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REACTIONS OF DISSOLVED CHEMICALS EXTRACTED FROM MANURE OR COMPOST WITH SOILS AND SOIL CONSTITUENTS

BY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Reactions of Dissolved Chemicals Extracted from Manure or Compost with Soils and Soil Constituents submitted by Claudia Cecilia Gomez in partial fulfillment of the requirements for the degree of Master of Science in Soil Science.

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ABSTRACT

The potential for manure and compost to contaminate the environment depends in part on the movement of soluble C, N and P constituents into surface and groundwater. Concentrations of dissolved organic C (DOC), as high as 1 g l^{-1}, have been observed in puddles at the base of some compost piles and large quantities of DOC are extractable from manure. Soluble N and P are readily extracted from manure and compost. Transport of solutes is controlled by sorption onto soil. Sorption comprises diverse mechanisms ranging from precipitation to partitioning and adsorption. The extent of these mechanisms is in turn a function mainly of the content and quality of the soil organic phase; the presence of minerals that would cause precipitation; and the hydrophobicity of the DOC. I hypothesized that hydrophobic components of DOC would be more readily sorbed by the organic-rich A horizon, while hydrophilic components of DOC would be more readily sorbed by the mineral dominated B and C horizons resulting in horizon-specific fractionation. I also hypothesized that soluble N would be retained by soils in the form of NH_4-N and that phosphates would be strongly sorbed by the mineral components of soil.

Extract from manure and composted manure were equilibrated with surface and subsurface soil samples from an Eluviated Black Chernozem and sorption was measured, at equilibrium concentration, up to 1000 mg C kg^{-1} soil. Sorption of DOC extracted from compost was 6-8 times greater than that of DOC extracted from manure for both surface and subsurface soil samples. Characterization of the DOC, before and after exposure to soil, by CPMAS ^{13}C NMR did not indicate a significant difference in the chemical

composition of manure or compost extractable DOC. However, the ratio of absorbance values at 465 and 665 nm (E_4/E_6) for DOC increased after equilibration with soil for both surface and subsurface soil samples, suggesting that some components of DOC are more readily sorbed to soil than others. Sorption of N and P was up to 50 times greater than for DOC.

The movement of soluble compounds from manure and composted manure through intact soil cores was used to test the hypothesis that soil acts as a filter for suspended solids of manure and compost while soluble materials are not attenuated. Manure and compost were applied to intact soil cores, sampled from the Ah, Bt and Ck horizons of an Eluviated Black Chernozem, at a rate of 6.8 Mg ha^{-1} on a dry matter basis. DOC, suspended solids, soluble N and soluble P were detected in the leachates from manure amended soil cores but not in the leachates of cores receiving compost. DOC concentrations in the manure amended leachates were as high as 460 mg C l^{-1}. Solubilization of P occurred and N concentrations in the leachates were as high as 100 mg N l^{-1}. Results from this work are consistent with the previous sorption results that suggested reduced likelihood of leaching and groundwater contamination using compost as compared with manure. I conclude that mobile DOC from manure has the potential to contaminate surface and groundwater while the low mobility of DOC from compost eliminates most of this potential.

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GENERAL INTRODUCTION

Animal manures have long been recognized for their value as a nutrient source in the production of agricultural crops because they improve both physical and chemical properties of soil including increased aggregate stability, increased water holding capacity, reduced evaporation, and increased organic matter contents (Ghaly and Singh 1991). Janzen and McGill (1995) estimated that during 1991 livestock in Alberta excreted 271 000 tonnes of N and 79 000 tonnes of P, with much of that concentrated in small regions. Land application of manures is considered a suitable method for the disposal of this waste. Land application, or land farming as it is often called when applied to agricultural waste, is the intimate mixing or dispersion of wastes into the upper layer of the soil-plant system with the objectives of microbial stabilization, adsorption, immobilization, selective dispersion or crop recovery of nutrients, leading to an environmentally acceptable assimilation of waste (Overcash and Pal 1979). The application of raw organics can be problematic because they are bulky, contain excess water, emit odors, and are difficult to transport; they also contain unwanted components such as xenobiotics, disease organisms and/or weed seeds. Excess nitrogen leached and ammonia volatilized from land receiving manure are also a concern (Paul *et al.* 1994). Chang *et al.* (1990) have also reported that soil pH decreases with time when cattle feedlot manure is applied to soil as organic acids are produced as a result of microbial decomposition of manure.

Composting of organic wastes is a preferable option prior to land application. Composting is a thermophilic process whereby microorganisms oxidize readily decomposable organic compounds to carbon dioxide and convert others to stable organic matter (Garcia *et al.* 1991). Composting destroys disease organisms and weed seeds (Hadas and Portnoy 1994) and also reduces the bulk of the starting material by 40-60%. Although the use of composted material in soils has increased, investigations into the management of composts have been limited (Nodvin *et al.* 1986). Sustainable application of waste to soil is dependent on knowledge of the transformation and the fate of waste components within the soil profile (Keeling *et al.* 1994).

Although properly controlled composting can alleviate many of the problems associated with raw organics, environmental concerns exist regarding nutrient losses from manure and compost heaps resulting from water infiltration and runoff (Ulén 1993). We have observed concentrations of dissolved organic carbon (DOC) as high as 1 g l^{-1}, in puddles at the base of some compost piles.

Dissolved Organic Carbon

DOC is a heteropolydisperse organic material containing a range of organic compounds from simple sugars to complex fulvic and humic acids (Moore *et al.* 1992). Fulvic and humic acids are components of humic substances. Dissolved humic materials represent a major fraction of the total organic C compounds in natural waters, constituting 40-60% of the dissolved organic C present (Dahm 1981; Lee *et al.* 1993; Schlautman and Morgan 1993). Humic materials are amorphous, dark coloured, hydrophilic, acidic, partially aromatic, chemically complex organic substances that range in molecular weight from a few hundred to a few thousand daltons (Schnitzer 1982). Fulvic and humic acids are defined functionally by their solubility in dilute alkaline and acidic solutions. Humic acids are soluble in dilute alkali but are precipitated with acidification of the alkaline extract. Fulvic acids are soluble in dilute alkali and remain in solution upon acidification (Schnitzer 1982). The two fractions are chemically similar but differ in molecular weight and functional group content. Fulvic acids have a lower molecular weight and higher content of oxygen-containing functional groups (COOH, OH, C=O) per unit weight than humic acids (Schnitzer 1982). Both fractions exhibit a relatively high resistance to microbial degradation and possess the ability to form stable water-soluble and -insoluble complexes with metal ions and hydrous oxides and to interact with clay minerals (Schnitzer 1982). The quantity and composition of DOC will vary with the source of organic C.

DOC can be extracted from both aqueous and nonaqueous sources including lakes, rivers, soils, composts, peats, bogs, plants, sewage sludge, and leaf litter. Aquatic humic acids are considered to be the result of the complexation of the "leftovers" of microbial activities on lignins and other compounds found in the waters (Shimp and Pfaender 1985). Dissolved and aquifer bound organic C, resulting from the degradation and repolymerization of plant material, are common constituents in shallow aquifers (Dunnivant *et al.* 1992).

Carbon cycling in soils is an important process that involves the movement of large amounts of DOC within the soil profile. The primary mode of C transport in soils involves the solubilization of organic rich surface layers and its deposition in mineral B horizons. This is the major characteristic of podzolization (Vance and David 1992).

Carbon in its soluble form is the most readily available for microbial metabolism. Microbial populations in soil are concentrated in water films that fill pores and coat soil particles. Therefore only chemicals in solution are considered directly available for uptake by microorganisms (Ogram *et al.* 1985; Fan and Scow 1993). Decomposition of DOC by microorganisms can lead to the development of anoxic conditions which can lead to competition between plants and microbes for oxygen.

DOC, because of its dissolved state, is highly mobile in soils although its retention by soils is also an important process. DOC influences acidity because many of the reaction products of its decomposition are acidic. Nutrient availability, toxicity, and the transport of metals and contaminants within soil are also affected because of DOC's high affinity for inorganic and organic chemicals which can result in the retardation or enhancement of contaminant mobility (Jardine *et al.* 1990; Moore *et al.* 1992; del Castilho *et al.* 1993; Hsu *et al.* 1993). The degree to which these processes are observed is dependent on the concentration of DOC retained by soils which in turn is dependent on the chemical characteristics of the soil constituents and the DOC.

DOC Sorption

DOC is involved in sorption reactions with soil constituents and chemicals in solution. Sorption is used as a generic term to mean the uptake of a solute by a sorbent from solution or gas phase without reference to a particular mechanism (Chiou 1989). It includes the mechanisms of adsorption, a two dimensional "sticking on" of materials or condensation on surfaces or interior pores of a solid by physical or chemical bonding forces; partitioning, a three dimensional process better described as absorption or dissolution or uptake in which the sorbed organic chemical permeates the sorbent; and precipitation, the formation of a new three dimensional phase (Chiou 1989; McBride 1994). As a result of these processes, DOC may act as a cosolute or cosolvent in the soil solution. The rate of chemical degradation, photolysis, volatilization, transfer to sediments, and biological uptake may be different for the fraction of an organic compound that is bound to DOC compared to that which is not bound (Carter and Suffet 1982). Subsurface transport of inorganic and organic contaminants may therefore be strongly related to the movement of DOC through soil (Jardine *et al.* 1990).

The degree to which solubility enhancement of sorbed chemicals and their microbial availability is observed is a function of both the kind and type of DOC and soil present and the interaction of DOC with soil (Nodvin *et al.* 1986; Moore *et al.* 1992). Extractable iron and aluminum, mineralogy and organic C content are important controls on the tendency of soils to sorb DOC. Soil organic matter is similar in composition to DOC and sorption or retention of DOC by these soils is expected to be high since soil organic C possesses the greatest affinity for DOC (Chiou 1989). This assumption is based on the theory of "like sorbs like" which dictates that chemicals preferentially partition into or onto phases like themselves.

While organic C possesses the greatest affinity for DOC, soils containing $CaCO_3$ may also exhibit moderate DOC sorption capacities. Sorption of organic matter by calcareous soils has been documented and precipitation of organic C in calcium-rich lakes has also been established (Moore *et al.* 1992).

In mineral dominated horizons, sorption occurs at the surface of crystalline and non-crystalline clays. Soils high in clays with high specific surface areas show high levels of sorption (Nelson *et al.* 1990). Amorphous minerals play a predominant role in the retention of DOC in these horizons. Dahm (1981) reported the majority of DOC resulting from leaching of N-rich deciduous leaves was not susceptible to physical-chemical bonding to crystalline clays of montmorillonite, kaolinite, and chlorite but showed considerably more sorption (40 times) onto amorphous aluminosilicate clays and hydrous oxides of iron and aluminum. Jardine *et al.* (1989) observed that the sorption of DOC, extracted from stream water, onto soil was significantly reduced with the removal of iron oxides and hydroxides while Moore *et al.* (1992) observed a positive correlation between DOC sorption, peat source, and extractable iron and aluminum concentrations.

The mechanisms by which DOC sorbs onto soil surfaces are largely unknown. A number of mechanisms may be involved in the removal of reactive solutes by soil, including ion exchange, precipitation-crystallization, structural substitution, chelation, physical adsorption, and partitioning (Nodvin *et al.* 1986; Moore *et al.* 1992).

Previous studies have concluded non-crystalline hydroxides and oxyhydroxides play an important role in sorption of organic solutes through hydrogen bonding, ligand exchange with surface-coordinated hydroxyls, or bridging with polyvalent cations (Donald *et al.* 1993). Sorption of DOC may also occur through nonspecific electrostatic ion exchange reactions with clay colloids that have permanent or pH dependent charge (Donald *et al.* 1993). Sorption capacities have been related to the surface area of soils, therefore soils low in clay would have low sorptive capacities (Nelson *et al.* 1990). Anion exchange may account for some of the sorption of DOC observed in soil. Jardine *et al.* (1989) and Guggenberger and Zech (1992) observed a competitive exchange between

DOC and sulfate. As the concentration of DOC in the system increased, the binding of sulfate onto soils was decreased.

Partitioning results because of "hydrophobic interactions", a combination of relatively small van der Waals bonding forces and a substantial thermodynamic gradient which drives organic molecules out of the aqueous phase and onto solid soil constituents. The thermodynamic driving force is the increase in entropy which results from the breakdown of the highly structured coordination shell of water molecules surrounding hydrophobic solutes such as DOC (Schlautman and Morgan 1993). Schnitzer and Kahn (1972) suggest humic material consists of a broken network of poorly condensed aromatic rings with appreciable numbers of disordered aliphatic or alicyclic structures attached around an aromatic core. The building blocks of humic structure are thought to be phenolic and benzenecarboxylic acids which are joined by hydrogen bonds and van der Waals forces to form relatively stable aggregates. The humic material is thought to have an open structure which allows for a considerable number of voids of varying dimensions, and the arrangement is expected to be sensitive to changes in pH, salt concentration, and valence of cations. The voids could trap organic compounds, provided the compounds had proper molecular sizes to fit. Hydrophobic cavities would be sites where van der Waals bonding forces between organic molecules and DOC could occur as part of the overall hydrophobic interaction (Schlautman and Morgan 1993).

DOC-Mediated Contaminant Transport

DOC's high affinity for inorganic and organic chemicals has implicated it in the transport of metals and contaminants through the soil profile. Most work to investigate the role of DOC in solubility enhancement of compounds has used pure fulvic or humic acids, either commercial or isolated from soil and water bodies, as surrogates for DOC. Humic substances, once dissolved, can increase the apparent water solubility of nonpolar hydrophobic compounds, bind organic compounds, and decrease the availability of chemicals to microorganisms (Landrum *et al.* 1984). It is generally accepted that humic acids have a greater binding potential than do fulvic acids.

Chiou *et al.* (1986) investigated the solubility enhancement of p,p'-DDT, 2,4,5,2',5'-PCB, 2,4,4'-PCB, lindane and 1,2,3-trichlorobenzene by soil humic materials. They observed increasing water solubility for p,p'-DDT, 2,4,5,2',5'-PCB and 2,4,4'-PCB as the concentration of humic acid was increased. Solubility enhancement was also achieved by exposing these pollutants to soil fulvic acid and aquatic humic and fulvic acids but the degree of enhancement was 4-fold and 5 to 7-fold that observed with soil humic acids, respectively. They postulated that a linear relationship existed between the apparent solubility of a compound and the concentration of the cosolute and that solubility enhancement is reduced with the increasing water solubility of the organic chemical. Hence, lindane and 1,2,3-trichlorobenzene, both of which are highly water soluble, would show minimal changes in their solvency. Carter and Suffet (1982) also observed a high degree of binding between DDT and commercial and aquatic humic acids as greater than 75% of added DDT was found bound to humic acid following a dialysis sorption study.

Lafrance *et al.* (1991) provided both complementary and contradictory evidence to that presented by Chiou *et al.* (1986). Lafrance *et al.* (1991) observed that aldicarb, a highly water soluble organic (6000 mg l^{-1}) was poorly bound by commercial fulvic and humic acids, a result consistent with Chiou *et al.*'s (1986) theory regarding the increased solvency of highly water soluble compounds. Lindane and PCP were observed to be strongly bound by humic acids, and to a lesser degree by fulvic acids. However, PCP was bound more strongly than lindane despite PCP's greater water solubility (Lafrance *et al.* 1991).

"Partition-like" interactions between solutes and organic acids are believed responsible for solubility enhancement. Chiou *et al.* (1986), in an attempt to explain the degree of partitioning with various solutes, used phenylacetic acid as a cosolute in their experiments. The results observed with humic and fulvic acids were not reproducible using phenylacetic acid. Solubility enhancement was postulated to occur as a result of the size of the cosolute molecules. As humic acids are bigger than fulvic acids, humic acids are assumed to have a sufficiently large intramolecular nonpolar organic environment for promoting a "partition-like" interaction with relatively nonpolar organic solutes (Chiou *et al.* 1986).

