrient concentrations:

a) installation of a large network of peizometers to monitor changes in the water table and lateral subsurface flow; these could be sampled at frequent intervals to assess the contribution of lateral subsurface flow to nutrient export;

b) installation of soil moisture probes at upland, midslope and lowland areas in the catchment to further monitor changes in the water table and the progression of the wetting front and assess soil moisture prior to rain events;

c) sampling of soil before and after events at several depths (right down to the tile line) before and after storm events to determine soil nutrient pools prior to rainfall and how nutrient levels change throughout the soil profile due to rainfall (many studies do not quantify available soil nutrient pools prior to rainfall); and

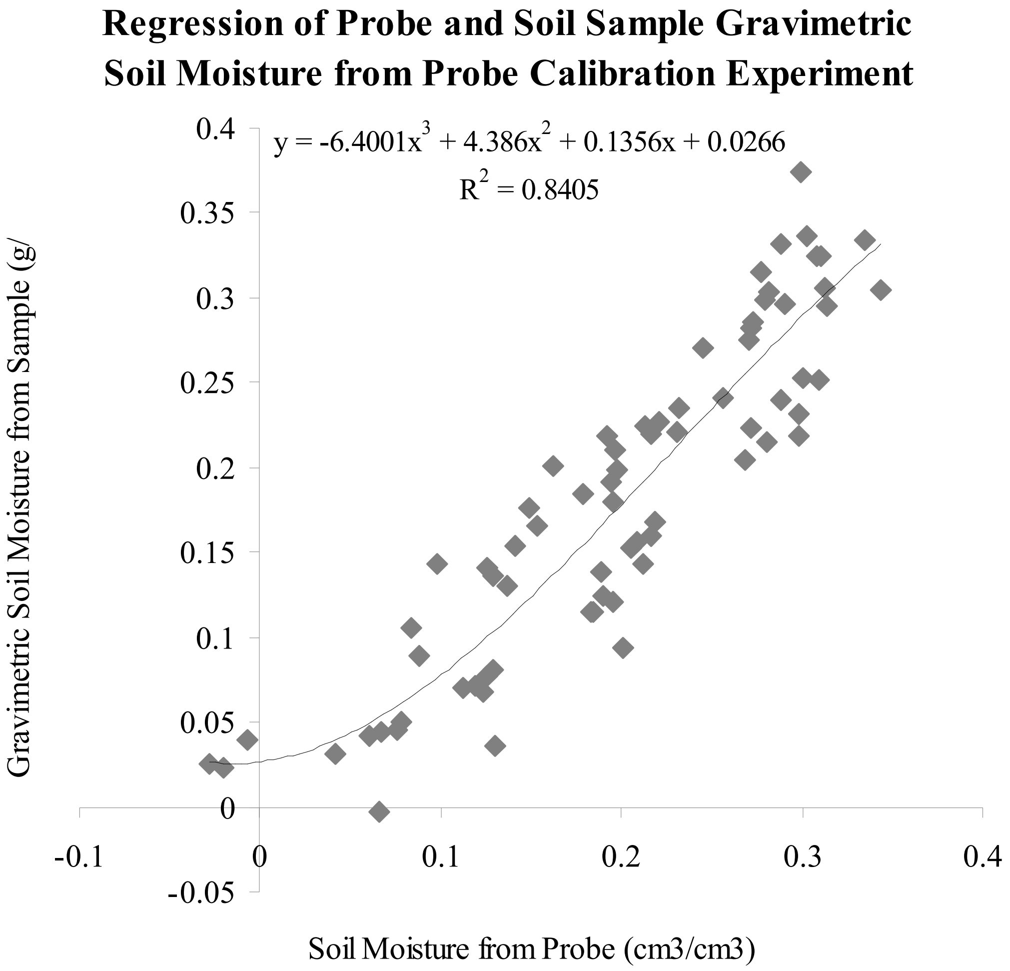
d) the use of isotopes to differentiate between ‘new’ and ‘old’ water in tile effluent and streamflow.

