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Fate of Nutrients Under an Irrigated, Manured Field, Southern Alberta

By

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A THESIS

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ABSTRACT

Groundwater in an unconfined, sandy aquifer shows evidence of impact from manure use. Average groundwater concentrations of NO₃-N and TP are 38 mg/L and 0.26 mg/L, respectively. Nitrate concentrations are being naturally attenuated by a combination of heterotrophic and/or autotrophic denitrification and dissimilatory nitrate reduction. Geochemical and $\delta^{34}\text{S}$ data indicate that autotrophic denitrification dominates in the aquifer. Dissimilatory nitrate reduction is an important process at the seepage meters. Significant masses of P are being stored in the soil zone and aquifer. Phosphorus transport is being attenuated by adsorption. Simple Ca- and Fe-phosphate minerals may also be precipitating. Annual discharges of N and P are 62 and 0.80 kg yr⁻¹, respectively. Oscillations in water levels in the Battersea Drain cause seasonal bank storage. Temporal trends in seepage and surface water chemistry are statistically similar suggesting the rate of N and P release is representative of upgradient fields along the Battersea Drain.

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DEDICATION

This thesis is dedicated to my grandparents (Peter and Marie Rawn) and my parents (Bryan and Carol Zilkey) who taught me, from a very early age, the importance of a clean groundwater supply and for many wonderful memories of family times at our cottage in Ponemah, Manitoba.

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CHAPTER 1: INTRODUCTION

1.1 Background

Agricultural practices are major contributors to surface and groundwater quality impairment (Puckett, 1995). However, very little research on the impacts of manure on groundwater can be found in the literature. Common manure constituents include the nitrogen and phosphorus species, sulfate (SO_4), chloride (Cl), microorganisms, and pathogens. This is of particular importance in southern Alberta, where high densities of Intensive Livestock Operations (ILOs) have led to a manure surplus on a regional scale. Many farmers in the region use manure as an economic alternative to commercial fertilizers. Additionally, many of the fields are irrigated, thereby adding to the downward flux of manure nutrients (McLin, 1990).

Several factors affect the nutrient content of manure, including animal type, manure management system, storage methods, amount and type of bedding used, application method, animal diet, composting techniques, and climate (Eghball & Power, 1994). As a result the nutrient content of manure is highly variable (Table 1-1). Estimates of nutrients contained in manure from grain- and concentrates-fed cattle in the United States indicate that each animal excretes approximately 145 g N and 42.7 g P per day (Eghball & Power, 1994).

Manure nutrients can be transported downward to the groundwater or overland to nearby surface water bodies. Downward transport, or leaching, has been considered a particularly important pathway for manure salts (chloride and sulfate) and nitrate. Phosphorus is generally considered to be immobile in the soil profile due to its tendency to adsorb to Al and Fe oxyhydroxide coatings on sediment and calcite surfaces, and/or precipitate as various P minerals (Rajan, 1975; Ryan et al., 1984; Sims et al., 1998). Surface runoff is considered to be the dominant transport pathway for P and can be an

Table 1-1: Selected dry solid nutrient concentrations (as percent dry weight) in beef cattle feedlot manure. Olson et al. (1999) is from southern Alberta.

Nutrient	Zhang et al., 1998	Eghball et al., 1997	Overcash et al., 1983	Olson et al., 1999
N	1.14	1.09	1.9	1.8
P	0.40	0.44	0.65	0.174 (PO ₄)
K	0.82	3.05	2	1.23
Ca	1.33	0.99	1.3	0.21
Mg	0.29	0.43	0.69	0.10
Na	-- ¹	1.27	0.74	0.33
Fe	0.16	--	0.56	1.35
Mn	0.14	--	0.038	0.031
Cl	--	--	1.4	0.06
S	--	--	0.5	0.46
Moisture	--	--	--	47.2
OM	--	--	--	44

¹ not available

important variable when applying manure to a field or determining tillage conditions. Between 1.3 and 5.5% of the manure mass applied to the no till experimental crop plots was removed by surface runoff following simulated rainfall events (Gilley & Eghball, 1998). Although this does not represent a significant portion of the amount applied, it can be significant in the context of water quality and highlights the need to consider nutrient and pathogen transport potential when evaluating manure and compost application practices under various tillage conditions.

The Code of Practice for Responsible Livestock Development and Manure Management in Alberta (Alberta Agriculture Food and Rural Development (AAFRD), 2000; Appendix E) use soil total N concentrations as the basis for nutrient loading. The N:P ratio of fresh manure is generally similar to crop needs. Since gaseous forms of N are lost during storage, application, and in the soil, P is invariably applied in excess of crop requirements, resulting in an accumulation of P in the soil and groundwater environments over time. Any accumulation of nutrients can potentially represent a long-term source available for future groundwater and surface water impacts. It is, therefore,

essential to understand the dynamics and transport processes that may or may not affect this nutrient pool.

1.2 Nitrogen Issues

Inorganic nitrogen (N) can occur in both oxidized and reduced forms in groundwater. The most common dissolved forms of inorganic N include nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) (Fetter, 1993). Organic N is also present in manure; e.g. as amino acids and the urea compounds. Since the NO_3^- species are not strongly sorbed and do not form common minerals, NO_3^- is considered to be mobile in aqueous environments.

Nitrate pollution of groundwater is important from both health and environmental perspectives. Nitrate is known to cause methemoglobinaemia (blue-baby syndrome) in infants (Comly, 1945; Craun et al., 1981; Johnson et al., 1987) and has been linked to reproductive toxicity and various forms of gastric cancers due to the formation of nitrosoamines following consumption of nitrate impacted water (Fan & Steinberg, 1996). The Canadian Drinking Water Guideline maximum allowable concentration (MAC) for nitrate has been set at a maximum of 10 mg-N L^{-1} (Minister of Health (MOH), 1996). Where nitrite is considered separately from nitrate, a maximum concentration of nitrite of 1 mg-N L^{-1} is recommended.

From an environmental perspective, N is a nutrient, and will promote growth of plant species in aquatic environments. Nitrogen was once considered to be the most limiting nutrient in estuaries and oceans (Ryther & Dunstan, 1971), but more recent information indicates that P is more limiting in all aquatic systems, including oceans (Toggweiler, 1999; Tyrell, 1999). The relatively low dependence on N concentrations is related to the availability of atmospheric N for fixation by aquatic organisms.

Nitrogen enrichment of ground- and surface water is a risk due to the high mobility of nitrate. Nitrogen can be transported as dissolved nitrate in surface runoff or subsurface flow, or in solid form during soil erosion.

However, in many instances the process of denitrification (groundwater) and/or biologic uptake (surface water) naturally attenuate the concentration of nitrate in water.

1.2.1 Sources of Nitrate

Nitrate is derived from several natural and anthropogenic sources. Pockets of groundwater containing high nitrate concentrations ($>100 \text{ mg-N L}^{-1}$) occur in glacial tills in southern Alberta, and are of geologic origin (Hendry et al., 1986b; Rodvang et al., 1998). As well, high levels of nitrate contamination (average: 250 mg L^{-1}) in ground waters of Runnels County, Texas were determined to be derived from soil organic nitrate (Kreitler & Jones, 1975). The occurrence of geologic nitrate associated with organic-rich shale has been documented in North Dakota and eastern Montana (Power et al., 1974), Nebraska and South Dakota (Boyce et al., 1976), Colorado (Reeder & Berg, 1977), and California (Strathouse et al., 1980; Holloway & Dahlgreen, 1999). Nitrate contamination also includes point and non-point (NPS) anthropogenic sources including septic systems, commercial fertilizers, manure application, and atmospheric emissions.

Anthropogenic nitrate contamination is particularly prevalent in shallow water table aquifers associated with high densities of agricultural activity on coarse-textured soils; including cropped land (either irrigated or dryland), intensive livestock operations and low woodland to cropland ratios (Egboka, 1984; Richards et al., 1990; Gillham, 1991; Komor & Anderson, 1993; Lampman, 1995; Nolan et al., 1997; Goss et al., 1998; Rudolph et al., 1998). Several state or provincial water quality surveys found that between 3 and 100% of water wells in agricultural regions had groundwater with levels of nitrate in excess of the maximum allowable concentration (MAC) (Hill, 1982; Kross et al., 1993; Mehnert et al., 1995; Richards et al., 1996; Gosselin et al., 1997; Hudak, 1998; Williams et al., 1998). The main causes cited for the

Table 1-2: Common redox reactions in groundwater environments. Organic carbon is the electron donor. Equation (2) represents heterotrophic denitrification (Freeze & Cherry, 1979).

Reaction Type	Reaction
Aerobic Oxidation (1)	$O_2 + CH_2O \rightarrow CO_2 + H_2O$
Denitrification (2)	$CH_2O + 4/5NO_3^- \rightarrow 2/5N_2 + HCO_3^- + 1/5H^+ + 2/5H_2O$
Manganese Reduction (3)	$CH_2O + 2MnO_{2(s)} + 3H^+ \rightarrow 2Mn^{2+} + HCO_3^- + 10H_2O$
Iron Reduction (4)	$CH_2O + 4Fe(OH)_{3(s)} + 4H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 10H_2O$
Sulfate Reduction (5)	$CH_2O + 1/2SO_4^{2-} \rightarrow 1/2HS^- + HCO_3^- + 1/2H^+$
Methane Fermentation (6)	$CH_2O + 1/2H_2O \rightarrow 1/2CH_4 + 1/2HCO_3^- + 1/2H^+$

contamination were commercial and manure fertilizers. In addition, in areas where irrigation is required for crop production, nitrate contamination is a particularly common and widespread problem (Power and Scheppers, 1989; Spalding and Exner, 1993).

1.2.2 Denitrification

Denitrification is a natural, bacterially-mediated process whereby nitrate is transformed to nitrogen gas via reduction by electron donors that can include organic matter, Fe, S, and other reduced species (Trudell et al., 1986; Korom, 1992). There are four general requirements for denitrification:

1. the presence of N oxides (NO_3^- , NO_2^- , NO, N_2O);
2. anaerobic conditions or restricted oxygen availability;
3. the presence of denitrifying bacteria, and;
4. suitable electron donors (Korom, 1992).

Denitrification can proceed by either heterotrophic or autotrophic pathways. Heterotrophic denitrification uses organic carbon as an electron donor and proceeds according to Eq. 2 in Table 1-2 assuming an ample supply of electron donors are present. Once oxygen in the groundwater is depleted (Eq. 1), bacteria will begin to reduce nitrate (Eq. 2). After the nitrate is consumed, manganese (Eq. 3), iron (Eq. 4), and sulfate (Eq. 5) are sequentially

Table 1-3: Autotrophic denitrification reactions in groundwater (Korom, 1992).

Reaction Type	Reaction
Pyrite Oxidation	$5\text{FeS}_2 + 14\text{NO}_3^- + 4\text{H}^+ \rightarrow 7\text{N}_2 + 10\text{SO}_4^{2-} + 5\text{Fe}^{2+} + 2\text{H}_2\text{O}$
Iron Oxidation	$2\text{HNO}_2 + 6\text{Fe}^{2+} + 6\text{H}^+ \rightarrow \text{N}_2 + 6\text{Fe}^{3+} + 4\text{H}_2\text{O}$

reduced, followed by methane fermentation (Eq. 6). If organic carbon is limiting (either in quantity or lability), NO_3^- may be reduced via autotrophic denitrification, which utilizes reduced inorganic species (i.e. sulfur, iron, manganese) as electron donors. Typically, autotrophic denitrification proceeds when nitrate is introduced into an environment where these reduced species are present. In this case, nitrate will be removed by autotrophic denitrification in the absence of organic carbon (Korom, 1992). Typical reactions for autotrophic denitrification are included in Table 1-3.

Although denitrification is not thought to proceed at dissolved oxygen concentrations above 2 mg L^{-1} (Gillham & Cherry, 1978) or Eh values greater than $0.28 \pm 0.2 \text{ V}$ (Spalding & Parrott, 1994), several studies have indicated that the availability of labile electron donors is the key factor in determining the denitrification potential of an aquifer (Smith & Duff, 1988; Gillham, 1991; Hiscock et al., 1991; Seitzinger, 1994; Clay et al., 1986; Pfenning & McMahon, 1996). Plant residues (McCarty & Bremner, 1993), and natural geologic reduced iron and sulfur are important sources of these electron donors. As these tend to be less abundant with depth, denitrification is suggested to be limited in aquifers with water tables at a depth of 2-3 m or greater (Starr and Gillham, 1993).

According to the equations outlined in Table 1-2 and Table 1-3, heterotrophic denitrification is characterized by decreasing concentrations of nitrate, oxygen, and organic carbon coupled with increasing concentrations of bicarbonate. Increasing sulfate and iron concentrations coupled with decreased nitrate and oxygen concentrations suggest autotrophic denitrification may be occurring. In some cases, increased ammonium suggests

the occurrence of dissimilatory denitrification, a process in which nitrogen is conserved within the system (Tiedje et al., 1982; Bulger et al., 1989).

Many aquifers in which denitrification occurs have a distinct redoxcline separating zones of nitrification and zones of denitrification (i.e. Bulger et al., 1989; Pedersen et al., 1991; Postma et al., 1991; Robertson et al., 1996). The most renowned example is the Fuhrberg Feld Aquifer near Hannover, Germany (Kolle et al., 1985; Frind et al., 1990). At this site, autotrophic denitrification by pyrite oxidation is the dominant pathway for nitrate reduction. This has produced groundwater with high sulfate and increasing hardness, contributing to the water quality problems in the region.

Several other factors affect the potential for an aquifer to naturally attenuate nitrate levels by denitrification. Lower groundwater flow rate, higher temperatures, low dissolved oxygen concentrations, and a pH between 7.0 and 8.0 all favor denitrification (Hiscock et al., 1991; Montgomery et al., 1996).

1.2.3 Agricultural Nitrate in Southern Alberta

From 1993 to 1997, seven irrigated sites in three irrigation districts in southern Alberta were investigated to determine the source and fate of nitrate in groundwater, and the potential for this groundwater to adversely affect local surface water (Rodvang et al., 1998). In areas where manure and fertilizer were applied at rates exceeding crop requirement, nitrate was leached to shallow groundwater through both sandy and clay-rich sediments. This resulted in elevated nitrate concentrations (2-3x MAC) in shallow groundwater (<7 m bgs) below fertilized and manured fields. Seventy-one percent of groundwater samples from the unconfined aquifer in the eastern portion of the Lethbridge Northern Irrigation District (LNID) contained nitrate above background levels; 35% of the samples were unacceptable for human consumption.

Geochemical and isotopic evidence indicates that denitrification completely removes nitrate below the redoxcline in aquifers (Postma et al., 1991) and aquitards (Robertson et al., 1996; Rodvang & Simpkins, 2001). Geochemical evidence also indicates denitrification occurs in some oxidized sediments with high nitrate concentrations, but to a much more limited extent (Rodvang et al., 1998; Rodvang & Simpkins, 2001). Increasing nitrate concentrations in shallow groundwater in oxidized sediments at some locations in southern Alberta suggests that denitrification is not entirely effective at nitrate attenuation (Rodvang et al., 1998).

1.3 Phosphorus Issues

Phosphorus (P) is essential for life. From an agricultural standpoint, adequate supplies of P are necessary for seed and root formation, crop quality, strength of straw and accumulation and release of energy during cell metabolism (Haygarth & Jarvis, 1999). Phosphorus in fertilizers and animal manure and/or concentrates are imported to agricultural systems in order to sustain productivity. However, too much P is not necessarily a "good thing". Agricultural crops only take up 5-10% of the applied fertilizer in the first year (Greenwood et al., 1980) obtaining the remainder of the necessary P from the residual soil pool (Sibbsen & Sharpley, 1997). As a result, agricultural soils must have a pool of residual P larger than the crop requirements for any single crop in order to ensure adequate crop nutrition.

Agricultural P is being increasingly linked to eutrophication of surface waters in many countries around the world. Evidence for cultural eutrophication from agriculturally derived P in northern Europe includes:

- agricultural P sources are becoming dominant in determining the eutrophication status of British waters (Moss et al., 1996);
- problems with nutrient accumulation in surface waters in the Netherlands are predominantly due to agricultural sources (Steenhoven & Oostrom, 1979).

- accumulating levels of soil P in six major rivers in northern Ireland have caused an upward trend in reactive P loading to surface water (Foy et al., 1995);
- orthophosphate levels increased 21% between 1965 and 1972 in the River Frome (SW England) (Heathwaite et al., 1996);
- concentrations of orthophosphate in the Slapton Catchment of SW England are estimated to have increased 133% since 1925 (Burt et al., 1996).

In North America, non-point source (NPS) pollution resulting from agricultural practices has been identified by the USEPA as the major source of contamination in streams and lakes (Puckett, 1995; Litke, 1999). More specifically, eutrophication resulting from agriculture has been linked to 60% of the river contamination, 50% of the lake contamination, and 34% of the estuary contamination in the United States (Parry, 1998). Additionally, a direct correlation has been found between stream water quality and levels of agricultural inputs in small stream basins of Alberta (Anderson et al., 1998).

The USEPA has not established freshwater quality criteria for P as yet, but the USEPA marine and estuarine criteria is $0.10 \mu\text{g L}^{-1}$ elemental P (Parry, 1998). The Alberta Surface Water Guideline for P (as total organic and inorganic) is 0.05 mg-P L^{-1} (Alberta Environment (AENV) 1999).

1.3.1 The Phosphorus Cycle

The phosphorus cycle is quite complex. The P cycle is a sedimentary cycle and does not have a significant atmospheric component (Corbridge, 1985; Schlessinger, 1991) with the exception of trace phosphine emissions from volcanoes (Correll, 1998). Instead, most of the global P store is locked up in igneous (as the apatite minerals) and sedimentary (phosphites) rocks. Once released, P can be transported and stored in the hydrosphere and the pedosphere. There is no natural biogeochemical process that will permanently remove P from these sinks.

Phosphate from rocks is released very slowly through natural weathering processes. However, human intervention has caused an increased rate of removal from the rock reservoir by mining and extraction (Schlessinger, 1991). This artificially removed P, used primarily in the production of fertilizer, is rapidly cycled into the hydrosphere and pedosphere.

In aquatic systems, P occurs only in its pentavalent form and may be present as orthophosphate (PO_4^{3-}), pyrophosphate, longer-chain pyrophosphates, organic phosphate esters, and phosphodiester and organic phosphonates (Correll, 1998). It is delivered to surface water as a mixture of dissolved and particulate forms, comprising a complex mixture of the different molecular forms of pentavalent P.

Once delivered to a surface water body, P is retained by a combination of biological assimilation and deposition of sediments and biota on the bottom sediments. This efficient trapping of P makes these systems very sensitive to excessive inputs and can lead to eutrophication of the lake, reservoir, or estuary.

1.3.2 Eutrophication

Surface water bodies can be highly sensitive to P accumulation. If the system is oligotrophic (low primary production) most of the P will be stored in the bottom sediments (Correll, 1998). However, in highly productive or eutrophic systems, the bottom waters often become anoxic during the growing season and P stored in the bottom sediments is released due to decreased sorption and increased mineral solubility, diffusing back into the water column (Mayer et al., 1999).

Eutrophication can become greatly accelerated when P levels in the water are between 0.01-0.02 mg L⁻¹ (Auer et al., 1986; Correll, 1998), and a system is considered P saturated when TP concentrations exceed 0.04 mg L⁻¹ (Auer et al., 1986). This is an order of magnitude smaller than the TP levels

required for crop growth ($0.2-0.3 \text{ mg L}^{-1}$), emphasizing the importance of controlling P losses to limit eutrophication (Daniel et al., 1998).

Nutrient enrichment of surface water by carbon (C), nitrogen (N) or P promotes biological productivity and disrupts the natural balance of water systems. Whole lake experiments have shown that the natural biota can adjust to N and C deficiencies by atmospheric fixation (Schindler, 1977). However, since P must be derived from external (non-atmospheric) or internal sources and biological activity requires a relatively low P to N ratio (1:16; Correll, 1998), P is considered to be the most limiting nutrient in fresh- and saltwater bodies on a global scale (Schindler, 1977; Toggweiler, 1999).

Once nutrient supplies in a surface water body are exhausted, oxygen levels in the water are depleted as a result of death and decomposition of the biota. This ultimately leads to suffocation of the more sensitive and commercially important aquatic organisms (i.e. fish) (Litke, 1999). Additionally, excessive biologic production leads to increased water temperatures, evaporitic water loss, and sedimentation, and impedes water flow and navigation. Highly eutrophic water bodies cannot be used as a drinking water supply as they tend to develop an unacceptable taste and odor in the finished water. Cyanobacterial blooms, common to eutrophic waters, contribute to summer fish kills, taste and odor problems in drinking water and trichloromethane production during water chlorination due to release of hepato- and neuro-toxins upon their death.

The potential for agriculturally derived P to affect surface water bodies in Alberta is great. Many of the surface water bodies in Alberta, are naturally highly productive (mesoeutrophic) and therefore very sensitive to further P enrichment by either internal or external sources (Howard et al., 1999). Compared with the boundary for eutrophy (0.04 mg L^{-1} ; Auer et al., 1986), the Alberta Surface Water Guideline for phosphorus (0.05 mg L^{-1}) is high.

1.3.3 Phosphorus Transport Processes

Agronomists traditionally view P as being immobile in soil (Haygarth & Jarvis, 1999), and much research has focussed on determining the sources and sinks of agricultural P. Over application of manure and inorganic fertilizers can result in an accumulation of P in the soil. This has agronomic implications only when exceptional amounts of accumulation have occurred. The transfer of this stored P to surface water bodies can represent a serious, long-term risk for water quality.

Hydrologic processes are considered the most important factor affecting the P transport regime (Haygarth and Jarvis, 1999; Haygarth et al., 2000), and are spatially and temporally variable. The dominant mechanisms for P transfer are generally considered to be surface erosion and runoff (Gburek & Sharpley, 1998; Sims et al., 1998). As a result, subsurface runoff, or P leaching, has, until recently, rarely been considered an important pathway for the transport of agricultural P to surface waters (Stollenwerk, 1996; Sims et al., 1998).

The amount of P transported in surface runoff is affected by several factors including climate, agricultural practices, and soil types. Generally, export of P in surface runoff is higher in early spring and summer; times coincident with both application and increased overland flow (Liu et al., 1997). In semi-arid to arid regions overland flow may occur only rarely. Surface runoff (overland flow) is limited by the higher infiltration rate in arid regions, whereas higher moisture storage in soils of humid regions permits increased runoff (Howard et al., 1999). However, overland flow can still occur in response to very heavy rainfall events. Export of P from the Peel-Harvey estuarine system in western Australia was found to be positively correlated with application rates of P fertilizer, presence of dairy farming and alluvial clay soils, and negatively correlated with beef farming (Birch, 1982). Additionally, no-till versus till conditions and crop residue type can impact the transfer of P in surface runoff (Eghball & Gilley, 1999).

Phosphorus transport by leaching or subsurface flow has not been considered a dominant transfer process due to its tendency to adsorb to sediment grains and/or precipitate as P minerals. Several studies have considered P leaching from the standpoint of artificial (tile) drainage systems and preferential flow through macropores. More recently, the identification of distinct PO_4^{3-} plumes in septic system effluent has highlighted the need for a better understanding of the factors affecting subsurface P transport.

Engineered agricultural land drainage, including tile drains, permeable fill materials, ditches, and arterial drainage, will influence the pathways of P transfer (Haygarth et al., 2000). Several studies have documented the export of P from agricultural lands via tile drain systems.

- Heckrath et al. (1995) considered transport of P from soils containing different P concentrations and found that on five occasions between 1992 and 1994, the TP and DP concentrations from plots receiving commercial P fertilizer exceeded 1 mg L^{-1} . Above values of 60 mg-P kg^{-1} , the P losses in drainage water were closely related to the P concentrations of the soil as measured by the Olsen method.
- Concentrations in drainage water from nine tile-drained soils exceeded the Quebec water quality standard ($0.03 \text{ mg-TP L}^{-1}$) at 52% and 24% of the sites in 1994 and 1995, respectively (Beauchemin et al., 1998).
- Four tile drains in east-central Illinois contributed 65-69% of the dissolved phosphorus export between 1995 and 1996 (Xue et al., 1998).

Transport of P in artificial drainage systems, like tile drains, is not surprising. Preferential flow paths will naturally develop in the permeable fill and available sorption sites will quickly become filled. Once the groundwater reaches the drain pipe minimal opportunities for further P attenuation exist.

Distinct and extensive PO_4^{3-} plumes have been found in septic system effluent, and in one instance, PO_4^{3-} was found to be as mobile as NO_3^- in a

loamy sand aquifer (Childs et al., 1974). Phosphate plumes have been well documented at several sites in southern Ontario. Plumes vary in length between 20 m (Robertson, 1995) to over 70 m (Harman et al., 1996; Ptacek, 1998; Zanini et al., 1998) and are characterized by steady state concentrations with little attenuation along the flow path. A more extensive plume (800 m) has been identified at a decommissioned septic system in Cape Cod, Massachusetts (Stollenwerk, 1996). Although elevated phosphate levels have not migrated as significant a distance as previously noted for other septic plumes, the plume is discharging to a local pond and is estimated to be a source of P for 10 years after discontinuation of septic system use in 1995. Whelan (1988) noted that the acidic nature of septic effluent may limit the adsorption potential of calcareous sands due to dissolution of carbonate and release of previously sorbed P.

Phosphorus transport is also possible in soils where there are well-developed preferential flow paths, and in soils amended with manure and/or with limited adsorption ability. In a laboratory experiment, larger (≥ 3 mm) macropores, or biopores, tended to adsorb the least amount of PO_4^{3-} (Jensen et al., 1998). This is due to the passage of solutes in the center of the pore at a higher velocity than the lateral diffusion rate, thereby "protecting" the PO_4^{3-} from adsorption. A decrease in a soil's ability to adsorb P can also occur naturally, as is the case at Lake Bysjon, Sweden (Vanek, 1993). Due to natural leaching of calcium from the soils over the past 3000 years, which lowered the sorption capacity of the soil, groundwater phosphorus is being discharged to Lake Bysjon, thus elevating its trophic status.

1.3.4 Phosphorus Attenuation Mechanisms

Phosphorus is not removed from groundwater systems by natural biogeochemical reactions, as is nitrogen (denitrification). However, its transport can be attenuated in two ways:

- 1) phosphate ions can adsorb onto clay minerals (Fox & Malati, 1993) or calcite (Tunnesi et al., 1999), and onto Al and Fe hydroxide coatings on sediment grains (Rajan, 1975; Fetter, 1993);
- 2) where appropriate ions are supersaturated in solution and the thermodynamic constraints are met, secondary P minerals may precipitate out of solution.

1.3.5 Phosphate Adsorption Processes

The movement of phosphorus in groundwater is attenuated by its tendency to adsorb onto charged sediment surfaces. Adsorption is the process whereby charged ions cling to the charged surfaces of solid particles due to their electrostatic attraction (Fetter, 1993). For phosphorus, the phosphate anion is attracted to positively charged surfaces of the surrounding sediments and held there by electrostatic forces. This occurs predominantly where there are Al or Fe oxy-hydroxide coatings on grains (Rajan, 1975; Ryden et al., 1977; Lijklema, 1980), an abundance of clay minerals (Chen et al., 1973; Fox & Malati, 1993), or in highly calcareous sands (Freeman & Rowell, 1981; Ryan et al., 1984; Shaviv & Shachar, 1989; Gonzalez-Pradas et al., 1993; Tunesi et al., 1999).

Phosphate sorption is typically described by "sorption isotherms" that relate the equilibrium solution concentration to the amount of phosphate sorbed. In natural systems, where sorption is rapid compared with the flow velocity, it can be described by an equilibrium sorption isotherm. The two most commonly applied equilibrium isotherms are the Freundlich and Langmuir isotherms.

The Freundlich isotherm is a more general equilibrium isotherm (Fetter, 1993) that is described by the following equation:

$$C^* = KC^N \quad (1)$$

where K and N are constant, C is the equilibrium concentration and C* is the amount of P sorbed expressed as a mass ratio of the P to dry sediment. If the

sorption characteristics of a system can be described by a Freundlich isotherm then a plot of C as a function of C^* yields a curvilinear relationship. The Freundlich isotherm has been widely applied to the sorption of soils for a wide variety of metals and organic compounds, including sulfate, cadmium, copper and zinc, molybdenum, organo-phosphorus and pesticides, *p*-chlorinated residues, parathion, and related compounds (Fetter, 1993). However, the Freundlich isotherm assumes an infinite number of sorption sites are available within the soil system, and is therefore prone to overestimate the amount of sorption possible in a given soil system.

The Langmuir sorption isotherm was developed to account for the finite number of sorption sites available to an ion in solution (Fetter, 1993). When all these sites are filled, sorption can no longer occur. The Langmuir isotherm is described by:

$$\frac{C}{C^*} = \frac{1}{\alpha\beta} + \frac{C}{\beta} \quad (2)$$

Where α is an adsorption constant related to the binding energy ($L\ mg^{-1}$) and β is the maximum amount of solute that can be adsorbed by the solid ($mg\ kg^{-1}$). If experimental data, plotted as C^* as a function of C , has a curved shape which approaches a maximum value, then sorption follows the Langmuir sorption isotherm. If C/C^* is plotted against C , the same data will be linear. The maximum ion sorption, β , is the reciprocal of the slope of the line, and the binding energy, α , is the slope of the line divided by the intercept.

Phosphate sorption has been described and modeled as a two step process: an initial fast step followed by a longer slow step. The fast step is generally recognized to be the formation of electrostatic complexes between the phosphate anion and positively charged sediment surfaces, and will hereafter be referred to as P sorption. There are currently two paradigms to describe the slow step:

- (1) diffusion of phosphate into the sediment grain (Ryden et al., 1977; Ibrahim & Pratt, 1982; Barrow, 1983a; Detenbeck & Brezonik, 1991a), and
- (2) formation of insoluble or sparingly soluble P compounds (Chen et al., 1973; Enfield et al., 1981; Freeman & Rowell, 1981; Shaviv & Shachar, 1989; Tunesi et al., 1999).

The latter is related to P mineral precipitation, and will be discussed in the next section.

Phosphate sorption is controlled by several factors related to the aqueous system. Where there are higher concentrations of phosphate ions in solution, sorption will proceed at a faster rate. This has been found to be true in both laboratory (Ibrahim & Pratt, 1982; Notodarmojo et al., 1991; Gonzalez-Pradas et al., 1993; Fox & Malati, 1993) and field studies (Onar et al., 1996). Increasing concentrations of Fe, Al, organic C, and CaCO₃ (Ryan et al., 1984; Gonzalez-Pradas et al., 1993; Chand et al., 1995; Beauchemin et al., 1996), increasing cation exchange capacity (Chand et al., 1995) and increasing ionic strength (Parveen, 1995) cause increased phosphorus adsorption in soils of all types. Higher pH values (Lijklema, 1980; Detenbeck & Brezonik, 1991b; Fox & Malati, 1993; Beauchemin et al., 1996) and more reducing conditions (Lijklema, 1980) will tend to decrease a soil's ability to attenuate phosphate levels by adsorption. Finally, increased shaking rate in the laboratory has been shown to increase sorption due to the mechanical breakdown of particles by abrasion, thereby increasing the number of sorption sites available (Barrow & Shaw, 1979; Fox & Malati, 1993).

The amount of phosphorus retained by a soil is also dependent on soil type, land use patterns, and fertilizer choice. Sandy soils typically have higher P concentrations in runoff than loamy (silty) soils (Notodarmojo et al., 1991). In a study examining the sorption and desorption kinetics of P in soils under contrasting land uses, agricultural soils were found to have a considerably lower sorption capacity than forested soils (Beauchemin et al., 1996). In

particular, the sorption capacity of the A and C horizons were decreased by 50 and 75% respectively. Soils associated with high animal densities and manure application were more at risk to leach P into drainage waters. At similar application rates, manure-P will more easily leach to shallow water tables in surficial aquifers than will inorganic fertilizer P (Eghball et al., 1996). The higher percentage of larger organic P molecules is thought to inhibit P sorption in the soil.

Although P sorption can attenuate P levels in groundwater the sorption complex does not represent permanent storage. Desorption tends to follow the same reaction kinetics as P sorption; an initially fast step, followed by a longer slow step (Munns & Fox, 1976; Barrow, 1983b). The desorption curve will mirror any subsequent sorption curves, but will never return to the original concentration before sorption occurred. Therefore, desorption cannot be thought of as absolute. One important consequence of desorption is that when the concentration of P drops below a threshold value, that representing an equilibrium between the solution and solid phases, P can begin to desorb and reenter solution (Richardson & Vaithyanathan, 1996), representing a long term source of P contamination.

1.3.6 Phosphorus Mineral Precipitation

The second phosphorus attenuation mechanism in the subsurface is the precipitation of P minerals. Phosphorus mineral precipitation has been noted to occur in septic system plumes, and in calcareous sands and lake sediments. Precipitation appears to control the magnitude of PO_4^{3-} in solution, whereas P migration velocity is governed by adsorption (Robertson, 1995; Zanini et al., 1998).

In general, the precipitation of phosphate minerals is controlled by the activities and presence of suitable ions, the redox conditions (Eh), and pH (Nriagu & Dell, 1974; Moore & Reddy, 1994; Tunesi et al., 1999), whereas the mineral assemblages are associated with source materials. Table 1-4 lists the

Table 1-4: Phosphorus minerals common to aqueous and/or low-grade diagenetic environments.

Mineral Name	Mineral Formula	K_{sp} ¹
Lipscombite	$Fe_3(PO_4)_2(OH)_3$	-- ²
Tinticite	$Fe_3(PO_4)_2(OH)_3 \bullet 3H_2O$	--
Cacoxenite	$Fe_4(PO_4)_3(OH)_3 \bullet 12H_2O$	--
Rockbridgite	$Fe_5(PO_4)_3(OH)_5$	--
Beraunite	$Fe_6(PO_4)_4(OH)_5 \bullet 6H_2O$	--
Laueite/Strunzite	$MnFe_2(OH)_2(PO_4)_2 \bullet 8H_2O$	--
Whitlockite	$Ca_3(PO_4)_2$	1.1×10^{-34}
Monetite	$CaHPO_4$	2.2×10^{-7}
Brushite	$CaHPO_4 \bullet 2H_2O$	--
Mitridatite	$CaFe_2(PO_4)_2(OH)_2 \bullet 8H_2O$	--
Foucherite	$CaFe_4(OH)_8(PO_4)_2 \bullet 7H_2O$	--
Anapaite	$Ca_2Fe(PO_4)_2 \bullet 4H_2O$	--
Heterosite	$FePO_4$	1.1×10^{-26}
Vivianite ¹	$Fe_3(PO_4)_2 \bullet 8H_2O$	10^{-36}
Reddingite	$Mn_3(PO_4)_2 \bullet 3H_2O$	--
Hydroxyapatite	$Ca_5(PO_4)_3OH$	10^{-128}
Strengite	$FePO_4 \bullet 2H_2O$	$10^{-21.6}$
Berlinite	$AlPO_4$	1.7×10^{-19}
Variscite	$AlPO_4 \bullet 2H_2O$	$10^{-22.1}$

¹ K_{sp} from Kraynov et al., 1993

² not available

most common phosphate minerals typically found in lake sediments and/or aquifers. Of these, hydroxyapatite is the thermodynamically least soluble (most stable) mineral in aqueous systems (Emerson, 1976) and vivianite is the most stable mineral under reducing conditions typical of bog sediments (Nriagu & Dell, 1974).

The most often cited phosphate minerals to occur in septic system plumes and/or lake sediments include: hydroxyapatite, vivianite, strengite, and variscite (Freeman & Rowell, 1981; Zanini et al., 1998). In some cases their presence has been verified by analytical techniques, but often is based on calculation of saturation indices by geochemical speciation programs. Where verified, the solid mineral products are typically amorphous and organic in

nature (Freeman & Rowell, 1981), and can occur as discrete authigenic grains and as grain coatings (Zanini et al., 1998).

Septic system plumes may contain a distinct phosphate plume, with steady-state concentrations lower than those in the septic effluent. The steady-state nature of the plume is assumed to indicate that the concentrations are being attenuated by P mineral precipitation. Several site-specific mechanisms have been proposed to explain this. Changes in redox or pH conditions can cause relatively rapid and transient changes in the groundwater chemistry, which can promote precipitation of insoluble Fe-P and Al-P phases in some aquifers (Zanini et al., 1998). In other systems, P minerals are thought to occur only in reducing zones in the plume (Ptacek, 1998) and this process is likely limited by low groundwater concentrations of Fe, Al, Ca, and P concentrations. Strengite, variscite, hydroxyapatite and other amorphous di- and octacalcium phosphates (Freeman & Rowell, 1981; Shaviv & Shachar, 1988) dominate these systems.

