

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

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Abstract

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 Fonsstad'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-term 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,

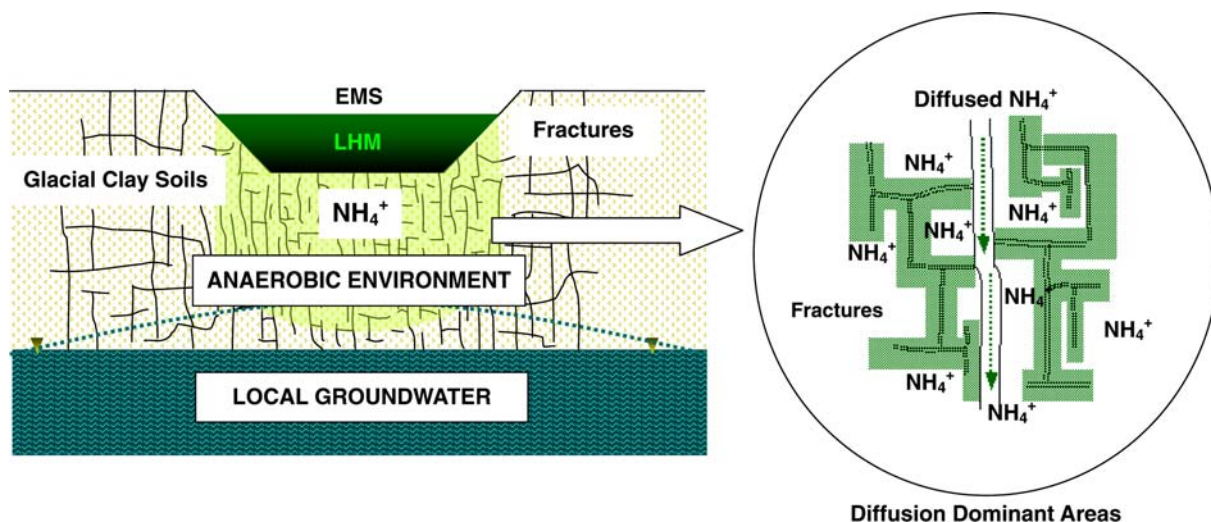


Fig. 1. Conceptual model for NH_4^+ diffusion along fractured glacial clays and/or clay tills in the Canadian Prairies. Note. EMS denotes earthen manure storage and LHM refers to liquid hog manure.

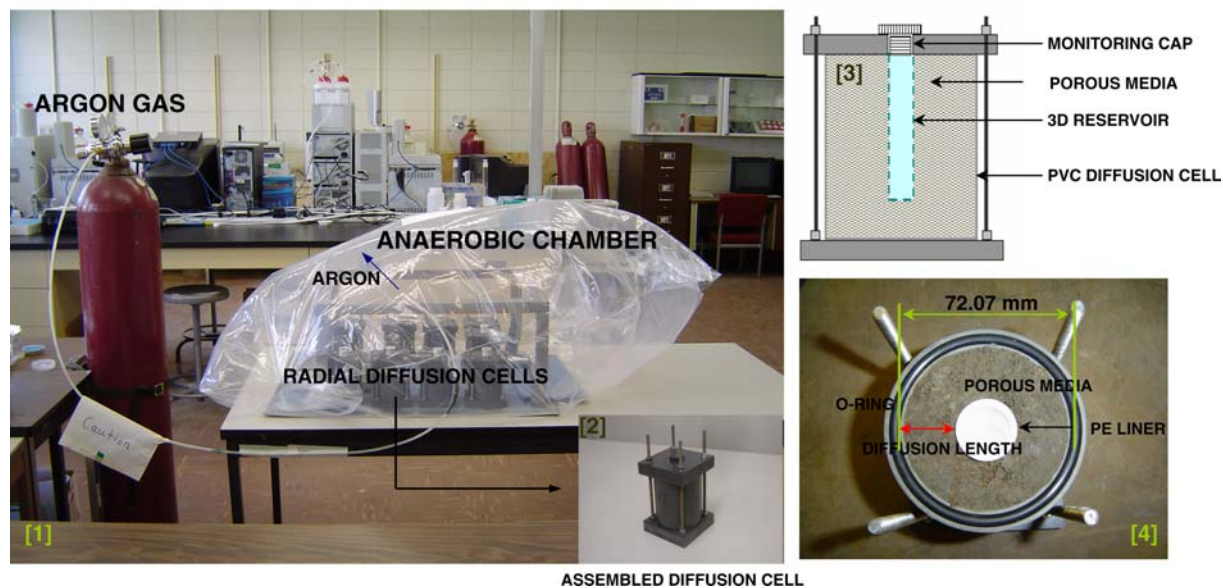


Fig. 2. Anaerobic radial diffusion cell setting and schematic of a radial diffusion cell.

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 $20 \text{ mL} \pm 0.08$, was filled with 20-mL ultrapure water (18.2 $\text{M}\Omega \text{ cm}$ and 0.7 $\mu\text{S}/\text{cm}$, 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 $20 \text{ mL} \pm 0.36$ 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 O₂ (DO), hardness, alkalinity, total dissolved solids (TDS) and total organic C (TOC).

The final step was to investigate the potential for NH₄⁺ desorption due to the infiltration of fresh water into the clay soils. To do this, 20-mL ultrapure 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 NH₄⁺ 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
<i>SPE (mg/L)</i>			
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 (NH₄OAc) 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 NH₄–N concentrations were 4–10 mg/L. The leached NO₃–N concentrations ranged from 3.4 to 8.6 mg/L. Nitrite was rarely detected because it rapidly oxidized to NO₃[–]. 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, NH₄⁺ 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 (CaCO₃), calculated by PHREEQC, was 0.2 for the liquid hog manure; consequently, calcite precipitation was expected during the experiment. Based on field alkalinity measurements CO₂ (g) in the liquid hog manure was oversaturated (SI value of 0.58) with respect to atmospheric CO₂ (SI of –3.51 for atmospheric CO₂ (g)). Degassing of CO₂ (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
<i>Cations</i>		
Ca	199	mg/L
K	1710	mg/L
Mg	6.4	mg/L
Na	611	mg/L
NH ₄	5241.5	mg/L
<i>Anions</i>		
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
<i>Carbonates</i>		
HCO ₃	14,300	mg/L
CO ₃	100	mg/L
OH	<100	mg/L
<i>Iron</i>		
Fe-dissolved	4	mg/L
<i>Organic carbon</i>		
Dissolved organic C (DOC)	4700	mg/L
Total organic C (TOC)	6510	mg/L
<i>Geochemical index</i>		
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 $\log P_{\text{CO}_2}$ 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-

