APPENDIX A - LITERATURE REVIEW

Ammonia Chemistry and Methods of Analysis

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Introduction

The following report presents general NH_3/NH_4^+ chemistry in environmental systems and investigates methods for analysis of NH_3/NH_4^+ in aqueous and gaseous phases as well as methods for determination of partitioning within different phases. This document also provides recommendations for the design of future experiments to investigate the partitioning of NH_3/NH_4^+ in laboratory systems. This will allow for a greater understanding of the ammonia gas injection technologies under consideration for remediation of uranium in the vadose zone at the Hanford site.

Objectives

As part of Task 3, Subtask 3.1, the objective of this literature review is to create a document to guide the design of future experiments. These experiments will focus on the determination of the physical mechanisms associated with the fate of ammonia in the Hanford subsurface through simplified experiments investigating the partitioning in bicarbonate-bearing suspensions, synthetic groundwater and Hanford sediments under variable pH and temperature conditions.

Background

Chemical Characteristics of Ammonia

Ammonia is a colorless gas, which is widely used in fertilizers, plastics, and explosives. NH_3 is a molecule with a triangular pyramid geometry and a strong dipole moment. It is capable of strong interactions in water including hydrogen bonding with water to create other species (Eqn. 1) and is very soluble in water (900 g/L at 0°C) (Battino, Seybold et al. 2011). Additional physical and chemical properties of ammonia are presented in Table 1. In aqueous solution it acts as a weak base, acquiring hydrogen ions from H_2O to yield in the production of ammonium and hydroxide ions.

$$H_2O + NH_3 \leftrightarrow NH_4^+ + OH^- \quad \text{p}K_b\text{=4.74} \qquad \text{Eqn. 1}$$
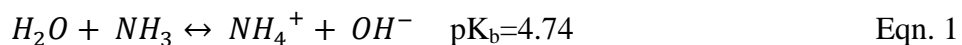
Production of hydroxide ions after ammonia gas dissolves in water contributes to its weakly alkaline properties in aqueous solutions. However, not all of the dissolved ammonia reacts with water forming ammonium ions. A substantial fraction remains in the molecular form in solution. The dissociation constant, K_b, is given by (Clegg and Brimblecombe 1989):

$$K_b = \frac{[NH_3](aq)[H^+]}{[NH_4^+](aq)} = 1.774 \times 10^{-5} \text{ at } 25^\circ C \qquad \text{Eqn. 2}$$

Conversely, the ammonium ion is a weak acid in aqueous solution due to its dissociation reaction with the formation of hydrogen ion and ammonia.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \quad pK_a=9.26 \qquad \text{Eqn.3}$$
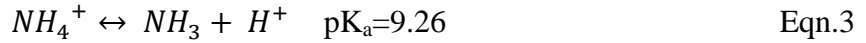
PH, electrolyte concentration and temperature are factors that affect the speciation and solubility in solution. The dissociation constant increases slightly with increasing temperature (Mackay and Shiu 1981, Weast, Melvin et al. 1988) and high electrolyte concentrations may lead to a decrease in solubility (Mackay, Shiu et al. 1979). Ammonia gas is present in equilibrium with NH_4^+ and with NH_3 in solution. Studies of ammonia volatilization have been based on liquid-gas equilibria (Eqn. 4) and ammonia gas solubility reaction (Eq. 1).

$$NH_3(g) \leftrightarrow NH_3(aq) \qquad \text{Eqn. 4}$$

The gas-liquid equilibrium is accounted for with Henry's law constant, K_H (Eqn. 5). Henry's law is only considered applicable to pure water and dilute systems (Wilhelm, Battino et al. 1977, Dean 1985, Betterton 1992, Ramachandran, Allen et al. 1996). For systems that are not pure water and contain many other chemical species, the constant is often referred to as an air-water distribution ratio (Ramachandran, Allen et al. 1996). However, for consistency, this report will refer to constants as Henry's law constants throughout the manuscript. In addition, a dimensionless Henry's law constant may be approximated for dilute solutions based on Eqn. 6 (Ramachandran, Allen et al. 1996), where c_G=molarity in the gas phase, c_L=molarity in the liquid phase, c_S=molarity of the solvent and H_i=dimensionless Henry's constant. The temperature relationship is known and can be expressed generically as an exponential function of the temperature of the solution using the Van't Hoff's relationship which was developed into an empirical equation by Arrhenius (Eqn. 7), where H=molar enthalpy of solvation of the solute and S=molar entropy of solvation of the solute (Helminen, Helenius et al. 2000, Lee, Mukherjee et al. 2013). Further, Eqn. 8 can be used to approximate the Henry's law constant for $NH_3(g)$ specifically at variable temperature (K) (Renard, Calidonna et al. 2004, Zhong, Szecsody et al. 2015). The ionization equilibrium is determined by the pH of the solution and the value of the equilibrium constant, K_A (Eqn. 9).

Table 1: Chemical properties of ammonia

Property		Value	References
Molecular weight		17.03 g/mol	(Le Blank, Madhavan et al. 1987)
Color		Colorless	
Physical state		Gas at room temperature	
Melting point		-77.7°C	
Boiling point		-33.35°C	
Specific gravity, 25°C		0.747 g/L	(Lide 1998)
pK_a, 25°C		9.25	
Density	Gas	0.7710 g/L	(Weast, Melvin et al. 1988)
	Liquid, -33°C, 1 atm	0.6818 g/L	(Windholz, Budavari et al. 1983)
	Aqueous solution, 28%, 20°C	0.89801 g/L	
	Vapor	0.5967 g/L	
Solubility in H_2O	25°C	0.187 (mole fraction)	(Wilhelm, Battino et al. 1977)
	0°C	42.8% (w/w)	(Le Blank, Madhavan et al. 1987)
	15°C	47% (w/w)	(Budavari, O'Neil et al. 1996)
	20°C	33.1-34% (w/w)	(Le Blank, Madhavan et al. 1987, Budavari, O'Neil et al. 1996)
	25°C	31-34% (w/w)	(Budavari, O'Neil et al. 1996)
	30°C	28% (w/w)	
	50°C	18% (w/w)	
Vapor Pressure	Anhydrous, 20°C	8.5 atm	(Sax and Lewis 1987)
	Anhydrous, 25°C	10.2 atm	(Daubert and Danner 1989)
	Aqueous, 28%, 25°C	2.9 atm	(Daubert and Danner 1989)
Henry's constant	0°C, atm-L/mol	0.0043 – 0.005	(Edwards, Maurer et al. 1978, Hales and Drewes 1979, Dasgupta and Dong 1986, Clegg and Brimblecombe 1989, Renard, Calidonna et al. 2004)
	5°C, atm-L/mol	0.005	(Brimblecombe and Dawson 1984)
	10°C, atm-L/mol	0.0069 – 0.0086	(Edwards, Maurer et al. 1978, Hales and Drewes 1979, Dasgupta and Dong 1986, Clegg and Brimblecombe 1989, Renard, Calidonna et al. 2004)
	25°C, atm-L/mol	0.0128 – 0.1* *Most commonly reported value – 0.017	(Van Krevelen, Hoftijzer et al. 1949, Robinson and Stokes 1970, Wilhelm, Battino et al. 1977, Edwards, Maurer et al. 1978, Hales and Drewes 1979, Dean 1985, Dasgupta and Dong 1986, Clegg and Brimblecombe 1989, Betterton 1992, Benjamin 2002, Renard, Calidonna et al. 2004, Sander 2015)
pH in water	1 N	11.6	(Windholz, Budavari et al. 1983)
	0.1 N	11.1	
	0.01 N	10.6	

$$P_{NH_3} = K_H[NH_3(aq)] \qquad\qquad \text{Eqn. 5}$$

$$H_i = \frac{C_G}{C_L} = \frac{K_H}{C_S RT} \qquad\qquad \text{Eqn. 6}$$

$$H_i = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad\qquad \text{Eqn. 7}$$

$$K_H = \frac{1}{e^{\left(-9.70+\frac{4092}{T}\right)}} \qquad\qquad \text{Eqn. 8}$$

$$K_A = \left[H^+(aq)\frac{[NH_3(aq)]}{[NH_4^+(aq)]}\right] \qquad\qquad \text{Eqn. 9}$$

The concentrations of NH_3 in the gas and liquid phases depend on the Henry's law constant K_h in atm/M and the fraction of $NH_3(g)$ that is converted to $NH_3(aq)$ or $NH_4^+(aq)$. The solubility of ammonia within a liquid as a function of its concentration is expressed using both the K_H and K_A values (Eqn. 10). Based on these principles, in systems that are open to the gas phase, the solubility of NH_3 remains constant but the total NH_3/NH_4^+ in the system can change with respect to pH and concentration in the gas and aqueous phase.

$$P_{NH_3} = K_H \frac{[AN\,(aq)]}{1+\frac{[H_3O^+(aq)]}{K_A}} \qquad\qquad \text{Eqn. 10}$$

The K_h of ammonia in dilute solution is 0.016 atm/M at a temperature of 25°C (Betterton 1992) (Table 1). Based on Henry's law, the solubility can be determined from this equation if the partial pressure of the gas and the constant are known. For a complete review of the concepts of Henry's law see Mackay and Shiu (1981) and Majer *et al.* (2008) (Mackay and Shiu 1981, Majer, Sedlbauer et al. 2008). For example, at 1 atm of partial pressure, the solubility of NH_3 at 25°C is equivalent to the inverse of the Henry's law constant or 62.5 M in pure H_2O. However, in a system open to the gas phase, the total solubility (NH_3 and NH_4^+) will be changing with pH and speciation changes as shown in Figure 1 below. Total solubility of NH_3 and NH_4^+ in water decreases as pH increases. Further, when pH increases the volatility of ammonia increases. The Henry's law relationship may break down at high concentrations (in excess of mole fractions of 0.01) (Mackay and Shiu 1981). However, these systems will not be considered here as environmental concentrations and those of the following experiments should not reach this level.