Conversely, P precipitation reactions in lake and bog sediments appear to be dominated by vivianite (Emerson, 1976; Postma, 1981) which may be present in its pure mineral form or in solid solution with reddingite. This is likely due to the higher incidence of reducing conditions in lake/bog sediments causing preferential precipitation of Fe²⁺-phosphates.

1.3.7 Phosphorus in Alberta

Alberta lakes, streams and rivers are different from those found elsewhere in North America (Howard et al., 1999). Many of the surface water bodies in Alberta are naturally productive (eutrophic). Further nutrient enrichment of surface waters in Alberta could lead to significant economic and environmental implications for public and animal health, the recreation and tourism industries, and could adversely affect aquatic life. Nonetheless, published research on these issues in Alberta is sparse.

Two lakes in northern and central Alberta were studied with respect to their trophic status and P characteristics. Amisk Lake, in northern AB, is thought to be naturally eutrophic (Manning et al., 1994). Low concentrations of ferric oxyhydroxides permit internally regenerated P to pass into the water column where it is readily available for algal growth. Narrow Lake, a mesotrophic lake in northern Alberta, receives P loads up to $58 \text{ mg m}^{-2} \text{ yr}^{-1}$ from groundwater discharge which exceed other internal and external P sources (Shaw et al., 1990). No source for the P was identified; however recycling of P in lake sediments as a source of P to the lake was mentioned as a source.

1.3.8 Analysis of Phosphorus in Soils

Current analytical techniques target five fractions of P: 1) total P (TP), 2) dissolved P (DP), 3) particulate P (PP), 4) biologically available P (BAP), and 5) plant available P (PAP) (Howard et al., 1999). Of these fractions, TP, DP, PP, and BAP are important in water analysis, while TP and PAP are important for soil analysis. When considering agricultural P contribution to water quality, BAP, DP, and PP are the key factors to consider. Current Alberta surface water guidelines are based on the concentration of TP in solution.

Total phosphorus (TP) includes all inorganic and organic forms of P in the soil (Howard et al., 1999). During analysis all forms of P present in the sample are converted to orthophosphate (PO_4^{3-}) using strong reagents and high temperatures to digest and dissolve all the soil P. The filtered leachate or water sample is then analyzed, either colorimetrically or by inductively coupled plasma mass spectrometry (ICP-MS), for PO_4 concentrations. Common methods include the perchloric acid digestion method (Olson & Sommers, 1982), and the sulfuric acid/hydrogen peroxide/hydrofluoric acid digestion method (Bowman, 1988).

Dissolved phosphorus (DP) is the fraction of P that is not retained by a $0.45 \text{ }\mu\text{m}$ membrane filter, and includes both inorganic and organic fractions.

Most of the organic DP is inert, whereas the inorganic DP is readily available for biologic use. Therefore the concentration of DP is not a direct measure of the bioavailability of P in aquatic systems.

Particulate P is the P fraction that is adsorbed onto particulate materials, which may include organic debris, soil particles containing Fe- or Al-hydroxides, or Fe-P, Al-P, or Ca-P minerals (Howard et al., 1999). In water analysis, PP concentrations are not measured directly; rather they are calculated as the difference between TP and DP concentrations. Particulate P is not immediately available for biologic uptake, however it can provide a long term, but variably available, source of P in lakes.

Biologically available P (BAP) is defined as "the amount of inorganic P that a P-deficient algal population can utilize over a period of 24 hours or longer" (Sonzogni et al., 1982), and includes DP and the bioavailable portion of PP (Sharpley & Smith, 1993). BAP is critical in assessing the risk of P loading and subsequent eutrophication of surface waters. Dissolved inorganic phosphate (PO_4^{3-}) is the form most readily available to aquatic plants for biologic production, but other forms of P (i.e. DP and PP) can be converted to PO_4^{3-} through natural biological processes or hydrolysis.

Most soil P analytical methods are used to identify P levels available for crop use. These methods use weaker extractants than are used for TP analysis, as the test is targeted at potentially-available P, which represents only a portion of the total P in the soil sample (Howard et al., 1999). There are numerous extraction methods, each with their own advantages and limitations depending on the soil pH, mineralogy, and organic matter content.

1.4 Objectives

The objectives of this thesis are threefold. First, to evaluate the ground-, seepage, and surface water quality at an irrigated, and manured field site in southern Alberta. Second, to assess the potential for natural nitrogen and phosphorus attenuation in the surficial aquifer by denitrification,

phosphate sorption and/or phosphorus mineral precipitation. Finally, to quantify the fluxes of nitrogen and phosphorus in direct runoff and groundwater flow from an agricultural field to an adjacent surface water body.

CHAPTER 2: GEOLOGIC SETTING

2.1 Bedrock Geology of Southern Alberta

Bedrock underlying the study area in southern Alberta comprises the soft, fresh, and brackish water sandstones, siltstones, and shales of the Upper Cretaceous Judith River and the overlying Bearpaw Formations (Rodvang et al., 1998). The Judith River Formation includes the Oldman and Foremost members, and is a series of fresh and brackish water deposits of finely interbedded and interfingering layers of bentonitic sandstone, carbonaceous shale, siltstone, mudstone, and lignite layers (Hendry et al., 1986a; Dawson et al., 1994; Rodvang et al., 1998). Layers and lenses of fine-grained sandstone, shale, and sandy shale are present throughout but are of limited lateral extent. The Oldman member overlies the Foremost member and is lighter in color, contains rare coal and massive sandstones. Conversely, coal is common and sandstone rare in the Foremost member.

The Bearpaw formation conformably overlies the Judith River Formation and largely comprises green and brown, soft, fissile, marine shales (Dawson et al., 1994). The shales commonly contain calcite concretions, bentonite seams and gypsum. Pyrite and cation exchange clays are important components of the unweathered bedrock, whereas carbonate minerals are not abundant. The high sodium and chloride contents are indicative of its deposition on the margin of an epeiric sea.

2.2 Quaternary Geology

Bedrock in southern Alberta is overlain by a series of glacial and post-glacial deposits (Lennox, 1993). The major Quaternary deposit is glacial till. Late Wisconsinian till was derived from Cretaceous bedrock and as such contains cation-exchange clays, calcite, and dolomite. Compositionally, the till contains 2-25% carbonate minerals, and 0.25 to 0.7% sulfur, predominantly

occurring as pyrite with minor sulfate from gypsum dissolution (Rodvang et al., 1998).

Two geochemically distinct zones have been defined in the till; an upper weathered zone and a lower unweathered zone (Hendry et al., 1986a; Hendry et al., 1986b). The weathered till is typically fractured, brown, and ranges between 4.6 and 18 m in thickness. The unweathered zone is discontinuous, gray, and unfractured. The contact between the two zones is generally abrupt, however in some areas a brown-gray mottled transition zone, up to 7 m in thickness, is present.

Till is overlain by a veneer to blanket of eolian, lacustrine, and/or fluvial sediment related to deglaciation and post-glacial processes (Rodvang et al., 1998). Surficial deposits in the study area are largely lacustrine sands, silt, and clayey sands ranging from 1 to 7 m in thickness. Compositionally, unweathered lacustrine sediments are similar to the underlying till.

2.3 Groundwater Quality in Bedrock and Till Aquifers

Groundwater in weathered till and bedrock is generally of poor quality (Table 2-1). Groundwater in till is slightly alkaline, with total dissolved solids (TDS) ranging from 10^3 to 10^4 mg L⁻¹, and high concentrations of Na, Ca, Mg, HCO₃, and SO₄ (Lennox, 1993). Groundwater in weathered till is dominated by Na and SO₄. High sulfate concentrations were derived from oxidation of reduced sulfur (mainly pyrite) incorporated into the till by bedrock erosion during glaciation (Van Stempvoort et al., 1994). Pyrite oxidation caused carbonate dissolution and the displacement of Na from exchange sites.

Groundwater in bedrock is dominated by Na and Cl, due to its deposition under brackish or marine conditions. Groundwater chemistry in bedrock is also influenced by pyrite oxidation, cation exchange, carbonate and gypsum dissolution, and mineral weathering.

Table 2-1: Geochemistry of groundwater from bedrock, and weathered and non-weathered till aquifers of southern Alberta. Concentrations are expressed in mg L⁻¹ (after Hendry et al., 1986a).

	Bedrock			Weathered Till			Nonweathered Till		
	Mean	S.D.	n	Mean	S.D.	n	Mean	S.D.	n
Na	1150	330	6	1915	1030	34	1138	460	4
Ca	64	80	6	405	108	34	750	960	4
Mg	24	29	6	323	180	34	88	61	4
SO ₄	1776	605	5	5290	2112	34	2352	1008	4
HCO ₃	885	116	6	732	256	34	1025	146	4
Cl	202	138	6	117	121	34	188	43	4
pH	8.0	0.1	5	7.1	0.4	30	7.3	0.6	3
Eh (mV)	100	100	13	150	100	36	-20	100	3

CHAPTER 3: MATERIALS AND METHODS

3.1 Site Selection

In order to meet the objectives of this thesis, several key requirements for a field site had to be satisfied. First, the site had to be located in the Battersea Drainage Basin of the Lethbridge Northern Irrigation District (LNID) of southern Alberta: an area with a dense population of intensive livestock operations (ILOs). Second, it had to be an irrigated field with a history of manure application. Third, it had to be located adjacent to a surface water body, and have a relatively simple groundwater flow system that discharged to the surface water. Finally, there could be no evidence for the dominance of discharge conditions, to eliminate the possibility that upward groundwater flow would obscure agricultural impacts.

3.2 Site Instrumentation

Drilling and instrumentation of the Battersea Field Site was completed in early June, 1999. Several test holes were drilled in the early spring at this site to investigate the groundwater flow direction, aquifer characteristics and therefore, suitability of the site. Drilling was conducted using a 10 cm (four inch) solid stem auger and soil samples were collected at 0.5-1.0 m intervals either off the auger or from soil cores. Drill logs detailing the geology of the site and installations were completed during drilling and are included in Appendix 1.

Instrumentation at the Battersea Field site includes nine multi-level samplers (MLS), and their associated water table wells (WTW), eight seepage meters (SM) and two mini-piezometers (MP) installed in the Battersea Drain. Multi-levels and WTW were installed approximately parallel with the groundwater flow path in the manured field, with a couple of installations in the improved pasture. It was not possible to install MLS or WTW near the Battersea Drain due to the presence of a subsurface utility corridor. All MLS

and WTW were built at the Alberta Agriculture Food and Rural Development lab in Lethbridge, Alberta. Press fit couplers were installed at a depth of 75 cm to allow MLS and WTW to be buried during seeding and harvest. Precipitation and irrigation were measured by a tipping bucket rain gauge installed at the site.

3.2.1 Multi-Level Samplers and Water Table Wells

The multi-level samplers comprise a center stalk with externally attached, individual sampling points placed at 50 cm intervals (Pickens et al., 1978; Figure 3-1). Center stalks are constructed from 1.27 cm ($\frac{1}{2}$ inch) PVC pipe and are screened over a 17 cm interval at their base with 20 slot PVC pipe. Individual sampling points are constructed from 0.32 cm ($\frac{1}{8}$ inch) spaghetti tubes that are screened at their base with Nytex® fabric secured with stainless steel wire. The spaghetti tubes are fastened to the center stalk with cable ties to prevent movement. The upper portion (situated above the ground surface) of the MLS is protected by 15 cm (six-inch) PVC casing. Water table wells are built from 5.08 cm (two inch) PVC pipe with 10 slot PVC screens (Figure 3-2). Silica sand was packed along the MLS and WTW in the aquifer zone. The upper portion of the drill hole was sealed with bentonite to prevent short-circuiting along the well casing.

3.2.2 Seepage Meters and Mini-Piezometers

Seepage meters were constructed from 45-gallon plastic drums cut off to 15 cm and inverted into the stream bed of the Battersea Drain to trap groundwater discharging to the surface water (Lee & Cherry, 1978). A hole was cut into the top of the seepage meter and plugged with a rubber cork with tygon tubing passed through. Samples were collected in 10 L plastic bags secured to the tygon tube with rubber bands. Seepage meters were installed such that the top of the meter was flush with the sediment surface at the base of the Battersea Drain. They were located, in pairs, at approximately 5 m intervals in the Drain.

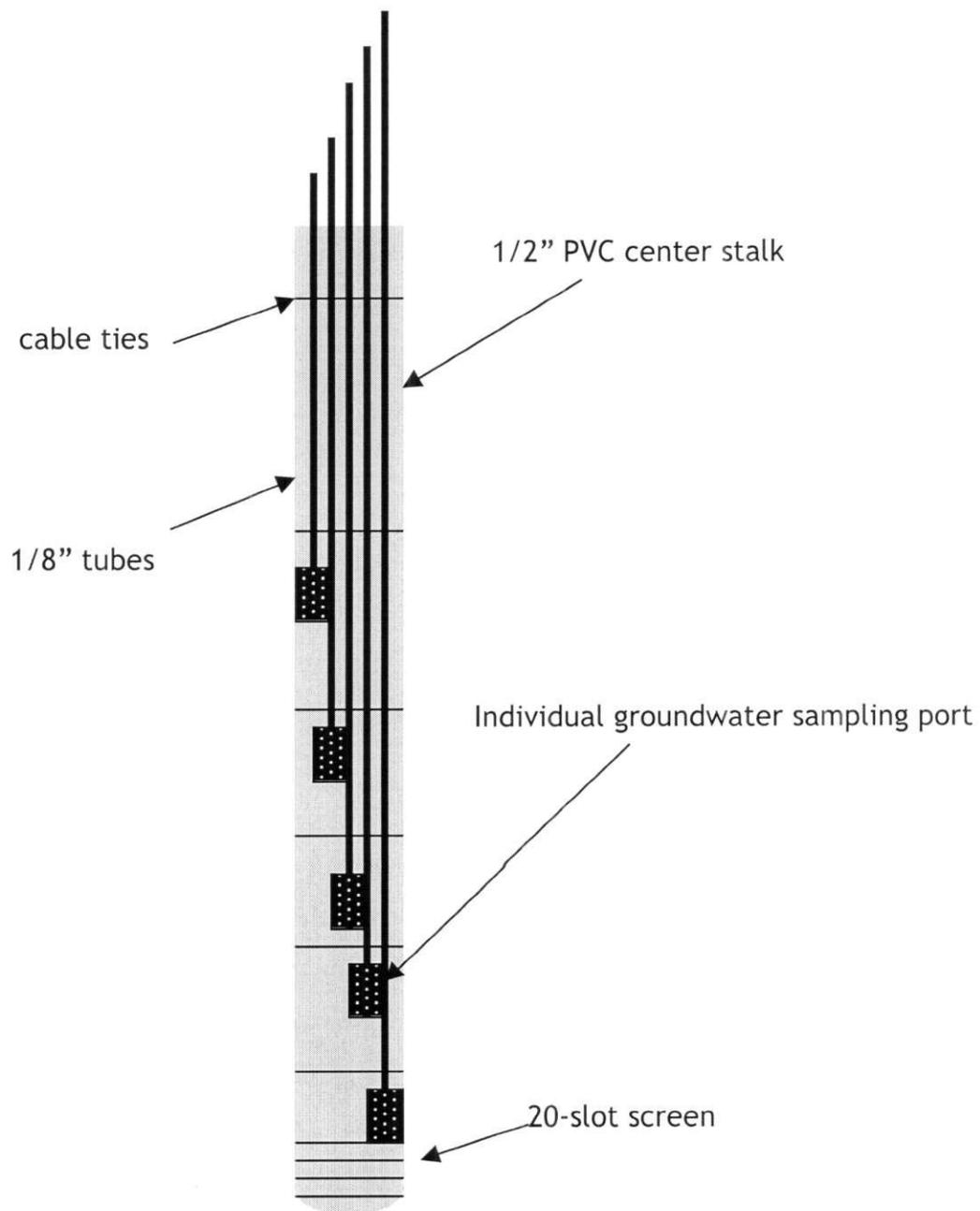


Figure 3-1: Schematic diagram of the multi-level sampler designed for use at the Battersea Field Site.

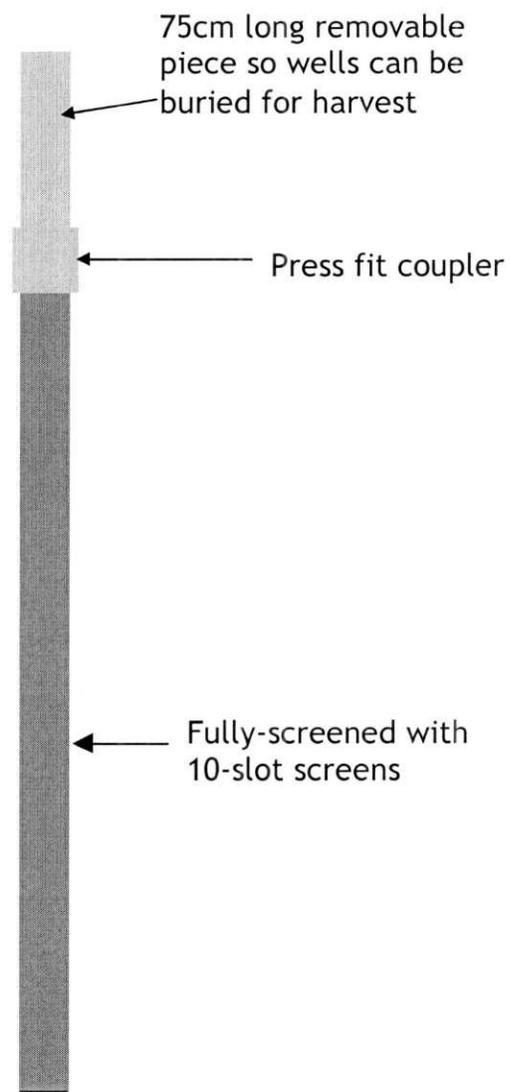


Figure 3-2: Schematic diagram showing water table well designed for use at the Battersea Field site.

Steel mini-piezometers were installed in the Battersea Drain in November to measure the hydraulic gradient at the base of the drain. Seepage meters and mini-piezometers were supplied by or constructed at the University of Calgary.

3.3 Aquifer Characterization

Hydraulic conductivity was determined by slug tests using downhole pressure transducers to record changes in water table elevation. Falling head and rising head tests were performed in the water table wells, thereby providing a bulk hydraulic conductivity for the formation. Each test took approximately 45 minutes to complete. Data analysis was done using the Hvorslev method (Hvorslev, 1951; Appendix 2).

Grain size distribution in the aquifer was determined by sieving dried, pre-weighed sediment samples through mesh screens, ranging in size from 2 mm to 0.03 mm. The separated fractions were weighed after sieving to determine the proportions of each sediment size fraction (Appendix 3).

3.4 Soil Sampling Protocol

A hand auger was used to collect soil samples from 28 evenly spaced locations at the Battersea field site, three of which were located in the improved pasture area (Appendix 4). Samples were collected from the following depth intervals: 0-15 cm, 15-30 cm, 30-60 cm, and 60-90 cm in the spring and fall of 1999 and 2000.

3.5 Water Sampling Protocol

A year-long monitoring program was conducted from June, 1999, through July, 2000. Water samples and field measurements were collected monthly from June through September and twice (October and March) in the winter (Table 3-1). Water samples for nutrient, anion, and major cation analyses were collected in acid-washed (10% HCl solution) 250 mL or 500 mL

Table 3-1: Sampling dates and event labels for the year-long monitoring program at the Battersea Field Site.

Sampling Date	Sampling Event	Comments
99-05-31	A	Sample analyses not included in this report.
99-06-07	B	Start of monitoring program.
99-07-02	C	
99-08-16	D	
99-10-20	E	Isotope samples collected in conjunction with nutrient samples.
00-03-23	F	
00-06-06	G	
00-07-11	I	Isotope and trace metal samples collected in conjunction with nutrient samples. End of monitoring program.

nalgene sample bottles. The total volume of each sample was 750 mL. Microbiological samples were collected in autoclaved 500 mL nalgene bottles. Duplicate samples and blanks were collected at each sampling event. While in the field, all samples were stored in coolers with icepacks.

Ground-, surface, and seepage water samples were filtered to 0.45 μm and preserved according to the protocol outlined in Table 3-2. With the exception of sampling event I, this was done at the AAFRD lab in Lethbridge, Alberta. Samples were vacuum filtered through 0.45 μm nitrocellulose filters and acidified with 10% H_2SO_4 to prevent microbiological activity. Because sampling event I was done in conjunction with isotope and trace metal sampling for a related, but separate study, in-line 0.45 μm filters were used in the field. Trace metal samples were acidified in the field with 5 mL of 90% HNO_3 .

3.5.1 Nutrient, Anion, and Major Cation Sampling Protocol

A total volume of 750 mL of ground-, seepage, and surface water were collected at each sampling event. Groundwater was sampled from each producing point using a GeoPump 2 peristaltic pump and tygon tubing. A

Table 3-2: Sample filtration and preservation protocol.

Analysis	Filtered (Y/N)	Acidified (Y/N)	Storage
Nutrients (NO ₃ , NO ₂ , NH ₄ , PO ₄ , DP, DOC)	Y	Y	Fridge at 4°C or freezer
Nutrients (TP)	N	Y	Fridge at 4°C or freezer
Anions (SO ₄ , Cl)	Y	Y	Fridge at 4°C or freezer
Anions (HCO ₃ , CO ₃)	Y	N	Fridge at 4°C or freezer
Major Cations (Ca, Na, K, Mg, Fe)	Y	Y	Fridge at 4°C or freezer
Microbiological (TC and FC)	N	N	Fridge at 4°C, <24 hrs

minimum of three casing volumes of water was purged and sample bottles were rinsed at least three times with groundwater prior to sample collection.

Surface water was collected from two locations: one upstream and one downstream of the site. Surface water samples were collected directly from the surface water body, approximately mid-way through the water column and, wherever possible, away from any external contaminant source. Sample bottles were rinsed a minimum of three times with surface water prior to sample collection.

Seepage meter samples were collected in 10 L bags attached to the seepage meters with rubber bands. Prior to attaching the sample bags to the seepage meters, one liter of deionized water was added to the sample bag to minimize seepage error (Isiorho & Meyer, 1999). This volume was reduced to 500 mL due to high seepage rates causing overflowing of the sample bags.

Sample bags were left on the seepage meters until a sufficient volume had been collected. The times varied depending on the hydraulic gradient and ranged from hours to days. The volume of water was measured in the field and 750 mL of sample collected. Any remaining water was discarded. At all times when attaching and removing the sample bags, the inlet hole was blocked to prevent contamination of the sample with surface water.

3.5.2 Microbiological Sampling

Ground-, surface, and seepage meter samples were collected for total and fecal coliform analysis. The samples were stored in a cooler with ice packs in the field, and stored at 4°C upon return to the lab. Groundwater samples were collected using tygon tubing attached to a GeoPump 2 peristaltic pump. All tubing was cleaned with 70% ethanol solution between samples to prevent cross-contamination. Seepage meter samples were collected following measurement of the seepage volume. The graduated cylinders were also rinsed with 70% ethanol between samples to prevent cross-contamination. Surface water samples were collected directly from the surface water body, approximately mid-way through the water column.

3.5.3 Field Measurements

Groundwater pH, Eh, DO, temperature, and EC were recorded for each sampling point at each sampling event. Field pH was measured using an Orion 250A portable pH meter and an Orion 9107 pH probe, calibrated using commercial solutions at pH 4.0, 7.0, and 10.0. EC was measured using a VWR Scientific 2052 EC meter and calibrated with KCl solution with an EC of 718 uSm/cm (at 25°C). Dissolved oxygen (DO) and temperature were measured using an YSI 55 downhole DO probe calibrated to 100% humidity. Electrical potential (Eh) of the waters was measured using an ORP Cole Palmer platinum Eh probe calibrated with Zobell's solution prepared according to the procedure outlined by Nordstrom (1977). All measurements were converted to the standard hydrogen electrode readings using the following formula: $E_h = E + E_R$, where E_h is the observed potential between the platinum band and a normal hydrogen electrode, E is the measured potential and E_R is the standard potential of the reference electrode. All field measurements were taken using a flow through cell constructed from a small rubbermaid container with holes cut into the top to permit insertion of the probes. The holes were specifically sized to the probes to minimize oxygen contamination. In addition, readings

were only taken once the flow-through cell began to overflow and the readings stabilized. Since deionized water was added to the seepage meter sample bags, field measurements were not recorded for seepage water.

3.6 Geochemical Analyses - Soil Samples

Soil samples were analyzed for K, Cl, PO₄-P, NO₃+NO₂, and NH₄ (Appendix 4). Both potassium and chloride were extracted in a 2:1 (mL:gm) H₂O extraction. Ten grams of soil was added to 100 mL of deionized water and shaken for one hour, then filtered. The filtrate was analyzed according to the procedures used for water analysis (Table 3-3).

Phosphate concentrations in soil were determined using the modified Kelowna method (SCDC Method S031). This method uses ammonium acetate, ammonium fluoride, and acetic acid to extract the phosphate bound to the sediment. The soil, extractant mixture was shaken for 30 minutes, and filtered. The filtrate was analyzed for phosphate concentration.

Nitrate + nitrite and ammonium concentrations were determined using the 10:1 KCl method. Ten grams of soil were mixed with 100 mL of 2N KCl and shaken for one hour, then filtered. The filtrate was analyzed for NO₃+NO₂ and NH₄.

3.7 Geochemical Analyses - Water Samples

Ground, seepage, and surface water samples were analyzed for nutrients (NO₃⁻, NO₂⁻, NH₄⁺, TKN, PO₄³⁻, TP, DP), anions (SO₄²⁻, Cl⁻, CO₃²⁻, HCO₃⁻), and major cations (Ca, Na, K, Mg, Fe) according to the methods listed in Table 3-3. With the exception of DOC and major cation analyses from sampling event D, all analyses were conducted at the AAFRD research lab in Lethbridge, Alberta. Water samples collected in conjunction with samples for isotopic analysis during Sampling event I were also analyzed for trace metals (Mn, As, Fe²⁺) at the University of Alberta Hospital laboratory.

Table 3-3: Suite of geochemical analyses and methods used for analysis of ground-, seepage, and surface water at the Battersea Field Site.

Species	Location	Method
Nitrate (NO ₃ -N)	AAFRD	TRAACS 800 Autoanalyzer; IM 782-86T
Nitrite (NO ₂ -N)	AAFRD	TRAACS 800 Autoanalyzer; IM 784-86T
Ammonium (NH ₄ -N)	AAFRD	TRAACS 800 Autoanalyzer; IM 780-86T
Total Kjeldahl Nitrogen (TKN)	AAFRD	TRAACS 800 Autoanalyzer; Standard Kjeldahl method
Orthophosphate (PO ₄ -P)	AAFRD	TRAACS 800 Autoanalyzer; IM 781-86T
Dissolved Phosphorus (DP)	AAFRD	TRAACS 800 Autoanalyzer; IM 787-86T
Total Phosphorus (TP)	AAFRD	TRAACS 800 Autoanalyzer; IM 787-86T
Dissolved Organic Carbon (DOC)	U of C	Technicon AutoAnalyzer II; IM 451-76W
Sulfate (SO ₄ ²⁻)	AAFRD	Milton Roy Spectronic 1001 Plus; Turbidimetric method
Chloride (Cl ⁻)	AAFRD	TRAACS 800 Autoanalyzer; IM 783-86T
Carbonate (CO ₃ ²⁻)	AAFRD	Man-Tech PC-Titrate; Acid titration
Bicarbonate (HCO ₃ ⁻)	AAFRD	Man-Tech PC-Titrate; Acid titration
Calcium (Ca)	AAFRD	Atomic Adsorption: Unicam 989
	U of C	Atomic Adsorption: PE Aanalyst 100
Magnesium (Mg)	AAFRD	Atomic Adsorption: Unicam 989
	U of C	Atomic Adsorption : PE Aanalyst 100
Sodium (Na)	AAFRD	Flame Photometer: IL 943
	U of C	Atomic Adsorption : PE Aanalyst 100
Potassium (K)	AAFRD	Flame Photometer : IL 943
	U of C	Atomic Adsorption: PE Aanalyst 100
Trace metals (Mn, As, Fe ²⁺)	CHR	ICP-MS ??

Nitrate, nitrite, ammonium, total kjeldahl nitrogen, phosphate, total dissolved phosphate (organic + inorganic), and total phosphorus (organic + inorganic) were analyzed on a TRAACS 800 autoanalyzer according to the methods listed in Table 3-3. Carbonate, bicarbonate, and lab pH and EC were measured by acid titration using a Man-Tech PC titrate unit. Sulfate was analyzed by the turbidimetric method using a Milton Roy Spectronic 1001 Plus. Major cation analyses conducted at AAFRD were done either by atomic adsorption (Ca, Mg) using an Unicam 989 spectrophotometer or by flame photometry (Na, K) using an IL 943 flame photometer. At U of C, all cation

analyses were done by atomic adsorption using a Perkin Elmer Analyst 100. Dissolved organic carbon was analyzed at the University of Calgary on the Technicon AutoAnalyzer II.

3.8 Microbiological Analyses

Total and fecal coliform analyses were conducted according to the membrane filtration procedure 9222B and 9222 D, respectively as outlined in Standard Methods for Water and Wastewater (A.P.H.A., 1998). Standard aseptic techniques were followed for all microbiological analyses.

Three volumes of water (100, 50, and 10 mL) were filtered, separately, through 0.45 μm Supor polyethersulfone or GN6 mixed cellulose ester membrane filters. The sides of the autoclaved nalgene filter apparatus were rinsed with deionized water to ensure that all bacteria in the sample were collected on the filter. Total and fecal coliform plates were incubated for 24 hours at 35°C and 44.5°C, respectively. Colonies were counted within 48 hours of incubation. Total coliform bacteria are identified by red colonies with a metallic sheen when grown on an Endo type medium. M-Endo media was used for total coliform analysis. Fecal coliform bacteria are various shades of blue when grown on M-FC medium. All atypical colonies were excluded from the counts.

3.9 Phosphate Sorption Experiments

Phosphate sorption experiments were conducted according to the procedure outlined in Fetter (1993). Eight soil samples were selected from the drill core samples to represent the surface sediment (S), unsaturated zone (V), and saturated zones. These samples and their intervals are listed in Table 3-4. Two rounds of experiments were completed; the first at higher concentrations to investigate the maximum sorption capacity of the sediments and a second using phosphate concentrations similar to those found in the groundwater at

Table 3-4: Sediment sample locations and intervals used in phosphate sorption experiments.

Sample ID	Location	Interval (m bgs)	Experimental Round
16-SZ ¹	NP16	3.27-4.15	High concentration
18-S ²	NP18	0.15-0.4	High concentration
18-SZ	NP18	2.0-3.0	Low concentration
18-SZ	NP18	3.9-4.5	Low concentration
27-SZ	NP19	2.0-3.0	Low concentration
27-SZ	NP19	3.6-4.5	Low concentration
29-UZ ⁴	NP29	0.94-1.5	High concentration
29-SZ	NP29	1.5-2.5	High concentration

¹SZ=saturated zone

²S = surface

³UZ = unsaturated zone

the Battersea field site. Approximately 100 g of sediment from each sample interval was weighed and then oven-dried for 24 hours to drive off the pore water and dry weights were recorded. Soil samples were sieved and the fraction of sediment smaller than 2 mm was isolated for phosphate sorption experiments. Seven 10g portions for each sample were weighed and stored in labeled bottles.

Each 10g sample was placed in a separate erlenmeyer flask and 100 mL of disodiumphosphate in 0.1M NaCl solution of varying concentrations (0, 1, 2.5, 5, 10, 20, 30, 40, 50 mg-PO₄ L⁻¹) was added to each flask. The flasks were then placed on a wrist action shaker and agitated gently for 4.5 days. Once removed from the shaker, the sediment-disodiumphosphate mixture was filtered to 0.45 μm and the filtrate was stored for analysis.

Phosphorus extractions were conducted to determine the amount of phosphorus currently being stored in the aquifer. Two extractions were done on each sample: (1) a strong acid extraction (100 mL of 1N HCl for 72 hours) to estimate sorbed plus mineral P, and (2) a weak acid extraction (100 mL of 10% HCl for 24 hours) to estimate sorbed P. Sediment samples from the same areas as those used for the phosphate sorption experiments were extracted as part of the experimental methodology. In addition, several samples were selected

from the improved pasture region. These are thought to represent background P values at the Battersea Field site, or values that are likely typical of the region. The extraction flask was agitated gently on a wrist action shaker, then filtered. The filtrate was stored for orthophosphate analysis. Filtrate from both sorption and extraction trials were analyzed for orthophosphate concentration using the Technicon AutoAnalyzer II, Industrial Method 94-70W/B.

3.10 Geochemical Modeling

Speciation calculations were conducted on groundwater at the Battersea Field Site using PHREEQCi (Version R_O_39) and the WATEQ4F database (Parkhurst & Appelo, 1999). Solution data and field measured parameters for each sampling point for sampling events D and I were used and saturation indices for all suitable P minerals and other minerals pertinent to determining groundwater geochemistry were calculated. These include; hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), anhydrite (CaSO_4), aragonite (CaCO_3), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), amorphous iron oxides ($\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$, $\text{Fe}(\text{OH})_3(\text{a})$, Fe_3OH_8), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and halite (NaCl). The simulations were deemed good if a) the speciation was appropriate and possible, b) appropriate valence states were calculated for all ions present in solution, and c) the percent error in the charge balance was less than 10%.

3.11 Sulfur Isotope Analysis

Eighteen samples were collected for ^{34}S isotope analysis of sulfur in sulfate, in mid-October, 1999. Thirteen samples were collected from MLS, three from seepage meters, and two from the Battersea Drain. Sample filtering and preservation was conducted in the lab at AAFRD. Isotope analysis was conducted in the Stable Isotope Lab in the Department of Physics and Astronomy at the University of Calgary.

Water samples were filtered and 1-5 mL of 10% BaCl₂ (volume dependent on sulfate concentration) were added to precipitate BaSO₄, then acidified to pH<2 to dissolve any precipitated BaCO₃. Precipitated BaSO₄ was collected on 0.45 μm millipore filters and washed with deionized water. The filters and precipitate were dried overnight in a 70°C oven. Finally, the dried filters + precipitate were weighed and the BaSO₄ was scraped off the filter for analysis.

Approximately 5 mg of BaSO₄ was mixed thoroughly with an agate mortar with 100 mL of a 1:1 V₂O₅-SiO₂ mixture and placed into a vertical glass tube that was closed at the bottom. Silica glass wool was placed on top of the mixture to prevent its escape during evacuation of the tube. Finally, approximately 2 g of copper wire was placed 2 cm above the glass wool.

Each sample tube was connected to the preparation line and evacuated. The copper wire was heated to a red glow by a torch until no appreciable outgassing was observed. This is done to remove any oxide coatings and volatile contaminants from the copper wire. The column was then heated to 900-950°C by a vertical electric furnace causing the BaSO₄ to thermally decompose, producing SO₃ and SO₂. SO₃ gas is converted to SO₂ gas by reduction on the hot copper wire. SO₂ gas is then caught in a cold trap by liquid nitrogen (-197°C). Any traces of CO₂ contamination are separated from the SO₂ cryogenically using a mixture of n-pentene and liquid nitrogen (-130°C). This is possible because the vapor pressure of SO₂ (<0.01 mm Hg) is much less than that of CO₂ (1.6 mm Hg), allowing the CO₂ to be preferentially pumped out of the tube with minimal loss of SO₂. The SO₂ gas is warmed by replacing the n-pentene-liquid nitrogen bath with a dry ice-alcohol bath (-90°C). This will retain any remaining traces of water. The sulfur isotopic composition of the SO₂ gas is determined by mass spectrometry and compared against prepared standards of seawater (-20‰) and Fisher (-2.7‰). There is a ±0.2‰ reproducibility with this method (Staniaszek, 1992).