The polarity and molecular configuration of the cosolute also appears to be important. Poly(acryl) acid, a linear polyelectrolyte similar in C (50%), O (44.4%) and H (5.6%) contents to fulvic acids did not enhance the solubility of DDT or PCB (Chiou *et al.* 1986). Poly(acryl) acid is dissimilar from fulvic acid in that it consists of a frequent and orderly arrangement of hydrophilic (carboxyl) groups to the C chain and to an extended chain structure which does not permit the formation of a sizable intramolecular nonpolar environment (Chiou *et al.* 1986).

The nature of the sorbate also plays a role. The high extent of binding for PCP with commercial humic acid observed by Lafrance *et al.* (1991) was attributed to the aromatic character of PCP as compared to lindane. Therefore, the PCP molecule is capable of directly intervening in hydrophobic bonding. Conversely, the saturated character of the lindane molecule allows less van der Waal's attraction forces with the planar aromatic structures of dissolved humic substances, leading to a lower binding extent than PCP (Lafrance *et al.* 1991).

It is generally accepted that nutrients are most readily available for microbial metabolism in their soluble form. Sorption of nutrients by DOC is implicated in reducing the bioavailability of chemicals. Experiments with humic acids and 2,4,6-trichloro-(^{14}C)-phenol (Robinson and Novak 1985), m-cresol, m-aminophenol, and p-chlorophenol (Shimp and Pfaender 1985), and benzylamine (Amador and Alexander 1988) resulted in reduced mineralization of these chemicals in the presence of humic acids. Mineralization was reduced as the extent of binding to humic acid increased. These findings are important from the standpoint of the bioremediation potential of these chemicals, in the presence of DOC, as sorbed chemicals may be metabolized to a lesser degree than free chemicals although their solubility may appear to be enhanced. DOC complexed chemicals while detectable by analytical methods may not be bio-available in the bound state. DOC sorption of chemicals can also be beneficial. Toxicity tests with *Daphnia magna* for diazinon, tetrabromobisphenol-A (TCP), 4-chloroanilin (4-CA) and pentachlorophenol indicated that the toxicity of diazinon and 4-CA to the water flea was reduced with the introduction of dissolved humic material (Lee *et al.* 1993).

The association of DOC with organic compounds in the solution phase has been proposed as the principle process affecting the sorption of organic compounds by solid sorbents. The processes taking place at the solid-solution interface, such as sorption of DOC and of DOC-associated organic compounds by solid sorbents, may also influence the sorption of organic compounds by solid sorbents (Lee *et al.* 1990). The influence of these reactions at the solid-solution interface have not been elucidated to date.

Lafrance *et al.* (1991), using aldicarb and dissolved humic substances, reported that although the sorption affinity of dissolved humic substances for aldicarb was minimal, the presence of dissolved humic substances slightly increased the sorption of aldicarb by soil containing 2.2% and 0.8% organic C (30% and 40% increase, respectively). Sorption kinetics for aldicarb remained unaffected.

Conversely, Lee *et al.* (1990) reported the sorption of napropamide onto montmorillonite in the presence of DOC decreased as compared to DOC free systems. As the amount of DOC was increased, the partition coefficient, K, for the reaction decreased from 0.33 (g DOC kg^{-1} clay)/(nmol m^{-3}) when no DOC was present to 0.09 (g DOC kg^{-1} clay)/(nmol m^{-3}) with 56.6 g DOC m^{-3} present. They speculated the K value decreased as a result of interactions between DOC and the clay. Sorption of DOC by the clay would result in a decrease in the total surface area available for sorption of napropamide. When soil was treated with napropamide and DOC, neither an increase in the amount of DOC nor the sorption of DOC by soil appeared to affect the sorption of napropamide by soil (Lee *et al.* 1990).

Objectives

The extent to which any of the above processes are observed is dependent on the concentration of DOC retained by soils which in turn is dependent on the chemical characteristics of the soil constituents and the DOC. The objective of this research was to investigate the extent to which DOC, extracted from manure and compost, sorbs to or is retained by soils and soil constituents. A secondary objective was to investigate the extent to which soluble N and P are sorbed by soils and whether they are influenced by the behaviour of DOC. To achieve these ends, two sets of experiments were undertaken. The first involved batch equilibration experiments in which manure and compost derived DOC, N and P were reacted with surface and subsurface soil samples of an Eluviated Black Chernozem. These experiments are described in Chapter 2 of this thesis. This set of experiments was useful in understanding the behaviour of DOC with soils and its constituents and to provide an idea of the potential sorptive capacity of soils for DOC, N and P. The second set of experiments concern themselves with *in situ* conditions. Batch equilibrations provide ideal conditions for sorption because they allow for the exposure of large surface areas to solutes whereas leaching experiments mimic *in situ* conditions better. Therefore, leaching experiments using soil cores from surface and subsurface horizons of an Eluviated Black Chernozem, amended with either manure or compost, were conducted in order to gain an understanding of the behaviour of soluble constituents in intact soils (Chapter 3). Chapter 4 of this thesis summarizes these experiments and provides a synthesis of the work and its implications to manure and compost management.

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Chapter 2

REACTIONS OF DISSOLVED ORGANIC CARBON, NITROGEN AND PHOSPHOROUS WITH SOILS AND SOIL CONSTITUENTS

Introduction

Nutrient losses from manure and compost are of concern with regard to contamination of surface and groundwaters. Concentrations of dissolved organic C (DOC) as high as 1 g l^{-1}, have been observed at the base of some compost piles and large quantities of DOC are extractable from manure. The potential for manure and compost to contaminate the environment depends largely on the movement of soluble C, N and P components into surface and groundwater.

Dissolved organic C (DOC) is a heteropolydisperse organic material containing a range of organic compounds from simple sugars to complex fulvic and humic acids (Moore *et al.* 1992). Soluble C influences soil pH since many of the reaction products from the decomposition of DOC are acidic. Nutrient availability, toxicity, and the transport of metals and contaminants within the soil are also affected because of DOC's high affinity for inorganic and organic chemicals which can result in the retardation or enhancement of contaminant mobility (Jardine *et al.* 1990; Moore *et al.* 1992; del Castilho *et al.* 1993; Hsu *et al.* 1993). DOC is a potential substrate for soil microorganisms and its decomposition can result in anoxic conditions leading to competition for O_2 between microbes, fauna and plants. The degree to which these processes are observed is dependent on the concentration of DOC retained by soils which in turn is dependent on the chemical characteristics of the soil constituents and the DOC.

Soluble N and P are two constituents readily extracted from manure and compost whose mobility may be influenced by or mimic that of DOC. Nitrate is the most soluble of the nitrogenous compounds and is subject to leaching and water transport (Paul and Clark 1989). Excess concentrations of NO_3^- in groundwaters have been associated with excess growth of plants and algae leading to eutrophication, health problems such as infant and animal methemoglobinemia, and the formation of carcinogenic nitrosamines through reaction with other nitrogenous compounds (Paul and Clark 1989). The fates of NO_3^- include: denitrification by microbes to NO_x or N_2, microbial uptake and use in amino acid synthesis, use by microbes as an electron acceptor under anaerobic conditions, leaching deep within the soil profile to groundwater or be transported off site by run-off, or it may accumulate in soil (Guenzi *et al.* 1978; Paul and Clark 1989; Paul *et al.* 1993).

Ammonium is less soluble than NO_3^- and is subject to volatilization and fixation by clays and soil organic matter rather than leaching. Up to 50% of total N in manure at the time of spreading can be lost as volatile NH_3 (Lauer *et al.* 1976). Manure is considered a good source of N for plants because 50-75% of it occurs in the form of NH_4^+ (Paul and Beauchamp 1995). Once NH_4^+ has been formed its fates include: plant uptake, utilization by microbes for the synthesis of amino acids, fixation in interlayer spaces of expanding clays, stabilization onto organic matter, and volatilization as NH_3 (Paul and Clark 1989; Paul and Beauchamp 1995).

Continuing additions of either fertilizer or manures causes enrichment of soil P, a dominant element controlling C and N immobilization by organisms (Paul and Clark 1989; Tran and N'dayegamiye 1995). Most soil phosphates are poorly soluble or insoluble, although P can be solubilized in the presence of CO_2 and organic acids (Paul and Clark 1989). Phosphates are known to cause algal blooms which result in eutrophication.

Sorption onto soil is an important control on transport of these soluble C, N and P components in the environment. Sorption is a generic term used to mean the uptake of a solute by a sorbent from solution or gaseous phase without reference to a particular mechanism (Chiou 1989). Sorption comprises diverse mechanisms ranging from precipitation to partitioning and adsorption.

The objectives of this study were to discover the extent to which DOC and consequently N and P from manure and compost would be sorbed or retained by soils and soil constituents. The underlying question is, do the soluble constituents extracted from manure and compost differ in their behaviour in soil and if so, how? I hypothesized that preferential sorption of DOC by soil constituents would result in horizon-specific fractionation of the DOC. The more hydrophobic components of DOC would be retained by the organic-rich A horizon leaving the remaining DOC negatively enriched with hydrophilic constituents which themselves would be preferentially sorbed by the mineral dominated B and C horizons. This hypothesis was based on the theory that nonionic organic molecules partition into organic phases which are similar in composition to the molecules rather than phases which are dissimilar (Chiou 1989). I also hypothesized that nitrogenous compounds in the form of NO_3^- would not be retained by soil, but that NH_4^+ would be retained by the soil matrix because of its positive ionic charge. Solubilization and subsequent mobility of P was not hypothesized to be significant even in the presence of organic acids extracted from manure and compost. These hypotheses were tested using batch equilibration experiments with manure and compost derived extracts.

Materials and Methods

Soil Samples

Soil samples were collected in the spring of 1994 from the Ah and Ck horizons of an Eluviated Black Chernozem at the Ellerslie Research Station in Edmonton, Alberta. The samples were air dried, sieved through a 2 mm sieve and stored at room temperature prior to the commencement of the study. Total C was measured by dry combustion and subsequent CO_2 determination using a high temperature (1300°C) LECO furnace. Total organic C of carbonate containing soil samples was determined by difference by first treating the subsurface soil samples with approximately 2 M HCl and heating at 80°C until no further frothing was observed. Soil pH was determined in deionized water and 10 mM $CaCl_2$ using a Fisher Accumet pH meter (Model 825 MP) as described by Hendershot *et al.* (1993). Particle size analysis was determined by the Buoyoucos hydrometer method as described by Kalra and Maynard (1991). Table 2.1 lists the soil characteristics.

Table 2.1. Selected soil characteristics.

Soil	Total Organic C (%)	Carbonate C (%)	pH		% sand	% clay	Texture Class
			water	0.01 M $CaCl_2$			
Ah	4.71	n a*	6.3	5.9	37	30	Clay loam
Ck	0.34	0.67	8.2	7.6	37	38	Clay loam

*n a = not analyzed

Compost and Manure Samples

Fresh cattle manure and urine, henceforth termed manure, were collected from the University of Alberta Dairy Unit at the Edmonton Research Farm in Edmonton, Alberta and were stored at 4°C. Composted cattle manure was obtained from Olds College in Olds, Alberta. Compost samples were air dried, sieved through a 2 mm sieve, and stored at room temperature prior to conducting the experiments.

Dissolved Organic Carbon Preparation

A subsample of manure was mixed with 20 mM K_2SO_4, amended with 10 µM $HgCl_2$ to retard microbial activity, at a rate of 1:17 dry manure to solution (w/w) and shaken for 2 hours on a reciprocal shaker at 200 rpm. Potassium sulfate was used to maintain the ionic strength of the DOC solutions. Manure derived DOC extracts (MS) were filtered through cheesecloth and 0.2 µm filters to remove suspended solids. The extracts were amended with approximately 0.5 g l^{-1} $CaSO_4$ to flocculate colloids and centrifuged for 20 min at 15 000 x *g*. DOC concentration was determined on an Astro 2001 System 2 Soluble Carbon Analyzer (Astro International Corporation, League City, Texas) by u.v.-promoted persulfate oxidation. The concentration of the stock solution was approximately 2800 mg C l^{-1}.

Compost derived DOC stock solutions (CS) were prepared in the same manner as MS solutions, however a ratio of 1:2 compost to solution (w/w) was used to maximize the quantity of DOC extracted. The concentration of organic C of the stock CS solution was approximately 1850 mg C l^{-1}. Both stock solutions were stored at 4°C prior to sorption experiments.

Batch Equilibration Experiments

A preliminary batch equilibrium experiment was conducted at increasing time intervals up to 32 hours with CS at a concentration of 280 mg C l^{-1} and a 1:10 ratio of soil to solution (w/w). Apparent equilibrium was reached at 16 hours. Based on these findings, 24 hours was chosen as an adequate duration for conducting the batch experiments.

For subsequent batch equilibrations, serial dilutions of the DOC stock solutions were prepared using 20 mM K_2SO_4 to yield concentrations ranging from 0 to 1850 mg C l^{-1} and the pH was adjusted to 6.5 with dilute H_2SO_4. Soil samples were shaken in triplicate with each of the dilutions, at a 1:10 soil to solution ratio, for 24 hours on a reciprocal shaker (200 rpm) in 50 ml Nalgene centrifuge tubes. Extracts were decanted and centrifuged for 20 min at 15 000 x *g*. Control samples of each DOC concentration were run simultaneously. The supernatant from the controls and samples was collected and analyzed for soluble C, total N, mineral N and total P.

Sorption isotherms for soluble C were constructed using the batch equilibration data. The equilibrium concentration of a solute (Ce) is that concentration of solute in the solution phase (solvent) that is in equilibrium with the solid soil phase (sorbent) at the end of the equilibration. The Ce was plotted against the concentration of solute that was originally added (Co) to the sorbent phase. These plots were used to calculate the partition coefficients (K_d) and uptake quantity (µg sorbate per g of sorbent) (x/m) for each of the DOC-soil combinations using the following equations.

$$K_d = \frac{\text{volume of DOC}}{\text{mass of soil}}\left(\frac{Co}{Ce} - 1\right) \tag{2.1}$$

$$\frac{x}{m} = K_d * Ce \tag{2.2}$$

The K_d value describes the affinity of a solute to partition onto a sorbent and is the slope of the plot x/m versus Ce when a linear isotherm is assumed. A linear sorption isotherm is the simplest model available to describe uptake of a solute by a sorbent and is defined mathematically by Equation 2.2. A linear isotherm describes a situation whereby a finite number of sorption sites exist and the energy required to sorb the first molecule to the sorbent is the same as the energy required to sorb all subsequent molecules. This mechanism of sorption is termed partitioning and usually holds true when solute concentrations are low. The greater the K_d value the greater the affinity of a solute to partition out of the solution phase onto the solid phase. Soil organic matter is the major sorbent of organic compounds (Chiou 1989) such that as the organic matter content increases so does sorption. Therefore, to compare the sorptive capacity of soils, they must first be normalized for organic matter content (f_{oc}). The organic matter normalized coefficient, K_{oc}, is calculated by dividing K_d by f_{oc}.

Similar sorption isotherms were constructed for N and P. Total soluble N was analyzed using the micro-Kjeldahl digestion method, with pretreatment to reduce NO_2^- and NO_3^- to NH_4^+, followed by colorimetric analysis on a Technicon Auto Analyzer II (Industrial Method No. 334-74 W/B) (McGill and Figueiredo 1993). The pretreatment was necessary since CS solutions are high in NO_3^- and the micro-Kjeldahl digestion method proved inadequate for accurately determining the NO_3^- concentration when compared to distillation-titration methods (Offord unpublished). Mineral N (NO_3-N and NH_4-N) was determined using the colorimetric technique with a Technicon Auto Analyzer II (Industrial Methods No. 487-77A and 98-70W, respectively).

The concentration of total P in the digested extracts was measured by the colorimetric method on a Technicon Auto Analyzer II (Industrial Method No. 334-74 W/B).

Electrical Conductivity and pH

Electrical conductivity and pH were measured for each sample and control supernatant following the batch equilibration. Electrical conductivity was measured using a YSI Conductivity Bridge (Model 31)and pH was measured with a Fisher Accumet pH meter (Model 825 MP). Samples were stored at 4°C prior to analysis. Measurements were made within 24 hours of collection.