To date, no studies have used all of the above equipment to fully characterize the hydrologic response of catchments and how this influences nutrient export. The end goal of this research is to be able to fully understand the processes that affect nutrient export from agricultural catchments and predict nutrient loading in surface and ground water using available nutrient pools, soil moisture, and soil structure.

Appendix

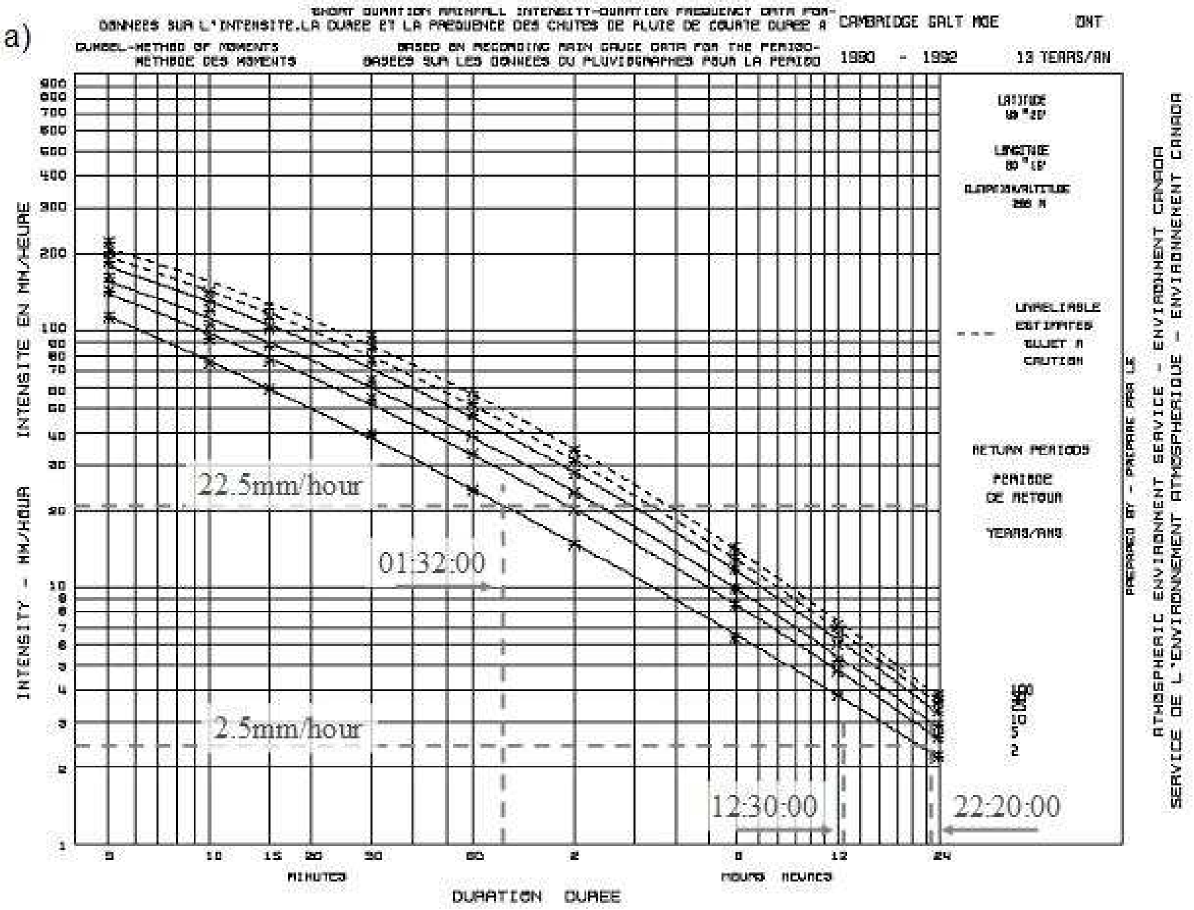
Supplementary Data

Calibration Curve from Calibrating the Soil Moisture Probes Used in the Hydrology Experiment