The mass flux (mol/m^2sec) can be estimated from the following equation (Mackay and Shiu 1981), where k_G=gas phase mass transfer coefficient, k_L=liquid phase mass transfer coefficient, c=ambient concentration, R=universal gas constant, and T=temperature (Eqn. 10). Under

environmentally relevant conditions, k_G and k_L are approximately 0.01 m/sec and 0.00005 m/sec for oxygen and water, respectively. Increasing the solute molecular weight will decrease both values slightly. However, the ratios are expected to remain relatively constant over different conditions (Mackay, Shiu et al. 1979).

$$N = \left[\frac{c - \frac{p}{H}}{\left(\frac{1}{k_L} + \frac{RT}{Hk_G}\right)} \right]$$

Eqn. 10

However, when H is small ($< 5 \times 10^{-3}$ atm*m^3/mol), as expected for NH_3 (g), then the equation can be reduced to Eqn. 11:

$$N = \left[\frac{k_G \times (CH - P)}{RT} \right]$$

Eqn. 11

In environmental systems, NH_3 and NH_4^+ may be present in the solid phase as well (i.e. minerals, soils and sediments). The partitioning from the gas phase to the solid phase for NH_3(g) may be represented in the same manner as the Henry's law coefficients described in Eqn. 5-6 with the aqueous phase concentration replaced by the solid phase concentration. The partitioning between the solid and liquid phases may be represented by an equilibrium K_d partitioning coefficient for each of the species present as shown in Eqn. 12-13 where the bracketed species represented the solid phase (sol) and aqueous phase (aqu) concentrations. For the purpose of this review, we will not consider kinetic rates. However, kinetic reactions could also be used to describe these systems. For sorption to the solid phase, a pseudo second order kinetic model has been used previously to describe sorption of NH_4^+ to zeolites as described by Eqn. 14-16 where q_{eq}=equilibrium sorption capacity, q_t=solid phase loading at time t, V_0=initial sorption rate in mmol/g*hr, K_2=pseudo second order rate constant (g/mmol*hr) (Guo, Zeng et al. 2007). The equilibrium sorption capacity for NH_3/NH_4^+ has been estimated previously using the Langmuir ($R^2 > 89\%$) and Langmuir-Freundlich ($R^2 > 98\%$) models for zeolites (Helminen, Helenius et al. 2000, Guo, Zeng et al. 2007), silica gel and alumina (Helminen, Helenius et al. 2000) and coir (Kithome, Paul et al. 1999). Several other models have been used for NH_3 and described previously including vacancy solution and potential theory (Helminen, Helenius et al. 2000) as well as first order, Bemmelen – Freundlich, and Temkin approaches for isotherm models (Kithome, Paul et al. 1999). However, the Langmuir models are considered the most appropriate for describing cation and anion sorption to soils (Kithome, Paul et al. 1999). Using Eqn. 15, V_0 and q_{eq} can be determined experimentally by plotting t/q_t versus t.

$$K_d = \frac{[NH_3(sol)]}{[NH_3(aqu)]} \qquad \text{Eqn. 12}$$

$$K_d = \frac{[NH_4{}^+(sol)]}{[NH_4{}^+(aqu)]} \qquad \text{Eqn. 13}$$

$$\frac{dq_t}{dt} = K_2 \times \left(q_{eq} - q_t\right)^2 \qquad \text{Eqn. 14}$$

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{q_{eq}}\right) \times t + \left(\frac{1}{V_0}\right) \qquad \text{Eqn. 15}$$

$$V_0 = K_2 \times q_{eq}{}^2 \qquad \text{Eqn. 16}$$
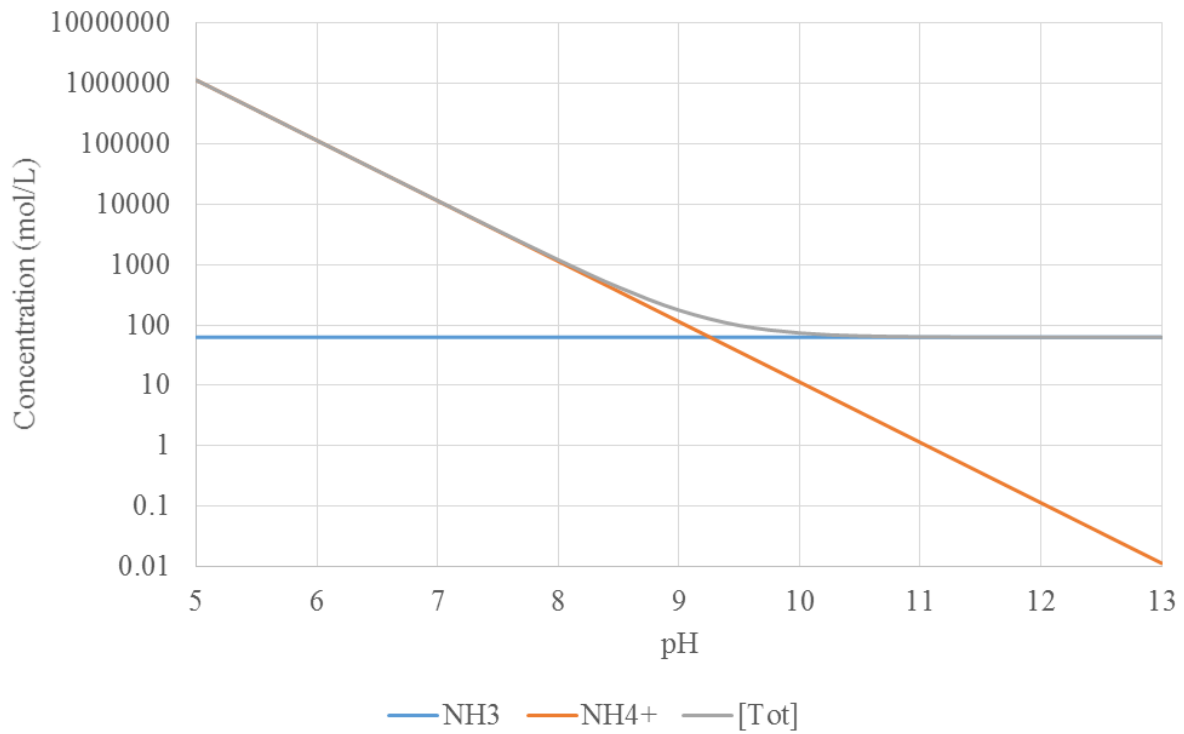
Figure 1: Ammonium (NH_3) and ammonia ($NH_4{}^+$) concentrations in pure/dilute H_2O at 25°C and gas partial pressure of 1 atm partial pressure of $NH_3(g)$ with respect to pH for a system open to the gas phase.

$$K_d = \frac{[NH_3(sol)]}{[NH_3(aqu)]}$$

$$K_d = \frac{[NH_4^+(sol)]}{[NH_4^+(aqu)]}$$

Solid
[soils, sediments, minerals]
$NH_3(ads)$ and $NH_4(ads)$

$$K_{H,sol} = \frac{[NH_3(g)]}{[NH_3(sol)]}$$

Liquid
[pore water]
$pK_a = 9.26$
$$NH_4^+ \leftrightarrow NH_3 + H^+$$

Gaseous
[air]
$NH_3(g)$

$$K_{H,aqu} = \frac{[NH_3(g)]}{[NH_3(aqu)]}$$
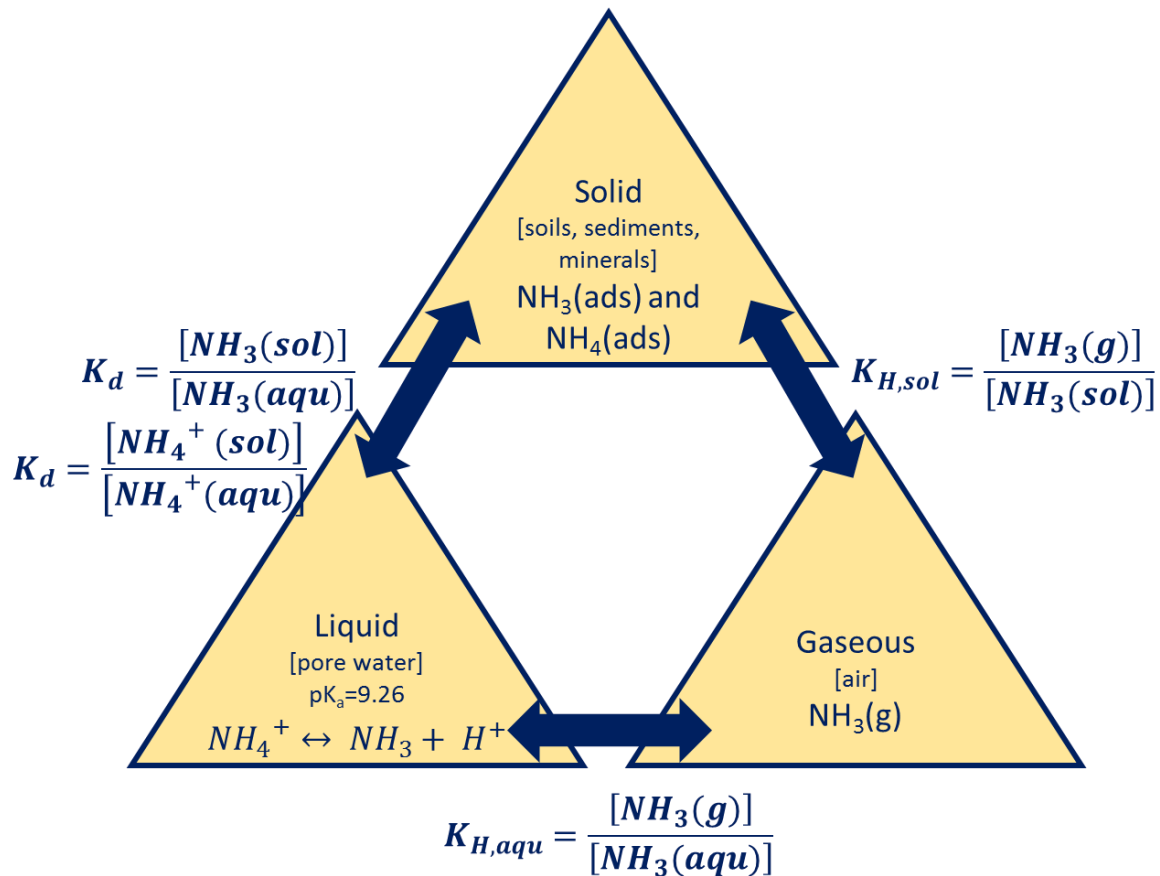
Figure 2: Representation of equilibrium partitioning of NH_3/NH_4^+ between the solid, liquid and gaseous phases with appropriate partitioning coefficients

Ammonia in the Environment

Ammonia in Soils and Sediments

Anhydrous ammonia or gaseous NH_3 in contact with moist soil dissolves and reacts with the water content to form ammonium and hydroxide ions causing the pH to increase and further reacts with the solid sediment phases. Pagans *et al.* modeled ammonia sorption to biofilter media using Henry's law and showed that the constant could change in three phase systems with respect to moisture content (Pagans, Barrena et al. 2006, Liang 2011). Zhong *et al*. confirmed that the rate of NH_3 gas diffusion is dependent on the water content with the soils (Zhong, Szecsody et al. 2015). An increase in pH also increases the rate of volatilization of ammonia by an order of magnitude for every unit above pH 6.0 (as shown in Figure 1 above) and even more so in environments of high temperature (Stevenson, Lovett et al. 1986). Therefore, ammonia volatilization is expected to be higher in alkaline soils than in acidic soils (Vlek and Craswell 1981, Singandhupe and Rajput 1989). Further, there is a strong correlation between the rates of

ammonia loss and carbonate concentrations (Jewitt 1942, Bharadwaj and Abrol 1978, Singandhupe and Rajput 1989, Hattfield and Follett 2008).

Previous work has investigated the sorption capacity of NH_3 on many different minerals and materials to better understand its sorption and reactivity with soils as well as for concentration and/or removal for industrial processes. Guo *et al.* estimated the exchange capacity of original and sodium zeolite at 1.03 and 1.14 mmol/g, respectively, in the presence of RO permeate water (Guo, Zeng et al. 2007). However, K^+ has a greater selectivity than NH_4^+ and, therefore, limits its use as an adsorbent material for removal of NH_4^+ environmental systems high in K^+ (Ames 1960, Guo, Zeng et al. 2007). Helminen *et al.* reported sorption capacities for $NH_3(g)$ at variable temperatures and pressures with reported values for zeolite (8.72 – 9.33 mmol/g at 93.8-97.8 kPa and 298K for two zeolite different samples), alumina (3.01 mmol/g at 98.3 kPa and 298K), silica gel (3.01 mmol/g at 94.3 kPa and 298K) and activated carbon (5.08 mmol/g at 94.3 kPa and 298K) (Helminen, Helenius et al. 2000). Kithome *et al.* (1999) investigated sorption of ammonium to coir with an adsorption capacity of 7778 mg N/kg at pH 5 and zeolite from pH 4-7 with an adsorption capacity of 14000 mg N/kg at pH 7 (Kithome, Paul et al. 1999). Previous work also reported that diffusion was the rate limiting step in the adsorption process for NH_4^+ to zeolites. The reaction energies were greater for the desorption process leading to the conclusion that sorption is reversible but desorption requires a greater net activation energy (Kithome, Paul et al. 1999).

