# The Dynamics of Potassium in some Australian soils

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# Abstract

Potassium (K) is a macro element in plant, animal and human nutrition and is regularly applied to agricultural land as a fertiliser or as a component of nutrients in irrigation wastewater. Soils contain variable quantities of potassium-bearing minerals and differ in their inherent K supplying capacity. Improving knowledge of the potassium cycle in soils is considered to be important for a better understanding of the productivity and sustainability of many ecosystems. This work combines soil analysis and mineralogical methods for characterising and quantifying the movement of different forms of potassium in Australian soils.

Dispersion of clay particles is one of the major processes responsible for the degradation of soil structure. Adsorbed sodium is traditionally considered to be a primary cause for poor soil structural stability. However, there is a knowledge gap in understanding the effect of adsorbed monovalent potassium on soil structure. Mixed results from the literature point to more research being required to explore the potential effect of applied $K^+$ on soil dispersive properties and the role of clay minerals in it.

Potassium is common in a wide variety of wastewaters and in some wastewaters is present at several hundred to several thousand mg/L.  Potassium is taken up by expandable clays leading to its fixation and illitisation of smectitic and vermiculitic layers. Clays have a major effect on soil physico-chemical properties, and hence the addition of wastewaters to soils may lead to mineralogical changes in the soils that affect these properties.

The aim of this work was to improve our understanding of potassium dynamics in Australian soils with emphasis on soil clay mineralogical properties. Soils from different regions of Southern Australia were used. Studies on pure clays have been included to understand the fundamental processes involved in potassium cycle in soils.

The results show that applied potassium can cause dispersion of soil but to a lesser extent than sodium. Potassium cations also could increase soil hydraulic conductivity to some extent when applied to a soil with high sodium content by substituting the $Na^+$ on exchange sites. Exchangeable potassium can cause dispersion of soil even if it is present in relatively small amounts (Exchangeable Potassium Percentage < 4%), particularly in soils with dominant illite/kaolinite mineralogy. The use of Exchangeable Cation Ratio is tested as an indicator of soil dispersion because it reflects the combined effects of potassium and sodium as dispersive agents.

Illitic and illitic-kaolinitic soils are more prone to dispersion than soils with dominant smectitic clay. This is due to their differences in clay microstructure and fabric when interacting with water. Turbidity and zeta potential could effectively reflect soil clay dispersive properties. But to understand the meaning of zeta potential for dispersive properties of soils we should have prior knowledge of the mineralogy of the soil studied. TEM and XRD methods could assist in providing a better understanding of the processes occurring in soil.

Application of potassium rich wastewater on four clayey soils from Southern Australia induced changes in the 2:1 clay assemblages of the soils. XRD diagrams and chemical composition of clays extracted from untreated and treated soils were determined. Characterisation of the effect of wastewater treatment on clay fraction either by decomposition of XRD patterns into their component phases or chemical analysis of the mineral content of the studied clays gave consistent results. In 3 of the 4 soils, shifts in peak positions occurred towards more illitic components along with increases in K and sometimes also Mg and Na contents of soil clays. Peak decomposition showed trends towards the formation of interstratifications of illite with smectite at the expense of smectite and an alteration of poorly-crystallised illite into its more well-ordered forms. The results show that illitisation may occur as a result of the addition of K-rich wastewaters to clayey soils. Growers and agricultural managers should consider soil clay mineralogy before irrigating with potassium-rich wastewater.

# Declaration

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Serhiy Marchuk

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# Chapter 1 Introduction

Potassium (K) is a macro element in plant, animal and human nutrition (Simonsson et al., 2009). The K ion is necessary for the functioning of all living cells, and is thus present in all plant and animal tissues; it is also a key element for plant growth. Potassium is regularly applied to agricultural land in many areas (Rangel, 2008). Improving knowledge about the K cycle is considered to be important for a better understanding of the productivity and sustainability of many ecosystems (Tripler et al., 2006).