CHAPTER 4: GEOLOGY & HYDROGEOLOGY OF THE BATTERSEA SITE

4.1 Location of Field Site

The selected field site is located within the Battersea Drainage basin of the Lethbridge Northern Irrigation District (LNID) of southern Alberta (Figure 4-1). The LNID is located immediately north of Lethbridge, and east of Picture Butte, Alberta. It is bounded to the north and west by the legal boundaries of the County of Lethbridge. The Little Bow and Oldman Rivers form the eastern and southern boundaries, respectively. The LNID is one of 13 irrigation districts in southern Alberta, which provide water for 1.3 million acres of agricultural land; 11% of this land is located in the LNID.

4.2 Climate

Average annual precipitation in Lethbridge is approximately 401 mm yr^{-1} (based on the past 50 years) with 62% occurring between May and September (Rodvang et al., 1998). The average evapotranspiration, measured in Lethbridge for the last 50 years, is 1196 mm yr^{-1} (Rodvang et al., 1998), exceeding precipitation by a factor of three. Recharge rates in coarse lacustrine sediments in the LNID ranges between 1.9 and 6.4 cm yr^{-1} , and averages 3.4 cm yr^{-1} based on water balance calculations (Rodvang et al., 1998).

Monthly precipitation and irrigation measured at the Battersea site averaged 83 mm (May to September) for the monitoring period (Table 4-1; Appendix 5). Average monthly precipitation in Picture Butte (where available) and Lethbridge was 49 mm over the same time period. Precipitation was comparable to the 30-yr average for the region in 1999; however 2000 was significantly drier (Figure A5-2; Appendix 5).

The average annual temperature in the Lethbridge area (30-yr average) is $5.4 \text{ }^{\circ}\text{C}$ (January: -9.6°C , July: 18.4°C). The temperature trends over the

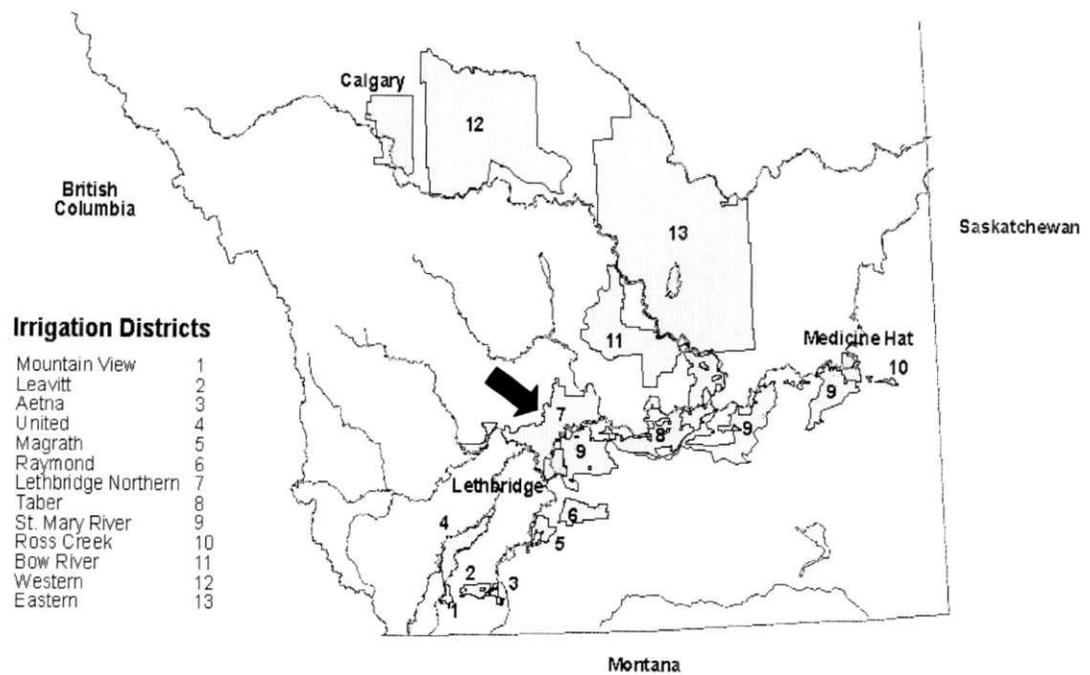


Figure 4-1: The thirteen irrigation districts of southern Alberta. The Lethbridge Northern Irrigation District (LNID) is indicated by the arrow and number 7.

Table 4-1: Monthly precipitation and irrigation amounts measured in the tipping bucket rain gauge at the Battersea site.

Month	Precipitation + Irrigation (mm)	
	1999	2000
May	---1	31.49
June	26.67	78.99
July	135.13	199.64
August	53.32	90.93
September	---	48.77

¹ no precipitation or irrigation measured

monitoring period closely match the regional long-term averages (Figure A5-1; Appendix 5).

4.3 Land Use in the LNID

The LNID comprises 155 000 acres of cropland (AAFRD, 2000). The principal crops in 1999 were forage (~60%), and cereals (~27%). Irrigation in the region is predominantly by either center pivot (45%) or wheel move (52%) irrigation systems. Irrigation began in 1923 and currently over 90% of agricultural land in the LNID is irrigated. Intensive livestock operations in the County of Lethbridge are dominated by beef and poultry, followed by hog and cow/calf operations.

4.4 Site Description

The selected field site, hereafter referred to as the Battersea site, comprises a quarter-section of an irrigated, manured, cropped field in the LNID of southern Alberta. The field site is bounded to the north by the Battersea Drain and to the east by a provincial trunk highway (PTH) (Figure 4-2). Crop rotation since 1989 has been canola-barley-alfalfa-barley-wheat-corn (Pollemans, personal communication; John Pollemans, Agricultural Foreman of the Battersea site, 2000). Crops have been predominately fertilized with

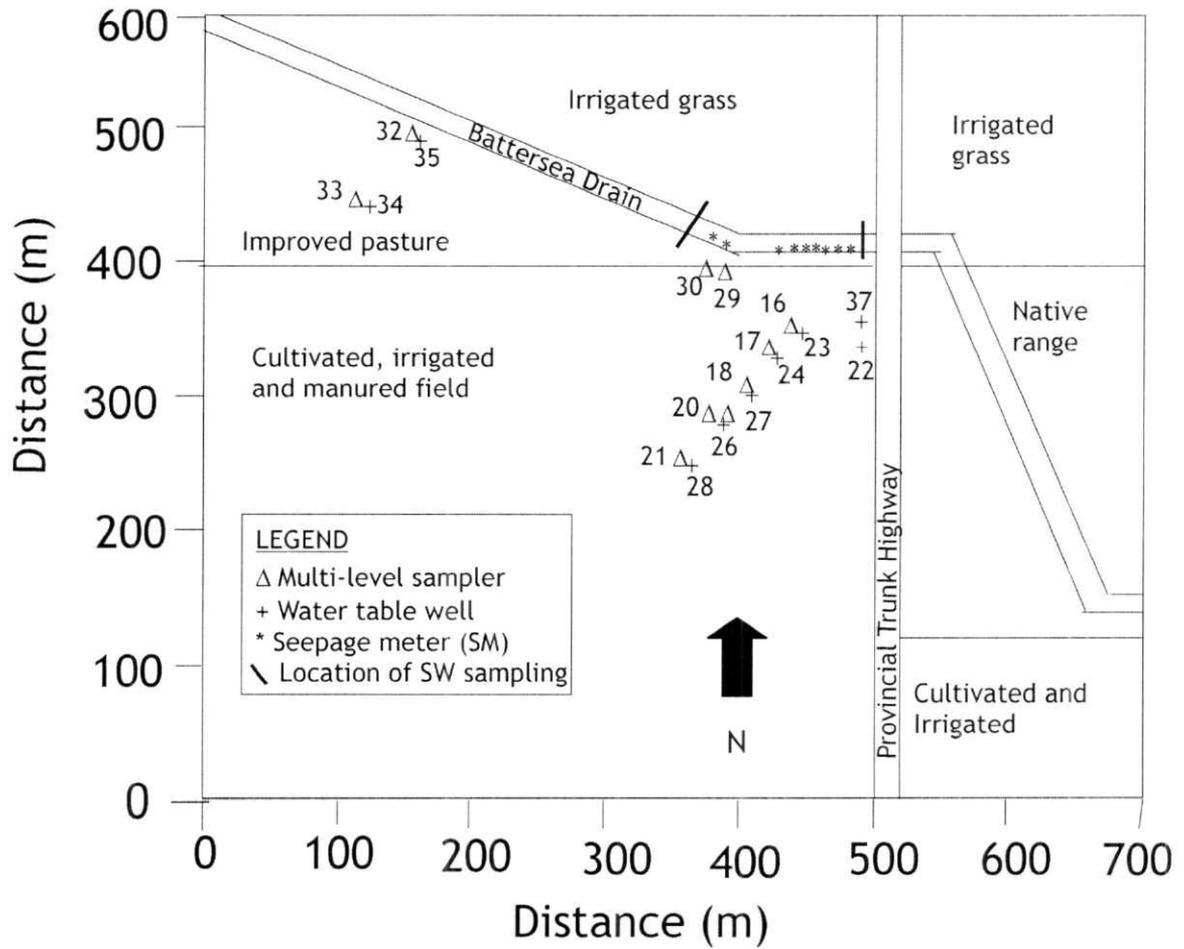


Figure 4-2: Map of Battersea field site showing locations of instrumentation and surface water (SW) sampling.

Table 4-2: Manure and fertilizer application rates (wet manure) for the Battersea field site since 1990 (Pollemans, personal communication; John Pollemans, Agricultural Foreman, Battersea Site, 2000).

Year	Manure	Fertilizer
2000	74 Mg/ha applied in spring	None
1999	74 Mg/ha applied in fall	0.11 Mg/ha Granular 46-0-0 in spring
1998	112 Mg/ha in fall	0.11 Mg/ha anhydrous ammonia in spring
1997	None	None
1996	112 Mg/ha in fall	None
1995	90 Mg/ha	None
1994	None	None
1993	None	0.056 Mg/ha anhydrous ammonia
1992	None	0.045 Mg/ha anhydrous ammonia
1991	None	None
1990	90 or 112 Mg/ha	None

manure, but there have been some historic applications of commercial fertilizer (Table 4-2).

Topographically, the Battersea site rises gradually away from the Battersea Drain towards the southwest (Figure 4-3; Appendix 6). A topographic high that runs diagonally northwest-southeast across the site slightly southwest of NP21 may represent a local flow divide. Groundwater north of this divide follows the local flow system (towards the Battersea Drain), whereas groundwater to the south follows the regional flow system (away from the Battersea Drain). There is a topographic low just southwest of this rise, potentially a location of depression focussed recharge.

Rare glacial scours can be seen in air photo but they are of limited extent. Many irrigation canals and engineered drains, like the Battersea, dissect the LNID creating summertime fluctuations in local groundwater flow systems. The Battersea Drain is typical of engineered drains in the region. It is characterized by steeply dipping banks and has a depth of approximately 4 m. The purpose of the Battersea Drain is to carry irrigation return flow (runoff,

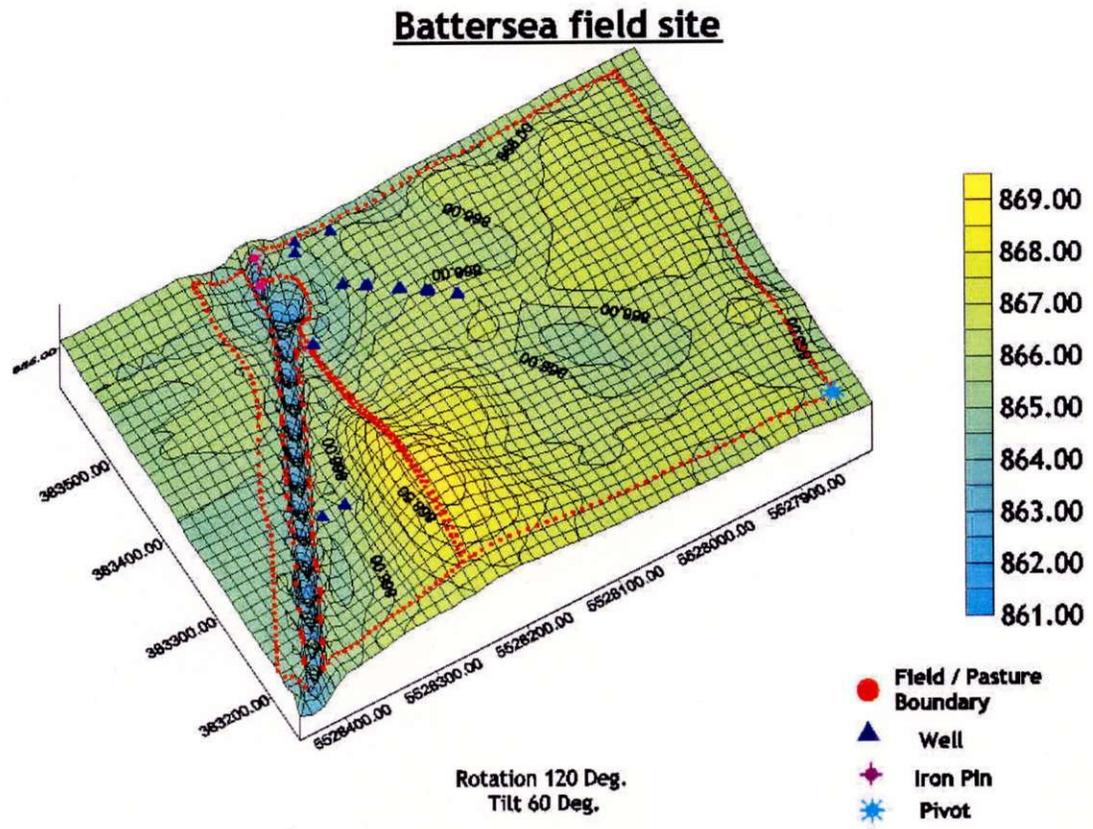


Figure 4-3: Surface topography of the Battersea field site.

unused irrigation water, subsurface drainage, and groundwater discharge) back to the Oldman River.

4.5 Geology of the Battersea Site

The Battersea site is underlain by well- to very well-sorted, fine to medium grained sand, silty-sand and muddy-sand (sandy loam) with some isolated and laterally discontinuous silty-clay lenses (Figure 4-4; Appendices 1 & 3). The average thickness of the sand unit is 4.2 m, and ranges between 1 m near the center-pivot at the southwest edge of the quarter-section, to 7.2 m near the Battersea Drain. The sand is lacustrine in origin and generally homogeneous. Graded bedding was observed in one location on the canal bank. Compositionally, the sand is calcareous, and dominated by quartz with some feldspar. It is conformably underlain by approximately 11 m of lacustrine clay, followed by a dense clay-loam to clay till to a depth of 75 m (Rodvang et al., 1998). The contact between the sand and clay varies from sharp to gradational throughout the site. The bottom sediments of the Battersea Drain are silty to muddy sands and gyttja with interbedded stringers of reduced organics.

4.6 Hydrogeology

The unconfined aquifer occupies about 9,000 ha between Iron Springs, the Little Bow and the Oldman Rivers. The sand is interbedded with fine- and medium-textured lacustrine deposits along the western and northern margins, and reaches a thickness of at least 27 m near the junction of the Little Bow and Oldman Rivers. The unconfined aquifer is currently used by several intensive livestock operations, and has been used as a water supply by farm families for at least 80 years.

The unconfined aquifer occurs in a very flat lacustrine basin where groundwater flow directions are influenced by minor changes in local topography, canals, surface drains, and pumped wells. Local flow directions

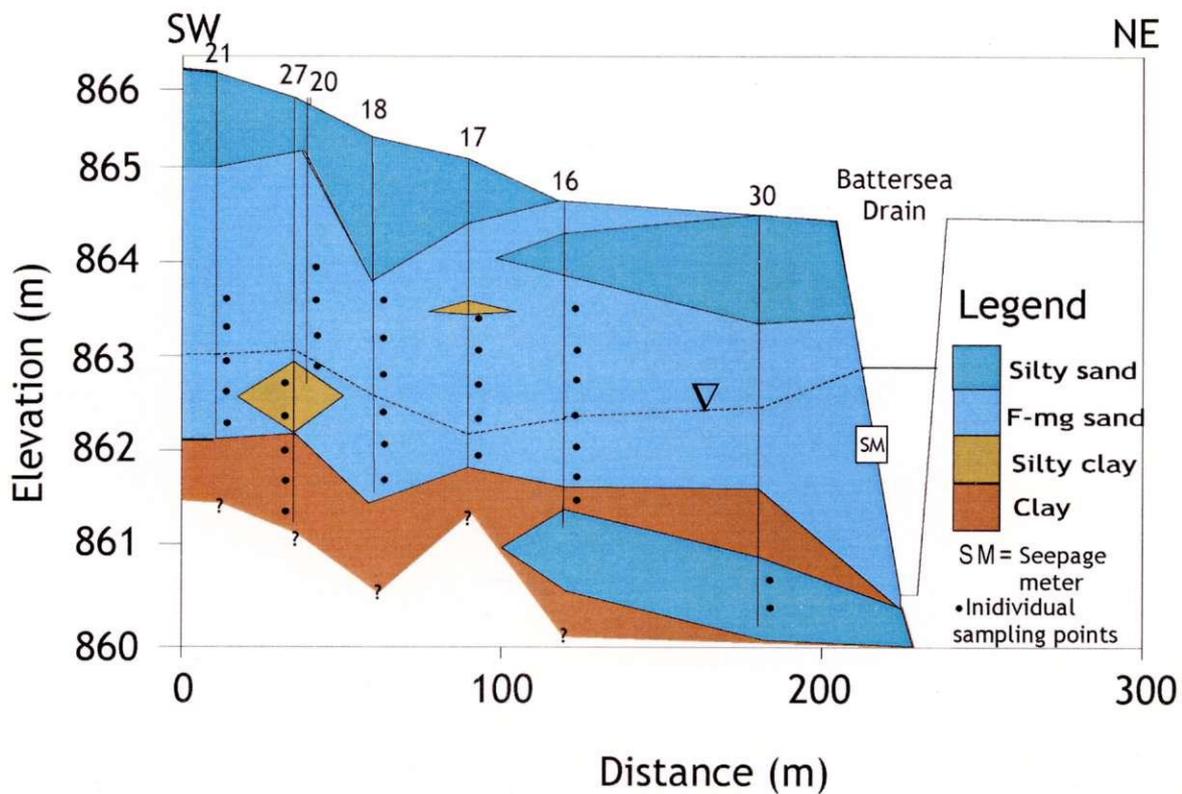


Figure 4-4: Cross-section from SW to NE at the Battersea field site showing the subsurface geology. The plotted water table is the average water table height during irrigation. F-mg sand = fine to medium grained sand.

vary over short distances and with seasonal conditions; particularly the amount of water in canals and surface drains. Regional groundwater flow is predominantly toward the east, recharging the Little Bow River. Locally, groundwater flows northeast towards the Battersea Drain, at an angle of 30° from north.

Hydrostratigraphically, the Battersea site is underlain by a shallow, unconfined, sandy aquifer that is further underlain by a clay aquitard. A silty sand lens in the clay layer appears to be a confined sandy aquifer of limited extent. Hydraulic heads typically decrease from the center of the Battersea site towards the Battersea Drain. The water table is generally near flat-lying and at an average depth of 3.4 m below ground surface. Water table elevations are lowest from fall to spring and highest in the summer during irrigation (Figure 4-5). The maximum seasonal fluctuation in water table elevation is approximately 60 cm.

Groundwater flow in the unconfined aquifer can be conceptualized as one-dimensional horizontal flow. Saturated thickness is a maximum of 2 m throughout the year, whereas the maximum length of the groundwater flow path at this site is approximately 330 m. Using an average horizontal gradient of 0.0075, the groundwater velocity is 0.09 m day⁻¹. Estimated maximum residence time in the aquifer is therefore 10 years.

4.6.1 Hydraulic Gradients - Aquifer

Hydraulic gradients vary along the flow path, and are dominantly horizontal towards the Battersea Drain (Table 4-3; Appendix 7). Reversals in this trend occur during the irrigation season, when the elevation of water in the Battersea Drain temporarily exceeds that in the aquifer. This creates a reversal of the horizontal gradient and causes bank storage along the length of the field site. The reversed gradient is generally limited to the region between NP16 and the Battersea Drain; however in one case (Aug-99; Table 3-4)

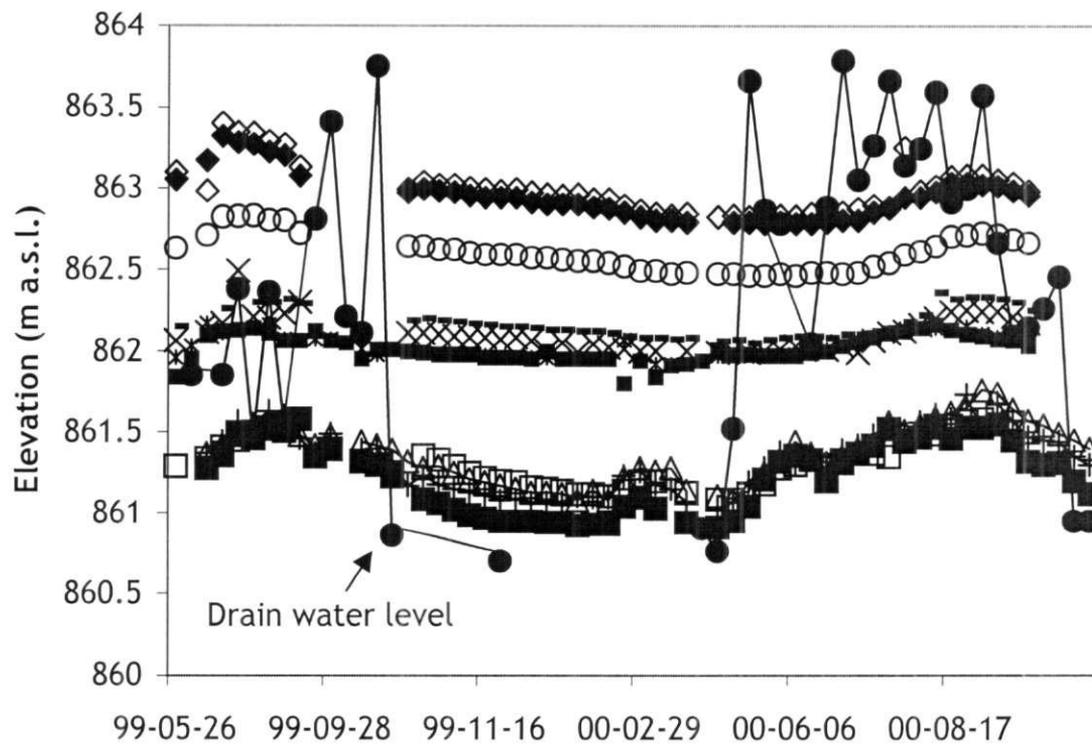


Figure 4-5: Temporal fluctuations in water table and surface water elevation at the Battersea site. (\diamond = WTW 28, \blacklozenge = WTW 26, \circ = WTW 25, $-$ = WTW 24, \times = WTW 23, \square = WTW 22, \blacksquare = WTW 37, $+$ = WTW 35, \triangle = WTW 34, \blacksquare = MLS 29, $*$ = MLS 30).

Table 4-3: Monthly average horizontal hydraulic gradients measured between water table wells at the Battersea field site. Negative gradients (away from the Battersea Drain) are bolded.

Month	28-26	26-25	25-24	24-23	23-B.D.¹
May-99	0.0017	0.014	0.0160	0.0300	-- ²
Jun-99	0.0045	0.016	0.0189	0.0019	0.0494
Jul-99	0.0023	0.014	0.0007	0.0106	0.0285
Aug-99	0.0018	0.012	0.0143	-0.0003	--
Sep-99	0.0012	0.012	0.0147	0.0029	--
Nov-99	0.0016	0.012	0.0145	0.0027	0.0457
Dec-99	0.0019	0.011	0.0144	0.0070	--
Jan-00	0.0019	0.011	0.0143	0.0029	--
Feb-00	0.0013	0.011	0.0140	0.0027	--
Mar-00	0.0012	0.011	0.0135	0.0143	--
Apr-00	0.0017	0.010	0.0135	0.0025	0.0410
May-00	0.0013	0.011	0.0133	0.0022	-0.0228
Jun-00	0.0018	0.011	0.0128	0.0024	-0.0297
Jul-00	0.0033	0.011	0.0133	0.0018	-0.0404
Aug-00	0.0016	0.011	0.0120	0.0036	-0.0311
Sep-00	0.0013	0.010	0.0140	0.0038	-0.0127
Average	0.0018	0.012	0.0134	0.0057	0.0330

¹ B.D. = Battersea Drain

² data not available

extended as far into the site as NP17. Gradients return to normal once irrigation ceases and the Drain water level drops.

Vertical gradients are predominantly upward, but vary from location to location and with time (Table 4-4). Upward gradients occur throughout the year, but dominate during the growing season with one exception (Jun-99).

4.6.2 Hydraulic Gradient - Battersea Drain surface water - sediment interface

The vertical hydraulic gradient in the bottom sediments of the Battersea Drain was variable over time (Appendix 7), and is loosely related to water levels in the drain. In general when the surface water level is higher, the gradient will tend to be negative, (i.e. losing stream). Conversely, when the water level is lower, the gradient will be positive (i.e. gaining stream). The

Table 4-4: Monthly average vertical hydraulic gradients measured between the multi-level samplers and their corresponding water table wells. Negative (downward) gradients are bolded.

Month	16-23	17-24	18-25	20-26	27-26	21-28
May-99	0.007	0.06	0.02	0	0.003	0.02
Jun-99	0.01	-0.05	0.01	-0.009	0.0008	-0.21
Jul-99	0.05	0.24	0.006	0.04	-0.003	0.005
Aug-99	0.06	0.09	0	-0.03	-0.005	-0.02
Sep-99	-- ¹	--	--	--	--	--
Oct-99	0.006	0.07	0.01	0.05	0.002	0
Nov-99	0.005	0.07	0.01	-0.03	0.0007	0
Dec-99	-0.01	0.09	0.007	-0.13	-0.002	0.03
Jan-00	0.003	0.1	0.01	0	0	0.02
Feb-00	0.003	0.09	0.005	-0.08	0.004	0.01
Mar-00	-0.45	0.15	0.01	-0.13	0.002	-0.03
Apr-00	0.003	0.05	0.01	--	0	0.01
May-00	0.005	0.07	0.003	0.1	0.004	-0.009
Jun-00	0.007	1.2	0.01	0.14	-0.002	-0.005
Jul-00	0.02	0.04	0.009	0	0.004	0.09
Aug-00	0.006	0.1	0.006	-0.04	-0.0009	0.004
Sep-00	-0.008	0.06	0.009	0	0.001	-0.001
Average	-0.02	0.15	0.009	-0.007	0.0005	-0.005

¹ Data unavailable

maximum and minimum gradients were 0.84 and -0.58, respectively. The mini-piezometer (MP) was often submerged during the monitoring period. Therefore, no assessment of the drain gradient was possible at water levels in excess of the height of the MP, or approximately 1 m water depth.

4.6.3 Hydraulic Conductivity

The bulk hydraulic conductivity (K) of the sand aquifer is $5.5 \times 10^{-5} \text{ m s}^{-1}$ (4.75 m da^{-1}) and ranges from 1.3×10^{-6} to $9 \times 10^{-5} \text{ m s}^{-1}$ ($0.11 - 7.8 \text{ m da}^{-1}$; $n=4$, $\sigma=3.7$) (Appendix 2). Using the measured K and thickness at each water-table well, transmissivity varies between $5.6 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at the southwestern edge of the site and $3.0 \times 10^{-2} \text{ m}^2 \text{ s}^{-1}$ near the Battersea Drain. The average K of the sediments at the base of the Battersea Drain is $7.96 \times 10^{-8} \text{ m s}^{-1}$ (2.5 m yr^{-1}).

This value is typical of silts and suggests the presence of a silt layer overlying sandy aquifer material, typical of streams.

4.6.4 Overland Flow

A collection trench was installed approximately parallel to the Battersea Drain and at the edge of the cultivated field to collect surface runoff. No overland flow was collected nor observed at the Battersea field site during this study. Since 2000 was significantly drier than the long term average, there is a decreased likelihood for generation of episodic overland flow during storm events. The collection trench was not protected from irrigation inputs (i.e. not covered). Therefore, it was not possible to differentiate between irrigation volume and any contribution from surface runoff. Therefore, overland flow during irrigation events cannot be completely ruled out.

4.6.5 Battersea Drain Flow Rate

Water flow in the Battersea Drain varied seasonally during the monitoring period, in response to varied contributions from irrigation canals and regional return flow (AAFRD, 2000; unpublished data). Generally, flow rate was highest during the summer months (average: $0.43 \text{ m}^3 \text{ s}^{-1}$ (15 cfs)) and decreased in the fall. The high summer flow rate comprises un-used irrigation water and return flow from irrigated fields along the Battersea Drain. Water in the drain was frozen over the winter; however some flow was noted under and alongside the ice (average $0.03 \text{ m}^3 \text{ s}^{-1}$ (1.0 cfs)).

4.6.6 Seepage Rate

Seepage rate was highest in the seepage meters located east of the irrigation lagoon (SM1-4, SM7-9) (Figure 4-6, Table 4-5). This is the lowest topographic point in the Battersea Drain at this site, therefore it would be expected that groundwater discharge would be highest here. Average annual seepage ranged between $0.14 \text{ L m}^{-2} \text{ da}^{-1}$ (SM6) and $60 \text{ L m}^{-2} \text{ da}^{-1}$ (SM9) for

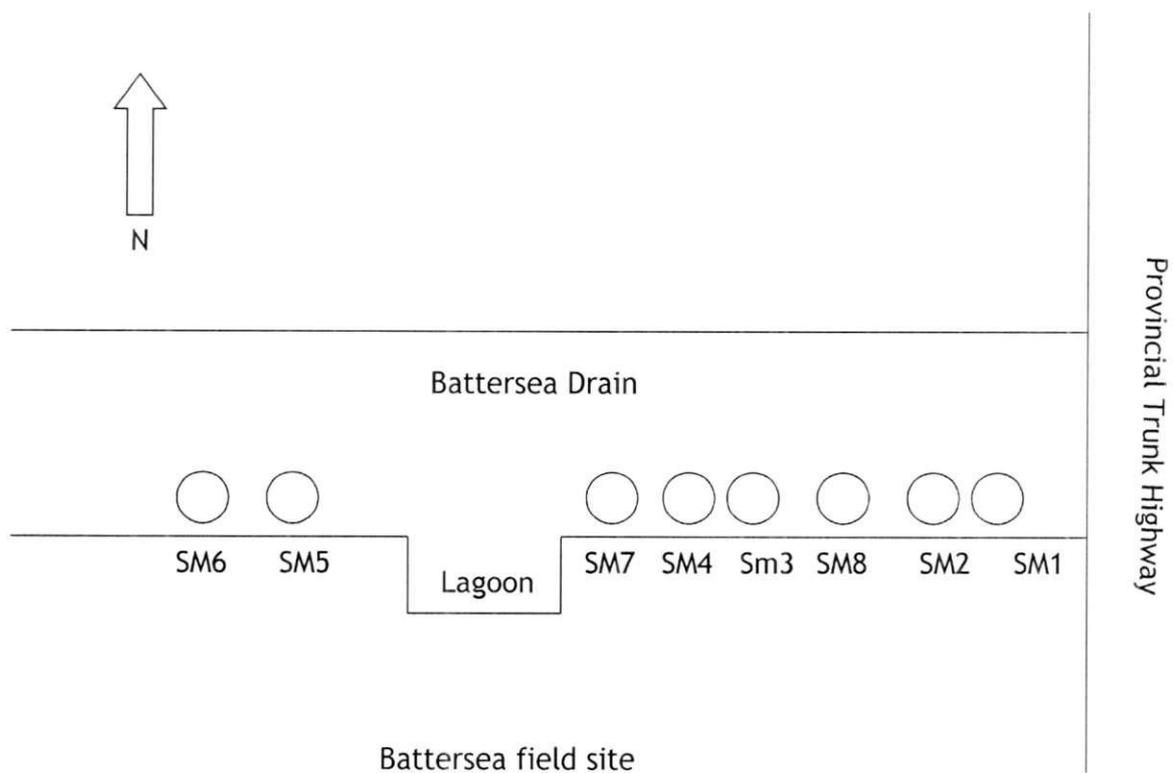


Figure 4-6: Schematic diagram showing approximate locations of seepage meters installed in the Battersea Drain at the Battersea field site. North is to the bottom of the diagram and the field site to the top. SM = seepage meter.

Table 4-5: Monthly average seepage rates ($\text{L m}^{-2} \text{ da}^{-1}$) for each seepage meter over the monitoring period.

	SM1	SM2	SM3	SM4	SM5	SM6	SM7	SM8	SM9
May 99	-- ¹	--	0.45	1.07	--	0.14	--	--	--
Jun 99	0.03	0.66	0.66	0.28	0.72	0.48	--	--	--
Jul 99	2.72	2.79	2.21	2.17	0.69	0.55	--	--	--
Aug 99	--	--	--	--	--	--	--	--	--
Sep 99	0.24	1.21	1.86	0.35	0.35	0.21	0.35	0.28	--
Oct 99	25.9	2.20	26.6	14.89	2.24	0.76	0.10	15.0	--
Nov 99	6.59	92	42.66	33.45	2.93	0.38	0.69	31.34	--
Dec 99	S.F. ²	S.F.							
Jan 00	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.
Feb 00	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.
Mar 00	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	S.F.	43.10
Apr 00	12.9	0.66	39.17	45.66	3.69	4.90	4.59	77.24	65.83
May 00	-3.14	0.76	2.34	3.93	-0.79	-0.79	0	0.76	--
Jun 00	n.a. ³	44.3	14.86	11.90	-1.24	-0.90	6.66	31.59	--
Jul 00	n.a.	85.6	20.89	20.76	-1.24	-1.83	15.17	65.69	--
Aug 00	n.a.	89.2	20.17	19.10	-2.93	-2.14	14.72	38.79	--
Sep 00	n.a.	130.4	26.45	27.55	-0.83	-0.83	16.93	119.6	--
Oct 00	n.a.	73.4	12.48	20.97	-2.10	-2.10	20.34	39.10	--

¹ seepage not measured

² S.F. = stream frozen over seepage meters, no seepage measured

³ n.a. = not available - bank caved over seepage meter

individual seepage meters. The overall annual seepage rate, across all locations, was $20 \text{ L m}^{-2} \text{ da}^{-1}$ ($0.02 \text{ m}^3 \text{ m}^{-2} \text{ da}^{-1}$).

Several temporal trends were also identified in the data (Table 4-5, Figure 4-7). During irrigation (May through August of 1999), average seepage rate at all seepage meters was negligible. Seepage then increased in September of 1999, and presumably remained higher during the winter months. However, because the water in the Battersea Drain was frozen over the seepage meters, sampling was not possible. A sharp decrease in the seepage rate occurred in May, 2000 in response to a rapid increase in Drain water level. This was closely followed by increased, but variable, seepage rates through to the end of October, 2000.

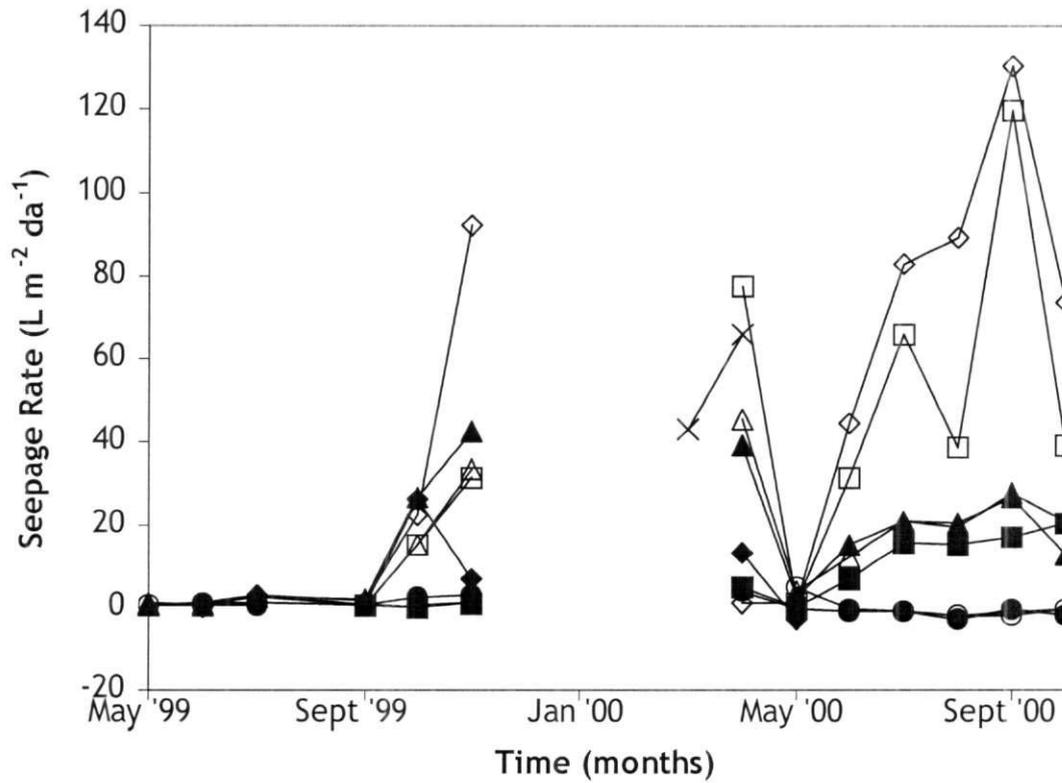


Figure 4-7: Change in seepage rate over time by location. No seepage was measured during the winter months as the water in the Battersea Drain was frozen over the seepage meters. (♦ = SM1, ◇ = SM2, ▲ = SM3, △ = SM4, ● = SM5, ○ = SM6, ■ = SM7, □ = SM8, X = SM9).