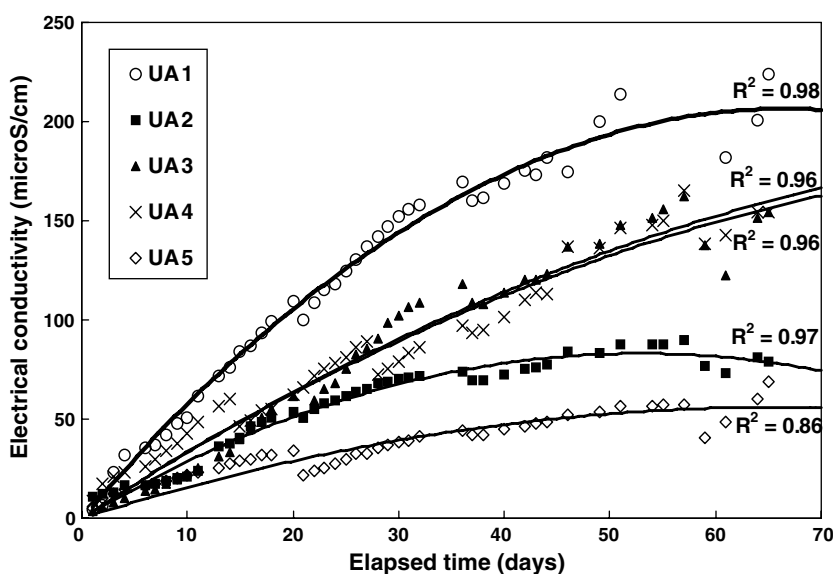


Fig. 3. Monitored electrical conductivity of the reservoirs during the diffusive equilibrium process.

Table 3
Reservoir monitoring results for major cations (unit: mg/L)

Major cations	Cell ID	Initial pore fluid	Initial liquid manure	Diffusion-day 10	Diffusion-day 60	Desorption-day 60
NH ₄ ⁺	UA Cell 1	<1.0	5242	2423	508	298
	UA Cell 2	<1.0	5242	2417	3177	59
	UA Cell 3	<1.0	5242	1767	1067	35
	UA Cell 4	<1.0	5242	–	136	18
	UA Cell 5	<1.0	5242	1093	169	30
K ⁺	UA Cell 1	10	1710	1260	856	20
	UA Cell 2	10	1710	1340	1370	72
	UA Cell 3	6	1710	1260	854	31
	UA Cell 4	6	1710	–	408	23
	UA Cell 5	4	1710	1120	726	42
Na ⁺	UA Cell 1	28	611	530	460	110
	UA Cell 2	<20	611	540	600	60
	UA Cell 3	<20	611	1520	420	90
	UA Cell 4	21	611	–	320	80
	UA Cell 5	<20	611	510	460	90
Ca ²⁺	UA Cell 1	16	199	190	250	110
	UA Cell 2	<10	199	150	80	80
	UA Cell 3	13	199	180	180	120
	UA Cell 4	13	199	–	360	110
	UA Cell 5	<10	199	250	260	120
Mg ²⁺	UA Cell 1	6	6.4	15	89	45
	UA Cell 2	<2	6.4	8	17	36
	UA Cell 3	3	6.4	14	68	34
	UA Cell 4	3	6.4	–	92	29
	UA Cell 5	<2	6.4	28	106	25

stantial decrease of NH₄⁺ in the reservoirs occurred under the anaerobic conditions (Table 4). After a 10-day period, it was observed that approximately 53% of the initial NH₄⁺ amount (mole) in the reservoir had diffused to the soils. Ammonium diffusion, initiated by a single injection of liquid hog manure, was almost complete within 60 days (with an average 91% of the initial NH₄⁺ diffused into the soil samples).

Table 5 shows the comparison between measured concentrations on diffusion-day 60 and the diluted concentrations for cations and anions. The diluted concentrations, which represent equilibrium concentrations after the diffusion and desorption processes, were calculated based on the mass balance between the diffused and remaining ions in the reservoirs and the estimated pore fluid volume (130–170 mL). In comparison with measured and calculated equilibrium concentrations, NH₄⁺ did not reach theoretical equilibrium. The measured NH₄⁺ concentrations in Cell UA1, 4 and 5 were about 55–84% lower than the expected equilibrium concentrations (see Table 5 and Fig. 5a). The significant concentration gradient for NH₄⁺ between

background pore fluid (less than 1 mg/L, Table 3) and liquid manure (5241 mg/L) forces a dramatic decrease of effluent concentration in the reservoir. The measured concentrations of NH₄⁺ were considerably lower than the equilibrium concentrations. This reflects significant retardation of NH₄⁺ through the tortuous paths in the fine materials. (It is noteworthy that Cell UA2 data were unusual because some rock materials in the cell blocked manure transport; Cell UA2 data were thus neglected for the most part of this portion of the analysis).

