

# **CEC and Kd Determination in Landfill Performance Evaluation**

**A Review of methodologies and preparation of standard materials for  
laboratory analysis**

**R&D Technical Report P1/254/01**

# **CEC and $K_d$ Determination in Landfill Performance Evaluation**

## **A Review of methodologies and preparation of standard materials for laboratory analysis**

R&D Project Record P1/254/01

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This report summarises CEC and  $K_d$  methodologies, the results of validation experiments, and recommends methodologies for the determination of CECs and  $K_{ds}$ . The information within this document is for use by EA staff and others wishing to study and model pollutant migration around landfill sites.

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# CONTENTS Page

## LIST OF TABLES II

## LIST OF FIGURES ERROR! BOOKMARK NOT DEFINED.

<b>1.</b>	<b>INTRODUCTION</b>	<b>1</b>
<b>2.</b>	<b>DETAILS OF SAMPLED LITHOLOGIES</b>	<b>1</b>
2.1	Mercia Mudstone Group	1
2.2	Lower Oxford Clay	1
2.3	Lower Chalk	1
2.4	Gault Clay	2
2.5	Sherwood Sandstone Group	2
2.6	Lincolnshire Limestone	2
<b>3.</b>	<b>LABORATORY METHODS</b>	<b>2</b>
3.1	Sample preparation	2
3.2	X-ray diffraction analysis	3
3.3	CEC methodologies	3
3.4	Statistical evaluation of the CEC data	7
3.5	$K_d$ methodology	9
	<b>APPENDIX</b>	<b>A-1</b>

## LIST OF TABLES

Table 3.1	Results from tests for normality (Geary's A) and for outliers (Grubb's T and the coefficient of skewness), with critical values at the 99% confidence level for these tests.	7
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## **1. INTRODUCTION**

This R&D Project Record accompanies R&D Technical Report P340. It contains all the analytical data, statistical evaluation data, sample details and laboratory procedures generated by the British Geological Survey in the course of completing a series of CEC and  $K_d$  validation experiments on behalf of the Environment Agency.

## **2. DETAILS OF SAMPLED LITHOLOGIES**

### **2.1 Mercia Mudstone Group**

Dorket Head Quarry [SK 595 465] Ibstock Building Products Ltd. The brick pit at Dorket Head exploits mudstones from the lower 20 metres or so of the Gunthorpe Formation. Two clays are quarried in the brick pit, the Red Clay and the Ivory Clay. The Red Clay is a 14.5 metre thick, reddish brown, blocky silty mudstone. Strongly cemented, dolomitic, coarse siltstone layers 30 cm thick comprise 10% of the thickness of the unit, and are known locally as 'skerries'. The Ivory Clay, which occurs higher in the sequence, is a reddish brown, blocky siltstone up to 2.3 metres thick, which is weathered more intensely than the Red Clay. The sample comes from a stockpile of screened material at the quarry and is representative of both clays.

### **2.2 Lower Oxford Clay**

Quest Quarry [TL 030 425] Hanson Brick Ltd. The Lower Oxford Clay comprizes bituminous shales and calcareous mudstone, which contain about 5% of finely divided carbonaceous material. The top 6 metres of material in the quarry is discarded because of its low calorific value in its weathered state. Approximately 15 metres of material underlying this is excavated, leaving 1 metre of material above the Kellaway Sands. The sample was collected from the hopper which links the excavation bucket to the brick factory, and is representative of this 15 metre section. A number of the former quarries in this area are being used as landfills. Further information on the Lower Oxford Clay is contained in Highley and Cameron (1995).

### **2.3 Lower Chalk**

Barrington Quarry [TL 396 504] Rugby Cement. This sample was collected from recently worked material at the quarry face. The Totternhoe Stone hard band is prominent in the face and is probably well represented in the sample. The Totternhoe Stone is underlain by the Chalk Marl, a rhythmic sequence of bluish grey marls and hard buff marly limestones, and is overlain by the Grey Chalk a greyish-white to white massively bedded chalk containing numerous pyrite nodules. A description of this unit, including chemistry, is given in Harrison et al. (1990).

## **2.4 Gault Clay**

Barrington Quarry [TL 396 504] Rugby Cement. The Gault is a Lower Cretaceous sequence of clays, mudstones, thin siltstones and occasional thin bands of phosphatic nodules. The sample was collected from outcrop in an area at the base of the quarry which is due to become a landfill site for cement kiln dust, a special category waste generated by the cement plant. Further information about the Gault may be found in Forster et al. (1994).

## **2.5 Sherwood Sandstone Group**

Burntstump Quarry [SK587 500] Tarmac Quarry Products Yorks and East Midlands. The quarry extracts the Nottingham Castle Sandstone, the upper of two formations defined in the Sherwood Sandstone Group in the area. The rock is a buff to pale red-brown sandstone with subordinate conglomerate, siltstone and mudstone. Marl horizons are visible in the quarry face, but none was included in the sample, which was collected from the quarry face prior to screening. Details of the local geology are given in Charsley et al. (1990).

## **2.6 Lincolnshire Limestone**

Longwood Quarry [TF 062 593] is one kilometre southwest of the village of Blankney in Lincolnshire. The formation is of Bajocian (Middle Jurassic) age, and was worked at the quarry for building stone and agricultural lime. A license for inert waste exists in part of the quarry. The sampled material is from boreholes drilled as part of a NERC/AFRC funded project into 'Pollutant transport in soils and rocks'. The boreholes appear to intersect the Lower Lincolnshire Limestone Formation, from the Blankney to Sproxton Members.

# **3. LABORATORY METHODS**

## **3.1 Sample preparation**

30 kg of each sample was crushed to 2 mm nominal maximum particle size using a laboratory jaw crusher, then dried (apart from the Gault Clay, Lower Oxford Clay and Lower Chalk) in a fan-assisted oven at 35 °C for 24 hours, before homogenization on a roller blender for a further 24 hours. Sub-samples were separated at this stage for the  $K_d$  validation experiments. 20 kg of each homogenized sample was stored for future use.

10 kg of each homogenized sample was reduced to  $<200 \mu\text{m}$  for further  $K_d$  experiments and for the CEC validation experiments using several methods: rotor-speed mill fitted with a 200 microns internal screen (Mercia Mudstone, Gault Clay); agate tema mill (Sherwood Sandstone, Lower Oxford Clay and Lower Chalk); cross-beater mill fitted with a 200 microns internal screen (Lincolnshire Limestone). The resulting  $<200 \mu\text{m}$  fractions were re-homogenized on a roller blender for 6 hours then sub-sampled into 100 x 100 g test samples using a rotary sample splitter, and stored in sealable containers.

## 3.2 X-ray diffraction analysis

XRD analysis was used to establish the bulk and clay mineralogy of the samples.

### 3.2.1 Sample preparation

For whole rock (bulk) analysis, about 3 g of each crushed sample was micronized under acetone for ten minutes, dried in an oven at 55 °C then back-loaded into standard aluminium sample holders.

For clay mineral analysis, a <2 μm fraction oriented mount was prepared using about 20 g of jaw-crushed material per sample. The Lincolnshire Limestone and Lower Chalk samples were hand-ground in a pestle and mortar to pass a 500 μm sieve, then leached using buffered sodium acetate/acetic acid at pH 5.3 to remove carbonate and facilitate extraction of the clay. The other samples were hand-crushed to <2 mm. The crushed and/or leached samples were dispersed in 150 ml of de-ionised water using ultrasound for approximately 3 minutes. The resulting suspensions were sieved on 63 μm and the <63 μm fraction placed in a 250 ml measuring cylinder and allowed to stand. 1 ml of 0.1 M 'Calgon' (sodium hexametaphosphate) was added to the suspensions to prevent flocculation. After a period dictated by Stokes' Law, a nominal <2 μm fraction was removed and dried at 55 °C. 100 mg of the <2 μm material was re-suspended in a minimal amount of distilled water and pipetted onto a ceramic tile in a vacuum apparatus to produce an oriented mount. The clay mounts were Ca-saturated using 2 ml 1 M CaCl<sub>2</sub>·6H<sub>2</sub>O solution and washed twice to remove excess reagent before being air-dried.

### 3.2.2 Analysis

XRD analysis was carried out using a Phillips PW1700 series diffractometer using Co-Kα radiation and operating at 45 kV and 40 mA. For bulk analysis the micronized powder mounts were scanned over the range 2-50 • 2θ at a scanning speed of 0.7 • 2θ /minute. The oriented mounts were scanned over the range 1.5-32 • 2θ in both air-dried and ethylene glycol-solvated states at a scanning speed of 0.5 • 2θ /minute. Diffraction data were analysed using the PC-based Phillips X'Pert software coupled to an ICDD database.

Labeled XRD profiles obtained from the oriented mounts of the fine fractions are presented in the Appendix as Figures 1 to 6.

## 3.3 CEC methodologies

### 3.3.1 BaCl<sub>2</sub>/triethanolamine method

#### Reagents

- Triethanolamine solution, pH = 8.1: dilute 90 ml of triethanolamine ([HOCH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>N) with water to about 1 litre and adjust the pH to 8.1 by adding about 140 – 150 ml of 2 N HCl. Dilute with water to 2 litres, mix and protect from carbon dioxide during storage.



- Barium chloride solution (2 N): dissolve 244 g of barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in water and dilute to 1000 ml with water.
- Buffered  $\text{BaCl}_2$  reagent: mix equal volumes of triethanolamine solution and barium chloride solution.
- Magnesium sulphate solution (0.05 N): Dissolve 6.20 g of magnesium sulphate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) in water and dilute to 1000 ml.
- EDTA solution (0.02 N): dissolve 3.723 g of EDTA (disodium salt) in water and dilute to 1000 ml.
- Ammonia buffer: dissolve 7 g of ammonium chloride in 57 ml of ammonia solution, s.g. 0.88, and dilute to 100 ml with water.
- Indicator: dissolve 0.25 g of Solochrome Black 6B in 50 ml of ethanol.

### Procedure

1. Weigh 5.0 g of sample into a 250 ml poly bottle.
2. Note the weight of the bottle and its contents (M1).
3. Add 100 ml of buffered  $\text{BaCl}_2$  reagent and agitate the mixture on a shaker for 1 hour.
4. Centrifuge at 1500 rpm for 15 minutes and discard the supernatant liquid.
5. Add a further 200 ml of buffered  $\text{BaCl}_2$  reagent.
6. Agitate the mixture for 1 hour on a shaker then leave overnight.
7. Centrifuge at 1500 rpm for 15 minutes and discard the supernatant liquid.
8. Add 200 ml of distilled water and agitate on a shaker for a few minutes.
9. Centrifuge at 1500 rpm for 15 minutes and discard the supernatant liquid.
10. Note the weight of the bottle plus contents (M2).
11. Pipette 100 ml of  $\text{MgSO}_4$  into the bottle, mix well and leave for 2 hours, agitating on a shaker occasionally.
12. Centrifuge at 1500 rpm for 15 minutes and decant the supernatant liquid into a stoppered flask or bottle.
13. Pipette a 5 ml aliquot of this solution into a 100 ml conical beaker and add 5 ml of ammonia buffer, plus 6 drops of indicator.
14. Titrate with standard EDTA (Titre A1 ml).
15. Titrate a 5 ml aliquot of  $\text{MgSO}_4$  (Titre B ml).

## Calculation

The sample titre (A1) must be corrected for the effect of the volume of liquid retained by the centrifuged sample after the water wash:

$$\text{Corrected titration (A2)} = A1 \frac{(100 + M2 - M1)}{100 \text{ ml}}$$

$$\text{CEC} = (B - A2) \times \frac{100}{5} \times 0.02 \times \frac{100}{5}$$

$$= 8(B - A2) \text{ meq/100 g}$$

If the CEC exceeds 50 meq/100 g the determination should be repeated using less sample and the calculation adjusted accordingly.

### 3.3.2 SrCl<sub>2</sub> method

#### Procedure

1. Weigh 2.50 g of sample into a disposable centrifuge tube.
2. Add 40 ml of 1.26 M SrCl<sub>2</sub>·2H<sub>2</sub>O (33.59%).
3. Shake on a flatbed shaker for 10 minutes at 250 rev/min.
4. Centrifuge at 2500 rpm for 10 minutes.
5. Decant 20-25 ml into a sterilin tube for analysis by ICP-OES (see below).

Five portions of HN05 and PCB standards were prepared and analysed using 1.25 g sample. A blank was also prepared.

Three portions of Gault Clay, Lower Chalk and Sherwood Sandstone plus a blank were also extracted in 40 ml portions of 0.63 M SrCl<sub>2</sub>·2H<sub>2</sub>O.

Note: to reduce costs, the sample-solution ratio described above is scaled-down compared to that described originally by Edmeades and Clinton (1981); 2.5 g of sample in 40 ml of reagent compared to 5.0 g of sample in 80 ml of reagent.

#### Analysis

Individual cations extracted in the SrCl<sub>2</sub> solution were analysed by ICP-OES (Inductively coupled plasma optical emission spectrometry) at the British Geological Survey using a Fisons/ARL 3580 Quantovac machine. All solutions were run at x20 dilution (0.063 M,

16.8 g/litre). Standards were matrix-matched and a five point calibration used up to the following range maxima:

Al 1 ppm; Ca 100 ppm; K 5 ppm; Mg 5 ppm; Mn 1 ppm; Na 5 ppm.

The Lincolnshire Limestone and Lower Chalk samples were diluted further to confirm the high Ca values, which were over-range for the calibration.

### 3.3.3 Methylene Blue (MB) method

#### Procedure

1. Weigh 2.00 g into a 600 ml beaker and add 300 ml de-ionised water. (Note: a sample mass smaller than 2 g can be used if the CEC is known to be high).
2. Place a magnetic stirrer into the beaker, place on a magnetic stirring plate and mix until the sample is dispersed uniformly.
3. Determine the pH of the slurry and add sufficient sulphuric acid (0.1 N) to bring the pH to between 2.5 and 3.8. Continue stirring whilst the pH is being adjusted and for a further 10 to 15 minutes after the last addition of acid.
4. Re-test the pH and add, if required, more acid to restore the pH to within the desired range.
5. Using a burette, add 5 ml of methylene blue solution to the slurry and stir for a further 1 to 2 minutes.
6. Using a glass stirring rod take a drop of slurry and place on the edge of a piece of filter paper.
7. Observe the appearance of the drop. The end point is indicated by a light blue halo around the edge of the drop. Add further methylene blue solution in 1 ml increments (up to 5 ml if the CEC is known to be high) with 1 to 2 minutes stirring after each addition until the end point is reached.
8. When the end point is thought to be reached, continue stirring for a further 2 minutes and re-test. Add more methylene blue solution if necessary, stir for 2 minutes and re-test again.

#### Calculation

$$\text{MBI meq/100 g} = (E \times V/W) \times 100$$

Where: E = milli-equivalents of methylene blue per ml  
V = ml of methylene blue solution added per sample  
W = weight of sample (corrected for moisture at 105 °C)

The pH of samples with high calcite levels was adjusted using 5 N sulphuric acid.

### 3.4 Statistical evaluation of the CEC data

#### 3.4.1 Homogeneity testing

Ten splits of each of Lower Chalk (LC), Sherwood Sandstone (SS), Gault Clay (GC), Lower Oxford Clay (LOC) and Lincolnshire Limestone (LL) were analysed in duplicate. Ten splits of a coarser fraction of the Sherwood Sandstone (SSC) were analysed in duplicate. Ten splits of Mercia Mudstone (MM) were analysed in triplicate. CEC analysis was performed using the BaCl<sub>2</sub>/triethanolamine method.

The homogeneity of the materials has been assessed by statistical analysis of the data derived from these analyses. For each sample, the data set was tested for normality using Geary's A-test, then tested for outliers using Grubb's T-test and the coefficient of skewness. The results of these statistical tests are shown in Table 1.

**Table 3.1 Results from tests for normality (Geary's A) and for outliers (Grubb's T and the coefficient of skewness), with critical values at the 99% confidence level for these tests.**

	MM	LC	SS	GC	LOC	LL	SSC	Critical values		
								n=20	n=30	
Geary's A	0.839	0.755	0.820	0.899	0.858	0.902	0.791	upper	0.905	0.886
								lower	0.688	0.707
Grubb's T	1.840	2.215	1.929	2.059	1.783	1.606	2.001	2.884	2.745	
Skewness	-0.214	0.530	-0.325	0.687	0.100	0.239	-0.157	1.11	0.986	

Data for MM were calculated from 30 data points and use critical values for n=30.

Data for the other materials were calculated from 20 data points and use critical values for n=20.

All the data sets satisfy a normal distribution at the 99% confidence level i.e. all calculated values of Geary's A fall within the range defined by the upper and lower critical values. No outliers were identified by the tests used i.e. all calculated values of Grubb's t and the magnitudes of the coefficients of skewness were less than the respective critical values. Although it is common to perform statistical tests at the 95% confidence level, the 99% confidence level was used in this study owing to the lower accuracy inherent in the analytical method compared to modern instrumental methods.

Initial assessment showed an apparent bias between the different batches of data. This was assessed by the F-test for sample variance and then the t-test, assuming equal variance or unequal variance, as appropriate, depending upon the outcome of the F-test. The significance of the difference between between-sample variance and within-sample variance was tested by analysis of variance (ANOVA). An overall mean, standard deviation and relative standard deviation (RSD) were also calculated for those materials in which a bias between the

analytical batches was identified, and for SSC data which are distributed less tightly. All statistical tests were conducted using Microsoft Excel. Results of these further statistical tests are presented in Tables A1-A7 of the Appendix.