Further, the kinetics of adsorption of NH_3/NH_4^+ to solid materials has shown that a langmuir isotherm is most often the best fit for minerals. Witter and Kirchman measured ammonia and ammonium adsorption to peat, zeolite and basalt at variable pH and ammonia concentrations with a Langmuir isotherm providing the best fit (Witter and Kirchmann 1989). Kithome *et al.* modeled ammonium adsorption to zeolite from pH 4-7 with a best fit described by Langmuir and Freundlich isotherms (Kithome, Paul et al. 1999). Helminen *et al.* measured ammonia sorption to zeolite, alumina, silica gel and activated carbon at partial pressure from 1 to 100 kPa with best fits described by a Langmuir-Freundlich isotherm (Helminen, Helenius et al. 2000). Overall, the strongest sorption capacity is reported for zeolite samples with the following trend in sorption capacity by mass: zeolite > coir > activated carbon > silica gel ~ alumina.

Ammonia in Aquatic Environments

Besides temperature and pH which are discussed in theory in previous sections, bicarbonate and other ions and components in the solutions may influence partitioning, reactivity and adsorption. Further, it is generally accepted that increases in dissolved electrolytes can decrease solubility and increase Henry's constants (Setschenow 1889). Based on experiments with variable salts (0 – 0.1 M), surfactants (0 – 100 mg/L), and humic materials (0 – 10 mg/L), Henry's constants for various volatile organic solvents including TCE and toluene were statistically different at a 95% confidence level and may vary by as much as 35% in complex mixtures (Yurteri, Ryan et al. 1987). In addition, changes in partitioning were not predictable (without clear trends). Further work by Gossett reported that salinity must be > 0.2 M KCl to cause a 10% increase in constants for volatile chlorinated hydrocarbons (Gossett 1987), but the combined effect of ions and surfactants was much more significant as shown by Yurteri *et al*. (Yurteri, Ryan et al. 1987). This is due to many complex changes occurring including changes in hydration and solvation, electrostatic and van der Waals interactions, internal pressure effects and 'salting out' (Battino and Clever 1966, Yurteri, Ryan et al. 1987). The values of the K_b and K_h of ammonia in text books are applicable for deionized water or dilute solutions (Wilhelm, Battino et al. 1977, Dean 1985, Betterton 1992, Ramachandran, Allen et al. 1996). However, bicarbonate and other ions may change these parameters as they impact the buffering properties of solutions, soil and sediment systems. Ammonium salts such as chloride, nitrate, and sulfate are very soluble in water (Weast, Melvin et al. 1988); therefore, changes in pH will not normally result in the formation of ammonium precipitates.

Previous work has recorded a significant discrepancy between ammonia concentrations measured in air and rainwater compared with conventional solubility theories (Hales and Drewes 1979). Szecsody *et al*. 2011 noted that the approach to equilibrium of $NH_3(g)$ partitioning in a Ca- and Mg-carbonate saturated groundwater was significantly slower than in distilled deionized water with less partitioning to the aqueous phase at equilibrium (Szecsody, Truex et al. 2012). Previous work also reported that aqueous CO_2 concentrations in equilibrium with the atmosphere could affect the solubility of $NH_3(g)$ solubility by nearly an order of magnitude (Hales and Drewes 1979), but this theory was disproven by further experiments in equilibrium with atmospheric CO_2 (340 ppm) over a range of NH_3/NH_4^+ concentrations from 75-1200 μM (Ayers, Gillett et al. 1985). However, the presence of ions must be considered to accurately evaluate

ammonia gas solubility in environmentally representative water systems. Therefore, further ions and mechanisms must be explored. In addition, Norton reported that the vapor pressure of NH_3 in solutions increased with increasing OH concentration for a range of (Norton and Pederson 1994). Table 2 below summarizes the activity coefficients for various ions in the presence of ammonia using the Pitzer method. These values are based largely on ion size and charge and allow for some comparison of the effect of ions (Clegg and Brimblecombe 1989).

Table 2: Activity coefficients (λ) comparison as summarized by Clegg and Brimglecombe (1989)

i	$\lambda_{N,i}$
NH_4	0
Na	0.0175
K	0.0454
Cl	0
NO_3	-0.003
SO_4	0.14
CO_3	0.18

Case Study: Ammonia in Tank Waste at Hanford and Savannah River Site

There is a significant amount of ammonia accumulating in aqueous tank waste from the Manhattan project at both the Savannah River Site in South Carolina and Hanford Reservation in Washington due to production of ammonia from components within the waste stream, thermal and radiolytic processes (Mahoney 2000). These wastes are a part of a high salt and high base waste stream. Therefore, previous work has measured equilibrium Henry's constants within synthetic tank wastewater in order to optimize the allowable ammonia concentrations and headspace. Table 3 – 4 summarizes the constants measured at variable temperatures and ionic strength for these purposes. Constants for the Savannah River site were measured using a multiple headspace extraction method via headspace chromatography (based on Chai and Zhu methodologies) whereas constants for Hanford were estimated based on vapor pressure and solubility measurements (Norton and Pederson 1994, Norton and Pederson 1995, Chai and Zhu 1998, Mahoney 2000, Swingle, Poirier et al. 2000).

Table 3: Henry's constants for simulated tank waste at Savannah River Site (Swingle, Poirier et al. 2000)

Simulated Savannah River Site Tank Waste (atm-kg/mol)		
Temp. (°C)	6.2 M Na, 1.7 M OH	12.6 M Na, 2.3 M OH
25	0.04182	0.140
30	0.05081	0.159
40	0.07375	0.202
50	0.10471	0.253
60	0.13228	0.312
70	0.1992	0.379
80	0.2681	-
90	0.35461	-

Table 4: Henry's constants for simulated tank waste at the Hanford reservation (Norton and Pederson 1994)

Simulated Hanford Tank Waste (atm-kg/mol) Temperature (°C)						
Simulant	25	30	40	50	60	70
0.5 M NaOH	0.0198	0.0240	0.0348	0.0494	0.0686	0.0936
1 M NaOH	0.0205	0.0252	0.0376	0.0548	0.0781	0.1093
2.5 M NaOH	0.0384	0.0469	0.0684	0.0978	0.1369	0.1882
3.99 M NaOH	0.0499	0.0604	0.0871	0.1230	0.1703	0.2316
5.47 M NaOH	0.0690	0.0829	0.1177	0.1637	0.2234	0.2997
6.95 M NaOH	0.1074	0.1274	0.1763	0.2393	0.3191	0.4185
3.4 M OH, 6.2 M Na	0.0418	0.0508	0.0737	0.1047	0.1457	0.1992
2.3 M OH, 12 M Na	0.1403	0.1592	0.2024	0.2531	0.3116	0.3784

Anthropogenic Ammonia in the Environment

Ammonia/um is widely used in industry for synthesis of fertilizers, nitric acid, urea, melamine, explosives, dyes and plastics (Helminen, Helenius et al. 2000), is produced in large amounts due to various agricultural activities and is currently being used for remediation purposes. Therefore,

much research has begun to determine its fate in the environment for regulatory and monitoring reasons as well as environmental impact.

Ammonia in Agriculture

There is a need in the agricultural industry to monitor NH_3/NH_4^+ concentrations in the air, soil and water to monitor their overall nitrogen budgets, understand the effects on the environment and to determine cost efficiency of methods. Some of the actions to be monitored include releases due to cattle, swine and other animals, $NH_3(g)$ injection for fertilization of crops, and conventional aqueous application of ammonium-based fertilizers. For example, Thompson and Meisinger monitored NH_3 loss due to volatilization and denitrification in the mid-Atlantic region (Thompson and Meisinger 2005) and Trierweiler and Bishop measured ammonia volatilization on wet versus dry soils (Trierweiler and Bishop 1983). Further, Sigandhupe and Rajput reported that total NH_3 volatilization increased with an increase in application amount (comparing 40, 80 and 120 kg-N/ha applied as urea, 28.2 to 31.8 kg-N/ha losses) but the percent of NH_3 volatilized decreased with increasing application amount (70.5% losses at 40 kg-N/ha versus 26.5% losses at 120 kg-N/ha) for field experiments in an alkaline soil with pH 9.3-10.2 (Singandhupe and Rajput 1989). The increasing concentration of NH_4^+ and pH in the aqueous phase led to an increase in the concentration gradient and volatilization rates of NH_3. The formation of unstable ammonium carbonate species may have further accelerated volatilization as it is an extremely rapid process (rate constant of 24.6 seconds) and would not limit the overall volatilization process (Jewitt 1942, Emerson, Grunwald et al. 1960, Bharadwaj and Abrol 1978). Hence, the rate of NH_3 loss is directly related to the concentration in solution for this high pH, high carbonate system (Vlek and Craswell 1981, Singandhupe and Rajput 1989). Previous researchers reported volatilization of as much as 87% of NH_3 applied at pH 10.6 (Jewitt 1942, Gupta 1955, Macrae and Ancajas 1970, Basdeo and Gangwar 1976, Bharadwaj and Abrol 1978, Sahrawat 1980, Singandhupe and Rajput 1989)

However, livestock production is the major source of $NH_3(g)$ emission to the environment from agricultural activities (Phillips, Scholtens et al. 2000, Phillips, Lee et al. 2001). The EPA estimates that 71% of NH_3 emissions in the United States are due to livestock production (Roe, Spivey et al. 2004). Therefore, many of the methodologies discussed within this review are a product of the agricultural industry. Further, the need for a better understanding of NH_3

partitioning is shown by the model developed by Anderson *et al.* as it could not adequately predict ammonia levels in swine confinement buildings (Anderson, Smith et al. 1987).

The dissociation constant of NH_3 in swine anaerobic lagoon samples was 50% of the value for deionized water at 25 and 35°C but nearly 94% of the value at 15°C (Arogo, Westerman et al. 2003). It is significant that these researchers reported a large difference between the lagoon samples and deionized water at elevated temperature. It shows that there are still phenomenon occurring in the more complex swine lagoon samples that is not entirely understood. In addition to the effects of ions on partitioning in aqueous systems, sorption of NH_3 to suspended solids may also effect the partitioning and speciation of ammonia gas. Anderson *et al.* (1987) previously reported a dependence of partitioning in swine manure at pH 6.5 on the fraction of CO_2 and H_2S and Zhang (1992) reported partitioning coefficients at 20% of water in liquid swine manure with 1% total solids (Anderson, Smith et al. 1987, Zhang 1992). However, Henry's law constants for NH_3 were approximated for field-moist broiler litter mixed with 450 mL of distilled deionized water at 23°C in a closed system and values are within 5% of reported values for dilute aqueous solutions (Liang 2011).

