CEC & K_d Determination in Landfill Performance Evaluation

A review of methodologies and preparation of standard materials for laboratory analysis

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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 Environment Agency staff and others wishing to study and model pollutant migration, particularly around landfill sites.

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EXECUTIVE SUMMARY

LandSim is a probabilistic quantitative risk assessment model issued by the Environment Agency for use by regulatory staff in landfill performance evaluation. LandSim takes into account factors such as liner and leachate-removal system and design, and the geological and hydrogeological regimes beneath and around the site in question. Among the input values required for the model is the cation exchange capacity (CEC) of geological materials around the landfill and the partition coefficient (K_d) of key solutes in leachates. CEC can be defined as the sum of exchangeable cations that a mineral, rock or soil can adsorb at a specific pH. K_d represents overall sorption of a particular species in leachate, irrespective of process. Both CEC and K_d are critical parameters in modelling the ability over time of the geosphere to retard the migration from landfill sites of leachates in groundwater.

Site-specific values for CEC and K_d have in the past often not been obtained because of the time and expense involved, and because of the absence of appropriate reference standards for calibrating methods. The LandSim manual provides default values for these parameters based on those published in the open literature for typical lithologies.

The principal aims of this study are to recommend standard methods for determining CEC and K_d in geological materials, to produce reference standards for calibrating these methods, and to extend the list of suggested default values currently available in LandSim. The intention is to encourage the adoption within UK laboratories of standard methods for determining CEC and K_d, and to maximize interlaboratory consistency.

The report is in two parts. Section 1 is a review of methods for determining CEC and K_d, which concludes with recommendations for validation experiments to evaluate and compare methods short-listed for adoption as ‘standards’ for providing input to LandSim. The CEC methods are: the $BaCl_2$ (‘compulsive displacement’) method; the $SrCl_2$ (single displacement and summation) method; and the methylene blue (sorption of an inorganic dye) method. Although these methods differ considerably in detail, each offers a combination of relative simplicity, adequate precision and practical advantages over other methods.

Section 2 outlines the results of the validation experiments. CEC and K_d have been determined on six ‘reference’ materials: Sherwood Sandstone, Mercia Mudstone, Gault Clay, Lower Oxford Clay, Lower Chalk and Lincolnshire Limestone. Each of these is an important UK lithology, and the site of existing or possible future landfill development. X-ray diffraction (XRD) analysis has been used to identify mineral constituents and provide a basis for interpretation of CEC results.

CEC work

The $BaCl_2$ method provides generally well constrained results, though some variation between batches of the same sample point to small, consistent variations in laboratory practice (Table A). The $SrCl_2$ method produced results broadly comparable to the $BaCl_2$ method for carbonate- and sulphate-free samples, but grossly over-estimated the CEC of the Lincolnshire Limestone, Lower Chalk and Gault Clay, all of which contain calcite as a major component. The methylene blue method, the simplest and quickest of the three, produced consistent CEC values which are generally significantly lower than corresponding results obtained using the $BaCl_2$ method.

Table A Results of the CEC determinations

Lithology	$BaCl_2$ method			$SrCl_2$ method			MBI method		
	Mean	Sd	RSD	Mean	Sd	RSD	Mean	Sd	RSD
Sherwood Sstn <2000 µm	4.55	0.48	10.6	2.41	0.11	4.36	3.05	0.22	7.21
Sherwood Sstn <200 µm	8.86	0.87	9.9	14.46	0.61	4.23	4.41	0.28	6.43
Mercia Mudstone	12.88	0.55	4.3	11.66	0.19	1.62	8.83	0.18	2.05
Lincolnshire Limestone	13.31	1.34	10.1	203.42	6.66	3.27	<2.00	N/A	N/A
Lower Chalk	17.88	0.83	4.7	212.10	3.69	1.74	5.45	0.46	8.38
Lower Oxford Clay	30.82	0.47	1.5	38.55	0.62	1.61	20.72	0.83	4.01
Gault Clay	34.37	1.80	5.2	136.79	4.41	3.22	25.25	0.47	1.88

CEC units are meq / 100 g
Sd = standard deviation
RSD = relative standard deviation (in %)

The $BaCl_2$ method is recommended for adoption as the standard for determining CEC input to LandSim and similar models. It is already widely used for determining CEC in soils, and has been shown in this study to provide consistent results and to be suited to a wide range of geological materials.

Mean results reported for the $BaCl_2$ method in Table A can be used as default values for LandSim where site-specific values are not available. However, because these results were obtained from crushed rock samples they are likely to be higher than actual CEC of the same material in the natural environment.

The $SrCl_2$ method should not be used for CEC determination in geological materials, principally because the presence of minerals such as calcite and gypsum, which are common in many lithologies, leads to substantial over-estimation of CEC.

The methylene blue method, which has the attraction of speed and simplicity, could be used to provide advisory CEC values on geological materials.

K_d work

Of the contaminants likely to be encountered in landfill leachate, ammonium ion is one of the most widespread because it is generated during the biological decomposition of waste. Under anaerobic conditions it is not oxidized to nitrogen, nitrite or nitrate, and in aqueous solution can percolate unchanged because it will not precipitate. Because it is toxic it can pose a threat to the environment, particularly watercourses, and is therefore significant in pollution plume delineation. In terms of screening employing LandSim it is the most important contaminant to model. Its sorption behaviour, expressed in the form of its partition coefficient, K_d, was examined for the six ‘reference’ materials. A recommended methodology was arrived at, by:

1) selecting fast, robust, accurate and inexpensive equipment
2) adopting a simple, easy-to-use technique
3) using quantities of materials that ensured maximum accuracy and consistent results
4) analyzing environmentally realistic concentrations and testing with authentic leachate

Table B summarizes benchmark values for input to LandSim.

Table B Summary of K_d results from laboratory batch experiments

Lithology		Ammonium concentration						
	Expt pH	10 mg/l Av K_d	10 mg/l K_d range	40 mg/l Av K_d	40 mg/l K_d range	Expt pH	Leachate* Av K_d	Leachate* K_d range
Sherwood Sstn <2000 µm								
Sherwood Sstn <2000 µm	8.3	1.36	1.19 - 1.56	1.31	0.98 - 1.84			
Sherwood Sstn <2000 µm	6.2	0.43	0.29 - 0.67					
Sherwood Sstn <200 µm	8.4	1.79	1.70 - 1.90	1.70	1.11 - 2.06			
Lower Chalk <2000 µm	8.1	2.06	1.98 - 2.18	1.97	1.72 - 2.13			
Lower Chalk <200 µm	8.0	1.63	1.29 -1.92	1.20	0.89 - 1.50	6.7	0.03	-0.03 - 0.09
Mercia Mudstone	8.0	7.78	7.30 - 8.53	5.49	5.21 - 5.88	7.0	5.24	4.64 - 5.72
Lower Oxford Clay	7.2	1.48	1.47 - 1.50	2.27	2.10 - 2.50			
Gault Clay	7.9	6.91	6.86 - 7.03	6.25	6.09 - 6.43			
Lincolnshire Lmst	7.4	0.77	0.71 - 0.82	0.66	0.63 - 0.69			

K_d measurements are in ml/g
* Ammonium concentration 4.24 mg/l

Reference samples, in the form of 100 g <200 µm splits of the six selected lithologies, with details of their experimentally determined CEC and K_d values, are available on request from the British Geological Survey[1]. Detailed results, including all analytical and statistical

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[1] Sample lithologies available from Dr D J Morgan at BGS, Sir Kingsley Dunham Centre, Keyworth, Nottingham, NG12 5GG, Tel: 0115 936 3100 subject to a handling and carriage cost.

evaluation data, XRD profiles, laboratory procedures and sample details, are presented in a separate document, the R&D Project Record (P1/254/01).

KEY WORDS: Cation Exchange Capacity, Aquifers, Retardation, Absorption, Risk Assessment

1. REVIEW OF METHODS FOR DETERMINING CEC AND K_d IN GEOLOGICAL MATERIALS

1.1 Introduction

The Environment Agency has recently issued, for use by regulatory staff, a probabilistic quantitative risk assessment model called LandSim which is used to evaluate landfill performance. LandSim takes into account such factors as liner and leachate-removal system and design, and the geological and hydrogeological regimes beneath and around the site in question. Among the input values required for the model are the cation exchange capacity (CEC) and partition coefficient (K_d). The uncertainty in these values is expressed by a triangular distribution for this input, and minimum, most likely and maximum values are entered. Default values are provided for these parameters based on literature values for typical lithologies.

The default values provided in LandSim are limited to a relatively small number of species and minimum values tend to be conservative. This is logical because it is always possible to postulate conditions under which a particular contaminant will be mobile. For instance metals, which are strongly sorbed in cationic form, may not be sorbed at all if they are complexed with carbonate or with organic molecules.

To keep the analysis in LandSim simple, steady-state models are used. Necessarily, steady state models are for single scenarios. In reality, situations change and a series of assessments which represent different scenarios for the landfill must be carried out. For example, leachate composition and geochemical conditions in the vicinity of the landfill may be very different in the early and late stages in the life of a landfill. The manual suggests that a reasonable estimation of landfill risk can be obtained by analysing the system at three times:

5) prior to closure
6) immediately after closure
7) 50 years after closure

Both CEC and the partition coefficient may change with time as the geochemical conditions change. The CEC is a function of the mineralogy but this may change as, for example, chalk dissolves in acid leachates, new phases are formed and coatings of iron oxyhydroxides dissolve or develop under changing redox conditions. The partition coefficient depends not only on the mineralogy but also on solution chemistry and, of course, the solution chemistry will change with time and distance from the landfill.

Because of this, the most difficult stage in the estimation or measurement of these parameters will be the selection of materials and conditions under which to make the measurements. Geochemical conditions will be continuously changing. Thus not only will the water chemistry change, but the mineralogy and surface chemistry of the solid phases may also change as precipitation/dissolution, redox reactions etc occur.

It is probably reasonable to assume that the CEC in the vertical pathway is exhausted by the time the landfill is closed. LandSim calculates the time taken to exhaust the CEC and the effect that this has on travel times and maximum concentrations released. Partition coefficients, however, are more difficult to estimate because future geochemical conditions are unknown.

1.2 Geology

The Major Aquifer formations encountered in the UK are the Chalk and Upper Greensand, Jurassic limestones, Permo-Triassic Sherwood Sandstones, Magnesian limestone, Carboniferous limestone and Lower Greensand , as described in the Environment Agency's Policy and Practice for the Protection of Groundwater (EA, 1998). Any experimental programme should concentrate on these geologic formations although it should not be too rigid. Extensions to minor aquifer formations could be considered if necessary.

1.3 Subsurface transport

During subsurface transport, reactive solutes are subject to a variety of hydrophysical and chemical processes. The major hydrophysical processes include advection and convection, dispersion and diffusion, compaction and consolidation, and radioactive decay. The key chemical processes are complexation including hydrolysis and acid-base reactions, oxidation-reduction, dissolution-precipitation, adsorption and ion exchange. The combined effects of all these processes must satisfy the conservation of mass. Traditional solute transport models (including LandSim) often incorporate the effects of hydrophysical processes rigorously but over-simplify chemical interactions among aqueous species, and account for heterogeneous reactions with empirical approaches such as the linear (K_d approach) and nonlinear (Freundlich) isotherms. Sophisticated chemical models on the other hand, incorporate a variety of chemical approaches but assume a no-flow (batch system). In the past decade, coupled models accounting for complex hydrophysical and chemical processes, with varying degrees of sophistication, have been developed (Jennings *et al*. 1982; Liu and Narashima, 1989a and 1989b; Read *et al*. 1991; Yeh and Tripathi, 1991). These models can simulate the chemical processes such as aqueous complexation, precipitation-dissolution, sorption-desorption, ion exchange, redox and acid base reactions simultaneously. They are, however, mathematically and conceptually complex. They require a large amount of detailed thermodynamic and geochemical data and need enormous computer power.

LandSim is designed to be a simple screening tool. It is a probabilistic model and requests a minimum, most likely and maximum values for the distribution coefficient (K_d). It does not allow for changing geochemical conditions along the flow path.

1.3.1 Sorption

Most chemicals in solution or suspension do not show the same mobility in groundwater as in the water itself. Retardation is controlled by different processes, including ideal ion exchange, precipitation/dissolution, chemical substitution, isotopic exchange and filtration. The terms adsorption or sorption generally include electrostatic adsorption (e.g. ion exchange), physical adsorption and specific adsorption, but exclude precipitation and filtration. All three types of sorption are dependent on the chemical form of the sorbate in solution. Parameters like Eh, pH, ionic strength and concentrations of the sorbant and complexing species influence adsorption by controlling speciation and also the surface chemistry of the aquifer material.

To quantify sorption, one typically measures the distribution of the adsorbate between the solid phase and the solution phase. Such a value is often called a 'K_d' or 'R_d'. Confusion arises because the term 'distribution coefficient' is also used much more selectively to refer to reactions such as binary ion exchange in which the reaction is reversible, equilibrium has been established and the K_d is constant over the concentration range of interest. The partition coefficient, measured in laboratory experiments, is an empirical parameter which measures overall sorption irrespective of the actual processes occurring and is, therefore, better described by the term 'distribution ratio', or R_d. Computer codes for safety assessment and site selection rely on the distribution coefficient concept and assume reversibility and equilibrium but it is as well to distinguish between K_d and R_d when making measurements (Reardon, 1981).

Many thousands of sorption measurements have been made and compilations of data put together for use in performance assessment and groundwater modeling (Sheppard, 1984; Higgo, 1988; McKinley, 1991; Berry, 1992). These databases are of limited value because each R_d value is specific to a particular experiment and it is impossible to extrapolate outside the experimental range.

Sorption mechanisms

A brief discussion of different sorption mechanisms follows:

(i) *Ion exchange* is rapid and largely reversible. The ability of a mineral such as a clay mineral to engage in ion exchange is determined by two factors:

1) the first, which is not pH-dependent, is due to the negative overall charge on the lattice structure resulting from isomorphous substitution of one atom by another of lower valency, e.g. aluminum for silicon. In the presence of water, compensating cations on the surfaces may be exchanged with other cations in solution.

2) The second, which is pH-dependent, arises from the broken bonds at the edge of clay mineral layers which are balanced by adsorbing H^+ or OH^- ions to achieve full co-ordination of the surface atoms. However, the area of these edges is small for clay minerals (1% for smectite) so that the net charge on the lattice is determined mainly by the degree of isomorphous substitution that has occurred.

When sorbed cations are free to exchange with other cations in solution, the exchange equilibria between any two cations can be expressed in terms of an equilibrium constant, the *selectivity coefficient*, K, which can be used to predict the relative activities of sorbed and solute species as:

$$nA + mBX \leftrightarrow mB + nAX$$

$$K = \frac{[B]^m[AX]^n}{[A]^n[BX]^m}$$

where: A and B are cations, X is the sorbing substrate and square brackets denote activities

Aquifer material may consist of a variety of sorbing substrates, each with its own set of selectivity coefficients governing exchange. This poses problems in describing ion-exchange equilibria and a common approach is to apply a bulk selectivity coefficient for each cation pair and a bulk cation-exchange capacity. However, this approach may not be suitable if the exchange characteristics of each of the sorbing components of the substrate are markedly different.