During the NH₄⁺ diffusion period, Cl[–] did not equilibrate. As shown in Table 5, the measured Cl[–] concentrations were higher than the calculated equilibrium concentrations (i.e., three and four times higher). It is inferred that Cl[–] would not diffuse into the porous media. Chloride played a key role in achieving charge balance during the NH₄⁺ diffusion. Fig. 5(b) and (c) show the measured and diluted concentrations of K⁺ and Cl[–]. Chloride preferentially exists as an ion pair with K⁺ in the effluent. In addition, inverse diffusion of the excess Ca and Mg caused these elements to pair with Cl[–] as CaCl₂⁰ and MgCl₂⁰ in the reservoir. As shown in

Table 4
Reservoir monitoring results for major anions (unit: mg/L)

Major anions	Cell ID	Initial pore fluid	Initial liquid manure	Diffusion-day 10	Diffusion-day 60	Desorption-day 60
Cl ⁻	UA Cell 1	20	1380	1110	706	135
	UA Cell 2	<20	1380	1150	1040	69
	UA Cell 3	<20	1380	1120	684	101
	UA Cell 4	<20	1380	–	468	131
	UA Cell 5	<20	1380	1040	751	132
PO ₄ ³⁻	UA Cell 1	<1	1270	313	294	8
	UA Cell 2	<1	1270	282	199	47
	UA Cell 3	<1	1270	297	199	11
	UA Cell 4	<1	1270	–	41	5
	UA Cell 5	<1	1270	144	80	13
HCO ₃ ⁻	UA Cell 1	200	14,300	6670	3890	751
	UA Cell 2	200	14,300	8920	11,500	704
	UA Cell 3	200	14,300	6570	5100	801
	UA Cell 4	200	14,300	–	2730	579
	UA Cell 5	100	14,300	5810	3260	637
SO ₄ ²⁻	UA Cell 1	24	9	3	5	12
	UA Cell 2	6	9	3	2	4
	UA Cell 3	16	9	3	4	1
	UA Cell 4	16	9	–	3	2
	UA Cell 5	6	9	3	5	6
NO ₂ ⁻ /NO ₃ ⁻	UA Cell 1	<0.04	1	0.4	D.L.	0.3
	UA Cell 2	<0.04	1	0.4	D.L.	<2
	UA Cell 3	<0.04	1	0.4	D.L.	<0.2
	UA Cell 4	<0.04	1	–	D.L.	<0.2
	UA Cell 5	0.05	1	0.4	D.L.	<0.2

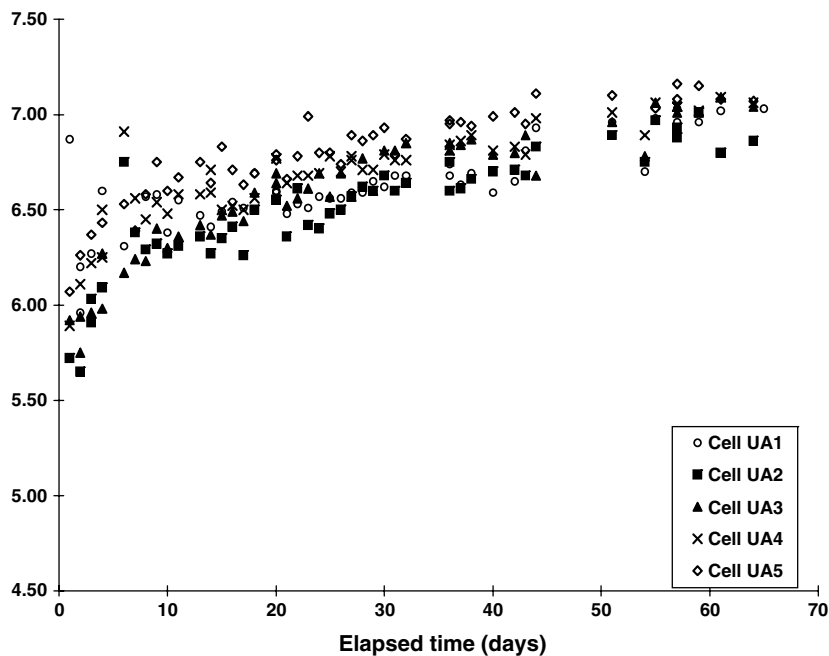


Fig. 4. Monitored reservoir pH during the diffusive equilibrium process.

Table 5
Measured concentrations vs. diluted concentrations (equilibrium) (unit: mg/L)

Analyte	Cell ID	Diffusion-day 60		Final pore fluid after desorption	
		Measured conc.	Diluted conc.	Measured conc.	Diluted conc.
NH ₄ ⁺	Cell UA1	508	1117	29	1050
	Cell UA2	3177	1106	59	704
	Cell UA3	1067	930	35	815
	Cell UA4	136	559	18	545
	Cell UA5	169	1079	30	1058
K ⁺	Cell UA1	856	306	20	191
	Cell UA2	1370	291	72	117
	Cell UA3	854	237	31	145
	Cell UA4	408	187	23	148
	Cell UA5	726	269	42	190
Na ⁺	Cell UA1	460	119	110	57
	Cell UA2	600	109	60	33
	Cell UA3	420	extrac.	90	extrac.
	Cell UA4	320	84	80	53
	Cell UA5	460	100	90	50
Ca ²⁺	Cell UA1	250	42	110	8
	Cell UA2	80	42	80	32
	Cell UA3	180	35	120	16
	Cell UA4	360	33	110	extrac.
	Cell UA5	260	26	120	extrac.
Mg ²⁺	Cell UA1	89	5	45	extrac.
	Cell UA2	17	2	36	0.2
	Cell UA3	68	3	34	extrac.
	Cell UA4	92	3	29	extrac.
	Cell UA5	106	0.1	25	extrac.
Cl ⁻	Cell UA1	706	244	135	149
	Cell UA2	1040	235	69	103
	Cell UA3	684	194	101	120
	Cell UA4	468	165	131	120
	Cell UA5	751	217	132	135
SO ₄ ²⁻	Cell UA1	5	23	12	22
	Cell UA2	2	7	4	7
	Cell UA3	4	16	1	15
	Cell UA4	3	15	2	15
	Cell UA5	5	7	6	6

Note. extrac. refers to the solutes extracted from the soils to the reservoir during the diffusion period.

Fig. 5(c), the charge balance error for Cl⁻ vs. K–Ca²⁺–Mg²⁺ pairs ranged from 4% to 9% in the effluent solution. During the desorption process, Cl⁻ concentrations were closer to equilibrium.

Potassium and Na⁺ diffusion was impacted by cation competition and a lower concentration gradient when compared with NH₄⁺. The concentrations of Na⁺ increased in the reservoir during the 60-day desorption period which indicates that exchangeable Na⁺ diffused from the porous media to the reservoir.

