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Cation exchange due to the diffusion of ammonium from livestock effluent through glacial clay soils

W.J. Chang [1], R. Donahue *

Department of Civil and Environmental Engineering, 3-068 Markin/CNRL Natural Resources Engineering Facility, University of Alberta, Edmonton, Alta., Canada T6G 2W2

The objective of this study was to experimentally simulate interactions between liquid manure and soil in diffusion-dominant areas beneath earthen manure storage (EMS). A previous radial diffusion cell method was modified to include an anaerobic chamber that employed a plastic glove bag supplied with inert Ar gas. Anaerobic conditions were maintained during the entire run time of the experiment. Little oxidation of NH_4^+ occurred; consequently, NO_3 and NO_2 concentrations were lower than the detection limit. Chloride played a key role in redistribution of major cations and anions resulting from the NH_4^+ diffusion. Linear NH_4^+ and K^+ adsorption isotherms were obtained. The resulting distribution coefficients, K_d, for NH_4^+ ranged from 0.3 to 0.4 L/kg. Significant NH_4^+ exchange reactions led to an average increase in hardness of 137% in the reservoirs, due to extraction of exchangeable Ca and Mg. Geochemical mixing modeling using PHREEQC adequately simulated the linear NH_4^+ adsorption at low dissolved NH_4^+ concentrations (<30 mM). The predicted manure volumes to cause NH_4^+ saturation were 1.0 1.4 mL/g for the glacial clay soil samples.
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1. Introduction

Manure produced by intensive livestock operations has been a public concern due to the substantial volume generated. An earthen manure storage (EMS) system, constructed with local geological material, is a common means to store liquid manure in Western Canada. Old EMS systems (older than 20 a), which are scattered throughout Alberta, have

no engineered liner or barrier system to prevent the seepage of liquid manure (Alberta Agriculture, Food and Rural Development, 2001).

The current Alberta regulations for EMS strictly enforce the need for an engineered liner system to protect groundwater and surface water resources (Alberta Agriculture, Food and Rural Development, 2004). Nevertheless, the presence of NO_3^- and NO_2^-, which is commonly caused by the leakage of liquid manure from EMS, has frequently exceeded water quality guidelines. In reality, 32–87% of the water resources in areas of low- to high-intensive livestock operation regions in Alberta exceeded the Maximum Contamination Level

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(MCL) of NO_3^- for aquatic life (Alberta Agriculture, Food and Rural Development, 1998, 2004).

In order to evaluate a budget of excess N under an EMS environment, the long-term diffusion effect and the interaction of liquid manure and local soils should be considered, in addition to the seepage loss of liquid manure from EMS facilities. In this study, therefore, diffusion is identified as a major transport process between liquid manure and the local soils used for the construction of EMS. The rationales for the consideration of diffusion are as follows: (1) molecular diffusion, which is the slowest contaminant transport mechanism, should be examined for long-term risk assessment and a decommissioning strategy to address unlined old EMS; and (2) EMS in the Canadian Prairies is generally located in glacial clay and/or clay tills with diffusion-dominated hydrogeologic regimes.

Ammonium, which is the most abundant form of N in liquid hog manure, is regarded as the source of NO_3^- contamination in aquifers. According to Fonstad's (2004) field measurement for fluid throughout EMS, low dissolved O_2 concentrations, ranging from 0.3 to 1.3 mg/L, led to anaerobic conditions in subsurface areas of the EMS. Eh readings of less than 100 mV, and high organic C concentrations of approximately 6000 mg/L, also cause N to remain in the NH_4^+ form. Excessive NH_4^+ can be transported to the aerobic zones of an aquifer and then be oxidized to form NO_3^- and/or NO_2^- (Kreitler and Jones, 1975; Wassenaar, 1995; Fukada et al., 2004; Hudak, 2000; Widory et al., 2004; Zebarth et al., 1999).