The periods of low seepage occurred during the summer in both 1999 and 2000. This corresponds to the irrigation period when Drain water levels are elevated, due to increased return flow, and the Battersea Drain acts as a losing stream. Conversely, the seepage rate increased both years when water levels in the drain dropped and the hydraulic gradient in the bottom sediments was positive (gaining stream).

CHAPTER 5: RESULTS & DISCUSSION

5.1 Soil Chemistry

There are no significant differences between average soil concentrations of K, Cl, NO_3+NO_2 , PO_4 , and NH_4 in the manured field and improved pasture regions of the Battersea site (Table 5-1; Appendix 4). However, average soil $\text{NO}_3\text{-N}+\text{NO}_2\text{-N}$ concentrations are slightly higher in the manured field than in the improved pasture which is consistent with manure application. Similarity between average soil K, Cl, and PO_4 concentrations in the field and pasture suggests that manure may have been historically applied to the improved pasture area. The landowner stated that it was doubtful that manure had been applied therefore fresh manure from cows grazing in the improved pasture is a more likely nutrient source.

Average soil concentrations of $\text{PO}_4\text{-P}$ and K generally decrease with depth (Figure 5-1; Appendix 4). Conversely, an initial decrease in average soil Cl, $\text{NO}_3\text{-N}+\text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$ is followed by an increase with depth. Since NO_3 , NH_4 and Cl are mobile, this trend is consistent with downward leaching in the soil profile. The trends of decreasing soil $\text{PO}_4\text{-P}$ and K with depth are consistent with adsorption to sediments, and derivation from an agricultural source such as manure.

There is little variation in average surface soil concentrations along a transect from the center of the field to the Battersea Drain (Figure 5-2). Increased concentrations could indicate nutrient concentration by overland flow and/or locally higher rates of manure application. Soil $\text{PO}_4\text{-P}$ tends to increase towards the Battersea Drain in the interval of 15 to 60 cm below the ground surface, while soil $\text{NO}_3\text{-N}+\text{NO}_2\text{-N}$ increases in the 60 to 90 cm interval. Since these variations are occurring at depth, it is unlikely that they result from overland flow. Rather, they are probably attributable to local variations in the rate of manure application coupled with decreased crop uptake along the edge of the field and preferential flow paths.

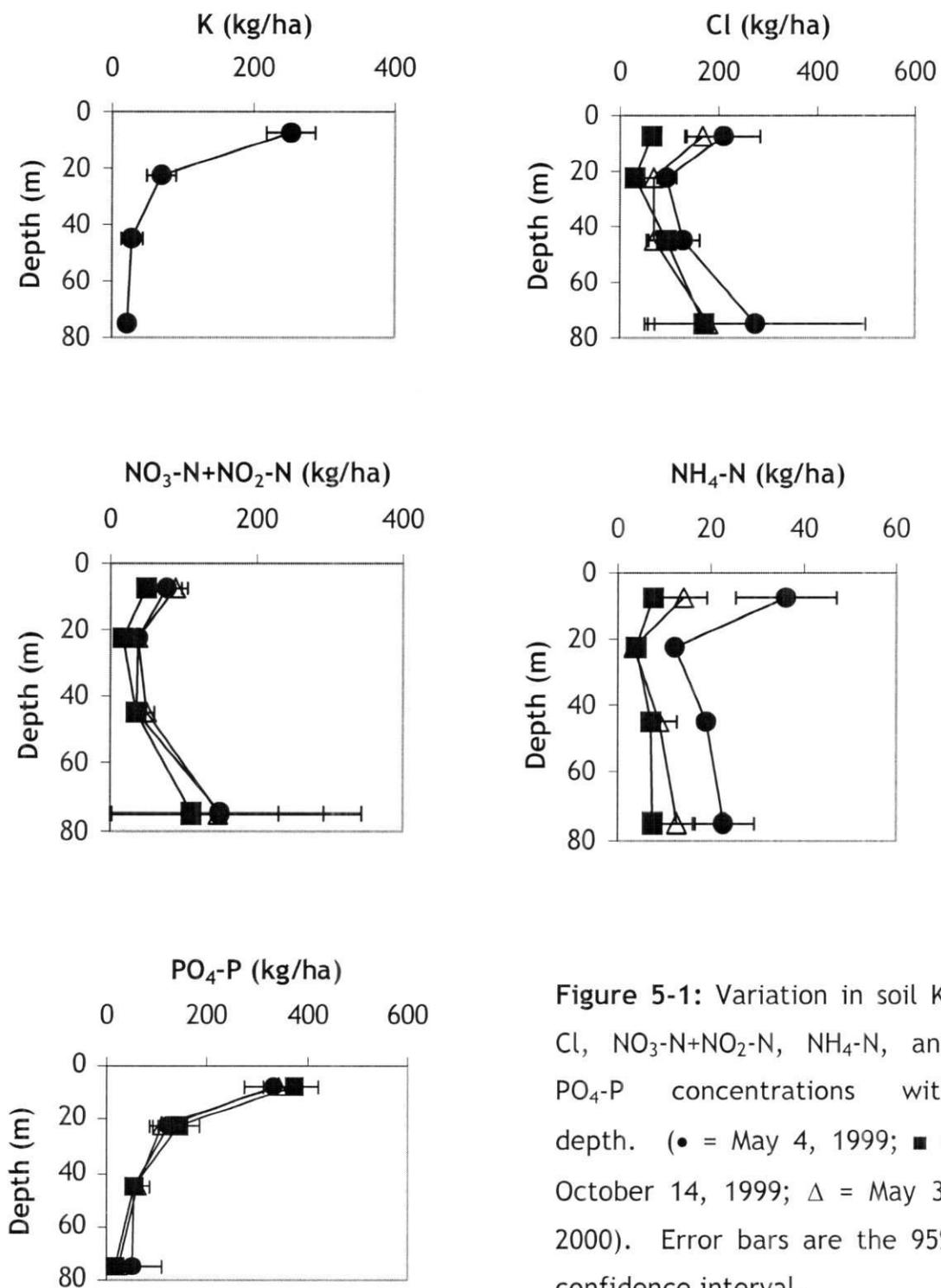


Figure 5-1: Variation in soil K, Cl, NO₃-N+NO₂-N, NH₄-N, and PO₄-P concentrations with depth. (• = May 4, 1999; ■ = October 14, 1999; Δ = May 3, 2000). Error bars are the 95% confidence interval.

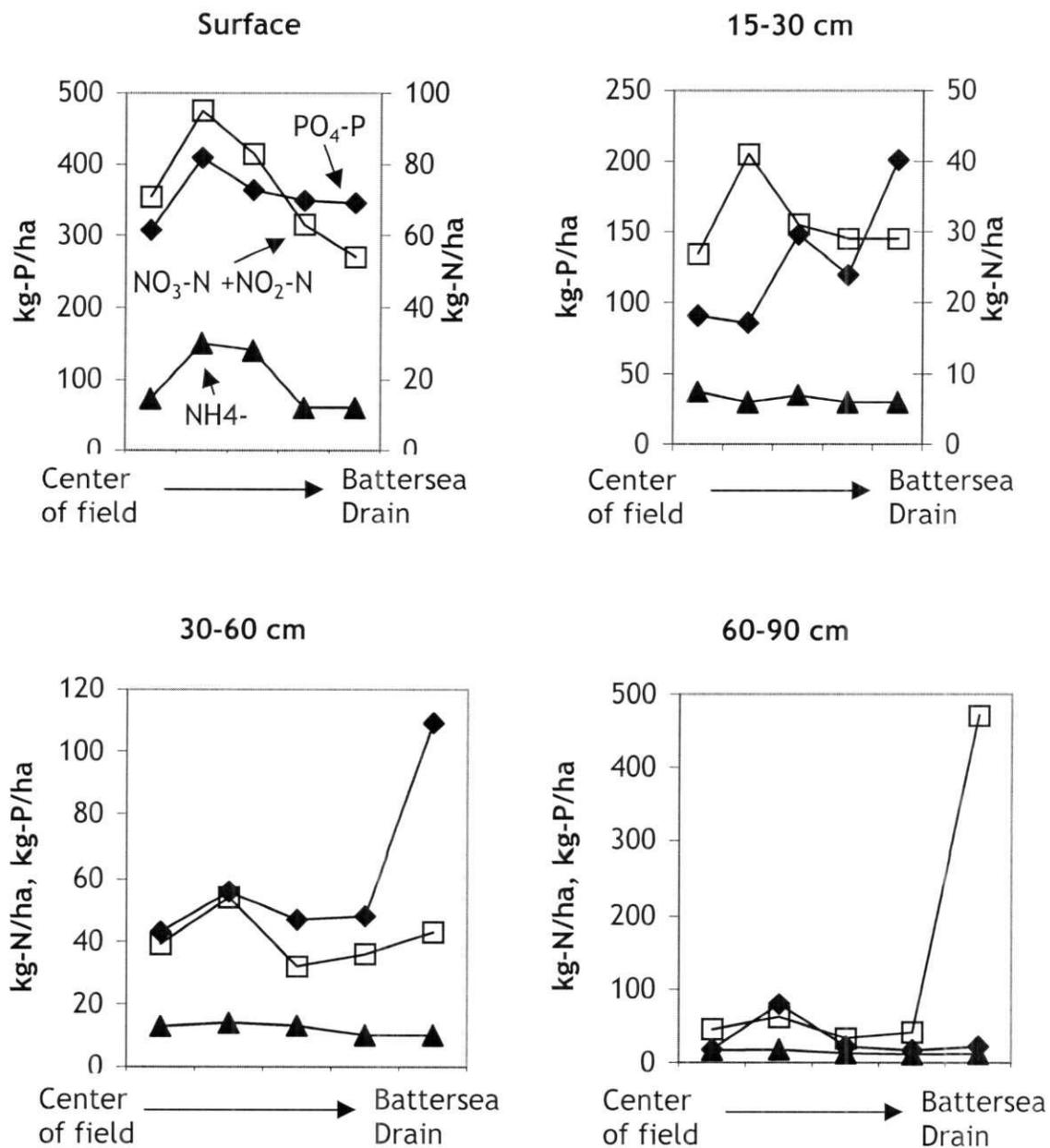


Figure 5-2: Variation in soil $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$, and $\text{NH}_4\text{-N}$ concentrations across the manured field.

Table 5-1: Average soil concentrations (kg/ha) in the upper 90 cm of the soil profile in the manured field and improved pasture at the Battersea site. (S.D.)

	Date (yy-mm-dd)	Manured Field (n=88)	Improved Pasture (n=24)
K	00-05-03	92 (114)	99 (98)
Cl	99-05-04	183 (347)	153 (242)
	99-10-14	84 (171)	110 (161)
	00-05-04	116 (151)	140 (183)
PO ₄ -P	99-05-03	140 (176)	141 (124)
	99-10-14	147 (168)	149 (155)
	00-05-04	135 (144)	134 (121)
NO ₃ -N+NO ₂ -N	99-05-03	80 (296)	56 (76)
	99-10-14	56 (182)	42 (67)
	00-05-04	84 (221)	71 (81)
NH ₄ -N	99-05-03	24 (21)	20 (6)
	99-10-14	6.4 (2.7)	7 (3)
	00-05-04	9 (10)	11 (13)

5.2 Water Chemistry

Groundwater at the Battersea site has been subdivided into two types; 1) groundwater under the irrigated, manured field (FGW), and 2) groundwater under the improved pasture (PGW). This has been done in an attempt to compare the effects of manure and fertilizer use on groundwater quality to a site 'background' groundwater quality. The improved pasture region of the Battersea site is thought to have received no known historical manure or fertilizer applications and is currently used for cattle grazing. It was hoped that shallow groundwater under the improved pasture will show minimal impact from manure use although the possibility of impacts from both upgradient and deeper groundwater are recognized.

5.2.1 General Results

Groundwater (field and pasture) at the Battersea field site is slightly reducing ($E_{h_{av}}=444$ mV; S.D.=78, n=76), neutral ($pH_{av}=7.3$; S.D.=0.89, n=93), mildly oxic ($DO_{av}=2.82$ mg L⁻¹; S.D.=1.74, n=93) and has an average temperature (T) of 11°C (S.D.=2.7, 91) (Appendix 9). Average groundwater conductivity is $1.93 \mu\text{Sm cm}^{-1}$ ($\sigma=0.88$, n=92). Surface water is moderately reducing ($E_h=318$ mV; n=1), oxic ($DO=5.5$ mg L⁻¹; n=1), slightly acidic ($pH=5.8$; n=1) and has an EC of $0.33 \mu\text{Sm cm}^{-1}$ (n=1) (Appendix 11). Although there is little variation between the field groundwater (FGW) and pasture groundwater (PGW) with respect to the Eh, EC, pH, T, and concentrations of major cations and anions, DO and nutrient concentrations do vary with location. (Table 5-2; Appendix 9). Field groundwater contains higher concentrations of NO₃, NO₂, PO₄, and Cl consistent with higher rates of manure application on the field compared with the pasture.

Anions, cations, nutrients, and field measured parameters exhibit both similarities and differences in groundwater, seepage water (Appendix 10), and surface water (Figure 5-3). Average concentrations of Mg, Na+K, Cl, SO₄, NO₃, and PO₄ in seepage water are intermediate between those in FGW, and surface water suggesting dilution of groundwater concentrations by surface water during bank storage. Variations in nutrient concentrations may also reflect natural attenuation of groundwater concentrations along the flow path and/or local variations in redox conditions.

Field groundwater (FGW) is Ca-Mg-SO₄ to Ca-Mg-HCO₃ type. Similarly, the groundwater under the improved pasture (PGW) is Ca-Mg-SO₄ type. These are typical of groundwater in oxidized medium lacustrine sediments of the LNID (Rodvang et al., 1998). Seepage and surface water are Ca-Mg-SO₄ to Ca-Mg-HCO₃ type.

Table 5-2: Average concentrations of nutrients, cations, and anions in field and pasture groundwater (GW), seepage (SM) and surface water (SW) at the Battersea site. Concentrations are reported in mg L⁻¹ unless otherwise indicated (S.D., n).

	Field GW	Pasture GW	SM	SW
NO₃-N (10 mg L ⁻¹) ¹	30 (16, 88)	2 (0.3, 4)	4 (16, 88)	3 (5, 69)
NO₂-N (1 mg L ⁻¹)	0.4 (1.7, 88)	0.09 (0.17, 4)	0.06 (0.09, 188)	0.03 (0.05, 69)
NH₄-N	0.04 (0.09, 88)	0.18 (0.23, 4)	1.20 (2.17, 184)	0.10 (0.19, 68)
PO₄-P	0.09 (0.33, 88)	0.01 (0.01, 9)	0.20 (1.27, 183)	0.01 (0.007, 66)
TP (0.05 mg L ⁻¹) ²	0.22 (0.51, 88)	0.09 (0.09, 3)	0.39 (1.12, 159)	0.05 (0.026, 55)
DP	0.10 (0.36, 88)	0.02 (0.01, 3)	0.17 (0.85, 159)	0.07 (0.37, 56)
DOC	10 (5.5, 86)	8.2 (9.4, 6)	7.5 (4.76, 158)	5 (3, 50)
SO₄ (500 mg L ⁻¹)	715 (737, 86)	1139 (460, 3)	680 (670, 188)	450 (533, 69)
Cl (250 mg L ⁻¹)	59 (26, 88)	30 (8, 4)	28 (29, 188)	17 (23, 69)
HCO₃	494 (75, 88)	354 (14, 4)	598 (1296, 188)	236 (111, 69)
Ca	150 (80, 17)	131 (0, 1)	138 (65, 15)	45 (2, 2)
Mg	159 (76, 17)	107 (0, 1)	91 (48, 15)	26 (0.2, 2)
Na	169 (256, 17)	111 (0, 1)	54 (24, 15)	32 (2, 2)
K	3.5 (5.5, 17)	4 (0, 1)	3 (1.5, 18)	3 (0.06, 2)
Fe	0.057 (0.068, 27)	0.075 (0, 1)	0.10 (0.12, 9)	0.07 (0.06, 4)
TC	5 (8, 18)	--³	90 (87, 3)	118 (17, 2)
FC	0 (0, 18)	--	103 (46, 3)	127 (5, 2)

¹ Drinking water guideline (Health Canada, 1999)

² Alberta Environment Interim surface water guideline (1999)

³ data not available

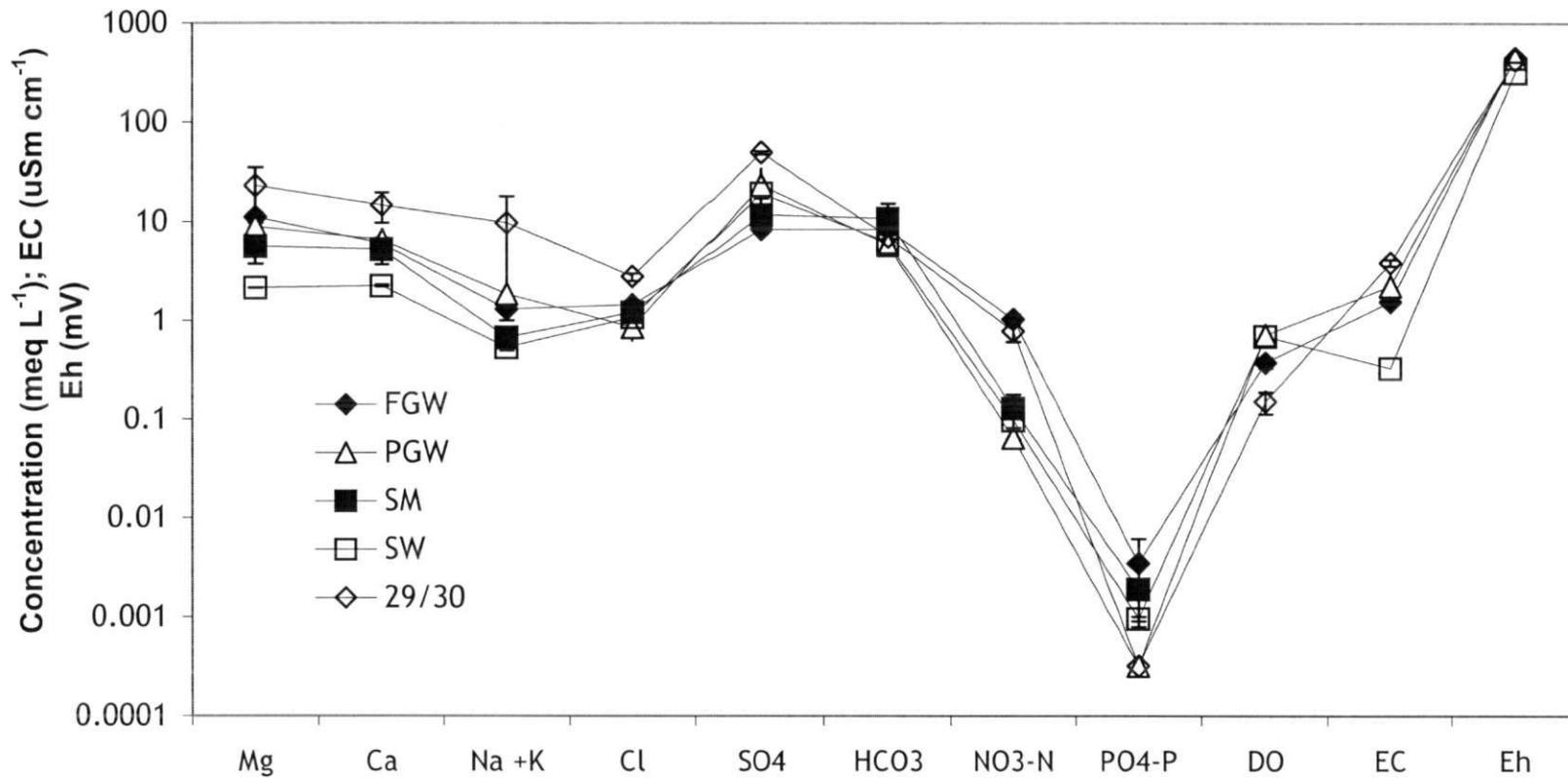


Figure 5-3: Schoeller diagram for major cations, anions, nutrients, and selected field measurements in ground-, seepage, and surface water at the Battersea Field site. FGW = groundwater under the manured field, PGW = groundwater under the improved pasture, SM = seepage water, SW = surface water, 29/30 = data from piezometers 29 & 30. Error bars indicate the 95% confidence interval.

5.2.2 Comparison with Regional Groundwater

Groundwater in fine-textured sediments in the LNID contains much higher concentrations of Na, Mg, SO₄, and Cl than groundwater in the unconfined aquifer (Rodvang et al., 1998). Natural salt concentrations also probably vary in the aquifer. Locations that receive groundwater discharge from fine-textured sediments probably contain higher natural salt concentrations than locations where the sands are thick and homogeneous.

Salt concentrations are significantly higher at MLS 29 & 30 than in the remainder of the study area (Table 5-3, Figure 5-1). These MLS are located on the edge of the manured field, and are completed in a sandy lens in the clay aquitard. Although average NO₃-N and HCO₃ concentrations at MLS 29 & 30 are similar to those in the FGW, the concentrations of Cl, SO₄, Na, Mg, and Ca, and the average EC are significantly higher. This suggests discharge from finer-textured sediments may have contributed salts to MLS 29 & 30. Nitrate and phosphorus concentrations are not higher at MLS 29 & 30 than in the rest of the FGW suggesting the salts are natural, and not related to agricultural contamination.

Due to varying salt contributions from fine-textured sediments, it is difficult to define a single natural background chemistry for the aquifer. Average concentrations from 16 piezometers in the aquifer that contain nitrate are listed in Table 5.3, along with the chemistry from one piezometer that did not contain nitrate. It is evident that salt concentrations are slightly higher in FGW from the study area, compared with average concentrations in the remainder of the LNID. The thinness of the regional aquifer in the study area may have contributed to the high salt concentrations. Alternatively, salts from manure may have leached into shallow groundwater in the study area.

Groundwater under the improved pasture (PGW) has similar NO₃, HCO₃, and K concentrations to LNID background (Table 5-3). However, concentrations of SO₄, Cl, Ca, Mg, and Na are significantly higher than background concentrations suggesting fine-textured sediments may have contributed salts

Table 5-3: Average concentrations of selected nutrients, anions, cations, and DO at the Battersea site and representative background and agriculturally impacted data from the LNID (S.D., n).

	Battersea Site			LNID (Rodvang et al., 1998)	
	Field GW	MLS 29 & 30	Pasture GW	Background	Impacted
NO₃-N (10 mg L ⁻¹) ¹	32 (16, 73)	24 (10, 15)	2 (0.3, 4)	0.1 (0, 1)	15 (14, 16)
NH₄-N	0.04 (0.09, 73)	0.02 (0.06, 15)	0.18 (0.23, 4)	0 (0, 1)	0.008 (0.002, 16)
DOC	9 (5.8, 72)	13 (0.82, 14)	8.2 (9.4, 6)	--²	7.7 (0.27, 2)
SO₄ (500 mg L ⁻¹)	410 (116, 73)	2425 (172, 13)	1139 (460, 3)	88 (0, 1)	239 (268, 16)
Cl (250 mg L ⁻¹)	51 (20, 73)	98 (17, 15)	30 (8, 4)	4.6 (0, 1)	29 (22, 16)
HCO₃	507 (72, 73)	428 (35, 15)	354 (14, 4)	467 (0, 1)	376 (79, 16)
Ca	120 (31, 14)	293 (87, 3)	131 (0, 1)	102 (0, 1)	106 (39, 16)
Mg	133 (30, 14)	280 (125, 3)	107 (0, 1)	37 (0, 1)	80 (60, 16)
Na	79 (36, 14)	588 (442, 3)	111 (0, 1)	23 (0, 1)	37 (16, 30)
K	2 (1.4, 14)	10 (12, 3)	4 (0, 1)	3.5 (0, 1)	6 (3, 16)
Fe	0.05 (0.06, 22)	0.03 (0, 1)	0.075 (0, 1)	--	0.09 (0.25, 14)
DO	3 (1.6, 74)	1.2 (0.6, 15)	5.67 (1.3, 4)	--	0.4-0.6

¹ Drinking water guideline (MOH, 1996). ² data not available

to the aquifer in this area or they may be from groundwater under the manured field. The geologic field logs (Appendix 1) indicate that the single sampling point in the PGW is installed in a fine sandy loam that has light gray and black laminations. Therefore, the low $\text{NO}_3\text{-N}$ and high $\text{NH}_4\text{-N}$ concentrations in PGW could be due to denitrification. Phosphorus concentrations are fairly low in the PGW (Table 5-2), which, combined with the low NO_3 concentrations and gray (i.e. unoxidized) sediments, is consistent with less contamination in the PGW.

Agriculturally impacted groundwater in unconfined, fine to medium grained lacustrine aquifers in the LNID is characterized by elevated concentrations of NO_3 , Cl, Na, and SO_4 (above background) and low levels of dissolved oxygen (Table 5-3; Rodvang et al., 1998). Average concentrations of $\text{NO}_3\text{-N}$, Ca, Mg, HCO_3 , Cl, Na, K, and NH_4 in FGW at the Battersea site are comparable to regional, agriculturally impacted groundwater. However, DO concentrations (2.7 mg L^{-1}) are five times higher than those sampled elsewhere in the LNID (0.5 mg L^{-1}). The saturated thickness of the sandy aquifer at the Battersea site is 1-2 m on average, whereas the sites sampled by Rodvang et al. (1998), average several meters in thickness. The relative thinness of the surficial aquifer at this site would permit transport of oxygen throughout the aquifer, resulting in higher DO concentrations than might be expected in agriculturally impacted water. In spite of the elevated DO concentrations, the FGW is characteristic of agriculturally impacted groundwater in the LNID.

5.2.3 Geochemical Correlations

A simple linear regression analysis was conducted on the geochemical groundwater, seepage water, and surface water data. All data from the PGW and cation data from surface water was excluded because the data set was limited to 2 or 3 points per ion. This resulted in r^2 values of 1, regardless of the likelihood of there being a statistically significant relationship. Data from MLS 29 & 30 have also been excluded due to the naturally elevated Cl and SO_4 concentrations that could mask agricultural impacts. Correlations are

considered statistically significant if the r^2 -value is equal to or greater than 0.25 ($r \pm 0.5$). This value was arbitrarily selected to ensure that at least half of the data set conformed to the relationship

Nitrate and chloride concentrations are strongly correlated in groundwater (Figure 5-4; Table 5-4), seepage water (Table 5-5), and surface water (Table 5-6), suggesting the ions originate from a single source. Although NO_3 can be derived from several sources, including manure and fertilizer application, septic systems, atmospheric emissions, and natural geologic processes, manure is the most likely source at this site. Sodium chloride is commonly added to beef cattle feed and in areas of irrigation and low precipitation, like the LNID, salt accumulation due to manure application can be a problem (Eghball & Power, 1994). Previous work in the LNID found a similar correlation between $\text{NO}_3\text{-N}$ and Cl concentrations in groundwater, which was attributed to manure application (Rodvang et al., 1998). The negative correlation between NO_3 and Fe is consistent with redox controls on $\text{NO}_3\text{-N}$ concentrations.

There appears to be two separate trends in Figure 5-4 related to chloride concentrations. The FGW at lower Cl concentrations and data from MLS 29 & 30 at higher concentrations. The latter are completed in finer-textured sediments that contain groundwater with higher natural Cl concentrations. The two trendlines are offset approximately 55 mg L^{-1} but have similar slopes. This suggests that although there is higher natural Cl at MLS 29 & 30, the addition of Cl and NO_3 from manure has been at a similar rate as in the field groundwater.

Reduced N (NH_4 and TKN) in groundwater (TKN only), seepage, and surface water samples is positively correlated with P concentrations (Figure 5-5). This is typical of reducing conditions. Nitrate is reduced and phosphorus becomes more mobile due to the dissolution of the sorption complexes (Moore Jr. & Reddy, 1994).

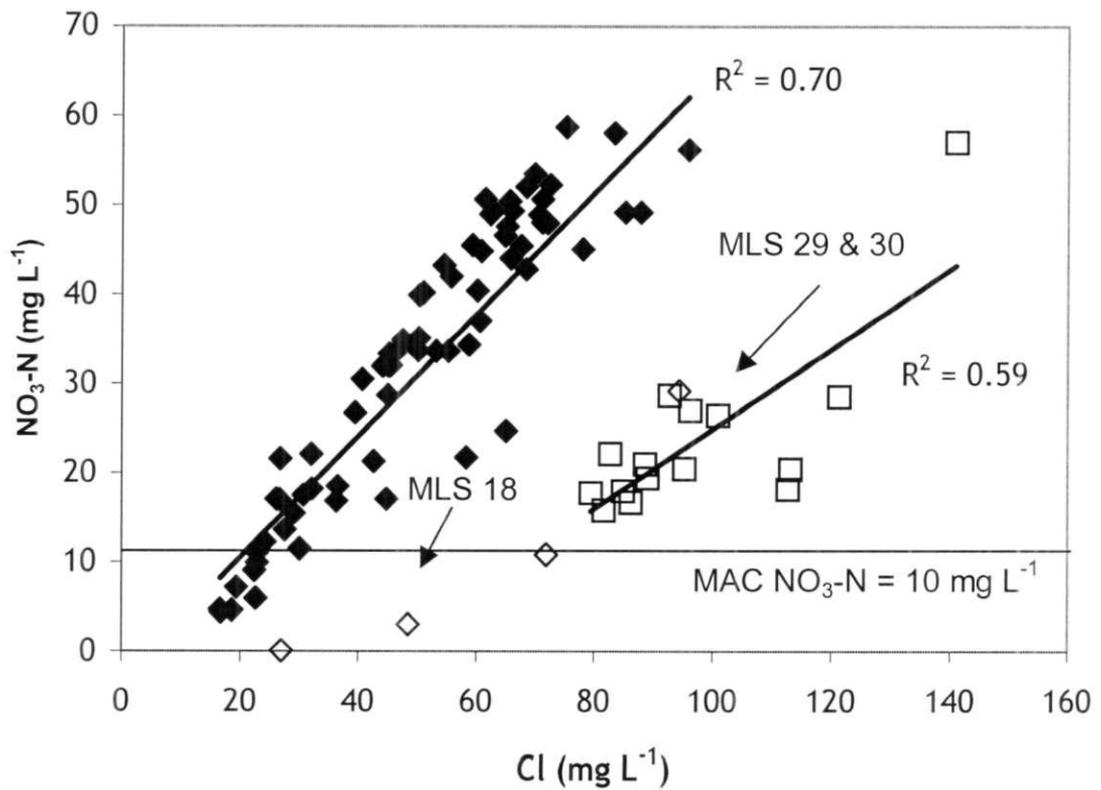


Figure 5-4: Relationship between NO_3 and Cl concentrations in the field groundwater. Note the separation of data from MLS 18, 29 & 30 from the overall trend due to higher chloride concentrations.

Table 5-4: Correlations between nutrients, anions, and cations in field groundwater (FGW) expressed as r^2 value. Negative correlations are underlined. Significant correlations ($r^2 \geq 0.25$) are bolded.