Spectrophotometric Analysis

The absorbance of each of the supernatants was measured with a Unicam SP 1800 Ultraviolet Spectrophotometer at 465 and 665 nm and their E_4/E_6 values calculated by using the ratio of absorbance at 465 nm to the absorbance at 665 nm. All samples were diluted with K_2SO_4 to approximately 200 mg C l^{-1} and the pH was adjusted to between 7 and 7.5 prior to analysis as suggested by Chen *et al.* (1977).

E_4/E_6 ratios have traditionally been used to characterize humic and fulvic acids from soils. Schnitzer and Khan (1972) propose light absorption increases with an increasing concentration of C in aromatic nuclei as opposed to aliphatic side chains. Kononova (1966) believes a low ratio reflects a more condensed aromatic character. Chen *et al.* (1977) concluded molecular size governs E_4/E_6 ratios such that large molecular weight compounds would have low ratios and would contain a high C content, but little O, CO_2H groups and total acidity. Rather than focus on the meaning of E_4/E_6 ratios, for the purposes of these experiments these ratios were used as measures of change between solutions before and after reaction with soil. It was assumed that two solutions which are different in composition quantity and/or design should have different ratios.

Characterization of DOC Solutions by CPMAS ^{13}C NMR

Solution state NMR is often the preferred method for characterization of organic compounds because of its high resolution, however, due to the heterogeneity of DOC and the high molecular weight of the DOC components, solid state NMR was used. Dilutions of MS and CS were prepared to a final concentration of 1260 mg C l^{-1} using 20 mM K_2SO_4 and the solution pH adjusted to 6.5 with dilute H_2SO_4. Samples were mixed with soil at a ratio of 5:1 solution to soil (w/w) and equilibrated for 24 hours on a reciprocal shaker at 200 rpm. Samples and controls were centrifuged for 20 min at 15 000 x *g* and the supernatant was dried at 55°C. The dried material was ground with a marble mortar and pestle. The proportions of aliphatic-C, aromatic-C, carboxyl-C, and carbonyl-C of the dried extracts were determined by NMR at the Department of Chemistry, University of Alberta (Xing 1994).

From the obtained spectra, the percent aliphatic-C was calculated using the ratio of peak area of 0-106 ppm to the total area of 0-220 ppm. The same approach was used to calculate the percentages of the other C groups (Table 2.5).

Polarity Index

The polarity indices of samples before and after reaction with soil were calculated using the results of the NMR analyses (Xing 1994). The polarity index (PI) is an indicator of the ratio of O+N to C of organic compounds. This index provides an indication of the sorptive behaviour of materials based on their organic character. The following equation developed by Xing (1994) was used to calculate the PI of the samples,

$$PI = 0.702 - 0.00353\ AR \tag{2.3}$$

where AR is the percent of aromatic C in the sample as measured by NMR.

Results

Batch Equilibration Experiments and Isotherms

Sorption of Soluble C

Both the Ah and Ck soil samples sorbed soluble C under the conditions tested. The Ah and Ck soil samples sorbed large quantities of DOC ranging from 400 μg C g^{-1} soil (MS + Ah) to 5100 μg C g^{-1} soil (CS + Ck) (Table 2.2). Sorption of soluble C follows a linear isotherm for all cases tested indicating the mechanism of sorption or retention is partitioning (Fig. 2.1). A linear isotherm describes a situation whereby a finite number of sorption sites exist and the energy required to sorb the first organic molecule is the same as the energy required to sorb subsequent organic molecules. Table 2.2 outlines the average parameters for each of the soluble C sorption isotherms based on three replicates. The sorption coefficient, K_d, describes the affinity of materials to partition onto soil and is 6 to 8 times greater for CS than for MS (Table 2.2). Subsurface soil samples sorbed 1.5 to 2 times more DOC than did surface soils as observed by the greater x/m values for Ck samples as compared to Ah samples for similar Ce values. The K_d value normalized for organic C concentration, K_{oc}, is 19 and 25 times greater for CS and MS DOC solutions respectively equilibrated with subsurface soil samples than for surface soil samples despite the fact that Ck soil samples contain one tenth the organic C concentration of Ah soil samples (Table 2.1). Compost derived DOC equilibrated with Ck soil samples yielded the greatest K_{oc} value, 973 ml g^{-1} (Table 2.2).

Table 2.2. Soluble C isotherm results for batch equilibrations of manure and compost derived DOC with soils.

Sample	K_d (ml g^{-1})	K_{oc} (ml g^{-1})	Ce (mg l^{-1})	x/m (mg C g^{-1} soil)
MS + Ah	0.3	6.4	1470	0.4
MS + Ck	0.6	162.2	1400	0.8
CS + Ah	2.4	51.0	1450	3.5
CS + Ck	3.6	973.0	1430	5.1

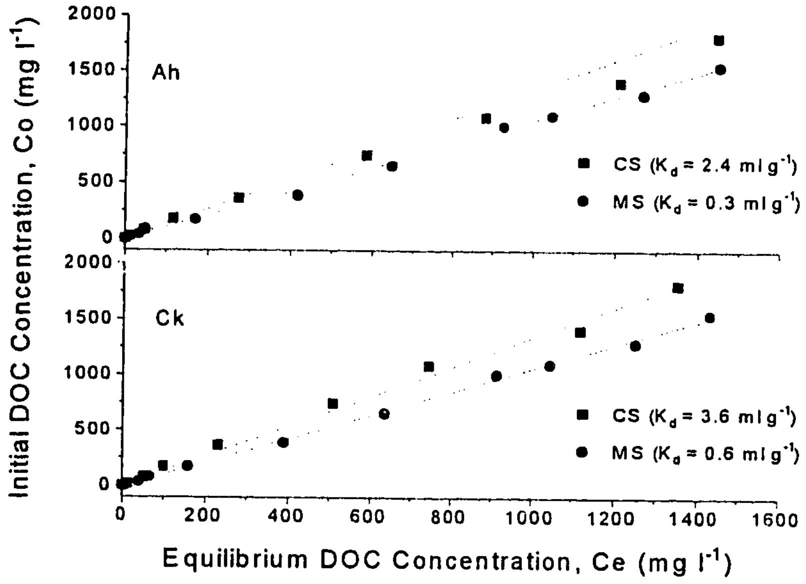

Figure 2.1. Sorption isotherms for the uptake of DOC by Ah and Ck soil samples.

Sorption of Soluble N and P

Soluble N was retained strongly by Ah and Ck soil samples as observed by the high sorption K_d values (Table 2.3). Maximum sorption of total N was achieved when CS was equilibrated with Ck soil samples (K_d = 2.72 ml N g^{-1} soil). Subsurface soil samples retained more total N than Ah soil samples (Table 2.3). For the CS treatment, N as NO_3-

N accounted for 93% of the total N while NH_4-N accounted for only 4% of the total N added. The opposite was true for the MS treatment where 80% of the total N added was accounted for by NH_4-N while only 0.01% was accounted for by NO_3-N. The NO_3-N concentrations measured in the supernatants for MS treated soils were near the detection limit of the Technicon Auto Analyzer II.

The maximum quantity of MS derived total N sorbed was 603 μg N g^{-1} soil by Ck soil samples and the quantity of CS derived total N was 449 μg N g^{-1} soil by the Ck soils (Table 2.3).

Total P added to the soil systems was 6 times higher with CS than with MS. Soluble P extracted from CS was retained more strongly than total P extracted from MS (Table 2.3). Manure extracted P was only retained by the Ck soil samples. Reaction of MS with Ah soil resulted in desorption of P (Table 2.3).

The sorption isotherms for soluble N and P follows a linear isotherm. Isotherm values could not be calculated for the sorption of NO_3-N extracted from manure by soils due to the low concentrations of NO_3-N detected in these samples. Similarly, calculations of x/m could not be made for NH_4-N from manure with Ck, total P from manure with Ah, and total P from compost with Ck due to negative Kd values. The isotherm parameters for sorption of N and P are listed in Table 2.3.

Table 2.3. Sorption isotherm parameters for N and P from batch equilibrations of manure and compost derived DOC with soils.

Total N

Sample	K_d (ml g^{-1})	Ce (mg l^{-1})	x/m (mg g^{-1} soil)
MS + Ah	2.5	232	0.57
MS + Ck	2.7	227	0.60
CS + Ah	1.8	169	0.31
CS + Ck	2.7	165	0.45

NO_3-N

Sample	K_d (ml g^{-1})	Ce (mg l^{-1})	x/m (mg g^{-1} soil)
MS + Ah	--	nd	--
MS + Ck	--	nd	--
CS + Ah	1.1	176	0.20
CS + Ck	1.3	165	0..22

NH_4-N

Sample	K_d (ml g^{-1})	Ce (mg l^{-1})	x/m (mg g^{-1} soil)
MS + Ah	2.2	193	0.42
MS + Ck	-0.01	190	--
CS + Ah	3.9	7.4	0.03
CS + Ck	33.7	2.5	0..08

Total P

Sample	K_d (ml g^{-1})	Ce (mg l^{-1})	x/m (mg g^{-1} soil)
MS + Ah	-1.3	ds	--
MS + Ck	1.5	2.6	0.01
CS + Ah	33.1	3.8	0.13
CS + Ck	-3.5	3.7	--

nd = not detected
ds = desorption

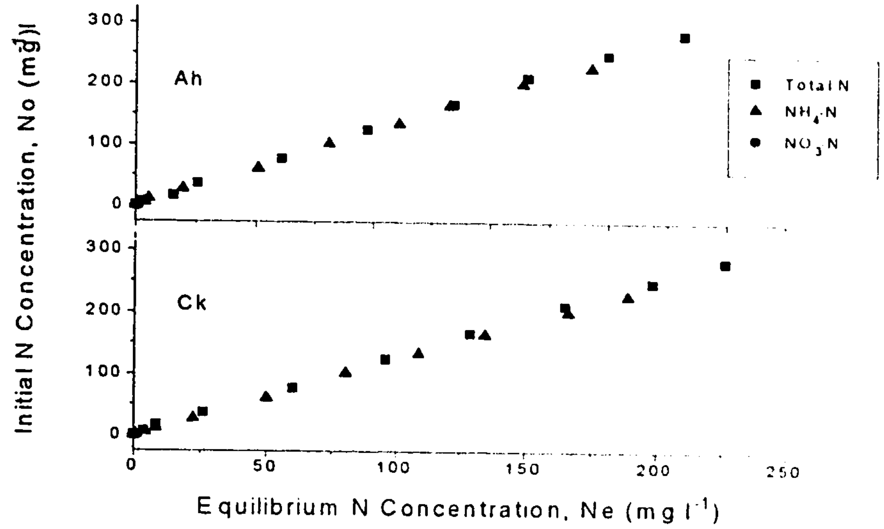

Figure 2.2.a. Sorption isotherms for the uptake of N extracted from manure by Ah and Ck soil samples.

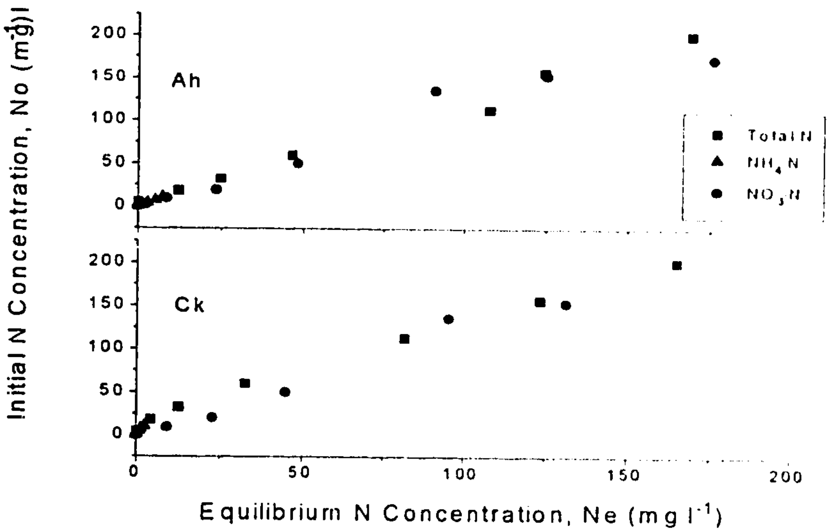

Figure 2.2.b. Sorption isotherms for the uptake of N extracted from compost by Ah and Ck soil samples.

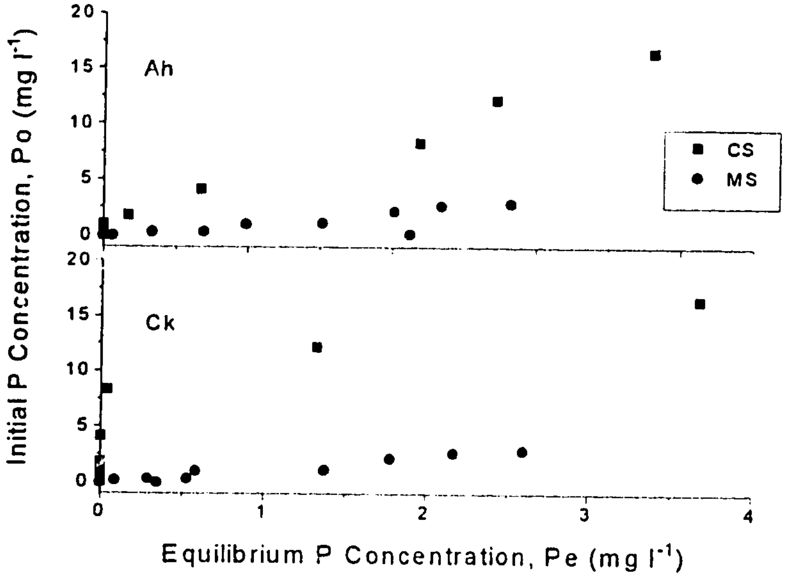

Figure 2.3. Sorption isotherms for the uptake of P by Ah and Ck soil samples.

Electrical Conductivity and pH

The EC of the isotherm samples increased with increasing DOC concentration. This is illustrated in Fig. 2.4 where, sample 11 represents a Ce of approximately 1450 mg C l^{-1} while sample 1 represents a Ce of 0 mg C l^{-1}. The EC of samples tended to decrease following reaction with soil to a similar value irrespective of soil type. The EC of CS treated samples were consistently higher than for MS treated samples, consistent with a greater concentration of salts or DOC in compost extract as compared to manure extract. In the case of soils, those possessing an EC of >2 dS m^{-1} are classified as saline (Hausenbuiller 1985).

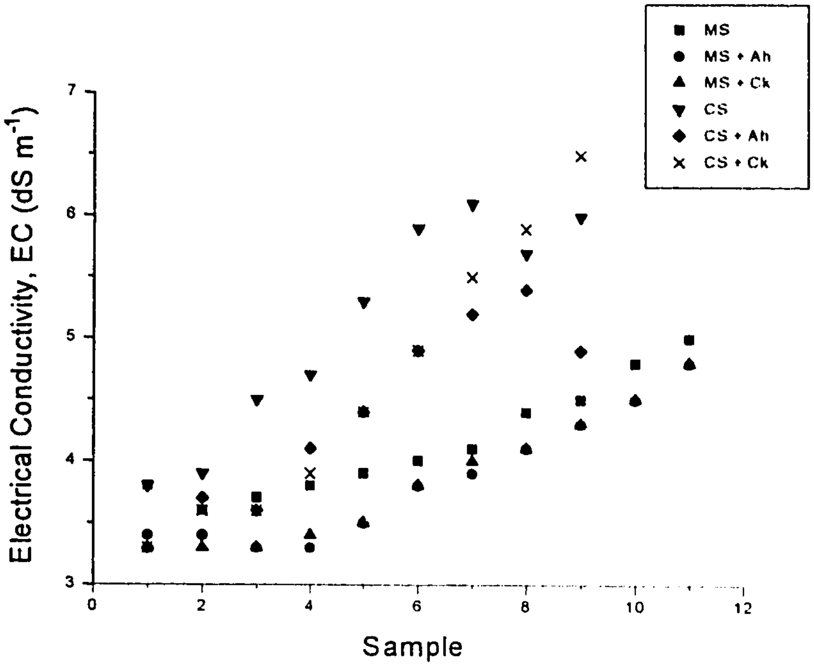

Figure 2.4. Electrical conductivity of Ah and Ck soil samples following equilibration with manure and compost derived DOC.