Fig. 1 provides a conceptual model of NH_4^+ diffusion along fractured glacial clays and/or clay tills in the Canadian Prairies. The fractures in the glacial deposits play a key role in the long-tem redistribution of NH_4^+ through molecular diffusion and adsorption (D'Alessandro et al., 1997; Donahue et al., 1999). Adsorbed and aqueous phase NH_4^+ may prevail between the fractures. Aqueous phase NH_4^+ in a major fracture is gradually attenuated. Significant cation exchange with the clays in contact with NH_4^+-rich liquid manure can be a primary cause of strong NH_4^+ adsorption. This may lead to changes in pore fluid chemistry due to the replacement of cations present in the clays.

2. Methods

2.1. Anaerobic radial diffusion cell method

2.1.1. Cell preparation

Minimally disturbed (stainless steel Shelby tube) glacial clay soils were collected during a geotechnical site investigation at Ponoka, Alberta (Cell UA1–5). The samples were extruded and trimmed to fit in the radial diffusion cell. Fig. 2-[4] shows the geometry of the PVC Teflon radial diffusion cell (RDC). To construct a reservoir hole in the soil sample in the RDC, the trimmed top surfaces of the soils were drilled along the central axis of the cylindrical RDC (OD, 27 mm; ID, 24 mm; H,
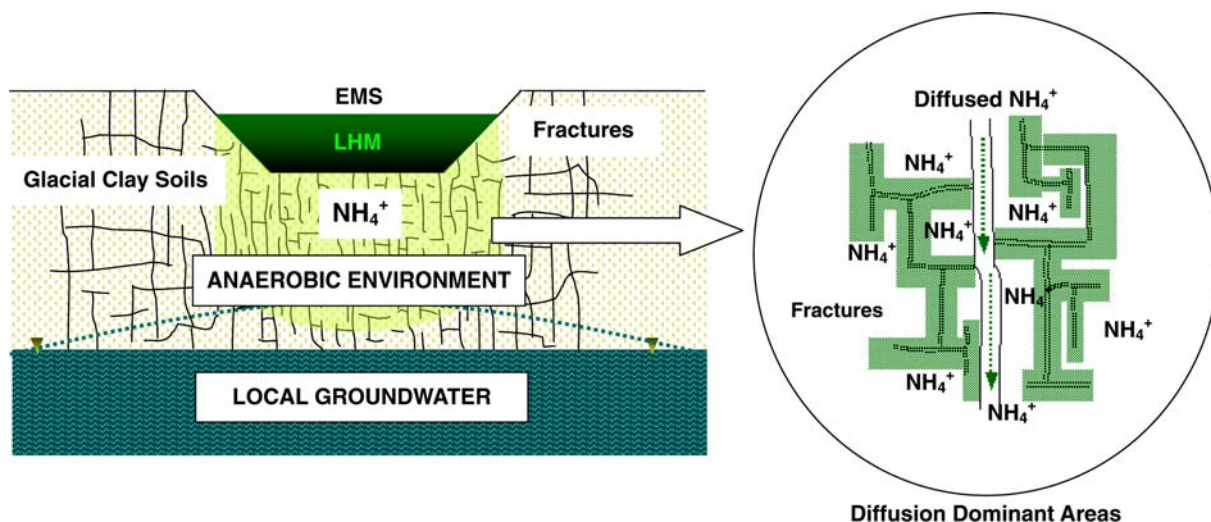