Exchangeable Ca and Mg greatly increased in the pore fluids during the NH₄⁺ diffusion period. Cal-

cium concentrations increased up to 26–81% of initial concentrations in Cell UA1, 4 and 5. The inverse Ca diffusion from the porous media to the reservoir is attributable to exchange reactions. Calcite precipitation in Cell UA2 and 3 caused the decrease in Ca concentrations in the reservoirs. Significant Mg inverse diffusion occurred due to exchange reactions during the 60-day diffusion periods. The Ca and Mg extracted by exchange reactions led to a substantial increase in the reservoir's hardness (Fig. 6). This is because Ca (0.412 nm) and Mg (0.428 nm) ions have a larger hydrated radius than does NH₄⁺ (0.331 nm) or K⁺ (0.331 nm) (Volkov et al., 1997). The larger

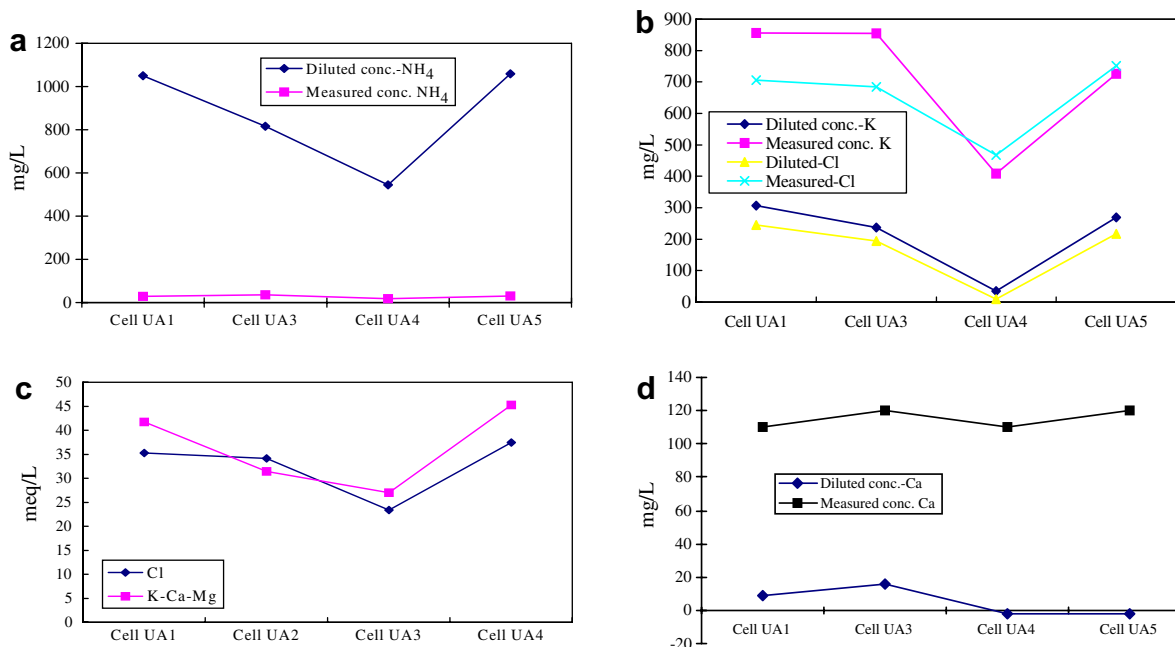


Fig. 5. (a) Measured vs. diluted NH_4^+ concentration. (b) Measured vs. diluted K^+ and Cl^- concentration. (c) Milli-equivalent of Cl^- vs. K^+ , Ca^{2+} and Mg^{2+} . (d) Measured vs. diluted Ca^{2+} concentration.

ions cannot percolate through the collapsed interlayer of minerals where adsorbed NH_4 and K are located and are forced back into solution (Lumbanraja and Evangelou, 1994). However, in a binary system of K^+ and NH_4^+ , NH_4^+ has the ability to expand the vermiculite interlayer by chemisorption processes and the NH_4^+ can exchange with the K (Lumbanraja and Evangelou, 1994).

According to the 2-year column studies on smectite-rich clay-swine effluent, conducted by Fonstad et al. (2001), Na , Mg and Ca on the exchange sites were displaced by K and NH_4 . This caused an increase in pore fluid hardness for the long-term soil–effluent interaction. Von Breyman and Suess (1988) discovered that Mg was displaced by NH_4^+ exchange in marine sediment within an anoxic environment. The extracted Mg was approximately 40% of the total adsorbed NH_4^+ . Clay mineralogy and CEC were similar to the soils employed in this experiment.

Accordingly, NH_4^+ diffusion caused by chemical potential resulted in a redistribution of major cations and anions in the pore fluid. In particular, Cl^- , which is well known as a conservative ion, is more likely to be attenuated in the clay pore space or dispersed to the reservoir to charge balance the

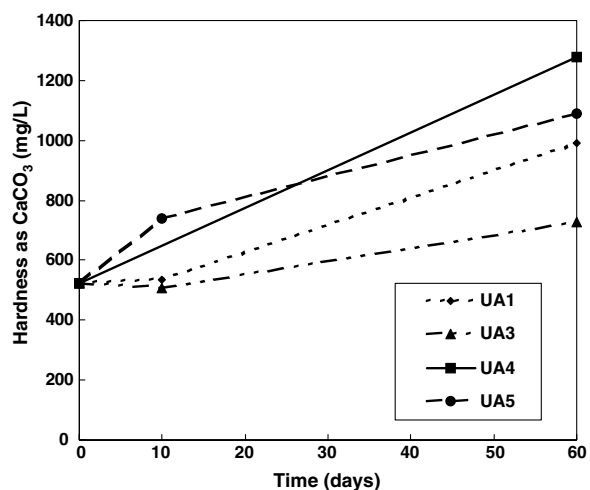


Fig. 6. Elevated hardness in all the reservoirs during the diffusion process: Average increase in hardness as CaCO_3 of 137%.

solutions to account for the adsorption or desorption of exchangeable K , Ca and Mg .