The pH of the extracts remained constant over the course of the batch equilibrations however, all values differed from the starting pH of 6.5 (Fig. 2.5). The pH of the control samples rose to approximately 7 and remained there for the duration of the experiments. The Ah samples reached pH values of 6.8 when treated with either MS or CS. The values were slightly lower when Ah soil samples were treated with CS but this difference was not significant. The smaller change in pH of Ah extracts relative to the control samples may be due to the presence of organic acids in the Ah soil which has a pH of 5.9 when measured in 10 mM $CaCl_2$ (Table 2.1). The pH of Ck sample extracts rose to an average of 7.6 when treated with either MS or CS. This rise in pH can be attributed to the presence of carbonates in Ck soil (66% of total soil C) (Table 2.1).

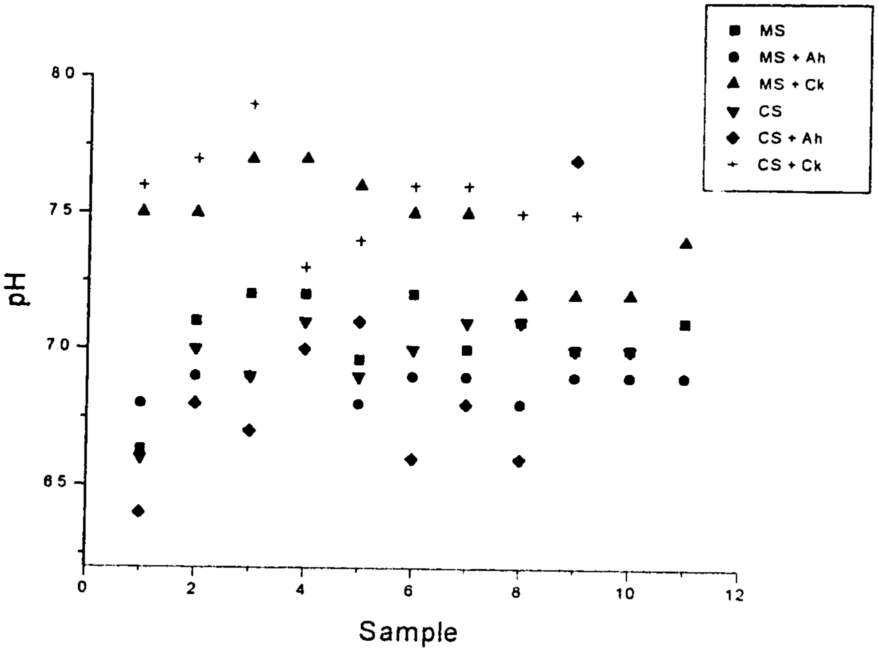

Figure 2.5. pH of Ah and Ck soil samples following equilibrium with manure and compost derived DOC.

Spectrophotometric Analyses

The E_4/E_6 ratios of the DOC solutions differed before and after equilibration with soil. In all cases, reaction of DOC with soil samples resulted in an increase in the ratio as compared to the controls (Table 2.4). The E_4/E_6 ratios for DOC solutions derived from compost were higher than for manure derived DOC when alone or following reaction with soil. In both cases, the greatest change in the E_4/E_6 value was observed following reaction of the DOC with subsurface soil samples (Table 2.4).

Table 2.4. Spectrophotometric results for batch equilibration samples.

Sample	E_4/E_6*	Standard Deviation
MS Control	6.0	1.0
MS + Ah	7.0	2.0
MS + Ck	8.4	0.7
CS Control	7.3	0.7
CS + Ah	9.5	0.8
CS + Ck	12.0	1.0

CPMAS ^{13}C NMR and Polarity Indices

The organic C compositions of the DOC solutions before and after equilibration with soil were determined using CPMAS ^{13}C NMR. NMR results revealed little difference between the compost derived DOC solutions and the manure derived DOC prior to mixing with soil (Table 2.5). In general, the percent aliphatic C for MS was greater than that of CS and the percent aromatic C of CS was greater than that of MS, however the differences observed were slight (Table 2.5). Reaction with soil did not change the organic C composition of the solutions despite retention of 22 to 40% of the added DOC by soil constituents (Table 2.5). Generally, reaction of MS with soil resulted in a decrease in aliphatic C, a slight increase in aromatic C and a decrease in carboxyl C (MS + Ah only). Reaction of CS with soil resulted in an increase in aliphatic C, a decrease in aromatic C and a decrease in carbonyl C (CS + Ck only). Changes in aliphatic and aromatic C concentrations were greatest when DOC was reacted with Ck soil samples. Definitive conclusions about the character of DOC removed from solution cannot be made because of the large degree of overlapping between NMR peaks of DOC and DOC + soil spectra. The differences in organic C composition, when expressed as PI, are small indicating there is no difference between the ratio of (O+N)/C of MS and CS alone or between the treated samples.

Table 2.5. Constituents of MS and CS before and after equilibration with soil samples as determined by CPMAS ^{13}C NMR and polarity index.

Sample	Aliphatic-C[†] (0-106)[*]	Aromatic-C (106-160)	Carboxyl-C (160-190)	Carbonyl-C (190-220)	Polarity index
MS	63.27	22.03	12.99	1.69	0.62
MS + Ah	62.50	22.62	14.29	0.59	0.62
MS + Ck	60.82	22.81	14.62	1.75	0.62
CS	56.88	26.69	13.49	2.93	0.61
CS + Ah	58.12	24.50	14.81	2.56	0.62
CS + Ck	60.54	24.59	13.51	1.35	0.62

[†] Values are given as percent of total spectral area.

*Denotes chemical shifts in units of parts per million.

Discussion

DOC Sorption

Sorption is used as a generic term to mean the uptake of a solute by a sorbent from solution or gas phase without reference to a particular mechanism (Chiou 1989). It includes the mechanisms of adsorption, a two dimensional "sticking on" of materials or condensation on surfaces or interior pores of a solid by physical or chemical bonding forces; partitioning, a three dimensional process better described as uptake in which the sorbed organic chemical permeates the sorbent; and precipitation, the formation of a new three dimensional substance (Chiou 1989; McBride 1994).

Sorption of DOC by soils, under the conditions tested, follows a linear isotherm and is described by Equation 2.2 (Fig. 2.1). A linear sorption isotherm is the simplest model available to describe uptake of a solute by a sorbent and generally holds true for low solute concentrations. A linear isotherm describes a linear relation, between solute concentration in the organic phase and that in the solvent phase, which exists over a wide range of solute concentrations and the mechanism of sorption at work is assumed to be partitioning (Chiou 1989). Partitioning results because of "hydrophobic interactions", a combination of relatively small van der Waals bonding forces and a thermodynamic gradient which drives organic molecules out of the aqueous phase and onto solid soil constituents (Chiou 1989; Schlautman and Morgan 1993). Fundamental to linear isotherms for soils and aqueous systems is that the molar heat of sorption of the compound is constant and independent of solute concentration (Chiou 1989).

Soil organic matter is the main sorbent of nonionic organic compounds such that as organic matter content increases so does sorption (Chiou 1989). Based on these hypotheses, the Ah soil samples should have sorbed greater quantities of DOC than Ck soil samples assuming partitioning is the mechanism of sorption. For the DOC-soil combinations tested, this assumption did not hold true as observed by the K_d and K_{oc} values (Table 2.2).

The partition coefficients calculated for the DOC-soil systems suggest the affinity of DOC to partition onto soils differs for different soil and DOC types. DOC was strongly sorbed by both the Ah and Ck soil samples from the Eluviated Black Chernozem with quantities sorbed ranging from 400 μg C g^{-1} soil to 5100 μg C g^{-1} soil (Table 2.2). The K_d and K_{oc} values were 1.5 to 2 times and 19 to 25 times greater, respectively, for subsurface soil samples amended with DOC than surface soil samples despite the Ah soil samples containing 10 times more soil organic C (Tables 2.1 and 2.2). When normalized to organic C content, the Ck soil samples were more efficient at sorbing organic solutes than the soil organic matter of the Ah soils. Based on this evidence we conclude the affinity to sorb DOC differs for different soil types and may not be related exclusively to organic C content, as it is much lower in Ck horizons and therefore should not sorb larger quantities, but that other mechanisms of sorption are at work in these systems such as precipitation of Ca-DOC complexes.

The affinity of DOC to partition onto soil also differs for different DOC types. The K_d values for MS treated samples were 6 to 8 times lower than for CS treated systems (Table 2.2). Therefore, compost derived DOC is more strongly sorbed than manure derived DOC. Composting is a thermophilic aerobic process which results in the formation of CO_2 and more stable organic matter (Garcia *et al.* 1991). Deiana *et al.* (1990) concluded based on ^1H and ^{13}C NMR, FTIR and visible spectroscopies that humic acids extracted from manure compost were aromatic in character and similar to humic acids originating from soil. Consequently, it can be surmised that the concentration of aliphatic more hydrophilic organic compounds should be greater in manure than compost, since these molecules are more labile than the aromatic more hydrophobic organic compounds which are left following composting. This is consistent with NMR results reported here (Table 2.5). Hydrophobic compounds are more effective at binding other hydrophobic compounds, such as those which make up soil organic matter, than hydrophilic compounds (Carter and Suffet 1982; Jardine *et al.* 1989). It follows that CS should be the more hydrophobic of the DOC's tested and therefore should be sorbed more strongly by soil organic matter. However, simple partitioning of DOC onto soil organic matter does not explain the enhanced sorptive capacity of the mineral dominated Ck soil samples as compared to the organic-rich Ah samples.

Several possible mechanisms exist to explain the phenomenon of enhanced sorptive capacity of DOC by soils low in organic matter where minerals are responsible for most chemical reactions. The EC's of the DOC and DOC-soil extracts were high, starting at 3.25 dS m^{-1} and reaching a maximum of 6.5 dS m^{-1} (Fig. 2.4). High EC values are associated with high salt and DOC concentrations. The salts present in DOC, the DOC itself and the minerals which occur in soil samples from the Ck horizon are prerequisites for precipitation reactions. This hypothesis would be consistent with the sorption results which indicate that CS is sorbed more strongly than MS (Table 2.2). Compost derived DOC had a consistently higher EC than MS indicating a greater concentration of soluble salts or ionizable DOC and therefore a greater potential for the formation of precipitation products. This is also consistent with the finding that CS was sorbed most strongly by Ck soil samples which contain carbonates (Tables 2.1 and 2.2). Soils containing $CaCO_3$ have been reported to exhibit moderate DOC sorption capacities (Moore *et al.* 1992) which may be attributed to precipitation. Further support for this hypothesis may be drawn from the observation that EC readings dropped following reaction of DOC with soil suggesting a reduction of soluble salts possibly as newly formed calcium-precipitates (Fig. 2.4). Precipitation is likely a predominant mechanism at work in the DOC-Ck systems.

In mineral dominated horizons, adsorption results from the surface area of crystalline and non-crystalline clays such that soils high in clay will have higher surface areas and potentially more sorption sites than those low in clay (Dahm 1981; Jardine *et al.* 1989; Nelson *et al.* 1990). Sorption results from nonspecific electrostatic ion exchange with clay colloids that have permanent or pH-dependent charge (Nelson *et al.* 1990). While both soil types used in these experiments are classified clay loams, the Ck soil sample contains 8% more clay (Table 2.1) which may account for some of the sorption taking place in these systems.

Simple partitioning onto organic matter may not be the only mechanism of DOC loss from solution in organic-rich soil-aqueous systems. Biodegradation of DOC will influence "apparent sorption" in DOC-Ah systems. DOC is a potential substrate for microorganisms and microbial activity of the abundant population of the organic-rich Ah soils will increase following introduction of DOC. Dahm (1981) reported 97% of initial DO^{14}C, extracted from alder leaves, was taken up by microbes and either incorporated into biomass or respired as CO_2 over a 48 hour period. Supplemental experiments by this researcher indicated that as much as 30% of "apparently sorbed" DOC may be lost as CO_2 resulting from mineralization from DOC-Ah soil mixes (Gomez, unpublished).

Changes in pH influence the sorptive potential of sorbents (Carter and Suffet 1982; Lee *et al.* 1990; Schlautman and Morgan 1993). Decreases in solution pH reduce the charge on humic polymers in solution rendering them less hydrophilic. These molecules become more effective at binding hydrophobic compounds or binding to hydrophobic soil organic matter (Carter and Suffet 1982). The pH of the DOC-soil extracts remained unchanged over the course of the equilibrations, however pH's did differ by treatment (Fig. 2.5). All samples were initially adjusted to pH 6.5 prior to batch experiments, however, the pH of Ah treated samples stabilized at or near 6.8 while Ck treated samples remained at or near 7.6 (Fig. 2.5). These results support the conclusion that sorption should be favoured in DOC-Ah systems, but, this is inconsistent with the findings of this research. The influence of pH on DOC sorption may be masked by other processes at work under the test conditions.

Nature of DOC Sorbed by Soils

The original hypothesis I wished to address with this work was whether preferential sorption of DOC occurred for different soils. I hypothesized the more hydrophobic constituents of DOC would be preferentially sorbed by the organic-rich Ah horizon while the more hydrophilic constituents would be preferentially removed by the mineral dominated B and C horizons. To test these hypotheses, DOC extracts before and after equilibration with soil were characterized using spectrophotometric analysis (E_4/E_6) and ^{13}C NMR.

E_4/E_6 ratios have traditionally been used to characterize humic and fulvic acids from soils. Consensus as to how to interpret these values does not exist. Schnitzer and Khan (1972) propose light absorption increases with an increasing concentration of C in aromatic nuclei as opposed to aliphatic side chains. Kononova (1966) believes a low ratio reflects a more condensed aromatic character. Chen *et al.* (1977) concluded molecular size governs E_4/E_6 ratios such that large molecular weight compounds would have low ratios and they would contain a high C content, but little O, CO_2H groups and total acidity. Rather than use these ratios to characterize DOC, I chose to use them as qualitative indicators of change. Differences in quantity or quality of organic C in DOC extracts should be reflected in the absorbance measurements and consequently the E_4/E_6 value.

The E_4/E_6 ratios for both MS and CS increased following reaction with soil when compared to control samples (Table 2.4). The ratios were consistently higher for CS than for MS treated samples. These results imply the starting materials, MS and CS, and the equilibrium solutions are different in composition from each other. Thus, different constituents of DOC are present in each of these 6 solutions, either in quantity or quality of C, and therefore, different C constituents were removed by each of the soils.

The ratios were consistently greater following mixing with Ck soil as compared to Ah soil (Table 2.4). The conclusions drawn by Chen *et al.* (1977) provide conflicting evidence to what was observed with these experiments. According to Chen *et al.* (1977) if a high ratio is associated with low molecular weight compounds then we can infer solutions of CS contain a greater proportion of low molecular weight compounds than MS solutions, a conclusion not consistent with the process of composting. As the ratios increase after equilibration with soil, we can conclude that a reduction in higher molecular weight compounds has occurred, the greatest change occurring following reaction of DOC with Ck soil samples (Table 2.4). Large molecular weight organic compounds generally contain a lower O and H content and higher C content than low molecular weight compounds and are generally more hydrophobic and aromatic in nature. Partitioning of hydrophobic compounds is favoured over hydrophilic compounds onto soil organic matter, and the data support the conclusion that these materials are also more susceptible to precipitation.

Nuclear magnetic resonance was used in an attempt to quantify the changes in DOC following reaction with soil. NMR results revealed some differences between MS and CS. In general, MS contained a greater proportion of aliphatic C than CS and consequently CS contained a greater proportion of aromatic C than MS (Table 2.5). The proportions of aliphatic and aromatic C did not change significantly following reaction with soil. A slight decrease in aromatic C content was observed when CS was reacted with soil and a slight decrease of aliphatic C content was observed when MS was reacted with soil. The NMR results do not provide conclusive evidence to support the hypothesis of preferential sorption. Polarity indices were the same for all test conditions (Table 2.5).