(ii) Surface complexation is the dominant cause of charge on the surface of non-silicate oxide minerals, where it arises mainly from unshared O and OH species resulting from broken surface bonds. The magnitude and sign of the charge varies with pH. At the zero point of charge (ZPC) the net surface charge is zero and the anion and cation exchange capacities are equal and at a minimum. When conditions are more alkaline than the ZPC, the oxide surface is negatively charged. When conditions are more acidic than the ZPC, the oxide surface is positively charged. Typical values for the ZPC are pH 2.0 for kaolinite, pH 2.5 for silica gel, pH 6.7 for goethite and pH 8.2 for gibbsite. In addition to this purely electrostatic bonding some ions may be adsorbed by 'specific adsorption' or 'ligand exchange' regardless of their charge or activity in solution. Specific adsorption of anions lowers the ZPC, while specific adsorption of cations raises the ZPC. The mechanism appears to be a direct co-ordination of the surface metal cation with the oxy-ions or replacement of a hydroxyl group directly co-ordinated to the surface metal cation.

If sorption is by surface complexation to oxide or hydroxide surfaces, values may range from zero to $>10^6$ ml/g for the same material as the pH increases. The sorption edge, i.e. the pH range over which sorption increases from 0 % to 100 %, is frequently in the pH range 6 to 7, i.e. within the pH range for natural groundwater.

(iii) Precipitation is not a true sorption process but it has the same effect and experimentally it is often difficult to make a distinction. Changes in solution pH may cause the release of contaminants bound by precipitation.

(iv) The movement and fate of organic contaminants is governed largely by sorption and biodegradation. Sorption is often affected in a significant way by only two factors: the hydrophobicity of the contaminant, and the fraction of natural organic carbon in the subsurface matrix (Karickhoff *et al.* 1979, 1981; Brown and Flagg, 1981; Reinhard *et al.* 1984; Rutherford, *et al.* 1992). Organic contaminants partition almost exclusively onto the organic carbon fraction (f_{OC}) in soil or aquifer material, if f_{OC} constitutes at least 1% by weight of the material. If it is less than 1%, organic carbon may not be the primary surface onto which organic compounds partition. There is a critical level of soil or aquifer organic

carbon at which sorption onto organic matter equals sorption onto mineral surfaces. McCarty *et al*. (1981) showed that this level depends on the surface area of the soil (S_a) and the octanol-water partition coefficient, K_{OW}, of the organic compound; they derived the relationship:

$$f^*_{oc} = \frac{S_a}{200\ (K_{ow})^{0.84}}$$

This equation suggests that soils or aquifers with low organic carbon content would retain organic compounds with high K_{OW} values but might not retain those with low K_{OW} values.

A number of researchers have developed relationships between K_{OW} and K_d or partition coefficient with respect to the organic fraction (K_{OC}). Schwarzenbach and Westall (1981), looking at methylated and chlorinated benzenes, found that the equation

$$K_{OC} = K_d = 0.40 \times f_{OC} \times (K_{OW})^{0.72}$$

was valid primarily for f_{OC} >0.001 (= 1% by weight). For f_{OC} <0.0005 the regression equation tends to underestimate K_d.

Karickhoff *et al*. (1979, 1981) gave different equations for different groups of compounds. For example:

$K_{OC} = 0.63K_{OW}$ (miscellaneous organics)
$\log K_{OC} = 1.00 \log K_{OW} + 1.377$ (45 organics, mostly pesticides)
$\log K_{OC} = 0.94 \log K_{OW} - 0.346$ (five polyaromatic compounds)

Most of the log K_{OC} values computed using these equations fall within one standard deviation of the geometric mean (Fetter, 1993) and, for screening purposes using LandSim, selecting a relationship formulated for a similar organic and an aquifer material should be sufficiently accurate. K_{OW} values are available in the literature for a large number of compounds (e.g. Verschueren, 1983). Relationships between K_{OW} and solubility, and also molecular structure and topology, have also been formulated (Olsen and Davis, 1990). Computer programs (e.g. 'LOGKOW' marketed by Syracuse Research Corporation) have been developed which calculate the log K_{OW} based on the structure of the organic molecule. In general, calculated values are close to measured values.

1.4 Landfill pollution plumes

Leachate composition varies significantly among landfills, depending on waste composition, waste age and landfilling technology. Landfill leachates usually contain:

1) dissolved organic matter, expressed as chemical oxygen demand (COD) or total organic carbon (TOC); it includes fatty acids (particularly in the acid phase of waste stabilization) and more refractory compounds such as carbohydrate- fulvic- and humic-like compounds
2) anthropogenic compounds originating from the specific waste
3) inorganic macrocomponents - Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, Fe^{2+}, Mn^{2+}, Cl^{-}, SO_4^{2-} and HCO_3^{-}
4) heavy metals such as Cd, Cr, Cu, Pb, Ni and Zn

An overview of their probable sorption behaviour is given below. Section 1.5 considers the implications for LandSim of sorption behaviour of the various contaminants. Sections 1.6 and 1.7 review methods for determining cation exchange capacities and distribution ratios, respectively.

1.4.1 Probable sorption behaviour in a landfill pollution plume

(i) Organic matter in leachate: Sorption of leachate organic matter onto aquifer material seems to be of only minor significance, but there is usually a rapid drop in TOC concentration as the organic matter degrades. Microbiological attack with a decomposition procedure is difficult to describe mathematically since the amount of biodegradation depends on factors such as nutrients and redox conditions. Computer programs such as MGSE (Microbial Growth in Subsurface Environments) have been used successfully for relatively simple systems (Noy *et al*. 1996). For landfills it has been suggested that biodegradation be described using an exponential decay and half-life in a manner similar to radioactive decay (Bütow and Lühr, 1988). However, in the long term degradable organics will have decomposed and, for modeling purposes, adjusting leachate composition to that of aged waste and assuming low K_d values for the refractory carbohydrate-, fulvic- and humic-like compounds is probably the best policy.

(ii) Anthropogenic-specific organic compounds constitute only a few percent of the total amount of dissolved organic carbon in the leachate but they are important because many are not biodegraded readily and they may be toxic at very low concentrations. Estimation of K_d values from a knowledge of K_{OW} and the organic content of aquifer material is not a strictly

satisfactory approach. If sorption were to be relied upon to protect a vulnerable aquifer from such a compound it would be advisable to make some partition coefficient measurements.

(iii) Inorganic macrocomponents The mobility of inorganic contaminants depends on a complex network of interactions between transport and speciation. Cations tend to be retarded through adsorption and precipitation reactions. Complexation by soluble organic matter may, on the other hand, inhibit this retardation. Anions should generally be quite mobile.

Adsorption reactions depend on the availability of efficient sorbents (e.g. clays or Fe and Mn oxyhydroxide minerals), and on factors such as pH, Eh, ionic strength and speciation. Precipitation reactions are also affected by pH, Eh, alkalinity and the presence of sulphide in the leachate environment. The extent of organic complexation is influenced by the concentration and nature of the organic molecules in the leachate. All these processes, as well as solid phase changes, are controlled by the biological reactions that regulate the concentration and form of the organics and redox conditions in the plume environment. The fate of inorganic contaminants will therefore be influenced by the fate of organics.

Aquifer material usually has a low cation exchange capacity compared with topsoils and sediments that contain high concentrations of clay and organic material. However, the exchange capacity may still be very significant. The ratio of cations on the exchange sites depends not only on selectivity coefficients, but also on the concentration ratios in solution. In a leachate plume, several cations will be present at the same time with different affinities for the exchange sites and in different concentrations (Dance and Reardon, 1983; Reardon and Dance, 1983). This creates a complex front of travelling peaks in the plume as the plume composition changes due to ion exchange. In many pristine aquifers the cation exchange sites are dominated by Ca, Mg and, at low pH, protons. In saline soils Na will dominate. When exposed to leachate with higher ionic strength and different relative cationic composition, the saturating cations (e.g. Ca, Mg, Na) will be expelled and move with the leachate front. This has been observed frequently and is referred to as the hardness halo (Christensen, 1994, Nicholson *et al*. 1983).

Ca and Mg are also influenced by complexation and dissolution/ precipitation. Attenuation of NH_4 and K will be significant, whereas Na will be retarded only slightly. Fe^{2+} and Mn^{2+} in the leachate will be subject to ion exchange, oxidation, dilution and precipitation as sulphides or carbonates. Reactions involving ferric oxyhydroxides are important because dissolution of such phases by leachate can add significantly to groundwater contamination, and their re-precipitation further down-flow may decrease heavy-metal concentrations by co-precipitation. If conditions in the leachate are reducing, Fe(III) and Mn(IV) will be reduced and may dissolve together with any co-precipitated elements. However, oxidation and re-precipitation should occur further downstream if conditions become oxidizing (Nicholson *et al.* 1983).

Ammonium is released during the biological decomposition of waste. Once in solution in leachate within the anaerobic environment of a landfill it undergoes minimal further reaction and is available to percolate from wastes into underlying strata. Retardation of ammonium by cation exchange has been shown to be significant even in aquifers with low cation exchange capacities, and it will be separated from NO_3^- as the two species are transported in the direction of groundwater flow. Estimates of NH_4^+ migration rates based on sorption measurements and cation exchange capacity can provide a reasonable approximation. However, biological processes can affect the distribution of nitrogen among the different species (NH_4^+, NO_3^-, NO_2, NH_3 and N_2) under differing redox and pH conditions. Both NH_4^+ and NO_3^- can serve as nutrients for microbial growth (assimilation) and, in addition, be electron donors (Behnke, 1975; Pedersen *et al.* 1991). Nash and Kahn (1981) stated that "the presence of ammonium in a leachate plume is often the first clear indication of pollution. High ammonia concentrations usually indicate nearness of a landfill site and anaerobic degradation in progress. Total absence of ammonia and the presence of nitrate indicates a fair distance from the site and aerobic conditions being reached".

Ceazan *et al.* (1989) evaluated the role of cation exchange in the retardation of ammonium (NH_4^+) and potassium (K^+) transport in a shallow sand and gravel aquifer. This was achieved by observing the distributions of NH_4^+ and K^+ within a plume of sewage-contaminated groundwater, and conducting small-scale tracer tests and batch sorption experiments on aquifer material. Both NH_4^+ and K^+ were transported approximately 2 km in the 4 km plume. A retardation factor, R_f (i.e. the ratio of velocity of unretarded species to velocity of NH_4^+/K^+), may be calculated[2], and in this case $R_f = 2.0$. Small-scale tracer tests demonstrated that NH_4^+ and K^+ were retarded ($R_f = 3.5$) relative to an unreactive tracer. A batch sorption isotherm was determined by mixing 50 g portions of wet sediment with 100 ml of uncontaminated groundwater (pH = 6.3). This was spiked with six different NH_4^+ concentrations ranging from 0.25 to 25 mg/l as N. Equilibration was for 1 hour at 23 °C. The isotherm was linear over the concentration range studied giving a R_d value of 0.34 ml/g.

Anion exchange sites in aquifer material are very few, and non-reactive anions such as chloride will not be retarded. Sulphate and bicarbonate are frequently involved in chemical reactions and their behaviour cannot be modeled using simple retardation factors. Arsenic and selenium form anionic complexes and should normally be treated as anions, even though precipitation and reduction may occur.

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[2] R_f may be related to K_d by the expression: $R_f = 1 + (e\,K_d/\varepsilon)$, where e = bulk density and ε = porosity

Heavy metals seldom constitute a groundwater pollution problem at landfills because landfill leachates usually contain relatively low concentrations of heavy metals, and they are subject to strong attenuation by both sorption and precipitation. In the reducing zones around a landfill most heavy metals have very low solubilities and, in the sulphate-reducing zone, even small concentrations of sulphides will precipitate all heavy metals except chromium. Thus, strongly reducing conditions should prevent the mobility of heavy metals even in the presence of high concentrations of dissolved organic matter. Transport could be possible under mildly reducing conditions (not sulphidic). Oxidizing environments should limit the solubility of heavy metals. Where heavy metals are transported through the various redox zones (i.e. from an anoxic to an oxic environment) surrounding a landfill under neutral pH conditions, nickel is predicted to be the most mobile cationic heavy metal (Vogl and Angino, 1985; Bourg, 1992).

Attempts to study sorption of metals in landfill pollution plumes have shown how sensitive measured R_d values are to leachate/groundwater composition. Thus, Majone (1993) examined the adsorption of lead from leachates originating in controlled landfills for municipal solid wastes. R_d values ranging from 1 ml/g to 33 ml/g were found, sorption being highly dependent on pH and lead concentration. The R_d was very sensitive to Pb^{2+} concentration at high pH values (8.5, 8.0 and 7.0) but was insensitive at lower pH values (6.0, 5.0, and 4.0). Christensen (1992, 1994) studied the sorption of low concentrations of Cd on to two mineral soils from unpolluted soil solution and waste leachates (compost, incinerator slag, sewage sludge) using laboratory batch experiments. He found that the Cd distribution coefficient was 30 to 250 times smaller from waste leachates than from unpolluted soil solution. The effect of pH on the Cd distribution coefficients was less consistent in waste leachate than in unpolluted soil solution, varying from hardly any effect to a seven-fold increase for a pH increase of approximately one unit.

1.5 Implications for LandSim

From the above discussion it would appear that the most important contaminants that need to be considered when running LandSim are ammonium and anthropogenic organic compounds known to be in the leachate. All contaminants need to be considered on a case by case basis:

- metals will probably be retarded strongly, but the fact that organic and inorganic complexes may be mobile means that the minimum default value for K_d should normally be zero. Maximum values for K_d could be measured in batch experiments using pristine rock, trace metal concentrations and natural or synthetic groundwater. These maximum values would be conservative because they ignore the even higher values that may occur under reducing conditions.

- Elements such as As, Se and Hg that tend to form anionic complexes in groundwater should be allocated R_d values of zero although they too can be immobilized under reducing conditions.

- K_d values for anthropogenic organic compounds can be estimated with sufficient accuracy from a knowledge of the K_{OW} and the organic content of the aquifer material. Again the default value should be zero.

- K_d values for ammonium will be related to the CEC of the aquifer material but, for greater confidence, should be measured.

1.6 Determination of cation exchange capacity

1.6.1 Theoretical basis of cation exchange capacity measurement

Definitions

Clays and other minerals can adsorb cations and anions and retain them in an exchangeable form. Exchangeable ions normally associated with clay minerals are: the cations Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+ and Al^{3+}, and the anions SO_4^{2-}, Cl^-, PO_4^{2-} and NO_3^-. *Ion exchange capacity* can be defined as the total ionic charge of the adsorption complex active in the adsorption of ions (Bain and Smith, 1987). It is normally measured at pH 7 and reported as milli-equivalents per 100 grams (meq/100g) or as centimoles of positive charge per kilogram (cmol [+] kg^{-1}). The exchange capacity of minerals, rocks and soils can be considered from two main viewpoints: anion-exchange capacity, which is not mentioned further, and cation-exchange capacity, which is the subject of this section.

Cation-exchange capacity (CEC) can be defined as the sum of exchangeable cations that a mineral, rock or soil can adsorb at a specific pH. In other words, it is a measure of the negative charges carried by the sample. The net charge on the lattice of a mineral is determined by the degree of isomorphous substitution that has occurred. In most rocks and soils, clay minerals play the dominant role in governing CEC.