Fig. 1. Conceptual model for NH_4^+ diffusion along fractured glacial clays and/or clay tills in the Canadian Prairies. *Note.* EMS denotes earthen manure storage and LHM refers to liquid hog manure.
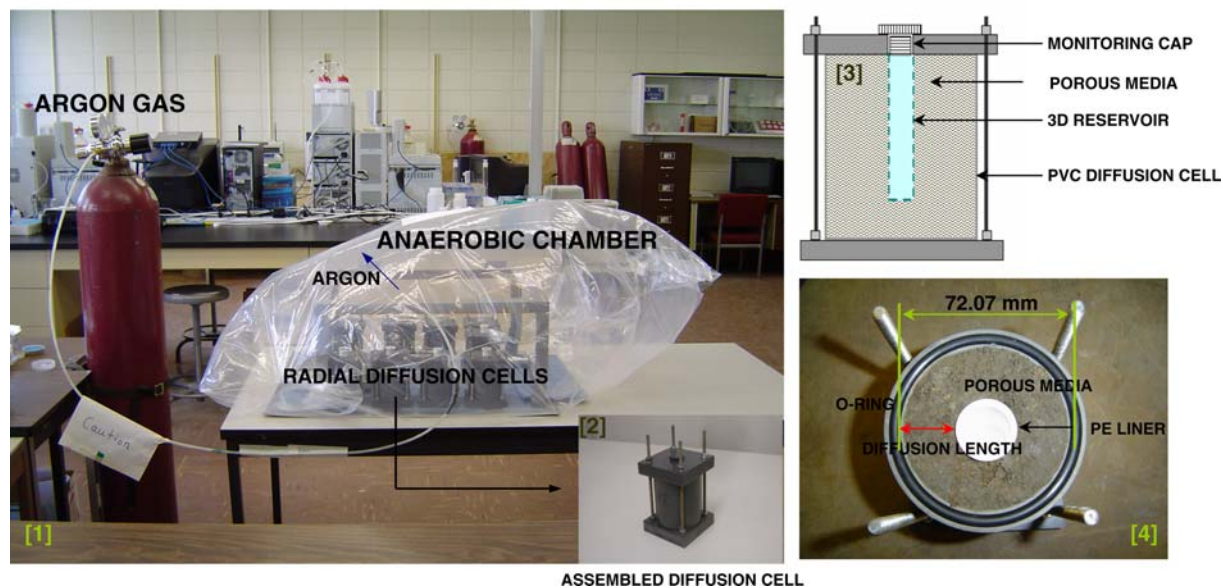
Fig. 2. Anaerobic radial diffusion cell setting and schematic of a radial diffusion cell.

70 mm). These were not drilled down to the absolute bottom of the cells in order to allow three-dimensional radial diffusion into the porous media (Fig. 2-[3]). The typical reservoir depth was 70 mm from the top surface, and the average height of all the cells was 90 mm. A polyethylene (PE) porous liner (X-5306 Porex®-25 μm fine) was inserted into the drilled hole. The intact core samples were then enclosed with O-ring seals and with the square-shaped upper plates of the cells. The cell preparation was conducted as quickly as possible to minimize disturbance of, and moisture loss from, the soil samples.

2.1.2. Diffusive equilibrium and monitoring reservoir

After setting up the five diffusion cells, each central reservoir, which had an inner volume of 20 mL ± 0.08, was filled with 20-mL ultrapure water (18.2 MΩ cm and 0.7 μS/cm, Barnstead). The ultrapure water was allowed to equilibrate with the soil for 60–90 days, depending on the types of soil samples (Van der Kamp et al., 1996), to quantify the initial soil pore fluid chemistry. This procedure essentially dilutes the original pore fluid chemistry of the soil sample by the volume of the reservoir (0.84–0.87 times dilution). In order to confirm that diffusive equilibrium of the pore fluids had occurred, the electrical conductivity (Orion® 130A) of the reservoir solutions was measured by using a microelectrical probe and the pH change (Accumet®

AR50) of the reservoirs was monitored (Van der Kamp et al., 1996).

Stagnant electrical conductivity response of the reservoirs was regarded as completing diffusive equilibrium. After equilibrium was achieved, the pore fluids were sampled from the diffusion cells and filtered using syringe filtration (Waterman® nylon membrane filter paper 0.45 μm). Major cations and anions of the pore fluid were analyzed by ion chromatography (IC), Dionex® 2500 (Applied Environmental Geochemistry Research Facility at the University of Alberta).

2.1.3. Anaerobic conditions and injection of liquid hog manure

A four-hand glove bag (Fig. 2) was used to replicate the anaerobic environment beneath EMS, Fig. 2-[1]. Argon gas was added three or five times per day to maintain O_2-limited conditions in the glove bag chamber. The anaerobic chamber was to separate the diffusion cells from the atmospheric environment of the laboratory room. It was critically important to maintain anaerobic conditions during the routine monitoring program.