	NO ₂	NH ₄	TKN	PO ₄	TP	DP	DOC	SO ₄	Cl	HCO ₃	Ca	Na	K	Mg	Fe
n	(73)	(73)	(73)	(73)	(73)	(73)	(72)	(73)	(73)	(73)	(14)	(14)	(14)	(14)	(22)
NO ₃	<u>0.03</u>	0	<u>0.08</u>	<u>0.11</u>	<u>0.15</u>	<u>0.10</u>	0	<u>0.02</u>	0.70	0.30	0.04	0.29	0.07	0.70	0.27
NO ₂		0.19	0.39	0.35	0.16	0.37	0.22	0	0.02	0.02	<u>0.19</u>	<u>0.08</u>	0.01	<u>0.09</u>	0.36
NH ₄			0.04	0.02	0.01	0.02	0.17	0.18	0.01	<u>0.01</u>	<u>0.06</u>	<u>0.17</u>	0.05	<u>0.06</u>	0.47
TKN				0.83	0.76	0.81	0.08	0.01	0	<u>0.01</u>	0	<u>0.11</u>	0.14	0	0.35
PO ₄					0.81	0.98	0.06	0.01	0	0.01	0.12	0.46	0	0.13	0.64
TP						0.77	0.05	0.01	<u>0.02</u>	<u>0.01</u>	<u>0.05</u>	0.45	0.03	<u>0.20</u>	0.51
DP							0.09	0.01	0	<u>0.01</u>	<u>0.10</u>	0.44	0.01	<u>0.13</u>	0.63
DOC								0.05	0.02	0.04	0.11	0.03	0.67	0.06	<u>0.05</u>
SO ₄									0	0.29	0.61	0	0.31	0.05	0
Cl										0.33	0.07	0.07	<u>0.01</u>	0.78	<u>0.03</u>
HCO ₃											<u>0.12</u>	0.10	<u>0.02</u>	0.23	<u>0.02</u>
Ca												0.03	0.15	0.16	0.03
Na													0.08	0.13	0.41
K														0.01	<u>0.04</u>
Mg															<u>0.11</u>

Table 5-5: Correlation between nutrients, anions, and cations in seepage water expressed as r^2 values. Negative correlations are underlined. Significant correlations ($r^2 \geq 0.25$) are bolded.

n	NO ₃ (188)	TKN (159)	PO ₄ (183)	TP (159)	DP (159)	Cl (188)	HCO ₃ (188)	Ca (15)	Na (15)	K (15)	Mg (15)	Fe (9)
NO ₃		<u>0.02</u>	<u>5E-04</u>	<u>0.024</u>	<u>0.01</u>	0.37	1E-04	0.015	0.037	<u>0.014</u>	PE-04	0.007
NO ₂		0.003	0.004	0.023	0.016	0.18	0.003	0.046	0.24	0.003	0.058	0.38
NH ₄		0.84	0.35	0.72	0.50	0.052	0.009	0.48	0.65	0.058	0.47	0.097
TKN			0.50	0.69	0.51	0.071	0.008	0.33	0.44	0.54	0.35	0.20
PO ₄				0.77	0.99	0.006	0.006	0.45	0.43	0.13	0.52	0.28
TP					0.77	0.014	0.010	0.47	0.59	0.54	0.59	0.45
DP						0.002	0.007	0.44	0.43	0.58	0.53	0.26
DOC						0.003	0.005	0.35	0.68	0.14	0.29	0.23
SO ₄						0.34	0.47	0.43	0.29	0.093	0.36	0.009
Cl							0.09	0.18	0.24	4E-05	0.14	<u>0.002</u>
HCO ₃								0.62	0.60	0.26	0.75	0.45
Ca									0.67	0.11	0.94	0.31
Na										0.08	0.72	0.47
K											0.075	0.18
Mg												0.41

Table 5-6: Correlations between nutrients, anions, and cations in surface water expressed as r^2 values. Negative correlations are underlined. Significant correlations ($r^2 \geq 0.25$) are bolded.

n	NO ₃ (69)	NO ₂ (69)	NH ₄ (68)	TKN (55)	PO ₄ (66)	TP (55)	DP (56)	DOC (50)	SO ₄ (69)	Cl (69)	CO ₃ (69)	HCO ₃ (69)
NO ₃		0.43	0.23	0.55	<u>0.0021</u>	0.031	0.14	0.42	0.78	0.85	0.002	0.76
NO ₂			0.029	0.15	0.0007	0.056	0.23	0.15	0.41	0.46	0.088	0.26
NH ₄				0.50	<u>0.0012</u>	0.63	0.0002	0.26	0.38	0.27	<u>0.074</u>	0.58
TKN					0.0006	0.32	0.11	0.64	0.80	0.75	0.047	0.69
PO ₄						0.0022	<u>0.0025</u>	3E-06	<u>0.0061</u>	<u>0.0012</u>	<u>0.0062</u>	<u>0.009</u>
TP							0.22	0.35	0.31	0.14	<u>0.016</u>	0.48
DP								<u>0.069</u>	0.11	0.022	0.034	0.024
DOC									0.60	0.61	<u>0.0028</u>	0.59
SO ₄										0.89	0.0067	0.79
Cl											0.0057	0.75
CO ₃												<u>0.057</u>

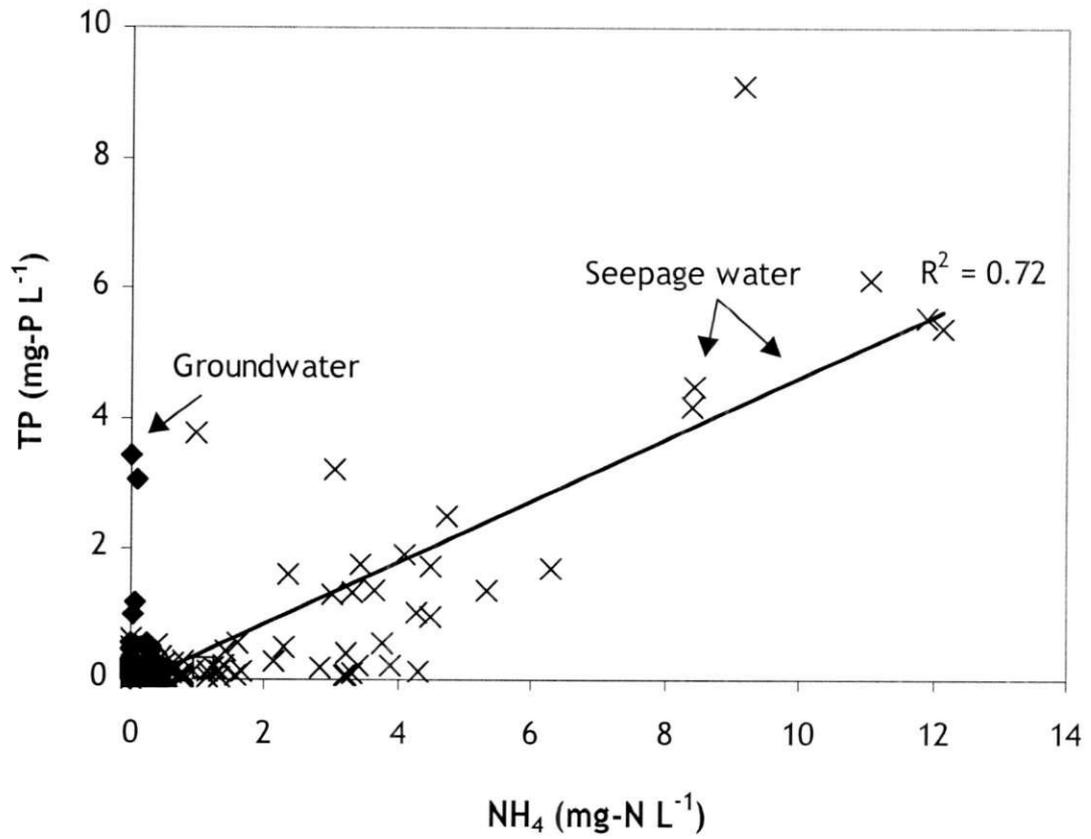


Figure 5-5: Relationship between NH_4 and TP concentrations in groundwater, and seepage water at the Battersea site. The trendline is calculated for seepage water data.

Unlike NO_3 , TP, DP, and $\text{PO}_4\text{-P}$ concentrations are not significantly correlated with chloride in groundwater under the manured field (Figure 5-6). The lack of correlation may suggest that P and Cl are not derived from the same source (manure). However, it is more likely that the lack of correlation is caused by non-conservative behavior since there is evidence that P is derived from a surface source.

Phosphorus concentrations in precipitation in southern Alberta are negligible. Although the main source for P at this site is thought to be manure, some P may be naturally present in the aquifer (geologic P). Phosphorus concentrations, particularly PO_4 and DP, typically decrease with depth below the water table (Figure 5-7), whereas $\text{NO}_3\text{-N}$ and Cl concentrations remain constant (Figure 5-8) due to their higher mobility in groundwater. The P/Cl ratios follow the same trend as P with depth (Figure 5-9). Higher concentrations of P in the upper region of the aquifer coupled with a decreasing P/Cl ratio with depth indicate that P has been derived from the surface. $\text{NO}_3\text{-N}$ and Cl have leached to greater depths. The PO_4/TP ratio also decreases with depth in the aquifer (Figure 5-10) suggesting that some of the TP may be natural.

A comparison with data from uncontaminated groundwater in the LNID (Rodvang, personal communication; Joan Rodvang, Hydrogeologist, Alberta Agriculture Food and Rural Development) indicates that P at the Battersea site is not geologic in origin. Furthermore, the decrease in PO_4 with depth below the water table suggests it is mainly derived from agriculture. The strong correlation between NO_3 and Cl in the surficial aquifer (Figure 5-2) indicates they are both derived from manure. Although P in the aquifer is not strongly correlated with Cl, the data suggests this is due to depth controls. Chloride has leached to greater depths than PO_4 , causing the P/Cl ratio to decrease with depth (Figure 5-6). Although geologic sources may contribute a small proportion of the TP, the data indicates there is a significantly higher contribution from agricultural sources than natural ones.

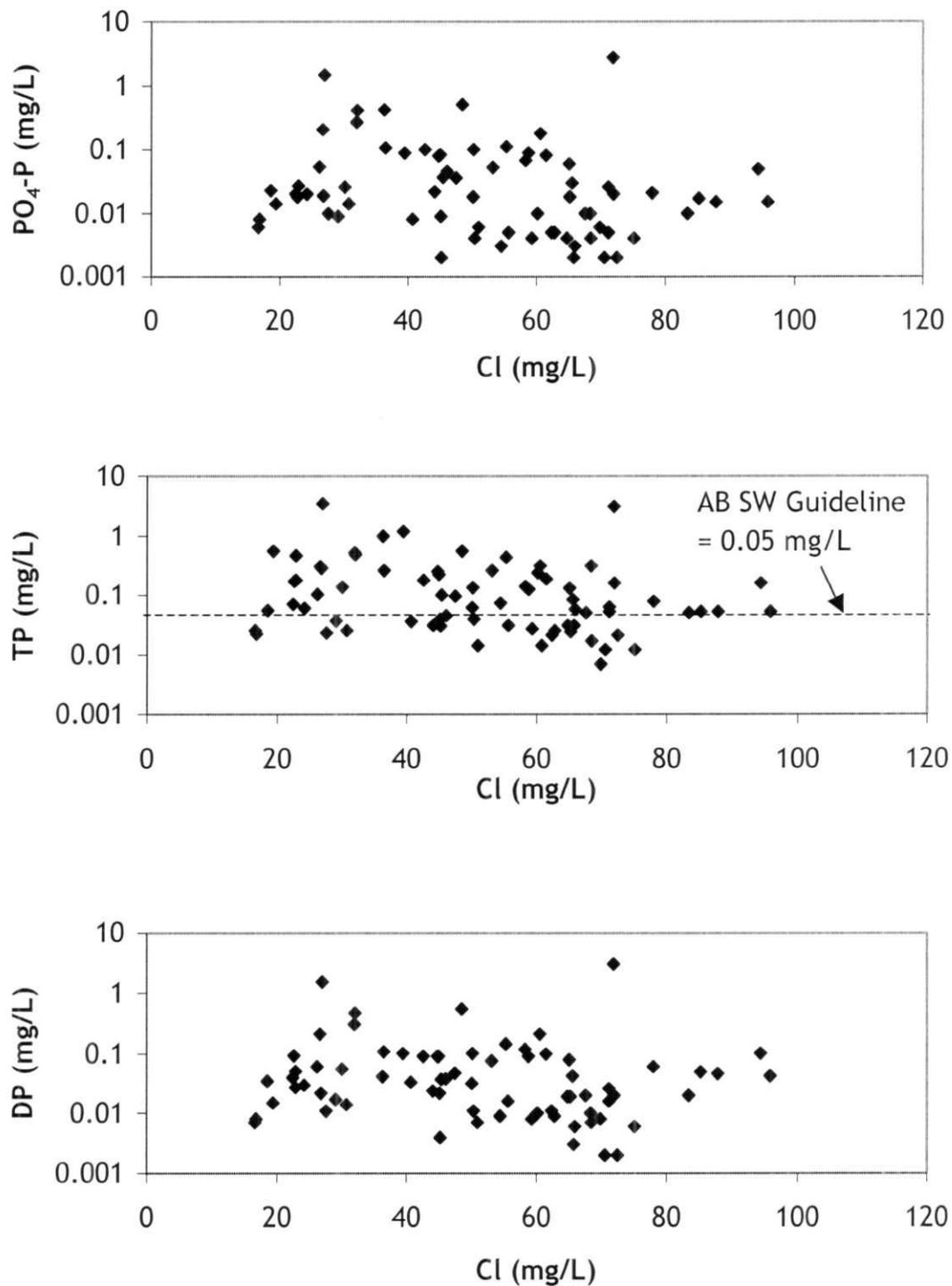


Figure 5-6: Relationship between P and Cl in groundwater at the Battersea site. Note the lack of correlation between the P species and Cl concentrations.

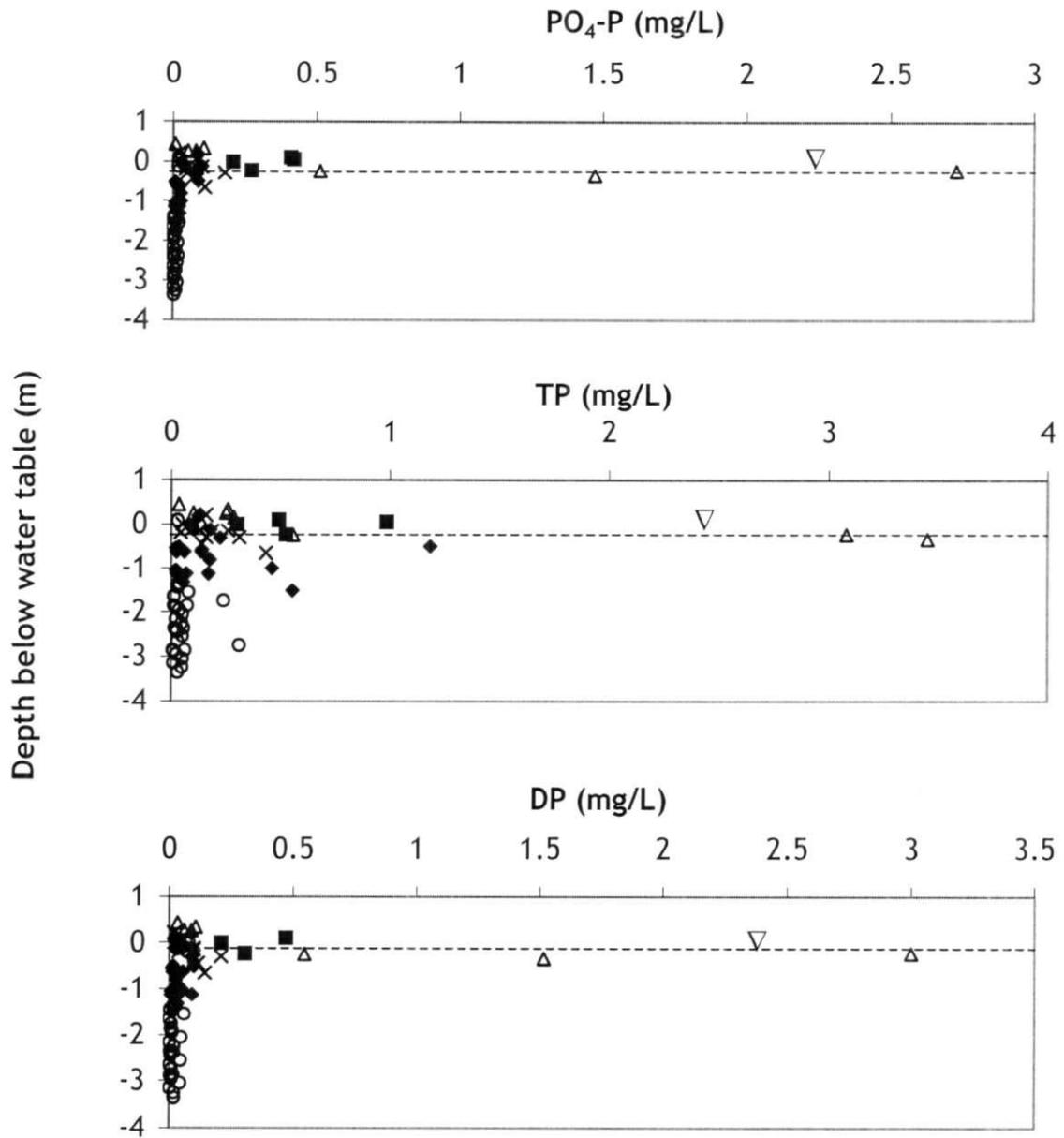


Figure 5-7: Variation in P concentrations with depth below the water table. Concentrations of P are highest at the water table and decrease with depth. (◆ = MLS 16; ■ = MLS 17; △ = MLS 18; ○ = MLS 27/20; X = MLS 21.

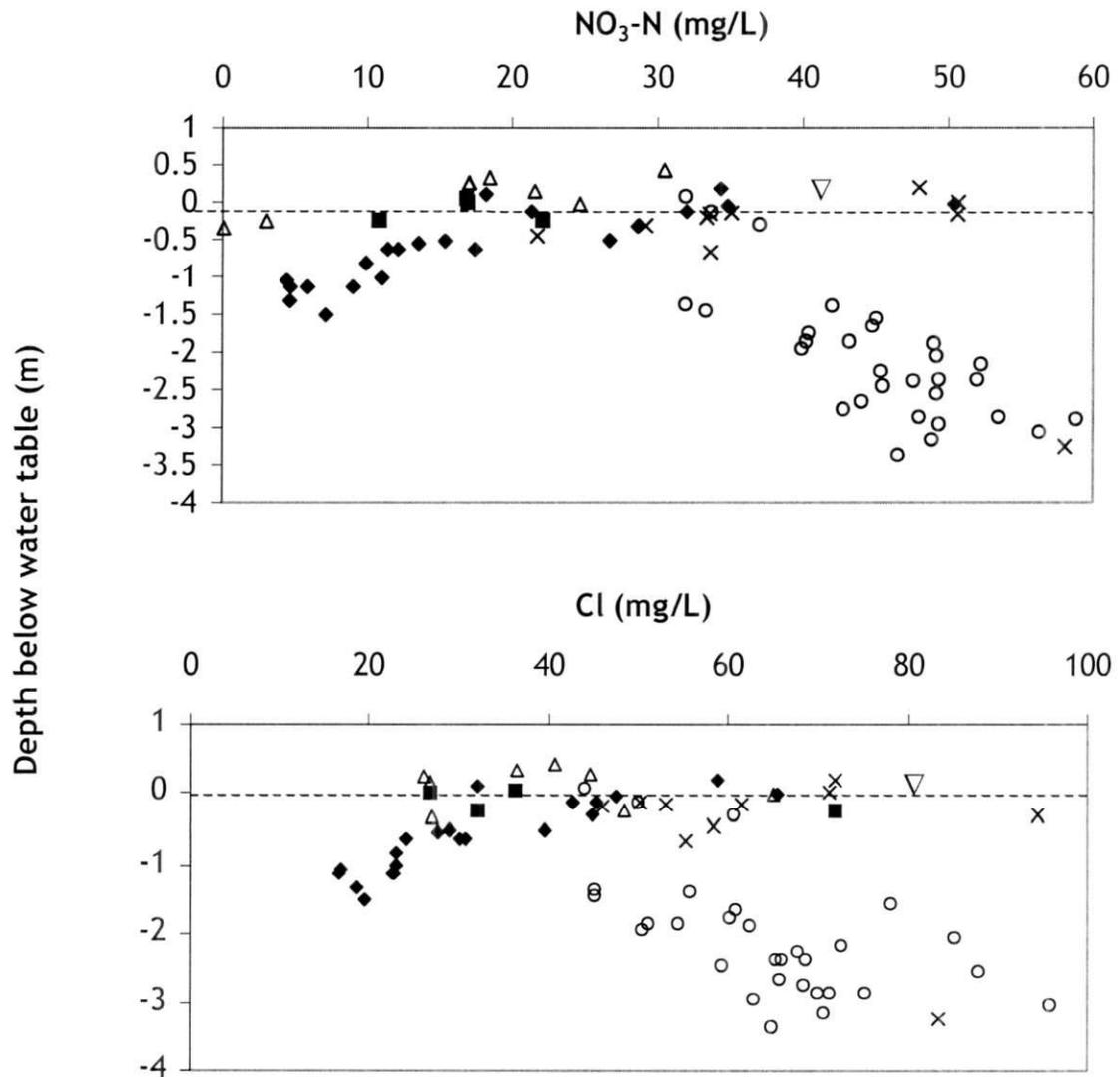


Figure 5-8: Variation in NO₃-N and Cl concentrations with depth below the water table. ◆ = MLS 16; ■ = MLS 17; △ = MLS 18; o = MLS 27/20; X = MLS 21.

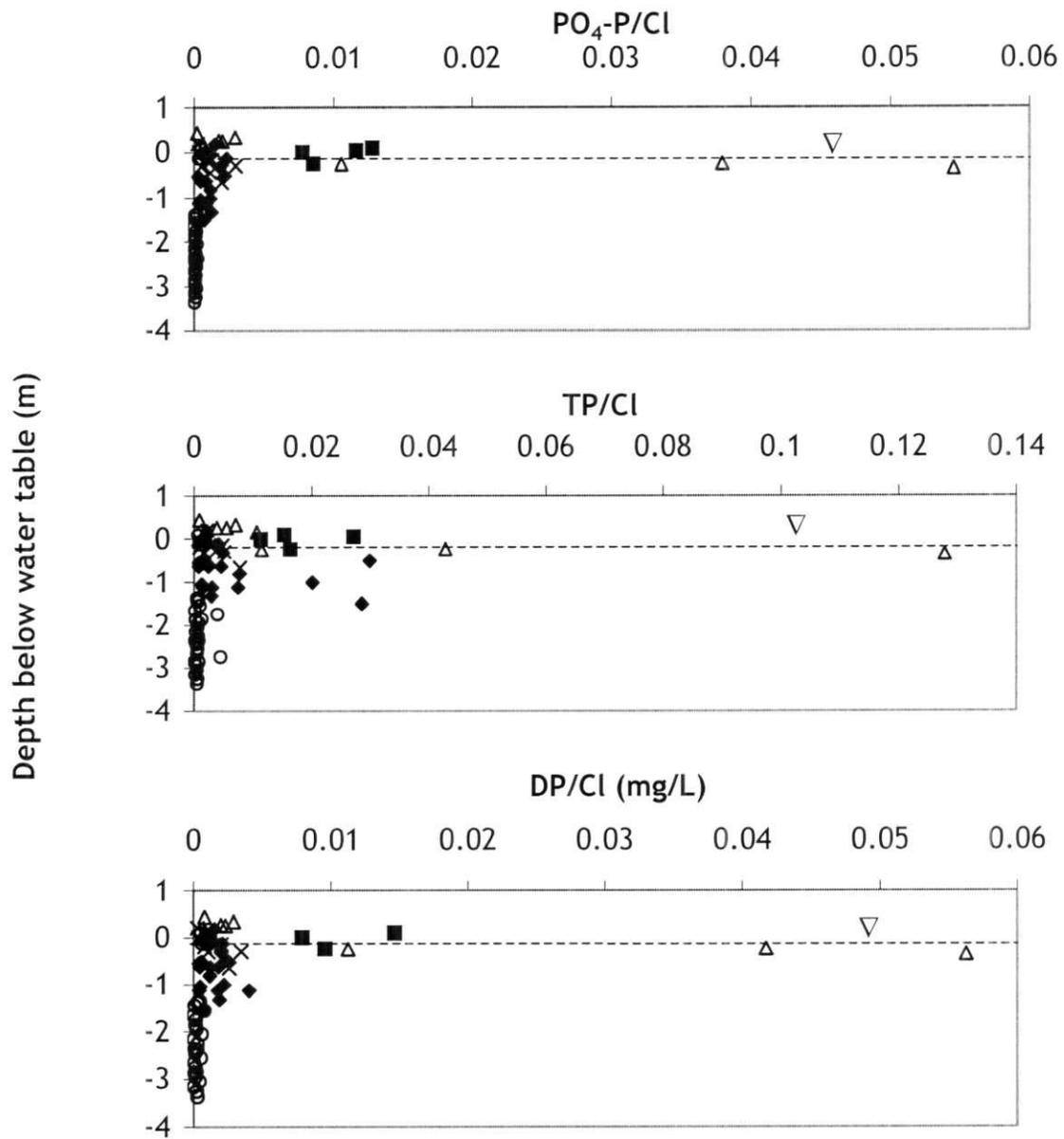


Figure 5-9: Variation in the P/Cl ratios with depth below the water table. \blacklozenge = MLS 16; \blacksquare = MLS 17; \triangle = MLS 18; \circ = MLS 27/20; \times = MLS 21.

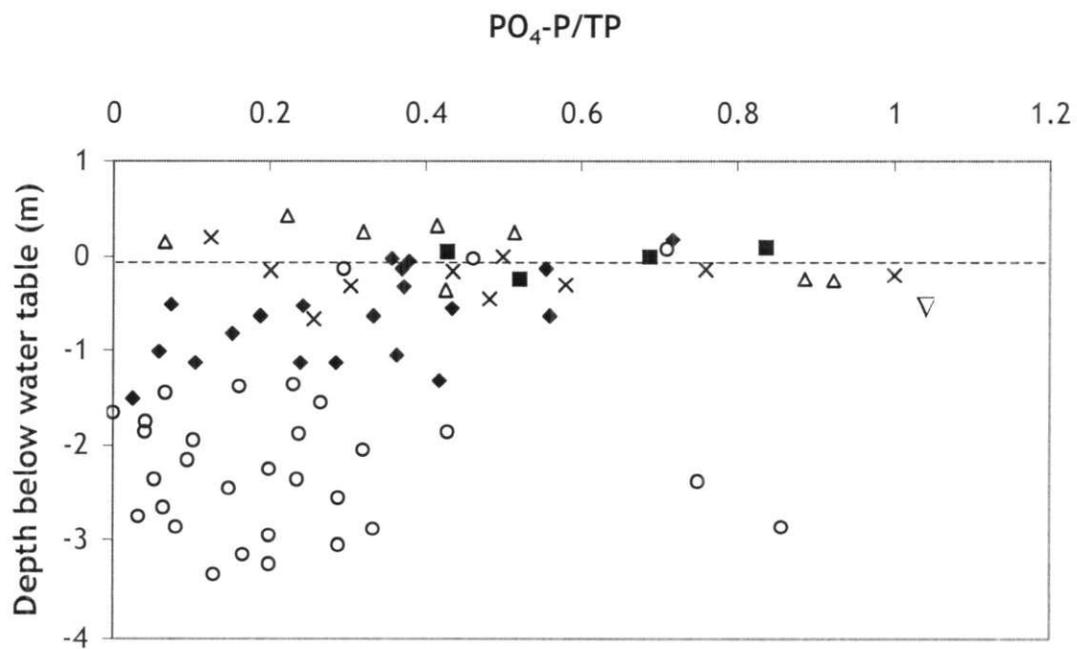


Figure 5-10: Variation in PO₄-P/TP ratio with depth below the water table.

◆ = MLS 16; ■ = MLS 17; △ = MLS 18; ○ = MLS 27/20; X = MLS 21.

Phosphorus is positively correlated with groundwater and seepage water Fe concentrations (Figure 5-11; Tables 5-4 & 5-5) although these correlations may be affected by a few data points. Increased concentrations of Fe are common in reducing environments due to the dissolution of Fe oxyhydroxide coatings and Fe oxide minerals (Moore Jr. & Reddy, 1994). Reducing environments also favor P release due to dissolution of sorption complexes (Figure 5-12). There was no relationship between P and pH of any waters.

5.2.4 Water Quality - Comparison with Federal and Provincial Guidelines

Ground-, seepage, and surface water show evidence of agricultural impact, and all waters exceeded some water quality criteria (Table 5-7). Common manure contaminants include NO_3 , P, SO_4 , Cl, and pathogenic and nonpathogenic microorganisms (Gosselin et al., 1997; Macler & Merkle, 2000). All of these, where present in excess, can have detrimental effects on the utility of the water resource. As a result, maximum allowable concentrations (MAC) for drinking water quality have been set for health (NO_3 , SO_4 , microorganisms), and aesthetic (Cl) reasons. Phosphorus does not pose a known health threat. However, excess P in surface water can cause eutrophication, thereby minimizing the recreational and resource potential of the surface water body. Therefore, P concentrations in both ground- and surface water have been compared against the Alberta provincial surface water guideline (0.05 mg L^{-1} as TP).

5.3 Chloride

5.3.1 Variation Along the Groundwater Flow Path

Groundwater Cl concentrations decrease along the flow path (Figure 5-13). Since Cl is conservative, this decrease is probably due to mixing with Cl-poor water. Isotopic analysis of the $\delta^{18}\text{O}$ content of the groundwater suggest that the higher Cl groundwater under the manured field may be mixing with

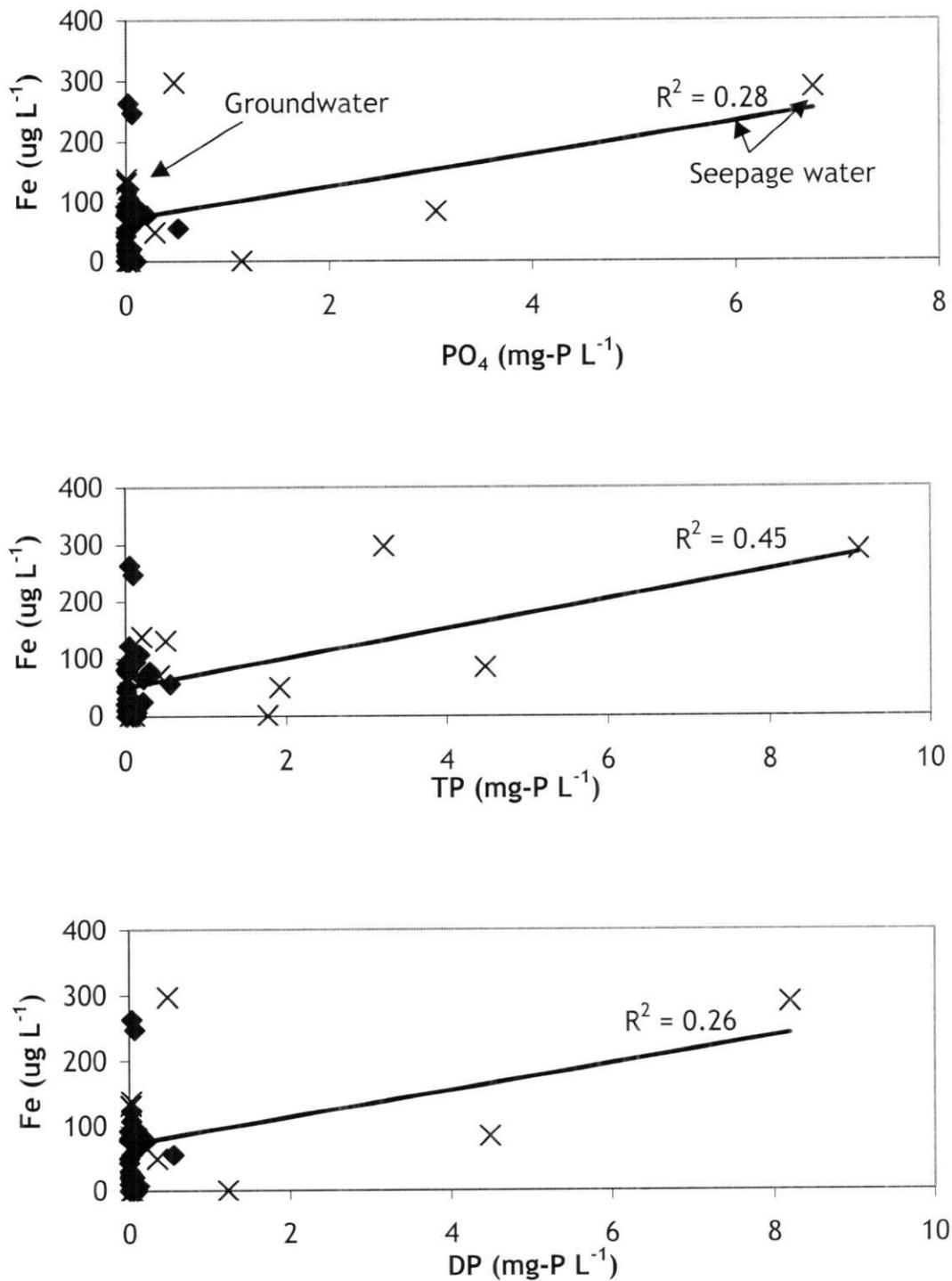


Figure 5-11: Relationship between P and Fe concentrations in groundwater and seepage water. Trendlines are included for seepage water data.

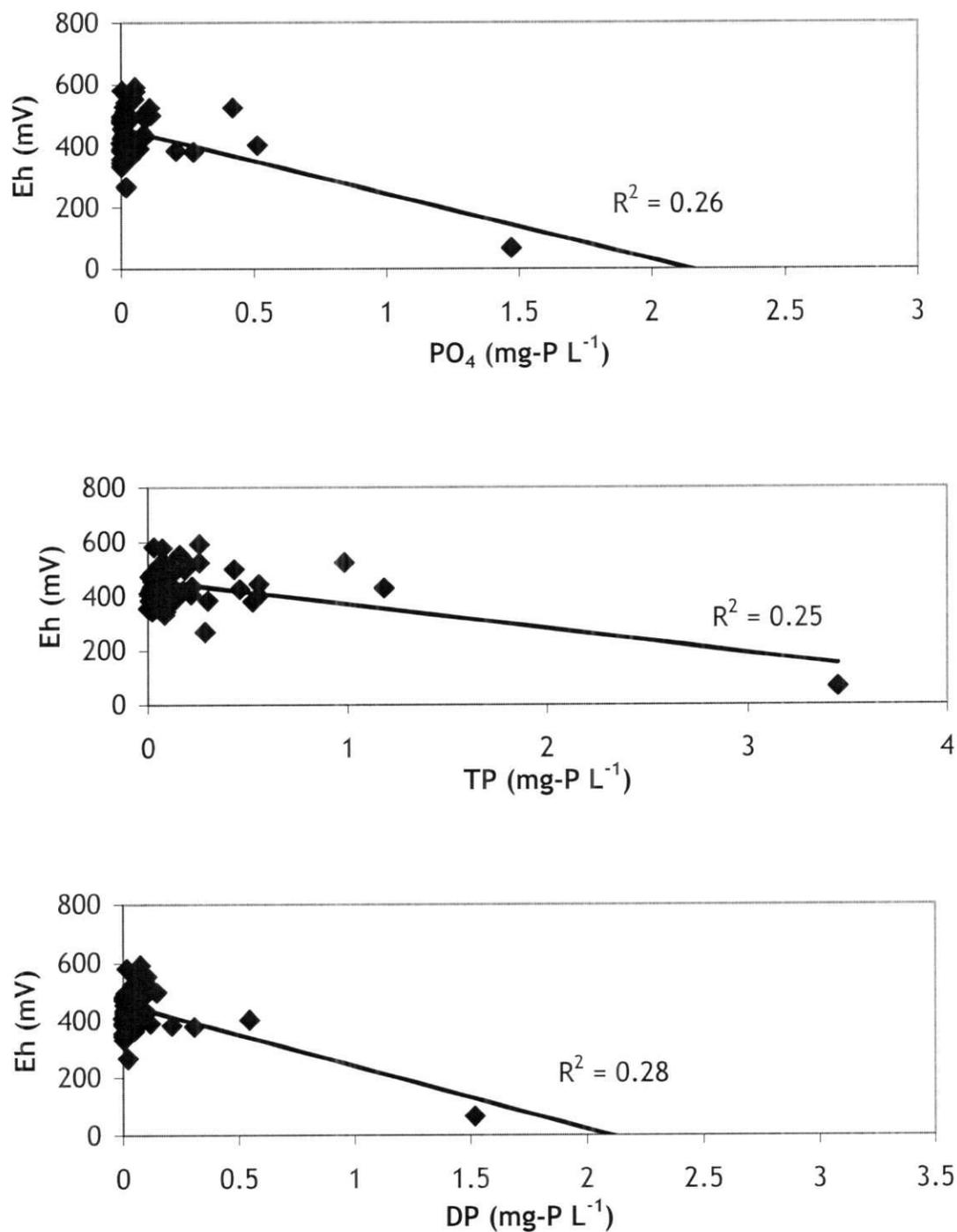


Figure 5-12: Relationship between groundwater P concentrations and Eh.

Table 5-7: Percentage of water samples that exceed the MAC or surface water guideline (as mg L⁻¹) for common manure contaminants. (maximum concentration, minimum concentration).

	NO ₃ -N	TP (as P)	SO ₄	Cl	TC	FC
Guideline	10	0.05 ¹	500	250 ²	0 ³	0 ³
Background⁴	0	n.a. ⁵	15.5	0	n.a.	n.a.
FGW	90 (59, 0.07)	68 (3.5, 0)	27 (2618, 226)	0 (141, 17)	74 (30, 0)	0 (0, 0)
PGW	0 (2.5, 1.9)	67 (0.19, 0.027)	100 (1499, 620)	0 (39, 20)	n.a.	n.a.
SM	8 (49, 0)	66 (9.11, 0)	52 (5198, 0)	0 (174, 0)	100 (117, 2)	67 (65, 0)
SW	21 (12, 0.09)	32 (0.198, 0.02)	48 (1659, 39)	0 (75, 0)	100 (100, 76)	100 (155, 156)

¹ Alberta Interim Surface Water Guideline (AE, 1999).

² Aesthetic objective

³ concentrations as cfu (colony forming units)/100 mL

⁴ (Rodvang et al., 1998)

⁵ n.a. = not available

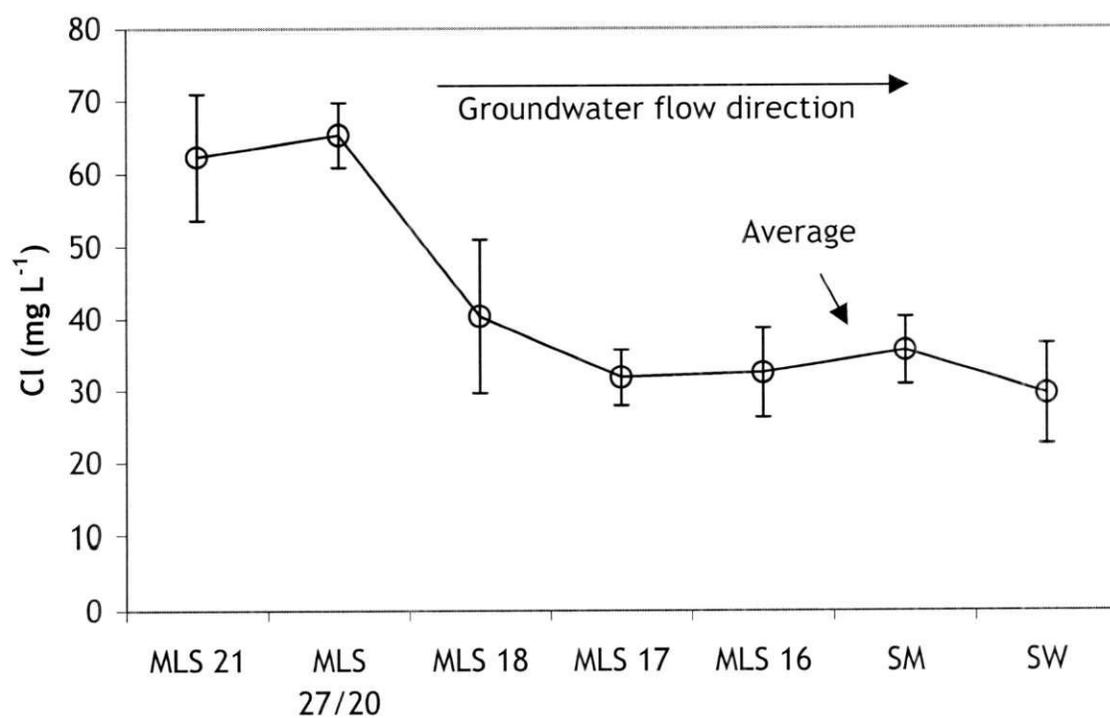


Figure 5-13: Variation in Cl concentrations along the groundwater flow path. The error bars represent the 95% confidence interval.

older, deeper, isotopically depleted groundwater with lower chloride concentrations (J.E. McCallum, M.Sc. candidate, Department of Geology & Geophysics, University of Calgary, in progress). A topographic low in the upper surface of the clay aquitard is located under MLS 18 (Figure 4-4). This, coupled with the dominantly upward hydraulic gradients at MLS 17 & 18 (Table 4-4), suggests that the point of discharge for deeper groundwater to the unconfined aquifer could be located in this region. This is consistent with the trend in Cl concentrations shown in Figure 5-13.