Environmental Remediation with Ammonia Gas
While gas remediation is usually considered for volatile organic compounds, it can be useful for inorganic contaminants as well. There are three classes of remediation by gas phase injection as described previously (1) direct removal of contaminant vapor from groundwater, (2) manipulation of master geochemical variables and (3) injection of gaseous stabilizing agents (Denham and Looney 2005). Because inorganic contaminants are highly affected by solution chemistry, injection of gas phases that change the chemistry (class two) could be useful in vadose zone remediation of inorganic metals and radionuclides (Denham and Looney 2005, Dresel, Wellman et al. 2011). However, it must be noted that these geochemical changes within the subsurface are often temporary unless they are moving the system towards its natural equilibrium. The partitioning of NH_3 and NH_4^+ within each of the phases present in the subsurface vadose zone environments (gas, liquid and solid) must be fully understood in terms of the anthropogenic impacts. Figure 2 represents the equilibrium partitioning of the major species within each of the phases. However, these partitioning coefficients assume equilibrium and cannot differentiate interactions such as those occurring in systems with various microbes

present (i.e. nitrification). In addition, the injection of $NH_3(g)$ may significantly effect the pH of the system. Therefore, it is essential that the sediment proton or OH^- adsorption capacity is known. The sediment proton adsorption capacity is directly correlated to the mineral dissolution of soils based on the mass of base added to the system (Szecsody, Truex et al. 2013).

The fate of the NH_3/NH_4^+ in the environment during remediation processes is still under investigation. Previous work has shown that NH_3 gas injection can be used for remediation of volatile organic compounds and inorganic metals and radionuclides (including acid mine drainage) (Skousen, Hilton et al. 1996, Denham and Looney 2005, Szecsody, Truex et al. 2012). Denham and Looney (2005) have summarized developmental stages for direct removal (for Hg, I, C, and Rn), geochemical variable manipulation by pH and redox (for U, Cr, As, Tc) adjustment, and stabilizing reagents including gaseous phosphate (for Pb, Cd, U, and Sr) and hydrogen sulfide (for Cu, Ni, Cd, Hg, Pb) removal as specific gas remediation technologies. Ammonia gas injection to acid mine drainage waters has been shown to be effective at neutralizing the sulfuric acid in the waters as well as precipitating heavy metals from solution (Faulkner and Skousen 1991, Skousen, Hilton et al. 1996). However, $NH_3(g)$ injection could lead to biostimulation and eutrophication in some environmental systems.

Case Study: Remediation of Uranium with Ammonia Gas

The Hanford site in Washington has approximately 200,000 kg of uranium within the subsurface as a result of improper disposal and accidental releases following plutonium production (Corbin, Simpson et al. 2005, Zachara, Brown et al. 2007). The mobility of uranium (U) in the groundwater at Hanford is relatively high based on its low K_d at pH 8 $(0.11 - 4\ L/kg)$ (Zachara, Brown et al. 2007, Szecsody, Truex et al. 2013), small retardation factor 1.43 (Szecsody, Truex et al. 2013), and presence as the more mobile U(VI) species (McKinley, Zachara et al. 2007). It must be noted that the goal of remediation in this case study is to decrease the flux of uranium to the groundwater from the vadose zone through reduction of contaminant mobility in the subsurface. In determining the remediation technology, there was a desire to inject gas instead of liquid as the contamination exists in the vadose zone (with a groundwater table as much as 100 m deep) in an area that receives minimal annual rainfall and, therefore, has minimal water content within the vadose zone. This is particularly difficult because of the depth of the vadose zone as options for deep vadose zone remediation are much less developed than shallow or

saturated system technologies (Dresel, Wellman et al. 2011). Dresel *et al*. provides a brief discussion of the positive and negative aspects of vadose zone remediation technologies (Dresel, Wellman et al. 2011). The site mineralogy consists largely of quartz, plagioclase, K-feldspar, calcite, and clays (with the clay fraction consisting largely of illite, smectite and chlorite) (Szecsody, Truex et al. 2013). Hanford formation sediments investigated by Wan *et al*. reported a cation exchange capacity in the range of 1.7 – 18 meq/100g (Wan, Larsen et al. 2004).

Basic injections (including injection of the weak base NH_3) may lead to the slow dissolution of silica-containing minerals such as quartz, montmorillonite, muscovite and kaolinite (Wan, Larsen et al. 2004, Wan, Tokunaga et al. 2004, Szecsody, Truex et al. 2012, Szecsody, Truex et al. 2013). This results in an increase in dissolved Si^+ and Al^{3+}. Small increases in Na^+, K^+, $Fe^{2+/3+}$, Cl^-, F^- and SO_4^{2-} have also been reported (Szecsody, Truex et al. 2012, Szecsody, Truex et al. 2013). Increases of Ca^{2+} and Mg^{2+} were not reported in laboratory experiments but Ca^{2+} ion increases were reported in column experiments with injection of uranium in 0.1 M NaOH and 1 M $NaNO_3$ (Szecsody, Truex et al. 2013). Further, Szecsody *et al*. (2013) has shown that basic solutions co-disposed with uranium may lead to an increase in the retardation of uranium (to 1.76 compared to 1.43 in groundwater) within the subsurface and showed evidence of precipitation of uranium (Szecsody, Truex et al. 2013). However, the high ionic strength conditions produced by the basic injection may lead to desorption and mobilization of uranium as slightly greater effluent concentrations were measured in comparison of pH 8 groundwater versus 0.1 M NaOH with maximum effluent concentrations of 6.0 μM and 9.1 μM, respectively. The mechanisms leading to formation of uranyl precipitates and the specific species forming are still not understood. Szecsody *et al*. predicted that uranium precipitation should be a dominant process under highly alkaline conditions (pH 13) with Na-boltwoodite formation which occurs from pH 9.5 – 13 (Szecsody, Truex et al. 2013). However, precipitation and sorption of uranium with aluminosilicates and carbonates in alkaline conditions may also occur (Szecsody, Truex et al. 2012, Szecsody, Truex et al. 2013). Szecsody *et al*. theorizes that the initial (within the first hour) loss of uranium from suspension is the result of sorption and precipitation while the long term losses (over 10 – 100's of hours) are due to precipitation as it occurs on the time scale of silica dissolution (Szecsody, Truex et al. 2013). Sorption is expected to be minimal under these conditions (high pH, high ionic strength), therefore, precipitation should be the dominant mechanism. The specific precipitates that may form under $NH_3(g)$ injection conditions have yet

to be identified. However, some precipitates have been identified from previous waste disposal sites and efforts at Hanford. Nano-crystalline U precipitates (from large-volume, alkaline waste disposal) and aluminosilicates with low, homogenously distributed concentrations of U (from continuous leakage of acidic or neutral wastes) have been identified in contaminated sediments at Hanford without $NH_3(g)$ treatment. Those characterized from the large-volume, alkaline waste disposal are U(VI) species associated with silicate minerals that are likely Na-boltwoodite (Catalano, Heald et al. 2004, McKinley, Zachara et al. 2007). However, Szecsody *et al*. could not confirm changes in Na-boltwoodite concentrations by EXAFS and XANES of sediments exposed to $NH_3(g)$ in laboratory experiments and selective extraction procedures can only give an indirect measurement of uranium association with various phases (Szecsody, Truex et al. 2010, Szecsody, Truex et al. 2010, Szecsody, Truex et al. 2012, Szecsody, Truex et al. 2013). In addition, there are additional precipitates that have yet to be identified within the Hanford site vadose zone (Zachara, Brown et al. 2007).

 In addition, the partitioning of the $NH_3(g)$ during injection and long-term needs further investigation as partitioning coefficients within relevant waters and sediments has not yet been investigated. While $NH_3(g)$ injection has not yet begun at the Hanford site, preliminary plans are to inject 48 cm/min flow rates 0.5 m from the injection wells (Zhong, Szecsody et al. 2015). Preliminary work on the injection of $NH_3(g)$ was instigated by Szecsody *et al*. (2011). $NH_3(g)$ was injected in laboratory experiments as described previously. Temporarily, the pH of the system increased from 8 to 11-13 upon ammonia injection (Szecsody, Truex et al. 2012). This resulted in increased pore water cations and anions due to mineral dissolution. While the increased pH could possibly increase the mobility of uranium due to its formation of carbonate species at high pH, this is expected to be a short-term, intermediate phenomenon. By six months after injection in laboratory experiments, the pH in laboratory experiments decreased by at least two pH units. This reduction in pH led to an order of magnitude decrease in Ca and Mg ions, three order of magnitude decrease in Fe(III) and a 50% decrease in Si and Na ions. Therefore, it is expected that two phenomenon ultimately occur as a product of ammonia injection: (1) U precipitates as solubility decreases (as pH moves back towards neutral) and (2) U minerals are coated with non-U, low solubility precipitates. Therefore, while the aqueous phase changes were not long-term, the formation of precipitates and coated minerals may provide a long term solution for the site. The results of the experiments estimate that 93% less mass of U may be

leached with 5% $NH_3(g)$ injection versus untreated sediments (Szecsody, Truex et al. 2012). This work reported a retardation factor of 363 for $NH_3(g)$ (based on the liquid to gas mass ratio) that was calculated for columns packed with sediments with a 4% water content (99.73% of the $NH_3(g)$ was partitioned to the pore water) and agree well with experimental data (Szecsody, Truex et al. 2012). Further work by Zhong *et al*. (2015) reports that 85% less U is immobilized from columns treated with 5 and 15% v/v $NH_3(g)$ (versus untreated) (Zhong, Szecsody et al. 2015).

Future research needs for uranium remediation by NH_3-gas injection

1. Knowledge of NH_3 transport in porous media (Zhong, Szecsody et al. 2015)
2. Determination of geochemical reactions caused by ammonia addition to the subsurface (Zhong, Szecsody et al. 2015)

Methods

A method must be chosen to analyze the concentration of NH_3 and NH_4^+ in suspension as well as the solubility of NH_3 gas in liquids in the presence of variable ions, soil, temperature and pH. The solubility will be best approximated through the determination of Henry's law constant. In addition, these tests are a vital step in determining the interaction of NH_3 gas with the high-carbonate soils and pore waters at Hanford site as well as its mobility in these environments. In the following sections several methods for determination of gaseous and aqueous NH_3/NH_4^+ concentrations and solubility will be evaluated. For detection of NH_3/NH_4^+, we will include methods using a gas-sensing electrode and colorimetric methods. For determination of solubility we will include both static and dynamic equilibrium methods. It must be noted that Henry's law constants are difficult to determine experimentally and have often been estimated from thermodynamic data such as vapor pressure or solubility in the past (Mackay and Shiu 1981, Ji, Boisvert et al. 2008). However, only methods based on direct measurement of equilibrium gas and liquid phase concentrations to calculate Henry's law constant will be presented here.

Methods for the Determination of NH_3/NH_4^+ in Aqueous Solutions

Direct measurement of NH_3 is confined to drinking waters, clean surface water and nitrified wastewater effluent (APHA, AWWA et al. 1985). For high concentrations, high interferences and other water sources, a distillation step is generally required. Upon collection of samples,

residual chlorine should be destroyed by pretreatment with de-chlorinating agent. For samples that cannot be immediately analyzed, they should be preserved with either 0.8 mL conc. H_2SO_4/L sample or 0.5 mL 1.0M HCl/L and stored at 4°C until analysis (acid should be neutralized with KOH or NaOH immediately prior to analysis). Previous researchers have acidified with as much as 1 mL of sulfuric acid in 9 mL of sample to decrease volatilization of NH_3 (Ndegwa, Vaddella et al. 2009). However, the standard methodology recommends 0.8 mL conc. H_2SO_4/L to reduce losses.