Potassium is quite abundant in soils, the total soil K pool constitutes a large K-resource with between 3000 and 100 000 kg ha$^{-1}$ in the upper 0.2m of the soil profile depending on parent material, soil type and mineralogy (Sparks, 1987). However, the availability of this soil K for the crop depends on the ability of the soil to release K and on the crop itself (Johnston, 2003). The major source of potassium for plants in soils is from clay minerals (Velde and Barré, 2010) which are the most reactive inorganic components in soil systems (Barré et al., 2009). Soils contain varying amounts of K-bearing minerals and, along with K added with irrigation wastewater, fertilizers and manures, they constitute a major reserve of K (Andrist-Rangel et al., 2006). As well as acting as sources of K, some minerals may at times act and behave as sinks for K-fixation. The fixation process involves adsorption of K ions on to sites in the interlayers of illite, vermiculite and highly charged smectite and their intermediate phases (so-called mixed layer or interstratified minerals), resulting in a collapse of the interlayer space. Whether minerals act as sinks or sources for K depends on the K concentration in the soil solution (McLean and Watson, 1985). Understanding and measuring the inherent potential of soils to deliver potassium (K) to crops and the key soil properties that are related to their K status is becoming increasingly important for the development of long-term sustainable agricultural systems (e.g., Öborn et al., 2005).

## 1.1 Research aim and objectives

The general aim of this work was to improve our understanding of potassium dynamics in Australian soils with emphasis on soil clay mineralogical properties.

Specific objectives for this study were:

- examine the influence of major exchangeable cations ($Ca^{2+}$, $Mg^{2+}$, $Na^{+}$ and $K^{+}$) and $K^{+}$ in particular, on physical and chemical properties of soils with contrasting mineralogy and the differences induced by different cations on the soils;

- investigate the effect of different vegetation regimes on clay mineralogy and potassium status of one of the South Australia's most common soils – a Chromosol;
- investigate the effect of exchangeable and soluble $K^+$ on soil hydraulic properties and clay dispersion and determine how the clay minerals could be modified through application of potassium;
- determine whether irrigation with wastewater high in potassium could change the clay mineral assemblage of soils and hence how it could influence soil properties that are important for agriculture;
- demonstrate applicability of modern soil and clay investigation methods and techniques for characterising and quantifying the effect of applied potassium on soil and soil clay minerals.

The practical aim was to increase the state of knowledge of the role of potassium in Australian soil.

## 1.2 Thesis organisation

This thesis is divided into 9 chapters, including the Introduction and the Literature Review, with the relevant literature being reviewed at the start of each experimental chapter.

**Chapter 1:** introduces the main topic of the study – potassium in Australian soils; the aim and objectives; and the structure of this thesis.

**Chapter 2:** provides an overview on the state of knowledge on the potassium status in soil and the important role of clay minerals in the potassium cycle.

In **Chapter 3,** I have developed the laboratory procedures for studying the effects of the application of potassium on clay minerals using the most common reference clay – Wyoming bentonite. I have used this procedure in further experiments. The changes in clay structure were verified using the X-ray diffraction technique (XRD) with specific software, which enabled identification of these changes.

**Chapter 4**: investigates how cation exchange and related physical properties are influenced by the type of cations in different type clay minerals.

**Chapter 5:** examines the influence of major exchangeable cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$) on the colloidal behaviour of soils with contrasting mineralogy. I also studied the structural differences induced by different cations using XRD, zeta potential and particle size measurements.

**Chapter 6** consisted of two parts. In the first, a field based study, I investigated the variability of the clay fraction of one of the South Australia most common soils – a Chromosol, with depth and under different vegetation regimes. In the second, laboratory study, I evaluated the influence of exchangeable $K^+$ on the dispersive behaviour of the clay fraction of the Chromosol using traditional analytical methods, XRD and TEM.

**Chapter 7**: describes studies of possible effect under laboratory conditions of irrigation with wastewater on the mineralogy of four Australian clayey soils under laboratory condition. The aim was to determine whether irrigation with wastewater high in potassium could change the clay mineral assemblage of soils. The changes in clay composition and properties were monitored using the decomposition of digital XRD data and through chemical analysis of digested clay fractions before and after treatment with wastewater.

**Chapter 8**: investigates 17 dispersive soils from different areas of Australia with varied cropping histories and management practices, except that they all had exchangeable $K^+/Na^+$ ratios > 1. The purpose of this experiment was to determine and quantify the influence of high exchangeable potassium content on various physical and chemical properties of these soils and their dispersive behaviour.