A similar Cl trend (i.e. decreasing concentrations along a flow path) was found at a site in Connecticut (Clausen et al., 2000). At this site, chloride concentrations in the sandy surficial aquifer decreased in the last 2.5 m of groundwater flow prior to discharging into a stream. The decreased Cl concentrations were attributed to mixing of Cl-rich groundwater with upwelling Cl-poor groundwater from an underlying till.

5.3.2 Variation in Seepage Meters

Average chloride concentrations at the Battersea site are highest in the field groundwater, lowest in surface water and intermediate in seepage water (Table 5-2). Since Cl is conservative, the intermediate concentrations in the seepage water are most likely due to mixing of groundwater (Cl-rich) and surface water (Cl-poor) during bank storage. Dilution of groundwater along the flow path may also be affecting concentrations in the seepage water.

5.4 Nitrogen

5.4.1. Variation along the Flow Path

Nitrate and ammonium concentrations are variable as groundwater flows towards the Battersea Drain (Figure 5-14). Likewise, $\text{NO}_3\text{-N:Cl}$ and $\text{NH}_4\text{-N:Cl}$ molar ratios are also variable along the flow path. Since Cl is conservative in groundwater, Cl molar ratios have been plotted to remove the dilution effects

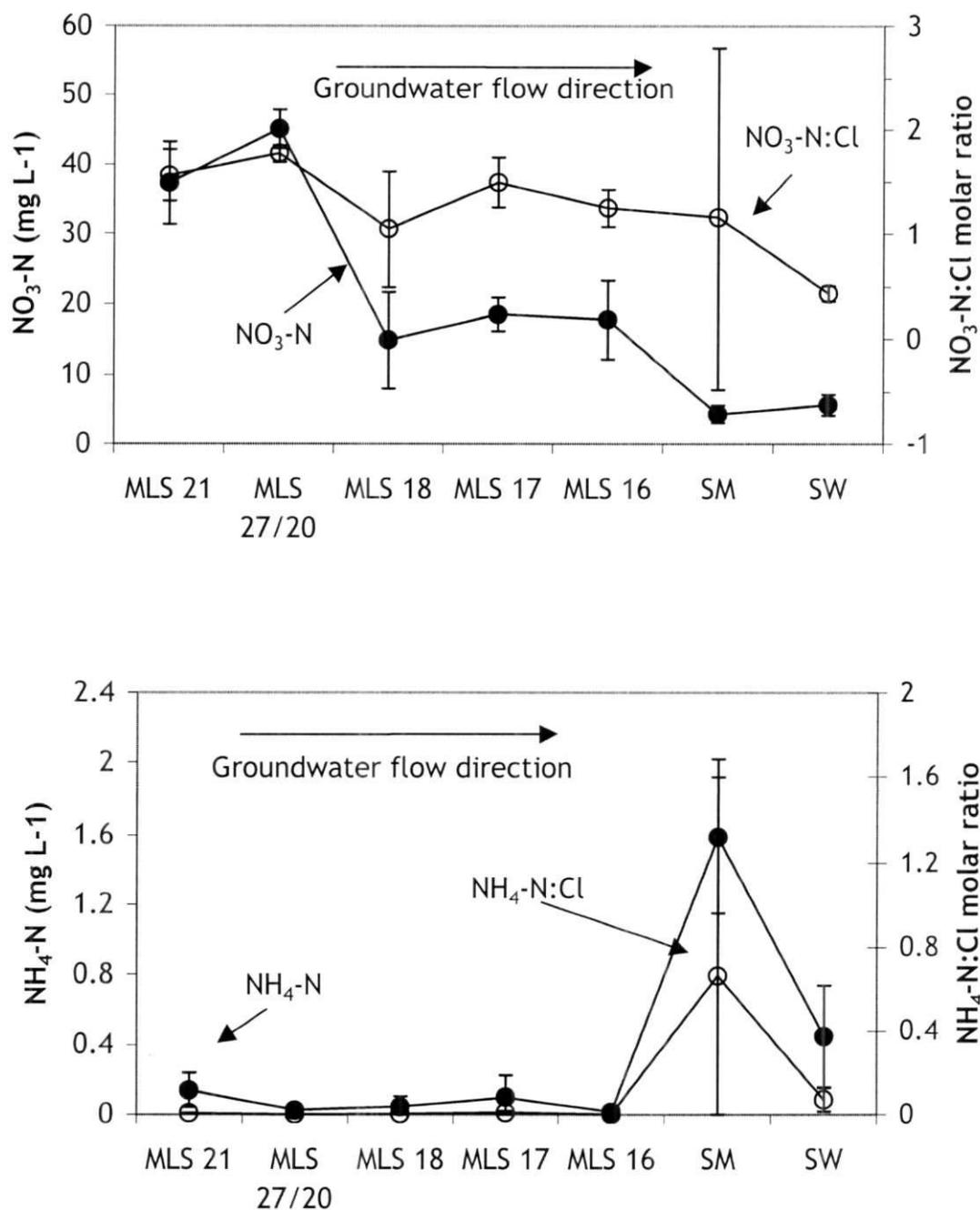


Figure 5-14: Variation in NO₃-N and NH₄-N concentrations and NO₃-N:Cl and NH₄-N:Cl molar ratios along the groundwater flow path. Error bars represent 95% confidence interval.

from upwelling groundwater at MLS 18.

Average groundwater $\text{NO}_3\text{-N}$ concentrations increase, then significantly decrease as groundwater flows in the aquifer sediments. There is less variation in the molar ratio plot suggesting that the decrease is due, in part, to dilution of groundwater $\text{NO}_3\text{-N}$ concentrations. Average $\text{NO}_3\text{-N}$ concentrations are lower in the seepage and surface water than in the aquifer. Average groundwater $\text{NH}_4\text{-N}$ concentrations tend to increase when $\text{NO}_3\text{-N}$ concentrations decrease, with the largest increase in the seepage water. Concentrations in the seepage water are highly variable suggesting the local redox conditions at the seepage meters are also variable. The coincident variation between $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations suggests that NO_3 is being locally reduced to NH_4 in the aquifer (near MLS 18) and in the seepage meters.

5.4.2 Evidence for Denitrification

Nitrogen is predominantly present as NO_3 in groundwater at the Battersea site (Table 5-2). Nitrate is the dominant form of N in oxic, non-reducing groundwater, and therefore, would be expected to predominate at this field site. Nonetheless, significant levels of $\text{NO}_2\text{-N}$ (max: 11 mg-N L^{-1}) and $\text{NH}_4\text{-N}$ (max: 0.49 mg L^{-1}) were found in groundwater suggesting that small patches of less oxic, more reducing groundwater may exist in the aquifer. Groundwater upwelling near MLS 18 (as indicated by ^{18}O isotopes and decreasing Cl concentrations (Figure 5-13)) could cause locally reducing conditions at this point. Reduced sediments were found at MLS 18 during drilling. Alternatively, small patches rich in organic matter have been hypothesized to be 'hotspots' for NO_3 reduction (Jacinthe et al., 1998). Whatever the actual cause, NO_3 reduction is not complete (N is conserved) and may indicate that dissimilatory NO_3 reduction is occurring.

Nitrate, unlike chloride, is non-conservative in groundwater systems and concentrations may be naturally attenuated by denitrification. The two most prevalent pathways for denitrification are via the reduction of organic carbon

(heterotrophic denitrification) or oxidation of reduced sulfur (autotrophic denitrification). Denitrification may occur either across a redoxcline (i.e. with depth) or along a groundwater flow path (i.e. where flow paths are dominantly horizontal). No distinct redoxcline was found in sediments at the Battersea site (Appendix 1), but several of these trends occur along the groundwater flow path.

Nitrate concentrations and molar ratios are variable (Figure 5-14), but generally decrease along the flow path. At the same time, the SO_4^- and HCO_3^- :Cl molar ratios gradually increase in the aquifer, with a large, but variable increase as water is discharged to the Battersea Drain (i.e. in the seepage meters) (Figure 5-15). Sulfate and bicarbonate are produced during autotrophic and heterotrophic denitrification, respectively (Tables 1-2 & 1-3).

Since Cl is conservative in groundwater, and derived from the same source (manure) as NO_3^- , a changing molar ratio is assumed to remove the effects of dilution from upwelling groundwater and reflect changes in the concentration of the non-conservative element. The NO_3^- :N:Cl molar ratio decreases by 20% in the aquifer and a further 8% prior to discharging to the surface water (Table 5-8, Figure 5-14). The SO_4^- :Cl and HCO_3^- :Cl molar ratios increased 50% and 111%, respectively, in the monitored portion of the aquifer and a further 850% and 550% prior to discharging to the Battersea Drain. The observed decrease in NO_3^- :N:Cl and increase in SO_4^- :Cl and HCO_3^- :Cl molar ratios in the aquifer region and in seepage meters suggest that both autotrophic and heterotrophic denitrification are occurring.

5.4.3 Heterotrophic Denitrification

Geochemical evidence presented by Rodvang et al. (1998) suggests that denitrification does occur under irrigated, manured fields in the LNID. If heterotrophic denitrification was occurring at the Battersea site, decreased concentrations of DOC and NO_3^- -N would occur in conjunction with increasing concentrations of HCO_3^- . Although the NO_3^- :N:Cl and HCO_3^- :Cl molar ratios do

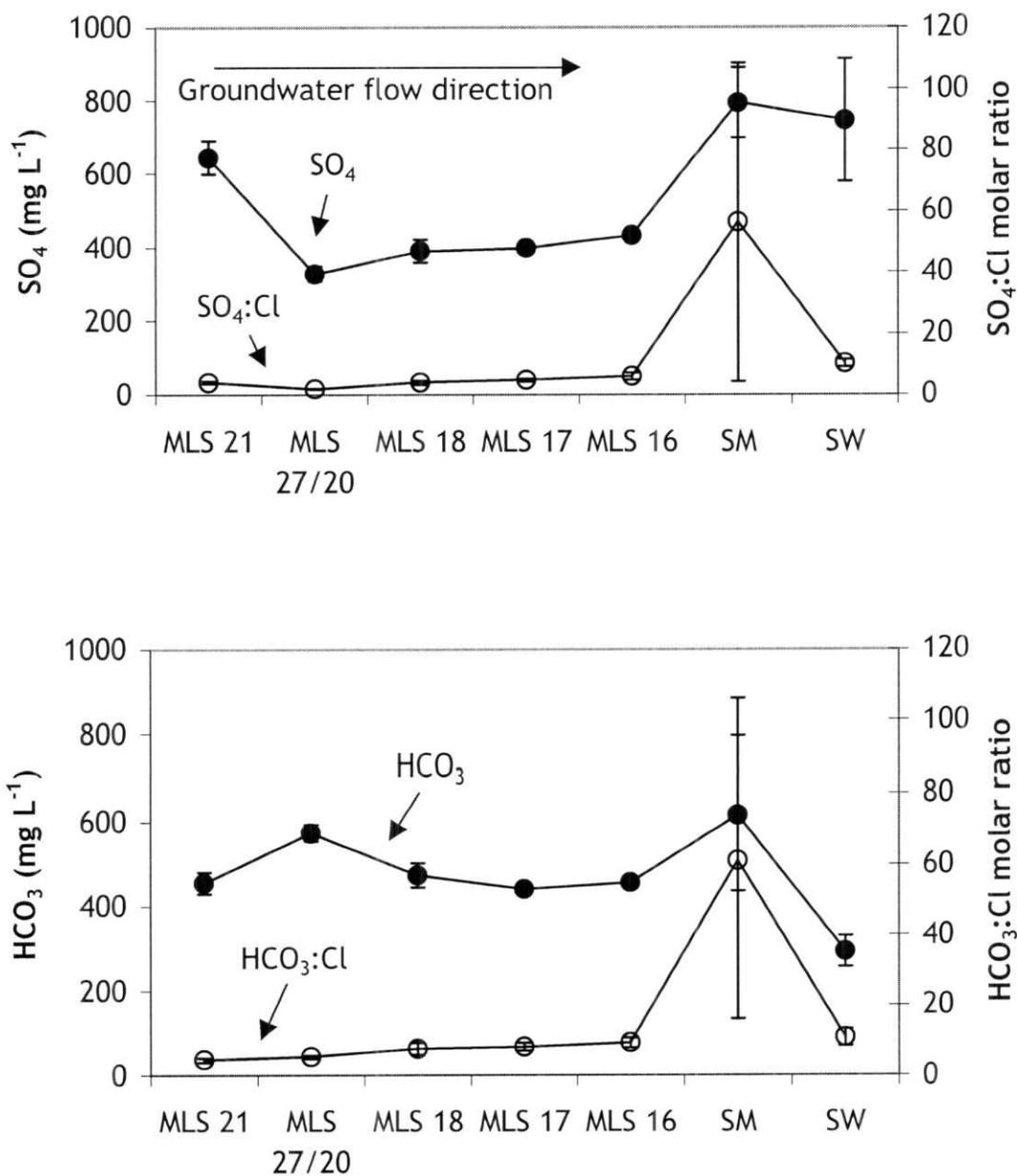


Figure 5-15: Variation in SO_4 and HCO_3 concentrations and $\text{SO}_4:\text{Cl}$ and $\text{HCO}_3:\text{Cl}$ molar ratios along the flow path. Error bars represent 95% confidence interval.

Table 5-8: Average NO₃-N-, SO₄-, HCO₃-, DOC-, and NH₄-N:Cl molar ratios along the groundwater flow path.

	NO ₃ -N:Cl	DOC:Cl	SO ₄ :Cl	HCO ₃ :Cl	NH ₄ -N:Cl
NP21 ¹	1.56	0.63	3.95	4.43	0.0036
NP16 ²	1.25	0.65	5.93	9.39	0.0074
SM ³	1.15	1.70	56.26	61.07	0.12

¹ start of monitored flow path

² end of monitored flow path

³ seepage meters - point of discharge to surface water

conform to this trend (i.e. decrease and increase respectively), there is negligible net change in the DOC:Cl molar ratio along the flow path (Table 5-8).

At the Battersea site, DOC is probably derived from manure with some contribution from plant residues in the soil. Deeper, fine-textured sediments contain groundwater that is higher in DOC (Rodvang et al., 1998). Therefore, upwelling groundwater discharging along the flow path may be increasing DOC concentrations while decreasing Cl concentrations. Although there is an increased DOC:Cl molar ratio near MLS 18, there is no correlation between DOC concentration and $\delta^{18}\text{O}$ suggesting that this is not the source (Figure 5-16).

Organic carbon molecules are typically complex carbon chains and not easily degraded. Therefore, the DOC present in the aquifer may not be labile and therefore not available to act as an electron donor. It is therefore unlikely that heterotrophic denitrification is the dominant process for N attenuation at this site, although it cannot be ruled out. Extremely high SO₄ concentrations in piezometers located beside a feedlot in the LNID were consistent with autotrophic denitrification (Rodvang et al., 1998).

5.4.4. Autotrophic Denitrification

Pyrite oxidation is a biochemical reaction mediated by microorganisms of the family *Thiobacillus* or the genus *Desulfovibrio* or *Desulfotomaculum* (Langmuir, 1997; Table 1-3). It occurs when pyrite and other reduced forms of

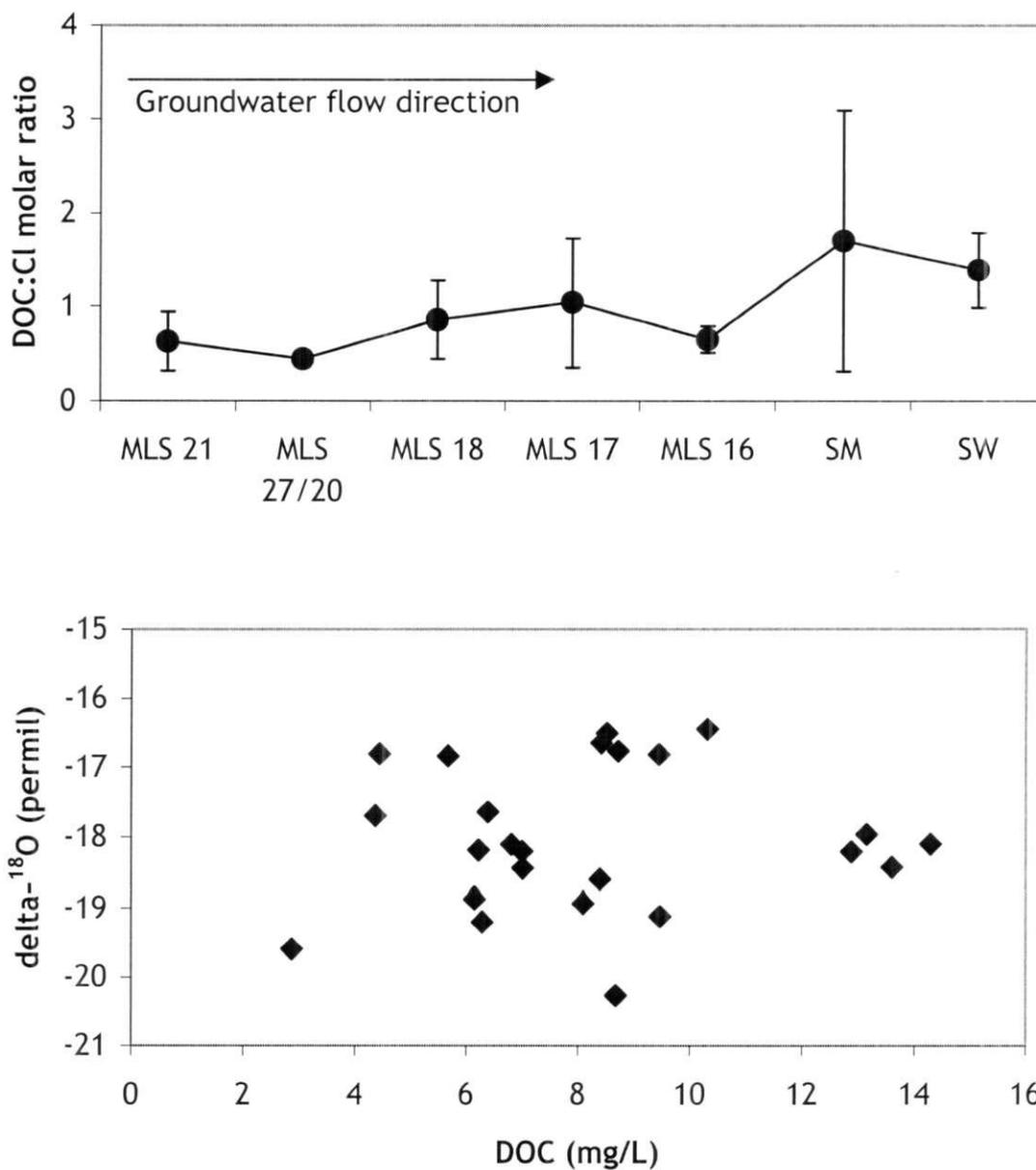


Figure 5-16: Variation in the DOC:Cl molar ratio along the flow path (upper graph) and the relationship between DOC and the $\delta^{18}\text{O}$ of the groundwater. The lack of correlation suggests that increased DOC at MLS 18 is not derived from the upwelling isotopically depleted groundwater.

sulfide are exposed to oxidized species (including NO_3), and can contribute significant amounts of SO_4 to groundwater (Apello & Postma, 1994). Pyrite oxidation with denitrification (autotrophic denitrification) occurs where organic carbon is not available as an electron donor, either as a result of low concentrations or the presence of non-labile forms. It is characterized by decreasing concentrations of NO_3 coupled with increasing concentrations of SO_4 in groundwater.

Although the concentrations of both $\text{NO}_3\text{-N}$ and SO_4 are variable along the flow path, there is less variation in the trends of the molar ratios (Figures 5-14 & 5-15) that suggest that autotrophic denitrification is occurring. Localized decreases in the $\text{NO}_3\text{-N:Cl}$ molar ratio are coincident with increases in the $\text{SO}_4\text{:Cl}$ molar ratio. These occur near MLS 18 and in the seepage meters, although trends in the latter are highly variable. The potential for autotrophic denitrification is further supported by the ^{34}S isotopic analysis.

Sulfur in SO_4 becomes increasingly depleted in ^{34}S as the groundwater SO_4 concentration increases (Figure 5-17). If $\delta^{34}\text{S}$ is plotted against the inverse of the SO_4 concentration, a significant ($r^2=0.29$) linear relationship exists between them. This relationship is typically associated with depletion of the heavier isotope due to oxidation of a more depleted, reduced sulfur species. There is also a trend toward isotopic depletion along the groundwater flow path (Figure 5-18). This coupled with the decreasing $\text{NO}_3\text{-N:Cl}$ and increasing $\text{SO}_4\text{:Cl}$ molar ratios suggests that autotrophic denitrification is attenuating $\text{NO}_3\text{-N}$ concentrations.

Sulfate minerals have very positive $\delta^{34}\text{S}$ values, ranging from +10 to +35 ‰ (Clark & Fritz, 1997). Fertilizers also have quite positive $\delta^{34}\text{S}$ values and reduced S in manure can range from 0 to +40‰ (Bernhard Mayer, Associate Professor, Dept. of Geology & Geophysics, University of Calgary, 2000). The $\delta^{34}\text{S}$ values for S in SO_4 at this site range between -3 and -8 ‰ (Table 5-9). Therefore, it is possible to eliminate dissolution of sulfate minerals as a potential source for the isotopic variation even though their saturation indices

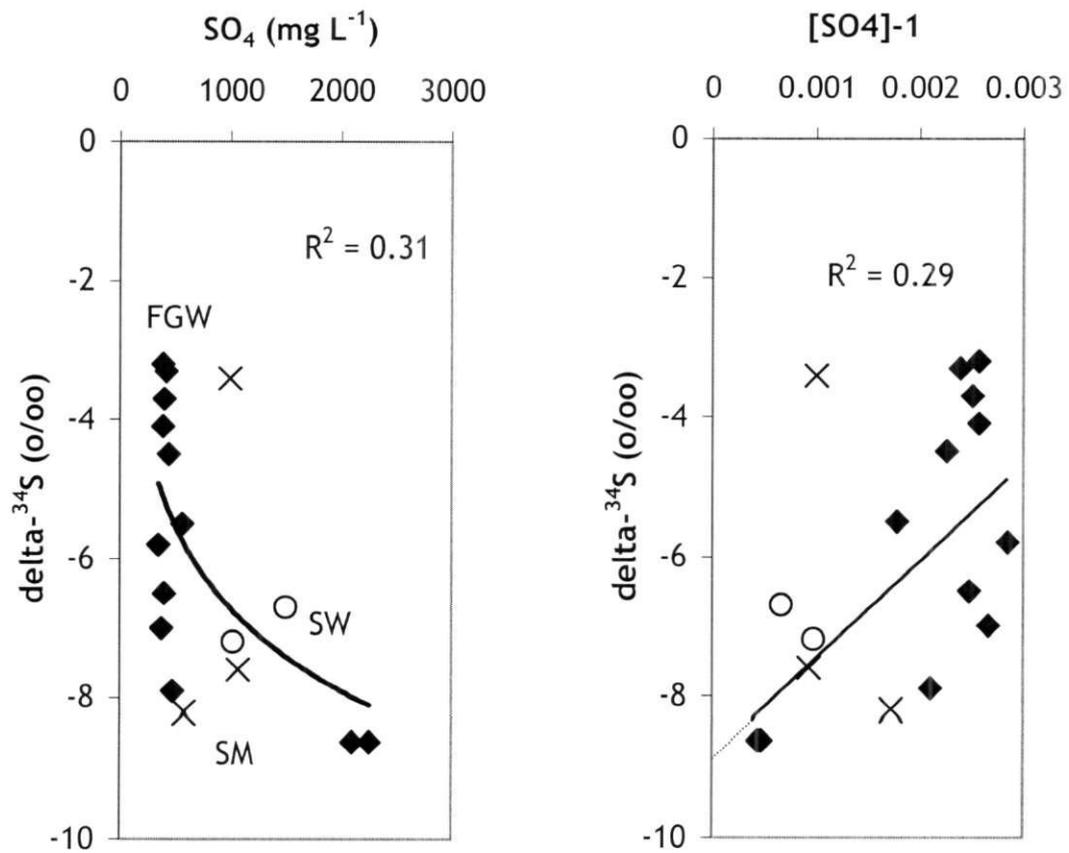


Figure 5-17: Relationship between SO₄ concentrations and $\delta^{34}\text{S}$ in SO₄ in ground, seepage, and surface water samples (Oct, '99). FGW = field groundwater (\blacklozenge), SW = surface water (o), SM = seepage meter (x)

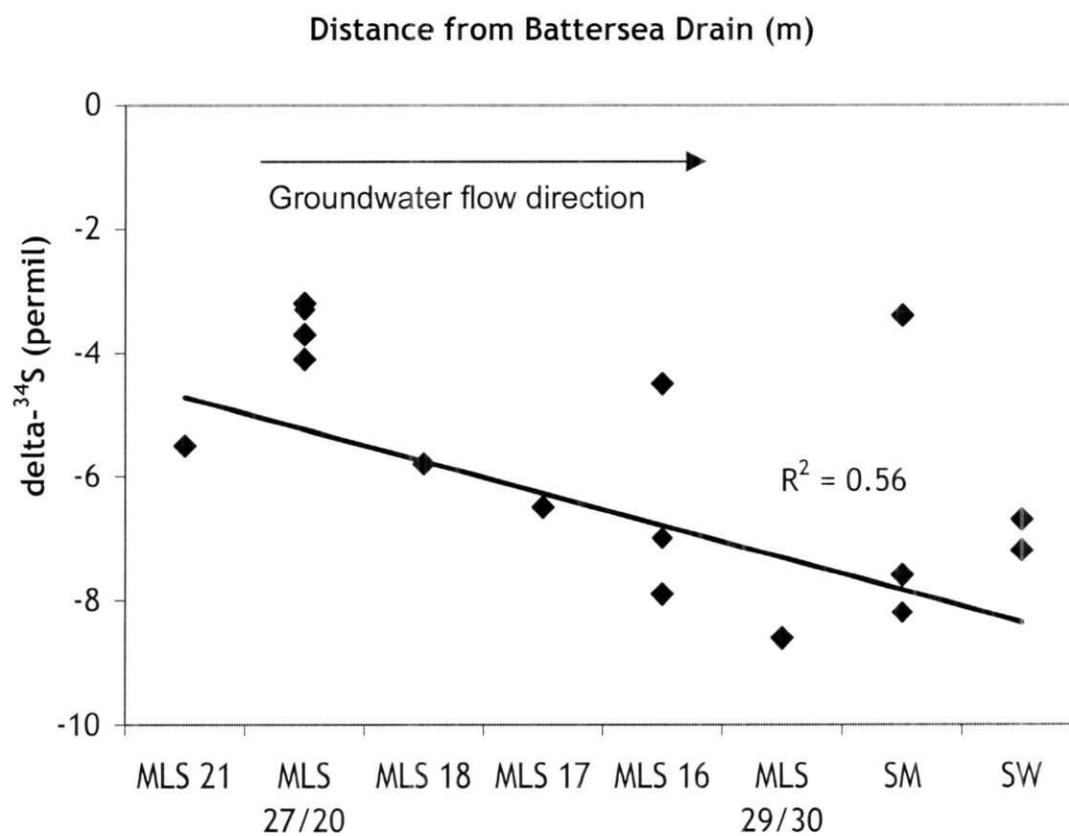


Figure 5-18: Relationship between $\delta^{34}\text{S}$ and distance along the flow path.

Table 5-9: $\delta^{34}\text{S}$ composition of S in SO_4 in field ground-, seepage, and surface water at the Battersea site (Oct, '99). MLS are recorded as piezometer number - port number (i.e. 16-1), where port 1 is the deepest sampling point.

Piezometer #	[SO_4] (mg L^{-1})	$\delta^{34}\text{S}$ (‰)
16-1	476	-7.9
16-2	442	-4.5
16-3	375	-7.0
17-1	403	-6.5
18-2	351	-5.8
21-1	562	-5.5
27-2	389	-3.2
27-3	399	-3.7
27-4	418	-3.3
27-5	389	-4.1
30-1	2257	-8.6
30-2	2101	-8.6
Upstream SW ¹	1501	-6.7
Downstream SW	1021	-7.2
SM-1 ²	1069	-7.6
SM-2	1000	-3.4
SM-3	581	-8.2

¹ SW = surface water

² SM = seepage meter

suggest anhydrite and/or gypsum dissolution is occurring along the flow path. (Figure 5-19). Reduced organic S from manure cannot be eliminated as a potential source as there is no isotopic data available from this site. However, a more likely scenario is the microbiologically mediated oxidation of a reduced inorganic S source, such as pyrite.

The $\delta^{34}\text{S}$ value of S in SO_4 from oxidation of pyrite is usually slightly depleted from that of its sulfur source. This reflects the kinetic isotope effects caused by preferential selection of the lighter isotope by the bacteria mediating the process. The $\delta^{34}\text{S}$ value of S in SO_4 derived from a reduced sulfur source will never attain the $\delta^{34}\text{S}$ value of the reduced sulfur due to mixing of two distinct isotopic sinks; pyrite in the clay and SO_4 in groundwater. The $\delta^{34}\text{S}$ value of the sulfide source can be estimated by determining the y-intercept

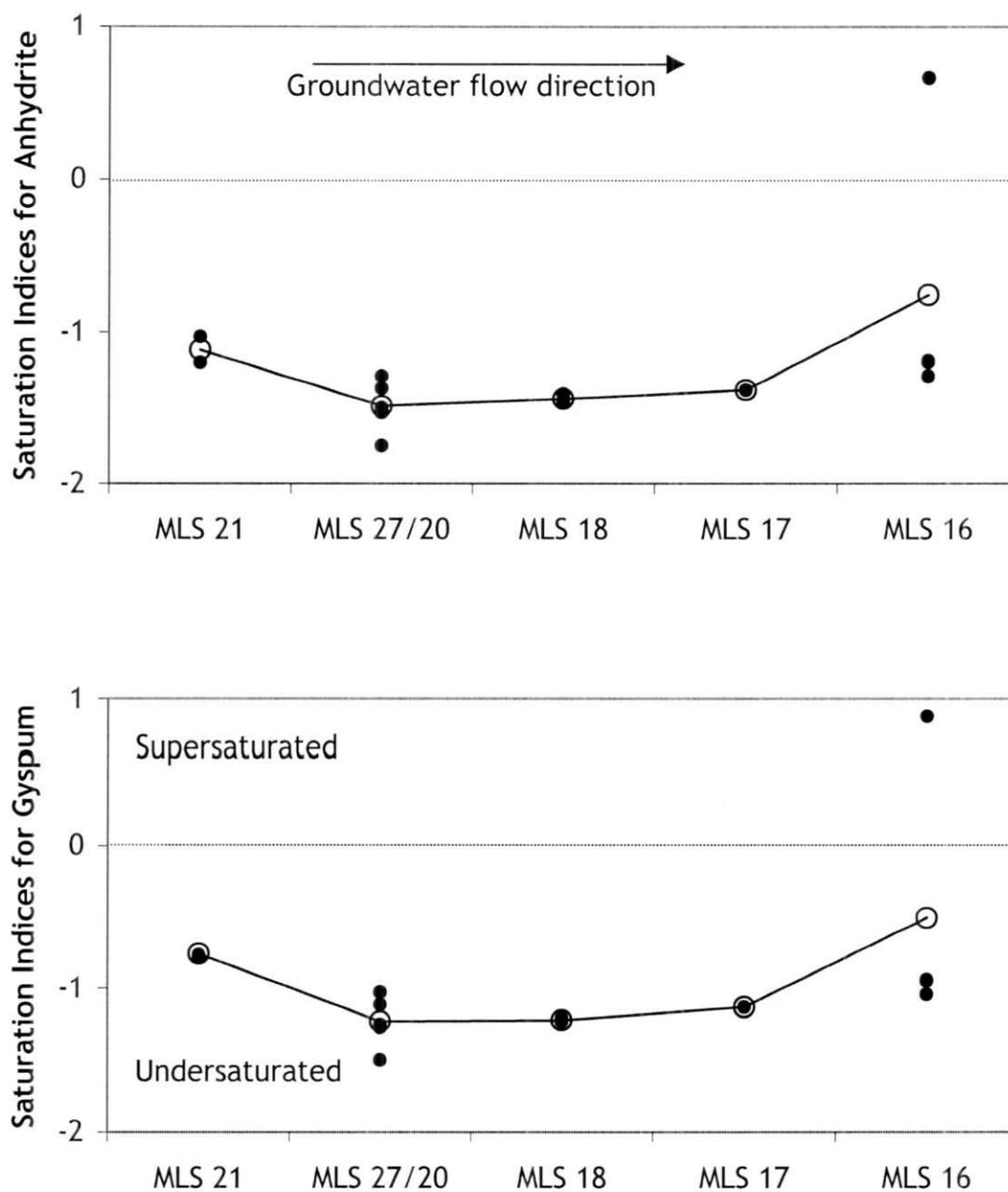


Figure 5-19: Variation in saturation indices of anhydrite and gypsum along the groundwater flow path. Negative values indicate undersaturation (dissolution). Positive values indicate supersaturation (precipitation).

value of the extrapolated curve defining the relationship between $\delta^{34}\text{S}$ and the $[\text{SO}_4]^{-1}$ (Figure 5-17). The estimated $\delta^{34}\text{S}$ value for the SO_4 source at the Battersea field site is approximately -9 ‰ which is within ± 2 ‰ of the $\delta^{34}\text{S}$ values for S in pyrite in glacial drift in the region (Hendry et al., 1986; Hendry, 1989).

5.4.5 Dissimilatory Nitrate Reduction

Dissimilatory nitrate reduction (DNR), the bacterially mediated conversion of NO_3 to NH_4 , has been recognized in waste-water contaminated groundwater (Smith & Duff, 1988; Bulgar et al., 1989). This is a much less desirable N attenuation process as the reduction of NO_3 to N_2 gas is not complete. Instead, the reduced N remains available (as NH_4) to be converted back to its original form (NO_3) once the groundwater moves to a more oxidic environment. Generally, DNR is thought to occur in electron-rich environments where there is a high ratio of potential electron donors with respect to NO_3 (Tiedje et al., 1982). Additionally, organic carbon and low redox potential in soils tend to increase the formation of NH_4 (Buresh & Patrick, 1978).

Ammonium is present in groundwater, seepage water and surface water (Table 5-2) at the Battersea site, indicating that DNR might be occurring. Increased concentrations of $\text{NH}_4\text{-N}$ tend to occur when $\text{NO}_3\text{-N}$ concentrations decrease (Figure 5-14), suggesting that some of the NO_3 is being locally reduced to NH_4 . It has been previously stated that high concentrations of NO_2 and NH_4 in groundwater may be due to reduction in patches rich in organic carbon or locally reducing microenvironments. Of more importance, however, is the high concentration of NH_4 in seepage water (average: 1.2 mg L^{-1}).