A material can be described as homogenous if the between-sample variance is not significantly greater than the within-sample variance at a given confidence level. If  $F$  is less than  $F_{\text{critical}}$  then the difference between the between-sample variance and the within-sample variance is not significant at the 99% confidence level. A value of  $F < 1$  indicates that the between-sample variance is less than the within-sample variance.

The t-test identified significant bias between the two batches of analyses of LC, SS, GC and LL. Any bias between the batches for MM, LOC and SSC was found to be not significant at the 99% confidence level.

The between-sample variance for MM and SSC is not significantly greater than the within-sample variance at the 99% confidence level. The low value of  $F$  calculated after ANOVA for OxC means that the criterion for homogeneity is satisfied by default. The low values of  $F$  ( $\ll 1$ ) calculated after ANOVA for LC, SS, GC and LL are likely to be caused by the large discrepancies between the two batches of data, as identified by the t-test. However, analysis of all twenty data for these latter four materials shows a relative standard deviation of between 5% and 10%. These materials may therefore be sufficiently homogeneous to allow determination of CEC with an error of  $\pm 10\%$ , bearing in mind the bias identified by the t-test.

In summary, MM, LOC and SSC are sufficiently homogeneous (at the 99% confidence level) for use as reference materials for the determination of CEC by the  $\text{BaCl}_2$ /triethanolamine method, although the spread of data in SSC is greater than that of MM and LOC. The statistical tests identify too great a bias between batches of analytical data for an assessment of the homogeneity of LC, SS, GC and LL. However, these materials may be sufficiently homogeneous to allow determination of CEC with an error of  $\pm 10\%$ .

### 3.4.2 Comparison of methodologies

Replicate analyses were made by each of the methods for each of the materials. Five replicate sub-samples were taken from one split and analysed by the  $\text{SrCl}_2$  method. Five (or three of GC and LL) replicate sub-samples were taken from the same split and analysed by the MBI method. As described above, two or three replicate sub-samples were taken from the same split and analysed by the  $\text{BaCl}_2$ /triethanolamine method. Data from five different splits were used for the comparison exercise because the  $\text{BaCl}_2$ /triethanolamine method was used on fewer splits than the two other methods because the observed bias between batches described above might have influenced the comparison unduly. Data from each of these splits, together with calculated means and standard deviations, are presented in Table A8 of the Appendix.

The MBI method generally gives rise to lower CEC values than the other methods. The  $\text{SrCl}_2$  method generally gives rise to higher CEC values than the other methods, an order of magnitude higher for LC, GC and LL. Broadly speaking, the precision of the  $\text{SrCl}_2$  and  $\text{BaCl}_2$ /triethanolamine methods is comparable and tends to be better than the MBI method. Further comment on the differences between the methods is not possible as the source data come from splits sub-sampled in different ways.

## 3.5 $K_d$ methodology

### 3.5.1 Introduction

The following sections describe research undertaken to determine  $K_d$  for aqueous ammonium ion on the geological materials described in Section 2. Consideration of the likely generation and fate of contaminants in landfill leachate highlights  $K_d$  for ammonium ion as an appropriate input for LandSim (see accompanying R&D Technical Report P340).

Although the term  $K_d$  is used to describe the quantity determined in these experiments, it should be borne in mind that what is actually being determined should strictly be referred to as  $R_d$ . The distribution coefficient ( $K_d$ ) is a true thermodynamic quantity, which applies to simple reversible systems that are in equilibrium, and is in practice difficult to determine. On the other hand, the distribution ratio ( $R_d$ ), determined in laboratory experiments, is empirical and measures overall sorption regardless of the contributions of the various sorption processes (Reardon, 1981). A batch technique was employed to determine  $K_d$  experimentally in preference to flow-through columns; compared to column experiments, the batch method is relatively simple, inexpensive and can generate rapidly a considerable amount of data. Technical difficulties of high back-pressure (with subsequent failure/leakage of fittings etc) and elution of fines when attempting to achieve flow through columns of finely ground materials led to this aspect of  $K_d$  study being abandoned. However, a recently conducted field study (Trick et al. 1999) examining retardation of ammonium ion through the Sherwood Sandstone, yielded  $K_d$  values between 1.1 ml/g and 1.6 ml/g. These are in close agreement with the batch  $K_d$  value of about 1.3 ml/g derived in this study.

### 3.5.2 Preliminary work

Three initial batch experiments ( $K_d$  Expt 1 to  $K_d$  Expt 3) were performed using a colorimetric method for ammonium ion determination (Fraser and Russell, 1969). However, this was laborious and prone to interferences. Subsequently, a fast and robust gas-sensing electrode technique (Section 3.5.3) was adopted which provided an inexpensive and much more effective way of measuring ammonia in aqueous solutions. Use of the electrode is specified in the recommended methodology.

#### Calibration curve (Colorimetric determination)

A number of ammonium chloride standards ranging from 0 to 5 mg/l were prepared. To these were added specific reagents (see below), before colour development by heating in a water bath at 37 °C for 10 minutes. Absorbance of the standards was measured in 1 cm glass cuvettes on a Pye UniCam SP8-100 dual beam spectrophotometer set to 667 nm with a bandwidth of 1nm. The reference cuvette contained purified water (Purite)\*.

- Ammonia: top standard containing 4.815 mg/l ammonium chloride in Purite.
- Reagent A: 8.5% sodium salicylate/ 0.06% sodium nitroprusside in Purite.
- Reagent B: 0.25% sodium dichloroisocyanurate in 0.3 M sodium hydroxide.
- \*Purite: Distilled, de-ionised, charcoal-filtered and bacteriologically-filtered water.  
(StillPlus HP, Purite Ltd, Bandet Way, Thame, Oxon, UK)

## Experimental procedure

Approximately 12 g of Mercia Mudstone was suspended in 190 ml 0.03 M NaCl in a 500 ml glass Duran bottle, and allowed to equilibrate through constant stirring. The sodium chloride was used to produce a synthetic groundwater of known ionic strength. A 1 ml portion of a known concentration of ammonium chloride was dispensed by Gilson pipette into the Duran bottle. At various time intervals, 10 ml of the slurry was removed, filtered and processed with the standard reagents noted above, and its absorbance measured by the spectrophotometer. The final ammonium concentration was determined by comparing the absorbance obtained from the sample with that generated from the calibration curve.

## Results

Results are summarized in the Appendix (Tables A.10 to A.12). They show that  $K_d$  remained roughly constant (approximately 2 ml/g) even though there was a ten-fold decrease in ammonium concentration between  $K_d$  Expt 1 and  $K_d$  Expt 2. However, there was a large standard deviation on these measurements indicative of an inappropriate solid/solutions ratio (i.e. M/V), and the accuracy of  $K_d$  in these experiments needs to be treated with some caution. These were essentially scoping experiments, and greater accuracy would be achieved by increasing M/V (see Table 1.7 in the accompanying R&D Technical Report P340).

### 3.5.3 Recommended methodology

#### Introduction

On the basis of the scoping experiments, the colorimetric method was abandoned in favour of a selective gas-sensing electrode that could measure dissolved ammonia in aqueous solutions. This produced fast, economical, accurate and reproducible results with reduced interference. The response of the electrode obeyed the Nernst equation in the range 0.01 to 18 000 mg/l ammonium ion in aqueous solution.

In response to the low  $K_d$  values obtained in the scoping experiments, the solid solutions ratio (M/V) was increased from 0.065 to 0.4 to improve the accuracy of  $K_d$ .

The following sections describe the revised procedure for determination of ammonium  $K_d$  in a range of geological materials.

#### Pre-Equilibration

Eighteen 30 ml polycarbonate Oakridge (Nalgene) centrifuge tubes with screw-cap closures were labeled then weighed. 10 g aliquots of the chosen geological material and 25 ml portions of 0.03 M NaCl were added to each tube and pre-equilibrated on a rotary shaker (Stuart Scientific Ltd) at 36 rpm.

After 72 hours, fifteen of the tubes were removed and allowed to settle under gravity. The pH of the supernatant in each was measured using an Orion pH electrode attached to an Orion EA 940 IonAnalyzer meter.

A 1 ml portion of 250 mg/l ammonium chloride concentrate was added to each of five of the tubes using a Gilson dispensing pipette; 1 ml of a 1000 mg/l solution was added to each of a further five. This resulted in ammonium concentrations of 10 and 40 mg/l, respectively. The remaining five tubes, designated as controls, received 1 ml portions of 0.03 M NaCl. The contents of each tube were mixed, allowed to settle and the pH re-measured, before all fifteen were returned to the shaker.

Meanwhile, the three untreated tubes were centrifuged at 4000 rpm for 15 minutes. To remove any colloidal material, the supernatant was filtered (MWCO 30,000 Daltons i.e. < 3 nm dia.) by centrifuging at 4000 rpm for 6 minutes in an Amicon Centriprep-30 cell (Millipore UK, Ltd). The filtrate, suitably preserved, was analysed for major cations and anions by ion chromatography. Results are presented in Table A.9 of the Appendix.

### **Equilibration**

After the 1 ml additions and a further 48 hours on the rotary shaker, the fifteen treated tubes were removed from the shaker and centrifuged for 15 minutes at 4000 rpm. After noting their weights, each supernatant was transferred to a clean Oakridge tube and its pH measured, before acidifying with 1 drop of 8 M HCl, and re-measuring the pH. The acidification was necessary to keep ammoniacal nitrogen in the ammonium ion form, preventing its loss as ammonia gas.

Each supernatant was filtered, as before, through a Centriprep cell, and the ammonium concentration of a weighed 10 g of the resulting filtrate was determined (Section 3.4).

The composition of solutions used in the pre-equilibration and equilibration stages are given on page A-9 of the Appendix.

### **Ammonia measurement**

An Orion Ammonia Electrode model 95-12 (QuadraChem Ltd.) was used in conjunction with an Orion 940A meter, set to measure millivolts (mV), attached to a printer (Citizen iDP 3540). Prior to first use, and thereafter weekly, the electrode tip was fitted with a fresh standard hydrophobic membrane. The required quantity of internal filling solution was poured into its outer body according to the instruction manual. Detailed information on use and characteristics of the electrode can be found in the instruction manual. A number of steps, outlined below, had to be taken prior to measuring samples.

### **Electrode slope**

The electrode slope test served to check that the electrode was functioning properly. 'Slope' is defined as the difference in mV observed with a ten times change in concentration. To measure the slope, 10 g Purite water was weighed accurately into a 24 ml glass vial fitted with an open-hole screw cap. 0.2 g ISA (Ionic Strength Adjuster [QuadraChem, Ltd]) was dispersed in the water using a Pasteur pipette. A small PTFE stirrer bar was placed in the solution and the vial placed on a magnetic stirrer. The ISA contains concentrated sodium hydroxide and an acid-base indicator. Any sample it is added to, unless very acidic, becomes



alkaline with pH >11, as shown by the indicator colour, and at this pH any ammonium ions in the sample are converted rapidly to ammonia which is then measured by the electrode.

The tip of the ammonia electrode was introduced carefully into the solution at an acute angle via the hole in the cap. This prevents air bubbles forming on the membrane, which can lead to erroneous results. After a short equilibration, readings were downloaded to the printer during a 3-4 minute measuring period. Since Purite water contains such low levels of ammonia, close to the electrodes' lower sensitivity range, this particular reading is subject to some variation. It did not, however, influence the final analysis.

After calculating the average of the readings taken, the electrode was removed briefly from the vial, rinsed in distilled water, and dried gently with a tissue. Before returning it to the solution, 0.1 ml of 0.1 M ammonium chloride standard (QuadraChem Ltd) was dispersed in the vial. Readings taken by the printer were noted and averaged. The electrode was removed and rinsed once more, before adding a further 1.0 ml of the standard (a ten times increase in concentration), and the readings again noted and averaged.

The difference between the readings, taken after the first and second additions of 0.1 M ammonium chloride standard, is defined as the slope of the electrode. It should fall within the range -54 to -60 mV when the solution temperature is between 20-25 °C. If a slope outside this range was obtained, the troubleshooting guide in the instruction manual was consulted before proceeding further.

### **Calibration standards**

The second step involved calibrating the electrode with standards covering the expected range of the samples to be measured. The standards chosen, 0.0001 M (approximately 1.8 mg/l) and 0.01 M (approximately 180 mg/l), were prepared from the 0.1 M ammonium chloride standard and Purite water, using a serial dilution technique.

As with the slope check, 10 g of each was weighed into a vial, and 0.2 g ISA solution dispersed in it. The more dilute standard was always measured first, the results in mV averaged, and the actual concentration in mg/l calculated. A two-point calibration curve of result (+ 100 mV), against the log of the calculated concentration was constructed, and a linear curve fit applied. The equation obtained was used to convert readings in mV to ammonium concentrations in mg/l for any samples measured that day (see Appendix page A-11 for examples).

To check the stability of the standards and reproducibility of the electrode, vials containing the two standards were sealed with Parafilm™ and re-measured after the measurement period.

Slope checking and calibration were performed at least once a day.

### **Sample measurement**

After calibration, the concentration of ammonium ions in supernatants from the experiments was determined. As before, 10 g of liquid was weighed out and 0.2 g of ISA added, and results collected over a short time period.

To avoid cross-contamination, it was particularly important to measure the most dilute samples first. Hence, the five control samples were always measured first, followed by the tubes to which 10 mg/l ammonium had been added, before finally measuring those with 40 mg/l added. The electrode was rinsed thoroughly in distilled water between samples.

If there was an appreciable interval between sample measurements, the electrode's membrane was prevented from drying by storage in 10 g of 0.001 M ammonium chloride solution containing 0.2 g ISA. Before measuring samples again, the 0.0001 M and 0.01 M standards were re-measured and a new calibration equation obtained for any subsequent samples.

Once the ammonium concentration in mg/l had been calculated from the calibration, appropriate values were entered into the  $K_d$  equation and  $K_d$  calculated.

### 3.5.4 Results and discussion

Data from each of the fourteen experiments is provided in Tables A.10 to A.23 of the Appendix.  $K_d$  was calculated using the following relationship (see accompanying Technical Report):

$$K_d = [(I-F)/F] \times (V/M)$$

Where:

I	=	Initial ammonia concentration, mg/l
F	=	Final ammonia concentration, mg/l
V	=	Volume of liquid, g
M	=	Mass of solid, g

These four parameters are noted in the relevant headings of tables in the Appendix. Results have been summarized below according to the geological material used.

Attempts to conduct experiments at various pHs were confounded by two major limitations:

- all the materials had a large buffering capacity as a consequence of their carbonate contents. Thus, the Lower Chalk, Gault Clay and Lincolnshire Limestone (composed principally of calcite), and the Mercia Mudstone, Sherwood Sandstone and Lower Oxford Clay, (with appreciable dolomite and/or calcite components), resisted reductions in pH upon acidification.
- Ammonium ions are unstable at high pH undergoing conversion to ammonia ( $pK_a = 9.24$  at 20 °C). The  $K_d$  experiments were conducted in the pH range 6.2 to 8.4. Between pH 6 and pH 7.5 all ammoniacal nitrogen in aqueous solution is in the form of ammonium ions at 20 °C; at pH 8 about 5% is in the form of ammonia and at pH 8.4 this rises to about 15%.

In determining  $K_d$ , the experiments (all except one) were conducted with no pH adjustment; pH therefore resulted from pre-equilibration of the geological material with the neutral 0.03 M NaCl (pH 7). This is referred to as 'natural pH'.

The effect of concentration on  $K_d$  was investigated using ammonium chloride spikes that produced initial ammonium ion concentrations of 10 mg/l and 40 mg/l. The range was limited by the need to maximize the accuracy of values obtained for  $K_d$ . Given that the scoping

experiments indicated that  $K_d$  values for ammonium on the chosen geological materials were likely to be low, then minimizing the value  $F/I$  would lead to greater accuracy. Lowering of  $F/I$  is achieved by employing a low initial concentration. Setting this against the limit of accurate detection of the electrode and the need for realistic environmental concentrations led to the chosen range.

Because ammonium ions can be utilized as nutrients by micro-organisms there was potential for biotic processes that could affect  $K_d$  determination. While this would be unlikely for the experiments conducted with artificial groundwater prepared from sterile pure water, there was a stronger possibility of it occurring in experiments involving authentic leachate. Rather than attempt sterilization in such cases, and possibly introduce perturbations, other nitrogenous species in solution (i.e. nitrite and nitrate ions) were monitored at the start and finish of the experiments. Changes in these would indicate that ammonium ions were being used microbially. However both species remained effectively constant in both experiments involving the leachate and hence it was assumed that biological action was having no influence upon measured  $K_d$  (Table A.9).

- *Sherwood Sandstone*

Comparing the  $K_d$  obtained from the coarse material (particle size 0-2 mm) with that of the ground form (<200  $\mu\text{m}$ ) indicated the effect of size reduction upon sorption (Tables A.13 and A.16):  $K_d$  increased from approximately 1.35 ml/g for the unmodified material to 1.75 ml/g when the size was reduced. The increase can be attributed mainly to an increase in the specific surface areas of the various constituents. The  $K_d$  behaviour is reflected in a higher CEC value for the fine sandstone compared with the coarse.