Maintenance of the anaerobic environment in and around the diffusion cells is a key requirement for simulating the reducing conditions of the EMS. For the entire experimental period, including

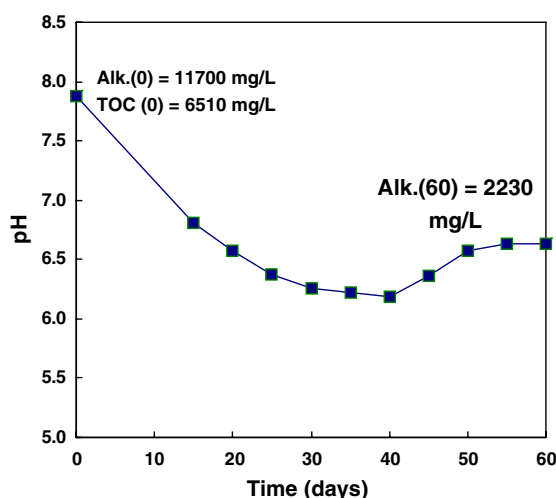
the desorption process (185 days), the presence of O_2 was strictly limited by adding Ar gas into the chamber. As a result, NH_4^+ , the reduced form of N compounds, was not oxidized to NO_3^- or NO_2^- in any of the diffusion cells (see Table 4). This fact is key evidence of the importance of maintaining the anaerobic environment in the diffusion cells. In addition to N compounds, it is possible for SO_4^{2-} to be reduced in the cells. Sulfate levels decreased from 46% to 80% of the initial content in all cells (Cell UA1–5). The authors also smelled sulfide during the sampling and measuring of the raw liquid hog manure that came in contact with the glacial clay soils.

4.1.2.1. pH changes during diffusion. As shown in Fig. 7, the measured reservoir pH rapidly dropped from 7.9 to 6.2 within the first 40 days, and then increased to 6.6 over the next 20 days. It is understood that the increase in H^+ ions in the reservoir is due to the diffusion of H^+ from the pore fluid. The pH difference between pore fluid (pH 7) and effluent (pH 7.9) resulted in H^+ diffusion (Reaction 1). The predicted pH value for the effluent was between pH 7 and pH 7.8 at equilibrium; however, the final effluent pH was equilibrated at 6.2. It is possible that a cation-exchange reaction between NH_4^+ and H^+ (Reaction 2) decreases the pH in the reservoir that contains effluent. When NH_4^+ diffuses into the pore fluids, NH_4^+ concentrations increase in

that pore fluid. The NH_4^+ with a high mole fraction is better able to occupy the exchange sites on clay minerals and thus exchange H^+ . Consequently, the exchangeable H^+ diffusion may be directly associated with the pH decrease in the reservoirs.

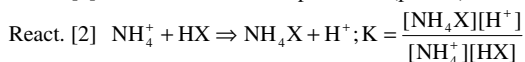
Reaction 3 in Fig. 7 shows that NH_4^+ adsorption by cation exchange causes chemical regeneration when major cations exist in pore fluid (Semmens et al., 1997). As NH_4^+ occupied the exchange sites (X^-), the major cations (M) on the clays were extracted from the sites. The cations released from the exchange sites then formed a complex with HCO_3^- ($MHCO_3$) in the pore fluid. According to speciation calculations by PHREEQC, Ca, Mg and Na preferably form complexes with HCO_3^- . Eventually, the NH_4^+ adsorption caused by cation exchange results in a decrease in HCO_3^- in the reservoir. In reality, as shown Fig. 7, the measured alkalinity for all the cells decreased significantly, to 64–81% of the initial alkalinity.

The elevated Ca concentration, generated by the exchanged Ca, and the already elevated HCO_3^- concentration reacted quickly enough to maintain equilibrium in the reservoir solution (Fig. 7, Reaction 4). The SI for calcite by PHREEQC speciation calculation ranged from 0.05 to 0.2; therefore, the calcite precipitation generated by the exchangeable Ca^{2+} diffusion caused a H^+ concentration increase in the effluent reservoir.

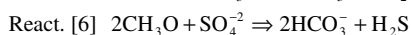
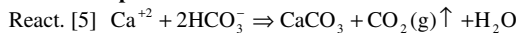


Decrease in pH in the reservoir:

React. [1] H^+ diffusion between pore fluid (pH 7.0) and manure (pH 7.9).



Increase in pH in the reservoir:



Cf. Eh-pH diagram for S-O₂-H₂O system (Langmuir, 1997).

NOTE

X^- : exchange site with monovalent

M: major cations (Ca, Mg, K, Na)

Alk. (0) and (60): measured alkalinity on day 0 and day 60

TOC (0) and (60): measured TOC on day 0 and day 60.

Fig. 7. Change in pH during the diffusion periods and related geochemical reactions in the diffusion cells.

In contrast, after 40 days, an increase in pH was observed in all of the reservoirs (Fig. 7). Exsolution of CO_2 (g) occurred due to reactions between the exchanged Ca and HCO_3^- in the liquid hog manure (Reaction 5). The elevated Ca and alkalinity concentration and the developing CO_2 (g) caused the increase in pH levels in the reservoir after 40 days. The measured reservoir pH increased from 6.2 to 6.6 after 40 days. The substantial decrease in TOC in the reservoirs supported the oxidation of organic compounds (e^- donor) as well as SO_4^{2-} (e^- acceptor) reduction during the interaction periods (Reaction 6). The measured TOC decreased in the reservoirs, to 63% from 86% of the initially determined TOC. Sulfate reduction by the oxidation of organic C was also indicated by the increase in pH after 40 days. Based on the measured pH levels for all reservoirs, pH ranged from 6.6 to 7.9 after 40 days. According to the Eh–pH diagram for the S– O_2 – H_2O system (Langmuir, 1997), H_2S and HS^- will be the dominant S forms in the anaerobic pore fluid at the measured pH levels. Furthermore, clay minerals in the cells will buffer the acidity that is generated by NH_4^+ diffusion. It is known that clays have a mineral-controlled buffer capacity that is remarkably resistant to acidity, particularly in comparison to associated carbonates (Langmuir, 1997).