Pretreatment by Distillation

Briefly, begin with a 500 mL sample (or diluted to 500 mL, unless the NH_3-N concentration is less than 100 µg/L, then 1000 mL sample) with a neutral pH. Then add 25 mL of borate buffer and adjust pH to 9.5 with 6N NaOH. Once the sample flask is transferred to the distillation apparatus, distill at a rate of 6 to 10 mL/min with the tip of the delivery tube below the acid receiving solution (either boric acid or sulfuric acid depending on method as described below). Further details of this method are outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA et al. 1985).

Equipment: borosilicate glass flask (800-2000 mL) attached to a vertical condenser, pH meter and electrode, borosilicate flask (500-1000 mL)

Electrode Measurement of NH_3

The ion-selective electrode uses a hydrophobic, gas-permeable membrane to separate the sample solution from the electrode solution. It has an applicable range of 0.03 to 1400 mg NH_3-N/L (APHA, AWWA et al. 1985). A calibration curve is prepared based on decimal dilutions from 1000 to 0.1 mg NH_3-N/L of a stock NH_4Cl solution or certified standard. Estimation of concentrations may also be completed through the method of standard addition. The sample pH must be raised to 11 to convert all aqueous species to $NH_3(aq)$ as shown in Figure 1 and all samples, blanks and standards should be run in parallel. The distillation step is unnecessary for this method. If a distillation step is preferred, the NH_3 should be trapped in 0.04 N H_2SO_4. High concentrations of ions may affect this measurement, but color and turbidity do not. Amines are a positive interference while mercury and silver will have the opposite effect by complexing with ammonia. At concentrations less than 0.8 mg NH_3-N/L there is a tendency to overestimate the NH_3 concentration for distilled and effluent water samples. Further, below 1 mg NH_3-N/L, the

electrode responds more slowly and may need 5-10 minutes to reach a stable reading. During measurement, samples must be consistently stirred (but not so much that air bubbles are sucked into solution) and pH adjusted to 11 with NaOH only after electrode is submersed (as some ammonia may be lost from a basic solution). Further details of this method are outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA et al. 1985).

Equipment: Meter with expanded mV capabilities or ion specific meter, ammonia-selective electrode, magnetic stirrer and PTFE-coated stir bar

Titration Methods

For high NH_3 concentrations (greater than the stated ranges for the colorimetric methods or 5 mg/L), the titration method coupled with a required distillation step into boric acid is preferred over colorimetric methods (APHA, AWWA et al. 1985). Volatile alkaline compounds, such as hydrazine and amines, may interfere with titrimetric results. Following distillation into boric acid indicator solution (10 mL indicator, methyl red and methylene blue, in 1 L), titrate ammonia in distillate with standard 0.02 N H_2SO_4 titrant until indicator turns a pale lavender color. The full methods are outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA et al. 1985).

Colorimetric Methods

Colorimetric methods generally have better detection limits than titration, although there are some interferences (Ndegwa, Vaddella et al. 2009). Three colorimetric methods are described below with each being applicable to different concentration ranges. With these methods it is vital that blanks, standards and samples are all prepared under the same conditions including temperature, ionic strength and reaction time. Therefore, variable HCO_3^- solutions will be used to create blanks that are representative of the samples pulled from 0-100 mM HCO_3^- suspensions. Further calibration curves must be completed for each new batch of samples within the expected range of the samples at the time of sample measurement. It must be noted that each of the methods presented below estimate total NH_3 and NH_4^+ in solution instead of one species or the other.

Nesslerization Method

The nesslerization method has reported detection limits of 2 µg NH_3-N/L with an upper range of 5 mg NH_3-N/L but the reproducibility suffers below 100 µg/L (APHA, AWWA et al. 1985).

Interferences include turbidity, color, and substances precipitated by the hydroxyl ion (i.e. magnesium and calcium). Error within the method for domestic wastewaters without pretreatment can be as high as 1-2 mg/L. Interferences may be removed by the distillation step into boric acid or, with less efficiency, by precipitation with zinc sulfate and alkali precipitates. Alkali elements may form turbidity when treated with Nessler reagent, but EDTA can be used to inhibit precipitation. In addition, glycine, hydrazine and some amines will react with the reagents to interfere with the characteristic yellow color. Some organic compounds (i.e. ketones, aldehydes, alcohols and some amines) may also cause a yellowish or greenish color or increased turbidity on nesslerization following the distillation step but may be boiled off at low pH following distillation. However, undistilled samples with residual chlorine will need to be treated with a dechlorination agent. Briefly, 50 mL of sample at neutral pH is mixed with 1 mL of nessler reagent and mixed. The samples are ready for measurement after 10 minutes. Because this method is carried out at a neutral pH, it is expected that the major species present in this system is NH_4^+. Therefore, this method evaluates total NH_3 and NH_4^+ in suspension. For concentrations from 0.4 – 5 mg/L, a wavelength of 400-425 is suitable for measurement of the yellow color with a 1-cm light path. If the path length is extended to 5 cm, 5 – 60 µg/L can be determined. Above 10 mg/L, the brown hues should be measured from 450 – 500 nm. In addition, visual standards can be prepared in the event that access to a spectrophotometer is not available. The full methods are outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA et al. 1985).

Equipment: Spectrophotometer for use at 400-500 nm and path length at least 1 cm or filter photometer (blue filter may be necessary for high concentrations), pH meter and electrode

Phenate Method

The phenate method has a detection limit of 10 µg NH_3-N/L with an upper range of 500 µg NH_3-N/L (APHA, AWWA et al. 1985). If alkalinity exceeds 500 mg $CaCO_3$/L, color or turbidity is present, or the sample has been preserved in acid, the distillation step into 0.04 N sulfuric acid is required. It must be noted that samples will be from 0 – 100 mM HCO_3^-, and, therefore, will be above these limits and require distillation. Briefly, to a 10 mL sample in a 50 mL beaker with stirrer add 0.5 mL of $MnSO_4$ solution and place on stir plate. After adding 0.5 mL HCl, immediately add 0.6 mL dropwise of phenate reagent. Color formation is complete after 10

minutes and stable for 24 hours and should be measured between 600 – 660 nm wavelengths. The full methods are outlined in *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA et al. 1985).

Equipment: Spectrophotometer for use at 600 – 660 nm wavelength and path length of 1 cm or filter photometer with a red-orange filter, magnetic stirrer and stir plate, glass beaker (50 mL)

Ammonium Salicylate Method

Hach has developed a field kit for this measurement which was incorporated in several previous papers due to its ease of use (Szecsody, Truex et al. 2012, Zhong, Szecsody et al. 2015). They have developed several different methods ranging in detection from 0.015 – 47 mg-NH_3/L (Hach 2014). In addition, these methods have been previously adapted for determination in seawater (Bower and Hansen-Holm 1980). The detection range for the laboratory methods are 5 to 500 μg N/L. Briefly, this method transfers 25 mL of sample, calibration standard or blank to a 50 mL Erlenmeyer flask and then adds 3 mL of salicylate-catalyst solution (0.0025% sodium nitroprusside catalyst and 4% sodium salicylate) and 5 mL of alkaline-citrate solution. After 1 hour but before 3 hours, the absorbance is read between 640 and 680 nm. In freshwater, the maximum absorbance occurs at 680 nm. However, in seawater, the absorbance is shifted to 640 nm. This illustrates the importance of preparing standards of similar ionic strength to samples for measurement.

Equipment: 50 mL erlenmeyer flasks, stopper flasks, spectrophotometer with 1 cm light path, vortex stirrer and water bath

Methods for the Determination of Gaseous NH_3

The following methods for determination of gaseous ammonia involve either direct measurement or the capture of ammonia in liquids ('trapping') and solids for measurement. It must be noted that the methods described within this text are for the laboratory scale. Appropriate field methods have been reviewed previously (Phillips, Lee et al. 2001). Further, care must be taken in electing equipment and materials that do not absorb NH_3 gas. Silicone is one example of a material that does absorb NH_3 gas (Phillips, Lee et al. 2001).

Direct Measurement of NH₃ Gas

Direct Measurement of NH$_3$ Gas

There are many different methods that have been utilized in the literature for detection of NH$_3$(g). Two methods were used previously by Zhong *et al*. (2015): (1) PerkinElmer Ultraviolet Absorbance detector at 20 nm which was used for concentrations less 0.5% v/v, took about 10 minutes per sample and needed ~20 mL volume (2) Drager gas sampler and colorimeter tubes designed for NH$_3$(g) concentration less than 10% v/v which took about 20 seconds per sample and needed ~100 mL volume. Liang also measured the gas phase using a photoacoustic spectrophotometer (INNOVA, model 1421) with a reported detection limit of 0.2 ppm. However, gas chromatography is the most common method for gas-phase analysis.

Gas chromatography

The use of gas chromatography in the testing of headspace gases or vapor in a sample vial prevents direct contact with liquids or solids and the complexity of the sample matrix can be diminished and even avoided (Zhu and Chai 2005). A method reported by Yamamoto *et al*. (1994) collects NH$_3$(g) into a GC column packed with 15% polyethylene glycol of mean molecular weight of 6000 and 5% potassium hydroxide solution on Chromosorb 103 (Yamamoto, Nishiura et al. 1994, Phillips, Lee et al. 2001). This method has a demonstrated range of 2-100 ppb and detection of 0.02 ppb.

Methods of Trapping NH$_3$ Gas

Acid trap methods are considered inexpensive, reliable and accurate, but inconvenient for high-frequency sampling (Phillips, Lee et al. 2001, Hafner, Meisinger et al. 2012). Methods have been outlined previously by Thompson and Meisinger (Thompson and Meisinger 2005) and generally utilize an excess of a dilute solution of a strong acid for capture of NH$_3$(g). Most ammonia traps use either boric acid, sulfuric acid, orthophosphoric acid or another strong acid. However, boric acid is generally used in conjunction with titration methods of measurement and sulfuric acid for colorimetric methods (APHA, AWWA et al. 1985, Ndegwa, Vaddella et al. 2009). A drawback of these methods is that they are generally not continuous sampling methods. However, some modifications can be made as outlined in the Citric Acid Method below. It is important to understand the principles because too little acid will result in a poor trap efficiency but too much acid will reduced detection limits. Boric acid traps with a concentration of 2% and gas flow rate of 118 mL/min were recently used but researchers did not

report a capture efficiency (Liang 2011). Previous field reports have seldom estimated the necessary conditions required for optimum performance but have reported the following parameters for sulfuric acid traps: flow rate of 3-4 L/min, 18-650 mL traps, with sulfuric acid concentrations of 0.05-0.9 mol/L (McInnes, Kissel et al. 1985, Genermont, Cellier et al. 1998, Rana and Mastrorilli 1998, Cabrera, Kissel et al. 2001, Shi, Parker et al. 2001, Cole, Clark et al. 2005, Guiziou and Beline 2005, Todd, Cole et al. 2006) (as compiled by Ndegwa et al., 2009). With sulfuric acid, the volume and molarity of acid necessary can be estimated based on the following stoichiometry when the expected ammonia emissions are known. However, previous work utilized a safety factor of two (Ndegwa, Vaddella et al. 2009). Nonetheless, the efficiency of their traps significantly decreased with increasing amounts of NH_3 to be trapped even when the stoichiometric capacity was significantly greater (with efficiency falling below 80% with masses of NH_3 greater than 100 mg).

$$H_2SO_4 + 2NH_3 \leftrightarrow (NH_4)_2SO_4 \qquad \text{Eqn. 17}$$
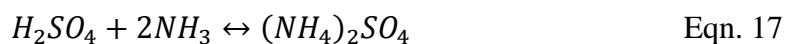
An increase in the depth of the acid by three led to an absolute efficiency increase of 8% and a decrease of the flow rate by two led to an increase of 4%. Following the gas trapping procedure, acidification of samples with 1 mL sulfuric acid to 9 mL of sample will reduce volatilization of $NH_3(g)$ (Ndegwa, Vaddella et al. 2009). However, the methods outlined in the *Standard Methods for the Examination of Water and* Wastewater it is recommended that samples be preserved with either 0.8 mL conc. H_2SO_4/L sample or 0.5 mL 1.0M HCl/L and stored at 4°C until analysis (APHA, AWWA et al. 1985).