Intensity-Duration Frequency Rainfall Curves for a) Cambridge Gale MOE and b) Hamilton A.

a)


SHORT DURATION RAINFALL INTENSITY-DURATION FREQUENCY DATA FOR-
DONNEES SUR L'INTENSITE,LA DUREE ET LA FREQUENCE DES CHUTES DE PLUIE DE COURTE DUREE A
CAMBRIDGE GALT MOE
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GUMBEL-METHOD OF MOMENTS
METHODE DES MOMENTS
BASED ON RECORDING RAIN GAUGE DATA FOR THE PERIOD-
BASEES SUR LES DONNEES DU PLUVIOGRAPHES POUR LA PERIOD
1980 - 1992
13 YEARS/AN
LATITUDE 43 °20'
LONGITUDE 80 °19'
ELEVATION/ALTITUDE 268 M
UNRELIABLE ESTIMATES SUJET A CAUTION
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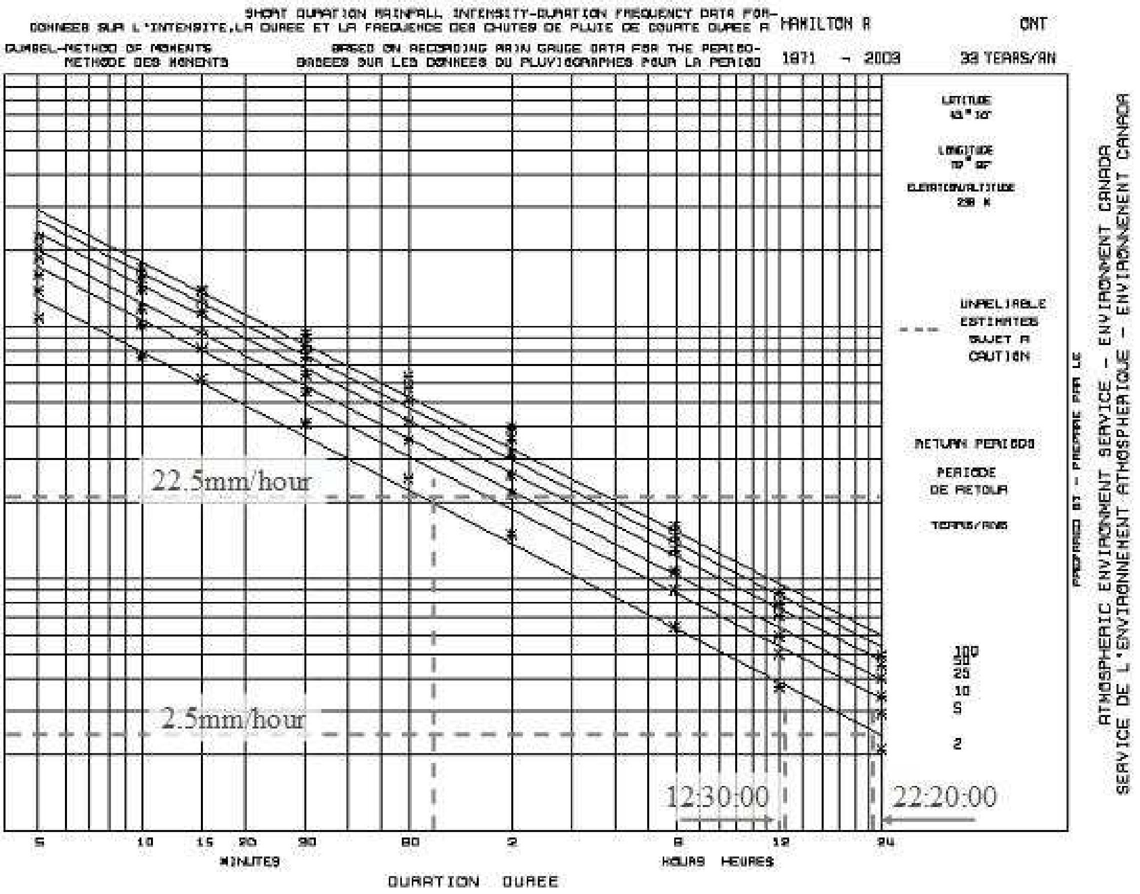
b)