Consequently, NH_4^+ diffusion resulted in a pH decrease in the pore fluid of all the diffusion cells

in addition to a substantial increase in hardness. The initial pore fluid pH 7.0 decreased to between 6.2 and 6.6 because of H^+ diffusion resulting from the initial pH difference, the cation exchange of NH_4^+ for H^+ and Ca^{2+} , and calcite precipitation. Therefore, it is possible that changes in pH and hardness can be simple indicators of the need to investigate NH_4^+ plumes in EMS areas.

4.1.3. Diffusion-controlled adsorption

Using the anaerobic RDC method, linear NH_4^+ and K^+ adsorption isotherms ($R^2 = 99\%$) were developed in relation to the equilibrium activity of the reservoir (Fig. 8). The activities were determined by PHREEQC speciation calculation based on the Davies equation for activity coefficients. High cation-exchange capacity and diffusion-controlled adsorption primarily affected the linearity of NH_4^+ and K^+ adsorption isotherms. It was assumed that the smectite-rich soil samples with high CEC values (21.2–43.3 meq/100 g) had sufficient exchange sites to adsorb 80–90% of the NH_4^+ injected into the cells. Von Breyman and Suess (1988) also showed that a linear relationship exists between adsorbed NH_4^+ and dissolved NH_4^+ concentration. The adsorbents were smectite-rich clay soils with high CEC (i.e., 84.2 meq/100 g). The dissolved NH_4^+ concentrations ranged from 5.3 to 36 mM. Additionally, Lumbanraja and Evangelou (1994) obtained a linear NH_4^+

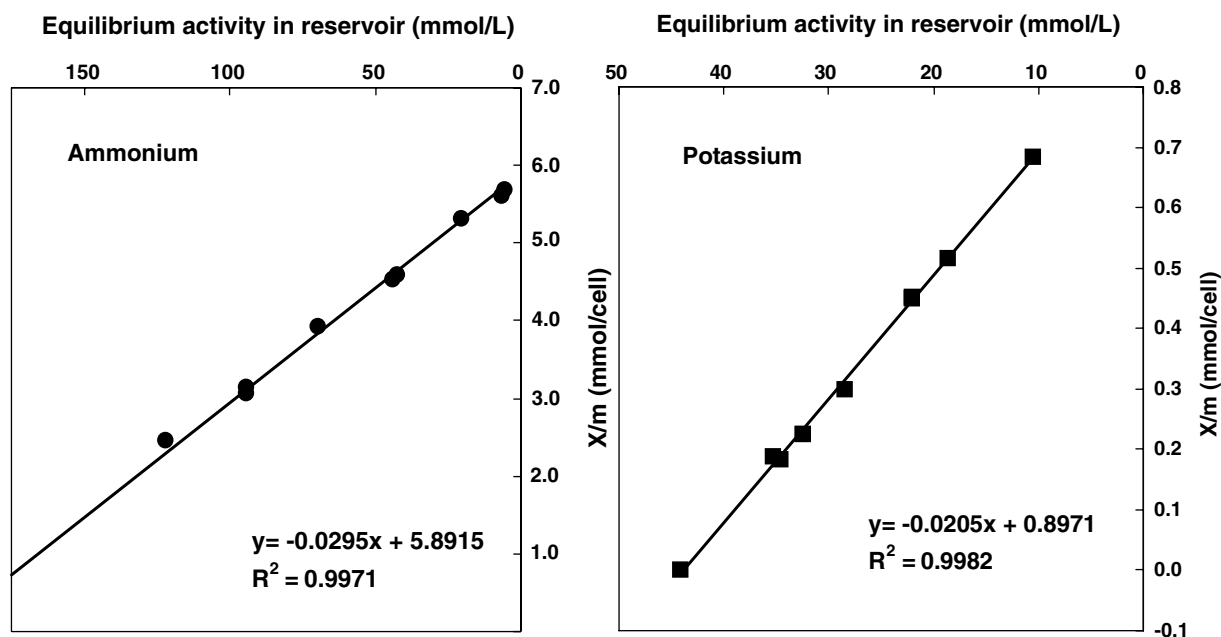


Fig. 8. Linear NH_4^+ and K^+ adsorption isotherms under anaerobic conditions using the RDC method.

adsorption in a low dissolved NH_4^+ level (20 mM) as well; in their experiment, NH_4^+ competed with K^+ for the exchange sites on vermiculite and smectite-type clay.

In addition to high CEC, NH_4^+ adsorption was a function of diffusion time, a result also known as the diffusion-controlled adsorption process. The mechanism of diffusion-controlled adsorption may be divided into five steps (Kithome et al., 1998): (1) diffusion of NH_4^+ through the pore fluid up to the smectite particle; (2) diffusion of NH_4^+ through the smectite particles; (3) chemical exchange between NH_4^+ and exchangeable cations on exchange sites in the interior of the smectite minerals; (4) diffusion of the displaced cations out of the interior of the mineral; and (5) diffusion of the displaced cation through the solution away from the smectite minerals. The diffusion-only process in the cells reflected both the heterogeneity and tortuosity of the intact core samples. Therefore, even when the source NH_4^+ was highly concentrated (5242 mg/L), the NH_4^+ dissolved in pore fluid was equilibrated at low concentrations.

The clay-rich soil samples selectively adsorbed and/or desorbed major cations in pore fluid. The competition for the limited adsorption sites depended on constituent mole fraction, ionic charge and ionic size (hydrated radius). In particular, NH_4^+ predominated at the adsorption sites because NH_4^+ with a high mole fraction in the source – about 45% – had more chances to occupy the sites compared to other co-existing cations. Ammonium was also preferred on adsorption site due to the presence of K^+ in solution. James and Harward (1964) and Mortland (1968) showed that while NH_4^+ and K^+ have the same hydrated radius, NH_4^+ adsorption was enhanced in the presence of K^+ . The adsorbed NH_4^+ tends to expand soil's interlayer allowing it to internally diffuse onto a surface and displace trapped interlayer K^+ and structural K^+ (Lumbanraja and Evangelou, 1994). Lumbanraja and Evangelou (1994) observed that K^+ adsorption, when in competition with NH_4^+ , was suppressed, whereas NH_4^+ adsorption was enhanced in binary ($\text{NH}_4^+\text{-K}^+$) and ternary ($\text{NH}_4^+\text{-K}^+\text{-Ca}^{2+}$) systems.