Reducing pH from the 'natural pH' (8.3-8.4) to pH 6.2 (by addition of 8 M HCl) reduced  $K_d$  from 1.36 ml/g to 0.43 ml/g (Table A.15). The 'natural pH', adopted by the aqueous phase after pre-equilibration, was undoubtedly influenced by the basic nature of the dolomite and calcite components. At the 'natural pH', which is at or above the ZPC of all constituents of the sandstone, the net negative charge on the matrix would be greater than at pH 6.2, when charge reversal would have occurred on the surfaces of some of the components, e.g. haematite ZPC 6.7, calcite ZPC 8.4 (Stumm and Morgan, 1971). This would result in fewer sites for cation sorption at the lower pH. However, the probable major cause for reduction in  $K_d$  is dissolution of calcite and dolomite due to addition of the acid. The calcium ion concentration rose by a factor of 10, to approximately 1000 mg/l (Table A.9), compared with the 'natural pH' experiments. A much greater concentration of calcium ions in solution would reduce ammonium sorption through increased competition for ion exchange sites. A slight rise in pH was noted over the duration of this experiment suggesting that attainment of an equilibrium pH was slow. By the time it was measured as part of the chemical analysis (conducted some time after the  $K_d$  experiment) it was up to 7.44. For this reason, no further attempts were made to alter pH in the  $K_d$  experiments.

Over the concentration range studied,  $K_d$  was constant for both the coarse sandstone (1.31 at 10 mg/l  $\text{NH}_4$ : 1.36 at 40 mg/l  $\text{NH}_4$ ) and the fine sandstone (1.79 at 10 mg/l  $\text{NH}_4$ : 1.70 at 40 mg/l  $\text{NH}_4$ ). Though this implies that the sorption isotherm over this range is linear, it should not be extrapolated beyond the experimental data range because of the empirical nature of such isotherms.

- *Lower Chalk*

The primary influence on the 'natural pH' of the  $K_d$  experiments with this material was the carbonate phase, calcite in this case, leading to a 'natural pH' of about 8. Perhaps surprisingly, the coarse material (0-2 mm), examined in  $K_d$  Expt 5, yielded a higher  $K_d$  (Table A.14) than did the fine material (<200  $\mu$ m) examined in  $K_d$  Expt 8. However, the experiment with the coarse chalk was conducted over 72 hours compared with 48 hours for the fine chalk, and slow attainment of equilibrium may have been responsible for the difference.

With either fine or coarse material there was very little difference in  $K_d$  values between the low and high ammonium chloride concentrations. Thus, for the fine material,  $K_d$  varied between 1.2 ml/g (40 mg/l  $NH_4$ ) and 1.6 ml/g (10 mg/l  $NH_4$ ). The variation was even smaller for the coarse material, i.e.  $K_d$  was 2.0 ml/g (40 mg/l  $NH_4$ ) and 2.1 ml/g (10 mg/l  $NH_4$ ). As with the Sherwood Sandstone, this suggests a linear sorption isotherm over the range of concentration investigated.

In  $K_d$  Expt 12, landfill leachate containing 4.24 mg/l ammonia was used to assess the effect of contaminated groundwater on  $K_d$ . The chalk is closest in geology to the existing formation at the landfill site from which the leachate was collected.  $K_d$  results were very low (Table A.21), ranging from -0.03 ml/g to 0.09 ml/g. As with the aqueous phase in the low pH experiment involving Sherwood sandstone, a high concentration of aqueous calcium ions (372 mg/l) was present in the leachate (Table A.9). The effect of this would be to diminish sorption of ammonium ions through ion exchange site competition.

- *Mercia Mudstone*

$K_d$  values for this material were calculated originally using the colorimetric method (Section 3.5.2) with an exploratory solid-solution ratio, and produced results that were considered unreliable. The experiment was repeated with the ammonia electrode method and the recommended solid-solution ratio.  $K_d$  Expt 9 produced the highest  $K_d$  results for each ammonium chloride concentration of all the geological materials tested (Table A.18). However, the CEC was comparatively low. This may reflect the presence of illite as a major component of the clay fraction: ammonium ions behave differently from most other cations with illite and will enter and displace exchangeable potassium cations from the interlayer positions.

As this material gave the highest  $K_d$  values with the artificial laboratory groundwater (0.03 M NaCl spiked with ammonium chloride solution), a second experiment was performed using the landfill leachate.  $K_d$  Expt 13 produced comparably high  $K_d$  results (Table A.22).

- *Lower Oxford Clay*

$K_d$  Expt 10 was run with this material as the solid phase and produced low  $K_d$  values (Table A.19). In contrast, the CEC was relatively high (approximately 31 meq/100 g). The composition of the aqueous phase after pre-equilibration revealed elevated ionic concentrations of calcium (718 mg/l), magnesium (152 mg/l), potassium (150 mg/l) and sodium (900 mg/l). Inhibited sorption of ammonium ions could therefore be expected on the basis of exclusion through competition from other cations.

- *Gault Clay*

Gault Clay, used in  $K_d$  Expt 11, produced high  $K_d$  values (Table A.20) and also yielded the highest CEC values. Both parameters indicate the strong influence of the clay fraction on the sorption behaviour of this material.

- *Lincolnshire Limestone*

The final experiment performed in this series was  $K_d$  Expt 14, using the Lincolnshire Limestone as the solid phase and the 10 and 40 mg/l concentrations of ammonium chloride. Values obtained (Table A.23) were the lowest of the six geological materials tested. The CEC was also comparatively low (approximately 13 meq/100 g). This is probably due to the absence of a significant clay fraction and the dominance of constituents of low CEC, i.e. calcite, quartz, pyrite.

As with the Sherwood Sandstone and the Lower Chalk, there appeared to be a linear sorption isotherm over the concentration range investigated.

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## APPENDIX

Tables A.1 to A.8 contain statistical results from the CEC work.

Preparative guidelines for the various solutions used in the  $K_d$  experiments are listed on page A-10. The steps required to calibrate the ammonia electrode are noted on page A-12. Table A.9 contains information on the chemical composition of the 0.03 M NaCl after contact with each of the geological materials during pre-equilibration. Complete experimental data for  $K_d$  Expts 1 to 14 is provided in Tables A.10 to A.23.

XRD profiles are presented in Figures A.1 to A.6.



CEC-BaCl <sub>2</sub> /Trieth	batch 1	batch 2
SSC10	3.58	4.20
SSC20	4.83	4.47
SSC30	4.48	4.62
SSC40	4.50	3.83
SSC50	4.91	4.64
SSC60	4.45	5.01
SSC70	4.99	5.40
SSC80	4.76	5.36
SSC90	4.26	4.65
SSC100	3.87	4.11

**Table A.1**  
**CEC and statistical test data**  
**for the Sherwood Sandstone**  
**(<2000 μm) sample**

overall mean	4.55
standard deviation	0.48
relative standard deviation	10.6%

F-Test Two-Sample for Variances

	batch 2	batch 1
Mean	4.63	4.46
Variance	0.27	0.21
Observations	10	10
df	9	9
F	1.28	PASS
P(F<=f) one-tail	0.36	
F Critical one-tail	5.35	

t-Test: Two-Sample Assuming Equal Variances

	batch 2	batch 1
Mean	4.63	4.46
Variance	0.27	0.21
Observations	10	10
Pooled Variance	0.24	
Hypothesized Mean Difference	0	
df	18	
t Stat	0.76	PASS
P(T<=t) two-tail	0.46	
t Critical two-tail	2.88	

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
SSC10	2	7.78	3.89	0.19
SSC20	2	9.30	4.65	0.06
SSC30	2	9.11	4.55	0.01
SSC40	2	8.33	4.16	0.22
SSC50	2	9.55	4.78	0.04
SSC60	2	9.46	4.73	0.15
SSC70	2	10.39	5.19	0.08
SSC80	2	10.12	5.06	0.18
SSC90	2	8.92	4.46	0.08
SSC100	2	7.98	3.99	0.03

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.34	9	0.37	3.55	0.031	4.94
Within Groups	1.05	10	0.10			
Total	4.39	19		PASS		



CEC-BaCl <sub>2</sub> /Trieth	batch 1	batch 2
SS10	9.42	7.17
SS20	10.18	8.76
SS30	9.35	7.53
SS40	9.49	8.53
SS50	10.21	8.59
SS60	9.45	7.98
SS70	9.85	8.33
SS80	9.06	7.44
SS90	8.73	8.65
SS100	9.66	8.73

**Table A.2**  
**CEC and statistical test data**  
**for the Sherwood Sandstone**  
**(<200 μm) sample**

overall mean	8.86
standard deviation	0.87
relative standard deviation	9.9%

**F-Test Two-Sample for Variances**

	batch 2	batch 1
Mean	8.17	9.54
Variance	0.35	0.21
Observations	10	10
df	9	9
F	1.66	PASS
P(F<=f) one-tail	0.23	
F Critical one-tail	5.35	

**t-Test: Two-Sample Assuming Equal Variances**

	batch 1	batch 2
Mean	9.54	8.17
Variance	0.21	0.35
Observations	10	10
Pooled Variance	0.28	
Hypothesized Mean Difference	0	
df	18	
t Stat	5.74	FAIL
P(T<=t) two-tail	1.9E-05	
t Critical two-tail	2.88	

**Anova: Single Factor**  
**SUMMARY**

Groups	Count	Sum	Average	Variance
SS10	2	16.59	8.30	2.53
SS20	2	18.94	9.47	1.00
SS30	2	16.88	8.44	1.65
SS40	2	18.02	9.01	0.47
SS50	2	18.81	9.40	1.32
SS60	2	17.43	8.72	1.08
SS70	2	18.18	9.09	1.15
SS80	2	16.51	8.25	1.31
SS90	2	17.37	8.69	0.00
SS100	2	18.39	9.20	0.43

**ANOVA**

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.53	9	0.39	0.36	0.931	4.94
Within Groups	10.94	10	1.09			
Total	14.48	19			PASS	

CEC-BaCl <sub>2</sub> /Trieth	batch 1	batch 2	batch 3		
MM10	13.47	13.55	13.51		
MM20	13.63	13.22	12.80		
MM30	13.29	13.65	13.21		
MM40	13.76	12.79	12.90		
MM50	12.05	12.60	12.98		
MM60	12.90	12.11	13.11		
MM70	12.24	12.26	12.96		
MM80	12.92	12.50	13.34	overall mean	12.88
MM90	11.86	12.22	12.27	standard deviation	0.55
MM100	13.38	12.05	12.79	active st'ard deviation	4.3%

**Table A.3**  
CEC and statistical  
test data for the  
Mercia Mudstone  
sample

F-Test Two-Sample for Variances

	batch 1	batch 2	batch 2	batch 3	batch 1	batch 3
Mean	12.95	12.70	12.70	12.99	12.95	12.99
Variance	0.47	0.35	0.35	0.12	0.47	0.12
Observations	10	10	10	10	10	10
df	9	9	9	9	9	9
F	1.33	PASS	2.96	PASS	3.94	PASS
P(F<=f) one-tail	0.34		0.061		0.027	
F Critical one-tail	5.35		5.35		5.35	

t-Test: Two-Sample Assuming Equal Variances

	batch 1	batch 2	batch 3	batch 2	batch 3	batch 1
Mean	12.95	12.70	12.99	12.70	12.99	12.95
Variance	0.47	0.35	0.12	0.35	0.12	0.47
Observations	10	10	10	10	10	10
Pooled Variance	0.41		0.23		0.29	
Hypothesized Mean Difference	0		0		0	
df	18		18		18	
t Stat	0.88	PASS	1.34	PASS	0.16	PASS
P(T<=t) two-tail	0.39		0.20		0.88	
t Critical two-tail	2.88		2.88		2.88	

Anova: Single Factor  
SUMMARY

Groups	Count	Sum	Average	Variance
MM10	3	40.53	13.51	0.00
MM20	3	39.66	13.22	0.17
MM30	3	40.15	13.38	0.06
MM40	3	39.46	13.15	0.28
MM50	3	37.63	12.54	0.22
MM60	3	38.12	12.71	0.28
MM70	3	37.46	12.49	0.17
MM80	3	38.76	12.92	0.17
MM90	3	36.35	12.12	0.05
MM100	3	38.22	12.74	0.44

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5.23	9	0.58	3.16	0.015	3.46
Within Groups	3.68	20	0.18			
Total	8.91	29		PASS		

CEC-BaCl <sub>2</sub> /Trieth	batch 1	batch 2
LL10	14.70	12.92
LL20	15.47	12.98
LL30	14.89	11.95
LL40	14.48	11.51
LL50	12.85	11.46
LL60	14.17	12.48
LL70	14.68	12.16
LL80	15.44	11.97
LL90	13.38	12.05
LL100	14.40	12.33

**Table A.4**  
**CEC and statistical test data**  
**for the Lincolnshire**  
**Limestone sample**

overall mean	13.31
standard deviation	1.34
relative standard deviation	10.1%

**F-Test Two-Sample for Variances**

	batch 1	batch 2
Mean	14.44	12.18
Variance	0.68	0.26
Observations	10	10
df	9	9
F	2.58	PASS
P(F<=f) one-tail	0.087	
F Critical one-tail	5.35	

**t-Test: Two-Sample Assuming Equal Variances**

	batch 1	batch 2
Mean	14.44	12.18
Variance	0.68	0.26
Observations	10	10
Pooled Variance	0.47	
Hypothesized Mean Difference	0	
df	18	
t Stat	7.36	FAIL
P(T<=t) two-tail	7.9E-07	
t Critical two-tail	2.88	

**Anova: Single Factor**  
**SUMMARY**

Groups	Count	Sum	Average	Variance
LL10	2	27.62	13.81	1.58
LL20	2	28.44	14.22	3.10
LL30	2	26.83	13.42	4.32
LL40	2	25.99	13.00	4.43
LL50	2	24.30	12.15	0.96
LL60	2	26.65	13.32	1.41
LL70	2	26.84	13.42	3.19
LL80	2	27.41	13.71	6.03
LL90	2	25.43	12.71	0.87
LL100	2	26.73	13.36	2.13

**ANOVA**

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6.11	9	0.68	0.24	0.978	4.94
Within Groups	28.04	10	2.80			
Total	34.15	19			PASS	

CEC-BaCl <sub>2</sub> /Trieth	batch 1	batch 2
LC10	17.53	17.89
LC20	17.54	17.91
LC30	16.67	18.04
LC40	16.62	17.99
LC50	17.23	18.39
LC60	17.30	19.12
LC70	17.45	18.91
LC80	17.77	17.92
LC90	17.82	19.07
LC100	16.77	19.73

**Table A.5**  
**CEC and statistical test data :**  
**the Lower Chalk sample**

overall mean	17.88
standard deviation	0.83
relative standard deviation	4.7%

**F-Test Two-Sample for Variances**

	batch 2	batch 1
Mean	18.50	17.27
Variance	0.44	0.19
Observations	10	10
df	9	9
F	2.24	PASS
P(F<=f) one-tail	0.12	
F Critical one-tail	5.35	

**t-Test: Two-Sample Assuming Equal Variances**

	batch 2	batch 1
Mean	18.50	17.27
Variance	0.44	0.19
Observations	10	10
Pooled Variance	0.32	
Hypothesized Mean Difference	0	
df	18	
t Stat	4.89	FAIL
P(T<=t) two-tail	0.00012	
t Critical two-tail	2.88	

**Anova: Single Factor**  
**SUMMARY**

Groups	Count	Sum	Average	Variance
LC10	2	35.42	17.71	0.07
LC20	2	35.45	17.73	0.07
LC30	2	34.71	17.35	0.94
LC40	2	34.61	17.30	0.93
LC50	2	35.61	17.81	0.68
LC60	2	36.42	18.21	1.65
LC70	2	36.36	18.18	1.07
LC80	2	35.68	17.84	0.01
LC90	2	36.89	18.44	0.78
LC100	2	36.50	18.25	4.38

**ANOVA**

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2.65	9	0.29	0.28	0.966	4.94
Within Groups	10.59	10	1.06			
Total	13.23	19			PASS	

CEC-BaCl <sub>2</sub> /Trieth	batch 1	batch 2
LOC10	31.33	30.00
LOC20	31.65	30.48
LOC30	31.33	30.39
LOC40	30.85	30.33
LOC50	31.27	30.80
LOC60	31.20	30.63
LOC70	31.09	30.44
LOC80	30.63	30.18
LOC90	30.75	31.52
LOC100	30.52	31.05

**Table A.6**  
**CEC and statistical test data**  
**for the Lower Oxford**  
**Clay sample**

overall mean	30.82
standard deviation	0.47
relative standard deviation	1.5%

**F-Test Two-Sample for Variances**

	batch 2	batch 1
Mean	30.58	31.06
Variance	0.20	0.13
Observations	10	10
df	9	9
F	1.52	PASS
P(F<=f) one-tail	0.27	
F Critical one-tail	5.35	

**t-Test: Two-Sample Assuming Equal Variances**

	batch 1	batch 2
Mean	31.06	30.58
Variance	0.13	0.20
Observations	10	10
Pooled Variance	0.17	
Hypothesized Mean Difference	0	
df	18	
t Stat	2.64	PASS
P(T<=t) two-tail	0.017	
t Critical two-tail	2.88	

**Anova: Single Factor**  
**SUMMARY**

Groups	Count	Sum	Average	Variance
LOC10	2	61.32	30.66	0.89
LOC20	2	62.14	31.07	0.68
LOC30	2	61.72	30.86	0.44
LOC40	2	61.18	30.59	0.14
LOC50	2	62.07	31.04	0.11
LOC60	2	61.84	30.92	0.16
LOC70	2	61.53	30.76	0.21
LOC80	2	60.80	30.40	0.10
LOC90	2	62.27	31.14	0.29
LOC100	2	61.57	30.78	0.14