After creating the anaerobic chamber, the reservoirs in the five diffusion cells were filled with 20 mL ± 0.36 raw liquid hog manure, which was collected at the Swine Research and Technology Center (SRTC) at the University of Alberta (March,

2004). In order to measure the earlier response of the anticipated ion exchange, the effluents of about 20 mL (reservoir volume) were sampled from the reservoirs (~20 mL) after a 10-day diffusion period had elapsed. A short diffusion period is required to determine effective diffusion coefficients. The effective diffusion coefficient was determined by matching the rate of change in the pore chemistry of the reservoir. If the pore fluids are allowed to completely equilibrate a diffusion coefficient cannot be determined. The analysis of effective diffusion coefficients and other transport properties is beyond the scope of this manuscript but is presented in Chang (2005).

After sampling, fresh manure effluent was immediately re-injected into the reservoirs and the samples allowed to equilibrate. During the 60-day diffusion period, a routine monitoring program assessed the effluent chemistry; this included the measurement of electrical conductivity, pH, temperature, and mass change caused by evaporation and measuring and sampling losses.

After the 60-day diffusion period, the effluent was sampled from all the cells. Conventional water chemistry analysis was conducted on the collected effluent solution, including cation and anion concentration by IC analysis, electrical conductivity, pH, temperature, dissolved O_2 (DO), hardness, alkalinity, total dissolved solids (TDS) and total organic C (TOC).

The final step was to investigate the potential for NH_4^+ desorption due to the infiltration of fresh water into the clay soils. To do this, 20-mL ultra-pure water was injected into each reservoir in contact with the soil samples. The desorption duration was planned to continue for a further 60 days. Routine monitoring and water chemistry analysis were carried out during the desorption period.

2.2. Geochemical mixing models using PHREEQC

PHREEQC interactive version 2.6.0.1 (Parkhurst and Appelo, 1999), developed by the U.S. Geological Survey, was used for the geochemical mixing modeling. The simulations were divided into two modules: (1) SIMPLE MIX MODEL and (2) MIX MODEL. The SIMPLE MIX MODEL refers to the simulation of a single episode of the liquid hog manure injection. Hence, the SIMPLE MIX MODEL described the anaerobic RDC experiment with a single liquid hog manure injection. The

MIX MODEL aimed to simulate the maximum number of injection episodes to achieve full NH_4^+ saturation in soils.

3. Material characterization

3.1. Soils

The soils consisted of 31–34% sand and 65–68% clay. According to the United Soil Classification System (USCS), the sampled soils in this study were classified as sandy-lean clay (CL) for Cell UA1–2 at 1.5–2.3 m depth, and sandy-fat clay (CH) for Cell UA3–5 at 3–5.3 m depth. Hydrometer tests and wet sieve analysis were performed for the soil classification at the Geotechnical Laboratory at the University of Alberta. The total porosity estimated by gravimetric water content typically ranged from 0.32 to 0.42. Volumetric water contents were 32–33% for Cell UA1 to UA2, and 37.5–42% for UA3–5.

X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses were used to identify the clay mineralogy of the samples. The XRD results indicated that the soil samples were

Table 1
Geochemical properties of the soil samples

Geochemical index	Group 1	Group 2	Group 3
Cation-exchange capacity (meq/100 g)	21.2	43.3	34.2
Total N (%)	0.06	0.08	0.04
Organic matter (%)	1.5	1.5	1
Total organic C (%)	0.74	0.77	0.48
SPE (mg/L)			
Na	63	60	61
Ca	54	52	73
Mg	23	19	23
K	6	11	15
$N–NH_4$	4	7	10
Cl	67	31	24
SO_4	150	102	130
$N–NO_3$	9	3	4
$N–NO_2$	2.5	2	0.96
pH	7.9	8	8.18
EC (mS/cm) at 25 °C	0.39	0.34	0.38
SAR	1.83	1.81	1.60
ESR	0.03	0.03	0.02
ESP	2.67	2.64	2.34

Note. (1) Group 1, Cell UA1 and UA2; Group 2, Cell UA3 and UA4 and Group 3, Cell UA5. (2) SPE denotes saturated paste extraction. (3) EC, electrical conductivity; SAR, sodium adsorption ratio; ESR, exchangeable sodium ratio; ESP, exchangeable sodium percent.

composed of smectite and illite with lesser amounts of plagioclase, chlorite and kaolinite. Minor quantities of K feldspar were detected as well. The soil samples from Ponoka consist of 60% smectite in the clay fraction within a framework sand/silt.