Equilibrium, selectivity and fixation in clay minerals

Equilibrium between cations in solution and those adsorbed on exchange sites depends on the nature of the potentially exchangeable cation population and properties of the clay mineral structure. In smectites (e.g. montmorillonite, beidellite), for instance, the preference for monovalent cations decreases in the order Cs>Rb>K $_4$>Na>Li. This represents the lyotropic series, and it indicates the greater attraction of smectite surfaces for less hydrated cations. In a mixed-cation solution, sorption of Cs would thus be preferred to sorption of Na, and if Na was originally present in exchange sites it would be displaced by Cs. However, other factors also influence selective sorption and fixation of cations by clay minerals. The smaller alkali cations, with their greater polarizing power, acquire large and diffuse hydration sheaths and induce much flexibility in expanding interlayer spaces. The least hydrated strongly basic cations such as K, Rb, Cs, Sr and Ba can cause this interlayer space to collapse, thus 'locking' the exchange sites. In general, the higher the layer charge of the mineral the more strongly the cation is fixed; there is also evidence that cations are fixed more strongly by clays in which the layer charge arises primarily by substitutions in the tetrahedral sheet.

pH-dependency of CEC in clay minerals

Although the CEC of a clay mineral arises largely from a charge imbalance in the clay structure, contributions to the CEC may occur from broken cation bonds exposed at the edges of the clay layers. (Note that these are not exchangeable cations on the clay crystal surfaces, but cations [e.g. Al, Fe] that form the crystal structure of the clay lattice). In general, this contribution to the net negative charge on the clay layer (i.e. the CEC) increases with increase in pH. Broken bond surface occupies an appreciable proportion of the total crystal area of kaolinite but a much lower proportion of the crystal area of smectitic clays. Consequently, the pH-dependent charge due to broken bonds is more important for kaolin minerals than for smectite.

Measuring CEC

The vast majority of methods for determining CEC in rock and soil samples depend on displacing exchangeable cations and compensating negative charges with an *index cation* which is introduced by washing the sample in a salt solution. Thereafter, CEC can be determined in one of several ways, as described below. It is clearly important that the index cation be preferred or held more tightly by the surface than the cations being replaced. For this reason Cs^+, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} have been used commonly as index cations.

Measurement of CEC is complicated by several factors. These include:

- dissolution of soluble salts, $CaCO_3$ and gypsum, leading to overestimation of CEC.

- Specific adsorption (fixation) of K and NH_4 in the interlayer position in vermiculites and micas (including illite or hydrous mica). This can result in either over- or underestimation of exchangeable K when NH_4 is used as an extractant, depending on whether the NH_4 ion moves through the interlayer positions replacing the K, or whether it causes collapse of the edges, preventing further exchange. Although specific adsorption of K and NH_4 can influence measured CEC values, its effect will be relatively insignificant in most instances.

- Specific adsorption of trivalent cations such as Al^{3+} or Fe^{3+} on surfaces, leading to an underestimation of CEC.

In general, errors can be reduced by using a method of CEC determination that employs reagents of a similar concentration and pH to those of the sample to be analysed. For this reason a method buffered at pH 7.0 or 8.2 using relatively high concentrations of saturating and extracting solutions is often used to decrease errors due to the dissolution of $CaCO_3$ and gypsum. In acidic materials, solutions buffered at pH 7.0 or 8.2 are less effective in replacing trivalent cations, and unbuffered methods provide a better estimate of the CEC and exchangeable cations (Hendershot *et al*. 1993).

The ammonium ion was, for a long time, the most commonly used index cation for several reasons:

- it is amongst the most preferred of cations in the lyotropic series and this selectivity, coupled with extremely weak hydration, enables the NH_4^+ ion to move rapidly to a well-defined number of exchange sites, sealing off access to other sites.

- Because it has to be used in concentrated solutions for efficient and rapid displacement, the high solubility and cheapness of all ammonium salts is relevant.

- The pH of ammonium salts can be adjusted easily, which is useful if pH-dependence is a factor in measuring the CEC of a particular material.

- Ammonium salts interfere least in flame and other photometric methods.

However, use of NH_4 as an index cation also has drawbacks. For 1:1 minerals[3] (kaolinite and halloysite) low CEC values are obtained because ammonium cannot replace aluminium and hydrogen completely, and for 2:1 minerals (vermiculite, micas, illite) the ammonium index ion may become fixed and therefore not exchangeable. For these and other reasons many alternative index cations have been investigated.

Most methods for determining CEC employ shaking, centrifugation and decantation operations in the saturation and extraction of the index cations, and washing the sample after saturation of the index cation. An extremely large number of variants of the CEC-determining methods are produced by different combinations of pretreatment, index cation, salt, solvent, washing procedure and determinative technique for the ions. Kelley (1948) and Thomas (1977) have reviewed the background of CEC measurements comprehensively. Metson (1956) and Grim (1968) reviewed methods for clay minerals, and Chapman (1965) and Rhoades (1982) those for soils. The following section draws mainly on relatively recent publications, many of which describe improvements to older methods.

1.6.2 Review of methods for determining CEC

Introduction

The coverage of methods for determining CEC in this section is not exhaustive, but the principal methods and their variants are included, and a clear indication is given of the type and range of methods available. As described above, the vast majority of methods depend on displacing exchangeable cations by an index cation. These can be grouped as ‘displacement methods’. Once exchangeable cations have been displaced by the index cation, there are five principal ‘types’ of method for determining CEC. These are shown in Figure 1.1, and each is described separately below. The various methods, the salts and cations used, and reference publications in which the method is described in detail are summarized in Table 1.1. A brief list of the advantages and disadvantages associated with each method is also presented in Table 1.1; however this is limited to those pointed out by the noted authors and is not intended to be a comprehensive assessment. Each of the methods listed in Table 1.1 has been

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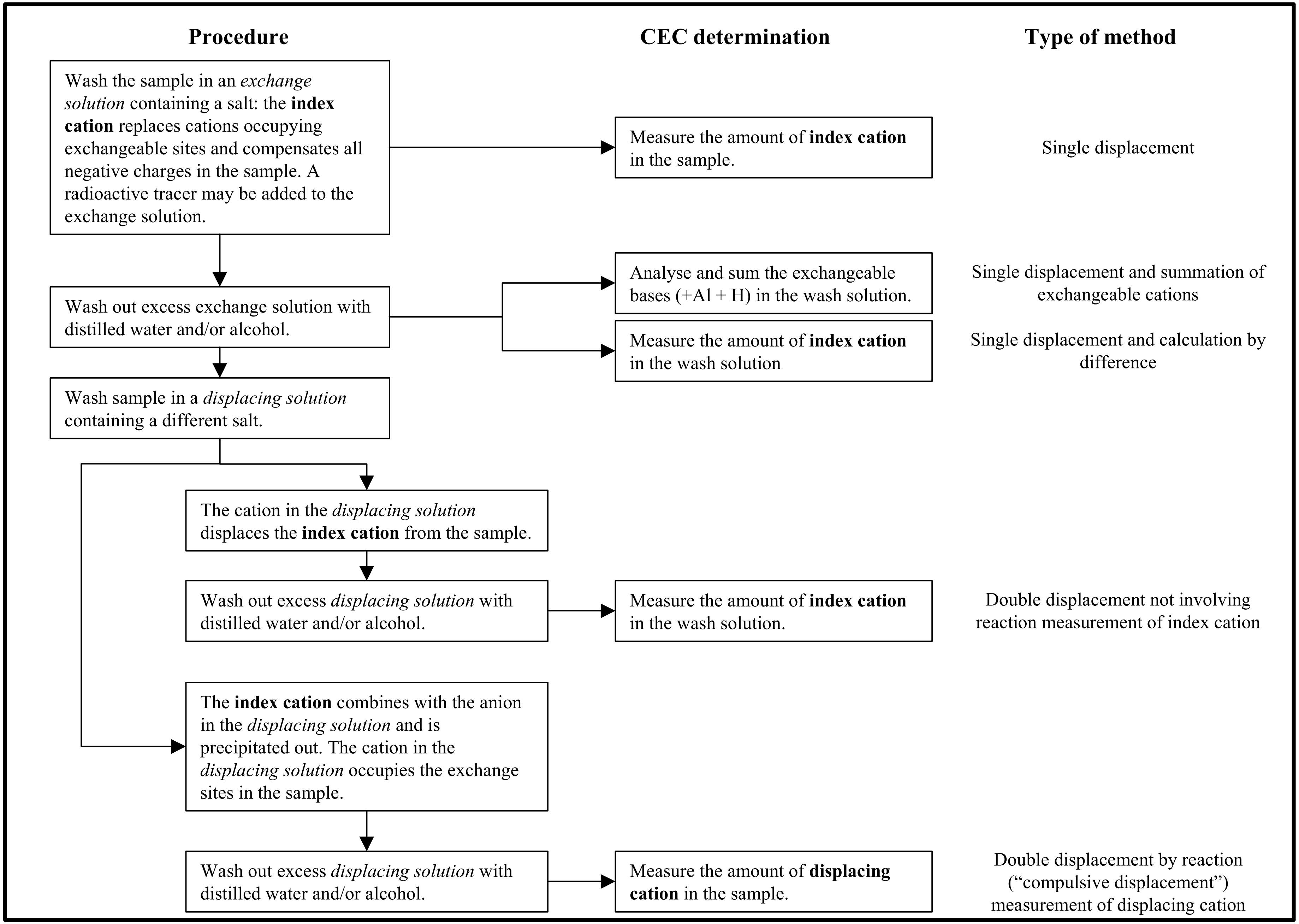
[3] Clay minerals are layer silicate crystals. The basic structural units in layer silicates are silica sheets (in tetrahedral coordination) and brucite or gibbsite sheets (in octahedral coordination). In 1:1 clay minerals (kaolinite and halloysite) each layer in the crystal consists of one tetrahedral sheet and one octahedral sheet. In 2:1 clay minerals (vermiculite, micas, illite) each layer has two silica tetrahedral sheets between which is an octahedral sheet.

assigned a number. These numbers appear in brackets at appropriate points in the following text.

Figure 1.1 Summary of displacement methods for CEC measurement



Wash the sample in an *exchange solution* containing a salt: the **index cation** replaces cations occupying exchangeable sites and compensates all negative charges in the sample. A radioactive tracer may be added to the exchange solution.

Measure the amount of **index cation** in the sample.

Single displacement

Wash out excess exchange solution with distilled water and/or alcohol.

Analyse and sum the exchangeable bases (+Al + H) in the wash solution.

Single displacement and summation of exchangeable cations

Measure the amount of **index cation** in the wash solution

Single displacement and calculation by difference

Wash sample in a *displacing solution* containing a different salt.

The cation in the *displacing solution* displaces the **index cation** from the sample.

Wash out excess *displacing solution* with distilled water and/or alcohol.

Measure the amount of **index cation** in the wash solution.

Double displacement not involving reaction measurement of index cation

The **index cation** combines with the anion in the *displacing solution* and is precipitated out. The cation in the *displacing solution* occupies the exchange sites in the sample.

Wash out excess *displacing solution* with distilled water and/or alcohol.

Measure the amount of **displacing cation** in the sample.

Double displacement by reaction (“compulsive displacement”) measurement of displacing cation

Displacement methods

a) Single displacement and measurement of index cation

In single displacement methods the amount of index cation adsorbed on the sample is measured directly or calculated and the CEC is determined from this. This approach is complicated by the possibility that the sample contains a significant amount of the same element as the index cation, either in the minerals or in porewaters. The smaller the CEC of the sample, the bigger a potential problem this becomes. A precise analytical characterisation of the untreated sample is required to quantify 'background' levels of the index cation. Straightforward single displacement methods for determining CEC are virtually unused at the present day.

One way to avoid this problem is to label the index cation with a radioactive isotope. Several such methods have been described. Blume and Smith (1954), for example, used ^{45}Ca (1) and Bache (1970) used ^{133}Ba (2). After treatment of the sample, the concentration of the isotope in the sample is used to calculate CEC. Chhabra *et al*. (1975) described an isotopic dilution method in which soil samples were equilibrated with 0.01*N* $Ca(NO_3)_2$ at pH 7 then equilibrated isotopically in a similar solution containing a ^{45}Ca radioisotope. CEC was obtained from the change in radioactive content of the equilibrium dialysate using liquid scintillation counting. Methods involving radioactive isotopes are rarely used, partly because of health and safety considerations, and partly because suitable radioisotopes are not readily available.

b) Single displacement and summation of exchangeable cations

In these methods, exchangeable cations are displaced from the sample by treatment with a salt solution and measured individually in the extractant. Although numerous methods have been developed for measuring exchangeable cations, they generally use one or other of two types of extractant: buffered or unbuffered salts. Comparisons of CEC methods (e.g. Gillman *et al*. 1983) have shown that buffered salt methods give higher CEC values than do unbuffered salt methods, if the samples being measured have a pH-dependent charge.

The most commonly used of these methods is one in which ammonium-acetate (NH_4OAc) is used to displace exchangeable bases and KCl is used for determining exchangeable Al and exchangeable acidity (3; e.g. Lavkulich, 1981; Horn *et al*. 1982; Hendershot and Duquette, 1986). The sum of exchangeable basic cations (by buffered or unbuffered salt extractants) plus exchangeable acidity (by unbuffered salt extractants) is known as the *effective CEC*

(ECEC or CEC_{eff}; e.g. Amacher *et al*. 1990). Because of its widespread use, the 'NH_4OAc method' has become a reference method with which others are often compared.

Edmeades and Clinton (1981) proposed a very simple, one-step exchange procedure that measures exchangeable cations and effective CEC using a single treatment with 1.26*M* $SrCl_2$ (4). Stuanes *et al*. (1984) used 1*M* NH_4NO_3 to displace the bases (i.e. basic cations) and Al (5), while Hendershot and Duquette (1986) and Hendershot *et al.* (1993) described a method using 0.1*M* $BaCl_2$ to displace exchangeable cations (6). Shuman and Duncan (1990) and Meyer *et al*. (1994) treated soil samples with an unbuffered 1*N* NH_4Cl solution (7).

The NH_4OAc method described above (3) was developed for standard analysis of a wide range of soil types. However, it requires an extended leaching and repeated extractions, and is tedious and time consuming because monovalent NH_4^+ does not exchange easily with divalent Ca^{2+} or Mg^{2+}. If ethylenediaminetetracetic acid (EDTA) is introduced into the NH_4OAc extractant, the process is speeded up and the exchange is completed within 1 or 2 minutes. However, the EDTA complexes very slowly with Al^{3+} at room temperature and not all of the Al^{3+} is removed with a single extraction. Consequently, EDTA is not an efficient extractant for the determination of exchangeable acidity. Qiu and Zhu (1993) proposed using NH_4OAc-1, 2-diaminocyclo-hexanetetracetic acid (DCTA) solution as an extractant for CEC measurement in acidic soils, so that both exchangeable bases and acidity could be determined simultaneously with a single extraction (8). DCTA not only has larger formation constants for Ca^{2+}, Mg^{2+} and Al^{3+} than EDTA, but the Al^{3+} complex also forms faster at room temperature (Zhu 1980).

c) Single displacement and calculation of CEC by difference

Use of rather concentrated solutions in the saturation step is often necessary to ensure a complete displacement of all exchangeable cations, and stems from the fact that the differences in affinities of ions for the exchange complex are usually not very large. The use of an index cation whose adsorption affinity for minerals in a sample is much larger than for all ions commonly present in the sample, irrespective of valency, would eliminate the need to use such concentrated solutions. In such a case, CEC could be determined simply by measuring accurately the amount of index cation in the saturating solution prior to treating the sample, and the amount in the extraction solution after treating the sample: CEC is the difference between the two. Furthermore, determination of both CEC and of exchangeable cations becomes a 'one-step' operation because both are obtained by analysis of the extraction solution.