**ANOVA**

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.96	9	0.11	0.33	0.943	4.94
Within Groups	3.17	10	0.32			
Total	4.13	19			PASS	

CEC-BaCl <sub>2</sub> /Trieth	batch 1	batch 2
GC10	33.00	32.20
GC20	32.28	33.25
GC30	33.72	32.77
GC40	38.08	32.75
GC50	36.63	33.28
GC60	35.86	33.67
GC70	36.32	33.29
GC80	36.33	33.68
GC90	37.07	33.92
GC100	36.10	33.22

**Table A.7**  
CEC and statistical test data for the Gault Clay sample

overall mean	34.37
standard deviation	1.80
relative standard deviation	5.2%

F-Test Two-Sample for Variances

	batch 1	batch 2
Mean	35.54	33.20
Variance	3.56	0.26
Observations	10	10
df	9	9
F	13.48	FAIL
P(F<=f) one-tail	0.00032	
F Critical one-tail	5.35	

t-Test: Two-Sample Assuming Unequal Variances

	batch 1	batch 2
Mean	35.54	33.20
Variance	3.56	0.26
Observations	10	10
Pooled Variance	N/A	
Hypothesized Mean Difference	0	
df	10	
t Stat	3.78	FAIL
P(T<=t) two-tail	0.0036	
t Critical two-tail	2.88	

Anova: Single Factor  
SUMMARY

Groups	Count	Sum	Average	Variance
GC10	2	65.20	32.60	0.32
GC20	2	65.53	32.76	0.47
GC30	2	66.49	33.25	0.45
GC40	2	70.83	35.42	14.20
GC50	2	69.91	34.95	5.60
GC60	2	69.54	34.77	2.40
GC70	2	69.61	34.81	4.60
GC80	2	70.01	35.00	3.51
GC90	2	70.99	35.50	4.96
GC100	2	69.32	34.66	4.14

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	21.02	9	2.34	0.57	0.791	4.94
Within Groups	40.65	10	4.06			
Total	61.67	19			PASS	

**Table A.8 Summary data – replicate analyses of one split, units meq/100 g. Data for BaCl<sub>2</sub> method are replicates from five different splits.**

Mercia Mudstone				Gault Clay				Oxford Clay			
	BaCl <sub>2</sub>	SrCl <sub>2</sub>	MBI		BaCl <sub>2</sub>	SrCl <sub>2</sub>	MBI		BaCl <sub>2</sub>	SrCl <sub>2</sub>	MBI
Analysis 1	12.90	11.70	8.92	Analysis 1	35.86	133.63	24.70	Analysis 1	31.20	38.74	20.72
Analysis 2	12.24	11.48	8.51	Analysis 2	36.32	139.09	25.52	Analysis 2	31.09	37.76	19.89
Analysis 3	12.92	11.87	8.92	Analysis 3	36.33	138.10	25.52	Analysis 3	30.63	38.04	19.89
Analysis 4	11.86	11.45	8.92	Analysis 4	37.07	131.07		Analysis 4	30.75	39.13	21.55
Analysis 5	13.38	11.80	8.92	Analysis 5	36.10	142.08		Analysis 5	30.52	39.08	21.55
mean	12.66	11.66	8.83	mean	36.34	136.79	25.25	mean	30.84	38.55	20.72
standard deviation	0.60	0.19	0.18	standard deviation	0.45	4.41	0.47	standard deviation	0.30	0.62	0.83
RSD	4.76%	1.62%	2.05%	RSD	1.25%	3.22%	1.88%	RSD	0.96%	1.61%	4.01%

Sherwood S'tone <2000				Sherwood S'tone <2000			
	BaCl <sub>2</sub>	SrCl <sub>2</sub>	MBI		BaCl <sub>2</sub>	SrCl <sub>2</sub>	MBI
Analysis 1	9.45	15.18	4.81	Analysis 1	4.45	2.39	2.81
Analysis 2	9.85	14.98	4.41	Analysis 2	4.99	2.54	3.21
Analysis 3	9.06	14.12	4.41	Analysis 3	4.76	2.41	3.21
Analysis 4	8.73	14.33	4.41	Analysis 4	4.26	2.25	3.21
Analysis 5	9.66	13.70	4.01	Analysis 5	3.87	2.45	2.81
mean	9.35	14.46	4.41	mean	4.47	2.41	3.05
standard deviation	0.46	0.61	0.28	standard deviation	0.44	0.11	0.22
RSD	4.87%	4.23%	6.43%	RSD	9.76%	4.36%	7.21%

Lincolnshire Limestone				Lower Chalk			
	BaCl <sub>2</sub>	SrCl <sub>2</sub>	MBI		BaCl <sub>2</sub>	SrCl <sub>2</sub>	MBI
Analysis 1	14.17	212.03	<2.00	Analysis 1	17.30	216.84	5.61
Analysis 2	14.68	202.39	<2.00	Analysis 2	17.45	213.03	4.81
Analysis 3	15.44	200.31	<2.00	Analysis 3	17.77	208.19	5.21
Analysis 4	13.38	194.76		Analysis 4	17.82	208.54	6.01
Analysis 5	14.40	207.60		Analysis 5	16.77	213.88	5.61
mean	14.41	203.42	<2.00	mean	17.42	212.10	5.45
standard deviation	0.75	6.66	N/A	standard deviation	0.42	3.69	0.46
RSD	5.23%	3.27%	N/A	RSD	2.43%	1.74%	8.38%

## Preparation of solutions used in the $K_d$ experiments

### 1 0.03 M NaCl

Weigh 1.76 g of sodium chloride

Wash into a 1 l graduated flask using Purite\* water

Make up to the mark with Purite water

### 2 250 mg/l ammonium chloride solution

Weigh 3.53 g of 0.1 M ammonium chloride standard into 25 ml graduated flask

Make up to the mark with 0.03 M NaCl

1 ml of this diluted to 25 ml is equivalent to 10 mg/l

### 3 1000 mg/l ammonium chloride solution

Weigh 13.93 g of 0.1 M ammonium chloride standard into 25 ml graduated flask

Make up to the mark with 0.03 M NaCl

1 ml of this diluted to 25 ml is equivalent to 40 mg/l

### 4 0.01 M (180 mg/l) ammonium chloride standard

Weigh 2.5 g 0.1 M ammonium chloride standard into 25 ml graduated flask

Make up to the mark with Purite water

### 5 0.001 M (18.0 mg/l) ammonium chloride standard

Weigh 2.5 g 0.01 M ammonium chloride standard into 25 ml graduated flask

Make up to the mark with Purite water

### 6 0.0001 M (1.8 mg/l) ammonium chloride standard

Weigh 2.5 g 0.01 M ammonium chloride standard into 250 ml graduated flask

Make up to the mark with Purite water

### 7 8 M HCl

Disperse 17.16 ml of 1 M HCl (s.g. 1.18) into 25 ml graduated flask

Make up to the mark with Purite water

\* Purite water

Distilled, de-ionised, charcoal filtered and bacteriologically filtered water



Table A.9 Chemical composition of 0.03 M NaCl in Purite after contact with geological material for 72 hours

LIMS code	Sample code	After 72 hour contact with	pH	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	HCO <sub>3</sub> mg/l	Cl mg/l	SO <sub>4</sub> mg/l	NO <sub>3</sub> mg/l	Cation total meq/l	Anion total meq/l	Balance %	NO <sub>2</sub> mg/l	NH <sub>4</sub> mg/l	Si mg/l	Mn mg/l	Total Fe mg/l	Al mg/l
06112-00001	Kd Expt 4	Sherwood Sst	7.64	33.53	14.04	587	15.8	57	1039	13.7	0.84	28.78	30.54	-2.97	<0.10	n/d	4.14	<0.001	<0.01	<0.02
06112-00002	Kd Expt 5	Lower Chalk	7.52	101.65	21.8	625	13.4	33	1028	222	1.16	34.41	34.19	0.32	<0.10	n/d	5.28	<0.001	<0.01	<0.02
06112-00003	Kd Expt 6	Sherwood Sst	7.44	1027	156	657	43.4	385	3125	14.4	0.73	93.96	94.78	-0.43	<0.10	n/d	20.4	4.62	<0.01	<0.02
06112-00004	Kd Expt 7	Sherwood Sst	7.64	38.47	19.7	610	33.2	82	1100	15.2	<0.80	30.93	32.71	-2.80	<0.20	n/d	3.88	0.015	<0.01	<0.02
06112-00005	Kd Expt 8	Lower Chalk	7.51	101.82	19.2	644	15.1	47	1138	183	<0.80	35.07	36.69	-2.26	<0.20	n/d	7.34	0.006	<0.01	<0.02
06112-00006	Kd Expt 9	Mercia Mdst	7.71	97.91	35.3	527	8.35	70	1154	30.0	<0.80	30.91	34.32	-5.23	<0.20	n/d	5.63	0.007	<0.01	<0.02
06164-00001	Kd Expt 10	Lower Oxford Clay	7.96	718	152.0	900	150	156	1114	2428	<0.80	91.45	84.54	3.93	<0.20	2.23	10.8	0.07	0.002	0.02
06164-00002	Kd Expt 11	Gault Clay	7.49	194	39.8	552	57.6	40.5	1145	247	2.80	38.46	38.14	0.41	<0.20	0.27	5.27	0.01	0.003	0.03
06185-00009	Kd Expt 14	Lincolnshire Lnast	7.59	777	23.6	610	32.2	102	1079	1792	<0.80	68.08	69.41	-0.97	0.23	n/d	4.63	0.01	<0.01	0.02

n/d = not determined

Chemical composition of Thriploew leachate

LIMS code	Sample code	pH	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	HCO <sub>3</sub> mg/l	Cl mg/l	SO <sub>4</sub> mg/l	NO <sub>3</sub> mg/l	Cation total meq/l	Anion total meq/l	Balance %	NO <sub>2</sub> mg/l	NH <sub>4</sub> mg/l	Si mg/l	Mn mg/l	Total Fe mg/l	Al mg/l	
06002-00020	Kd Expt 12/13	As received	7.39	372.00	7.40	351	19.3	920	550	238	1.13	35.80	35.64	0.22	<0.050	n/d	9.30	0.19	<0.05	0.30
06185-00001	Kd Expt 12	Contact with LC	n/d	n/d	n/d	n/d	n/d	482	337	13.3	n/d	n/d	n/d	n/d	0.33	n/d	n/d	n/d	n/d	n/d
06185-00002	Kd Expt 13	Contact with MM	n/d	n/d	n/d	n/d	n/d	501	215	14	n/d	n/d	n/d	0.19	n/d	n/d	n/d	n/d	n/d	n/d

## Calibration of ammonia electrode - example of steps involved

### 1 Calculated concentration of 0.01 M ammonium chloride standard

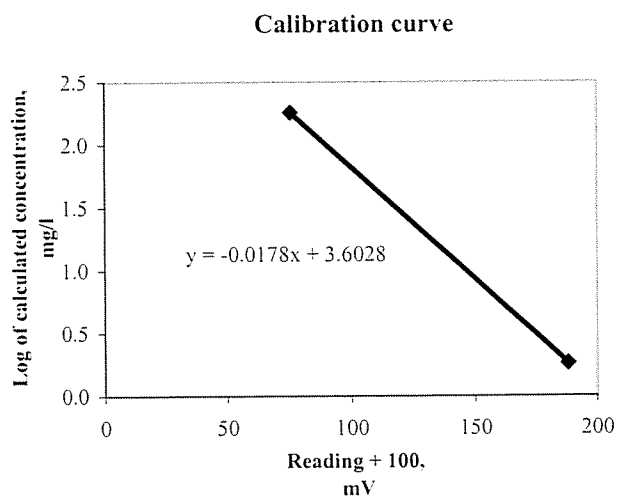
Wt of 0.1 M std in 0.01 M std g	Actual molarity M	0.01 M reading mV	Reading + 100 mV	Calculated concentration mg/l	Log of calc. concentration
2.5100	0.01004	-24.3	75.7	180.7200	2.2570

### 2 Calculated concentration of 0.0001 M ammonium chloride standard

Wt of 0.1 M std in 0.0001 M std g	Actual molarity M	0.0001 M reading mV	Reading + 100 mV	Calculated concentration mg/l	Log of calc. concentration
2.5100	0.000101	88.1	188.1	1.8144	0.2587

### 3 Plot graph of reading + 100 against log of calculated concentration

Reading + 100 mV	Log of calc. concentration
75.7	2.2570
188.1	0.2587



### 4 Perform linear curve fit

$$y = -0.0178x + 3.6028$$

### 5 Calculate y using reading + 100 value for x. Then antilog to obtain measured concentration of standards

Standard	Measured concentration mg/l
0.0001M	1.7973
0.01M	180.0280

### 6 Calculate concentration of ammonia in samples by substituting as for step 5

### K<sub>d</sub> determinations using colorimetric method

Table A.10 K<sub>d</sub> Expt 1: using 500 ml Duran containing 0.03 M NaCl with Mercia Mudstone and 1.0 M ammonium chloride

Sample number	pH sample	Weight mudstone g M	Total weight liquid g V	NH <sub>4</sub> conc after dilution mg/l I	Final NH <sub>4</sub> conc (measured) mg/l F	Date measured	K <sub>d</sub> ml/g	Average K <sub>d</sub> ml/g	Standard deviation	Relative St Dev %
1	5.68	12.10	190.32	94.12	86.51	3.9.98	1.38	1.7129	1.2688	74.08
2	7.21	12.10	190.32	94.12	78.57	3.9.98	3.11			
3	9.09	12.10	190.32	94.12	90.44	3.9.98	0.64			
Actual mg/l = 17913.6										

Table A.11 K<sub>d</sub> Expt 2: using 500 ml Duran containing 0.03 M NaCl with Mercia Mudstone and 0.1 M ammonium chloride

Sample number	pH sample	Weight mudstone g M	Total weight liquid g V	NH <sub>4</sub> conc after dilution mg/l I	Final NH <sub>4</sub> conc (measured) mg/l F	Date measured	K <sub>d</sub> ml/g	Average K <sub>d</sub> ml/g	Standard deviation	Relative St Dev %
1	8.42	12.37	191.08	9.41	10.72	4.9.98	-1.88	1.9844	2.8245	142.34
2	8.56	12.37	191.08	9.41	8.47	4.9.98	1.72			
3	8.06	12.37	191.08	9.41	7.30	4.9.98	4.47			
4	7.78	12.37	191.08	9.41	7.62	4.9.98	3.63			
Actual mg/l = 1791.36										

Table A.12 K<sub>d</sub> Expt 3: using 500 ml Duran containing 0.03 M NaCl with Mercia Mudstone

Sample number	pH sample	Weight mudstone g M	Total weight liquid g V	NH <sub>4</sub> conc after dilution mg L I	Final NH <sub>4</sub> conc (measured) mg L F	Date measured	K <sub>d</sub> ml/g	Average K <sub>d</sub> ml/g	Standard deviation
1	8.50	12.02	191.01	0	0.47	4.9.98	-15.89	-15.8910	0.0000
2	8.01	12.02	191.01	0	0.59	4.9.98	-15.89		
3	7.76	12.02	191.01	0	0.77	4.9.98	-15.89		
Actual mg/l = 0									

Table A.13 K<sub>d</sub> Expt 4: Coarse Sherwood Sandstone with 10 and 40 mg/l ammonium chloride after 48 hours slaking at 'natural pH'

Tube no.	Weight tube + lid g	Wt sst added g	Total weight g	Wt NaCl added g	Weight inc. liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weight liquid g	Calc. NH <sub>4</sub> Cl mg/l	Actual NH <sub>4</sub> Cl (see below) mg/l	Actual NH <sub>4</sub> Cl conc after dilution mg/l	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
		M							V			I				
1	12.48	10.03	22.51	24.02	46.53	7.89	0.00		24.02							
2	12.49	10.01	22.50	24.01	46.51	7.91	0.00		24.01							
3	12.52	10.01	22.54	24.04	46.58	7.96	0.00		24.04							
4	12.56	10.01	22.57	24.02	46.59	7.79	1.02	7.78	25.04	250.00	251.77	10.22	47.54	33.56	8.30	1.00
5	12.52	10.02	22.54	24.20	46.74	7.97	1.01	7.91	25.21	250.00	251.77	10.11	47.69	33.69	8.27	0.99
6	12.47	10.01	22.48	24.03	46.51	7.98	1.01	7.95	25.04	250.00	251.77	10.17	47.38	33.38	8.37	1.00
7	12.50	10.01	22.51	24.07	46.58	8.13	1.01	8.08	25.08	250.00	251.77	10.17	47.50	33.59	8.38	0.99
8	12.54	10.02	22.56	24.03	46.59	8.21	1.01	8.12	25.05	250.00	251.77	10.17	47.53	33.28	8.34	0.99
9	12.50	10.01	22.51	24.02	46.53	8.14	1.01	8.16	25.03	1000	997.74	40.12	47.43	33.33	8.34	1.00
10	12.48	10.01	22.49	24.08	46.57	8.09	1.01	8.13	25.08	1000	997.74	40.00	47.52	33.36	8.37	1.00
11	12.50	10.01	22.52	24.02	46.53	8.13	1.01	8.19	25.02	1000	997.74	40.13	47.49	33.29	8.37	1.01
12	12.54	10.03	22.56	24.12	46.68	8.12	1.01	8.22	25.13	1000	997.74	39.94	47.53	33.16	8.36	1.01
13	12.54	10.01	22.55	24.01	46.56	8.14	1.01	8.22	25.02	1000	997.74	40.18	47.49	33.16	8.36	1.01
14	12.53	10.03	22.56	24.12	46.68	8.03	1.00	8.18	25.12	0.00	0.00	0.00	47.62	33.40	8.39	1.02
15	12.52	10.03	22.55	24.18	46.72	8.07	1.01	8.15	25.18	0.00	0.00	0.00	47.54	33.36	8.39	1.01
16	12.49	10.03	22.52	24.09	46.60	8.14	1.01	8.16	25.09	0.00	0.00	0.00	47.49	33.49	8.33	1.00
17	12.53	10.00	22.53	24.02	46.55	8.12	1.01	8.10	25.02	0.00	0.00	0.00	47.50	33.40	8.35	1.00
18	12.50	10.03	22.53	24.01	46.54	8.13	1.00	8.19	25.02	0.00	0.00	0.00	47.44	33.46	8.33	1.01
19	12.58	10.00	22.59	24.02	46.61	8.16	1.01	8.12	25.03	0.00	0.00	0.00	47.55	33.42	8.36	1.00