Sorption of N and P by Soils

Sorption of N and P by soils followed linear isotherms as observed for DOC (Fig. 2.2 to 2.3). Total and mineral N were sorbed strongly by the soils tested as indicated by the high K_d values (Table 2.3). Calculations of sorption coefficients yielded K_d values up to 10 times greater than observed for DOC (Tables 2.2 and 2.3) Volatilization of N as NO_x and NH_3 is a dominant mechanism for the loss of N from solution in manured systems and this likely accounts for a portion of the N lost from solution during the equilibrations. Paul *et al.* (1993) observed nitrous oxide emissions were higher from soil following addition of manure slurries than following addition of composted manure. Ammonia losses can account for up to 50% of N depletion from manured soils (Lauer *et al.* 1976). Ammonia made up the majority of the mineral N detected from manure treated samples. Nonspecific electrostatic ion exchange reactions with soil organic matter and clay colloids is also an important mechanism of retention of NH_4-N. The positive ionic charge on NH_4^+ makes it susceptible to electrostatic bonding with the negatively charged sites of organic matter and clays. Sorption of NH_4^+ was not significant from CS onto soil despite high K_d

values due to the low concentrations of NH_4^+ found in the CS solution but this may be due to the competition for sorption sites from K^+, the background electrolyte (Table 2.3).

Compost derived total N is composed primarily of NO_3-N and its "sorption" was similar in both surface and subsurface soils. Precipitation may account for the bulk of the "apparently sorbed" NO_3^- to Ck soils. Nitrate left in solution will be available to undergo biological reduction to NH_4^+. Chen and Patrick (1981) reported in a simulated runoff system, the addition of C sources reduced the redox potential of the system and enhanced the rate of NO_3^- reduction. The most probable fate of the NO_3^- will be leaching. Leaching of NO_3^- has been reported to be significantly increased following the addition of fertilizers and manures (Angle *et al.* 1993).

Soluble P was detected in high quantities in MS and CS although CS solutions contained 6 times more total P than MS and CS extracted P but was not sorbed strongly by soils (Tables 2.3). Initial P concentrations in MS reached a maximum of 2.5 mg P l^{-1} in MS and 15 mg P l^{-1} in CS solutions (Fig. 2.3). Reaction of total P extracted from MS with Ah soil samples resulted in desorption of P (Po = 2.5 mg P l^{-1}, Pe = 2.76 mg P l^{-1}). Donald *et al.* (1993) reported that the hydrophobic neutral fraction of DOC enhanced the transport of P in forest soil. Phosphorous can be solubilized in the presence of organic acids and CO_2 (Paul and Clark 1989) and DOC is a heterogeneous mixture of organic acids of varying sizes. The steepness of the sorption curve for total P extracted from CS when reacted with Ck soil provides evidence that precipitation is likely the method of P retention occurring in the Ck-DOC systems. Phosphorous concentrations remain low until the soil matrix is saturated, at which time the excess P is observed in solution.

Conclusions

Sorption of DOC follows a linear isotherm for both surface and subsurface soils. The predominant mechanism of sorption in the Ah soils is partitioning while in the Ck soils it is precipitation. E_4/E_6 ratios provide some evidence to support the hypothesis of preferential sorption of DOC constituents by different soil types, but this was not validated by ^{13}C NMR results. Sorption of N and P follow a linear isotherm. Soils do not sorb P strongly and N losses from manure amended soils may be due in large part to volatilization rather than sorption. The presence of DOC may enhance reduction of N and solubilization of P.

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Chapter 3

LEACHING OF SOLUBLE CARBON, NITROGEN AND PHOSPHOROUS FROM INTACT SOIL CORES AMENDED WITH MANURE OR COMPOST

Introduction

The potential for manure and compost to contaminate the environment depends in part on the movement of soluble C, N and P constituents into surface and groundwater. DOC is implicated in enhancing the transport of inorganic and organic chemicals and can itself cause soil acidity and anoxic conditions as it is decomposed (Jardine *et al.* 1990). Excessive nitrogen leaching and ammonia volatilization from organic amendments are of concern (Paul *et al.* 1994). Nitrates, the most soluble of the N-compounds, have been implicated in eutrophication, infant and animal methemoglobinemia and the formation of carcinogenic nitrosamines (Paul and Clark 1989). Most inorganic phosphates are poorly soluble or insoluble but can move with other nutrients in surface runoff (Timmons *et al.* 1977; Paul and Clark 1989) and have been linked to algal blooms and eutrophication.

The sustainable application of organics to soil depends on knowledge regarding the transformation and fate of the various constituents within the soil profile (Keeling *et al.* 1994). Manure and compost application to land can occur under numerous weather conditions. Excessive fertilization prior to wet seasons increases the susceptibility of nutrient losses by surface runoff and leaching (Klausner *et al.* 1974). Manure disposal to land during periods of active thaw has been reported to result in large losses of soluble N and P as runoff (Klausner *et al.* 1976). Lauer *et al.* (1976) reported NH_3 volatilization from manure amended soils was precluded by subfreezing temperatures, snow cover and a rapid thaw which leached the ammoniacal N into the soil. Harding and Ross (1964) reported that freezing of soil samples increased the quantity of mineralizable N and that NO_3^- produced during freezing increased with increasing organic C contents.

Sorption is an important control on the mobility of soluble compounds and the magnitude of its influence is dependent on the characteristics of the soluble compounds and the soil. Previous experiments provided evidence that soluble C, N and P extracted from manure and compost were sorbed by soils (Chapter 2). Batch equilibration experiments provide ideal conditions under which sorption can occur, a situation not often found in intact soils. Column leaching studies on the other hand determine the extent to which sorption reactions influence the transport of soluble constituents through intact cores of soils. I addressed four basic questions with these experiments. Firstly, does soil act as a filter for suspended solids extracted from manure or compost? I hypothesized that particulate matter, which is transported with soluble constituents, should be retained within the soil matrix and that finer textured soils should retain more solids due to the large proportion of fine pores in clay textured soils. Secondly, is soluble C leached through intact soils? Based on previous work, I hypothesized that soluble C would be transported through intact soils and that DOC from manure would move more readily than compost DOC (Chapter 2). Nitrogen occurs primarily as NH_4^+ in manure extracts while NO_3^- is the predominant form of N in compost extracts (Chapter 2). Therefore, do compost amended cores leach more N than manure amended cores? I hypothesized that, due to the forms of mineral N found in manure and compost, that compost amended cores would leach more N than manure amended cores. Lastly, I wanted to answer the question of whether soluble P would leach through intact soils? Organic acids enhance the solubilization of organic P (Paul and Clark 1989), however, I hypothesized this solubilization would be insignificant and would not result in leaching of P from manure or compost amended soils.

Materials and Methods

Soil Samples

Intact soil cores were obtained from the Ah, Bt and Ck horizons of an Eluviated Black Chernozem from the Ellerslie Research Station in Edmonton, Alberta. Cores were sampled using PVC tubing cut to the dimensions 7.5 cm in diameter X 10 cm in height. The core bottoms were covered with glass wool and sealed using perforated plastic lids. Cores were stored at 4°C prior to the leaching experiments.

Frozen Soil Cores

Following moistening to field capacity nine intact cores sampled from the Ah horizon of an Eluviated Black Chernozem were stored frozen until the onset of the leaching experiments. The cores were wrapped with insulation prior to the leaching experiments. Leaching experiments were conducted in the same manner as for the non frozen samples.

Manure and Compost Samples

Fresh cattle manure and urine, henceforth termed manure (87% moisture), were collected from the University of Alberta Dairy Unit at the Edmonton Research Farm in Edmonton, Alberta and were stored at 4°C. Composted cattle manure was obtained from Olds College in Olds, Alberta. Compost samples were air dried, sieved through a 2 mm sieve and stored at room temperature prior to conducting the experiments.

Core Leaching Experiment

Prior to the leaching experiments, the intact cores were moistened to field capacity by saturating and draining for 24 hours. Treated cores were amended with manure or compost at a rate of 6.8 Mg ha^{-1} on a dry matter basis. Approximately 10 pore volumes or 2.5 L of 20 mM K_2SO_4, amended with 10^{-5} M $HgCl_2$ to retard microbial activity, were leached under gravity through each core. A nonreactive tracer (Br^-) was used to monitor the flow of solution. The frozen Ah soil cores (Ah-F) were amended, treated with K_2SO_4 and allowed to thaw. Leachate sampling of Ah-F began as soon as liquid began to move through the cores. Control samples were run simultaneously. Leachate samples were collected every 30 ml at the onset of the study and every 50 to 100 ml following the breakthrough of Br^-. All cores were run in triplicate and leachate samples were frozen following Br^- concentration measurements prior to further analysis.

Bromide Tracer

Bromide was used as a nonreactive tracer to monitor the flow of solution through the soil cores. Bromide concentrations were determined at 23°C using a Br^- selective electrode (Fisher Cat. No. 13-620-520; Fisher Calomel Reference Electrode Cat. No 13-620-51) on a Fisher Accmuet pH meter (Model 825 MP). Ionic strength was maintained using 5 M $NaNO_3$ (2ml l^{-1}). A standard curve for Br^- was constructed and the equation of the line (Eqn. 3-1) used to determine the concentration of Br^- in the leachates.

$$\text{mg Br}^- \ l^{-1} = \log^{-1}\left(\frac{\text{mV reading} - 121.8}{-60.2}\right) \qquad (3-1)$$

Suspended Solids

The resulting leachates were analyzed before and after centrifugation, for 20 min. at 15 000 x *g*, for suspended solids using a Baush and Lomb Spectronic 21 spectrophotometer set at 660 nm. The difference between absorbance before and after centrifugation was attributed to the quantity of solid material leached through each soil core.

Soluble C, N and P

A representative core was chosen from each of the treatments based on the Br- curve and suspended solid results and the leachate samples analyzed for soluble C, total N, mineral N and total P.

Soluble C concentration was determined on an Astro 2001 System 2 Soluble Carbon Analyzer (Astro International Corporation. League City, Texas) by u.v.-promoted persulfate oxidation.

Total soluble N was analyzed using the micro-Kjeldahl digestion method, with pretreatment to reduce NO_2^- and NO_3^- to NH_4^+, followed by colorimetric analysis on a Technicon Auto Analyzer II (Industrial Method No. 334-74 W/B) (McGill and Figueiredo 1993). The pretreatment was necessary since compost extracts contain high concentrations of NO_3^- and the micro-Kjeldahl digestion method proved inadequate for accurately determining the NO_3^- concentration when compared to distillation-titration methods (Offord unpublished). Mineral N (NO_3-N and NH_4-N) was determined using the colorimetric technique with a Technicon Auto Analyzer II (Industrial Methods No. 487-77A and 98-70W, respectively).

The concentration of total P in the digested extracts was measured using the colorimetric method on a Technicon Auto Analyzer II (Industrial Method No. 334-74 W/B).

Additions of C, N and P

Leaching experiments were simulated with manure and compost to determine the maximum quantities of C, N and P that could potentially be leached through the soil cores. Manure and compost were applied at the same mass rate as in the cores to glass wool held in a Buchner funnel. Fifty ml increments of 20 mM K_2SO_4 were applied to the samples and the leachates analyzed for soluble C using the Astro 2001 Soluble Carbon Analyzer.

Leachates containing the highest soluble C concentrations were analyzed for total N, mineral N and total P as described previously. Table 3.1 lists the maximum addition rate which could be made from 50 ml of K_2SO_4 passing through manure or compost at the application rates used.

Table 3.1. Maximum single dose addition of C, N or P to intact soil cores.

Sample	Soluble C (mg l^{-1})	Total N (mg l^{-1})	NO_3-N (mg l^{-1})	NH_4-N (mg l^{-1})	Total P (mg l^{-1})
Manure	842.0	58.3	0.6	38	0.5
Compost	161.0	14.9	5.9	2.1	0.4

Results

Bromide Breakthrough Curves

The concentration of Br^- in the leachates of each of the cores was monitored to ensure the flow of water through the cores. Bromide moved through each of the soil cores with its greatest retention time occurring in Ah soil cores (Fig. 3.1.a and 3.1.b). Movement of leachate was slowest through the Ck soil cores with 10 pore volumes of leachate requiring approximately 8 days to move through the cores, and fastest through the Ah-F and Bt soil cores with the same quantity of leachate requiring only 2 days to move through the cores (data not shown).

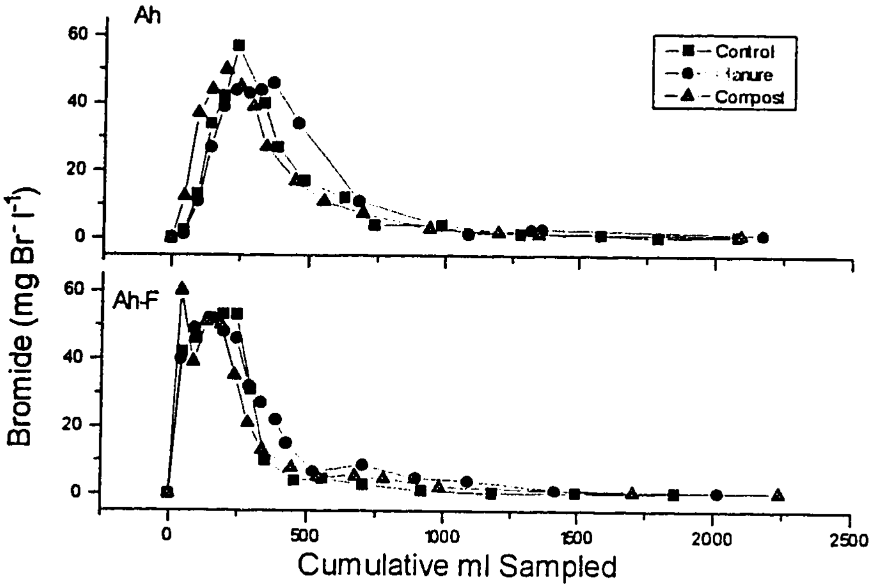

Fig. 3.1.a. Bromide breakthrough curves for Ah and frozen Ah soil cores amended with manure or compost.

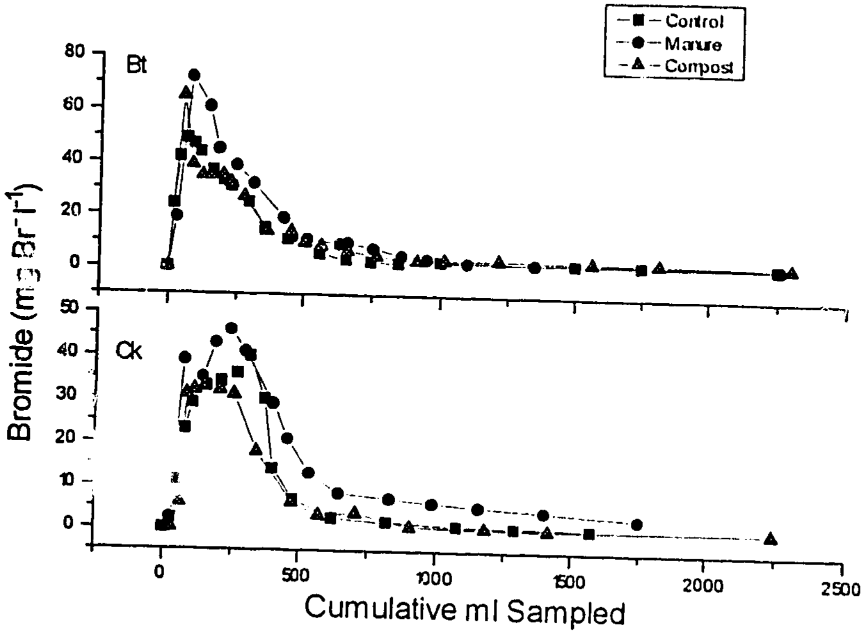

Fig. 3.1.b. Bromide breakthrough curves for Bt and Ck soil cores amended with manure or compost.