Pleysier and Cremers (1973; 1975) showed that the silver-thiourea (AgTU) complex ion, Ag(S=C-NH_2-NH_2), may serve such a purpose. Addition of a relatively small excess of this complex, relative to the CEC, is sufficient to ensure a complete saturation of the (soil) sample. The AgTU complex is also a powerful flocculant, which presents a further advantage in the separation of solid and liquid phases. Chhabra *et al*. (1975) presented a short and simple method (9) for the simultaneous measurement of CEC and exchangeable cations in soils using the AgTU complex. The method consisted of a single saturation of a one-gram soil sample with 0.01*M* AgTU solution which was buffered (pH=7) with 0.1*M* NH_4OAc. CEC and exchangeable ions were obtained by analysing the extract for Ag, Ca, Mg, K and Na. Results were practically identical to those obtained by the standard NH_4OAc method.

Morel (1957) first described the use of cobalt-hexamine trichloride ($[Co(NH_3)_6]Cl_3]$; CoHM) as an index cation for CEC determinations (10). As with the AgTU method, the sample is saturated with the CoHM ion and CEC is calculated by determining the difference in concentration of the CoHM in solution before exchange and in the post-exchange solution. Maes *et al*. (1991) proposed using CoHM as an index cation for measuring the CEC of 'intact' and dissolved soil humic substances. In this case, CoHM was used as an alternative to AgTU for measuring the CEC of the more hydrolyzable metal cations. Because CoHM is an inert complex with an extremely low ligand exchange rate, a ^{60}Co 'spike' was added during its synthesis, which was used to monitor all CoHM adsorption equilibria.

Ciesielski and Sterckeman (1997a) described a study in which they compared three different methods of exchanging CoHM with samples (single extraction; successive extractions; percolation) and three different methods of measuring CoHM ion concentrations in exchange solutions (spectrocolorimetric determination of ammonia nitrogen concentrations; determination of cobalt concentrations by flame atomic absorption spectrometry; determination of CoHM ion concentrations by direct spectrocolorimetry). They recommended the use of single extractions and direct spectrocolorimetric determination of the CoHM ion for routine analysis.

In determining the exchange properties of calcareous materials, addition of the exchange solution may cause carbonate dissolution, resulting in an overestimate of the exchangeable Ca concentration and therefore of CEC. Dissolution of other Ca-bearing minerals such as gypsum can also result in overestimation of exchangeable Ca. Although this source of uncertainty may be insignificant for materials with a high exchange capacity, it can be substantial for materials with a lower exchange capacity.

Several authors have attempted to minimize the interference of carbonate dissolution (Tucker, 1954; Carpena *et al*. 1972; Neal, 1977) by using either double-leaching techniques to account for the amount of mineral dissolved, or by using ethanol-based solvents to reduce mineral dissolution during the measurement procedure. Reardon *et al*. (1983) used the original pore water in glaciofluvial sand deposits as the solvent for the exchanging salt, as a means of reducing calcite dissolution interference (11). These authors tested three salts, NH_4Cl, CsCl and LiCl, for their suitability. CsCl was preferred because of its low tendency to dissolve carbonate, and because of the preference of Cs^+ on exchange sites. The method is suitable for determining the exchangeable cation population of calcareous sandy materials with CECs of less than 1 meq/100g, and the authors suggested it could be applied with reasonable accuracy and reproducibility to materials with exchange capacities as low as 0.1 meq/100g. The method was tested in, and found to be suited to, the field.

d) Double displacement not involving reaction, and measurement of index cation

In these methods, the index cation is displaced from the sample by a different cation introduced in a second (*displacing*) salt solution (Figure 1.1). The amount of index cation in the extractant is measured and represents the CEC. Bain and Smith (1987) described a procedure in which Na, introduced in the form of NaOAc solution, is displaced by NH_4 which is introduced as NH_4OAc (12). The amount of Na in the extractant represents the CEC.

Hendershot *et al*. (1993), in a method modified from Fey and LeRoux (1976) and James (1984) which was designed specifically for measurement of pH-dependent AEC-CEC (anion exchange capacity and cation exchange capacity), used Ca introduced as 0.05*M* $Ca(NO_3)_2$ as the index cation and K introduced as KCl as the displacing cation (13). Measurement of Ca and NO_3 concentrations allowed calculation of AEC-CEC.

In the majority of double displacement methods, excess saturating salt is removed from the sample by washing it (repeatedly, if necessary) with distilled water or alcohol (usually ethanol or isopropanol) or another salt, or a combination of these. Only after washing (and checking the extractants for levels of solution removed) is the displacing cation introduced in the second salt solution. Chapman (1965), Chhabra *et al*. (1975), Bain and Smith (1987) and others have described a method in which the index cation, NH_4, is introduced as NH_4OAc and, after saturation, excess salt is removed by washing with isopropanol. Na, introduced subsequently in the form of NaCl solution, displaces the NH_4 which is measured in the extractant (14). Careful monitoring of mass balance is required to ensure that desorption does not occur during washing. In a method used by Wada and Okamura (1980), NH_4 is again the index cation, this time introduced as 1*M* NH_4Cl, which is displaced by Na introduced as

$NaNO_3$ after washing (15). Matsue and Wada (1985), in a modification of the method of Gillman (1979; described below), proposed a method using five centrifuge-washing steps with 0.01*M* $SrCl_2$ to saturate the exchange complex and to displace bases and exchangeable Al (16). This is followed by one treatment with 0.5*M* HCl to extract the adsorbed Sr. The Sr is measured to produce a CEC value.

Zhao *et al*. (1997) described using Ca (introduced as 1.0*M* Ca cation solution at pH 7.0) as the index cation and displacing it with either 2.0*M* NaCl or 1.0*M* $CuSO_4$ after repeated washings in distilled water (17). Finally, Leinweber *et al*. (1993) and Hendershot and Duquette (1986) used Ba introduced as $BaCl_2$ as the index cation and replaced it with Mg introduced as $MgCl_2$ after repeated washings with distilled water (18).

Stuart and Vickers (1989) suggested a method (19) for determining CEC in calcium-rich samples in which the sample is saturated with Ca (in the form of $CaCl_2$ solution), washed repeatedly in ethanol and then saturated with a LiCl/CsCl displacing solution. The amount of calcium displaced by the second salt solution is measured and represents the CEC.

Table 1.1 Summary of CEC determination methods

No.	Type of method	Index cation	Saturating salt or solution	Displacing cation	Displacing salt or solution	References	Advantages	Disadvantages	Comments
1	Single displacement; radioactive tracer measurement of index cations	^{45}Ca	N/A	N/A	N/A	Blume & Smith, 1954; Chhabra et al. 1975		Requires working with radioactive materials.	
2	Single displacement; radioactive tracer measurement of index cations	^{133}Ba	N/A	N/A	N/A	Bache, 1970		Requires working with radioactive materials.	
3	Single displacement and summation of exchangeable cations	NH_4	1*M* NH_4OAc buffered to pH7.0	N/A	N/A	Lavkulich, 1981; Horn et al. 1982; Hendershot et al. 1993	Uses a relatively large sample size which helps to decrease sample variability; no decantation steps so no loss of sample; can be used to measure exchangeable cations and CEC or just exchangeable cations.	As with other methods in which NH_4^+ is used as an index cation, fixation of NH_4^+ and K^+ in phyllosilicates can cause over- or underestimation of exchangeable K^+.	If NH_4OAc is used alone, only exchangeable bases are measured in the extraction solution. KCl is often used in addition to NH_4OAc to displace exchangeable Al and acidity (H^+).
4	Single displacement and summation of exchangeable cations	Sr	1.26*M* $SrCl_2$	N/A	N/A	Edmeades & Clinton, 1981; Sänger-von Oepen et al. 1993	Simple, one-step exchange procedure; no problems due to dissolution of salts or carbonate minerals.		Results obtained using this method were in close agreement with those obtained from a more complex method involving NH_4OAc extraction for exchangeable bases and KCl extraction for Al and Mn.
5	Single displacement and summation of exchangeable cations	NH_4	1*M* NH_4NO_3	N/A	N/A	Stuanes et al. 1984			The salt solution displaces bases and Al.
6	Single displacement and summation of exchangeable cations	Ba	0.1*M* $BaCl_2$	N/A	N/A	Hendershot & Duquette, 1986; Hendershot et al.1993	Simple and rapid; Ba is a good flocculant and is able to displace trivalent cations; relatively low ionic strength of the equilibrating solution causes a smaller change in pH than more concentrated solutions.	The sum of displaced cations can be larger than true CEC due to soluble salts in the sample (but if a proportion of the cations in exchange positions are H^+, the sum of the other cations determined in the equilibrium solution will be less than the CEC).	
7	Single displacement and summation of exchangeable cations	NH_4	1*N* NH_4Cl	N/A	N/A	Shuman & Duncan, 1990; Meyer et al. 1994	Simple procedure; a single extraction solution can be analysed in one step.	Ca is underepresented in the extractants.	
8	Single displacement and summation of exchangeable cations	NH_4	NH_4OAc-DCTA	N/A	N/A	Qiu & Zhu, 1993	Use of DCTA in the extractant speeds up the exchange process dramatically compared to using NH_4OAc alone.		Method and comments similar to method no. 5, except the DCTA compound is added to the extractant.
9	Single displacement and calculation of CEC by difference	AgTU	0.01*M* AgTU solution	N/A	N/A	Chabbra et al. 1975	The high stability of the Ag-TU complexes ensures extremely low concentrations of free silver metal ions, preventing any interference of either carbonate or chloride by precipitation. Simple 'one-step' operation. Economically attractive.	AgTU solutions are unstable at pH>8 and subject to photochemical reactions.	0.1*M* NH_4OAc (pH=7) may be added for buffering purposes. Pleysier & Juo (1980) used the Ag-TU complex to displace exchangeable bases, and measured effective CEC by summation of ions in the extractant.
10	Single displacement and calculation of CEC by difference	CoHM	0.01*M* CoHM solution	N/A	N/A	Morel, 1957; Maes et al. 1991; Ciesielski & Sterckeman, 1997a,b			Not widely used.
11	Single displacement and calculation of CEC by difference	Cs	CsCl	N/A	N/A	Reardon et al. 1983	Carbonate dissolution is minimised; only a single exchange reaction is needed because Cs is not a major cation in groundwaters or in the sample; because it is a field test there are no problems of reaction during sample storage.		The method has been designed specifically for use on calcareous sandy material with CEC of less than 1 meq/100g.

Table 1.1 Summary of CEC determination methods

No.	Type of method	Index cation	Saturating salt or solution	Displacing cation	Displacing salt or solution	References	Advantages	Disadvantages	Comments
12	Double displacement not involving reaction; measurement of index cation	Na	NaOAc	NH_4	NH_4OAc	Bain & Smith, 1987		Relatively lengthy procedure: about four overnight washes are needed to saturate the index cation.	
13	Double displacement not involving reaction; measurement of index cation	Ca	0.05*M* $Ca(NO_3)_2$	K	1.0*M* KCl	Described in Hendershot et al. 1993; after James, 1984 and Fey & LeRoux, 1976			Designed specifically for measurement of pH-dependent AEC-CEC. After displacement by the KCl solution, both Ca and NO_3 concentrations are used for calculating AEC-CEC.
14	Double displacement not involving reaction; measurement of index cation	NH_4	1*M* NH_4OAc	Na	NaCl (in an acidified solution)	Chapman, 1965; Black, 1965; Chhabra et al. 1975; Bain & Smith, 1987		Relatively lengthy procedure: about four overnight washes are needed to saturate the index cation.	Since there is a danger that, on prolonged washing, ammonium ions are displaced by hydrogen ions, an alcohol solution (e.g. isopropyl alcohol) is used for washing. The alcohol keeps the clay flocculated, facilitating washing, filtration or sedimentation.
15	Double displacement not involving reaction; measurement of index cation	NH_4	1*M* NH_4Cl	Na	1*M* $NaNO_3$	Wada & Okamura, 1980		Many washings required.	Modification of the method of Schofield (1949); allows measurement of CEC at a known pH and electrolyte concentration (i.e. can be modified to match 'field' pH).
16	Double displacement not involving reaction; measurement of index cation	Sr	0.01*M* $SrCl_2$	H	0.5*M* HCl	Matsue & Wada, 1985	Single washing only required.		Allows measurement of CEC at a known pH and electrolyte concentration (i.e. can be modified to match 'field' pH). Exchangeable bases and Al (i.e. summation method for CEC) can be determined in collected 0.01*M* $SrCl_2$ washings for comparison.
17	Double displacement not involving reaction; measurement of index cation	Ca	1.0*M* Ca cation sol'n at pH7.0	Na or Cu	2.0*M* NaCl or 1.0*M* cupric sulphate	Zhao et al. 1997			
18	Double displacement not involving reaction; measurement of index cation	Ba	$BaCl_2$	Mg	$MgCl_2$	Leinweber et al. 1993; Hendershot & Duquette, 1986.			In the method of Leinweber et al. the BaCl2 solution was buffered at pH8.1 with triethanolamine. The two sets of authors used different salt concentrations in their solutions.
19	Double displacement not involving reaction; measurement of index cation	Ca	$CaCl_2$	Li/Cs	LiCl/CsCl	Stuart & Vickers, 1989	Greatly reduces interference from Ca.		Designed specifically for use with Ca-rich samples.
20	Double displacement by reaction ('compulsive displacement'); measurement of displacing cation	Ba	0.1*M* $BaCl_2$	Mg	0.025*M* $MgSO_4$	Bain & Smith, 1987; Gillman, 1979; Gillman & Sumpter, 1986; Hendershot & Duquette, 1986	Eliminates the repeated washing steps otherwise needed to replace the index ions. $BaCl_2$ has a strong replacing power without being preferentially adsorbed, and does not cause collapse of expanded phyllosilicates, as does K^+ or NH_4^+.	Materials containing high levels of SO_4 will precipitate $BaSO_4$ if $BaCl_2$ is added. Specific adsorption of SO_4 on sesquioxides in some soils can result in higher CEC measurements.	In a preliminary step, exchangeable bases and Al are extracted using 0.1*M* $BaCl_2$.
21	Double displacement by reaction ('compulsive displacement'); measurement of displacing cation	Ba	0.1*M* $BaCl_2$	Mg	0.02*M* $MgSO_4$	British Standards Institute, 1995; Ciesielski & Sterckeman, 1997b		The method suffers from interference from Ca^{2+} as calcite or gypsum in the sample. Also, the presence of any soluble salts gives values for the exchangeable cations that are higher than the actual exchangeable amounts.	Exchangeable bases can be measured in the $BaCl_2$ extract; the method described is a modification of the method proposed by Gillman (1979); the method is designed specifically for determining effective CEC and base saturation level.