**Chapter 9**: integrates and discuss key findings from the experimental chapters 3 – 8.

**Chapter 10**: summarises and concludes the key findings from the study and discusses recommendation for further research.

# Chapter 2. Literature Review

Potassium is the chemical element with the symbol K (Latin: kalium, from Arabic: al-qalyah - "plant ashes"), atomic number 19, and atomic mass 39.0983 and it is the seventh most abundant element in the earth's crust. Potassium was first isolated from potash ($K_2O$). Elemental potassium is a soft silvery-white metallic alkali metal that oxidizes rapidly in air and is very reactive with water, generating sufficient heat to ignite the evolved hydrogen. Potassium is the "universal cation" in biological systems. It is nontoxic, even at soil and plant levels far in excess of minimum requirements for optimum growth (Barak, 1999). Potassium in nature occurs only as ionic salts. As such, it is found dissolved in seawater, and as part of many minerals. The potassium ion is necessary for the functioning of all living cells, and is thus present in all plant and animal tissues. It is found in especially high concentrations in plant cells, and among foods, it is most highly concentrated in fruits.

The potassium chemical industry dates from 1861, following the development of the extraction process to recover potassium chloride from potassium and sodium chloride salt deposits (Stewart, 1985). Potassium chloride (KCl), known also as muriate of potash, is the most widely used source of potassium for agricultural crops (Kafkafi et al., 2001).

The exact function of potassium in plant growth has not been clearly defined. Potassium is the only essential plant nutrient that is not a constituent of any plant parts (McAfee, 2005). Potassium is associated with the movement of water, nutrients, and carbohydrates in plant tissue. If K is deficient or not supplied in adequate amounts, growth is stunted and yields are reduced. Various research efforts have shown that potassium:

- stimulates early growth
- increases protein production
- improves the efficiency of water use
- is vital for stand persistence, longevity, and winter hardiness of alfalfa
- improves the resistance to diseases and insects

These roles or functions are general, but all are important for profitable crop production (Rehm and Schmitt, 2002).

Excess potassium in the soil will reduce very considerably the amount of other cations the crop can take up, and this may lead to crop growth being badly upset by these induced deficiencies of other cations. The discussion on the general effects of potassium deficiency is complicated by the fact that it depends so much on the relative concentration of other elements, particularly sodium and calcium in the plant tissues (Russell, 1973).

The potassium cycle is almost entirely inorganic. A major role of potassium in living organisms is osmotic control and potassium is taken up, retained and excreted in ionic form ($K^+$). The amount of potassium in soil solution is relatively small but is in near equilibrium with usually the much larger amount of exchangeable potassium from which it is replenished. Soils also contain potassium in more slowly exchangeable forms which act as sources for crops. Potassium present in clay minerals (lattice-K) becomes available in exchangeable forms as these minerals weather. This is a long term process and the amount of potassium made available each year depends on the proportion and types of clay present in the soil (FWAG). The major forms in which potassium is held in soils and the changes it undergoes as it cycles through the soil-plant system are shown below (Figure 1) (Brady and Weil, 2008).