4.2. Geochemical mix models for the anaerobic RDC method

The NH_4^+ adsorption isotherm simulated by SIMPLE MIX MODEL was in agreement with

the RDC experiment result (Fig. 9). The adsorption simulation had lower and upper limits that were dependent on the estimated effective pore fluid volume. The input pore fluid volume ranged from 130 to 170 mL. Notably, the lower limit simulation was in agreement with the experimental results. Fig. 9 shows the total adsorbed NH_4^+ , both from the experiment (5.7 mmol/cell) and from the lower limit simulation (6.2 mmol/cell).

Estimated K_d ($\{\text{mg/kg dry soil}\}/\{\text{mg/solution}\}$) values for NH_4^+ ranged from 0.3 to 0.4 L/kg under anaerobic conditions and diffusion-only process. It was assumed that smectite-rich clay soil samples adsorbed all the diffused NH_4^+ because of the relatively large amount of clay with high CEC (21.2–43.3 meq/100 g, dried 531–634 g). However, K_d from radial diffusion cells accounts for a diffusive transport characterized by heterogeneity and tortuosity of in situ soils under competition and reducing conditions. No literature that addresses the distribution coefficients, K_d , for NH_4^+ when assessed by the anaerobic RDC method was available. However, in recent studies, Fonstad (2004) obtained 0.05–0.4 L/kg for K_d ; Thornton et al. (2001) reported 0.06–0.3 L/kg values; Erskine (2000) and Ceazan et al. (1989) showed a 0.5 L/kg value and 0.34–0.87 L/kg values for K_d , respectively. The K_d values of these

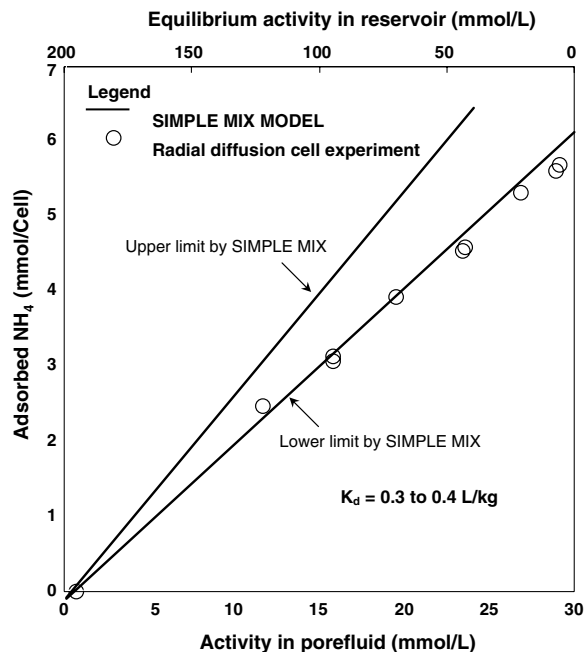


Fig. 9. Ammonium adsorption determined by the radial diffusion cell method and SIMPLE MIX MODEL.

previous studies vary because of the disparate types of adsorption experiments, the CEC, clay mineralogy, initial NH_4^+ concentration, and running time.

Fig. 10 demonstrates the simulation of the pore fluid chemistry during linear NH_4^+ adsorption. The anaerobic condition was maintained in the simulated pore fluid. Nitrate and NO_2^- were not produced in this model. Potassium in competition with NH_4^+ linearly diffused into the pore fluid. Diffusion of Ca and Mg into the soil samples was not significant in the simulation. Sulfate reduction was also simulated by changes in pore fluid chemistry.

According to the MIX MODEL results, the predicted liquid manure volumes for NH_4^+ saturation were 1.0–1.2 L/kg for sandy-lean clay samples and 1.4–1.7 L/kg for sandy-fat clay samples (706–1010 mL/cell, dilution effect was considered). Fig. 11 represents the number of mixing simulations that correspond to the required number of source injections of the initial injected NH_4^+ concentration, at 5242 mg/L. Thus, the predicted number of injections ranged from 35 to 40 for sandy-lean clays (Cell UA1 and 2) and from 43 to 51 for sandy-fat clay samples. About 20 mL of liquid manure per injec-