Groundwater seepage can be considered as a possible mechanism for the release of N to surface waters by displacing interstitial NH_4 during its migration through sediments (Belanger & Mikutel, 1985). Natural decreases in Eh and increased concentrations of NH_4 have been recognized in lake and bog sediments resulting from the anaerobic decomposition of organic matter (N

mineralization) (Mayer et al., 1999). Reducing environments favor high concentrations of electron donors that would promote the reduction of NO_3^- . Concentrations of TKN and NH_4^+ peak during periods of high groundwater discharge (from fall to spring). Therefore, increased $\text{NH}_4\text{-N}$ concentrations in seepage water could be due to DNR promoted by the enclosure of the drain bottom sediments by the seepage meters or natural development of anoxic conditions over the winter causing anaerobic decomposition of organic matter in the drain bottom.

5.4.6 Nitrogen Balance

Molar ratios of NO_3^- , NO_2^- , NH_4^+ , and TKN and Cl were compared to determine the relative importance of DNR versus autotrophic denitrification near MLS 18 and in the seepage meters (Table 5-10; Figure 5-20). These ratios have been normalized to chloride to remove any effects due to dilution.

The variation in Figure 5-20 highlights the occurrence of localized N loss at the Battersea site. There is apparently substantial gaseous N loss, from either DNR or denitrification, between MLS 16 and the seepage meters. Less significant gaseous N loss also occurs near MLS 18. Since the N again increases between MLS 18 and MLS 17, it is apparent that most of the N removal is occurring in the last part of the groundwater flow path prior to groundwater discharge to the Battersea Drain. This is similar to the trend noted by Clausen et al. (2000) where N attenuation was greatest in the last 2.5 m prior to groundwater discharge. Like at MLS 18, the presence of reduced sediments and organics in sediments of the Battersea Drain suggests that the N loss may occur immediately prior to discharge. Since it was not possible to instrument the site between MLS 16 and the Battersea Drain due to an underground utility corridor, the extent of N attenuation in this region cannot be assessed in detail.

Nitrogen loss at MLS 18 and in the seepage meters is coincident with increases in NO_2^- , NH_4^+ , SO_4^{2-} , HCO_3^- and organic N. Increases in the DOC:Cl molar

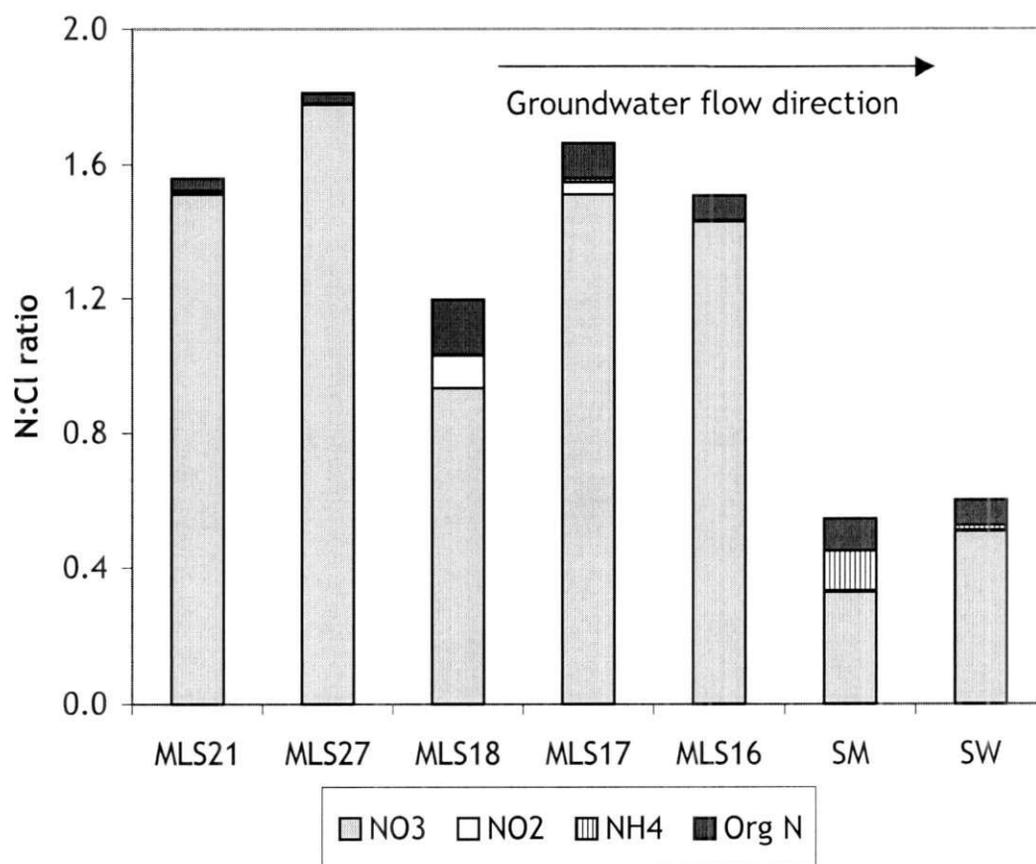


Figure 5-20: Summary of N balance results along the groundwater flow path at the Battersea site. Molar ratios have been normalized to Cl to remove dilution effects from upwelling groundwater at MLS 18.

Table 5-10: Summary of N balance results.

Location	Cl	NO ₃ :Cl	NO ₂ :Cl	NH ₄ :Cl	Org N:Cl	Total N:Cl
MLS 21	1	1.511	0.005	0.006	0.038	1.575
MLS 27/20	1	1.778	0.001	0.00015	0.031	1.968
MLS 18	1	0.932	0.098	0.003	0.164	1.134
MLS 17	1	1.511	0.037	0.011	0.104	1.617
MLS 16	1	1.429	0.002	0.001	0.076	1.588
SM	1	0.325	0.005	0.117	0.097	0.371
SW	1	0.507	0.004	0.015	0.075	0.510
Net loss	0	-1.004	-0.001			-1.065
Net gain	0			+0.009	+0.016	

ratio at both of these sites would argue against heterotrophic denitrification, however, the increase could be masking an actual decrease in the DOC concentrations. Isotopic data ($\delta^{34}\text{S}$) suggests that autotrophic denitrification is occurring along the groundwater flow path and could account for the N loss. However, neither process can account for the substantial increases in the HCO₃:Cl and SO₄:Cl molar ratios at the seepage meters (Table 5-8). There is an excess of HCO₃ and SO₄ being produced.

Upwelling groundwater in the aquifer could be contributing SO₄, HCO₃, and DOC to the system. However, no significant correlations were found between these species and the $\delta^{18}\text{O}$ of groundwater. Mineral dissolution and/or mixing with deeper groundwater higher in natural salts (i.e. similar to that at MLS 29 & 30) along the flow path could also be sources for SO₄ and HCO₃ in groundwater and seepage water.

Calcite, aragonite, and dolomite tend towards supersaturation along the groundwater flow path (Figure 5-21), whereas gypsum and anhydrite are undersaturated (Figure 5-19). Therefore, carbonate dissolution cannot be a source for increased bicarbonate in the aquifer, though the more acidic conditions in the Battersea Drain could be promoting dissolution which could

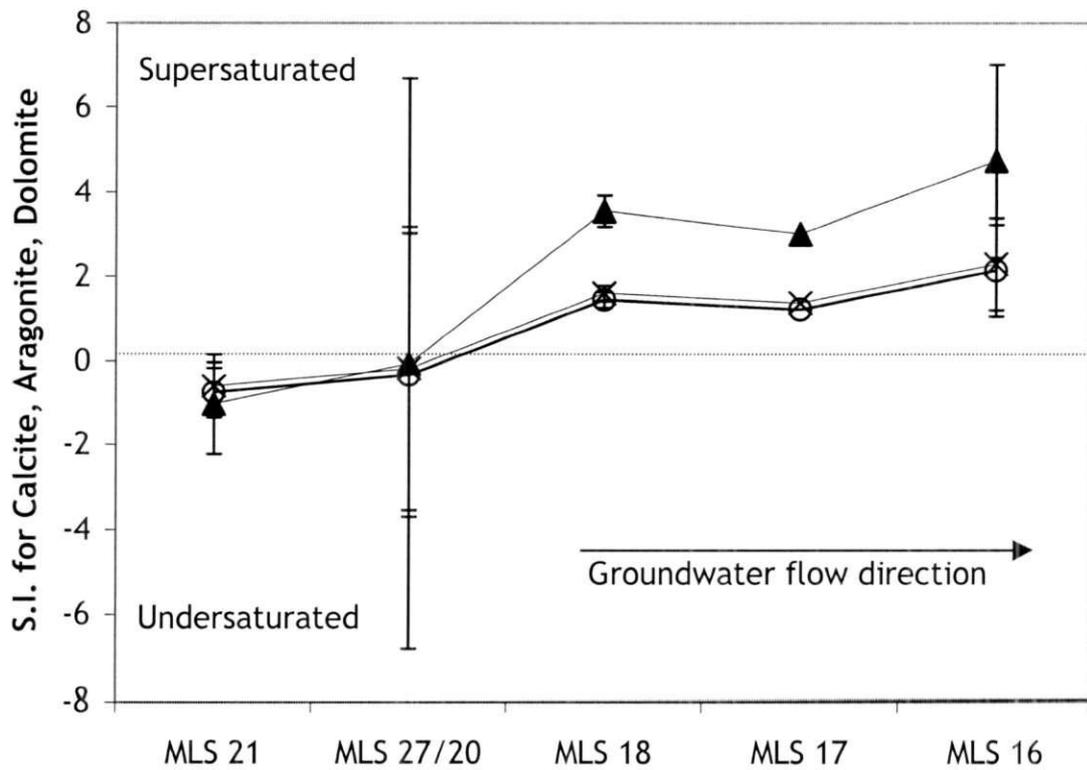


Figure 5-21: Variation in the saturation indices for calcite (o), aragonite (X), and dolomite (▲) along the groundwater flow path. Positive values indicate supersaturation. Negative values indicate undersaturation. Error bars represent the 95% confidence interval.

contribute to seepage as bank storage water is released. Sulfate mineral dissolution may be contributing sulfate, although the isotopic signature of the SO_4 argues against this.

Multi-level samplers 29 & 30 are completed in a sandy lens within the clay layer and their chemistry suggests the presence of naturally higher salt concentrations typical of fine-textured sediments in the LNID (Table 5-3). By comparing the average $\text{SO}_4:\text{HCO}_3$ ratios at MLS 29 & 30 (5.68), MLS 16 (0.96), and in the seepage water (1.44), the increase in SO_4 and HCO_3 concentrations at the seepage meters could be due to an 8% contribution from deeper groundwater.

There is a significant amount of $\text{NH}_4\text{-N}$ produced at the seepage meters. The increase in the $\text{NO}_3\text{-N}:\text{Cl}$ molar ratio between the seepage meters and surface water (Figure 5-20, Table 5-10) indicates that the NH_4 is re-oxidized in the surface water. The presence of reduced sediments in the Battersea Drain and the higher organic content of these sediments suggests that DNR is an important process as groundwater discharges to the Battersea Drain.

5.5 Phosphorus

5.5.1 Variation Along the Groundwater Flow Path

Total P concentration and the $\text{TP}:\text{Cl}$ molar ratio are variable along the groundwater flow path (Figure 5-22). However, DP concentration and the $\text{DP}:\text{Cl}$ molar ratio steadily decreases. The increases and decreases in TP concentration could indicate locally reducing patches in the aquifer (increases) and/or locally increased sorption capacity of the aquifer sediments (decreases). Increased groundwater and seepage water P concentrations are coincident with local increases in NH_4 concentrations and local decreases in NO_3 concentrations (Figure 5-14). This suggests that the more reducing conditions in these locations (at MLS 18, and in the seepage water) may be responsible for the release of previously adsorbed phosphate. Variations in aquifer sediments

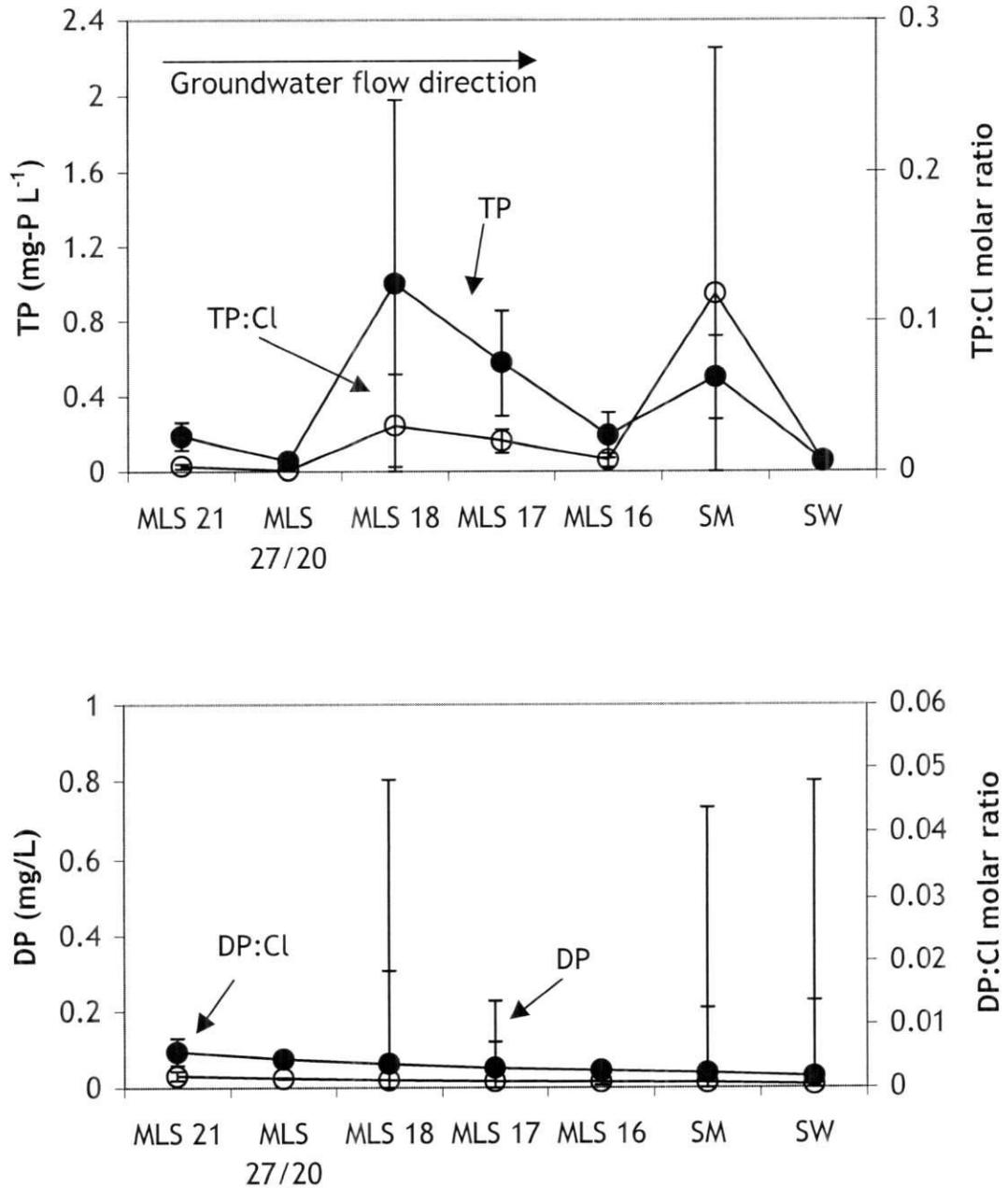


Figure 5-22: Variation in TP and DP concentrations and P:Cl molar ratios along the groundwater flow path. Error bars represent the 95% confidence interval.

Table 5-11: Phosphorus extraction data from aquifer sediments at the Battersea field site. Mass of P is expressed as mg-P/g sediment.

Sample ID	Depth (m bgs)	Weak (10%) Acid PO ₄ -P	Strong (1N) Acid PO ₄ -P
16-SZ ²	3.27-4.15	n.a. ¹	0.24
16-SZ	3.27-4.15	0.29	0.51
18-S ³	0.15-0.4	0.20	n.a.
18-SZ	2-3	0.35	0.40
18-SZ	3.9-4.5	0.56	0.47
27-SZ	2-3	0.21	0.61
27-SZ	3.6-4.5	0.22	0.46
29-USZ ⁴	0.94-1.5	0.15	n.a.
29-SZ	1.5-2.5	0.17	0.23
Average (S.D.)		0.27 (0.13)	0.42 (0.14)

¹n.a. = not available

² SZ = saturated zone

³ S = surface zone

⁴ USZ = unsaturated zone

may cause groundwater P concentrations to be lower at some locations. A greater capacity to adsorb phosphate could be caused by higher concentrations of Fe- and/or Al- hydroxides or calcite crystals at some locations. The steadily decreasing trend of DP:Cl molar ratio along the flow path suggests that the transport of P in groundwater is being attenuated.

5.5.2 Phosphorus Attenuation: Adsorption and P-mineral Precipitation Potential

Extraction data (10% HCl) from sediments at the Battersea site indicate that P is currently being stored in the aquifer (Tables 5-11 & 5-12; Appendix 13). However, there is no significant difference between the mass of P in aquifer sediments (0.27 mg-P g⁻¹ sediment) and background sediments (0.31 mg-P g⁻¹ sediment) in the improved pasture. The PGW has a similar chemistry to LNID background (Table 5-3), indicating it has not been impacted by agricultural practices. Fresh manure inputs from grazing cattle and the possibility of historic manure application may explain the similarity in the extracted P masses in the aquifers of the manured field and improved pasture.

Table 5-12: Phosphorus extraction data from pasture (background) sediments at the Battersea field site. Mass of P is expressed as mg-P g⁻¹ of sediment.

Sample ID	Depth (m bgs)	Weak (10%) Acid PO ₄ -P	Strong (1N) Acid PO ₄ -P
33SZ ¹	1.42-1.83	0.45	0.59
33SZ	1.83-3.58	0.21	0.27
32USZ ²	0.45-0.6	0.33	0.32
32USZ	0.6-0.9	0.24	0.37
32USZ	0.9-1.2	0.33	0.29
Average (S.D.)		0.31 (0.09)	0.37 (0.13)

¹ SZ = saturated zone

² USZ = unsaturated zone

Some of the P in the aquifer may be natural (geologic) suggested by the decreasing PO₄-P/TP ratio below the water table (Figure 5-10). However, the decrease in PO₄-P and DP below the water table indicates that P is dominantly derived from the surface.

The average mass of P measured in the surface and unsaturated zones (185 & 29USZ) is 0.17 mg-P/g sediment. The mass of P in the aquifer is up to 3 times higher and tends to increase with depth (Figure 5-23). However, soil PO₄-P depth profiles suggest that P leaching is being attenuated in the surface zone (Figure 5-1). The maximum sorption capacity, β , calculated from the Langmuir sorption isotherm (Figure 5-24), is 0.24 mg-P g⁻¹ sediment. The average mass of P currently sorbed to aquifer sediments exceeds this value suggesting that the sediments may be approaching saturation. The decreasing DP concentrations along the groundwater flow path (Figure 5-22) indicate that P transport is being attenuated in the aquifer.

The strong acid extraction (1N HCl) data from aquifer (0.42 mg-P g⁻¹ sediment) and background (0.37 mg-P g⁻¹ sediment) was not significantly different (paired t-test) from the weak acid extraction (Tables 5-11 & 5-12). This suggests that P is not being stored as P minerals, and adsorption is likely the dominant process attenuating P transport. Phosphate migration is controlled by sorption, whereas the concentration of PO₄-P is governed by the

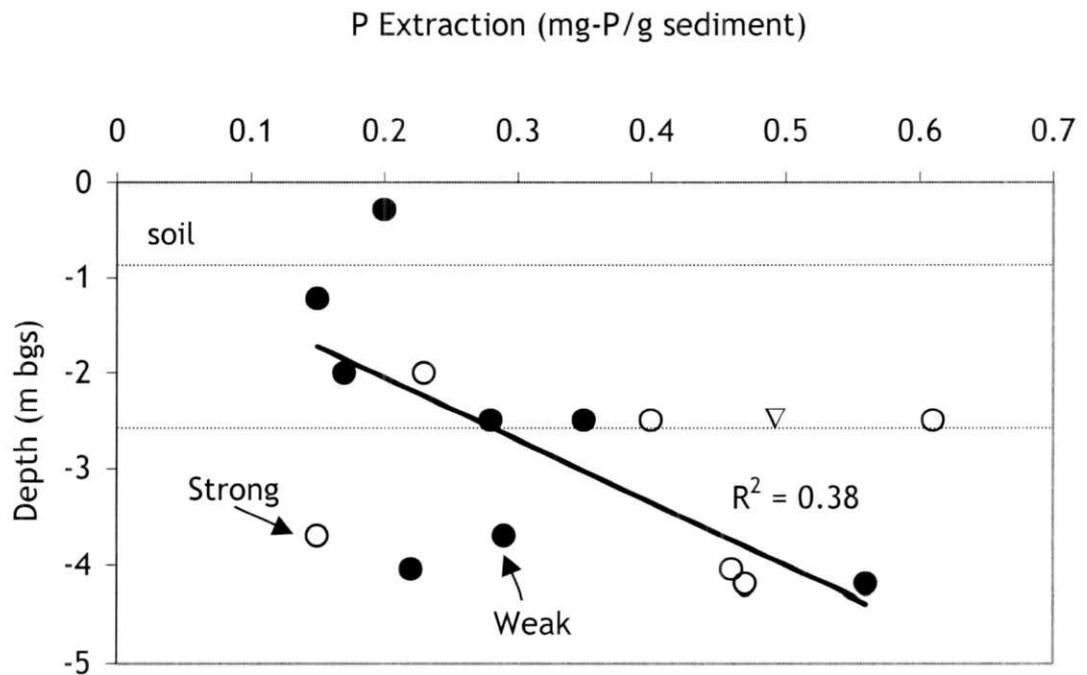


Figure 5-23: Variation in the extracted P mass with depth in the aquifer. The strong extraction data points are plotted for comparison only and have not been included in the linear regression. The plotted water table is the average water table depth.

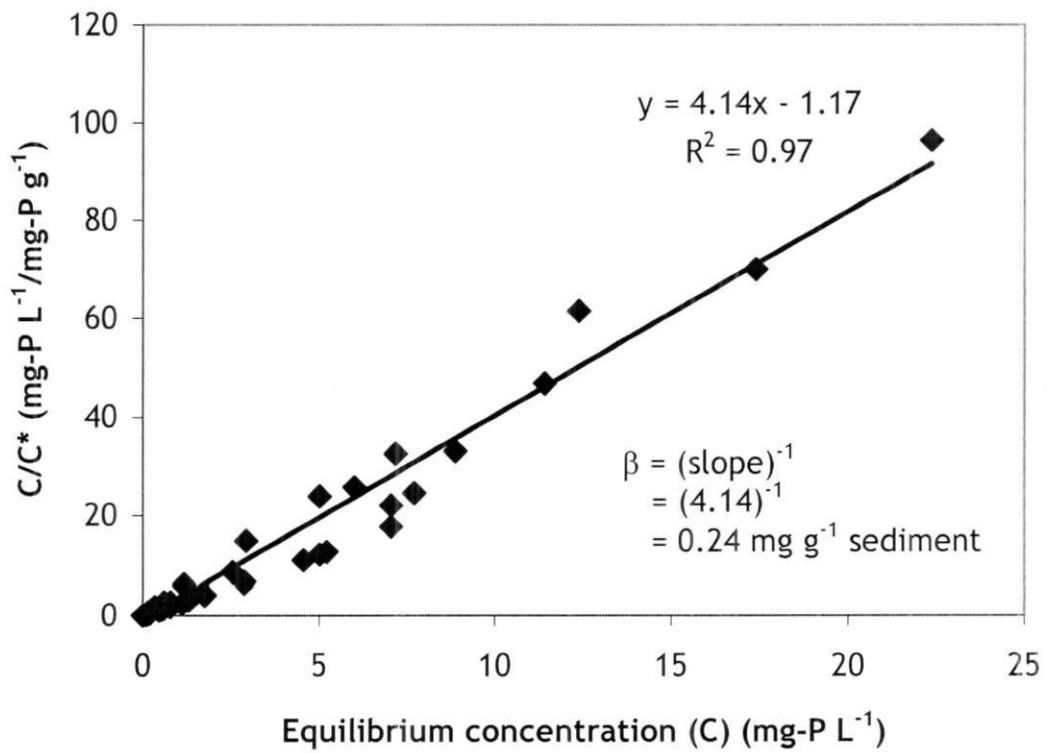


Figure 5-24: Langmuir sorption isotherm comprising all data from phosphate sorption experiments.

Table 5-13: Average saturation indices for specified minerals in groundwater at the Battersea field site. Negative values indicate undersaturation, and positive values indicate supersaturation.

	Average	Standard Deviation	n
Anhydrite (CaSO ₄)	-1.09	0.88	18
Gypsum (CaSO ₄ •2H ₂ O)	-0.83	0.56	18
Aragonite (CaCO ₃)	0.88	2.24	18
Calcite (CaCO ₃)	1.03	2.24	18
Dolomite (CaMg(CO ₃) ₂)	2.29	4.46	18
Halite (NaCl)	-6.84	0.67	18
Strengite (FePO ₄ •2H ₂ O)	-2.88	1.54	17
Vivianite (Fe(PO ₄) ₂ •8H ₂ O)	-21.20	4.66	17
Hydroxyapatite (Ca ₅ (PO ₄) ₃ OH)	1.65	0.67	17

constraints of phosphate mineral solubility (Robertson, 1995).

Steady-state groundwater P concentrations coupled with a fully utilized sediment sorption capacity were considered to be indicative of equilibrium with a P mineral phase in a septic system plume (Robertson, 1995; Harman et al., 1998). At the Cambridge site, the PO₄-P levels in the steady state plume remain consistently near 4 mg L⁻¹ with time (Robertson, 1995). The concentrations of PO₄-P at MLS 27 (upgradient) and MLS 16 (downgradient) at the Battersea site tend towards a concentration of 0.005 mg L⁻¹ over the study period (Figure 5-25), suggesting the system may be approaching steady state conditions. There is insufficient data to determine whether steady state conditions exist at the Battersea site, but the potential cannot be discounted.

Geochemical modeling indicates that the groundwater is currently saturated to supersaturated with respect to hydroxyapatite (HA) (Table 5-13) and tends towards supersaturation along the flow path (Figure 5-26). Hydroxyapatite supersaturation has been found in calcareous sand aquifers contaminated with septic system effluent (Robertson et al., 1991; Robertson, 1995; Harman et al., 1998) and authigenic P minerals have been found and characterized in aquifer sediments (Zanini et al., 1998). However, supersaturation does not guarantee that HA precipitation is occurring. Mineral

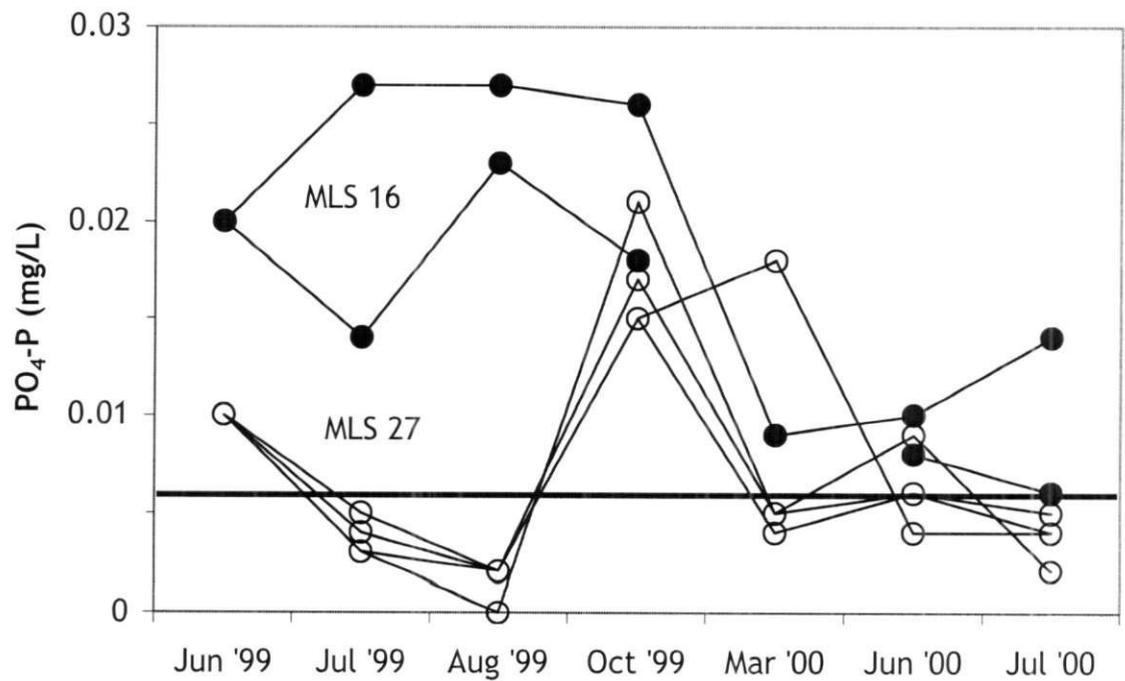


Figure 5-25: Variation in $\text{PO}_4\text{-P}$ concentrations at MLS 27 (upgradient) and MLS 16 (downgradient) over the study period. Note the tendency for $\text{PO}_4\text{-P}$ concentrations to approach 0.005 mg/L with time.

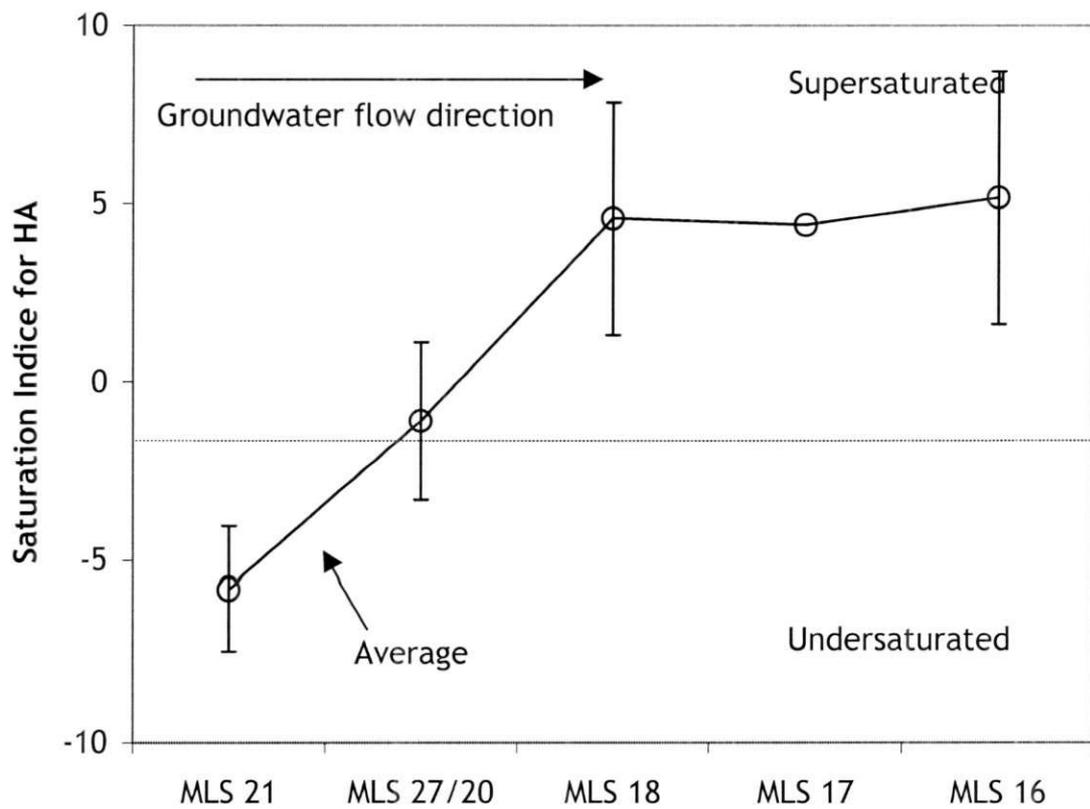


Figure 5-26: Variation in hydroxyapatite (HA) saturation indices along the groundwater flow path. Positive values indicate supersaturation, whereas negative values indicate undersaturation. Error bars represent the 95% confidence interval.

stability is controlled by many factors including the pH, Eh, aqueous concentrations, and kinetics.

Thermodynamically, HA is the most stable P mineral in natural waters (Emerson, 1976) and polluted waters are typically supersaturated with HA (Kraynov, 1993). Groundwater at the Battersea site is within the Eh and pH range for both hydroxyapatite and strengite stability (Figure 5-27 ;Moore Jr. & Reddy, 1994) but is only supersaturated with respect to hydroxyapatite (Table5-13).

Precipitation of hydroxyapatite is inhibited by several factors, including the presence of organic acids (Inskeep & Silvertooth, 1988), a Ca/Mg ratio less than 4.5 (Martens & Harriss, 1970), and absence of calcite surfaces or seed crystals (Moore Jr., et al., 1991). Organic acids (such as fulvic, humic, and tannic acids) tend to adsorb onto seed crystals, thereby preventing the nucleation of HA crystals (Inskeep & Silvertooth, 1988). Magnesium is chemically similar to calcium, but has a smaller ionic radius, and can therefore substitute for Ca in the HA crystal lattice, causing structural deformities and preventing crystallization of HA (Martins & Harriss, 1970). Finally, minerals require a nucleus to seed crystal growth when forming by authigenic processes. Absence of nuclei or calcite surfaces, that may act as nuclei, will prevent crystal formation.

Groundwater at the Battersea site is likely to contain organic acids presumably derived from the applied manure ($\text{DOC}_{\text{av}} = 10 \text{ mg-C L}^{-1}$; Table 5-2). In addition, the average Ca/Mg ratio in groundwater is 0.97, well below the threshold ratio of 4.5 necessary for HA crystallization (Martens & Harriss, 1970). Both calcite and aragonite tend toward supersaturation along the flow path (Figure 5-21), suggesting that calcite and/or aragonite crystals could be precipitating in the aquifer. While this would facilitate the precipitation of HA, the presence of organic acids and the low Ca/Mg ratio would tend to prevent its formation. It is therefore unlikely that HA is precipitating in groundwater at this site.

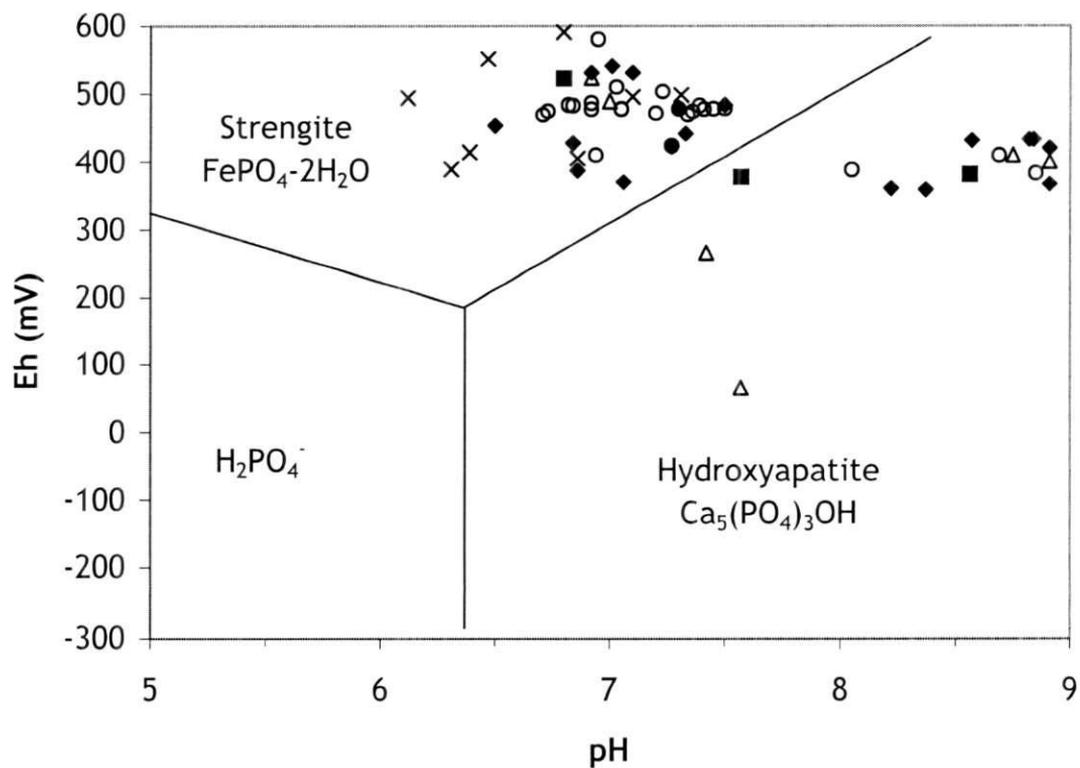


Figure 5-27: Distribution of field groundwater samples between the stability fields for hydroxyapatite and strengite. Stability field boundaries after Moore Jr. & Reddy (1994). \blacklozenge = MLS 16; \blacksquare = MLS 17; \triangle = MLS 18; \circ = MLS 27/20; \times = MLS 21.