Table 1.1 Summary of CEC determination methods

No.	Type of method	Index cation	Saturating salt or solution	Displacing cation	Displacing salt or solution	References	Advantages	Disadvantages	Comments
22	Double displacement by reaction ('compulsive displacement'); measurement of displacing cation	Ba	1.0*M* $BaCl_2$ solution buffered at pH8.1 using triethanolamine	Mg	0.02*M* $MgSO_4$	British Standards Institute, 1996	Use of triethanolamine in the $BaCl_2$ solution removes the problem of Ca^{2+} interference due to carbonate dissolution: a protective coat of $BaCO_3$ forms around any carbonate minerals, rendering them insoluble.		Exchangeable bases can be measured in the $BaCl_2$ extract; this method is a modification of Bascomb (1964), which was a modification of the Mehlich (1938;1942) method; it is designed for determining potential CEC and exchangeable cations.
23	Double displacement by reaction ('compulsive displacement'); measurement of displacing cation	Ba	0.2*M* $BaCl_2$/ 0.2*M* NH_4Cl	Mg	0.005*M* $MgSO_4$	Sumner et al. 1994	Time and labour are saved by estimating the quantity of water required to attain the specific conductance of a standard ionic strength, by measuring the EC of the solution and using an independently established calibration curve.		Modification of the methods of Gillman (1979) and Gillman & Sumpter (1986).

e) Double displacement by reaction ('compulsive displacement'), and measurement of displacing cation

In the compulsive exchange method of Gillman (1979) and Gillman and Sumpter (1986), the sample is saturated initially with Ba in the form of $BaCl_2$, then exchanged with Mg by reaction with $MgSO_4$, forming a precipitate of $BaSO_4$. The quantity of Mg adsorbed (= CEC) is estimated by loss from the $MgSO_4$ solution added. Because the Ba is removed from the sample by *reaction* (i.e. compulsively exchanged) there is no need for the repeated washing steps that would otherwise be needed to replace the index ions. Compared to some other exchange salts $BaCl_2$ has clear advantages: it is favoured by its strong replacing power without being preferentially adsorbed, and it does not cause collapse of expanded phyllosilicates, as does K^+ or NH_4^+ (Wada and Harada, 1969).

In the presence of calcite or gypsum, elevated CEC results can be obtained using the original compulsive displacement method because of interference of Ca in the reaction. Tucker (1954) suggested using an ethanolic solution of $BaCl_2$/triethanolamine to overcome this interference, and Bascomb (1964) described a compulsive displacement method which, after slight modification, was adopted as the British Standard method for determining CEC and exchangeable cations in soil samples (22).

Several variations on the compulsive displacement method have been proposed, all using $BaCl_2$ and $MgSO_4$ solutions (see Table 1.1, methods 20, 21 and 22). The method is suitable for use in laboratories which have minimal equipment; however the last step in the procedure is rather lengthy and involves the stepwise addition of water until the sample is brought to a standard reference ionic strength. Sumner *et al*. (1994) proposed a modification which eliminated this step by measuring the electrical conductivity (specific conductance) of the solution and predicting the quantity of water to be added from an independently established calibration curve (23). Results obtained using their modified method compared well with those obtained using the original Gillman and Sumpter method, indicating that the modification is accurate as well as time and labour saving.

Stuart and Vickers (1989) noted that these compulsive displacement methods did not solve the problem of interference by Ca released from dissolved gypsum. These authors tested three reagents ($BaCl_2$/ triethanolamine/ water; $BaCl_2$/ triethanolamine/ ethanol; LiCl/ CsCl/ ethanol) for reaction with calcite and gypsum and discovered that, although the addition of ethanol to the $BaCl_2$ reagent was effective in reducing the interference from calcite, it was less effective for gypsum. The LiCl/CsCl reagent was, however, much more effective in reducing interference from both minerals. On this basis the authors proposed a different method (19; described previously) for determining CEC in calcium-rich samples.

Other methods for determining CEC

a) Methods involving organic dyes

Early research on sorption of dyes such as auramine, methylene blue, methyl violet B and rhodamine 3B by clays (Emodi, 1949; Robertson and Ward, 1951; Ramachandran *et al*. 1962) showed that all gave CEC values that were close to each other and to those obtained by conventional methods. Subsequently, sorption of methylene blue (MB) has become established as a rapid and convenient means of determining CEC in a wide range of materials (Phelps *et al*. 1968; Hosking and Pike, 1985; Bensted, 1985).

The methylene blue molecule ($C_{16}H_{18}N_3SCl.3H_2O$) consists of an organic base in combination with an acid. It is a large, 'raft-shaped' molecule with approximate dimensions 16 x 8.4 x 4.7 Å (Kipling and Wilson, 1960) and replaces cations on clays irreversibly according to the following reaction:

Ca,Na-clay + methylene blue hydrochloride -> methylene blue-clay + Ca,Na-chloride

Absorption normally occurs with the largest surface of the MB molecule (134 Å^2) in contact with the clay surface. For some high-charge smectites which have surface charge densities as low as 100 Å^2 per exchange site, this means that monolayer coverage of the clay surface by MB molecules occurs before the charge imbalance on the structure is satisfied, and low CEC values may result.

Two approaches are used to measure MB CECs. In the first (Jones, 1964), an aqueous clay dispersion is titrated directly with a nominally 0.005 *M* solution of MB to an end-point that is recognized by spot testing the dispersion on a filter paper until a light blue halo of free dye appears around the darker dyed clay spot. This indicates that the adsorptive capacity of the clay is satisfied and that the free dye is spreading out into the filter paper. The second (e.g. Hang and Brindley, 1970) involves shaking a known amount of clay in a solution which contains an excess of MB molecules over that required to satisfy the exchange capacity. Following centrifugation, the optical density of the supernatant liquid is compared to that of the original solution, and the amount of dye absorbed by the clay is calculated by difference.

A number of factors may affect CEC determination using MB:

- care has to be taken in preparing standard MB solutions as the quality of this dye is variable, especially in relation to the water of crystallization.

- The steric hindrance effect noted above for high-charge smectites may lead to low CEC values.

- Thorough sample disaggregation is essential to ensure that all exchange sites are accessible to the large MB cation.

- When dissolved in water there is a tendency for the MB molecules to form dimers rather than monomers at concentrations $>10^{-3}$ mol dm^{-3}; this has implications for the measurement of optical density of MB solutions which is fundamental to the second of the two approaches above.

- Very small amounts of MB are absorbed by glassware (polypropylene containers are preferable).

Despite these possible drawbacks, the MB method has gained widespread acceptance as a rapid means of determining CEC.

b) CEC calculation by surface area measurement

Burrafato and Miano (1993) proposed a new method for measuring the CEC of clay minerals which involved titrating an aqueous suspension of clay with a surfactant (or surface active agent), namely hexadecylpyridinium chloride (CPC). During titration, the surface tension of the aqueous suspension is measured. The CPC has a strong affinity with clay surfaces, and the high repartition rate of CPC on the surfaces results in a high and constant surface tension value until the surfactant has saturated the clay surface. Once a mono-layer has formed, the adsorption of a second layer leaves an amount of free surfactant in equilibrium, which is able to drop to the lower value of the surface tension of water, which can be detected with high sensitivity and reliability. At the point of saturation, CEC (meq/100 g) = CPC_{added} (cm^3) x 10.

c) Sorption capacity measurement by sequential extraction

Salim *et al*. (1996) investigated the sorption characteristics of clayey calcareous sediments used to construct landfill bottom liners using a method called combined sequential extraction-sorption isotherm analysis (CSSA). By spiking samples with solutions containing high levels (~50 to 11,000 mg l^{-1}) of heavy metals (Pb, Ni and Cd) and carrying out sequential extraction analysis subsequently, they were able to construct sorption isotherms for the bulk sample and for the individual minerals within it. Using this method, the sorption capacities of individual minerals or components can be determined while they are together in a natural system.

1.6.3 Published comparisons of methods

In a study of about fifty soil samples covering a wide range of mineralogical composition, acidity and organic matter content, Chhabra *et al*. (1975) compared their AgTU method (9) with an ammonium-acetate method (14) and a ^{45}Ca dilution method (1). Three different variations of the AgTU method were tested:

- direct saturation of the soil sample with 0.01*M* AgTU solution without any pH adjustment;

- saturation with 0.1*M* AgTU solution adjusted to 0.1*M* in ammonium-acetate and a pH of 7.0, prior to treatment of the samples;

- presaturation of the samples with a 1*M* ammonium-acetate solution (pH=7), followed by centrifugation, decantation and saturation with unbuffered 0.01*M* AgTU solution.

Two variants of the ammonium-acetate method were used: a column percolation method and a centrifugation method. CEC values obtained using each method are summarized in Tables 1.2 and 1.3 along with corresponding pH and organic matter content.

Table 1.2 Comparison of CEC values (in meq/100g), as obtained by different methods, from 15 Belgian soil samples of low organic matter content (<1%). Modified from Chhabra et al. (1975).

Soil no.	pH (KCl)	%C	AgTU-a	AgTU-b	AgTU-c	NH_4OAc-percolation	^{45}Ca
1	6.0	0.09	9.3	10.50	9.66	9.75	10.7
2	5.7	0.12	10.2	11.21	10.24	12.75	11.4
3	4.8	0.09	8.7	11.05	10.97	11.75	10.7
4	4.3	0.24	9.2	11.55	11.03	12.75	13.6
5	4.3	0.27	0.9	1.49	1.20	1.75	3.0
6	4.1	0.36	20.0	19.55	19.22	20.75	21.5
7	4.6	0.06	12.6	14.03	14.20	14.25	14.1
8	4.5	0.06	10.9	13.48	13.21	13.25	12.7
9	4.2	0.09	9.5	11.48	10.68	9.00	11.0
10	4.1	0.09	10.0	12.63	12.21	12.75	11.3
11	4.5	0.03	11.2	13.37	13.17	13.00	12.0
12	5.5	0.75	6.2	7.14	6.90	8.00	8.7
13	6.1	0.66	4.4	4.86	4.85	5.90	6.5
14	4.9	0.72	6.4	7.69	7.77	8.75	8.8
15	6.0	0.72	9.9	10.56	N.D.	12.25	11.7
Mean values			9.29	10.71	10.37	11.1	11.18

Table 1.3 Comparison of CEC values (in meq/100g), as obtained by different methods, from 15 Belgian soil samples of high organic matter content (>1%). Modified from Chhabra et al. (1975).

Soil no.	pH (KCl)	%C	AgTU-a	AgTU-b	AgTU-c	NH_4OAc-percolation	NH_4OAc-centrifugation	^{45}Ca
16	4.0	1.08	4.87	6.95	6.76	7.50	10.45	10.3
17	3.7	10.40	15.10	27.40	31.80	28.00	33.00	42.4
18	3.6	3.42	3.86	9.15	13.24	9.50	11.00	18.7
19	4.1	1.39	6.10	8.70	8.27	8.25	10.15	9.7
20	3.6	11.7	16.30	29.10	33.00	26.75	36.00	38.7
21	3.6	3.36	7.50	12.65	13.31	14.25	16.40	16.5
22	3.6	2.34	6.60	11.72	10.50	11.75	14.50	19.7
23	3.4	9.66	14.60	28.90	36.00	30.25	41.90	51.6
24	6.2	1.14	6.00	6.20	6.30	7.50	8.25	8.5
25	6.5	1.33	9.60	9.13	8.30	9.50	10.35	10.5
26	5.8	1.68	11.90	13.70	13.18	13.00	13.45	13.1
27	5.3	1.80	9.60	10.90	10.88	12.00	11.60	14.8
28	6.0	2.07	10.0	10.30	9.75	10.75	10.30	11.9
29	5.7	2.87	11.60	12.80	13.50	12.50	14.10	14.5

30	5.5	2.78	13.0	14.00	13.44	14.50	16.00	16.7
Mean values			9.78	14.11	15.22	14.40	17.16	19.8

For samples with relatively low organic matter contents, the authors described the agreement between the different methods as ‘satisfactory’, the differences between the extremes being about 20%. Differences between samples with relatively high organic matter contents were, however, much more pronounced, with extreme values differing by a factor of 2 or 3. In virtually all cases the ^{45}Ca method gave the highest CEC values. The authors also stressed that, regardless of the organic matter content and the pH, the (b) procedure with AgTU produced CEC values nearly identical to the NH_4OAc percolation method, the difference being about 3% on average.

Edmeades and Clinton (1981) compared their $SrCl_2$ summation method (4) with the ‘standard’ method (3) employing NH_4OAc extraction for basic cations and KCl extractable Al and Mn, and found close agreement.

Hendershot and Duquette (1986) described a study in which three methods of determining CEC and exchangeable cations using $BaCl_2$ solution were compared on forest and agricultural soils. The methods were: the sum of cations displaced with 0.1*M* $BaCl_2$ (6); exchangeable Ba after saturation with $BaCl_2$ and displacement by $MgCl_2$ (18); and compulsive displacement (20). Results for the three methods are presented in Table 1.4. The results show that, when Al, Mn and Fe are included with Ca, Mg, Na and K in the sum of cations, the summation method (6) gave the same result as the other, more complex methods. The authors therefore recommended that this simple one-step method be used for routine analysis of acidic soils.

Table 1.4 CEC (cmol(+) kg^{-1}) and pH values for three methods using $BaCl_2$ as the saturating salt. Modified from Hendershot and Duquette (1986).

Sample no.	Soil	Horizon	Sum of cations	CEC $BaCl_2$-$MgCl_2$	CEC $BaCl_2$-$MgSO_4$	Exchange pH
1	Sainte Rosalie	Bg	34.22	27.72	32.50	5.86
2	Rideau	Ap	29.12	30.64	33.75	5.65
3	"	Bg	25.98	25.00	32.53	4.96
4	St-Urbain	Ap	32.72	33.49	37.75	5.59
5	"	Bg	22.60	22.42	24.75	5.89
6	Pin Blanc	Bhs	2.05	1.66	2.41	4.20
7	Lac des Moraines	Bsl	4.47	3.07	5.68	4.01
8	"	2Bw	1.13	0.57	1.91	4.28
9	Latuque	O1	49.86	43.93	N.D.	4.55
10	"	E	2.34	3.24	4.05	3.48
11	"	Bhs	3.84	4.78	8.21	4.11
12	"	C	0.35	0.15	2.73	4.81
13	Escoumins, M-13	O2	24.31	28.98	N.D.	3.49

14	"	Bs	0.21	0.36	3.24	4.59
15	Escoumins, M-15	O2	23.49	20.33	N.D.	3.79
16	"	Bs2	0.19	0.00	2.40	4.99
17	Escoumins, M-9	Bs1	1.43	1.39	4.31	4.34

Studies by Horn *et al*. (1982) and Gillman *et al*. (1983) have indicated that divalent cations, such as Sr or Ba, give comparable results to procedures using NH_4^+ salts and KCl for exchangeable bases and Al, respectively.

Ciesielski and Sterckeman (1997b) compared results obtained with three standardized methods for determining CEC and exchangeable cations in soils. The methods are based on different exchange reagents: cobalt hexamine trichloride (CoHM; 10); $BaCl_2$ (21); and NH_4OAc (14). Different exchange procedures were also compared: single extraction; successive extractions; and percolation. Values measured with Ba and CoHM as the index cations compared well, revealing the uniformity of the physicochemical processes involved. However, CEC values obtained with NH_4OAc as the index cation varied significantly from those obtained by the two other methods. The authors ascribed these differences to dissolution of carbonate minerals, the ability of ammonium to exchange fixed potassium, and to pH buffering of the extracts by the NH_4OAc. The authors also noted that the *quantity* as well as the nature of the index cation used would influence reaction yields. In balancing simplicity of use, cost and precision of results the authors concluded that a method using unbuffered CoHM as the index cation with a single extraction was most appropriate for determining CEC and exchangeable cations in soils.

In Van Olphen and Fripiat (1979), details are presented of interlaboratory determinations of CEC: three laboratories each used a different method to calculate CEC on the same clay samples. The methods used were: ‘compulsive displacement’ using $BaCl_2$ and $MgSO_4$ (similar to 20); NH_4OAc exchange with Kjeldahl determination of NH_4 on the washed clay (not included in Table 1.1); and NH_4OAc exchange, with determination of the NH_4 content of the washed clay with an ammonia electrode (not included in Table 1.1). Reasonable agreement was obtained between values determined by the different laboratories using the different methods, with results generally within 5% of the mean. In a second study, results were compared for CEC determinations obtained by different laboratories using the same method (the standard NH_4OAc method) on the same samples. The results revealed a relatively large spread in the data.