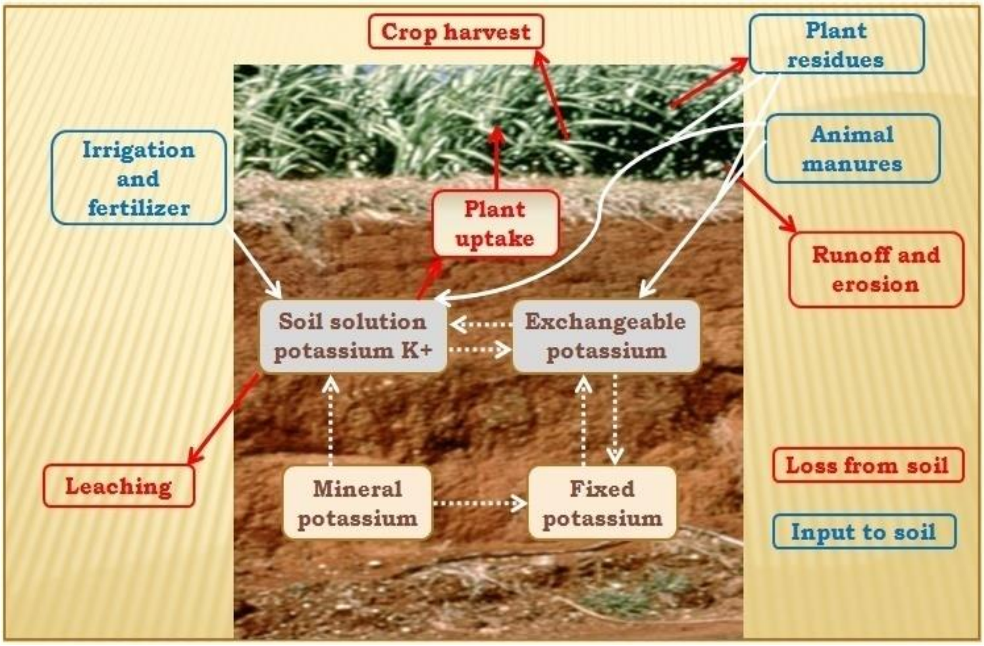


**Figure 1** The classical potassium cycle

## 2.1 Forms of Potassium in Soil

Potassium is quite abundant in soils, typically ranging from 0.5 to 4.0%. Of this, only a small part is present in water-soluble and exchangeable forms (potassium ion $K^+$), and readily available for plant uptake, usually less than 1% of the total. Apart from nitrogen, K is a mineral nutrient that plants require in the largest amount (Marschner 1995 in Scherer et al., 2003).

Potassium, among the mineral cation required by plants, is the largest in size ($r$ = 1.33 Å, Table 1). thus, the number of $O^{2-}$ ions surrounding it in mineral structures is high, 8 – 14, and consequently the strength of each K–O bonds is relatively weak. Potassium, relative to $Ca^{2+}$, $Mg^{2+}$, $Li^{+}$, and $Na^{+}$ ions, has a higher polarizability but $NH_4^{+}$, $Rb^{+}$, $Cs^{+}$, and $Ba^{2+}$ are some of the cations of interest which have even higher values (Table 1). Other things being equal, the higher the polarizability the more strongly the cation is attracted in exchange reactions (Helfferich, 1962) since the distance of closest approach is less (Rich, 1968).

In regard to hydration, however, potassium has a low hydration energy compared to $Mg^{2+}$, $Al^{3+}$, $Ca^{2+}$, $Na^{+}$, and $Li^{+}$ (Table 1). This means that in the interlayer space, $K^{+}$ ions would cause little swelling and have less effect on other groups, including organic molecules in the interlayer space, than the other ions commonly found in these positions (Rich, 1968).

**Table 1** Radius, polarizability and hydration energy of certain cations (after Rich, 1968)

| **Cation** | **Radius**, Å | **Polarizability**, Å$^3$ | **Hydration energy**, kcal/g.ion | |
|---|---|---|---|---|
| | | | First shell | Total shells |
| $Li^{+}$ | 0.6 | 0.02 | 71 | 74 |
| Na+ | 0.95 | 0.21 | 51 | 51 |
| K+ | 1.33 | 0.97 | 34 | 34 |
| Rb+ | 1.48 | 1.47 | 27 | 27 |
| Cs+ | 1.69 | 2.37 | 21 | 21 |
| Mg2+ | 0.65 | 0.17 | 300 | 411 |
| Ca2+ | 0.99 | 0.44 | 227 | 311 |
| Sr2+ | 1.13 | 0.84 | 189 | 263 |
| Ba2+ | 1.35 | 1.63 | 163 | 227 |
| NH4+ | 1.43 | 1.6 | 30 | 30 |
| H+ | Very small | Negative | - | - |

In soils, potassium is described as existing in three forms. These are generally agreed to be:

- unavailable
- slowly available
- readily available

All forms coexist at any point in time in soils and there is a constant change from one form to another (Figure 2). That is, these three forms are said to be in equilibrium with each other.

**Unavailable Potassium**: Depending on soil type, approximately 90-98% of total soil K is found in this form. Feldspars and micas are the primary minerals that contain most of the K. Plants cannot use the K in this crystalline-insoluble form. Over long periods of time, these minerals weather (break down) and K is released. This process, however, is too slow to supply the full K needs of field crops. As these minerals weather, some K moves to the slowly available pool. Some also moves to the readily available pool (see Figure 2).