Equipment: (based on Ndegwa et al., 2009) acid bottle trap (polypropylene cylinder sealed with vinyl stopper with 6.35 mm OD glass tube) or Dreschel bottle, critical orifice, variable area flow meter (Cole-Parmer, C-32460-42), vacuum pump (Gast MFG Corp., DOA-P104-AA), 4L sealed container, Teflon tubing at 6.35 mm ID

Continuous Citric Acid Method

A pH-based method using a citric acid trap was developed recently where the NH_3 is captured in a citric acid solution with continuous pH measurement (Hafner, Meisinger et al. 2012). This allows for estimation of NH_3 concentration based on speciation changes with pH over time in a single solution instead of repeated aqueous sampling and measurement of NH_3. At <1 mmol/kg of citric acid, acidic gases may cause significant interferences, but the linear measurement range

is from pH 2.8-4.0 with a capacity of 2.0 to 2.5 times the citric acid concentration. Concentrations of >100 mmol/kg of citric acid are not necessary. An increased citric acid concentration allows for greater NH_3 capacity at the expense of sensitivity of the method. Overall, the relative error of the method was <10% with an ammonia:citric acid ratio >0.25:1 (or approximately 10% of the total trap capacity) and recovery was 97-99% for aqueous suspensions from five trials. Field measurements were accurate down to 800 µmol/kg in solution. With a 100 gram trap solution and gas flow rate of 5 L/min, a concentration change of 300 µg/kg could be measured in suspension with a five hour sampling interval and with a gas concentration of 340 µg/m^3. However, the salicylate colorimetric method was accurate below 10 µmol/kg.

Equipment and materials: water bath, graduated cylinder (25-100 mL) or a syringe body (20 mL), 250 mL glass jar with Teflon-lined lid (I-Chem Septa jar, Thermo Fisher Scientific), 3mm inner diameter tubing, Accumet AR15 pH meter, Orion 91-02 or Accumet 13-6202-85 glass combination, AgCl reference pH electrode, pH buffers of initial citric acid concentrations (1, 10 and 100 mmol/kg with pH of 3.24, 2.63 and 2.09) and ammonium citrate (1, 10, 100 mmol/kg with pH of 5.48, 5.31, 5.00 at 20°C, respectively), anhydrous citric acid (Fisher, reported purity 100.0%), ammonium citrate (Fisher, 99.6% purity), ammonium chloride (Fisher, 99.6% purity)

Methods for Measuring the Partitioning of Gases in Suspension

Partitioning of compounds between the air-water interface is one of the most important processes affecting transport of chemical species in the environment (Hansen, Zhou et al. 1995, Ramachandran, Allen et al. 1996). Therefore, there are many methods for determining partitioning between the gas-liquid interface including equilibration of a batch mixture, flowing a film or stream of liquid through a gas, bubbling gas in liquid or flowing gas over a stationary liquid (Battino and Clever 1966). For determination of Henry's law constant (equilibrium partitioning) we will only use methods based on direct measurement of the aqueous and/or gas phase concentrations including: modified static (batch) and dynamic (time dependent) methods. It must be noted that some of the dynamic methods allow for determination of the rate of dissolution of the gas phase into the aqueous phase. Many more methods for determination of gas partitioning than those described here are in the review by Battino and Clever including gas chromatographic methods as well as manometer and volumetric methods (Battino and Clever 1966). Manometer and volumetric methods, while extremely accurate, are not included here

because they will not be applicable to environmental systems including those with variable electrolytes and minerals (Battino and Clever 1966). While many of these have been developed for volatile organic compounds, the protocols are applicable to $NH_3(g)$. With the exception of the dynamic equilibrium method and Mackay's method, each of these methods are closed, batch systems. In both the equilibrium partitioning and the static equilibrium method, the steady-state equilibrium of the solute is determined in an enclosed system and generally includes analysis of gas-phase samples. However, in the dynamic equilibrium method, equilibrium between the gas and aqueous phases is reached followed by monitoring of the gas phase decay. This can allow for the determination of both Henry's law constant and the hydrolysis loss rate (Lee, Mukherjee et al. 2013). The attainment of equilibrium is generally the most important factor in these methods (Battino and Clever 1966, Mackay, Shiu et al. 1979).

Static Headspace (Batch) Methods and Modifications

Static methods involve the equilibration of the gas and aqueous phases in a closed system with solute present at low concentrations. Although the methodology is simple and more environmentally applicable, these methods can incur large errors (as high as 60%) for materials with a low Henry's law constant (Ramachandran, Allen et al. 1996, Ji and Evans 2007, Ji, Boisvert et al. 2008, Szecsody, Truex et al. 2012). The samples must be dilute and below saturation to be described by Henry's law as described previously in this manuscript. In this method, generally only the equilibrium gas phase (unless explicitly stated) is measured and then the ratios of the gas phase measurements for a standard and the compound of interest are used to estimate the aqueous concentrations in order to determine Henry's law constants. Each vial has the same bulk quantity of the solute or compound of interest. The initial aqueous phase concentration generally must also be known for determination of constants by this method. Significant variations of these methods are described in the following sections. However, first, general methodologies developed by several researchers are further described.

The equilibrium partitioning in a closed system (EPICS) method involves measuring the concentration of a single volatile compound in the headspace of two sealed bottles having different liquid volumes (Lincoff and Gossett 1984, Hansen, Zhou et al. 1995). However, it assumes that equal masses of solute are in each bottle. Stock solutions are equilibrated for at least two weeks prior to preparation of samples which were equilibrated for approximately 24 hours with regular shaking. The error reported using these methods was 2-5% with the lower

range being due to modifications for more precise measurements of the masses of compounds in each bottle (Lincoff and Gossett 1984, Gossett 1987, Robbins, Wang et al. 1993). However, the protocol requires the exact knowledge of the mass ratio of the compound of interest in each of the bottles and cannot be used for determination in unknown matrices or environmental samples (Robbins, Wang et al. 1993) unless modified by measuring the initial mass of contaminant in the system. This modified method was successfully used to investigate water composition effects on partitioning of the model compounds TCE and toluene as well as seven additional chlorinated hydrocarbons and six aromatics (Yurteri, Ryan et al. 1987) and 13 different volatile chlorinated hydrocarbon compounds (Gossett 1987) but was not recommended for highly soluble compounds (dimensionless $H < 0.1$).

Equipment: 250 mL amber bottles, silicone rubber septum cap with poly(tetrafluoroethylene) liner, water bath, gas-tight syringe

Robbins *et al*. (1993) explains a version of this method where three vials are prepared with different headspace-to-aqueous volume ratios. Ramachandran *et al.* (1996) also describes a variation of this method but uses four vials with variable ratios. This method is applicable to a wide range of volatile and semi-volatile organic compounds including the highly soluble methyl tert-butyl ether (Robbins, Wang et al. 1993). This allows for an unknown initial aqueous concentration as long as each of the three or four solutions is identical with only measurement of equilibrium gas phase concentrations. Samples in these experiments are occasionally swirled over at least 30 minutes prior to measurement in a constant temperature water bath to allow for equilibration. Each of the experimentally determined aqueous phase concentrations and the calculated aqueous concentrations are the same at a 99% confidence level by a two-tailed, t-test statistical comparison. Headspace to liquid volume ratios of 7, 3.33 and 0.333 were found to be sufficient for a wide range of compounds (Robbins, Wang et al. 1993).

Equipment: 40 mL volatile organic analysis (VOA) vials (Supelco Inc, Part No. 2-3283) or 65 mL narrow-mouthed reagent bottles, silicone/poly(tetrafluoroethylene)-faced septa (Supelco Inc., Part No. 2-3292M) or rubber septa with Teflon tape to minimize adsorption of organic vapors, 22 gauge needles (Spinal-Tap Needle, Popper & Sons, Part No. 7307), Luer-Lock plastic syringe, 250 µL gas-tight, valve-locking microsyringe (Scientific Glass Engineering, Part No. 010507 and 0315243), water bath

Further, Chai and Zhu developed another simple batch method which was later used by Savannah River site scientists where samples are prepared in vials for an automatic headspace sampler coupled to a gas chromatography (Chai and Zhu 1998, Swingle, Poirier et al. 2000). In this method samples are equilibrated at temperature for 30 minutes prior to sampling and then re-sampled every ten minutes (a total of ten samples are pulled). Peak ratios are then compared to a known sample to estimate Henry's constants. Swingle *et al*. reported an error of 10 – 20% for this method and used the partitioning of methanol to water as a standard for comparison. This method is attractive because it is entirely automated.

Equipment: HP-5890 gas chromatograph, HP7963 automatic headspace sampler, and glass autosampler vials

Internal Standard Method

The internal standard method is a batch method that can be used to determine the Henry's law constant without knowledge of exact substrate concentrations or gas and liquid volumes for compounds with low dimensionless constant values ($< 10^{-3}$) (Ji and Evans 2007, Ji, Boisvert et al. 2008). Previous work has described similar methods in which the ratio of solubilities was determined for argon and nitrogen for comparison with other measurements (Benson and Parker 1961, Battino and Clever 1966). In work by Ji *et al*. (2008), dimensionless Henry's law constants are determined with an error of <10% (an average of 5.6% error) across temperatures from 5 to 25°C and constants ranging from 0.32-7.27 ($x10^{-3}$) for various aldehydes, ketones and nitriles. An average error of ~5% was also achieved in his previous work (Ji and Evans 2007). This method must have a gas volume to aqueous volume ratio of less than 1.0 so that the amount of the compounds transferred to the gas phase is very small (<1%) and uses an organic solvent to prepare standard solutions of the compounds of interest and internal standard (pentane in this work) (Ji and Evans 2007). The internal standard compound and the compound of interest (NH_3) must not be reactive with eachother or undergo significant degradation during the experiment (butyronitrile and 2-pentanone were used in previous work) (Ji and Evans 2007, Ji, Boisvert et al. 2008). These samples were prepared at concentrations of 5-40 ppm in 40 mL amber glass vials with septa and swirled for at least 30 minutes in a temperature controlled water bath prior to sampling of both the gas headspace and aqueous phase (Ji and Evans 2007).

Equipment: 5% dimethyldichlorosilane in tolume to deactivate inner surface of vials, 40 mL sample vials (Supelco), silicone/poly(tetrafluoroethylene)-faced septa caps with holed screw caps (Supelco), water bath, BioRad cooling water circulator, 500 µL gas-tight, valve-locking microsyringe (model 500 R-V-GT, Scientific Glass Engineering), Eppendorf micropipets

Dynamic Methods

The following methods are considered open systems where a gas phase is continuously injected into the solution of interest. Because there is continuous (or multiple) measurements of the concentrations with respect to time, these methods may allow for determination of the rate of partitioning. For both Mackay's Method and the Dynamic Headspace Method, the flow rate of the gas out of the solution is monitored. However, several researchers have employed similar protocols with open beaker-type systems to investigate environmental samples including groundwater (Genermont and Cellier 1997, Szecsody, Truex et al. 2012). These methods have been used to investigate the carbonate buffering capacity in systems that are saturated with Ca and Mg. However, the accuracy of the beaker-type methods has not been investigated and it is difficult to extract quantitative information as these systems are open to the atmosphere.