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-19 = controls

1.0 M NH<sub>4</sub> stock solution = 0.995 Actual mg/l 17913.99  
 250 mg/l NH<sub>4</sub> as molar : Tubes 4-8 0.014 251.77  
 1000 mg/l NH<sub>4</sub> as mol: Tubes 9-13 0.055 997.74  
 0 mg/l in tubes 14-19

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.13 (cont.) K<sub>a</sub> Expt 4: Coarse Sherwood Sandstone with 10 and 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

$K_a = (I-F)/F * (V/M)$

Spreadsheet continued

Tube no.	NH <sub>4</sub> ratio finish/start	Wt tube + sandstone g	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog F	K <sub>a</sub> ml/g	Average K <sub>a</sub> ml/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.68	26.46	1.00	2.10	11.12.98	82.3	182.30	0.84	6.92	1.19				
5	0.67	26.49	1.00	2.23	11.12.98	83.0	183.00	0.83	6.73	1.26				
6	0.64	26.47	1.00	2.19	11.12.98	84.0	184.00	0.81	6.47	1.43				
7	0.62	26.48	1.00	2.31	11.12.98	84.8	184.80	0.80	6.26	1.56				
8	0.65	26.72	1.00	2.39	11.12.98	83.4	183.40	0.82	6.62	1.34	1.36		0.15	10.71
9	0.72	26.64	1.00	2.27	11.12.98	46.7	146.70	1.46	28.82	0.98				
10	0.71	26.62	1.00	2.61	11.12.98	47.2	147.20	1.45	28.25	1.04				
11	0.70	26.66	1.00	2.28	11.12.98	47.2	147.20	1.45	28.25	1.05				
12	0.58	26.83	1.00	2.24	11.12.98	52.3	152.30	1.36	23.03	1.84				
13	0.61	26.81	1.00	2.16	11.12.98	50.9	150.90	1.39	24.36	1.62	1.31		0.40	30.29
14		26.72	1.00	2.23	11.12.98	144.9	244.90	-0.25	0.56					
15		26.75	1.00	2.26	11.12.98	191.6	291.60	-1.06	0.09					
16		26.51	1.00	2.22	11.12.98	193.4	293.40	-1.09	0.08					
17		26.58	1.00	2.24	11.12.98	189.9	289.90	-1.03	0.09					
18		26.47	1.00	2.24	11.12.98	193.3	293.30	-1.09	0.08					
19		26.67	1.00	2.26	11.12.98	189.9	289.90	-1.03	0.09			0.17	0.19	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-19 = controls

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.14 K<sub>a</sub> Expt 5: coarse Lower Chalk with 10 and 40 mg/l ammonium chloride after 72 hours shaking at 'natural pH'**

Tube no.	Wt tube + lid g	Wt chalk added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weight liquid g	Calc. NH <sub>4</sub> Cl mg/l	Actual NH <sub>4</sub> Cl (see below) mg/l	NH <sub>4</sub> conc after dilutio mg/l	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
		M							Y		I					
1	12.55	10.04	22.59	24.08	46.67	8.08			24.08							
2	12.50	10.02	22.53	24.42	46.95	8.16			24.42							
3	12.50	10.02	22.52	24.03	46.55	8.17			24.03							
4	12.46	10.03	22.48	24.38	46.86	8.11	1.00	8.25	25.38	250	252.98	9.97	47.76	34.34	8.13	1.02
5	12.49	10.03	22.52	24.07	46.59	8.12	1.00	8.24	25.07	250	252.98	10.08	47.51	34.00	8.14	1.01
6	12.48	10.03	22.50	24.36	46.87	8.14	1.00	8.23	25.36	250	252.98	9.97	47.79	34.43	8.15	1.01
7	12.49	10.01	22.50	24.01	46.51	8.14	1.00	8.23	25.01	250	252.98	10.10	47.43	33.96	8.16	1.01
8	12.49	10.01	22.50	24.04	46.54	8.21	1.00	8.22	25.03	250	252.98	10.08	47.41	33.99	8.12	1.00
9	12.51	10.00	22.51	24.43	46.94	8.24	1.00	8.21	25.43	1000	998.33	39.14	47.86	34.56	8.16	1.00
10	12.47	10.00	22.47	25.01	47.48	8.22	1.00	8.23	26.00	1000	998.33	38.30	48.33	34.88	8.11	1.00
11	12.52	10.01	22.54	24.03	46.57	8.18	1.00	8.20	25.03	1000	998.33	39.78	47.38	33.84	8.11	1.00
12	12.51	10.00	22.51	24.65	47.16	8.22	1.00	8.22	25.64	1000	998.33	38.78	48.08	34.68	8.13	1.00
13	12.47	10.02	22.48	24.43	46.91	8.22	1.00	8.23	25.42	1000	998.33	39.09	47.84	34.49	8.14	1.00
14	12.52	10.02	22.54	24.13	46.67	8.23	1.00	8.24	25.13	0	0	0.00	47.57	34.03	8.19	1.00
15	12.50	10.03	22.53	24.80	47.33	8.24	1.00	8.27	25.80	0	0	0.00	48.24	34.88	8.20	1.00
16	12.54	10.01	22.56	24.03	46.59	8.23	1.00	8.21	25.03	0	0	0.00	47.51	34.07	8.19	1.00
17	12.52	10.04	22.55	24.04	46.60	8.17	1.00	8.19	25.04	0	0	0.00	47.52	33.93	8.14	1.00
18	12.47	10.00	22.47	24.02	46.49	8.25	1.00	8.26	25.01	0	0	0.00	47.41	34.03	8.12	1.00
19	12.49	10.00	22.49	24.00	46.50	8.23	1.00	8.27	25.00	0	0	0.00	47.42	34.04	8.10	1.00

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-19 = controls

1.0 M NH<sub>4</sub> stock solution = 0.995 Actual mg/l 17913.99

250 mg/l NH<sub>4</sub> as molar 0.014 252.98

1000 mg/l NH<sub>4</sub> as mol 0.055 998.33

0 mg/l in tubes 14-19

**K<sub>a</sub> determinations using ammonia electrode method**

Table A.14 (cont.) K<sub>a</sub> Expt 5: coarse Lower Chalk with 10 and 40 mg/l ammonium chloride after 72 hours shaking at 'natural pH'

Spreadsheets continued

$$K_a = \frac{(F-E)}{F} \times (V/M)$$

Tube no.	NH <sub>4</sub> ratio finish/start	Wt tube + chalk g	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog F	K <sub>a</sub> mg/g	Average K <sub>a</sub> mg/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.54	25.92	1	2.20	14.12.98	82.3	182.3	0.73	5.36	2.18				
5	0.56	25.97	1	2.20	14.12.98	81.1	181.1	0.75	5.62	1.98				
6	0.55	25.88	1	2.24	14.12.98	81.6	181.6	0.74	5.51	2.05				
7	0.55	25.98	1	2.22	14.12.98	81.3	181.3	0.75	5.58	2.03				
8	0.54	25.91	1	2.22	14.12.98	81.7	181.7	0.74	5.49	2.09	2.06		0.07	3.62
9	0.60	25.86	1	2.10	14.12.98	46.2	146.2	1.37	23.32	1.72				
10	0.59	25.92	1	2.18	14.12.98	47.0	147.0	1.35	22.57	1.81				
11	0.54	26.01	1	2.31	14.12.98	48.2	148.2	1.33	21.50	2.13				
12	0.55	25.92	1	2.19	14.12.98	48.4	148.4	1.33	21.32	2.10				
13	0.55	25.89	1	2.21	14.12.98	48.3	148.3	1.33	21.41	2.10	1.97		0.19	9.55
14		26.01	1	2.27	14.12.98	164.9	264.9	-0.73	0.18					
15		25.87	1	2.23	14.12.98	150.9	250.9	-0.49	0.33					
16		25.94	1	2.23	14.12.98	181.9	281.9	-1.03	0.09					
17		26.10	1	2.20	14.12.98	187.4	287.4	-1.13	0.07					
18		25.88	1	2.21	14.12.98	176.6	276.6	-0.94	0.11					
19		25.92	1	2.26	14.12.98	183.2	283.2	-1.06	0.09		0.15		0.10	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-19 = controls

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.15 K<sub>a</sub> Expt 6: 10 g coarse Sherwood Sandstone with 10 mg/l ammonium chloride after 48 hrs shaking at pH 6.2**

Tube no.	Wt tube + lid g	Wt sst added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH + 2 drops 8 M HCl	pH + 1 more	pH + 1 more	pH + 2 more	pH + 2 more	pH + 2 more	pH + 2 more	pH + 2 more	pH + 2 more	pH after NH <sub>4</sub> Cl added g	Total weight liquid g	HCl added Id=0.035 g	Calc NH <sub>4</sub> Cl mg/l	actual NH <sub>4</sub> C (see below) mg/l	NH <sub>4</sub> C dilution mg/l
1	12.48	10.02	22.50	24.03	46.53		8.20	6.87	6.40	6.43	5.96					24.03				
2	12.55	10.00	22.56	24.12	46.68		8.27	6.90	6.42	6.48	6.00					24.12				
3	12.50	10.00	22.50	24.02	46.52		8.25	6.90	6.45	6.49	6.02					24.02				
4	12.56	10.00	22.56	24.15	46.71	8.05	8.26	6.91	6.46	6.50	6.03			1.00	6.06	25.16	25.51	250	254.26	10.16
5	12.55	10.01	22.56	24.02	46.58		8.26	6.90	6.48	6.50	5.99			1.00	6.08	25.02	25.37	250	254.26	10.20
6	12.52	10.02	22.54	24.12	46.66		8.31	6.86	6.48	6.51	6.07			1.00	6.17	25.12	25.47	250	254.26	10.14
7	12.49	10.01	22.50	24.39	46.89		8.26	7.00	6.50	6.53	6.04			1.00	6.17	25.39	25.74	250	254.26	10.03
8	12.49	10.00	22.50	24.04	46.54		8.24	6.93	6.49	6.55	6.05			1.00	6.11	25.04	25.39	250	254.26	10.16

Tubes 1-3 = wash for chemical analysis  
 Tubes 4-8 = 10 mg/l

1.0 M NH<sub>4</sub>Cl 1.00  
 250 mg/l NI 0.01

Actual mg/l 17913.99  
 254.26



**K<sub>d</sub> determinations using ammonia electrode method**

Table A.15 (cont.) K<sub>d</sub> Expt 6: 10 g coarse Sherwood Sandstone with 10 mg/l ammonium chloride after 48 hrs shaking at pH 6.2

$$K_d = (F - F^*) / F^* (V/M)$$

Spreadsheet continued

Tube no.	Wt after centrifuge	Wt liquid removed	pH liquid removed	pH ratio after NH <sub>4</sub>	NH <sub>4</sub> ratio finish/start	WT tube + sst	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog F	K <sub>d</sub> ml/g	Average K <sub>d</sub> ml/g	Standard deviation	Relative St Dev %
1																	
2																	
3																	
4	47.60	33.26	6.15	0.93	0.79	26.86	1	2.11	20.1.99	48.6	148.6	0.90	8.03	0.67			
5	46.77	32.37	6.23	0.94	0.85	26.89	1	2.38	20.1.99	46.8	146.8	0.94	8.63	0.46			
6	46.45	32.07	6.28	0.95	0.90	26.84	1	2.44	20.1.99	45.5	145.5	0.96	9.09	0.29			
7	46.29	31.96	6.29	0.94	0.87	26.85	1	2.43	20.1.99	46.5	146.5	0.94	8.73	0.38			
8	46.31	32.09	6.28	0.93	0.87	26.70	1	2.41	20.1.99	46.2	146.2	0.95	8.84	0.38	0.43	0.14	32.85

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.16 K<sub>a</sub> Expt 7: 10 g fine Sherwood Sandstone with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

Tube no.	Wt tube + lid g	Wt sst added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weigh liquid g	Calc NH <sub>4</sub> Cl mg/l	actual NH <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> (see below) mg/l	dilution	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
		M							V		I					
1	12.54	10.00	22.54	23.02	45.56	8.46			23.02							
2	12.46	10.03	22.49	23.03	45.52	8.49			23.03							
3	12.54	10.11	22.65	23.01	45.66	8.52			23.01							
4	12.50	10.01	22.51	23.02	45.53	8.33	1.03	8.13	24.06	250	253.12	10.87	46.49	19.86	8.48	0.98
5	12.47	10.01	22.48	23.09	45.57	8.31	0.98	8.28	24.07	250	253.12	10.31	46.32	19.69	8.45	1.00
6	12.49	10.02	22.50	23.09	45.59	8.31	0.99	8.36	24.08	250	253.12	10.38	46.42	19.79	8.43	1.01
7	12.55	10.00	22.55	23.02	45.57	8.32	0.98	8.32	24.00	250	253.12	10.36	46.47	19.87	8.44	1.00
8	12.49	10.02	22.51	23.01	45.51	8.48	0.99	8.37	23.99	250	253.12	10.40	46.42	19.69	8.42	0.99
9	12.49	10.03	22.52	23.02	45.54	8.40	0.98	8.31	24.00	1000	1001.45	41.06	46.30	19.58	8.37	0.99
10	12.53	10.01	22.53	23.01	45.54	8.44	0.99	8.29	23.99	1000	1001.45	41.20	46.37	19.70	8.37	0.98
11	12.52	10.02	22.55	23.04	45.58	8.42	0.99	8.29	24.02	1000	1001.45	41.07	46.25	19.48	8.40	0.98
12	12.50	10.02	22.53	23.07	45.59	8.38	0.98	8.33	24.04	1000	1001.45	40.76	46.40	19.64	8.37	0.99
13	12.47	10.01	22.48	23.21	45.70	8.42	0.97	8.35	24.19	1000	1001.45	40.36	46.54	19.76	8.36	0.99
14	12.49	10.01	22.50	23.07	45.57	8.39	1.00	8.33	24.08	0	0	0.00	46.51	19.84	8.47	0.99
15	12.49	10.00	22.49	23.04	45.53	8.39	0.98	8.22	24.02	0	0	0.00	46.33	19.63	8.45	0.98
16	12.58	10.00	22.59	23.03	45.61	8.32	0.99	8.33	24.02	0	0	0.00	46.37	19.83	8.48	1.00
17	12.52	10.01	22.53	23.04	45.56	8.36	0.99	8.32	24.02	0	0	0.00	46.44	19.76	8.47	1.00
18	12.50	10.00	22.50	23.11	45.61	8.39	1.01	8.29	24.11	0	0	0.00	46.52	19.89	8.47	0.99

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

1.0 M NH<sub>4</sub> stock solution = 1.00 actual mg/l = 17913.99

2.50 mg/l NH<sub>4</sub> as molar Tubes 4-8 0.01 253.12

1000 mg/l NH<sub>4</sub> as mol Tubes 9-13 0.06 1001.45

0 mg/l in tubes 14-18

**K<sub>d</sub> determinations using ammonia electrode method**

Table A.16 (cont.) K<sub>d</sub> Expt 7: 10 g fine Sherwood Sandstone with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'

$K_d = (F - F_0) / F_0 * (V/M)$

Spreadsheet continued

Tube no.	NH <sub>4</sub> ratio finish/start	Wt tube + sst g	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog mg/l F	K <sub>d</sub> ml/g	Average K <sub>d</sub> ml/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.58	26.62	1	2.16	20.1.99	54.8	154.8	0.80	6.27	1.76				
5	0.58	26.62	1	2.22	20.1.99	56.2	156.2	0.77	5.93	1.77				
6	0.59	26.62	1	2.32	20.1.99	55.6	155.6	0.78	6.08	1.70				
7	0.57	26.59	1	2.32	20.1.99	56.3	156.3	0.77	5.91	1.81				
8	0.56	26.67	1	2.14	20.1.99	56.8	156.8	0.76	5.79	1.90	1.79		0.07	4.11
9	0.68	26.72	1	2.34	20.1.99	17.3	117.3	1.45	27.95	1.12				
10	0.59	26.63	1	2.14	21.1.99	16.7	116.7	1.38	24.22	1.68				
11	0.59	26.77	1	2.30	21.1.99	16.5	116.5	1.39	24.42	1.64				
12	0.54	26.76	1	2.48	21.1.99	19.2	119.2	1.34	21.86	2.07				
13	0.54	26.78	1	2.46	21.1.99	19.3	119.3	1.34	21.77	2.06	1.72		0.39	22.71
14		26.66	1	2.15	20.1.99	117.6	217.6	-0.29	0.51					
15		26.69	1	2.33	20.1.99	130.0	230.0	-0.50	0.31					
16		26.54	1	2.14	20.1.99	135.0	235.0	-0.59	0.26					
17		26.67	1	2.09	20.1.99	141.9	241.9	-0.71	0.20					
18		26.62	1	2.42	20.1.99	139.1	239.1	-0.66	0.22			0.30	0.13	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.17 K<sub>a</sub> Expt 8: 10 g fine Lower Chalk with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