Suspended Solids

Absorbance of light at 660 nm by leachate solutions was used as an index of suspended solids. Suspended solids were only observed in cores amended with manure. Absorbance was least for suspensions leached through Ck soil cores and greatest for those leached through Bt soil cores (Fig. 3.2.a and 3.2.b). Absorbance reached a maximum of 1.14 for these suspensions compared from Bt cores with a maximum of 0.32 when leached through Ck cores. Previously frozen Ah soil cores allowed for large quantities of suspended solids to move through as in the case of Bt cores. A maximum absorbance of 0.6 was achieved with these cores (Fig. 3.2.a). Surface soil cores (Ah) allowed an intermediate quantity of solids to move through, reaching a maximum A_{660} of 0.42 (Fig. 3.2.a).

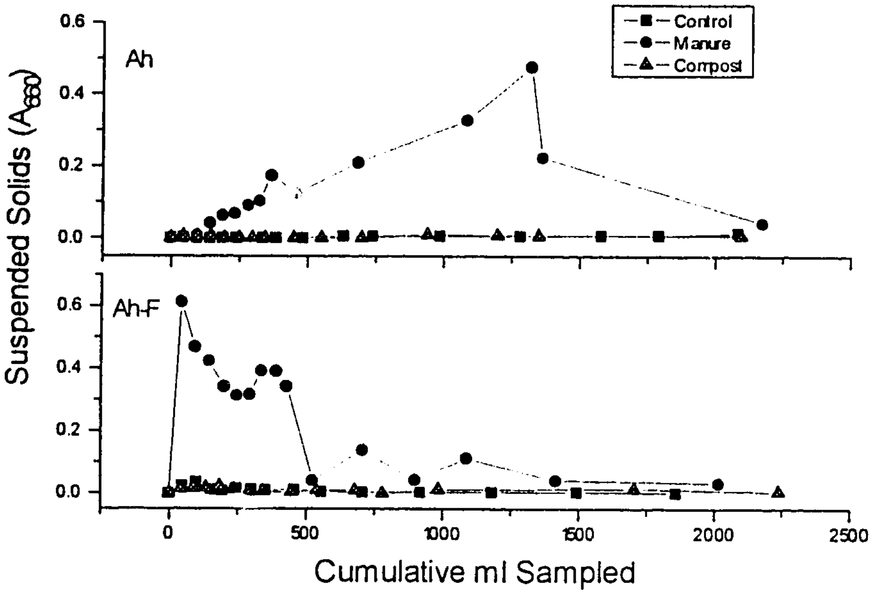

Fig. 3.2.a. Absorbance at 660 nm of leachates from Ah and frozen Ah soil cores amended with manure or compost.

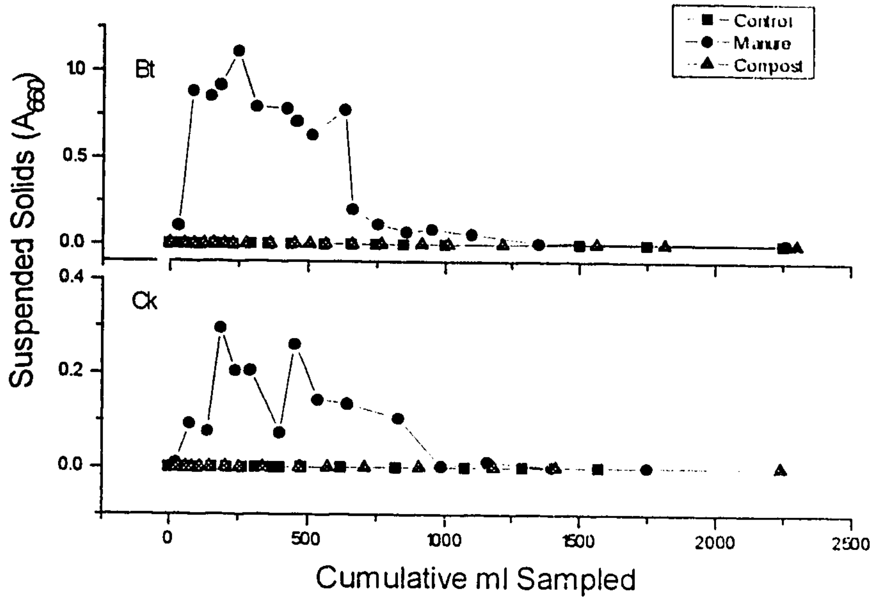

Fig. 3.2.b. Absorbance at 660 nm of leachate from Bt and Ck soil cores amended with manure or compost.

Leachate Analysis

Soluble C

Soluble C was detected in the leachates only from cores amended with manure (Fig. 3.3.a and 3.3.b). The highest concentrations of soluble C were detected in the leachates of the Bt (434 mg C l^{-1}) and Ck (462 mg C l^{-1}) soil cores. Soluble C movement through these cores paralleled the movement of Br^- and suspended solids (Fig. 3.1.b, 3.2.b and 3.3.b). Carbon was also readily leached through the Ah-F cores. A maximum concentration of 223 mg C l^{-1} was detected. The movement of C paralleled Br^- and suspended solids and, therefore, the bulk of the C was removed with the first 500 ml (Fig. 3.1.a, 3.2.a and 3.3.a). The Ah cores retained C the longest as observed by the broad breakthrough curve for soluble C (Fig. 3.3.a). Soluble C leached through Ah did not parallel in space or time, the movement of Br$^-$ however, the breakthrough curve for suspended solids was similar (Fig. 3.2.a). The maximum concentration of soluble C detected in any one leachate sample was 67 mg C l^{-1}, however, the net quantity of soluble C leached is similar to the other soil cores tested.

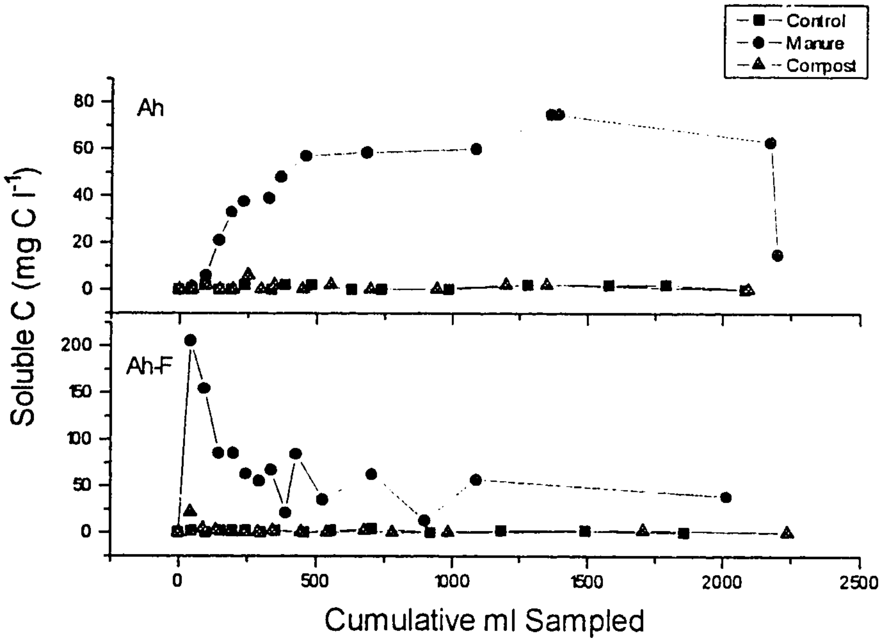

Figure. 3.3.a. Soluble C leached through intact Ah and frozen Ah soil cores amended with manure or compost.

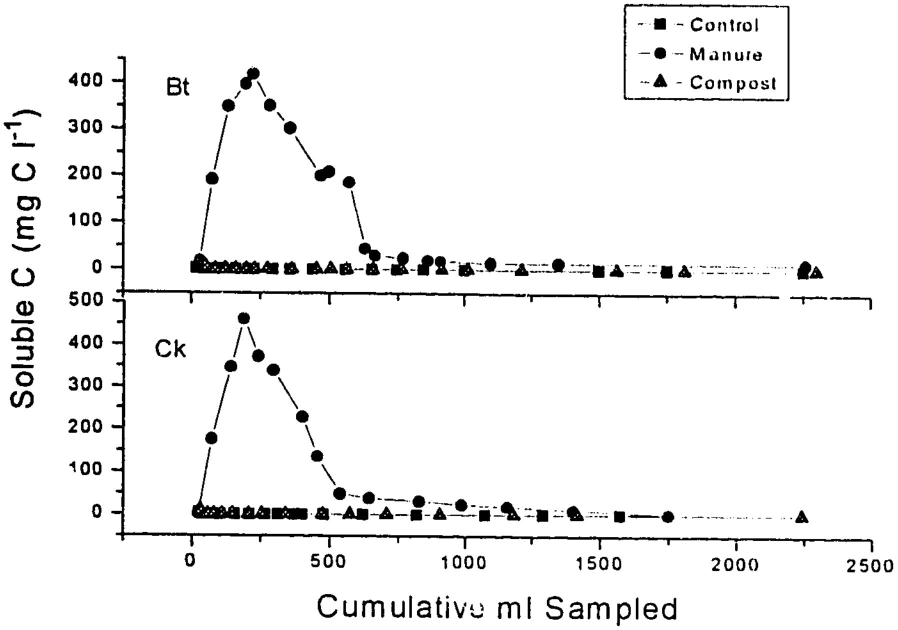

Figure. 3.3.b. Soluble C leached through intact Bt and Ck soil cores amended with manure or compost.

Total and Mineral N

Total N reached and maintained a concentration of 6-8 mg N l^{-1} in the leachates of control and compost amended Ah and Ah-F cores (Fig. 3.4.a and 3.4.b). Elevated total N concentrations were observed with cores amended with manure. Soluble N reached and maintained concentrations of 50 mg N l^{-1} in Ah and 97 mg N l^{-1} in Ah-F leachates of manure amended cores. Soluble N was leached more slowly through Ah cores and the elevated concentrations of N were maintained after leaching approximately 500 ml of 20 mM K_2SO_4. Conversely, Ah-F soluble N was leached quickly at the outset of the leaching experiment paralleling the movement of Br^-, suspended solids and soluble C.

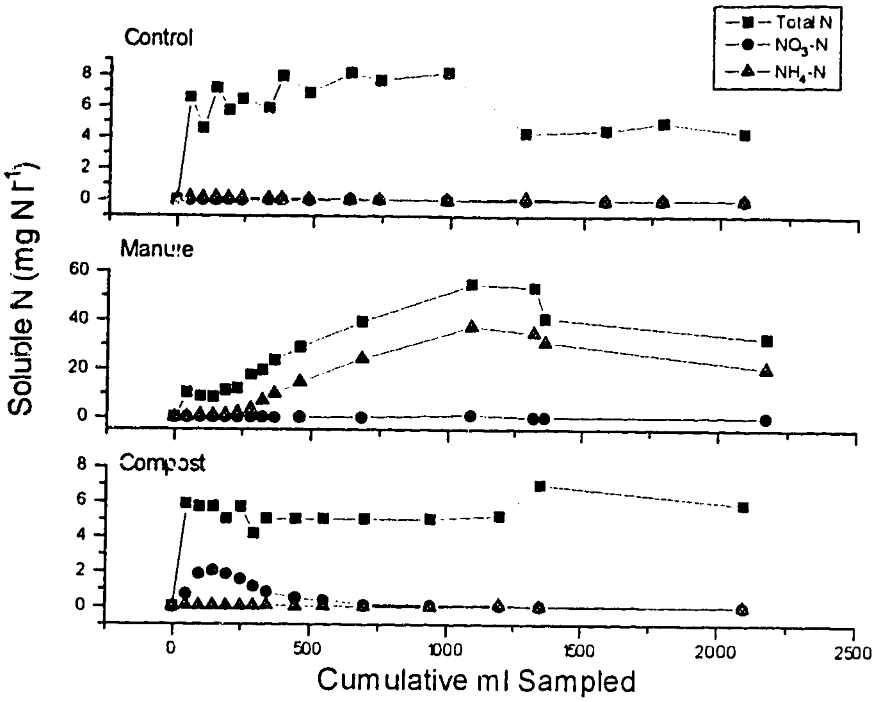

Figure. 3.4.a. Soluble N leached through intact Ah soil cores amended with manure or compost.

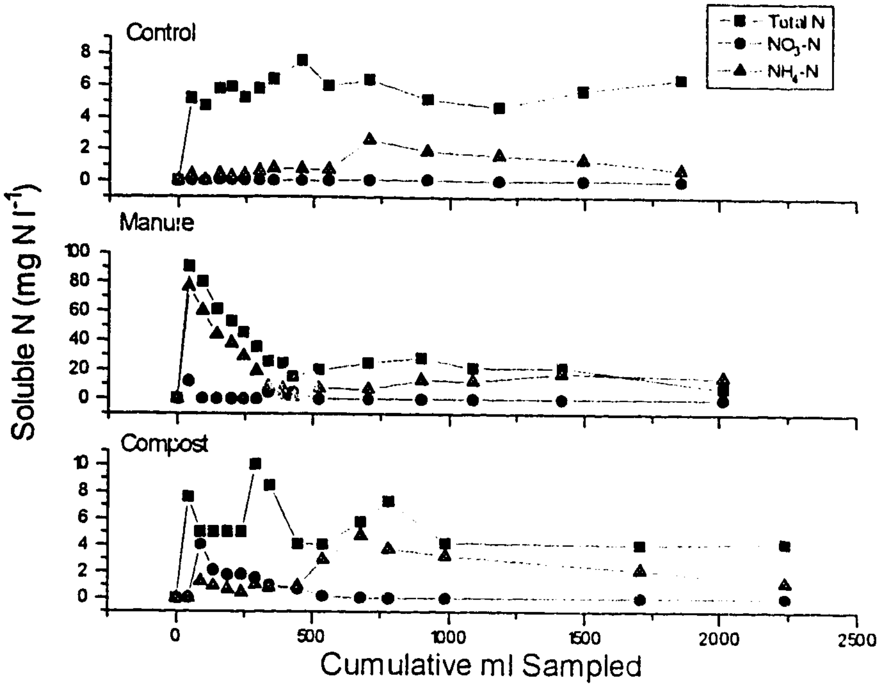

Figure. 3.4.b. Soluble N leached through intact frozen Ah soil cores amended with manure or compost.

Total N concentrations averaged 10 mg N l^{-1} from Bt controls and 6 mg N l^{-1} from Ck controls (Fig. 3.4.c and 3.4.d). These levels were achieved following leaching with approximately 50 ml of 20 mM K_2SO_4 and maintained throughout the experiment. Elevated total N concentrations were observed for manure amended Bt cores averaging 50-75 mg N l^{-1} (Fig. 3.4.c). Leachates from Ck cores amended with manure contained an average of 50 mg N l^{-1} (Fig. 3.4.d). Transport of soluble N did not follow the breakthrough curve of Br^- for any of the Bt or Ck cores tested.

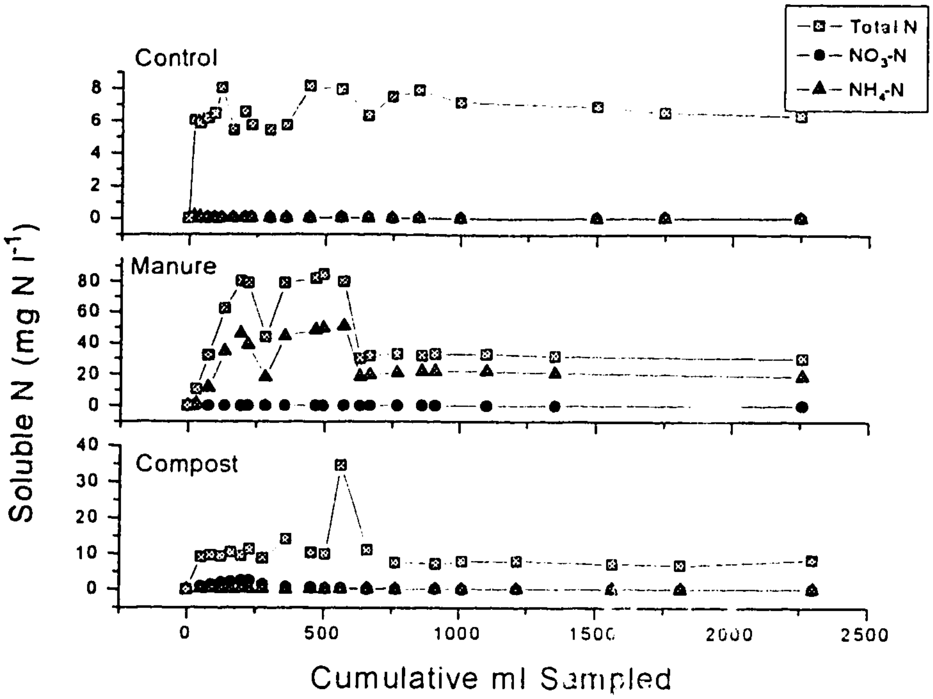

Figure. 3.4.c. Soluble N leached through intact Bt soil cores amended with manure or compost.