Kalra and Maynard (1994) compared CEC values obtained for calcareous and non-calcareous soils using seven different extractants. The results, summarized in Table 1.5, reveal some marked differences in CEC values. The $BaCl_2$ extractant gave the highest CEC values while the NH_4Cl solutions, particularly the unbuffered extractant, gave the lowest results. CEC values obtained using the unbuffered NH_4Cl were similar to those obtained using the NaOAc/NaCl/EtOH method. There was very little difference in CEC or exchangeable cations between buffered and unbuffered solutions of each extractant.

Table 1.5 CEC values in cmol (+) kg-1 determined using different extracting solutions. Modified from Kalra and Maynard (1994).

Sample type	Extractant						
	a	b	c	d	e	f	g
Calcareous soil	3.71	3.69	3.84	3.64	5.88	10.61	4.03
Non-calcareous soil	32.18	32.33	31.06	28.67	43.95	49.51	28.43
Non-calcareous soil	21.19	21.23	21.28	20.36	28.44	27.17	18.91

a = 1.0 M NH_4OAc pH 8.2
b = 1.0 M NH_4OAc pH 7.0
c = 1.0 M NH_4Cl pH 8.4
d = 1.0 M NH_4OAc unbuffered pH 5.0
e = i) 1.0 M $BaCl_2$ pH 8.2 ii) 0.5 M $MgCl_2$
f = i) 0.1 M $BaCl_2$ unbuffered pH 5.5 ii) 0.5 M $MgCl_2$
g = i) 0.4 M NaOAc/0.1 M NaCl/EtOH ii) 0.5 M $Mg(NO_3)$

Kalra and Maynard (1994) also presented tables detailing the amounts of individual cations (Ca, Mg, K and Na) extracted by each solution. The $BaCl_2$ solution extracted one-half to one-third less Ca than the NH_4OAc or NH_4Cl extractants, in the presence of carbonates. In the alkaline non-calcareous samples, however, the $BaCl_2$ extractants had the highest Ca concentrations. Similar trends were observed for Mg, but results for K were opposite to those for Ca and Mg. The highest K concentrations were obtained with buffered NH_4Cl, while the NH_4Cl solutions extracted more Na than either the $BaCl_2$ or the NH_4OAc extractants.

Pleysier and Juo (1980) compared CEC results from soils obtained using two methods: single extraction with dilute unbuffered AgTU solution (9); and the ‘standard’ method for determining effective CEC (3). Both methods gave essentially the same CEC values for 57 soils. Good agreements were also obtained between the dilute AgTU-extractable bases and *N* NH_4OAc-extractable bases. The dilute AgTU extraction gave slightly larger values of exchange acidity (Al+H) than the *N* KCl extraction for most soils. The authors concluded that the method using unbuffered AgTU is suitable for rapid, routine measurements of effective CEC and exchangeable cations for soils dominated by variable-charge colloids such as Fe- and Al-oxides and kaolins.

Table 1.6 compares CEC values for pure clay minerals obtained by the methylene blue (MB) method with those determined by an ammonium exchange method. With one exception, CECs obtained by both methods for kaolins show close agreement, whilst NH_4OAc CECs for illites are invariably higher than those determined by MB. The same applies for smectites, but in no case is the difference greater than 6.5%.

Table 1.6 Comparison of CEC values (in meq/100g) for pure clay minerals obtained by the methylene blue method with those determined by ammonium exchange.

Sample type	Sample	MB CEC	NH_4OAc CEC
Kaolins (from Taylor, 1985)	Supreme china clay	2.9	5.1
	China clay 10	3.4	3.4
	Snaittenbacher kaolin	1.4	1.8
	Kaolin I, India	7.03	7.12
	Kaolin II, India	5.94	6.0
Illites (from Taylor, 1985)	Fithian (API 35)	26.0	27.0
	Le Puy en Velay, France	22.6	26.6
	Illite von Fuzerradvany	17.8	18.6
Smectites (from Nevins & Weintritt, 1967)	Wyoming bentonite EG28	76.6	77.5
	Wyoming bentonite NE98	74.5	74.9
	Wyoming bentonite EG20	77.8	81.9
	Low yield bentonite EG16	71.8	76.4
	Low yield bentonite EG24	69.2	73.2
	Texas bentonite EG21	62.2	65.5

For thirty-seven soils with CEC values in the range 1.1-37.0 meq/100g, Savant (1994) found a linear relationship ($r^2 = 0.97$) between CECs determined by the MB and NH_4OAc methods.

1.6.4 Discussion

The method chosen as a standard for determining CEC values for input to LandSim will need to satisfy several criteria:

- it must be suited to a wide range of rock types (in particular those listed in Section 2), including some containing large proportions of carbonate and sulphate minerals.

- It should be straightforward; fewer steps in the methodology means less labour, less cost of reagents, less time *per* analysis and a better chance of obtaining consistent and reproducible results both within and between laboratories.

- Preferably, it should not involve reagents that pose a significant health risk to laboratory personnel and/or are difficult to deal with or dispose of.

- It needs to be sufficiently precise to provide meaningful data; however, unless the reaction efficiency[4] is known more accurately the methods described above will probably provide sufficiently precise data for input into LandSim in its present form.

- The analytical part of the method should involve a standard laboratory technique.

- It should have an established track record.

No general method exists that can be used reliably for all clay minerals, and each of the methods described in this report has advantages, limitations and drawbacks.

Comparison studies of the various direct displacement methods of determining CEC have shown that, generally speaking, there is little *significant* difference in results obtained using most of the methods. This is particularly so if potential sources of inaccuracy, such as dissolution of salts and minerals during saturation, are anticipated and steps are taken to minimize their effects. Studies that compared methods of directly measuring index cations and methods involving summation of, or straightforward measurement of, cations in extraction solutions produced essentially similar results. In other words, whether CEC or effective CEC is measured, the result is essentially the same. When these conclusions are considered in the context of the likely effect of reaction efficiency on *actual* CEC (as opposed to measured ideal CEC or calculated theoretical CEC) in rocks, it becomes clear that maximizing precision of results need not be the prime objective in identifying a suitable method for standard analysis. Put another way, there is no point in attempting to identify the most precise method for measuring CEC because factors such as reaction efficiency can potentially significantly reduce accuracy.

For these reasons very few of the methods for measuring CEC that have been described need be discounted on the basis of insufficient precision. Of more importance, particularly in the context of identifying a method which will be used widely and frequently, is the relative complexity of the methods, and the time, labour and cost of performing them. On the basis of

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[4] CEC values for a range of lithologies are available in the literature, and LandSim supplies a list of ‘suggested parameters’ for both CEC and partition coefficients. Values are supplied for a range of lithologies including chalk, sandstone and limestone from different aquifers, as well as clays and clay-sand mixtures. In the case of CEC, a correction is made for *reaction efficiency* (default values between 0.1 and 0.45) to allow for the fact that not all the sites will undergo cation exchange under *in situ* conditions.

such practical considerations, it is clear that single displacement methods offer considerable advantages over double displacement methods, which are inevitably more complex.

Of the single displacement methods, those that involve adding radioactive tracers to saturating solutions can be discounted because of the practical disadvantages of working with radioactive materials. Methods involving single displacement and summation of exchangeable cations are relatively straightforward, however those involving NH_4OAc and $BaCl_2$ solutions are prone to problems associated with fixation of cations and/or dissolution of minerals and, while the effects are probably relatively insignificant in the majority of cases, there may be occasions when more substantial errors occur. Only method 4 in Table 1.1, in which samples are saturated using a $SrCl_2$ solution, appears to offer a simple, one-step procedure with no associated problems due to dissolution of salts and carbonate minerals.

Methods that involve single saturation and calculation of CEC by difference appear to offer a good combination of precision and practicality. In Table 1.1, three variants of this method (9, 10, and 11) are shown, each using a different saturating solution. Of these, the AgTU method (9) may be impractical in some situations because AgTU solutions are unstable at pH>8. The CoHM method (10) appears to have no significant disadvantages, other than that it has not been used widely and has therefore not been tested on a wide range of materials. The CsCl method (11), in which CsCl is used as the exchange salt and the original pore solution in the sample is used as the exchange salt solvent, was developed specifically for use in the field on calcareous sandy materials of low exchange capacity (<1 meq/100 g). Although CsCl appears to have some important advantages as an exchange salt, the method would require modification and testing before a standard procedure for use in the laboratory, and suited to materials with a broader range of CEC, could be developed.

Double displacement methods, in general, are more complex and therefore less practical than single displacement methods, apparently without offering a significant advantage in terms of measurement precision. However, ‘compulsive displacement’ (22) has been adopted as the British Standard method, and as an international standard method, for determining CEC in soils. As such, it is very widely applied, it has been tested thoroughly on a wide range of materials, and is commonly used in studies comparing different methods for determining CECs.

The compulsive displacement method has two drawbacks when compared with most single displacement methods: the first is that there are potential health risks for laboratory personnel working with Ba and, because it is also harmful to the environment, there can be problems of disposal; the second is its relative complexity in terms of the number of reagents needed and the number of steps involved in the determination. However, because Ba is removed from the sample by *reaction* (i.e. compulsively displaced) there is no need for the repeated washing steps that are required to replace the index ions in other double displacement methods. Thus, assuming the potential health and environmental problems can be overcome, the compulsive displacement method has the advantage of being already widely used and, although less straightforward than single displacement methods, it is less complex than most other double displacement methods. Interference from Ca can affect CEC determinations by the compulsive exchange method in gypsum-bearing samples.

Methods using methylene blue dye are used widely and are very straightforward, particularly that described by Jones (1964). Comparison with the standard NH_4OAc method revealed differences in results of no more than 6.5%.

In summary, three 'key' types of method appear to offer a combination of relative simplicity, adequate precision and practical advantages. These are the single displacement and summation method (of these the method using $SrCl_2$ as the exchange salt (4) appears to have some advantages over those using NH_4 or $BaCl_2$), the 'compulsive displacement' method (22), and the methylene blue method of Jones (1964). Because these are radically different methods, and because they have so far been tested mainly on soils or on pure clay minerals, a comparative study using rock samples from the major aquifer formations encountered in the UK should be undertaken to determine more precisely their advantages, limitations and drawbacks before a single method (or a selection of methods) is proposed for adoption as standard for determining CEC input values for LandSim.

Although only limited data are available, CEC values obtained for the same sample using the same method by different laboratories show a considerable spread, in spite of precautions taken to obtain comparable results. Maximizing interlaboratory consistency in CEC measurements has three key requirements:

3) careful attention to experimental detail;
4) standardized experimental procedures;
5) certified reference materials with which individual procedures may be evaluated.

1.7 Determination of distribution ratios

Batch techniques and once-through-flow column experiments are the most common laboratory methods used to evaluate sorption. The batch method is appealing because of its apparent simplicity and its ability to generate a large amount of data in a short time. Column experiments allow observation of migration rates without significant rock alteration and can be used to study hydrodynamic effects (dispersion, colloidal transport etc) as well as chemical phenomena (multiple species, reversibility etc). However, equipment costs, time constraints, experimental complications and data reduction uncertainties make them unsuitable for a simple screening programme. This review will, therefore, concentrate on batch methods.

Batch techniques involve contacting the solid phase (disaggregated rocks, soils, sediments etc) with a solution containing the adsorbate (contaminant) of interest. In most instances the system is continuously agitated to facilitate mixing and contact. At specified times the solid and solution are separated and the resultant distribution of the adsorbate is determined. The timescale deemed to be required to attain equilibrium is somewhat arbitrarily chosen: usually seven to fourteen days for most reported data although it has been found that small changes occur after months or years.

The results are usually reported in terms of the distribution ratio, R_d, defined as

$$R_d = \frac{\text{concentration of the species on solid phase}}{\text{concentration of the species on the liquid phase}}$$

Any convenient units may be used for concentration and R_d has the dimensions volume/weight, usually ml/g or m^3/kg.

Distribution ratios are usually calculated from the initial and final concentration in solution using the formula

$$R_d = \frac{I - F}{F} \times \frac{\text{Volume}}{\text{Weight}}$$ where I and F = initial and final concentrations in solution

Any convenient concentration unit may be used (e.g. µg/l or cpm if a radiotracer is used).

Since

$$R_d \propto \frac{1 - F/I}{F/I}$$ the graph of R_d against F/I will be hyperbolic.

This means that the value of R_d will be very sensitive to small changes in solute concentration if F/I is small (usually when R_d is high) and very insensitive when F/I is large. In order to obtain reasonable accuracy it is advisable therefore to choose solid/solution ratios such that between about 25% and 75% of the solute is sorbed or F/I is between about 0.3 and 0.7.

For a given R_d, values of F and F/I change with solid/solution ratio (Table 1.7). Errors in calculated R_d, assuming a 10% analytical error throughout, are also given but this does not reflect the sensitivity of R_d to small changes in F. Clearly, if R_d is small (e.g. 2 ml/g) then a high solid/solution ratio should be used, bearing in mind that for the same system the higher the solid/solution ratios the lower the measured R_d value. If R_d is high a low solid/solution ratio (e.g. 1 g rock with 30 to 100 ml groundwater should be suitable for anticipated R_d values of 100 ml/g) should be used to ensure measurable concentrations are left in solution.

Table 1.7 Effect of solid/solution ratio on precision of Rd determinations

						If analytical error 10%	
I	m/v	v/m	F	F/I	I-F	error R_d	% error R_d
R_d =2							
1000	1	1	333.33	0.33	666.67	0.19	9.35
1000	0.5	2	500.00	0.50	500.00	0.49	24.49
1000	0.33	3	600.00	0.60	400.00	0.92	46.23
1000	0.2	5	714.29	0.71	285.71	2.21	110.40
1000	0.1	10	833.33	0.83	166.67	7.87	393.70
1000	0.03	30	937.50	0.94	62.50	65.86	3293.17
1000	0.02	50	961.54	0.96	38.46	180	9021
1000	0.01	100	980.39	0.98	19.61	714	35714
1000	0.002	500	996.02	1.00	3.98	17713	885657
R_d =10							
1000	1	1	90.91	0.09	909.09	0.15	1.49
1000	0.5	2	166.67	0.17	833.33	0.31	3.15
1000	0.33	3	230.77	0.23	769.23	0.50	5.00
1000	0.2	5	333.33	0.33	666.67	0.94	9.35
1000	0.1	10	500.00	0.50	500.00	2.45	24.49
1000	0.03	30	750.00	0.75	250.00	15.30	152.97
1000	0.02	50	833.33	0.83	166.67	39.37	394
1000	0.01	100	909.09	0.91	90.91	149.00	1490
1000	0.002	500	980.39	0.98	19.61	3571.41	35714
R_d =100							
1000	1	1	9.90	0.01	990.10	0.14	0.14
1000	0.5	2	19.61	0.02	980.39	0.29	0.29
1000	0.33	3	29.13	0.03	970.87	0.43	0.43
1000	0.2	5	47.62	0.05	952.38	0.73	0.73
1000	0.1	10	90.91	0.09	909.09	1.49	1.49
1000	0.03	30	230.77	0.23	769.23	5.00	5.00
1000	0.02	50	333.33	0.33	666.67	9.35	9
1000	0.01	100	500.00	0.50	500.00	24.49	24
1000	0.002	500	833.33	0.83	166.67	393.70	394

R_d =1000							
1000	1	1	1.00	0.00	999.00	0.14	0.01
1000	0.5	2	2.00	0.00	998.00	0.28	0.03
1000	0.33	3	2.99	0.00	997.01	0.42	0.04
1000	0.2	5	4.98	0.00	995.02	0.71	0.07
1000	0.1	10	9.90	0.01	990.10	1.42	0.14
1000	0.03	30	29.13	0.03	970.87	4.31	0.43
1000	0.02	50	47.62	0.05	952.38	7.25	0.73
1000	0.01	100	90.91	0.09	909.09	14.90	1.49
1000	0.002	500	333.33	0.33	666.67	93.54	9.35

The concentration-dependent nature of sorption processes must be emphasized. R_d typically increases as the concentration of sorbing solute decreases. Several isotherms have been developed to describe sorption behaviour at constant temperature but it must be stressed that these isotherms are empirical and should not be extrapolated beyond the range for which the experimental data are available. Probably the most widely used is the Freundlich isotherms *viz.*

$x = KC^N$ where: x = amount sorbed per unit weight of solid
C = equilibrium solute solution concentration
K, N are constants
i.e. $\log x = \log K + N.\log C$

and a plot of log x against log C gives N as the slope and log K as the intercept.