Tube no.	Wt tube + lid g	Wt chalk added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weigh liquid g	Calc. NH <sub>4</sub> Cl mg/l	actual NH <sub>4</sub> Cl (see below) mg/l	dilution	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
		M							V		I					
1	12.47	10.02	22.48	23.02	45.51	8.10			23.02							
2	12.56	10.01	22.56	23.02	45.59	8.09			23.02							
3	12.50	10.02	22.51	23.06	45.57	8.13			23.06							
4	12.52	10.01	22.53	23.32	45.85	8.10	1.00	8.00	24.31	250	254.40	10.43	46.77	20.59	8.06	0.99
5	12.47	10.01	22.48	23.13	45.61	8.07	1.00	8.09	24.13	250	254.40	10.54	46.55	20.39	8.02	1.00
6	12.57	10.00	22.57	23.20	45.78	8.05	1.00	8.08	24.20	250	254.40	10.49	46.71	20.40	8.09	1.00
7	12.53	10.02	22.55	23.06	45.60	8.09	1.00		24.05	250	254.40	10.53	46.55	20.32	7.88	
8	12.48	10.00	22.48	23.00	45.48	8.10	1.00		24.00	250	254.40	10.56	46.41	20.20	7.99	
9	12.47	10.01	22.48	23.01	45.49	8.05	1.00	8.08	24.01	1000	1000.27	41.63	46.44	20.30	8.02	1.00
10	12.51	10.00	22.51	23.02	45.54	8.03	0.99	8.09	24.02	1000	1000.27	41.41	46.47	20.30	8.04	1.01
11	12.51	10.01	22.51	23.04	45.55	8.04	0.99	8.09	24.03	1000	1000.27	41.36	46.47	20.17	8.02	1.01
12	12.53	10.00	22.54	23.10	45.63	8.10	0.99		24.09	1000	1000.27	41.22	46.56	20.34	8.01	
13	12.53	10.02	22.55	23.00	45.55	8.06	0.99		23.99	1000	1000.27	41.40	46.49	20.17	8.01	
14	12.52	10.02	22.54	23.07	45.60	7.83	0.96	7.92	24.03	0	0	0.00	46.46	20.20	8.00	1.01
15	12.52	10.03	22.54	23.10	45.65	7.96	1.00	7.92	24.10	0	0	0.00	46.56	20.37	8.02	0.99
16	12.46	10.02	22.48	23.04	45.51	7.97	1.00	7.95	24.03	0	0	0.00	46.38	20.30	7.99	1.00
17	12.49	10.00	22.49	23.05	45.53	7.94	0.99		24.04	0	0	0.00	46.47	20.39	7.96	
18	12.52	10.03	22.56	23.17	45.73	8.00	0.99		24.16	0	0	0.00	46.60	20.45	7.96	

Tubes 1-3 = wash for chemical analysis  
 Tubes 4-8 = 10 mg/l  
 Tubes 9-13 = 40 mg/l  
 Tubes 14-18 = controls

1.0 M NH<sub>4</sub> stock solution =  
 250 mg/l NH<sub>4</sub> as molar  
 1000 mg/l NH<sub>4</sub> as mol  
 0 mg/l in tubes 14-18

actual mg/l =  
 17913.99  
 254.40  
 1000.27

**K<sub>a</sub> determinations using ammonia electrode method**

Table A.17 (cont.) K<sub>a</sub> Expt 8: 10 g fine Lower Chalk with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'

$K_a = \frac{(F-F_0)}{F_0} \times (V/M)$

Spreadsheet continued

Tube no.	NH <sub>4</sub> ratio finish/start	Wt tube + chalk g	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog F	K <sub>a</sub> ml/g	Average K <sub>a</sub> ml/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.60	26.17	1	2.28	22.1.99	52.5	152.5	0.80	6.27	1.61				
5	0.61	26.16	1	2.16	22.1.99	51.7	151.7	0.81	6.47	1.51				
6	0.56	26.31	1	2.13	22.1.99	54.2	154.2	0.77	5.86	1.92				
7	0.57	26.23	1	2.26	22.1.99	53.7	153.7	0.78	5.97	1.83				
8	0.65	26.21	1	2.20	22.1.99	50.2	150.2	0.84	6.87	1.29	1.63		0.25	15.36
9	0.73	26.14	1	2.16	22.1.99	12.9	112.9	1.48	30.35	0.89				
10	0.69	26.16	1	2.15	22.1.99	14.4	114.4	1.46	28.59	1.08				
11	0.65	26.30	1	2.18	22.1.99	15.9	115.9	1.43	26.93	1.29				
12	0.66	26.23	1	2.20	22.1.99	15.7	115.7	1.43	27.15	1.25				
13	0.62	26.31	1	2.20	22.1.99	17.3	117.3	1.41	25.47	1.50	1.20		0.23	19.01
14		26.26	1	1.96	22.1.99	161.2	261.2	-1.08	0.08					
15		26.17	1	2.17	22.1.99	166.1	266.1	-1.17	0.07					
16		26.09	1	2.16	22.1.99	173.7	273.7	-1.30	0.05					
17		26.08	1	2.14	22.1.99	176.0	276.0	-1.34	0.05					
18		26.14	1	1.98	22.1.99	183.9	283.9	-1.48	0.03			0.06	0.02	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.18 K<sub>a</sub> Expt 9: 10 g Mercia Mudstone with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

Tube no.	Wt tube + lid g	Wt mdst added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weight liquid g	Calc. NH <sub>4</sub> Cl mg/l	actual NH <sub>4</sub> Cl (see below) mg/l	dilution	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
		M							Y			I				
1	12.44	10.01	22.45	23.02	45.47	7.84			23.02							
2	12.49	10.04	22.53	23.49	46.02	7.86			23.49							
3	12.51	10.02	22.53	23.18	45.71	7.78			23.18							
4	12.51	10.03	22.54	23.17	45.71	7.67	0.98	7.85	24.15	250	253.28	10.27	46.60	19.91	7.87	1.02
5	12.47	10.02	22.48	23.04	45.53	7.90	0.99	7.85	24.03	250	253.28	10.40	46.43	19.51	8.09	0.99
6	12.47	10.01	22.48	23.14	45.62	7.92	0.98	7.92	24.12	250	253.28	10.33	46.53	19.47	8.05	1.00
7	12.49	10.03	22.52	23.12	45.65	7.93	0.99		24.11	250	253.28	10.36	46.54	19.48	8.08	
8	12.50	10.05	22.55	23.19	45.74	7.90	0.99		24.17	250	253.28	10.35	46.63	19.52	8.15	
9	12.50	10.00	22.50	23.30	45.80	7.91	0.98	7.88	24.28	1000	1001.70	40.33	46.73	19.75	8.01	1.00
10	12.52	10.01	22.53	23.21	45.74	7.89	0.99	7.88	24.20	1000	1001.70	40.88	46.64	19.62	7.95	1.00
11	12.48	10.01	22.48	23.23	45.71	7.86	0.99	7.87	24.21	1000	1001.70	40.76	46.57	19.62	8.09	1.00
12	12.51	10.02	22.53	23.21	45.73	7.88	0.98		24.19	1000	1001.70	40.73	46.67	19.56	7.98	
13	12.55	10.00	22.55	23.66	46.21	7.90	0.98		24.64	1000	1001.70	39.94	47.15	20.05	8.08	
14	12.49	10.00	22.50	23.41	45.90	7.86	0.98	7.65	24.38	0	0	0.00	46.82	19.82	7.84	0.97
15	12.55	10.00	22.55	23.27	45.82	7.87	0.98	7.75	24.26	0	0	0.00	46.67	19.66	7.90	0.98
16	12.51	10.02	22.53	23.62	46.15	7.89	0.99	7.80	24.60	0	0	0.00	48.08	21.03	8.11	0.99
17	12.52	10.02	22.54	23.52	46.05	7.86	1.00	7.79	24.51	0	0	0.00	46.98	19.89	8.13	
18	12.48	10.03	22.51	23.53	46.03	7.90	0.99	7.89	24.51	0	0	0.00	46.96	19.40	8.08	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

1.0 M NH<sub>4</sub> stock solution =

250 mg/l NH<sub>4</sub> as molar

1000 mg/l NH<sub>4</sub> as molar

0 mg/l in tubes 14-18

actual mg/l =

17913.99

253.28

1001.70

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.18 (cont.) K<sub>a</sub> Expt 9: 10 g Mercia Mudstone with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

$K_a = (F - F^*) / F^* (V/M)$

Spreadsheet continued

Tube no.	NH <sub>4</sub> ratio finish/start	Wt tube + mudst g	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog F	K <sub>a</sub> ml/g	Average K <sub>a</sub> ml/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.22	27.05	1	2.07	27.1.99	80.4	180.4	0.35	2.26	8.53				
5	0.25	27.03	1	1.95	27.1.99	77.1	177.1	0.41	2.57	7.30				
6	0.24	27.06	1	2.30	27.1.99	78.1	178.1	0.39	2.47	7.65				
7	0.24	27.07	1	1.90	27.1.99	77.9	177.9	0.40	2.49	7.58				
8	0.23	27.11	1	2.13	27.1.99	78.6	178.6	0.38	2.43	7.86	7.78		0.47	5.98
9	0.29	26.97	1	2.11	27.1.99	38.7	138.7	1.07	11.78	5.88				
10	0.30	27.02	1	2.32	27.1.99	37.7	137.7	1.09	12.26	5.65				
11	0.31	26.95	1	2.20	27.1.99	37.3	137.3	1.10	12.45	5.50				
12	0.32	27.02	1	2.19	27.1.99	36.4	136.4	1.11	12.90	5.21				
13	0.32	27.09	1	1.85	27.1.99	36.6	136.6	1.11	12.80	5.22	5.49		0.29	5.22
14		27.00	1	2.23	27.1.99	164.8	264.8	-1.10	0.08					
15		27.01	1	2.50	27.1.99	167.9	267.9	-1.15	0.07					
16		26.99	1	2.15	27.1.99	169.1	269.1	-1.17	0.07					
17		27.04	1	2.06	27.1.99	166.8	266.8	-1.13	0.07					
18		27.09	1	2.12	27.1.99	168.6	268.6	-1.16	0.07			0.07	0.00	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

**K<sub>i</sub> determinations using ammonia electrode method**

**Table A.19 K<sub>i</sub> Expt 10: 10 g Lower Oxford Clay with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

Tube no.	Wt tube + lid g	Wt clay added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weight liquid g	Calc. NH <sub>4</sub> Cl mg/l	actual NH <sub>4</sub> Cl (see below) mg/l	dilution	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
1	12.48	10.02	22.50	22.00	44.50	7.04			22.00							
2	12.47	10.02	22.49	22.64	45.13	7.07			22.64							
3	12.49	10.01	22.50	22.23	44.73	7.09			22.23							
4	12.48	10.00	22.48	22.46	44.95	7.15	1.01	7.14	23.47	250	254.00	10.90	46.86	16.49	7.23	1.00
5	12.52	10.01	22.53	22.03	44.55	7.14	1.01	7.17	23.03	250	254.00	11.09	45.43	16.54	7.24	1.00
6	12.46	10.01	22.47	22.38	44.85	7.12	1.01	7.25	23.38	250	254.00	10.94	45.78	16.73	7.30	1.02
7	12.51	10.04	22.55	22.14	44.69	7.13	1.01	7.24	23.15	250	254.00	11.05	45.47	16.52	7.25	1.02
8	12.48	10.02	22.51	22.13	44.64	7.13	1.01	7.21	23.14	250	254.00	11.04	45.54	16.24	7.28	1.01
9	12.57	10.01	22.58	22.17	44.75	7.12	1.01	7.19	23.18	1000	1002.55	43.59	45.63	16.42	7.50	1.01
10	12.48	10.02	22.50	22.15	44.65	7.15	1.01	7.19	23.16	1000	1002.55	43.59	45.59	16.37	7.31	1.01
11	12.49	10.02	22.51	22.15	44.66	7.16	1.00	7.22	23.16	1000	1002.55	43.49	45.61	16.27	7.30	1.01
12	12.54	10.02	22.55	22.21	44.77	7.13	1.01	7.21	23.22	1000	1002.55	43.53	45.67	16.82	7.32	1.01
13	12.46	10.00	22.46	22.44	44.90	7.13	1.01	7.22	23.45	1000	1002.55	43.17	45.80	16.55	7.31	1.01
14	12.50	10.02	22.51	22.35	44.87	7.00	1.00	7.25	23.35	0	0	0.00	45.77	16.23	7.07	1.04
15	12.46	10.01	22.47	22.25	44.72	7.01	1.00	7.23	23.25	0	0	0.00	45.59	16.04	7.08	1.03
16	12.51	10.02	22.52	22.37	44.90	7.03	1.00	7.23	23.37	0	0	0.00	45.80	16.31	7.17	1.03
17	12.53	10.02	22.55	22.09	44.64	7.04	1.00	7.23	23.09	0	0	0.00	45.43	15.98	7.18	1.03
18	12.49	10.02	22.51	22.15	44.67	7.06	1.00	7.24	23.15	0	0	0.00	45.57	16.36	7.25	1.03

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

0.1 M ammonium standard solution : 0.10

250 mg/l NH<sub>4</sub> as molar : Tubes 4-8 0.014

1000 mg/l NH<sub>4</sub> as mol: Tubes 9-13 0.056

0 mg/l in tubes 14-18

actual mg/l =

1800.00

254.00

1002.55



**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.19 (cont.) K<sub>a</sub> Expt 10: 10 g Lower Oxford Clay with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

$K_a = (1-F)/F * (V/M)$

Spreadsheets continued

Tube no.	NH <sub>3</sub> ratio finish/start	Wt tube + clay g	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl reading mV	Reading + 100 mV	Log using formula	Antilog F	K <sub>a</sub> ml/g	Average K <sub>a</sub> ml/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.61	29.37	1	2.65	17.2.99	61.2	161.2	0.82	6.66	1.50				
5	0.61	28.90	1	2.24	17.2.99	60.9	160.9	0.83	6.74	1.49				
6	0.61	29.05	1	2.30	17.2.99	61.1	161.1	0.83	6.68	1.49				
7	0.61	28.94	1	2.38	17.2.99	60.9	160.9	0.83	6.74	1.48				
8	0.61	29.29	1	2.26	17.2.99	60.9	160.9	0.83	6.74	1.47	1.48		0.01	0.62
9	0.50	29.21	1	2.33	17.2.99	32.0	132.0	1.33	21.59	2.36				
10	0.51	29.22	1	2.29	17.2.99	31.5	131.5	1.34	22.03	2.26				
11	0.48	29.34	1	2.34	17.2.99	32.8	132.8	1.32	20.91	2.50				
12	0.52	28.83	1	2.43	17.2.99	30.7	130.7	1.36	22.75	2.12				
13	0.53	29.25	1	2.52	17.2.99	30.7	130.7	1.36	22.75	2.10	2.27		0.17	7.30
14		29.54	1	2.20	17.2.99	85.3	185.3	0.40	2.52					
15		29.55	1	2.27	17.2.99	86.7	186.7	0.38	2.38					
16		29.49	1	2.40	17.2.99	88.4	188.4	0.35	2.22					
17		29.45	1	2.81	17.2.99	88.7	188.7	0.34	2.20					
18		29.21	1	2.44	17.2.99	88.3	188.3	0.35	2.23			2.31	0.14	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