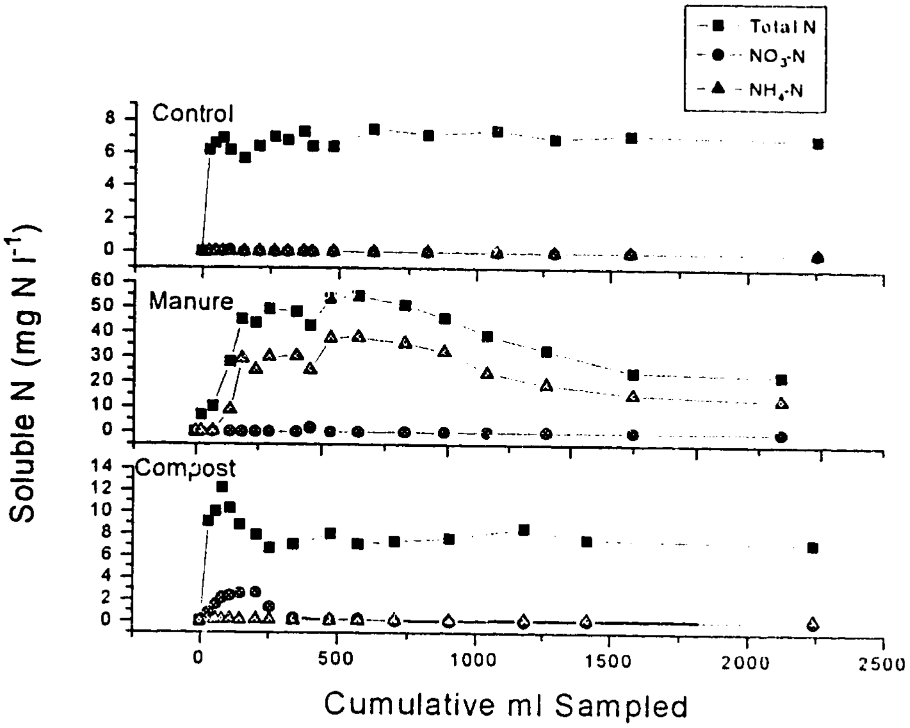

Figure. 3.4.d. Soluble N leached through intact Ck soil cores amended with manure or compost.

The main component of total N leached through the control soil cores is organic-N, as NO_3^- and NH_4^+ concentrations were near zero under control conditions (Fig. 3.4.a - 3.4.d). Ammonium-N accounted for the greatest proportion of total N from manure amended samples and its movement paralleled that of total N. Nitrate was the dominant form of N (up to 50% of maximum total N) recovered from compost amended Ah and Ah-F cores, however, total N concentrations were comparable to the controls (Fig. 3.4.a and 3.4.b). Nitrate levels were insignificant in the leachates of compost amended Bt and Ck cores (Fig. 3.4.c and 3.4.d).

Total P

Soluble P was detected in the leachates of control and compost amended cores at levels ranging from 0.5 to 1 mg P l^{-1} (Fig. 3.5.a and 3.5.b). Elevated P concentrations were observed in the leachates of cores amended with manure with the greatest quantity of P observed in the leachates of Bt cores, up to 6 times background (Fig. 3.5.b). Ah-F and Ck cores amended with manure leached up to 3 mg P l^{-1} (Fig. 3.5.a and 3.5.b). Phosphorous concentrations in Ah leachates averaged 1 mg P l^{-1} (Fig. 3.5.a). Movement of P did not parallel the breakthrough curves for Br^- or soluble C with the exception of Ah cores. Soluble P was retained longer by the Ah-F, Bt and Ck soils than were Br^- and soluble C.

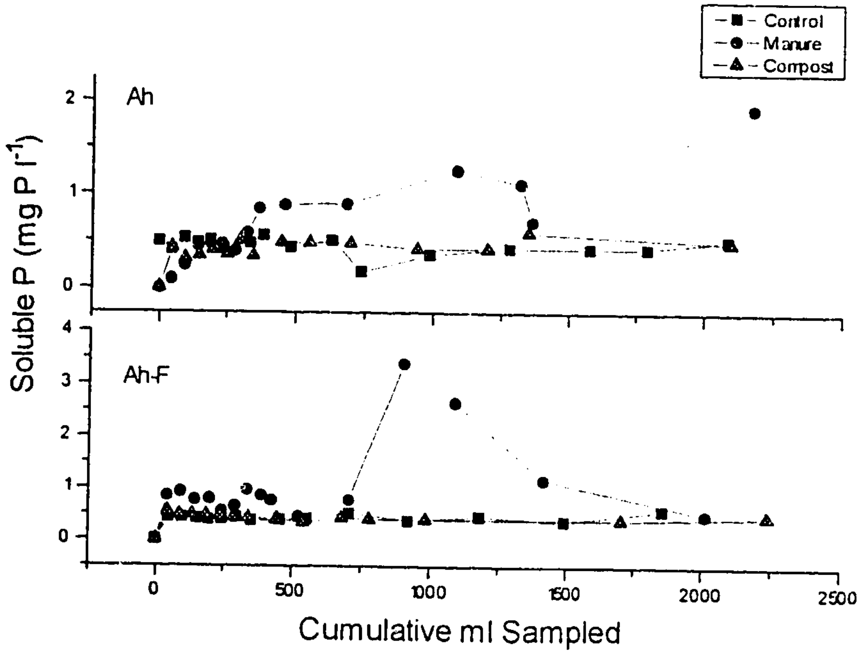

Figure. 3.5.a. Soluble P leached through intact Ah and frozen Ah soil cores amended with manure or compost.

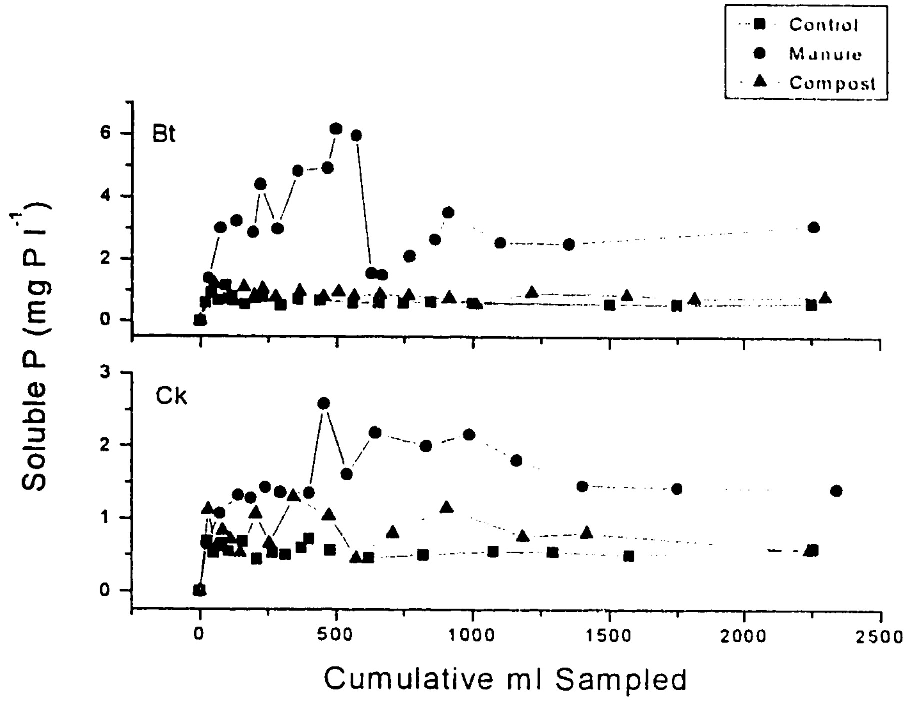

Figure. 3.5.b. Soluble P leached through intact Bt and Ck soil cores amended with manure or compost.

Discussion

Suspended Solids

The movement of soluble components from manure and compost through intact soil cores was used to test the hypothesis that soils act as a filter for suspended solids of manure and compost while soluble constituents move undisturbed. Absorbance at 660 nm was used as an index of solid matter concentration in suspension with increasing A_{660} correlating to an increase in solids concentration. The potential for transport of suspended solids existed with the three soils tested indicating soils may not act as filters.

Soil structure can create preferential flow channels for water and dissolved solutes which influences the characteristics of transport processes (Jury *et al.* 1991). The Ck soils possess the greatest potential to retain solid particles within their matrix (Fig. 3.2.b). These soils have a massive structure (Crown and Greenlee 1978) which, coupled with the high clay content (38%; Chapter 2), results in a dominance of fine pores making the Ck horizon superior for the retention of solid particles which are entrapped in the fine pore spaces.

The Bt soils possess a subangular-blocky structure with well defined vertical macropores (Crown and Greenlee 1978). The early elution of suspended solids from these soils can be attributed to the preferential flow of materials through the large channels (Fig. 3.2.b). Dispersion of the flow occurs as liquid moves rapidly through large channels and more slowly through finer pores.

The structure of Ah soil is a more homogenous granular structure which contains many fine random pores as well as some macropores (Crown and Greenlee 1978). The abundance of macropores is less than in Bt soils and their abundance of micropores is less than Ck due to the lower clay content of Ah soils. This results in an intermediate filter capacity when compared to Ck and Bt soils (Fig. 3.2.a and 3.2.b).

Freezing of Ah soils results in a reduction in the ability of the surface soil to retain or filter out suspended solids as compared to Ah (Fig. 3.2.a). As ice crystals form in soil pores they wedge apart some aggregates and compress others forcing them into closer, firmer contact (Hausenbuiller 1985). These actions result in the formation of large channels or macropores, similar to those found in Bt soils. Freezing removes water from the majority of the soil matrix causing the soil to dry (Hausenbuiller 1985). Re-wetting and subsequent expansion of the soil is slower than the rate of water movement thus, as the soils thaw, water and solids contained within the macropores flush easily out of the soil.

The breakthrough curves for the transport of suspended solids through soils occurred later and were more dispersed than those observed for the transport of the nonreactive tracer, Br^- (Fig. 3.2.a and 3.2.b). Concurrent or retarded transport of suspended solids relative to the tracer indicates the solids were retained to the same or greater extent than Br^-. The mechanism of retention is likely pore size exclusion whereby smaller solids move at the same rate as the tracer while larger solids must travel longer more tortuous paths due to their size relative to the fine pores. This is consistent with the filter capabilities observed for the three soils types where Ah and Ck soils, containing finer pores, have well dispersed suspended solids breakthrough curves relative to the Bt and Ah-F which have a greater proportion of macropores and consequently more abrupt breakthrough curves.

Transport of Soluble C

Previous investigations had concluded soluble constituents from manure were not as readily sorbed by soils as compost derived constituents (Chapter 2). The leaching of soluble constituents through intact soil cores was used to test the hypothesis that solubles from manure and compost are transported through soils.

Soluble C was detected only in the leachates of manure amended cores and reached a maximum of 462 mg C l^{-1} with Ck soils (Fig. 3.3.b). Soluble C leached readily through Bt and Ck cores. The breakthrough curves for soluble C transport occurred concurrently with those of Br^- suggesting **no net reaction** between soluble C and soil constituents; i.e. no sorption occurred nor was there pore size exclusion of soluble C molecules (Fig. 3.3.b). The maximum quantities of soluble C observed, 434 mg C l^{-1} for Bt and 462 mg C l^{-1} for Ck, account for approximately 50% of the potential loading from manure (Table 3.a). The large quantity of soluble C transported is consistent with previous findings which concluded soluble C extracted from manure was not strongly sorbed by soils (Chapter 2).

The soluble C breakthrough curve for manure amended Ah cores is broad, appearing over a wide leaching volume, unlike the sharp curve observed for Br^- (Fig. 3.3.a). We can deduce from the broadness of the curve that C is in reaction with Ah soil constituents either through sorption-desorption reactions or retardation of C molecules through pore size exclusion. Pore size exclusion is not a factor in the transport of soluble C through natural Ck horizons despite their high proportion of fine pores (Crown and Greenlee 1978). Therefore, we can conclude the movement of soluble C molecules is not being retarded in Ah soils since the proportion of fine pores is less than that found in Ck soils. Losses of C in this system likely occur via sorption-desorption reactions with soil constituents.

Soluble C concentrations in the leachates of manure amended Ah-F cores followed a similar pattern to Bt and Ck soils (Fig. 3.3.a). Soluble C was leached quickly and in high concentrations, reaching a maximum of 223 mg C l^{-1}. The breakthrough curve for C was similar to Br^- at the onset of the leaching experiment, however, as the cores thawed, the potential for retention of soluble C appears to have increased as soluble C was released more slowly but at elevated concentrations relative to the control (Fig. 3.3.a).

No soluble C was detected in the leachates of cores amended with compost (Fig. 3.3.a and 3.3.b). The nutrient loading, based on the Buchner funnel determinations, from compost was 20% that of manure despite identical mass application rates (Table 3.1). During aerobic decomposition of manure, formation of humified organic compounds results and a decrease in available nutrients is observed (Levi-Minzi *et al.* 1986; Riffaldi *et al.* 1988). The possibility exists that the labile C was not solubilized due to its low concentration or availability, however, this seems unlikely as C is readily extracted from compost upon exposure to water. The rate of C solubilization may play an important role since the manure was added moist to the cores and the compost was dry. Since compost derived soluble C is strongly sorbed by soils (Chapter 2), the time necessary to moisten the compost may have been sufficient to allow for sorption of molecules by soil as they moved into the solution phase.

The potential for transport of soluble C exists for all soils tested when amended with manure. Movement through subsoils or through thawing soils is rapid and occurs in higher concentrations when compared to surface soils. The degree of leaching may not be as dramatic as observed under these test conditions, especially with respect to Bt and Ah-F soil cores. Rapid flow rates, resulting from the experimental design, may not allow for sufficient contact time between DOC and soils for sorption to occur (Johnson and Farmer 1993). Soluble C is a potential contaminant since it influences soil acidity as many of the reaction products of its decomposition are acidic (Jardine *et al.* 1990). The decomposition of soluble C can also lead to anoxic conditions resulting in competition for oxygen. Nutrient availability, toxicity and the transport of metals and contaminants within the soil are also affected because of soluble C's high affinity for inorganic and organic chemicals (Jardine *et al.* 1990; Moore *et al.* 1992; del Castilho *et al.* 1993; Hsu *et al.* 1993).

Transport of Soluble N and P

Elevated concentrations of N (approximately 10 times the controls) were observed in the leachates of manure amended cores compared to controls (Fig. 3.4.a - 3.4.d). These concentrations were maintained throughout the leaching experiment with the exception of manure amended Ah-F cores. The Bt cores leached the most N (2 times above other cores) over the duration of the experiment while comparable amounts were leached by Ah and Ck cores; a consistent 50 - 60 mg N l^{-1} observed in each leachate sample. Freezing Ah cores altered the behaviour and distribution of N. Rather than detecting continuous leaching of N, from manure amended cores, a flush of N (≈10 times the control) was observed followed by a rapid decline to levels approximately twice the control (Fig. 3.4.b). This behaviour may be attributed to the formation of channels caused by freezing which result in the rapid transport of solutes through soil as observed with Bt cores (Jury *et al.* 1991). This readily leached N can meet with several fates while lying on the soil surface, leaching through soils, or once it reaches the groundwater.

The dominant form of N (≥70%) observed in the leachates of manure amended cores was NH_4-N with the remainder consisting of organic N. Despite the positive ionic charge on NH_4^+, it was not retained strongly by soils, however, this may be due to the high concentration of background electrolyte, K^+, which would out compete NH_4^+ for exchange sites on the soil matrix. Several fates await NH_4^+ as it leaches through soil.