SHORT DURATION RAINFALL INTENSITY-DURATION FREQUENCY DATA FOR-
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GUMBEL-METHOD OF MOMENTS
METHODE DES MOMENTS
BASED ON RECORDING RAIN GAUGE DATA FOR THE PERIOD-
BASEES SUR LES DONNEES DU PLUVIOGRAPHES POUR LA PERIOD
1971 - 2003
33 YEARS/AN
LATITUDE 43° 10'
LONGITUDE 79° 56'
ELEVATION/ALTITUDE 238 M
UNRELIABLE ESTIMATES
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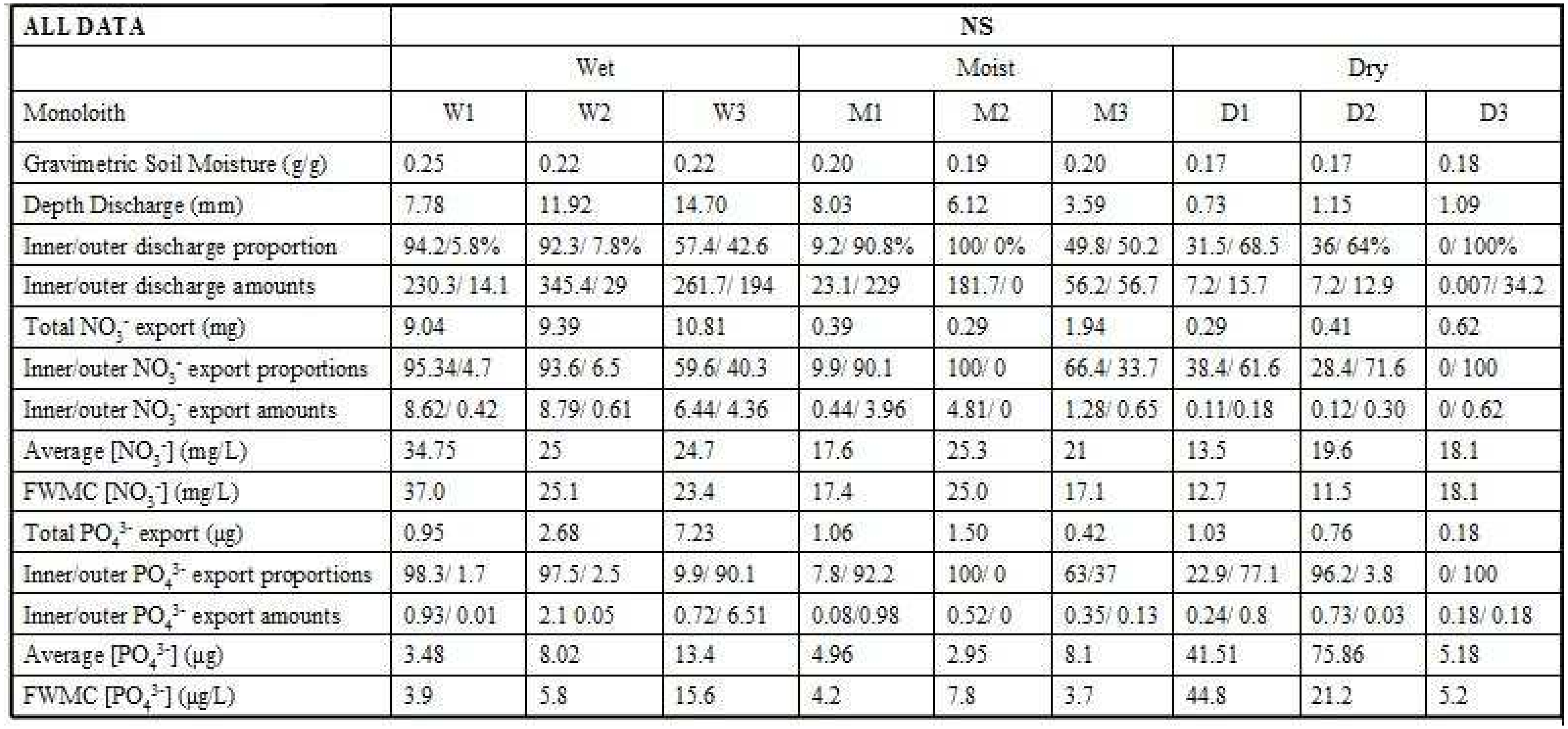
DURATION DUREE