**K<sub>a</sub> determinations using ammonia electrode method**

**Table A.20 K<sub>a</sub> Expt 11: 10 g Gault Clay with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

Tube no.	Wt tube + lid g	Wt clay added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weight liquid g	Calc. NH <sub>4</sub> Cl mg/l	actual NH <sub>4</sub> Cl (see below) mg/l	dilution	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
		M							Y			I				
1	12.46	10.01	22.47	24.04	46.50	7.66			24.04							
2	12.52	10.03	22.55	24.05	46.60	7.63			24.05							
3	12.53	10.00	22.53	24.02	46.55	7.69			24.02							
4	12.53	10.03	22.56	24.02	46.57	7.51	1.00	7.73	25.01	250	253.94	10.15	47.11	17.81	7.92	1.03
5	12.49	10.04	22.53	24.05	46.58	7.61	1.01	7.80	25.06	250	253.94	10.18	47.19	18.05	7.90	1.02
6	12.50	10.02	22.52	24.01	46.52	7.72	1.01	7.79	25.01	250	253.94	10.21	47.35	18.16	7.89	1.01
7	12.57	10.01	22.58	24.20	46.78	7.76	1.00	7.50	25.20	250	253.94	10.09	47.51	18.40	7.92	0.97
8	12.50	10.03	22.53	24.13	46.66	7.79	1.00	7.62	25.13	250	253.94	10.12	47.39	18.38	7.95	0.98
9	12.47	10.03	22.49	24.07	46.57	7.79	1.00	7.72	25.07	1000	1002.12	39.86	47.32	18.36	7.97	0.99
10	12.49	10.04	22.53	24.05	46.58	7.78	1.00	7.72	25.05	1000	1002.12	39.96	47.28	18.29	7.91	0.99
11	12.53	10.01	22.54	24.06	46.61	7.81	1.00	7.87	25.07	1000	1002.12	40.13	47.20	18.48	7.96	1.01
12	12.46	10.03	22.48	24.10	46.58	7.85	1.00	7.89	25.10	1000	1002.12	40.02	47.39	18.57	7.96	1.01
13	12.50	10.02	22.51	24.05	46.57	7.86	1.00	7.87	25.05	1000	1002.12	40.06	47.41	18.58	7.99	1.00
14	12.47	10.03	22.50	24.15	46.65	7.61	1.00	7.51	25.15	0	0	0.00	47.42	18.34	8.02	0.99
15	12.47	10.02	22.49	24.08	46.57	7.59	1.01	7.59	25.09	0	0	0.00	47.35	18.27	7.87	1.00
16	12.55	10.01	22.56	24.14	46.70	7.68	1.01	7.63	25.14	0	0	0.00	47.46	18.39	7.89	0.99
17	12.49	10.03	22.52	24.18	46.69	7.63	1.01	7.57	25.18	0	0	0.00	47.53	18.39	7.77	0.99
18	12.53	10.03	22.56	24.08	46.64	7.76	1.00	7.62	25.08	0	0	0.00	47.41	18.17	8.11	0.98

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

0.1 M ammonium standard solution : 0.10

250 mg/l NH<sub>4</sub> as molar : Tubes 4-8 0.01

1000 mg/l NH<sub>4</sub> as molar : Tubes 9-13 0.06

0 mg/l in tubes 14-18

actual mg/l = 1800.00

253.94

1002.12

**K<sub>a</sub> determinations using ammonia electrode method**

Table A.20 (cont.) K<sub>a</sub> Expt 11: 10 g Gault Clay with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'

$K_a = (F/RT) \ln(V/M)$

Spreadsheet continued

Tube no.	NH <sub>4</sub> finish/start	WT tube + clay g	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog mg/l F	K <sub>a</sub> ml/g	Average K <sub>a</sub> ml/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.27	29.30	1	2.11	18.2.99	74.7	174.7	0.43	2.70	6.87				
5	0.27	29.14	1	2.15	18.2.99	74.6	174.6	0.43	2.71	6.87				
6	0.27	29.18	1	2.16	18.2.99	74.5	174.5	0.44	2.72	6.86				
7	0.26	29.11	1	1.98	18.2.99	75.1	175.1	0.42	2.66	7.03				
8	0.27	29.01	1	1.87	18.2.99	74.8	174.8	0.43	2.69	6.91	6.91		0.07	0.99
9	0.28	28.95	1	2.21	18.2.99	39.3	139.3	1.05	11.16	6.43				
10	0.29	28.99	1	2.16	18.2.99	38.3	138.3	1.07	11.62	6.09				
11	0.28	28.71	1	2.18	18.2.99	38.9	138.9	1.05	11.34	6.36				
12	0.29	28.82	1	2.14	18.2.99	38.6	138.6	1.06	11.48	6.23				
13	0.29	28.83	1	2.18	18.2.99	38.3	138.3	1.07	11.62	6.12	6.25		0.15	2.35
14		29.07	1	2.10	18.2.99	132.4	232.4	-0.57	0.27					
15		29.08	1	2.28	18.2.99	135.3	235.3	-0.62	0.24					
16		29.06	1	2.09	18.2.99	141.7	241.7	-0.73	0.18					
17		29.13	1	2.33	18.2.99	173.2	273.2	-1.28	0.05					
18		29.23	1	2.34	18.2.99	163.0	263.0	-1.10	0.08			0.16	0.10	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

**K<sub>d</sub> determinations using ammonia electrode method**

Table A.21 K<sub>d</sub> Expt 12: 10 g Lower Chalk with 25 g Thriplow leachate

Tube no.	Wt tube + lid g	Wt chalk added g	Total weight g	Wt leachate added g	Weight +TR4 g	pH at start	Total liquid g	NH <sub>4</sub> Cl mg/l	Wt after centrifuge g	Wt liquid removed g	pH liquid removed	NH <sub>4</sub> liquid removed g	NI <sub>4</sub> ratio fin/start	Wt tube + chalk g	8 M HCl drops	pH now	Date meas.	NH <sub>4</sub> Cl mV	Reading +100 mV	Log using formula	Antilog	K <sub>d</sub> mg/g	Av. K <sub>d</sub> ml/g	St dev.	Rel. St dev %	K <sub>d</sub> =(F-F*)/(V/M)			
																										F	F*		
1	12.52	10.05	22.57	26.10	48.67	6.52	26.10	4.25	48.15	21.98	6.63	26.17		26.17			8.3.99												
2	12.55	10.05	22.59	26.07	48.66	6.52	26.07	4.25	48.57	22.38	6.67	26.19		26.19			8.3.99												
3	12.51	10.02	22.52	26.02	48.54	6.52	26.02	4.25	48.28	22.15	6.70	26.13		26.13			8.3.99												
4	12.47	10.00	22.48	26.03	48.50	6.52	26.03	4.25	48.03	21.97	6.73	26.06	1.01	26.06	1.00	4.98	8.3.99	62.00	162.00	0.63	4.30	-0.03							
5	12.52	10.03	22.55	26.03	48.58	6.52	26.03	4.25	48.30	22.16	6.68	26.14	1.01	26.14	1.00	3.05	8.3.99	62.00	162.00	0.63	4.30	-0.03							
6	12.58	10.03	22.62	26.09	48.70	6.52	26.09	4.25	48.67	22.44	6.71	26.24	0.97	26.24	1.00	3.43	8.3.99	63.20	163.20	0.61	4.10	0.09							
7	12.50	10.01	22.51	26.13	48.64	6.52	26.13	4.25	48.61	22.54	6.72	26.07	0.98	26.07	1.50	2.36	8.3.99	62.90	162.90	0.62	4.15	0.06							
8	12.53	10.01	22.54	26.08	48.62	6.52	26.08	4.25	48.60	22.47	6.74	26.13	0.98	26.13	1.50	2.14	8.3.99	62.80	162.80	0.62	4.17	0.05	0.03	0.06	211.11				

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = Thriplow leachate containing 4.2484 mg/l ammonium

**K<sub>a</sub> determinations using ammonia electrode method**

Table A.22 K<sub>a</sub> Expt 13: 10 g Mercia Mudstone (mudst) with 25 g Thriplow leachate

Tube no.	Wt + lid	Wt mudst added	Total weight	Wt leachate added	Wt + leachate added	pH at start	pH at liquid	Total NH <sub>4</sub> Cl	Wt after centrifuge	Wt liquid removed	pH liquid removed	NH <sub>4</sub> liquid removed	NH <sub>4</sub> ratio fm/start	Wt + mudst	drops	8 M HCl	pH now measured	Date	NH <sub>4</sub> Cl Reading	Log using formula	Antilog	K <sub>a</sub> ml/g	Av. K <sub>a</sub> ml/g	St dev	Rel. St Dev %	K <sub>a</sub> = (F-F)/F*(V/M)	
																										mg/l	F
1	12.48	10.02	22.50	26.04	48.55	6.52	26.10	4.25	48.34	21.35	6.97	0.36	26.99	1.50	2.83	8.3.99	87.70	187.70	0.18	1.53	4.64						
2	12.50	10.03	22.53	26.06	48.59	6.52	26.07	4.25	48.57	21.53	6.98	0.34	27.04	1.50	2.06	8.3.99	88.90	188.90	0.16	1.46	4.99						
3	12.55	10.01	22.56	26.00	48.56	6.52	26.02	4.25	48.48	21.38	6.99	0.34	27.09	1.50	2.06	8.3.99	88.90	188.90	0.16	1.46	4.99						
4	12.45	10.02	22.47	26.17	48.65	6.52	26.03	4.25	48.44	21.47	7.03	0.33	26.85	1.50	2.51	8.3.99	89.50	189.50	0.15	1.42	5.19						
5	12.47	10.01	22.47	26.04	48.51	6.52	26.03	4.25	48.28	21.37	7.03	0.32	26.87	1.50	2.26	8.3.99	90.90	190.90	0.13	1.34	5.65						
6	12.48	10.00	22.48	26.02	48.51	6.52	26.09	4.25	48.42	21.54	7.05	0.31	26.95	1.50	2.64	8.3.99	91.20	191.20	0.12	1.33	5.72						
7	12.48	10.00	22.48	26.09	48.58	6.52	26.13	4.25	48.52	21.65	7.06	0.31	26.95	1.50	2.64	8.3.99	91.20	191.20	0.12	1.33	5.72						
8	12.53	10.03	22.57	26.56	49.12	6.52	26.08	4.25	49.10	22.14	7.02	0.31	26.95	1.50	2.64	8.3.99	91.20	191.20	0.12	1.33	5.72						

Tubes 2,4,5 = wash for chemical analysis

Tubes 1,3,6-8 = Thriplow leachate containing 4.2484 mg/l ammonium

**K<sub>d</sub> determinations using ammonia electrode method**

**Table A.23 K<sub>d</sub> Expt 14: 10 g Lincolnshire Limestone (lst) with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

Tube no.	Wt tube + lid g	Wt lst added g	Total weight g	Wt NaCl added g	Weight inc liquid g	pH after wash	Wt NH <sub>4</sub> Cl added g	pH after NH <sub>4</sub> Cl	Total weight liquid g	Calc. NH <sub>4</sub> Cl mg/l	actual NH <sub>4</sub> Cl (see below) mg/l	dilution	Wt after cent g	Wt liquid removed g	pH liquid removed	pH ratio after NH <sub>4</sub>
1	12.52	10.01	22.54	24.06	46.60	7.30			24.06							
2	12.58	10.01	22.58	24.14	46.73	7.34			24.14							
3	12.46	10.00	22.47	24.14	46.60	7.43			24.14							
4	12.46	10.01	22.48	24.09	46.57	7.26	1.00	7.33	25.09	250.00	254.72	10.17	47.46	21.28	7.38	1.01
5	12.55	10.03	22.58	24.33	46.92	7.30	1.01	7.26	25.34	250.00	254.72	10.12	47.82	21.59	7.38	0.99
6	12.51	10.00	22.51	24.15	46.66	7.45	1.01	7.46	25.16	250.00	254.72	10.22	47.57	21.41	7.40	1.00
7	12.46	10.00	22.46	24.22	46.68	7.28	1.01	7.30	25.23	250.00	254.72	10.20	47.59	21.44	7.40	1.00
8	12.50	10.00	22.50	24.16	46.65	7.24	1.01	7.28	25.17	250.00	254.72	10.24	47.58	21.45	7.39	1.01
9	12.49	10.01	22.50	24.18	46.68	7.40	1.01	7.45	25.19	1000.00	1007.45	40.47	47.62	21.45	7.47	1.01
10	12.51	10.04	22.55	24.09	46.65	7.47	1.01	7.51	25.11	1000.00	1007.45	40.59	47.58	21.33	7.55	1.01
11	12.54	10.02	22.57	24.12	46.68	7.47	1.01	7.52	25.13	1000.00	1007.45	40.56	47.59	21.50	7.55	1.01
12	12.46	10.04	22.50	24.59	47.09	7.46	1.01	7.53	25.60	1000.00	1007.45	39.88	47.92	21.85	7.54	1.01
13	12.49	10.01	22.50	24.31	46.81	7.52	1.01	7.52	25.32	1000.00	1007.45	40.29	47.72	21.65	7.52	1.00
14	12.56	10.02	22.58	24.17	46.75	7.32	1.01	7.40	25.17	0.00	0.00	0.00	47.67	21.36	7.29	1.01
15	12.56	10.03	22.58	24.09	46.68	7.30	1.00	7.41	25.10	0.00	0.00	0.00	47.56	21.29	7.40	1.02
16	12.48	10.00	22.48	24.01	46.50	7.30	1.01	7.40	25.02	0.00	0.00	0.00	47.36	21.26	7.31	1.01
17	12.59	10.01	22.60	24.27	46.87	7.35	1.01	7.45	25.28	0.00	0.00	0.00	47.65	21.47	7.46	1.01
18	12.48	10.03	22.51	24.24	46.75	7.36	1.01	7.47	25.24	0.00	0.00	0.00	47.63	21.47	7.45	1.01

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls

0.1 M ammonium standard solution : 0.10000

250 mg/l NH<sub>4</sub> as molar s Tubes 4-8

1000 mg/l NH<sub>4</sub> as molar s Tubes 9-13

0 mg/l in tubes 14-18

1800.00

254.72

1007.45

actual mg/l =

**K<sub>d</sub> determinations using ammonia electrode method**

**Table A.23 (cont.) K<sub>d</sub> Expt 14: 10 g Lincolnshire Limestone (1st) with 10 or 40 mg/l ammonium chloride after 48 hours shaking at 'natural pH'**

$K_d = \frac{(F-F_0)}{F} * (V/M)$

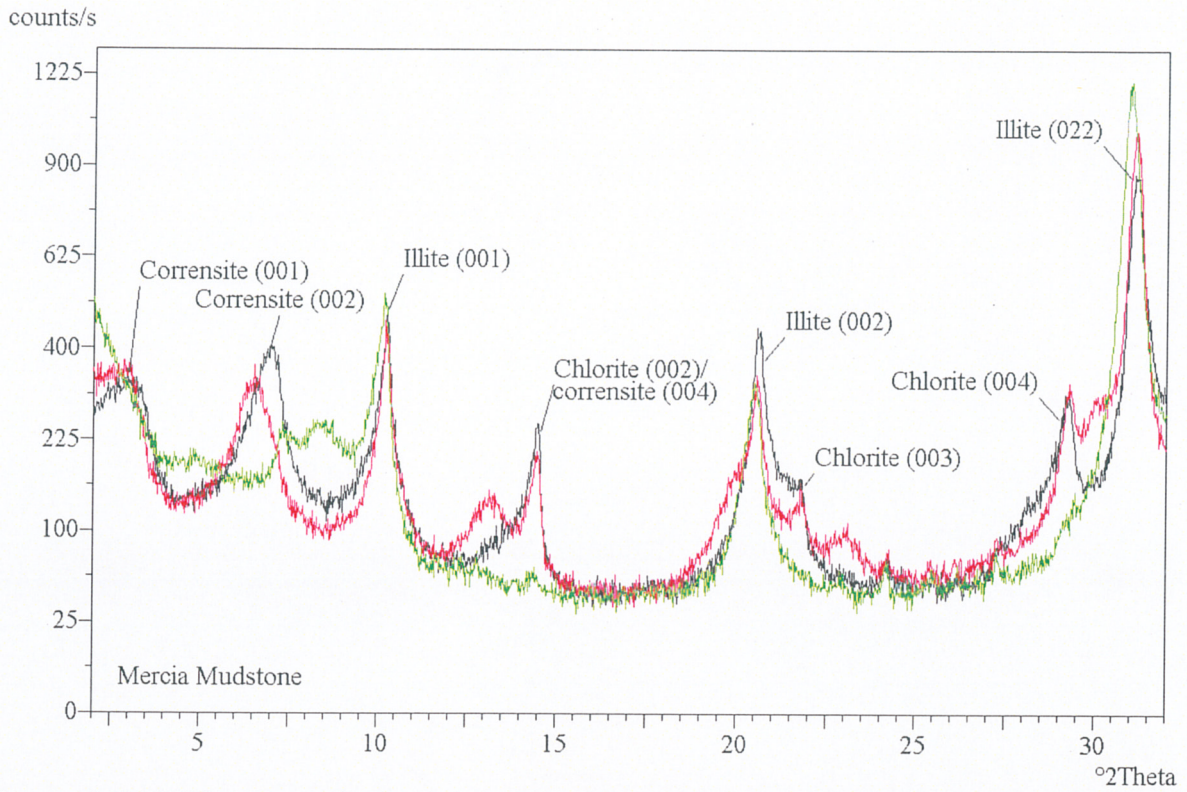
Tube no.	NH <sub>4</sub> ratio finish/start	Wt tube + 1st	8 M HCl drops	pH now	Date measured	NH <sub>4</sub> Cl mV	Reading + 100 mV	Log using formula	Antilog F	K <sub>d</sub> ml/g	Average K <sub>d</sub> ml/g	Blank average mg/l	Standard deviation	Relative St Dev %
1														
2														
3														
4	0.77	26.18	1	2.28	11.3.99	50.5	150.5	0.89	7.83	0.75				
5	0.77	26.23	1	2.16	11.3.99	50.7	150.7	0.89	7.76	0.77				
6	0.78	26.12	1	2.09	11.3.99	50.0	150.0	0.90	7.98	0.71				
7	0.75	26.14	1	2.11	11.3.99	50.9	150.9	0.89	7.70	0.82				
8	0.76	26.13	1	2.31	11.3.99	50.6	150.6	0.89	7.80	0.79	0.77		0.04	5.54
9	0.79	26.17	1	2.09	11.3.99	15.3	115.3	1.50	31.81	0.69				
10	0.79	26.24	1	2.28	11.3.99	15.2	115.2	1.50	31.93	0.68				
11	0.80	26.08	1	2.23	11.3.99	14.8	114.8	1.51	32.45	0.63				
12	0.80	26.07	1	2.23	11.3.99	15.3	115.3	1.50	31.81	0.65				
13	0.79	26.07	1	2.36	11.3.99	15.3	115.3	1.50	31.81	0.67	0.66		0.02	3.71
14		26.31	1	2.15	11.3.99	132.2	232.2	-0.52	0.30					
15		26.26	1	2.02	11.3.99	134.2	234.2	-0.55	0.28					
16		26.10	1	2.72	11.3.99	179.6	279.6	-1.34	0.05					
17		26.18	1	2.17	11.3.99	138.7	238.7	-0.63	0.23					
18		26.16	1	2.12	11.3.99	136.3	236.3	-0.59	0.26			0.22	0.10	