The cation-exchange capacities of the samples were determined by the conventional ammonium acetate (NH_4OAc) method (McKeague, 1981). The results were: 21.2 meq/100 g for Cell UA1–2; 43.3 meq/100 g for Cell UA3–4; and 34.2 meq/100 g for Cell UA5 (Table 1). The high CEC values reflected the 68% smectite present in the clay fraction of the samples.

A saturated paste extraction test (Carter, 1993) was conducted to examine geochemical properties of the soil samples (Table 1). A 1:1 volume ratio of air-dried soil to deionized water was adopted to create the saturated pastes (Hogg and Henry, 1984). The saturated pastes were then centrifuged to extract the soluble salts. The background NH_4–N concentrations were 4–10 mg/L. The leached NO_3–N concentrations ranged from 3.4 to 8.6 mg/L. Nitrite was rarely detected because it rapidly oxidized to NO_3^-. The measured soil pH typically ranged from 7.9 to 8.2 for the non-saline soils.

3.2. Liquid hog manure

Table 2 shows IC analysis for the initial liquid hog manure. Notably, NH_4^+ was a dominant species of which mole fraction is approximately 45%. Bicarbonate, K^+ and Cl^- were 36%, 7% and 6% in mole fraction, respectively. Calcium, Mg and Na in the manure were extremely limited (1–4%).

The measured electrical conductivity and pH of the manure were 23 mS/cm (25 °C), and 7.9, respectively. The DO reflected a very low level: 0.8 mg/L. The saturation index (SI) of calcite ($CaCO_3$), calculated by PHREEQC, was 0.2 for the liquid hog manure; consequently, calcite precipitation was expected during the experiment. Based on field alkalinity measurements CO_2 (g) in the liquid hog manure was oversaturated (SI value of 0.58) with respect to atmospheric CO_2 (SI of 3.51 for atmospheric CO_2 (g)). Degassing of CO_2 (g) from the reservoir was expected to occur during the experimental program, including the sampling and measuring of the reservoir solutions.

Table 2
Geochemical property of the liquid hog manure sample

Analyte	Results	Unit
Cations		
Ca	199	mg/L
K	1710	mg/L
Mg	6.4	mg/L
Na	611	mg/L
NH_4	5241.5	mg/L
Anions		
Cl	1380	mg/L
SO_4	9	mg/L
NO_3–N	1	mg/L
NO_2–N	1	mg/L
PO_4–P	1270	mg/L
Carbonates		
HCO_3	14,300	mg/L
CO_3	100	mg/L
OH	<100	mg/L
Iron		
Fe-dissolved	4	mg/L
Organic carbon		
Dissolved organic C (DOC)	4700	mg/L
Total organic C (TOC)	6510	mg/L
Geochemical index		
pH	7.9	pH
Conductivity (EC)	23	mS/cm
Hardness (as $CaCO_3$)	523	mg/L
Alkalinity	11,700	mg/L
Dissolved oxygen (DO)	0.8	mg/L
Density	1	g/mL
Total dissolved solid (TDS)	10,900	mg/L

4. Results and discussion

4.1. Geochemical interpretation for soil–liquid manure system

4.1.1. Initial pore fluid chemistry

Prior to sampling equilibrated reservoir solutions that were in contact with the soil samples, the required diffusive equilibrium time was predicted using ChemFlux (Fredlund and Stianson, 2003), which is a comprehensive transport-modeling tool based on the finite element method. In the 3D radial model, the conservative solute Cl^- diffuses from the porous media to the reservoir. The predicted equilibrium time ranged from 55 to 60 days when the equilibrium concentration for Cl^- reached 18–20 mg/L. Therefore, the reservoir solutions were sampled when the predicted 65-day period had elapsed and the pore fluid was regarded as representative of the soil samples. To confirm the diffusive equilibrium time, the electrical conductivity and

pH change in the reservoir solutions were measured (Van der Kamp et al., 1996). Fig. 3 shows that the determined diffusive equilibrium time ranged from 53 to 66 days for the Cell UA1, 2 and 5 samples. In the case of Cell UA3 and 4, the reservoir solution may not have completely equilibrated within the designed equilibrium time (65 days). The estimated equilibrium time for Cell UA3 and 4 ranged from 66 to 109 days. The elapsed time to reach equilibrium varied according to soil properties: particle size and clay fraction. It appeared that the soil samples with smaller particle size and more clay fraction resulted in a longer diffusive equilibrium time.