The estimated maximum residence time in the aquifer is 10 years. Therefore, if P mineral precipitation is occurring in groundwater at the Battersea site it is more likely that simpler Ca-phosphates, (i.e. brushite and/or monetite), may be forming. Although strengite is undersaturated in groundwater, the fact that FGW does lie in the stability field for strengite may suggest that simpler Fe-phosphates are also precipitating.

5.6 Bacteria

Total coliform (TC) bacteria were found in all waters at the Battersea site, whereas fecal coliform (FC) bacteria were detected only in seepage and surface water samples (Table 5-2). Contamination of groundwater by pathogenic microorganisms is generally believed to result from migration or introduction of fecal material into the subsurface (Gosselin et al., 1997). Primary sources of fecal contamination of public health concern include feces from other humans (i.e. leaching of private septic systems), and animals (i.e. originating from intensive livestock operations) (Gosselin et al., 1997; Macler & Merkle, 2000). The presence of coliform bacteria in groundwater is indicative of contamination by surface water. In particular, the presence of any bacteria from the FC group indicates that there has been contamination from fecal matter.

The presence of FC bacteria in the seepage water samples is problematic, as it may indicate contamination of the sample by surface water. However, there may be an alternate explanation. Bacteria and viruses are known to adsorb to sediment particles, which increases their chance of survival (Gerba, 1999). It is possible that the surface of the seepage meter bags could also be an ideal sorption site. Sample bags had a large opening with many folds where they were attached to the seepage meter outlet. These folds could provide an excellent location for bacterial attachment, as they would provide protection from other predatory microorganisms. Whenever seepage meter

samples were collected there was always a build-up of algae near the opening of the sample bag.

Bottom sediments of the Battersea Drain could also have been a site for bacterial adsorption and/or attachment. Both TC and FC are facultative anaerobes. The seepage meters were originally installed in late May of 1999, so there may have already been microorganisms present and possibly reproducing in the sediments enclosed by the seepage meters.

Surface water temperature in the Battersea Drain is generally around 25°C during the summer months. Although this is lower than the incubation temperatures for TC and FC analysis (32 and 44.5°C, respectively), it would still promote bacterial growth and reproduction. If any bacteria had sorbed or where otherwise attached to the opening of the seepage meter bags or present in the sediments under the seepage meters prior to installation, it is likely that they were also reproducing in that region.

Seasonal bank storage occurs along the length of the field site, in response to increased drain water levels during irrigation. As surface water moves into the sediments along the Battersea Drain FC bacteria could be carried with it. During the release of bank storage water, the bacteria may have been flushed into the seepage bags.

Contamination of the seepage meter samples, therefore could have occurred in one of three ways, or a combination of all three. The FC bacteria may have originated in the surface water or bottom sediments of the Battersea Drain and been subsequently carried with the seepage water as it discharged to the seepage meter bag. In either case, proliferation of the bacterial population may have occurred either in the sediments or in the seepage meter bag after transport. Alternatively, bacteria attached to the opening of the seepage meter bag could have contaminated the sample as it was being poured into the sample bottle. The exact mode of contamination is not known.

Table 5-14: Parameters used in the nutrient mass balances.

	Nitrogen	Phosphorus
Area of catchment	16 ha	16 ha
Area of seepage face	729 m ²	729 m ²
Recharge rate ¹	0.026 m/yr	0.026 m/yr
Manure application rate (wet)	52 Mg/ha/yr	52 Mg/ha/yr
Manure application rate (dry)	29.4 Mg/ha/yr	29.4 Mg/ha/yr
Moisture content of manure ²	40%	40%
Nutrient content of manure ³	1.8%	0.65%
Crop Uptake ⁴	120 kg/ha/yr	7.5%
Volatilization rate ⁵	20%	n.a. ⁶
Average depth to water table	2.7 m	2.7 m
Average saturated thickness	1.5 m	1.5 m

^{1,4} Rodvang et al., 1999

² Olson et al., 1999

³ Eghball & Power, 1994; Eghball et al., 1997; Zhang et al., 1998; Olson et al., 1999

⁵ Eghball & Power, 1994; Power et al., 1994; Eigenberg et al., 1998

⁶ n.a. = not applicable

5.7 Nutrient Transport

A mass balance was done to determine the transport (flux) and storage (pool) of N and P at the Battersea site. Nitrogen and phosphorus fluxes included the rate of nutrient application, nutrient movement in the aquifer and discharge to the Battersea Drain. Pools of N and P were identified in the soil and the aquifer. Parameters used in the mass balances are included in Tables 5-14.

5.7.1 Flux Calculations

Mass flux calculations were done for Cl, N, and P to estimate the rates of transport of nutrients at the Battersea site. Three fluxes have been identified in the system; manure flux, groundwater flux, and seepage meter flux.

The manure flux was calculated from the following formula:

$$(M_{A.R.-DRY} - M_{VOL} - M_{CROP}) * [X]_M * A_{RCH} \quad (1)$$

where $M_{A.R.-DRY}$ is the application rate of dry manure (kg/ha/yr), M_{VOL} is the volatilization rate of N, M_{CROP} is the crop uptake rate of N or P, $[X]_M$ is the Cl,

N, or P content of manure (% dry weight), and A_{RCH} is the area contributing groundwater recharge at the Battersea site (ha).

In order to observe mass flux changes in the aquifer, an upgradient (MLS 21 & 27) and downgradient (MLS 16) groundwater flux has been calculated according to the following formula:

$$R * A_{rch} * [X]_{FGW} = X_{IN} \quad (2)$$

where R is recharge ($m\ yr^{-1}$), A_{rch} is the area of the Battersea site contributing to recharge (16 ha), $[X]_{FGW}$ is the average concentration of Cl, N, or P in the groundwater ($mg\ L^{-1}$).

Seepage meter flux has been calculated from the seepage rate and average concentration in seepage water. Groundwater discharges to the Battersea Drain at an average rate of $20 \pm 34\ L\ m^{-2}\ da^{-1}$. Since there is a large potential variation in seepage rate and because nutrient seepage water concentrations have significant seasonal variations, a weighted average was used to calculate the discharge of nutrients from the aquifer. The weighted average was calculated from the following formula:

$$\frac{\sum(\text{seepage rate } (L\ m^{-2}\ da^{-1})) * ([X] (mg\ L^{-1}))}{\text{number of samples}} \quad (3)$$

where [X] is the concentration of the nutrient in the mass balance (i.e. Cl, N, P). The weighted average is then multiplied by the area of the seepage face in the Battersea Drain (m^2) to determine the mass per unit area with time.

Since Cl is conservative, it is unlikely to be stored in the system. Furthermore, the estimated maximum residence time in the aquifer (10 years) suggests that Cl concentrations are at or near steady-state. Therefore, the chloride fluxes have been fit to 100% to determine the recharge rate. Fluxes have been normalized to chloride to remove any dilution effects from upwelling groundwater at MLS 18 and bank storage.

5.7.2 Pool Calculations

Nutrients are being stored in two pools at the Battersea site; in the soil and unsaturated zones, and in the aquifer. Soil Cl mass was determined using the average soil Cl concentrations in the upper 90 cm of soil. Negligible Cl storage was assumed to occur between the soil zone and the water table. Soil N mass was calculated assuming the average soil concentrations between 0 and 90 cm remained constant over the depth to the water table (Figure 5-1). For P, the average soil concentration in the interval of 60 to 90 cm was extrapolated over the unsaturated depth below 60 cm (Figure 5-1). To convert soil PO₄ to soil TP, an approximation of [TP]=2*[PO₄] was used assuming that the inorganic (PO₄-P) fraction represented half of the total P in the soil. The mass in the aquifer was estimated by:

$$V_{H_2O} * [X]_{AVG} \tag{4}$$

where V_{H_2O} is the volume of water in the aquifer ($A_{RCH} * \text{Saturated thickness} * \text{porosity}$) using an assumed porosity of 40%, and $[X]_{AVG}$ is the average concentration of N or P in the groundwater.

5.7.3 Result of mass balance

The results of the mass balance calculations are presented in Figure 5-28. Chloride fluxes have been artificially balanced to reflect 100% transport through the Battersea site, and have been used to normalize the N and P fluxes.

Significant masses of N and P are stored in the soil pool although storage is not complete. Approximately 22% of the applied N is leaching to the aquifer whereas only 0.07% of the applied P is leaching downward. Phosphorus leaching is limited by its tendency to adsorb to sediment surfaces. Within the aquifer, 15% of the N is lost to denitrification along the flow path with a further 60% loss between MLS 16 and the seepage meters. This supports the previous observation that denitrification is predominantly occurring near the end of the groundwater flow path. Dissolved P flux is approximately 2.6 times

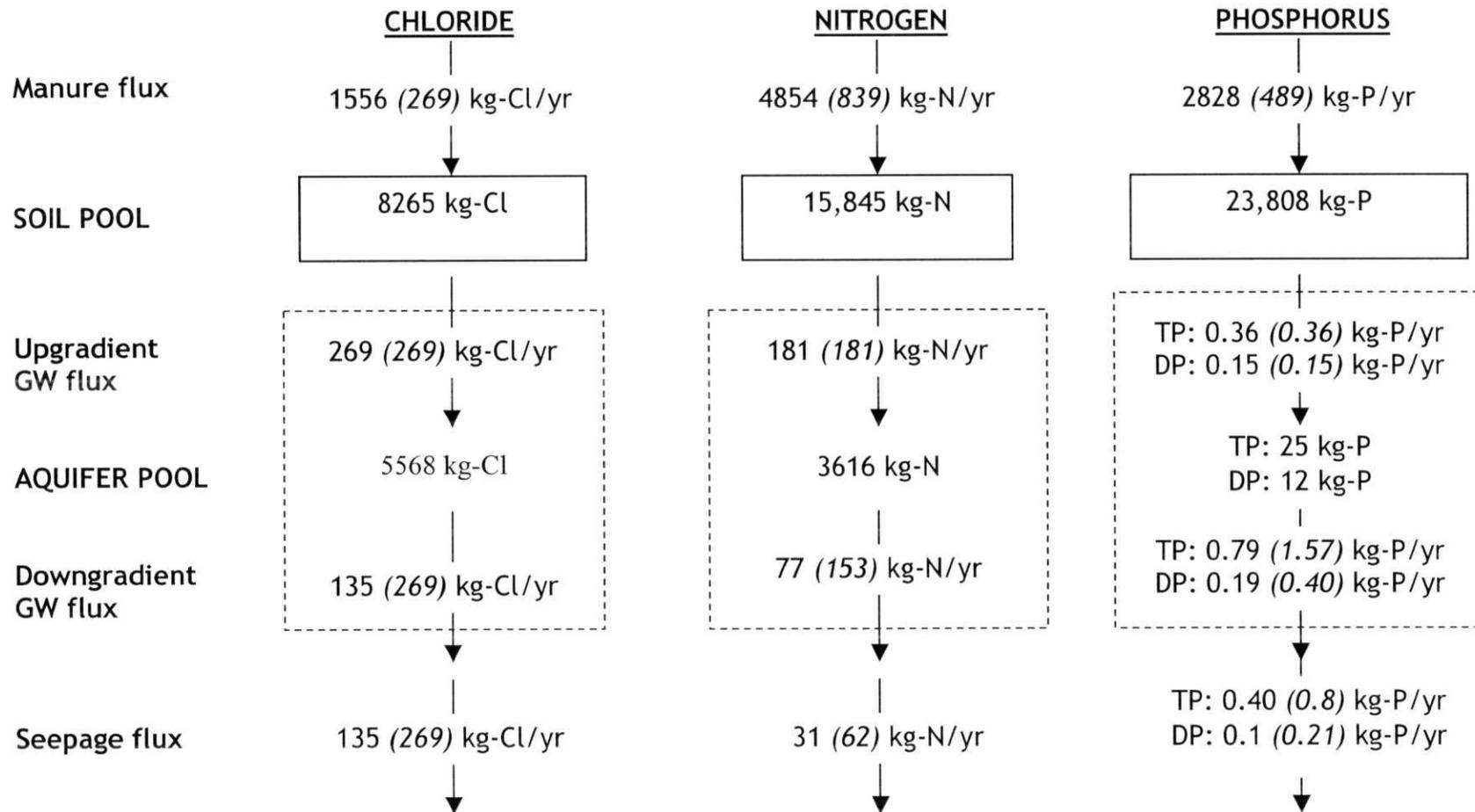


Figure 5-28: Flow chart showing Cl, N, and P storage and transport in the 16 ha catchment at the Battersea site. Italicized numbers are fluxes normalized to chloride.

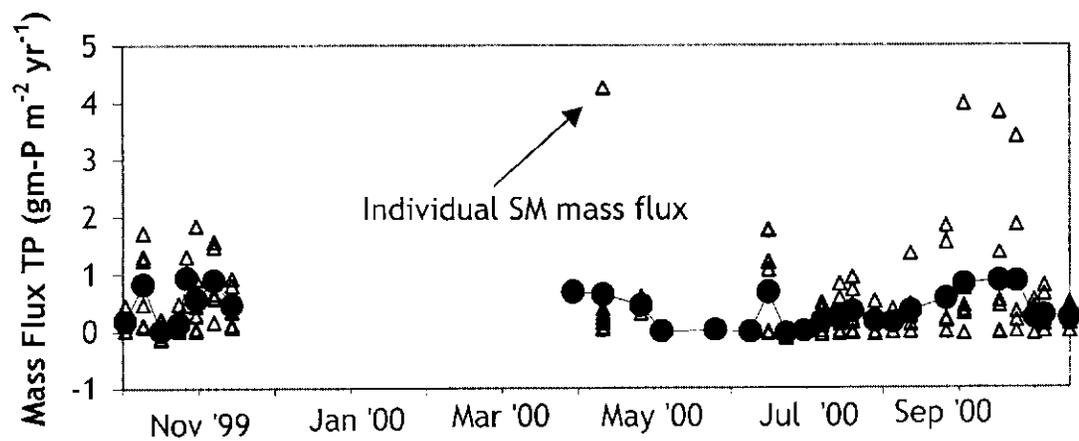
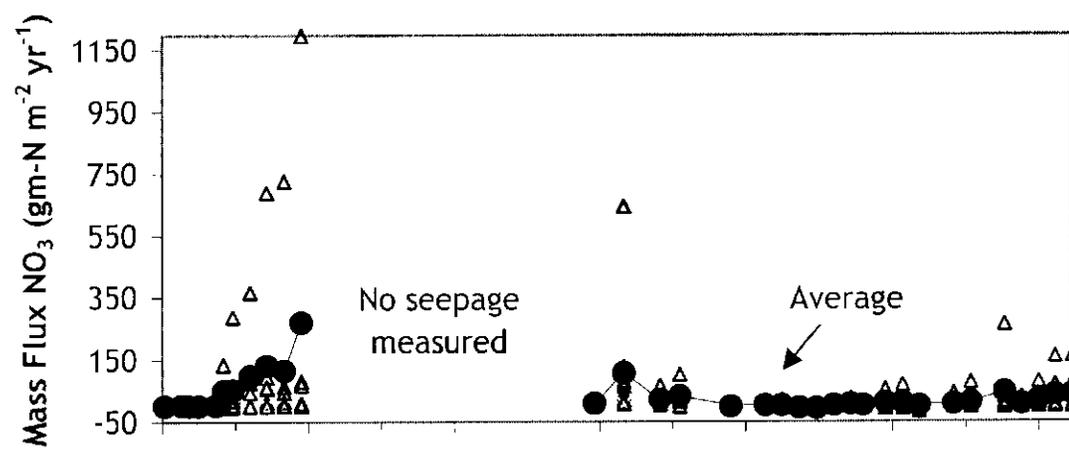
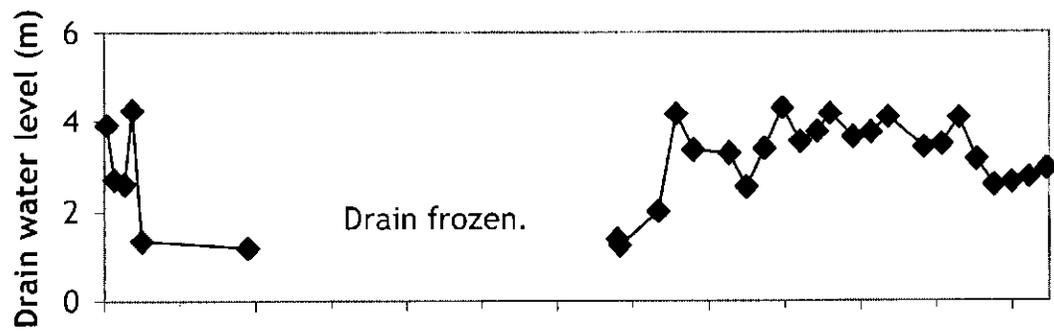
higher at MLS16 than at the start of the flow path, and then doubles in the seepage meter flux. Phosphorus release is probably due to the development of locally reducing conditions near MLS 18 and in the seepage meters. Nitrogen is discharging to the surface water at a rate of 62 kg-N/yr which represents 7.4% of the mass of manure applied annually. Phosphorus discharges to the Battersea Drain at a rate of 0.8 kg-P/yr ($1.1 \text{ g m}^{-2} \text{ yr}^{-1}$). This is a rate approximately 20 times higher than the P flux at a remote lake in northern Alberta (Shaw et al., 1990). Nonetheless, the discharge rate represents only 0.16% of the annual mass applied at the Battersea site.

5.8 Groundwater - Surface Water Interactions

Oscillations in the groundwater flow system, due to fluctuations in the elevation of water in the Battersea drain, result in bank storage along the length of the field site. Consequently when drain water levels are high (during irrigation), and the hydraulic gradient reverses, seepage is very low to negative. As the drain water level drops (after irrigation ceases), the horizontal hydraulic gradients return to normal and the seepage rates rapidly increase.

Mass fluxes of NO_3 and P in seepage water follow a similar trend (Figure 5-29). At high drain water levels, mass flux tends to be very low to negligible, whereas at low drain levels, mass flux is drastically increased. The onset of increased mass flux varies depending on the nutrient. Nitrate flux tends to increase gradually following a decrease in drain water level, whereas P flux is more sensitive to fluctuations in water level.

Whenever significant concentrations of P were measured in seepage water, elevated concentrations of reduced N (as NH_4 and TKN) were also present (Figure 5-5). Significant P release to Lake Tohopekoliga in Florida was promoted by reducing conditions artificially created by the enclosure of lake bottom sediments by seepage meters (Belanger & Mikutel, 1985). The presence of stringers of reduced sediments in the bottom of the Battersea



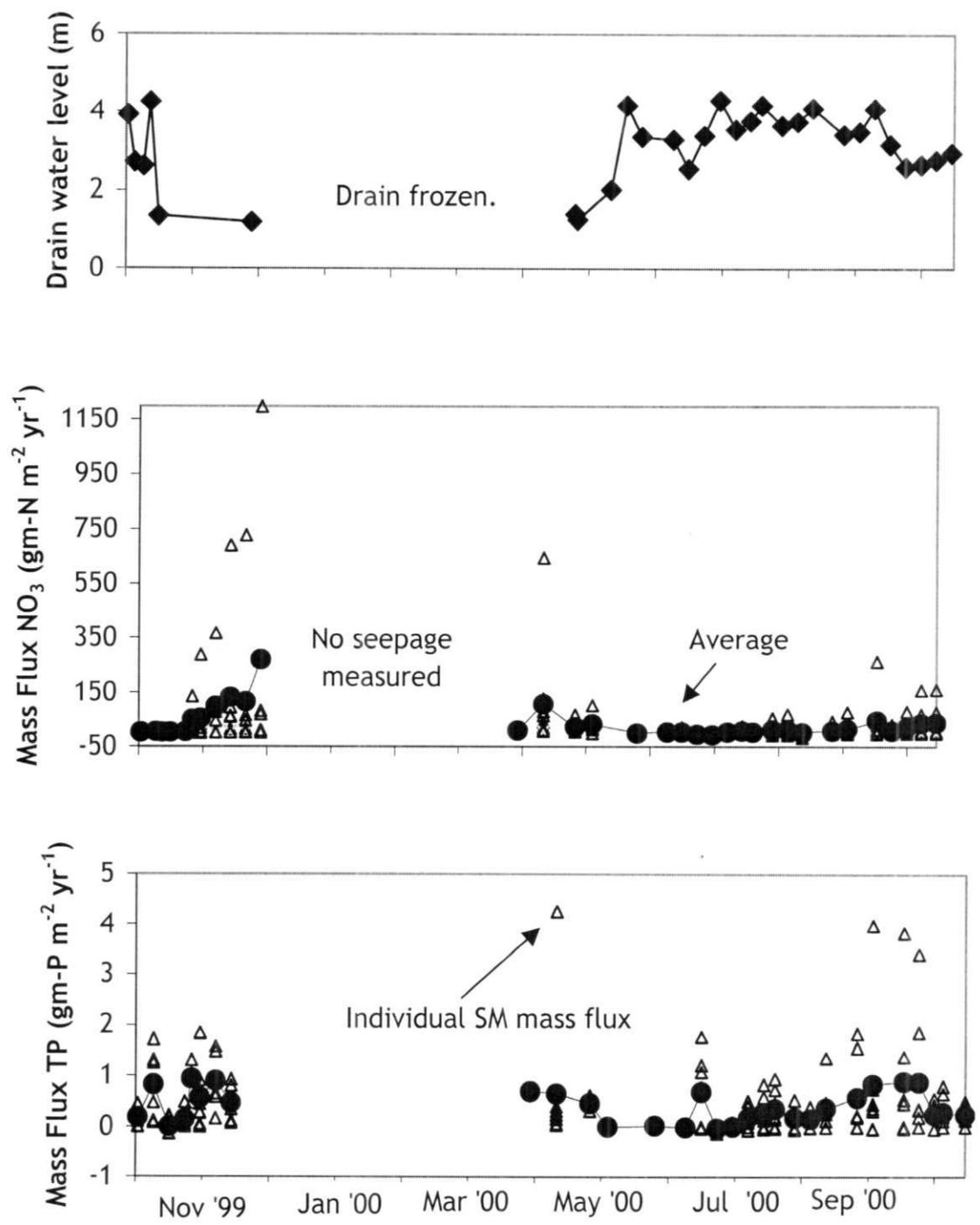


Figure 5-29: Variation in Drain water level and mass fluxes of NO₃ and TP over time. No seepage was measured during the winter. Both PO₄ and DP follow a similar trend as TP.

Drain, suggests that the sediments are naturally reducing, and the seepage meters are not creating these conditions. Phosphorus flux may be more responsive to fluctuations in drain water level because of immediate release of P from drain sediments once groundwater begins to discharge. The coincident release of P and reduced N in seepage water indicates NO_3 release is delayed simply because the initial N release is as NH_4 .

No statistically significant differences (2-way ANCOVA) were found to exist between the seepage and surface water chemistries (NO_3 , Cl, SO_4 , TP) with respect to the chemical variations over time (Figure 5-30). The Battersea Drain, like many other engineered drainage canals in the LNID was designed to artificially lower the local water table along its length. This suggests groundwater seepage is also affecting other drains in the LNID. Since the surface water chemistry varies in the same manner as the seepage water at this site, seepage from other fields probably follows similar trends. Ultimately, this suggests that the seepage meters are not responsible for the significant release of N and P to surface water, rather it must be due to natural development of anoxic conditions in the drain sediments.

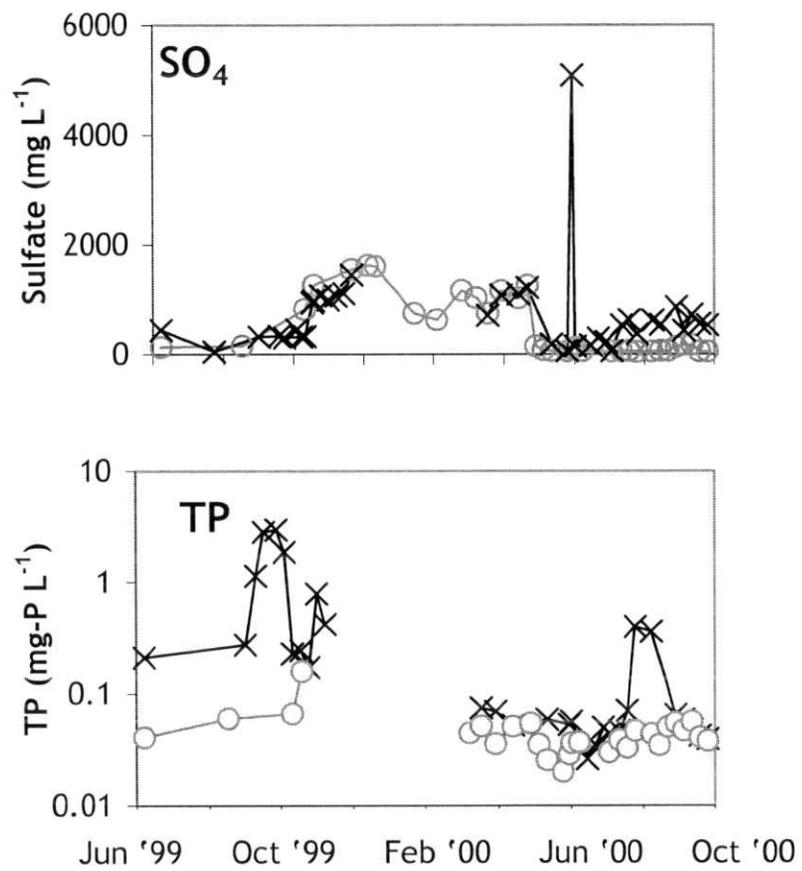
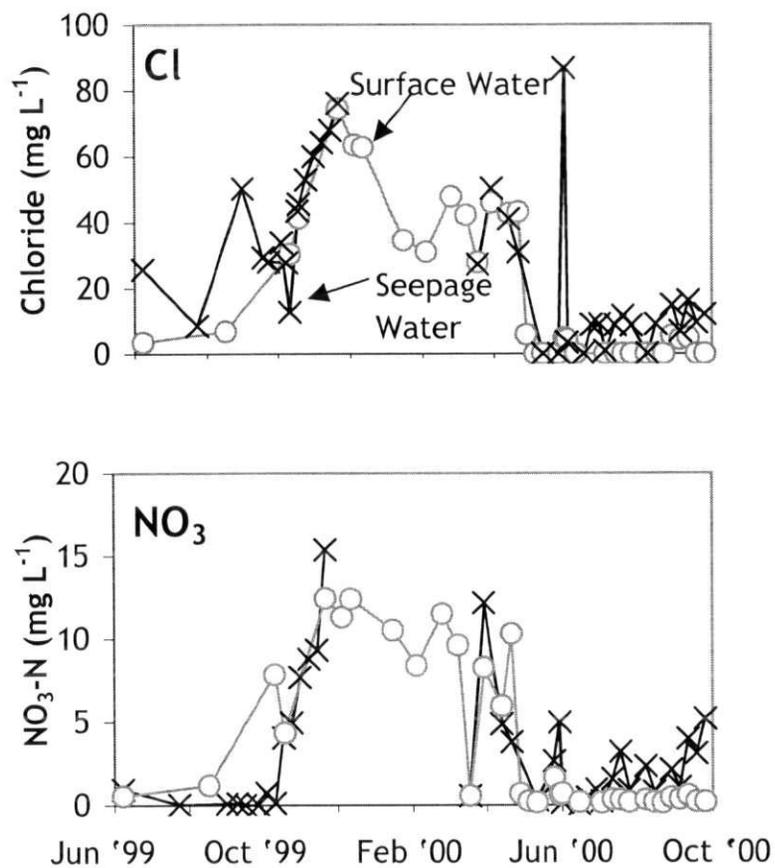


Figure 5-30: Variation in average concentrations of Cl, SO₄, NO₃, and TP in seepage (X) and surface (O) water over time at the Battersea field site.

CHAPTER 6: CONCLUSIONS

Groundwater at the Battersea site shows signs of impact from manure application. Concentrations of NO_3 , TP, SO_4 , Cl, TC, and FC, in excess of provincial and federal guidelines are present in groundwater, seepage water and surface water. Groundwater chemistry under the manured field is similar to that in other locations in the unconfined aquifer in the LNID. Nitrate is positively correlated with Cl, consistent with a manure source for both ions. Nitrate is negatively correlated with Fe, whereas total phosphorus is positively correlated with Fe. Both correlations are consistent with redox conditions. Groundwater P concentrations do not significantly correlate with Cl concentrations. Phosphorus concentrations are highest in the upper portion of the aquifer under the manured field, and the P/Cl ratio decreases with depth below the water table, consistent with a surface derived source of P at this site (i.e. manure).

The data suggest NO_3 concentrations in groundwater may be attenuated by a combination of autotrophic and/or heterotrophic denitrification and dissimilatory NO_3 reduction reactions. Nitrate reduction is predominantly occurring in localized areas in the aquifer and in the bottom sediments of the Battersea Drain. Dissolved organic carbon averages 10 mg L^{-1} in the unconfined aquifer, but concentrations do not substantially decrease along the flow path. Rather they increase near MLS 18. The lack of correlation between DOC concentration and the $\delta^{18}\text{O}$ of groundwater indicates that the increase in DOC concentrations is not due to upwelling groundwater. The observed variation in DOC concentrations suggests heterotrophic denitrification is not a dominant process, and that the DOC is present in forms that are not labile for denitrification.

Localized increases in SO_4 concentrations are coincident with decreases in NO_3 concentrations, suggesting autotrophic denitrification is occurring. Analysis of the $\delta^{34}\text{S}$ of S in SO_4 supports the occurrence of autotrophic

denitrification as the dominant N attenuation mechanism in the aquifer. Autotrophic denitrification is less desirable than heterotrophic denitrification due to the potential for significant increases in groundwater SO_4 concentrations.

The presence of elevated levels of NH_4 in groundwater and seepage water suggests that dissimilatory nitrate reduction (DNR) could also be occurring. Within the aquifer, high concentrations of NH_4 and NO_2 combined with low concentrations of NO_3 may be associated with patches rich in organic material and a locally reducing environment. Upwelling of deeper, nutrient poor groundwater near MLS 18 and/or locally reduced lenses may be the cause for the reducing conditions. High concentrations of NH_4 in seepage water are probably the result of flushing of NH_4 produced by DNR in the bottom sediments during periods of low groundwater discharge, when anoxic and reducing conditions develop in the drain-bottom sediments. An N-balance along the groundwater flow path suggests that DNR is an important N attenuation process in the seepage meters. Although DNR can reduce NO_3 concentrations in the groundwater, it is N-conservative, and therefore, not a desirable process over the long term.

Phosphorus is currently being stored in the aquifer sediments (average: 0.27 mg-P g^{-1} sediment). The maximum sorption capacity of the sediments is 0.24 mg-P g^{-1} sediment, suggesting that the aquifer is nearing saturation with respect to P adsorption. Phosphorus stored in saturated aquifer sediments is higher than the average concentration in the soil zone (0.17 mg-P g^{-1} sediment) and the mass of P extracted increases with depth. Although there is a significant mass of P stored in the soil zone, the trend of HCl-extractable P suggests that P is being leached to the water table. Increased PO_4/TP ratios with depth in the aquifer suggest that geologic P may be present. However, the decrease of both the P/Cl ratio and P concentrations with depth suggest that a significant mass of P is agriculturally-derived.

Total phosphorus concentrations are variable along the groundwater flow path. However, DP concentrations steadily decrease suggesting that P transport is being attenuated by P adsorption. Increased groundwater TP concentrations are coincident with increased NH_4 and decreased NO_3 concentrations indicating the presence of locally reducing microenvironments (i.e. at MLS 18 and seepage meters).

Geochemical modeling of groundwater indicates that the groundwater is saturated to supersaturated with respect to hydroxyapatite (HA) and that the saturation indices increase (i.e. HA becomes supersaturated) along the groundwater flow path. However, authigenic HA is not thought to be present in the aquifer sediments. Although groundwater P concentrations may be approaching steady state, the presence of organic acids and a low Ca/Mg ratio probably inhibit precipitation of HA. Groundwater samples are evenly distributed between the stability fields of strengite and hydroxyapatite, but strengite is undersaturated in the groundwater. However, simple Ca- and Fe-phosphates may be precipitating. Phosphorus concentrations extracted from aquifer sediments by strong acid were not significantly different than those extracted by weak acid suggesting P is not being stored as P minerals.

Nitrogen and phosphorus in groundwater are being transported to the adjacent surface water body (the Battersea Drain). Nitrogen loads of 62 kg-N yr^{-1} and TP loads of $0.80 \text{ kg-P yr}^{-1}$ (DP: $0.21 \text{ kg-P yr}^{-1}$) represent 7.4% and 0.16% of the masses reaching groundwater, respectively. Significant masses of N and P are stored in the soil and aquifer. Nitrogen flux decreases as groundwater moves through the aquifer, whereas P flux increases. The P release is related to the locally reducing zone at MLS 18 and in the drain sediments.

Oscillations in the groundwater flow system, due to fluctuations in the elevation of water in the Battersea Drain, result in bank storage along the length of the canal. When drain water levels are high, seepage rates and mass fluxes of NO_3 and P are low to negative. As the drain water levels drop, the hydraulic gradient reverses and both seepage rate and mass flux of NO_3 and TP

dramatically increase. Bank storage causes concentrations in seepage water to be intermediate between those of groundwater and surface water.

Phosphorus release is apparently more responsive than nitrate release to fluctuations in drain water level. Higher concentrations of reduced N in seepage water are coincident with higher P concentrations suggesting that the increased responsiveness of P is related to the redox conditions in the sediments of the Battersea Drain.

Temporal trends in seepage water and the surface water chemistries are not significantly different. Since the Battersea Drain receives seepage from agricultural fields along its length, the variation in N and P loads are more likely due to natural processes than to artificially reducing conditions caused by the enclosure of drain sediments by seepage meters. Furthermore, this suggests that the rates of N and P release at the Battersea site are not unique. Rather, they are probably typical upgradient fields along the Battersea Drain.

This study has important implications for management of the groundwater resources in the LNID. High levels of $\text{NO}_3\text{-N}$ and DP, like those at this site are typical of agriculturally impacted water in the LNID. Continued manure application at the current rates will only exacerbate the problem and could have future impacts on the water quality of other surface water bodies upstream of the site. Currently, Alberta's manure application guidelines are based on the N content of the soil. The mass of P in the soil at the Battersea site is 1.5 times greater than the mass of N. When manure is applied according to N guidelines, P tends to be applied at rates two or three times the crop requirements causing the P accumulation seen at this site. Although there is evidence for attenuation of P leaching in the surface zone, there is a finite amount that can be stored in the soil zone. Further inputs will eventually promote P leaching.

Nitrogen and phosphorus transport in the aquifer is being attenuated by denitrification and P sorption, with some indication that P mineral precipitation may be occurring. However, 90% of the groundwater samples

exceed the drinking water guideline for $\text{NO}_3\text{-N}$, and two-thirds exceeded the Alberta surface water guideline for TP. Heterotrophic denitrification is limited at the Battersea site by the presence of non-labile forms of DOC derived from manure. Natural denitrification could be promoted by introducing more labile forms of DOC. However, the development of reducing conditions in response to denitrification would promote P release due to dissolution of sorption complexes. Localized reducing conditions in the aquifer at the Battersea site are currently responsible for increasing the P flux along the flow path. Therefore, when considering nitrate remediation, it is important to consider the effect that practice may have on the P at the site. Since P cannot be permanently removed from a system, promotion of its artificial release could have serious implications for the trophic state of downgradient surface water bodies.

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