Tubes 1-3 = wash for chemical analysis

Tubes 4-8 = 10 mg/l

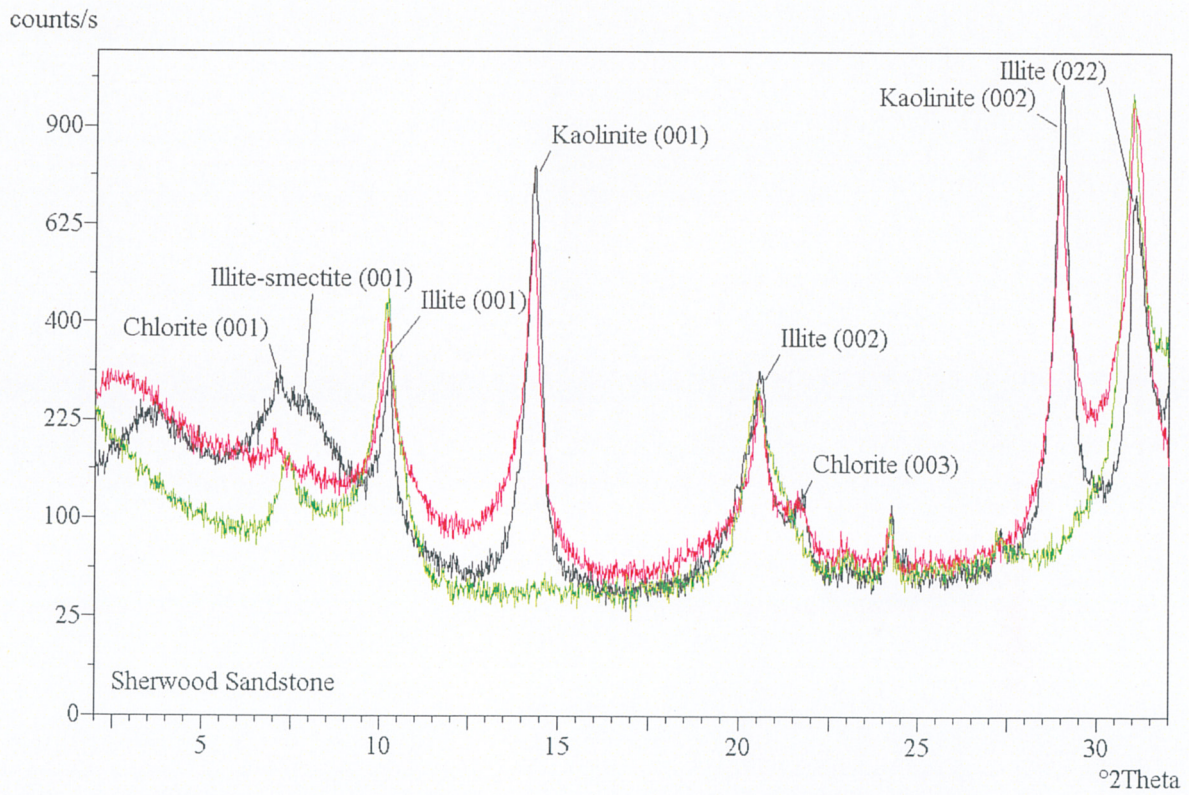
Tubes 9-13 = 40 mg/l

Tubes 14-18 = controls



**Figure A.1.** XRD traces obtained from the oriented mount prepared from the fine (clay) fraction of the Mercia Mudstone sample.

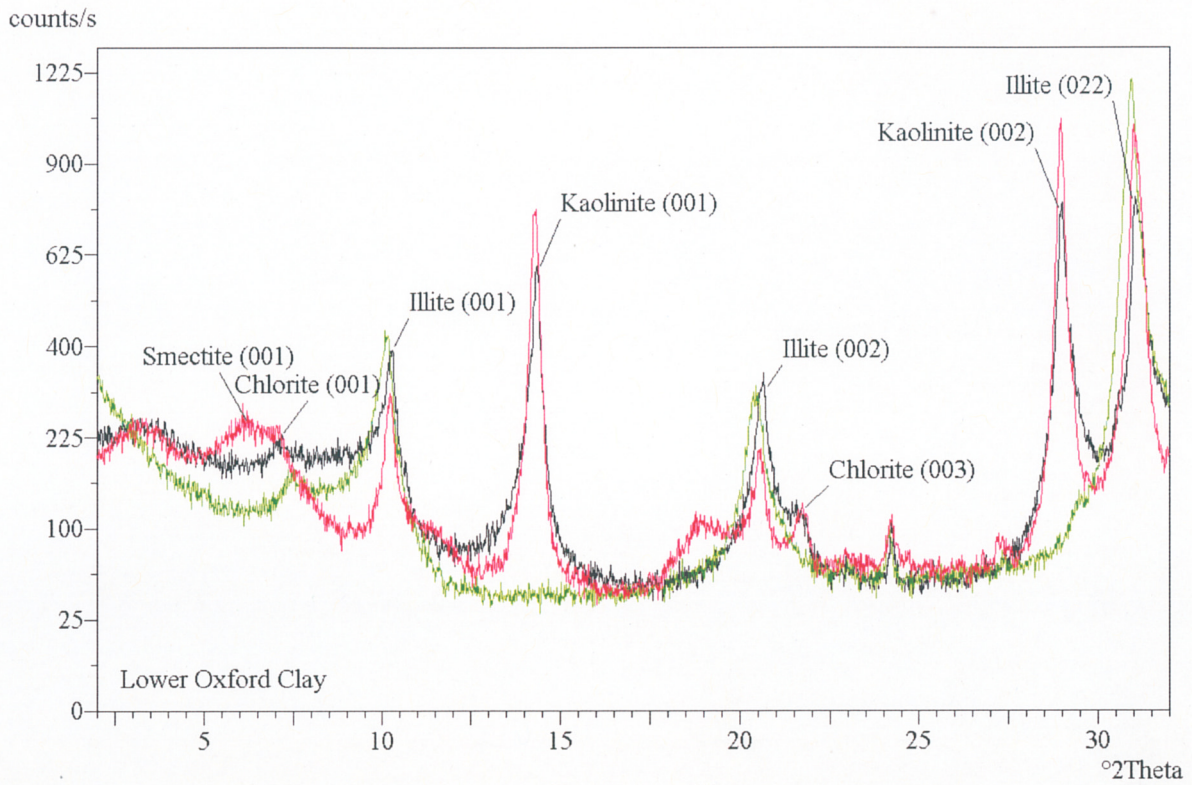
Black = air dried, red = glycol solvated state and green = after heating to 550 °C for 2 hours.



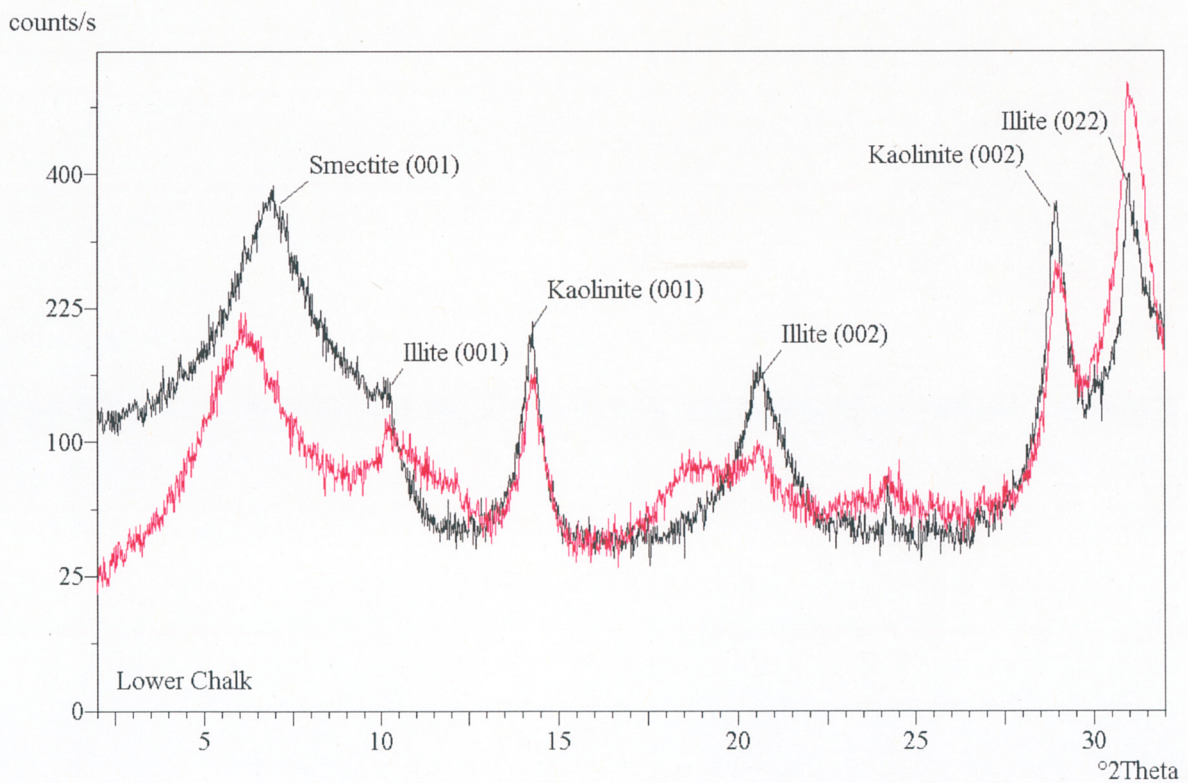
**Figure A.2.** XRD traces obtained from the oriented mount prepared from the fine (clay) fraction of the Sherwood Sandstone sample.

Black = air dried, red = glycol solvated state and green = after heating to 550 °C for 2 hours.

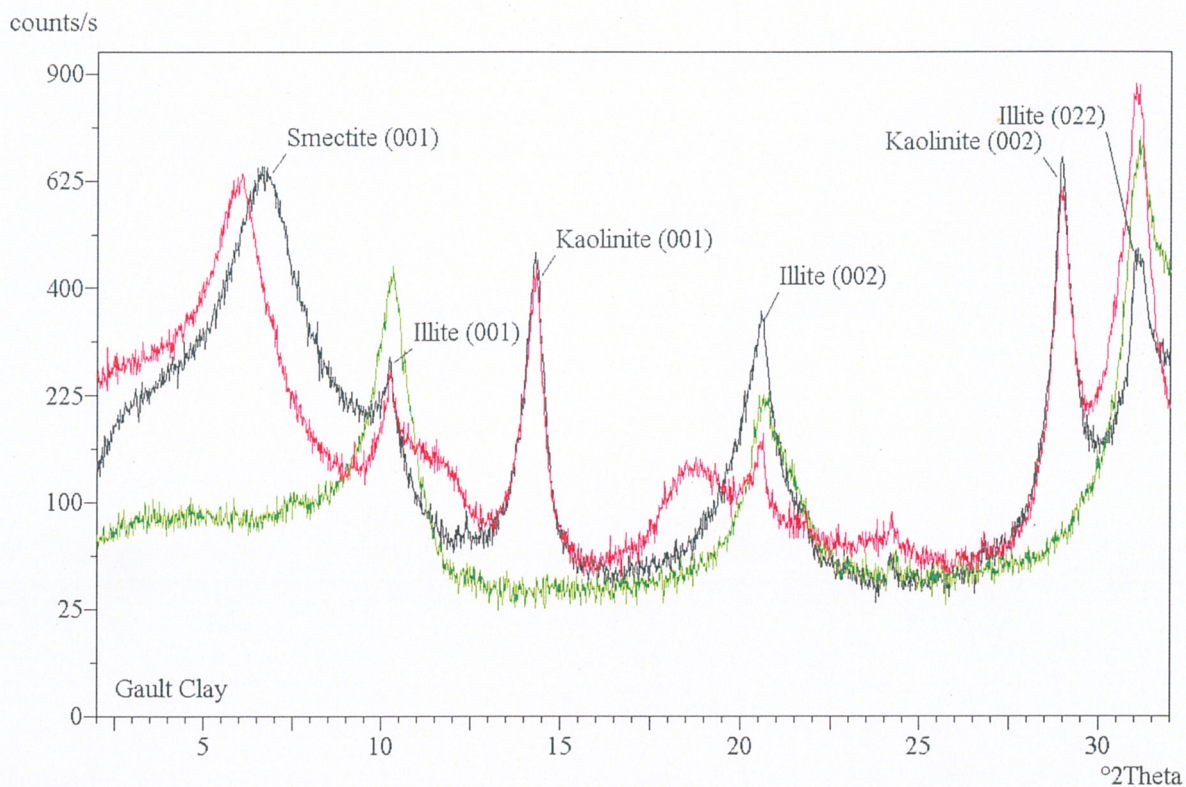




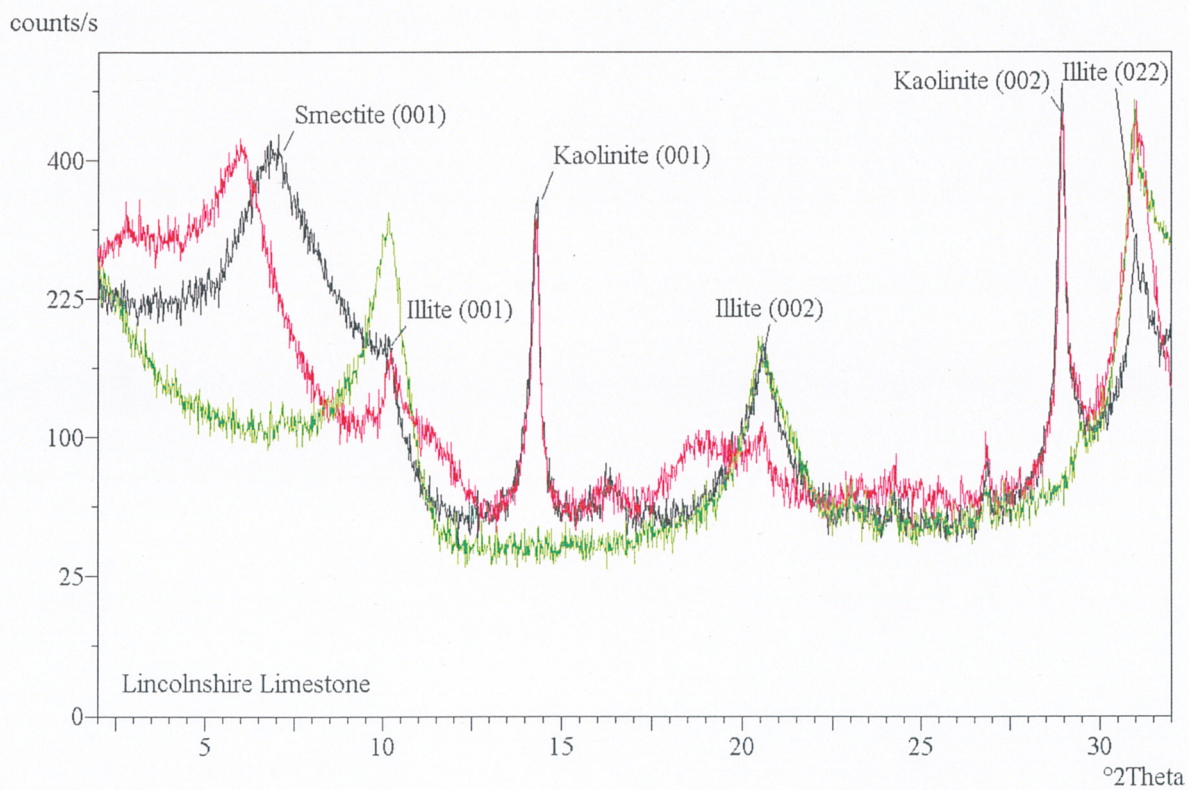
**Figure A.3.** XRD traces obtained from the oriented mount prepared from the fine (clay) fraction of the Lower Oxford Clay sample.  
 Black = air dried, red = glycol solvated state and green = after heating to 550 °C for 2 hours.



**Figure A.4.** XRD traces obtained from the oriented mount prepared from the fine (clay) fraction of the Lower Chalk sample.  
 Black = air dried and red = glycol solvated.



**Figure A.5.** XRD traces obtained from the oriented mount prepared from the fine (clay) fraction of the Gault Clay sample. Black = air dried, red = glycol solvated state and green = after heating to 550 °C for 2 hours.



**Figure A.6.** XRD traces obtained from the oriented mount prepared from the fine (clay) fraction of the Lincolnshire Limestone sample. Black = air dried, red = glycol solvated state and green = after heating to 550 °C for 2 hours.