The Freundlich model does not account for finite adsorption capacity at high concentrations of solute, but this does not hinder the modeling of adsorption of trace constituents. Over the sorbate concentration range in which the Freundlich isotherm is valid, the R_d may be calculated for any C by

$$R_d = KC^{N-1}$$

If N=1 the equation becomes linear, R_d is independent of concentration and equals the Freundlich constant K. It is common to find concentration-dependent sorption even at low solute concentrations and the value of N can be significantly different from one.

Sorption is extremely sensitive to a number of variables and for modeling purposes it is always advisable to simulate *in situ* conditions as closely as possible. Wherever possible, rock and associated groundwater from the site should be used. However, the fact that both mineralogy and groundwater chemistry may change along the flow path makes it difficult to obtain material that simulates the full suite of conditions. Some of the variables that have a marked effect on sorption are:

- *Mineralogy:* Sorption depends on the nature and charge of the mineral surface. The charge may change with pH of the groundwater. Minerals present at relatively low levels often dominate sorption behaviour (e.g. clays and iron oxyhydroxides). If organic compounds, such as humic acids, fulvic acids or anthropogenic contaminants, are present they may sorb onto the surfaces and change the sorption properties (Murphy and Zachara, 1995).

- *Speciation:* The speciation of the contaminant depends on the solution composition. Thus it may change with ionic strength, pH (metals may be cationic [e.g. Pb^{2+}] at low pH but present as hydroxides [e.g. $Pb(OH)_3^-$] at high pH), and Eh (reduced species are normally cationic and strongly sorbed). Pourbaix diagrams (i.e. pH vs Eh) of the type presented by Brookins (1988) are a useful guide to speciation. If organic compounds (e.g. fulvic acids or anthropogenic contaminants) are present they may form complexes with species of interest. For example, Ni^{2+} may sorb strongly whereas nickel fulvate or nickel acetate are only weakly sorbed.

  If more than one species is present simultaneously then the measured R_d will be a gross average value. For instance, if the contaminant happened to be distributed equally in the groundwater between two species that do not interconvert rapidly, one which did not sorb (R_d=0) and one which sorbed strongly (R_d = 1000), the batch method would yield an intermediate value of 30 ml/g in an experiment with a solid/solution ratio of 30. Use of the R_d value of 30 ml/g in subsequent mass transport calculations would not be conservative since 50% of the contaminant would move at the speed of the carrier solution.

- *Ionic strength:* If sorption is by cation exchange then R_d values will normally decrease with increasing ionic strength.

- *pH:* If minerals have a pH-dependent charge then sorption of cations will increase as pH increases, and sorption of anions will decrease. Frequently, the amount sorbed can increase from zero to 100% over a fairly narrow pH range (the sorption edge).

- *Eh:* At low Eh values many surfaces may be coated with iron oxide minerals. These may dissolve as conditions become reducing and sorption properties could change dramatically.

1.7.1 Experimental variables

Batch sorption measurements are made most conveniently in Oakridge centrifuge tubes. Rock and spiked groundwater are added, the tubes sealed and then shaken gently for the desired time. Phase separation is achieved by centrifugation or centrifugation plus filtration. The R_d values measured in such experiments are sensitive to a number of experimental parameters. The effect that these may have is discussed exhaustively in the literature (e.g. Serne and Relyea, 1982; Bradbury and Jeffries, 1985; Higgo, 1988; Puls *et al.* 1989).

- *Solid solution ratio and phase separation:* For a given set of experimental conditions, the parameter that seems to have the greatest effect on observed R_d is the solid/solution ratio together with the method of phase separation. Poor phase separation has the effect of leaving some sorbed contaminant with the solution phase. As a result, the measured concentrations in solution and on the solid are too high and too low, respectively, and the calculated R_d is too low. The higher the solid/solution ratio the greater this effect will be. Centrifugation and membrane filtration have both been used to separate the phases. Filtration through 30,000 or 10,000 Dalton filters gives more reproducible results than centrifugation, but sorption onto the filters must always be considered.

  Because the measured R_d is an average of the value for all the species present, it is often recommended that two different solid solution ratios be used. If two species with markedly different values are present then the two values obtained will be different. (Higgo and Rees, 1986; Higgo, 1988; Gschwend and Wu, 1985; Bradbury, 1985).

- *Water chemistry:* Ideally, groundwater in equilibrium with the rock should be used. In practice this is often impossible and a synthetic groundwater must be prepared either by equilibrating deionized water with crushed rock or by analyzing the groundwater and attempting to reproduce the composition using analytical reagents. This can then be equilibrated with the crushed rock for a few days. pH and Eh are important parameters; pH values should be as close as possible to *in situ* values. Eh is difficult to control, and for many purposes it is sufficient to measure R_d values under oxidizing conditions. R_d values measured under oxidizing conditions tend to be lower than those measured under reducing conditions and hence will be conservative.

- *Particle size and surface chemistry* of the solid phase can influence the distribution ratio markedly. As the particle size decreases, sorption often increases, possibly as a result of increasing surface area. If a particular sieved size fraction is chosen, certain minerals may be concentrated or depleted. The fraction may, therefore, not represent the mineralogy of the whole rock. For example, clay minerals will be enriched in the fine fraction. If unconsolidated sediment is under study the whole disaggregated sediment should be used. If crushed rock is used efforts should be made to avoid excessive fines. In general, the solid phase should be equilibrated with the groundwater for a few hours in order to equilibrate the exchange sites and dissolve any salts that may have precipitated during storage.

- *Contaminant concentration:* It is important to measure sorption in the concentration range of interest while taking care not to exceed solubility limits. Many measured R_d values are invalid because contaminant concentrations used in the experiments were too high, resulting in precipitation as well as sorption.

- *Method of contaminant addition:* pH adjustment after addition of an acid solution of the contaminant can result in supersaturation and colloid formation. To avoid this, contaminants should be added as salt solutions wherever possible.

- *Blank corrections:* In a sorption experiment the surface area of the container is small compared with that of the crushed rock and sorption to the container walls is likely to be negligible. If a blank is run without crushed rock sorption may be significant and corrections made on this basis will be too high. In general, it is better to make no blank correction.

1.7.2 Methodology recommended for scoping experiments

It is not possible to recommend a standard method for all rock types and contaminants. In the absence of any information about expected R_d values, literature data from the various reviews may provide some guidance as to the most appropriate methodology and probable order of magnitude. Simple preliminary experiments should be carried out along the following lines:

1) Obtain *in situ* groundwater or prepare synthetic groundwater. Filter through 0.2 µm filters. This removes fines and sterilizes[5] the groundwater. Measure pH and determine concentration of major cations and anions.

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[5] Note It is important to distinguish between biodegradation and sorption. Biodegradation results in changes in contaminant concentration and changes in the groundwater chemistry and surface chemistry of the solid. If biodegradation is likely, water and rock should be sterilized. The water phase can be filter-sterilized and the solid phase can be sterilized by autoclaving or by gamma irradiation. Higgo *et al.* (1994) found that addition of sodium azide or formalin reduced sorption, probably because of occupation of sorption sites. Other biocides, such as mercuric chloride, would presumably have the same effect.

2) Prepare solid phase by crushing if necessary. Particles should be less than about 1 mm but it is important to avoid production of colloidal material. If unconsolidated sediments are being studied do not dry or crush further. The moisture content of a separate sample should be determined by drying at 95 to 100 °C.

3) In duplicate, weigh about 1 g rock into 30 ml polycarbonate Oakridge centrifuge tubes. Autoclave if biodegradation is likely to occur. Equilibrate with 30 ml groundwater. Centrifuge (20 minutes at 10 000 rpm if clay content is high) and discard the aqueous phase. Weigh. Calculate weight of entrained water.

4) Spike groundwater by addition of contaminant. Contaminant concentration should be similar to that expected in the field. If possible, the spike should be in a solution of the same pH as the groundwater, e.g. as a salt. Check pH. Measure concentration of contaminant in the spiked groundwater.

5) Add 30 ml spiked groundwater to rock. Shake. Calculate actual concentration of spike after dilution with entrained groundwater.

6) Place tubes in an incubator and shake gently for seven days.

7) Centrifuge for ten minutes. Measure pH.

8) Filter supernatant through 30,000 Dalton membrane filter.

9) Measure contaminant concentration in supernatant (after acidification to <pH 2 where metals are being measured).

10) Calculate R_d from the formula

$$R_d = \frac{I - F}{F} \times \frac{\text{Volume}}{\text{Weight}}$$

11) where I and F = initial and final concentrations in solution. Remember to use dry weight (i.e. allowing for entrained water after washing and the moisture content if solid phase was not dry).

12) If necessary, repeat the experiment adjusting the weight of rock to give values of F/1 between 0.3 and 0.7.

13) If no adjustment is necessary and if the R_d value is >10 ml/g, repeat the experiment using a second solid/solution ratio in order to check whether or not more than one species (not readily interconvertible) is present.

1.8 References for Section 1

1.8.1 CEC references

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2. VALIDATION EXPERIMENTS AND PREPARATION OF STANDARD REFERENCE MATERIALS FOR CALIBRATION OF CEC AND K_d MEASUREMENTS

2.1 Introduction

CEC and K_d have been determined for six UK lithologies using the methods recommended in Section 1 of this report. Following statistical testing of sample homogeneity, the results have been used to compare the methods and assess their applicability to geological materials. Standard reference samples have been prepared from each of the six lithologies, against which regulatory staff can calibrate CEC and K_d measurements. Methods for determining CEC and K_d in geological materials that are suitable for adoption by the Environment Agency are recommended.

2.2 Lithologies selected for CEC and Kd determination

The six lithologies selected to be reference standards cover the range of UK geological materials likely to be of most interest in LandSim modeling: Sherwood Sandstone (SS), Mercia Mudstone (MM), Gault Clay (GC), Lower Oxford Clay (LOC), Lower Chalk (LC) and Lincolnshire Limestone (LL). Each of these is an important UK lithology, and the site of existing or possible future landfill development.

Each lithology is represented by a single sample. Each sample is broadly representative of its outcrop location but is not intended to be representative of the lithology as a whole. The Project Record contains details of the sampling sites and the sampled materials. Semi-quantitative mineralogical data for each sample were obtained by X-ray diffraction (XRD) analysis (Tables 2.1 and 2.2). XRD profiles and details of the XRD methodology are provided in the R&D Project Record.

Table 2.1 Summary of bulk XRD analysis results

Sample	Major component	Minor components	Trace components
Sherwood Sstn	Quartz	Orthoclase, dolomite, calcite	?Kaolinite, mica
Mercia Mudstone	Quartz	Dolomite, mica, chlorite, calcite, orthoclase	Hematite
Lincolnshire Lmst	Calcite	Quartz, pyrite	Albite, ?orthoclase

Lower Chalk	Calcite	Quartz	Mica, ?orthoclase
Lower Oxford Clay	Quartz	Calcite, kaolinite, mica, pyrite	Albite, ?smectite
Gault Clay	Calcite	Quartz, smectite, mica, kaolinite, pyrite	Dolomite, ?albite, ?orthoclase

Table 2.2 Summary of clay fraction XRD analysis results

Sample	Major component	Minor components	Trace components
Sherwood Sstn	Kaolinite	Illite, chlorite	Illite-smectite
Mercia Mudstone	Illite	Corrensite, chlorite	-
Lincolnshire Lmst	Smectite	Kaolinite, illite	-
Lower Chalk	Smectite	Kaolinite, illite	-
Lower Oxford Clay	Kaolinite	Illite, chlorite	Smectite
Gault Clay	Smectite	Kaolinite, illite	-

The clay assemblages are typical of these lithologies (Perrin 1971). Minerals identified in the clay fractions (Table 2.2) will play the dominant role in determining the CEC of the samples. However, all the samples contain calcite which, if allowed to dissolve during CEC determination, can lead to CEC values that are unrealistically high (see Section 2.3.4).

2.3 CEC determination

The six primary samples were crushed to <200 µm for CEC determination. A coarser fraction (2000 µm) was also prepared from the Sherwood Sandstone sample to enable an assessment of the influence of sample preparation on CEC values. CEC was determined for each sample using the $BaCl_2$, $SrCl_2$ and methylene blue index (MBI) methods. The reasons for choosing these methods, and a discussion of some of their advantages and disadvantages, are given in Section 1 of this report. The R&D Project Record contains further details of the sample preparation.

2.3.1 Methodology

Step-by-step procedures and key publications describing each of the methods are provided in the R&D Project Record. All CEC results were corrected for moisture content at 105 °C.

$BaCl_2$-triethanolamine method (shortened elsewhere to '$BaCl_2$ method')

The method used, a version of the popular 'compulsive displacement' method (see Section 1), is a slight modification of that described in Avery and Bascomb (1982) and of the British Standard method for determining CEC in soil. The use of triethanolamine in the procedure means that a protective coat of $BaCO_3$ forms around reactive Ca-rich minerals, rendering them insoluble and removing the problem of Ca interference due to mineral dissolution. The method is therefore suitable for determining CEC in calcareous and non-calcareous materials. Titrometric measurement of CEC was favoured over instrumental measurement because it is simpler, cheaper, often quicker and provides results of adequate precision for this task.

$SrCl_2$ method

The method used, a typical single displacement and summation method (see Section 1), is described in Edmeades and Clinton (1981). To reduce costs, the sample-solution ratio of 5.0 g of sample in 80 ml of reagent described in Edmeades and Clinton (1981) was scaled-down to 2.5 g of sample in 40 ml of reagent. Edmeades and Clinton determined CEC by summing milli-equivalent (meq) values for extractable Ca, Mg, Na, K, Mn & Al by atomic absorption spectrometry using an air acetylene flame. CEC was determined in the present study by summing meq values calculated from ppm levels of Ca, Mg, Na & K measured in extraction solutions by Inductively Coupled Plasma Optical Emission Spectroscopy.