Mackay's Method

This method was developed by Mackay *et al*. (1979) for measurement of partitioning of aromatic hydrocarbons (both liquid and solid phase hydrocarbons) in water in an open system. However, the authors note that this method could be used to determine how the presence of sorbents (i.e. minerals or organic matter), electrolytes or other gasses might affect solubility. Therefore, this method could be applicable to investigations of environmental systems. It must be noted that systems with solids present must remain turbid or well-mixed throughout measurement. With this method, Henry's constant is determined through a semilogarithmic plot of concentration versus time as the liquid concentration decreases during stripping with $N_2(g)$ at a flow rate of 50-500 cm^3/min after reaching equilibrium as described by equation 18.

$$ln\frac{C_{t,aqu}}{C_{0,aqu}} = -\left[\frac{H_{cp}\phi}{RTV}\right] \times t \qquad \text{Eqn. 18}$$

The initial equilibration of the liquid with the gas phase was accomplished through (1) equilibrating a hydrocarbon (or other contaminant) with water in a separate vessel and

transferring to the column or (2) by-passing the nitrogen stream after saturation with water through a vessel containing the hydrocarbon solution. Knowledge of the gas flow rate, liquid volume, and temperature must be known. However, only the liquid phase must be measured and only the relative change in concentration is necessary for determination of constants. Sampling frequency in experiments by Mackay *et al*. (1979) varied from every 2 min. to every 20 min. depending on volatilization. In addition, this method is most accurate at high concentrations and is not recommended for low concentration systems because only the liquid phase is measured. Yurteri *et al*. noted that this method failed in the case of 1,1-dichloroethylene due to its high volatility (Yurteri, Ryan et al. 1987). The error is estimated at 5% with measured values within 3% of those reported previously in literature (Mackay, Shiu et al. 1979). However, error could be 10-15% for sparingly soluble compounds that may sorb to vessel walls (Mackay and Shiu 1981). The primary source of error was the determination of initial equilibrium (Mackay, Shiu et al. 1979). To help reduce this source of error, columns with variable liquid volumes were used with the assumption that as liquid depth decreased, the contact time decreased, and the extent of equilibration would also be reduced. In addition, compounds with lower H and higher solubility (like NH_3) will approach equilibrium more quickly.

Equipment: Low-pressure line regulator (Matheson Model-70), rotameter (Brooks Sho-Rate 15-, Model 1355-02B-V), soap bubble flow meter (to measure exit flow rate), glass stripping vessel with sintered glass disk

Dynamic Headspace Method

This method has been described previously by Lee *et al*. (2013) to introduce undergraduate students to the chemistry laboratory. This experimental setup utilizes a bubble column (for solubility determination) and gas chromatography (for analysis of the volatile organic carbon molecule of interest). This method allows for determination of both Henry's law constant and the hydrolysis loss rate and requires only relative concentrations of the solute in the gas phase with respect to time based on Eqn. 19 where C_0 and C_t are the concentration of solute in the gas phase at equilibrium and at time, t, after equilibrium, respectively, k is the first order hydrolysis loss rate (sec-1), Φ is the gas flow rate, V is the volume, T is the temperature and R is the idea gas law constant. Figure 3 represents a schematic for determination of toluene solubility in water.

$$ln\frac{C_0}{C_t} = \left[\frac{\phi}{H_{cp}RTV} + k\right] \times t \qquad \text{Eqn. 19}$$

In this method a gas solution (N_2 + compound of concern) through water (600 mL for toluene and 80 mL for benzene nitrile) under atmospheric pressure at variable flow rates (500-800 cm^3/min for toluene and 700-1600 cm^3/min for benzene nitrile) with continuous monitoring of the gas phase. Generally, a more highly soluble compound utilized an experimental setup with lower volume of water and faster flow rates.

Equipment: fritted (6 mm diameter) bubble column, water bath, thermometer
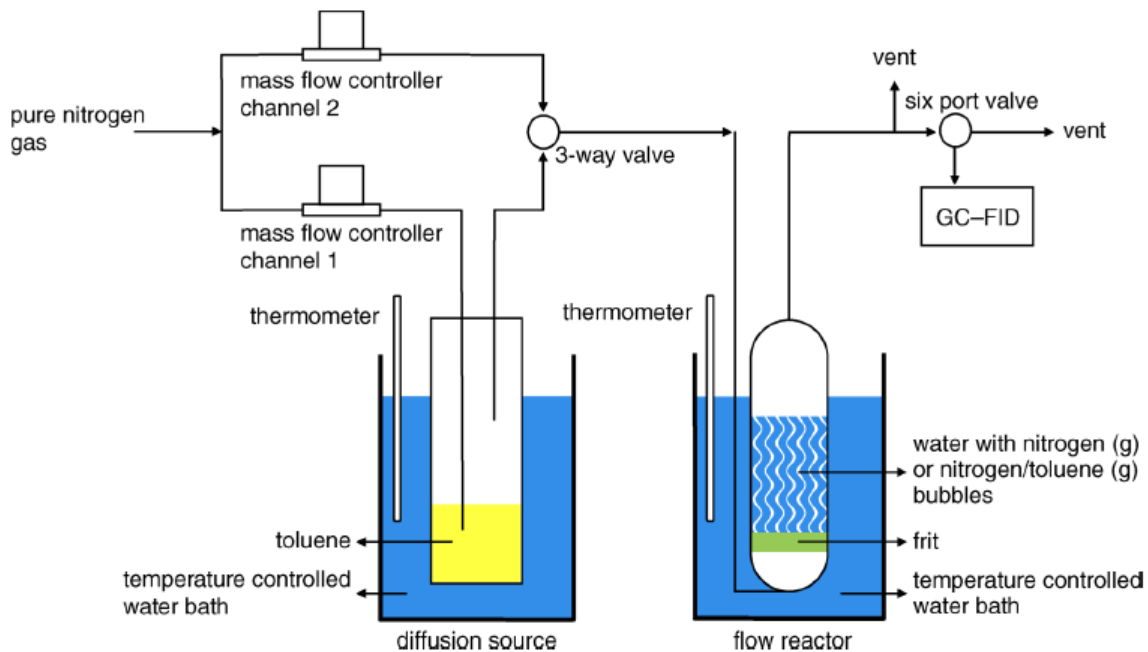
Figure 3: Schematic for Dynamic Equilibrium method for determination of Henry's constant (Lee, Mukherjee et al. 2013)

Methods for Measuring the Partitioning of Gases between the Solid and Liquid Phase in Environmental Systems

Laboratory Methods

Helminen et al. (2000)

Helminen (2000) measured equilibrium adsorption of gaseous NH_3 to solids by a static (batch) volumetric method with four grams of sorbent (zeolite, silica gel, alumina or activated carbon). This method utilized a pressure chamber and measured multiple isotherm points by calculating

adsorbed fractions based on initial and equilibrium pressures, system volumes and temperatures (Helminen, Helenius et al. 2000).

Equipment: Diffusion pump (Leybodiff 40), rotary oil pump (Edwards Speedvac 2), pressure gauge unit (Leybold-Heraeus Inficon CM3), capacitance manometer gauge for $0 - 1.33$ kPa range (LH Inficon CM100-G1000A), thermocouple, temperature-controlled water batch for 298 $- 343$K, electrically heated mantle, sample flask, liquid N_2 trap

Liang (2011)

A dissertation by Liang (Liang 2011) measured partitioning between broiler litter and water by equilibration without headspace in a glass jar sealed with Parafilm. Because Parafilm is permeable to water vapor (1 g/m^2-d) and ammonia has similar properties (molecule size and polarity), it may allow some ammonia to escape. However, without headspace, the authors theorized that ammonia escape was negligible as diffusivity in liquid is several orders of magnitude lower than air. Further, Henry's law constants were approximated for field-moist broiler litter (150 g) mixed with 450 mL of distilled deionized water at 23°C in a closed system (20.8 L total) based on measurement of outlet gas by photoacoustic spectrophotometer and aqueous NH_3(aq) by ion sensitive electrode every five minutes. The concentration of NH_3(aq) in suspensions was ~$2.7 \times 10_{-4}$ mol/L. The gas to liquid ratio is ~0.04 based on the assumption that the density of broiler litter is ~432 g/L as reported by Chastain (Chastain, Camberato et al. 2001). It is notable that the Henry's constants are within 5% of reported values for dilute aqueous solutions (Liang 2011).

Equipment: magnetic stir plate and stir bar, glass jar (8.5 cm diameter x 16 cm height), Parafilm, pH meter and electrode, ammonia ion selective electrode (Fisher Scientific, Model 13-620-508), air-tight container (Lock & Lock, 45 cm x 29 cm x 23.5 cm)

Kithome et al. (1999)

One gram zeolite was mixed with 20 mL of 840.6 mg as N/L of NH_4^+ and equilibrated on a shaker at 200 rpm for $5 - 180$ minutes at variable temperature. The aqueous phase was analyzed spectrophotometrically. Then, following a washing step in a 1:1 deionized water and acetone mixture, adsorbed NH_4^+ was extracted in 1 M KCl (Kithome, Paul et al. 1999).

Singandhupe and Rajput (1989)

Singandhupe and Rajput utilized a method described previously by Ventura and Yoshida which placed a semi-closed system in the fields consisting of a bottomless clear glass bottle (12.6 cm in diameter) with a Petri dish suspended with glass wool impregnated 25 mL of 1 N H2SO4 with a rubber stopper and glass tubbing to equalize pressure (Ventura and Yoshida 1977, Singandhupe and Rajput 1989).
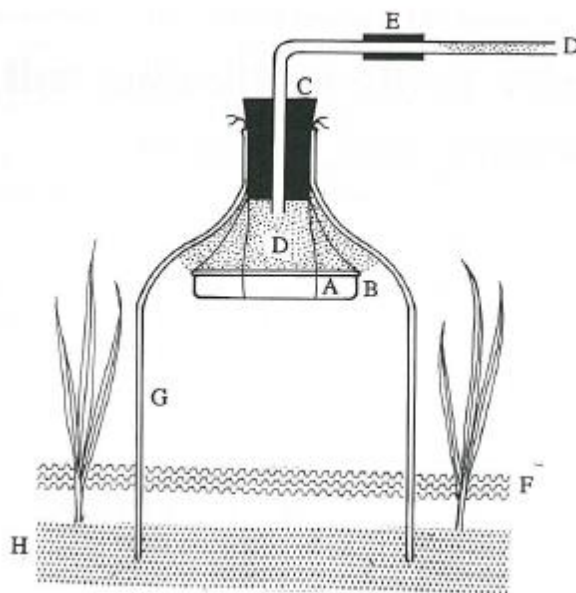
Figure 4: Schematic representation of the experimental setup utilized by Singandhupe and Rajput where A – wire, B – petri dish, C – rubber stopper, D – glass wool, E – glass tubing, F – water level, G – glass bottle, H – soil (Singandhupe and Rajput 1989)

Recommendations and Conclusions

For Sample Preparation

If there is greater than one hour prior to measurement, samples will be acidified with 0.8 mL H_2SO_4/L sample and stored in the refrigerator. By acidifying in sulfuric acid, samples can later be analyzed by colorimetric or NH_3(g)-sensing electrode (following pH adjustment back above 11) methods with minimal volatilization losses.