Table with all data from the short nutrient leaching event

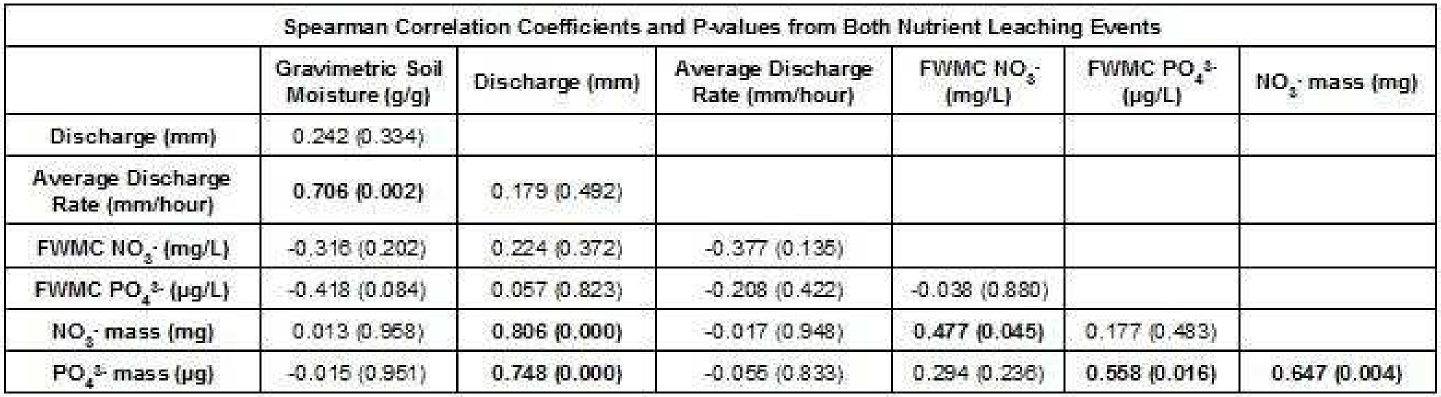


ALL DATA	**NS**								
	Wet			Moist			Dry		
Monoloith	W1	W2	W3	M1	M2	M3	D1	D2	D3
Gravimetric Soil Moisture (g/g)	0.25	0.22	0.22	0.20	0.19	0.20	0.17	0.17	0.18
Depth Discharge (mm)	7.78	11.92	14.70	8.03	6.12	3.59	0.73	1.15	1.09
Inner/outer discharge proportion	94.2/5.8%	92.3/ 7.8%	57.4/ 42.6	9.2/ 90.8%	100/ 0%	49.8/ 50.2	31.5/ 68.5	36/ 64%	0/ 100%
Inner/outer discharge amounts	230.3/ 14.1	345.4/ 29	261.7/ 194	23.1/ 229	181.7/ 0	56.2/ 56.7	7.2/ 15.7	7.2/ 12.9	0.007/ 34.2
Total NO_3^- export (mg)	9.04	9.39	10.81	0.39	0.29	1.94	0.29	0.41	0.62
Inner/outer NO_3^- export proportions	95.34/4.7	93.6/ 6.5	59.6/ 40.3	9.9/ 90.1	100/ 0	66.4/ 33.7	38.4/ 61.6	28.4/ 71.6	0/ 100
Inner/outer NO_3^- export amounts	8.62/ 0.42	8.79/ 0.61	6.44/ 4.36	0.44/ 3.96	4.81/ 0	1.28/ 0.65	0.11/0.18	0.12/ 0.30	0/ 0.62
Average $[NO_3^-]$ (mg/L)	34.75	25	24.7	17.6	25.3	21	13.5	19.6	18.1
FWMC $[NO_3^-]$ (mg/L)	37.0	25.1	23.4	17.4	25.0	17.1	12.7	11.5	18.1
Total PO_4^{3-} export (µg)	0.95	2.68	7.23	1.06	1.50	0.42	1.03	0.76	0.18
Inner/outer PO_4^{3-} export proportions	98.3/ 1.7	97.5/ 2.5	9.9/ 90.1	7.8/ 92.2	100/ 0	63/37	22.9/ 77.1	96.2/ 3.8	0/ 100
Inner/outer PO_4^{3-} export amounts	0.93/ 0.01	2.1 0.05	0.72/ 6.51	0.08/0.98	0.52/ 0	0.35/ 0.13	0.24/ 0.8	0.73/ 0.03	0.18/ 0.18
Average $[PO_4^{3-}]$ (µg)	3.48	8.02	13.4	4.96	2.95	8.1	41.51	75.86	5.18
FWMC $[PO_4^{3-}]$ (µg/L)	3.9	5.8	15.6	4.2	7.8	3.7	44.8	21.2	5.2