The initial pore fluid concentrations are presented in Tables 3 and 4. Ammonium, NO_3^- and NO_2^- concentrations were lower than detection limits according to the IC analysis. The charge balance errors for the total dissolved major cations and anions in the pore fluids ranged from 0.60% to 1.73%.

The pH of the reservoir increased with contact time, as shown in Fig. 4. The value of log P_{CO_2} ranged from 1.8 to 1.5 in cells UA1 to UA5. It is possible that developing CO_2 (g) in the pore fluids contributed to an increase in the pH of the reservoir solutions by calcite ($CaCO_3$) dissolution in the reservoirs. The saturation index (SI) of calcite ranged from 2.6 to 1.6 in the reservoir solutions, according to PHREEQC calculation. As a result of oversaturation of CO_2 (g) and dissolution of $CaCO_3$,

the reservoir solutions' pH increased on average from 6.1 to 7.0. Therefore, the pH of 7.0 is regarded as the representative pH of the synthesized pore fluids after diffusive equilibrium periods. The value of pH 7.0 will be used for the initial pore fluid chemistry data for geochemical models.

The monitored temperatures of the reservoirs ranged from 20 to 24.5 °C during the 65-day equilibrium period. The measured reservoir temperature was reasonably stable and equivalent to the temperature of the laboratory. It was assumed that a change in the reservoir temperature did not affect the initial pore fluid chemistry (Van der Kamp et al., 1996).

In order to complete water saturation, 5–17 mL of water was added to the soil samples in the diffusion cells. The added water volume was approximately 1.5–4.7% of the total volume of the soil in the cells. The effective pore fluid volume ranged from 130 to 170 mL. This estimation is based on mass balance equations that include 0.01–0.07% of evaporation loss and 0.38% of measurement loss. Both the initial pore fluid chemistry and the effective pore fluid volume were used for the geochemical mix models.

4.1.2. Change in pore fluid chemistry

Reservoir concentrations for the 10-day and 60-day periods of diffusion are presented in Tables 3 and 4. During the 60-day diffusion periods, a sub-
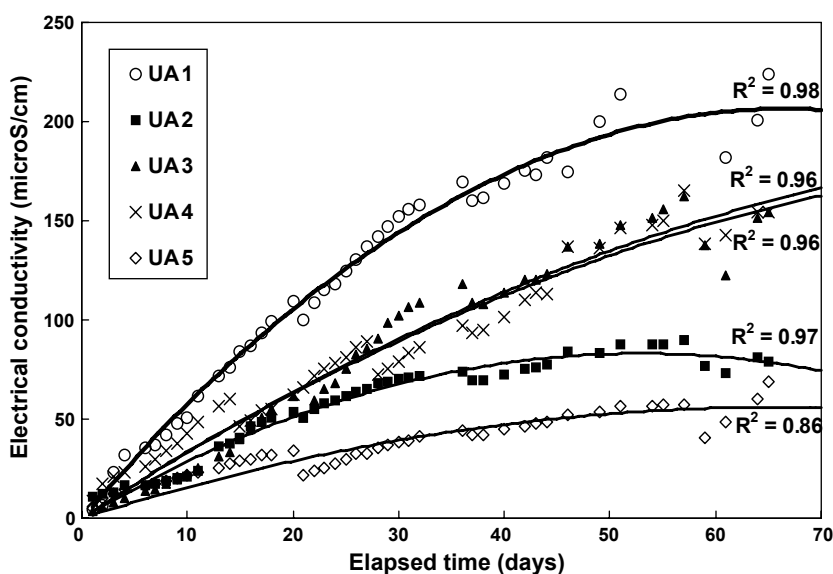

Fig. 3. Monitored electrical conductivity of the reservoirs during the diffusive equilibrium process.