For NH$_3$/NH$_4^+$ Measurement

For measurement of aqueous NH$_3$/NH$_4^+$, both the gas-sensitive electrode and the Nesslerizaation colorimetric method will be employed as complementary techniques. The electrode will be used due to its ease of use and ability to measure NH$_3$(aq) ions. However, select samples will also be analyzed by the colorimetric method to confirm accuracy. The Nesslerization colorimetric method has an applicable range of detection (detection limit of 2 µg NH$_3$-N/L with an upper range of 5 mg NH$_3$-N/L), rapid protocol and avoids alkalinity interferences through the addition of EDTA or Rochelle salt instead of a lengthy distillation step making it the simplest colorimetric method for total NH$_3$/NH$_4^+$ (with the least pretreatment).

For Determination of Partitioning

NH$_3$ can be introduced to the aqueous phase either as a gas or dissolved from a solid salt (like NH$_4$Cl) for determination of partitioning based on previous work (Ayers, Gillett et al. 1985, Arogo, Westerman et al. 2003). Both equilibrium and dynamic methods discussed in this review could be applied to environmental systems with solids as described previously and may include sampling at variable time points depending on the experimental setup. Static headspace (or batch) methods like the internal standard method and the modified EPICS method described by Robbins *et al*. (1993) and Ramachandran *et al*. (1996) are the most applicable to measurement of highly soluble species (like NH$_3$). While the aqueous to gas phase ratios have yet to be chosen, it must be noted that these experiments may require a large gas phase to have a measureable change in the aqueous phase due to the high solubility of the experiments. However, it would be simple to include soils in these systems at a later date. These experiments could also be designed with sacrifical samples to estimate the kinetic rate of partitioning if deemed useful.

The rate of loss of NH$_3$/NH$_4^+$ and Henry's constant could also be accurately measured by measuring the loss from a dynamic system using Mackay's (the dynamic headspace method is a similar method and should be applicable) methods. It must be noted that the dynamic systems must measure the rate of loss of the contaminant of concern to simplify the number of variables changing with time. Measurement during injection of NH$_3$ is not feasible in an open system because there is a rate of partitioning to the aqueous phase and a rate of loss from the aqueous phase simultaneously leading to two unknowns. Any experiments carried out with dynamic systems (with flow) will be run with a flow rate of 20 mL/min in order for comparison to

previous experiments (Zhong, Szecsody et al. 2015). Future issues may arise with the dynamic experimental setup as pH, conductivity and temperature may not be monitored continuously during the experiment. In addition, the current equipment would need to be modified to allow for appropriate mixing for experiments with Hanford soil present. The aqueous phase would also be difficult to measure as the column (Pyrex 31760) must be opened for sampling. However, gas phase measurements could be monitored through the use of acid traps followed by measurement of the aqueous concentration in the acid traps with the gas sensing electrode or colorimetric method and the current equipment may be modified to allow for simpler measurement and monitoring. Although previous works reported a significantly higher flow rate (3-4 L/min) when using gas traps, experiments would follow similar protocols (100 mL of 0.05 mol/L sulfuric acid) for acid traps and would utilize two traps in parallel in the event that 100% is not recovered within the first trap. It is likely that the recovery will be greater due to the decreased flow rate as noted previously where a decrease in flow rate of two led to a 4% increase in recovery (Ndegwa, Vaddella et al. 2009). The second acid trap will be necessary as previous scientists reported efficiencies near 80% for recovery of NH_3 masses greater than 100 mg (Ndegwa, Vaddella et al. 2009). Current experiments in open beaker systems (similar to preliminary experiments by Zhong *et al*.) have not reached greater than 52 mg of NH_3 in 100 mL aqueous suspensions (0.034 mol/L) (Zhong, Szecsody et al. 2015). However, it is likely that the total volume will be increased to 200 mL with the column setup. In addition, the height of acid that the gas bubbles through will be maximized in the traps as Ndegwa *et al*. also noted an increase in efficiency with increases in height of acid solutions.

Additional Considerations

For determination of partitioning, experiments should be conducted at constant ionic strength to allow for simpler modeling and to reduce the number of parameters changing throughout experiments. If batch partitioning experiments are performed, they should be at pH ~12 as > 99% of the NH_3/NH_4^+ will be present as NH_3 and a buffer will not be required to stabilize the pH. Figure 4 below summarizes the buffering capacity of 0.1 mol/L concentrations of common buffers within the basic pH range. At pH 12, the theoretical concentration of OH^- required to change the pH by 0.1 pH units is 2.3×10^{-3} mol/L without a buffer and 4.67×10^{-3} mol/L with 0.1 mol/L piperidine buffer (as shown in Figure 4-5 below). It will not be necessary to add an additional buffer for experiments unless NH_3 additions lead to concentrations that are greater

than 1.3 mol/L (current beaker experiments have reached a maximum of 0.034 mol/L) and addition of piperidine buffer will only double the buffering capacity (assuming that a pH fluctuation of up to 0.1 pH units is acceptable). Therefore, an additional buffer will not be necessary and will greatly simplify speciation calculations.
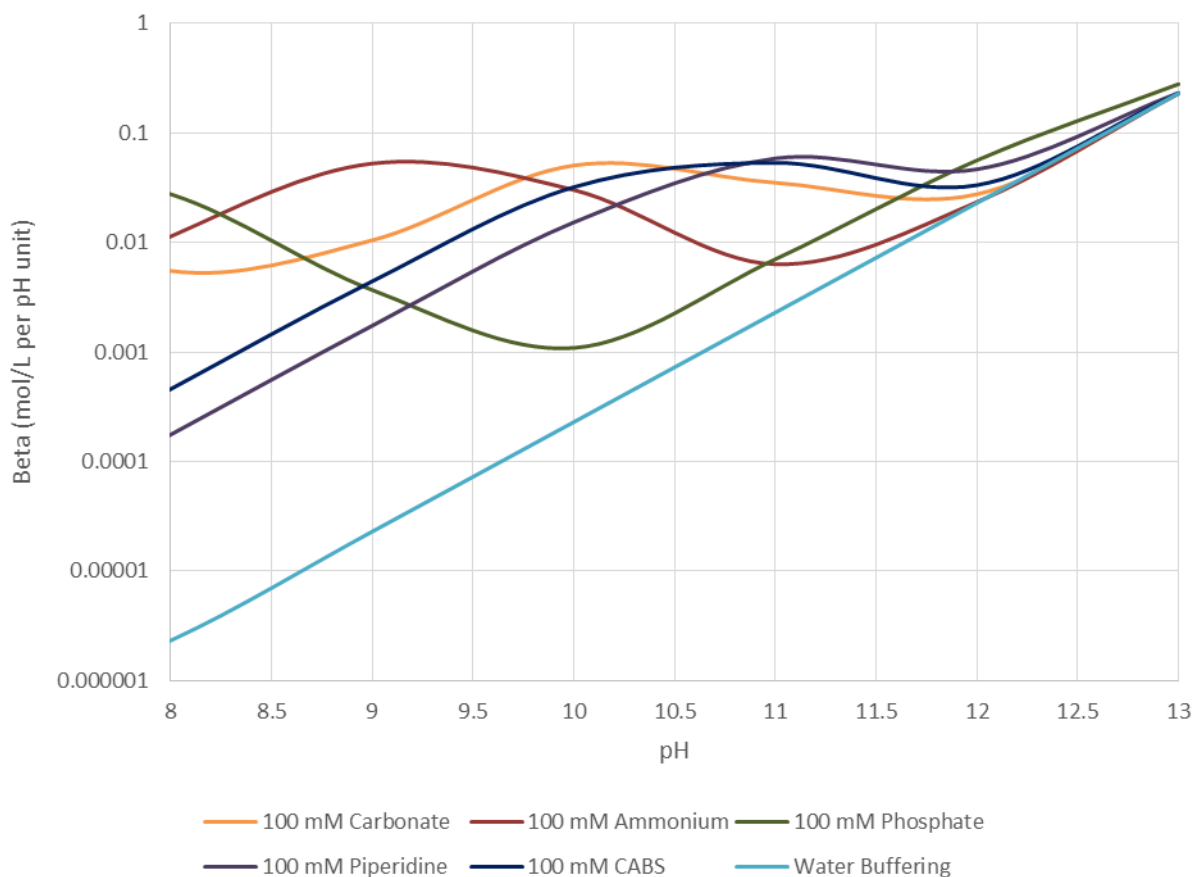

Figure 4: Buffering capacity in terms of mol/L of strong acid or base per pH unit versus pH for 100 mM concentrations of common buffers
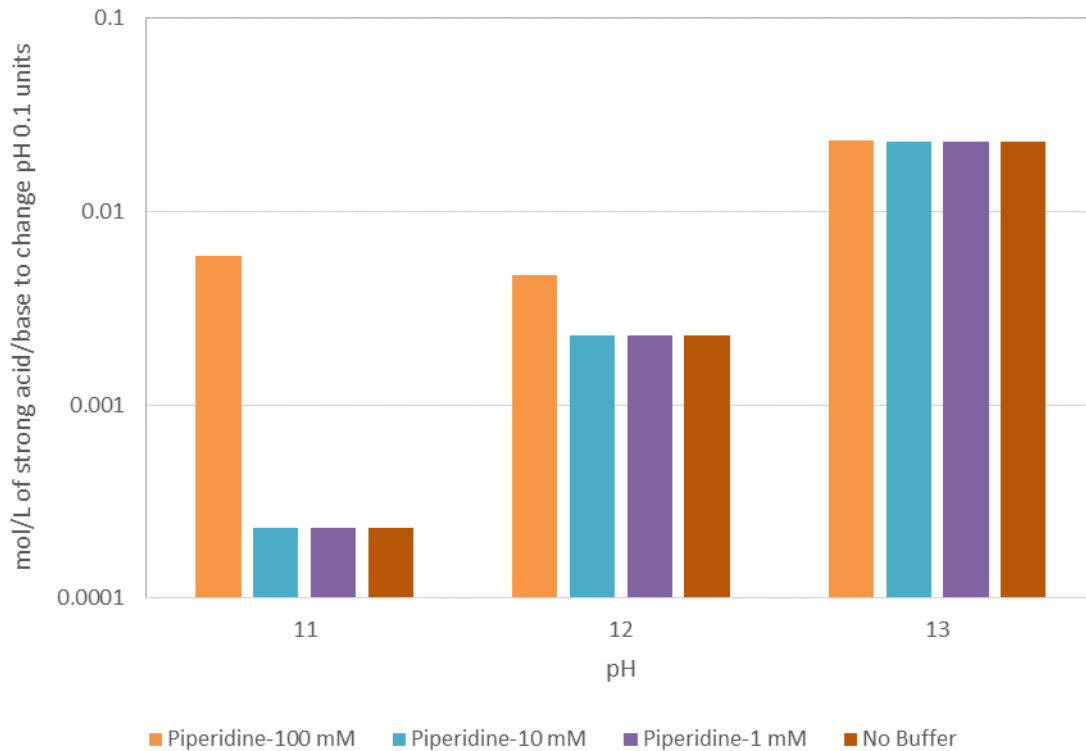
Figure 5: Comparison of the amount of strong acid or base required to change the pH of a suspension originally at pH 11, 12 or 13 by 0.1 pH units for variable concentrations of piperidine buffer and water

Note: 0.1 pH units was chosen as an acceptable fluctuation in pH for these experiments

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