Table with all data from the long nutrient leaching event

ALL DATA	**NL**								
	Wet			Moist			Dry		
Monoloith	W1	W2	W3	M1	M2	M3	D1	D2	D3
Gravimetric Soil Moisture (g/g)	0.18	0.18	0.16	0.15	0.15	0.15	0.14	0.12	0.14
Depth Discharge (mm)	23.18	16.25	16.18	3.82	14.89	4.21	5.17	3.11	9.18
Inner/outer discharge proportion	100/ 0%	100/ 0%	90.8/ 9.2%	8.8/ 91.2	98.2/ 1.9%	44.3/ 55.7	89/ 11%	96.4/3.6%	100/ 0%
Inner/outer discharge amounts	728.2/ 0	510.5/ 0	461/ 47	10.6/ 109.6	440.6/ 8.3	58.7/73.8	139.7/ 17.3	94/ 3.5	282.6/ 0
Total NO_3^- export (mg)	18.87	10.86	12.72	3.52	12.60	7.33	6.93	3.54	6.61
Inner/outer NO_3^- export proportions	100/ 0	100/ 0	94.7/ 5.3	21.3/ 78.7	98.6/ 1.4	67.5/ 32.5	88.1/ 11.9	99.6/ 0.4	100/ 0
Inner/outer NO_3^- export amounts	18.87/ 0	10.87/0	12.04/ 0.68	0.75/ 2.77	12.43/ 0.18	4.95/ 0.18	6.11/ 0.82	3.53/ 0.01	6.61/ 0
Average $[NO_3^-]$ (mg/L)	25.7	21.2	25.3	45.4	26.7	61.4	44.4	30.2	22.2
FWMC $[NO_3^-]$ (mg/L)	25.9	21.3	25.0	29.3	26.9	55.3	42.7	36.3	22.9
Total PO_4^{3-} export (μg)	7.07	6.70	6.43	1.27	6.38	148	0.97	0.76	3.57
Inner/outer PO_4^{3-} export proportions	100/ 0	100/ 0	83.5/ 16.5	32/ 68	98.5/ 1.6	99.2/ 0.8	89.8/ 10.2	100/ 0	100/ 0
Inner/outer PO_4^{3-} export amounts	7.07/ 0	6.70/ 0	5.37/ 1.06	0.4/ 0.9	6.3/ 0.1	146.7/ 1.2	0.9/ 0.1	0.8/ 0	3.6/ 0
Average $[PO_4^{3-}]$ (μg)	10.25	13.01	12.25	13.56	14.48	1586.2	6.04	11.48	13.55
FWMC $[PO_4^{3-}]$ (μg/L)	9.7	13.1	12.7	10.6	13.6	1117	6.0	7.8	12.4

All Spearman correlation coefficients from the nutrient leaching experiment (significant and non-significant).