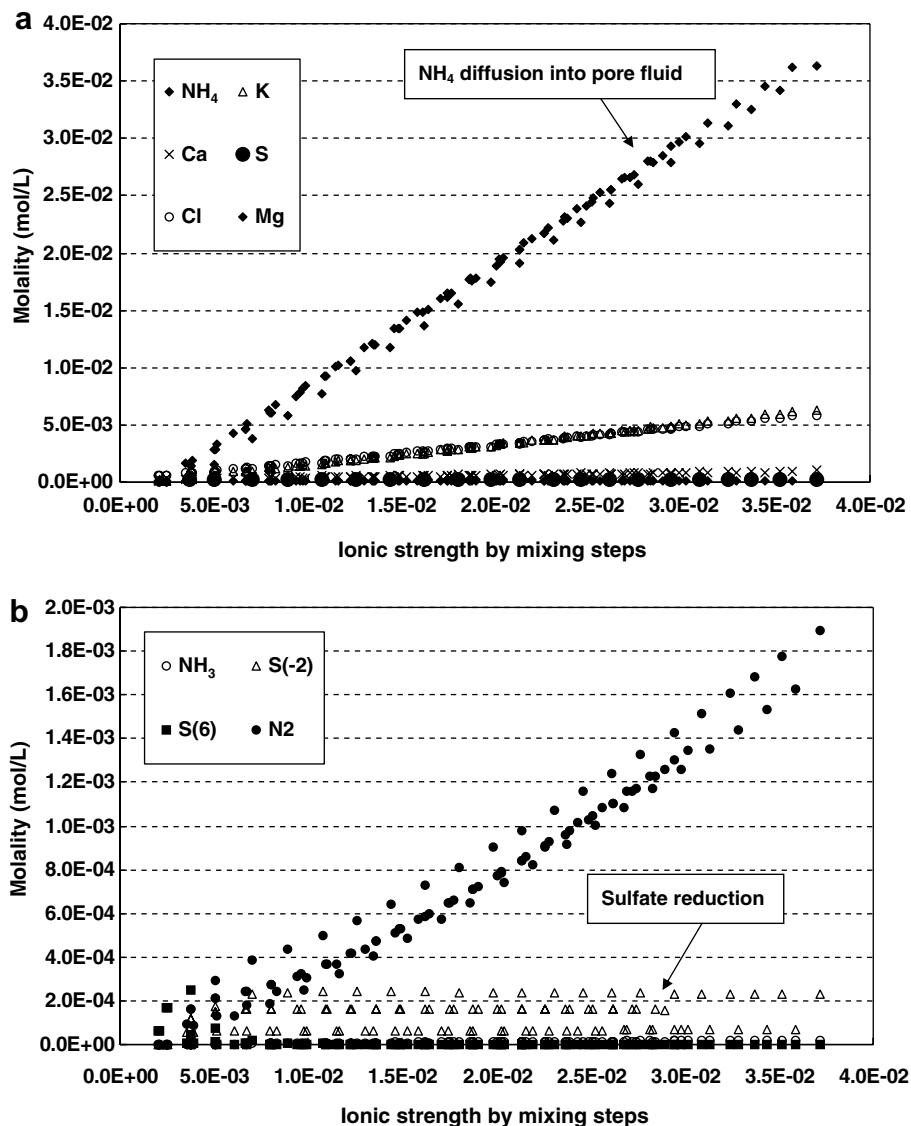


Fig. 10. Change in pore fluid chemistry simulated by SIMPLE MIX MODEL: (a) NH_4^+ and K^+ diffusion. (b) Reducing conditions in pore fluid.

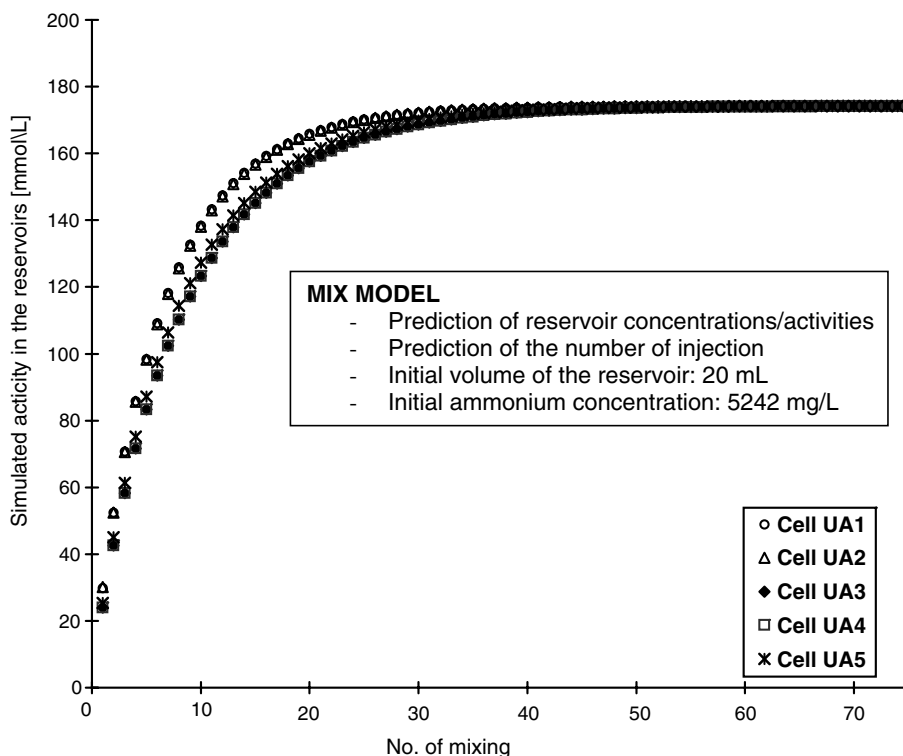


Fig. 11. Result of the MIX MODEL simulation.

tion was assumed. The NH_4^+ required to saturate exchange sites using an NH_4^+ solution concentration of 5242 mg/L ranged from 0.3 to 0.5 mol/kg (1.0–1.7 L/kg manure effluent), depending on the soil types.

5. Summary and conclusions

Maintenance of an anaerobic environment was the most critical issue in this experiment. For the entire experiment period (185 days), the O_2 level was strictly limited by means of an Ar gas environment. The preservation of reducing conditions during NH_4^+ diffusion was confirmed by NO_3^- and NO_2^- concentrations lower than the detection limit.

The geochemical response of reservoir pore fluid with diffusion time was investigated by monitoring reservoir chemistry with time. Ammonium diffusion driven by a chemical gradient resulted in a redistribution of major cations and anions in the pore fluid. Chloride played a key role in achieving charge balance during the NH_4^+ diffusion. Chloride did not behave as a conservative transport species. It was hypothesized that Cl^- was attenuated during diffu-

sion due to high concentrations of adsorbed NH_4^+ ion in the soils adjacent to the reservoir. Ammonium diffusion resulted in a pH decrease in the pore fluid of all the diffusion cells and more importantly a substantial increase in hardness (Ca and Mg) was observed. This increase in Ca and to a lesser extent Mg is an important indicator of an NH_4^+ plume (Fonstad, 2004).

High cation-exchange capacity and diffusion-controlled adsorption primarily affected the linearity of NH_4^+ and K^+ adsorption isotherms. The distribution coefficient, K_d , determined by a radial diffusion cell method ranged from 0.3 to 0.4 L/kg under competition with co-existing cations and diffusion-only mechanism.

The SIMPLE MIX MODEL adequately simulated the linear NH_4^+ adsorption at low dissolved NH_4^+ concentration (<30 mM) and changed pore fluid chemistry. Ammonium saturation capacity predicted by the MIX model ranged from 1.0 to 1.2 L/kg for sandy-lean clay samples and 1.4–1.7 L/kg for sandy-fat clay samples.

In conclusion, the anaerobic RDC method effectively satisfied the key requirements in characterizing the movement of NH_4^+ through glacial clay

soils; anaerobic conditions, diffusion-controlled adsorption, exchange reactions and competition.

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