Methylene Blue Index (MBI) method

This method requires only one reagent (methylene blue dye) and just a few steps to perform; consequently, it is the simplest, quickest and cheapest of the three methods. An aqueous sample dispersion is titrated directly with MB solution to an 'end-point' that is recognized by spot-testing on a filter paper. Improvement in detection of the end-point can be achieved by adding acid (5 N H_2SO_4) to buffer pH during the procedure. However, several of the samples examined in this study contained a substantial proportion of calcite, and a considerable volume of acid was required to buffer the solution. Unusually low MBI CEC results from these samples pointed to the possibility that the acid was affecting the properties of the clay mineral surfaces and artificially lowering the CEC. To test this, different quantities of acid (enough to buffer the pH to between 2.5 and 3.8; 1 ml; and none) were used during CEC determination using the MBI method on three samples. The results, outlined in the R&D Project Record, are ambiguous: although CEC values are slightly higher for splits where no acid was used, this may be because the end-point of the titration is determined less easily. The difference in the CEC values obtained using different quantities of acid is not sufficiently large to cause significant uncertainty in the accuracy of the results.

2.3.2 Analytical schedule and statistical evaluation

The analytical schedule was designed with three objectives: to enable statistical tests of sample homogeneity; to enable statistical tests of sub-sample homogeneity; and to enable inter-method comparison. Each of the six starting samples was crushed (coarse and fine fractions of the Sherwood Sandstone sample were prepared), homogenized and split into one hundred 100 g sub-samples (splits).

Homogeneity within each sample was tested by obtaining CEC values for every tenth split using the $BaCl_2$ method. This was repeated (twice in the case of the Mercia Mudstone sample) to produce separate batches of results which could be evaluated statistically.

Sub-sample homogeneity was tested by selecting one split from each sample and performing twelve CEC determinations: two using the $BaCl_2$ method, five using the $SrCl_2$ method and five using the MBI method (extra determinations were made on samples with high calcite contents, as described above and in the R&D Project Record).

The CEC results used in the homogeneity tests were also used to compare the three methods.

Full details of, and the data resulting from, the tests are provided in the R&D Project Record. The results are summarized below.

2.3.3 Homogeneity test results

Sample homogeneity can be assessed only in the context of the purpose for which the samples are intended. In the case of CEC determination, the degree of precision required is not high because of the inherent uncertainties concerning representivity of the sampled material and accuracy of the results (compared to actual CEC of geological materials in their natural state).

The Mercia Mudstone, Lower Oxford Clay and the coarse Sherwood Sandstone samples are sufficiently homogeneous (at the 99% confidence level) for use as reference materials for the determination of CEC by the $BaCl_2$/triethanolamine method. However, values obtained for the second batches of the Lower Chalk, Sherwood Sandstone, Gault Clay and Lincolnshire Limestone samples are consistently higher or lower than for the first batches, and the difference in results between the batches (up to about 10%) is too great for a statistical assessment of their homogeneity. The consistency of the difference between batches suggests strongly that the cause is not sample heterogeneity; it is more likely to reflect a small change in laboratory conditions between batch runs and/or operator bias in determining the end-point of the titration. These materials are therefore considered to be sufficiently homogeneous for use as CEC reference materials, though in the absence of more data to enable satisfactory homogeneity testing an error of ±10% should be expected. This is probably no greater than error associated with sample representivity and the accuracy of laboratory determinations compared with actual CEC in natural systems.

2.3.4 Comparison of methodologies

The results of the CEC determinations are summarized in Table 2.3.

Table 2.3 Summary of CEC results

Lithology	$BaCl_2$			$SrCl_2$			MBI		
	Mean	Sd	RSD %	Mean	Sd	RSD %	Mean	Sd	RSD%
Sherwood Sstn <2000 µm	4.55	0.48	10.6	2.41	0.11	4.36	3.05	0.22	7.21
Sherwood Sstn <200 µm	8.86	0.87	9.9	14.46	0.61	4.23	4.41	0.28	6.43
Mercia Mudstone	12.88	0.55	4.3	11.66	0.19	1.62	8.83	0.18	2.05
Lincolnshire Lmst	13.31	1.34	10.1	203.42	6.66	3.27	<2.00	N/A	N/A
Lower Chalk	17.88	0.83	4.7	212.10	3.69	1.74	5.45	0.46	8.38
Lower Oxford Clay	30.82	0.47	1.5	38.55	0.62	1.61	20.72	0.83	4.01
Gault Clay	34.37	1.80	5.2	136.79	4.41	3.22	25.25	0.47	1.88

Sd = standard deviation
RSD = relative standard deviation

Mean results obtained using the $BaCl_2$ method range from 4.55 to 34.37 meq/100 g. As expected, the results reflect the mineralogy of the samples: the lowest values are from the clay-poor sandstone and the highest values from the clay-rich samples. The results are broadly in line with published data for the same or similar lithologies.

Mean results obtained using the $SrCl_2$ method range from 2.41 to 212.10 meq/100 g. Results for the Sherwood Sandstone fractions, the Mercia Mudstone and the Lower Oxford Clay are slightly higher than those obtained using the $BaCl_2$ method, while those for the Lincolnshire

Limestone, Lower Chalk and Gault Clay are substantially higher. The latter samples contain calcite as a major component (Table 2.1). Because the $SrCl_2$ method employs unbuffered reagents, Ca-bearing minerals such as calcite, dolomite and gypsum, are dissolved and the resulting high Ca and Mg concentrations in the extraction solution lead to grossly elevated CEC values.

Mean results obtained using the MBI method range from <2.00 to 25.25 meq/100 g; results are generally lower than those obtained using the other methods. For the coarse Sherwood Sandstone fraction, the Mercia Mudstone, Lower Oxford Clay and Gault Clay the MBI results are around 30% lower than equivalent $BaCl_2$ results. The difference is considerably greater for the other samples. Low CEC values can be expected with the MBI method because monolayer coverage of clay particle surfaces by sorption of MB molecules occurs before the charge imbalance on the structure is satisfied.

Mean results for the coarse Sherwood Sandstone fraction are lower than for the fine fraction, regardless of the method used to determine CEC. However, the size of the difference between the two results varies considerably between the methods: CEC of the coarse fraction is about 25% lower using the MBI method, about 50% lower using the $BaCl_2$ method and over 80% lower using the $SrCl_2$ method. The lower CEC values of the coarse fraction are interpreted to reflect the mineralogical and textural characteristics of the Sherwood Sandstone, in which clay particles are to a large extent enclosed within a carbonate cement which is interstitial to the framework quartz and feldspar grains. In the <2000 µm fraction most of the clay particles will still be enclosed in carbonate, and CEC determined on such a fraction will be considerably lower than in the <200 µm fraction in which the carbonate cement has been ground finely, 'freeing' the clay particles. The $SrCl_2$ CEC value for the finer sandstone fraction is higher than values obtained using the other methods because of elevated Ca levels in the extraction solution caused by carbonate dissolution, as described above. The $SrCl_2$ CEC value for the coarser sandstone fraction is lower than might be expected, probably because of incomplete carbonate dissolution during the determination procedure, due to the relatively large particle size.

2.3.5 Summary and recommendations

The $BaCl_2$-triethanolamine method produces reliable results for a wide range of geological materials, including calcareous and non-calcareous rocks. It should be adopted by the Environment Agency as the standard method for determining CEC in geological materials. Titrometric measurement of CEC is quick, simple and cheap compared to instrumental analysis, and is sufficiently precise for the purpose of providing input to LandSim.

The $SrCl_2$ method involves a quick and simple extraction phase but requires instrumental CEC determination, which ultimately makes it potentially more time-consuming, complicated and costly than the $BaCl_2$ method. CEC values for lithologies containing little or no carbonate and Ca-sulphate minerals compare reasonably well with values obtained using the $BaCl_2$ method. However, grossly elevated CEC values are obtained from samples containing significant proportions of Ca-bearing minerals such as calcite, dolomite and gypsum because they dissolve in the unbuffered reagents, resulting in high Ca and Mg concentrations in extraction solutions. This method is therefore not suited to lithologies containing soluble Ca-rich minerals.

The methylene blue method is the simplest and quickest of the three. Results are significantly lower than are obtained using the $BaCl_2$ method and, because error is more significant on lower values, they will be less reliable. For these reasons, the methylene blue method is not as well suited to measuring the CEC of geological materials as the $BaCl_2$ method. Although it is recommended that the methylene blue method should not become the standard method for measuring the CEC of geological materials, it could be used to provide advisory values.

2.4 K_d measurements

K_d values for sorption of ammonium ion on each sample were determined using a simple batch technique. The detailed rationale for the recommended methodology may be found in the R&D Project Record.

2.4.1 Methodology

Full details and step-by step procedures including pertinent references are supplied in the R&D Project Record.

Essentially, the recommended methodology is based on the batch technique (see Section 1.7), in which a known mass of solid phase is shaken continuously with a solution containing a known concentration of the adsorbate of interest for a specified period of time. Some of the supernatant is then sampled and analysed for the adsorbate. The difference between the initial and final concentration of aqueous adsorbate is assumed to represent the amount of adsorbate sorbed onto the solid phase. This permits calculation of K_d, or strictly speaking R_d (see Section 1.7).

Attempts to employ column experiments as a means of calculating K_d from retardation factors were beset by technical problems. The fineness of the materials led to their elution in the aqueous mobile phase and caused high back-pressures resulting in leakage from fittings when flow was initiated. Accordingly, column techniques were dismissed in favour of the batch technique as the recommended procedure.

A colorimetric method of ammonium ion measurement was utilized initially but, because it was laborious and prone to interferences, it was superseded by a more convenient, robust, reliable and inexpensive gas-sensing electrode technique.

Use of a proprietary filtration device, capable of removing colloid-sized material from the aqueous phase, is recommended during phase separation (Higgo and Rees, 1986). The highly sorptive nature of colloids means that their presence in the aqueous phase can lead to erroneous determinations for the decrease in ammonium ion concentration.

All six reference materials contained calcareous constituents as major or minor components. Attempts to lower the pH at which K_d is determined can lead to dissolution of these phases and produce enhanced levels of calcium and magnesium ions in the aqueous phase. The subsequent increased competition of these ions for ion exchange sites can lead to decreased sorption and hence a decrease in K_d for the ammonium ions. For this reason the artificial groundwater used in K_d determination was prepared from a neutral salt, sodium chloride, its sole purpose being to mimic the ionic strength of typical leachates. The artificial groundwater was then pre-equilibrated with a given reference material and the ‘natural pH’ attained was employed in the K_d for ammonium ions that followed.

Results from the experiments are presented in Table 2.4 below, and are discussed in detail in the accompanying R&D Project Record.

Table 2.4 Summary of K_d results

Lithology		Ammonium concentration						
	Expt pH	10 mg/l Av K_d	10 mg/l K_d range	40 mg/l Av K_d	40 mg/l K_d range	Expt pH	Leachate* Av K_d	Leachate* K_d range
Sherwood Sstn <2000 µm	8.3	1.36	1.19 - 1.56	1.31	0.98 - 1.84			
Sherwood Sstn <2000 µm	6.2	0.43	0.29 - 0.67					
Sherwood Sstn <200 µm	8.4	1.79	1.70 - 1.90	1.70	1.11 - 2.06			

Lower Chalk <2000 µm	8.1	2.06	1.98 - 2.18	1.97	1.72 - 2.13			
Lower Chalk <200 µm	8.0	1.63	1.29 -1.92	1.20	0.89 - 1.50	6.7	0.03	-0.03 - 0.09
Mercia Mudstone	8.0	7.78	7.30 - 8.53	5.49	5.21 - 5.88	7.0	5.24	4.64 - 5.72
Lower Oxford Clay	7.2	1.48	1.47 - 1.50	2.27	2.10 - 2.50			
Gault Clay	7.9	6.91	6.86 - 7.03	6.25	6.09 - 6.43			
Lincolnshire Lmst	7.4	0.77	0.71 - 0.82	0.66	0.63 - 0.69			

K_d in ml/g
* Ammonium concentration 4.24 mg/l

In materials containing appreciable quantities of illite in the clay fraction the overall CEC may be low yet K_d for ammonium may be high because of the propensity of ammonium ions to enter and displace potassium ions from the interlayer spaces of illitic clays. This was found to be the case with Mercia Mudstone.

2.5 Reference materials

10 kg of each reference sample has been crushed, homogenized and divided into 100 g sub-samples. These are standard materials against which regulatory staff and site operators can calibrate their own measurements of CEC and K_d, and they are available, with details of the lithology and experimentally determined CEC and K_d values, on request from the British Geological Survey. Where independent CEC and/or K_d measurements are not available, the results of this work provide an indication of reasonable ‘advisory’ input values for models such as LandSim. It must be stressed, however, that the data are site-specific and are not intended to be representative of a particular lithology as a whole.

2.6 Conclusions

- The $BaCl_2$-triethanolamine method should be adopted as the standard method for determining CEC in geological materials. The method produces reliable results for a wide range of geological materials, including calcareous and non-calcareous rocks, sediments and minerals.

- Titrometric measurement of CEC is recommended: it is simpler, quicker and cheaper than instrumental methods and produces results of adequate consistency and precision for input to LandSim.

- The $SrCl_2$ method should not be used for CEC determination in geological materials, principally because the presence of minerals such as calcite and gypsum, which are common in many lithologies, leads to substantial over-estimation of CEC.

- The methylene blue method has the attraction of speed and simplicity, however results are generally lower than those obtained by the $BaCl_2$ method, less precise and less reliable. Although it is recommended that the methylene blue method should not become the standard method for measuring the CEC of geological materials, it could be used to provide advisory values.

- Sample selection and preparation play as important a role in CEC determination as the method used to measure CEC. Material sampled for CEC determination should be sufficiently representative of the lithology under examination to provide meaningful data. The preparation method should ensure that analysed samples are homogenized but not over-ground.

- In natural systems, *actual* CEC depends not only on the mineralogy of a rock, but also on the degree to which minerals that play an important role in governing CEC are accessible to groundwaters. CEC is a finite property and will change as exchange sites on minerals are occupied or exposed. It is therefore time-dependent, and may rise or fall in response to changing groundwater conditions.

- Mean CEC values obtained using the $BaCl_2$ method (Table 2.3) may be used as default values in LandSim, but it should be stressed that they are intended to be only a guide and are probably somewhat higher than actual CEC of the same materials in natural systems.

- Adoption of the batch technique is recommended as the standard methodology for the determination of K_d for ammonium ion on ground geological materials. It has the benefits of simplicity, ruggedness and economy. The method provided reasonably consistent results when used on the six reference materials, although not surprisingly RSDs tended to increase as K_d approached zero (see Appendices in accompanying R&D Project Record).

- The ammonium concentration range over which the K_d measurements were made was considered environmentally realistic (10 mg/l to 40 mg/l NH_4) and was compatible with securing maximum accuracy. The latter criterion also applied to the choice of solid-solution ratio.

- It is important to bear in mind that K_d is dependent on both mineralogy and the solution chemistry of the groundwater/leachate. Consequently, sorption will vary greatly with aqueous phase composition. So while the K_d values listed in Table 2.4 may be used as default values in LandSim, they are specific to the experimental conditions pertaining during their determination.

- The key parameters adopted, and those recommended for measurement of K_ds on ammonium ion, are:

    - Mass of ground solid : 10 g
    - Volume of liquid : 25 g
    - Initial ammonia concentrations : 10 and 40 mg/l
    - pH : 'natural' pH
    - Shaking action : rotary
    - Temperature : 20 °C
    - Pre-equilibration time : 72 hours
    - Equilibration time : 48 hours
    - Phase separation : Amicon Centriprep 30 filtration (> 3 nm dia.)
    - Ammonium measurement : gas-sensing ammonia electrode

2.7 References for Section 2

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