Nitrification, the biological oxidation of NH_4^+ or NO_2^- to NO_3^-, is rapid in moist soils at room temperature and even at 2-3°C (Harding and Ross 1964). The potential for denitrification, the biological reduction of NO_3^- or NO_2^- to N_2 or nitrous oxides, is high immediately following manure application and increases with moisture content and increasing concentrations of soluble C (Paul and Beauchamp 1995). The replenishment of O_2 depends on the soils' gaseous diffusion rate which decreases with increasing water contents and the decomposition or oxidation of soluble C results in low levels of dissolved O_2 (Guenzi *et al.* 1978). These are the prerequisites for denitrification and both conditions existed throughout these experiments. Guenzi *et al.* (1978) reported that nitrification and denitrification occur simultaneously in manure amended soils. Reducing microsites exist for denitrification and others for oxidative nitrification. An attempt was made to maintain saturated conditions throughout the experiment, however, oxidative periods likely did occur. Despite the tendency for nitrification-denitrification to occur under these test conditions, they did not have a significant influence on the leaching of NH_4^+.

Total N concentrations leached from compost were similar to those observed from the controls. Organic-N made up the largest proportion of total N (70-90%) with the remainder occurring as NO_3^-, with the exception of Ah-F. Nitrate is the most mobile of the nitrogenous compounds and is also susceptible to denitrification. The quantities leached by compost, under these test conditions, were insignificant relative to N leached from manure, less than 5 mg N l^{-1} (Fig. 3.4.a - 3.4.d). Manure N is stabilized during composting through microbial assimilation and humification (Hadas and Portnoy 1994). Castellanos and Pratt (1981) reported composted manures released less available N than fresh manure. Therefore, the absence of large quantities of N in the leachates of compost amended cores is not surprising. The possibility exists that, under the saturated conditions of these experiments, all NO_3^- released by the compost was lost through denitrification since denitrification rates increase as moisture contents increase (Paul and Beauchamp 1995).

Compost amended Ah-F leached similar quantities of NO_3^- as Ah, however, in addition, two times more NH_4^+ than NO_3^- was also detected (Fig. 3.4.a and 3.4.b). The appearance of NH_4^+ was not instantaneous as in the case of manure amended cores, but followed a lag period. Freezing leads to the death of a proportion of the microbial population in soils and the decomposition of this biomass yields NH_4^+ and CO_2 (Paul and Clark 1989). This may provide an explanation for the appearance of NH_4^+ in the leachates of the frozen cores.

Leaching of nutrients in the organic form appears to be an important mechanism for nutrient flux and removal (Donald *et al.* 1993). Most dissolved organic N and P in the soil solution has been found associated with hydrophilic acids and the neutral fraction of dissolved organic C (Schoenau and Bettany 1987; Qualls *et al.* 1991; Qualls and Haines 1991). The association of these nutrients with soluble C either as part of those same molecules or electrostatically adsorbed by soluble C, renders otherwise immobile nutrients mobile and subject to leaching (Donald *et al.* 1993). At least 20% and as much as 95% of the total N leached from the soils in this study was in the form of organic N. Liang *et al.* (1995) reported water soluble organic C increases net N mineralization in clay soils in quantities approximately equal to the amount of organic N added in water extracts.

Manure continues to mineralize and release N and C during the late fall and early spring thus the potential for the accumulation of N contaminants exists (Angle *et al.* 1993).

Elevated concentrations of P were observed with both amendments for all soils tested (Fig. 3.5. a and 3.5.b). Manure amendment caused a 1-2 times greater increase in soluble P concentrations than compost, however, the observed concentrations were still 2 to 5 times the maximum loading potential (Table 3.1). This may result from longer contact time between K_2SO_4 and manure and compost when on the surface of soil cores as opposed to on glass wool contained within Buchner funnels. Freezing caused an increase in soluble P leached from manure amended Ah-F, once thawing began, to levels observed from Bt cores. These data support the hypothesis that solubilization of soil P may have occurred under the test conditions. Soils contain an average of 0.5 to 1 μg P g^{-1} soil (Paul and Clark 1989). Organic acids have been reported to increase the solubility of soil P (Paul and Clark 1989; Donald *et al.* 1993) and yearly applications of manure increase the concentration of soil organic and inorganic P (Tran and N'dayegamiye 1995). Phosphate anions are insoluble or poorly soluble and strongly sorbed by mineral constituents such as clays and sesquioxides (Parfitt 1978; Paul and Clark 1989). Organic phosphate compounds, especially monophosphate esters, possess the potential for movement (Frossard *et al.* 1989). Frossard *et al.* (1989) reported in a study of Orthic Black Chernozemic, Grey Luvisolic and Calcareous Brown soils that organic-P compounds were more mobile than phosphate anions and may therefore by responsible for P leaching. Donald *et al.* (1993) reported that in a study with forest soils the hydrophobic neutral fraction of soluble soil C had the highest potential for mobility because it was not well sorbed by forest soils. They concluded the mobility of P-rich compounds was mediated by the potentially mobile hydrophobic neutral C fractions and these compounds were responsible for the redistribution of P from upland soil profiles to footslopes.

Conclusions

The potential for groundwater and surface water contamination exists when soils are amended with manure. Soils do not filter out suspended solids from manure but finer textured, amorphous structured soils with a high proportion of fine pores are best suited for retaining solid material. The potential for transport of soluble constituents exists with all the soils tested when amended with manure. Movement of solubles through subsoils or through thawing soils is rapid and results in higher concentrations of soluble constituents in the leachates than surface soils. Soluble C may enhance the transport and mineralization of manure N as well as aid in the solubilization and subsequent transport of manure, compost and soil P. Freezing of soils reduced the potential of surface soils to retain solid materials and enhanced the transport rate and quantity of soluble C, N and P through manure amended surface soils. Compost amended cores did not leach solids or soluble C or N. The lower mobility of compost constituents may reduce the potential for contamination of the environment when compared to manure.

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Chapter 4

SYNTHESIS

The potential for manure and compost to contaminate surface and groundwater depends on the transport of soluble C, N and P. The overall objective of this thesis was to investigate the extent to which DOC, soluble N and P, extracted from manure and compost, sorbed to or were retained by soils and soil constituents. To achieve this, batch equilibration and intact core leaching experiments were conducted using surface and subsurface samples of an Eluviated Black Chernozem, dairy manure and composted manure. Batch equilibrations were conducted to determine the potential for sorption by soluble constituents onto soil and to gain insight into the possible sorption mechanisms at work. Intact core leaching experiments were conducted to test the conclusions of the batch experiments *in situ*.

Summary

From the batch equilibration experiments several conclusions can be drawn. Soils sorb DOC, soluble N and P. Sorption of DOC follows a linear isotherm model for both surface and subsurface soils indicating that the mechanism of sorption in these systems is partitioning. A linear isotherm is the simplest model available to describe the retention of a solute by a sorbent and usually holds true for low solute concentrations. It describes a linear relationship between solute concentration in the organic phase and that in the solvent phase that exists over a wide range of solute concentrations (Chiou 1989).

Sorption of DOC is dependent on the characteristics of the DOC and the soil. Sorption of CS was 6-8 times stronger than MS by both soils. Hydrophobic compounds are more effective at binding hydrophobic compounds, such as soil organic matter, than hydrophilic compounds (Carter and Suffet 1982; Jardine *et al.* 1990). Composting results in the formation of humified organic compounds (Levi-Minzi *et al.* 1986; Riffaldi *et al.* 1988) which are more hydrophobic or aromatic than the starting manure. Compost derived DOC is slightly more aromatic (≈2-4%) than manure derived DOC (Chapter 2). Sorption by subsurface soils of DOC was 6-8 times greater than sorption by surface soils despite having an organic C content one-tenth that of surface soils. Organic matter is the main sorbent for organic molecules in solution (Chiou 1989), therefore another mechanism was at work in the subsurface soils. Since the Ck horizon was dominated by soil minerals and carbonate salts rather than organic matter. Therefore, the most probable mechanism for the removal of DOC by these soils is precipitation of DOC-mineral complexes or DOC-calcium precipitates. These results indicate that sorption of DOC differs for different soil types.

E_4/E_6 ratios and CPMAS ^{13}C NMR were used to characterize the nature of the constituents sorbed by each of the soil types. I hypothesized that hydrophobic constituents of DOC would be retained by organic-rich surface soils and hydrophilic constituents would be sorbed by mineral-rich subsurface soils. The E_4/E_6 values provided qualitative evidence to support the hypothesis of preferential sorption. The ratios increased following reaction of DOC with soil and were consistently higher for DOC-Ck systems. I conclude from these data that the equilibrium solutions for the DOC and DOC-soil mixes have different chemical compositions implying different constituents of DOC were removed by each of the soils tested. Nuclear magnetic resonance was used in an attempt to quantify these differences, however, due to the complexity of the DOC mixtures no definitive conclusion as to the chemical composition of the solutions could be made.

Soluble N was sorbed strongly by both soils and followed a linear isotherm. The predominant form of mineral N extracted from manure was NH_4^+ while mineral N was dominated by NO_3^- in compost extracts. Loss of N from manure treated samples may be better attributed to volatilization of NH_3 rather than sorption as the samples were well aerated throughout the batch experiments. DOC extracted from manure when reacted with Ah soil resulted in solubilization of P rather than sorption, though the concentration solubilized was small relative to what was added. Organic acids are known to enhance the solubilization of soil P (Paul and Clark 1989; Donald *et al.* 1993). Precipitation of P with mineral constituents accounts for the observed sorption of P by soils.

The conclusions drawn from the batch equilibration experiments were used to develop hypotheses for the core leaching study. We had observed that soils possessed the potential to sorb large quantities of solute but the question remained as to how that translated to the intact soil environment, particularly in the case of manure or compost amendment to frozen soil. In addition to the presence of soluble constituents *in situ*, suspended solids would also be present and capable of interacting with soil constituents. I hypothesized that soils would act as filters of suspended solids, but would allow for the movement of soluble compounds extracted from manure and compost. In particular, soluble C from manure would move more readily than soluble C extracted from manure. I predicted N as NH_4^+ and P would be sorbed by soils, based on the findings of the batch experiments.

Intact soil cores of Ah, Bt and Ck soils were amended with either manure or compost and leached. Suspended solids, soluble C and soluble N were detected in the leachates of manure amended cores. Fine textured soil retained the most solid mat[illegible] as a result of their large proportion of fine pores (Crown and Greenlee 1978), however complete filtering out of suspended solids did not occur as would be predicted by natural soil horizons such as Podzolic Bh and Bhf. Movement of soluble C and N through subsoils and thawing soils was rapid and resulted in higher solute concentrations within the leachates. Freezing of soils reduced the potential of surface soils to retain suspended solids or soluble compounds. Leaching of nutrients in the organic form is an important mechanism for nutrient flux and removal (Donald *et al.* 1993). At least 20% and as much as 95% of the total N leached through soils was in the organic form. Most dissolved organic N and P in the soil solution has been found associated with hydrophilic acids and the neutral fraction of dissolved organic C (Schoenau and Bettany 1987; Qualls *et al.* 1991; Qualls and Haines 1991). Elevated P concentrations were detected in the leachates of both manure and compost amended cores. I conclude P was solubilized in the presence of organic acids from manure and compost.

The results of the core leaching study confirmed the previous conclusion that manure derived DOC was more mobile than compost derived DOC perhaps due to MS's more hydrophilic character. Sorption of N compounds was as great for N extracted from manure as from compost in the batch equilibration experiments but large quantities of manure N were leached during the core study. Based on the batch equilibration experiments, P was predicted to be retained strongly by soils, however, this was not the case *in situ*, as P was solubilized and leached from both manure and compost. The lower mobility of compost constituents through intact cores was predicted by the batch equilibration experiments.

Implications

Janzen and McGill (1995) estimated that, during 1991, livestock in Alberta excreted 271 000 tonnes of N and 79 000 tonnes of P. Much of this is concentrated in small regions where the land base is not adequate for its effective use. There are many problems associated with manure application such as bulk, odour and the presence of weed seeds and pathogens (Paul *et al.* 1994). Composting is considered an effective means to minimize these problems. During aerobic decomposition of manure, humified organic compounds are formed and the quantity of available nutrients decreases (Levi-Minzi *et al.* 1986; Riffaldi *et al.* 1988). Despite this, concerns exist regarding nutrient losses from compost and manure (Ulén 1993). While the use of composts has increased, investigations into the management of composts have been limited (Nodvin *et al.* 1986).

The findings of this set of experiments sheds light on the behaviour of soluble components leached from manure and compost. While the potential exists for sorption of soluble C, N and P, the case is *in situ* is different. Manure and compost were applied at 6.8 Mg ha^{-1} on a dry matter basis, a moderate application rate for organic amendments. At this application rate, contamination of groundwater is a strong possibility with manure but not with compost. If disposal of manure or compost is the only objective of land application it would seem prudent to compost prior to applying. However, if use as a nutrient source is the goal of addition, further research needs to be conducted. The composting process results in more stable organic matter from which nutrients may not be readily extracted (Levi-Minzi *et al.* 1986; Riffaldi *et al.* 1988; Garcia *et al.* 1991). In such a case, higher application rates or repeated applications may be necessary and the impact of such applications cannot be predicted from this study.

Should compost not provide the required nutrient load for optimal plant growth, several considerations should be met prior to manure application. Application of manure may not always take place in the spring prior to seeding. Incorporation of manure to frozen soils reduced the potential for surface soil to retain suspended solids and soluble constituents (Chapter 3). Manure disposal during periods of active thaw has been documented as resulting in large losses of soluble N and P (Klausner *et al.* 1976). These losses were minimized when manure was applied and then covered with snow prior to thawing (Klausner *et al.* 1976) however, a rapid thaw can result in leaching of ammoniacal N into the soil under these conditions (Lauer *et al.* 1976). Therefore, application of manure at such times would simply result in a loss of valuable plant nutrients. The optimum time for manure application would be during periods of high evapotranspiration (Klausner *et al.* 1976) since application during wet seasons increases the susceptibility of nutrient losses by surface runoff and leaching (Klausner *et al.* 1974). Additionally, the influence of soluble C on other nutrients should be considered as DOC may enhance the mineralization of N and the solubilization of P. This is particularly important with manure DOC since it is the more mobile.

Future Research

These experiments have determined that soluble constituents from compost are less mobile than those of manure, yet the nutrient status of compost relative to manure is not known. As composting results in more stable organic matter (Garcia *et al.* 1991), the extraction of essential nutrients *in situ* may be more difficult with compost as compared to manure. Investigations into the extent of nutrient availability from compost are therefore required. Widespread use of composts is unlikely to occur unless it can be proven that composts are a valuable plant fertilizer, since the manufacture of composts can be costly. If increases in compost application are necessary, the maximum allowable rate of application must be determined in order to minimize nutrient losses and contamination. This may be accomplished using leaching experiments in which the application rates of compost are varied and the soil leachates are monitored.

To understand better the mechanisms at work in the sorption or retention of soluble constituents, tests with ^{14}C and ^{15}N would prove useful. The experiments conducted as part of this thesis provided clues as to the activities of soluble constituents but did not provide definitive evidence as to what components are most important. Mass balance of materials sorbed, volatilized and biologically mineralized would be invaluable to understanding how best to manage manures and composts to minimize nutrient losses that lead to environmental contamination.

As was observed by comparing batch equilibrations with core leaching studies, generalizations cannot readily be made as to the behaviour of soluble C, N and P in the environment. Therefore, field scale studies are essential. Precipitation, in Alberta, is not likely to reach the levels used in the leaching experiments, therefore, the leaching potential may be greatly reduced in the field. The presence of plants will also influence the mobility of nutrients as they are acted upon by plant roots. These experiments were also limited in that they only investigated one type of soil albeit all the horizons from that soil. Comparisons need to be made between soil types in order to draw broader conclusions.

Synthesis Statement

The decreased mobility of compost derived constituents may reduce or eliminate the potential to contaminate the environment when compared to manure.

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