Spearman Correlation Coefficients and P-values from Both Nutrient Leaching Events

	Gravimetric Soil Moisture (g/g)	Discharge (mm)	Average Discharge Rate (mm/hour)	FWMC NO_3^- (mg/L)	FWMC PO_4^{3-} (µg/L)	NO_3^- mass (mg)
Discharge (mm)	0.242 (0.334)					
Average Discharge Rate (mm/hour)	**0.706 (0.002)**	0.179 (0.492)				
FWMC NO_3^- (mg/L)	-0.316 (0.202)	0.224 (0.372)	-0.377 (0.135)			
FWMC PO_4^{3-} (µg/L)	-0.418 (0.084)	0.057 (0.823)	-0.208 (0.422)	-0.038 (0.880)		
NO_3^- mass (mg)	0.013 (0.958)	**0.806 (0.000)**	-0.017 (0.948)	**0.477 (0.045)**	0.177 (0.483)	
PO_4^{3-} mass (µg)	-0.015 (0.951)	**0.748 (0.000)**	-0.055 (0.833)	0.294 (0.236)	**0.558 (0.016)**	**0.647 (0.004)**

Spearman Correlation Coefficients and P-values from NS

	Gravimetric Soil Moisture (g/g)	Discharge (mm)	Average Discharge Rate (mm/hour)	FWMC NO_3^- (mg/L)	FWMC PO_4^{3-} (µg/L)	NO_3^- mass (mg)	PO_4^{3-} mass (µg)	Soil NO_3^- pools (µg per g dry wt)
Discharge (mm)	**0.850 (0.004)**							
Average Discharge Rate (mm)	0.405 (0.320)	0.429 (0.289)						
FWMC NO_3^- (mg/L)	**0.800 (0.010)**	0.617 (0.077)	0.667 (0.071)					
FWMC PO_4^{3-} (µg/L)	-0.567 (0.112)	-0.233 (0.546)	0.381 (0.352)	-0.367 (0.332)				
NO_3^- mass (mg)	**0.728 (0.026)**	0.636 (0.066)	0.619 (0.102)	0.477 (0.194)	-0.310 (0.417)			
PO_4^{3-} mass (µg)	0.433 (0.244)	**0.750 (0.020)**	0.500 (0.207)	0.433 (0.244)	0.350 (0.356)	0.218 (0.574)		
Soil NO_3^- pools (µg per g dry wt)	0.200 (0.606)	0.017 (0.966)	0.571 (0.139)	**0.717 (0.030)**	0.100 (0.798)	0.017 (0.966)	0.200 (0.606)	
Soil PO_4^{3-} pools (µg per g dry wt)	0.117 (0.765)	0.183 (0.637)	-0.190 (0.651)	0.250 (0.516)	-0.033 (0.932)	-0.469 (0.203)	0.450 (0.224)	0.183 (0.637)

Spearman Correlation Coefficients and P-values from NL

	Gravimetric Soil Moisture (g/g)	Discharge (mm)	Average Discharge Rate (mm/hour)	FWMC NO_3^- (mg/L)	FWMC PO_4^{3-} (µg/L)	NO_3^- mass (mg)
Discharge (mm)	**0.787 (0.012)**					
Average Discharge Rate (mm)	0.343 (0.366)	**0.800 (0.010)**				
FWMC NO_3^- (mg/L)	-0.527 (0.145)	**-0.700 (0.036)**	-0.583 (0.099)			
FWMC PO_4^{3-} (µg/L)	0.351 (0.354)	0.233 (0.546)	0.067 (0.865)	-0.183 (0.637)		
NO_3^- mass (mg)	**0.686 (0.041)**	**0.867 (0.002)**	**0.733 (0.025)**	-0.350 (0.356)	0.333 (0.381)	
PO_4^{3-} mass (µg)	0.653 (0.057)	0.617 (0.077)	0.300 (0.433)	-0.217 (0.576)	**0.683 (0.042)**	**0.700 (0.036)**

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