**Slowly Available Potassium**: This form of K is thought to be trapped between layers of clay minerals and is frequently referred to as being fixed. Growing plants cannot use much of the slowly available K during a single growing season. This slowly available K is not measured by the routine soil testing procedures. Slowly available K can also serve as a reservoir for readily available K. While some slowly available K can be released for plant use during a growing season, some of the readily available K can also be fixed between clay layers and thus converted into slowly available K (see Figure 2). The amount of K fixed in the slowly available forms varies with the type of clay that dominates in the soil.

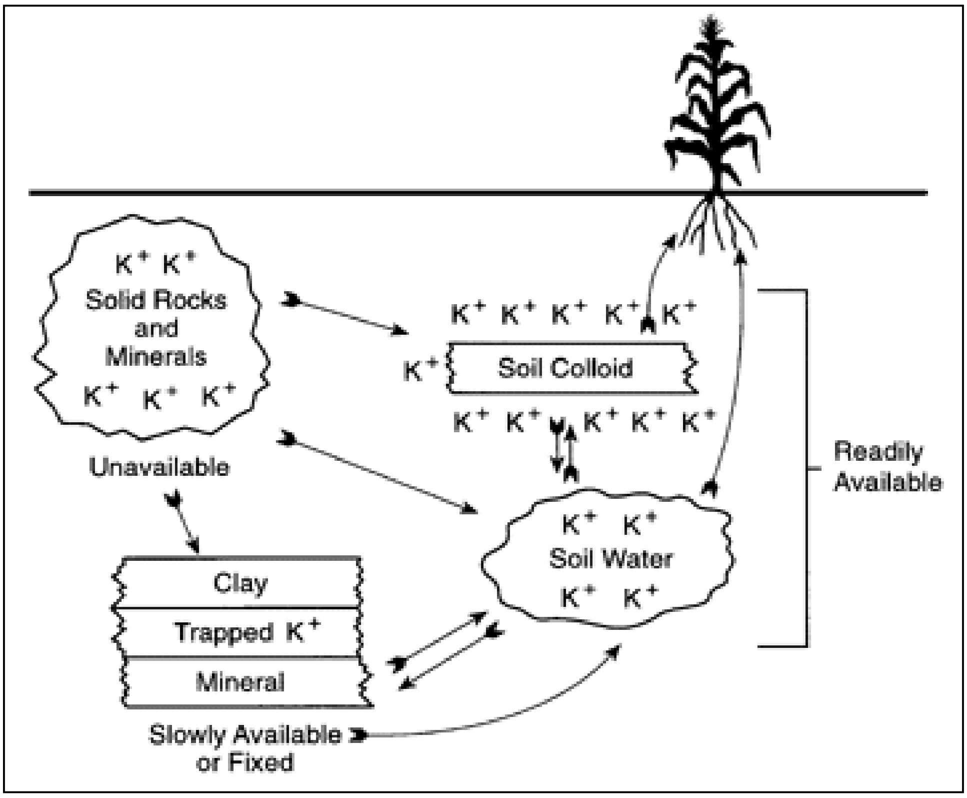


**Figure 2** Relationship among different form of potassium in the soil-plant system. (Source: Regents of the University of Minnesota)

**Readily Available Potassium**: Potassium that is dissolved in soil water (water soluble) plus that held on the exchange sites on clay particles (exchangeable K) is considered readily available for plant growth. The exchange sites are found on the surface of clay particles. This is the form of K measured by the routine soil testing procedure.

Plants readily absorb the K dissolved in the soil water. As soon as the K concentration in soil water drops, more is released into this solution from the K attached to the clay minerals. The K attached to the exchange sites on the clay minerals is more readily available for plant growth than the K trapped between the layers of the clay minerals.

The relationship between slowly available K, exchangeable K, and water-soluble K are summarized below:

Slowly available K

↑↓

Exchangeable K

↑↓

Water-soluble K

Notice that when the arrows go in both directions, one form of K is converted to another. The rate of conversion is affected by such factors as root uptake, fertilizer K applied, soil moisture, and soil temperature (Rehm and Schmitt, 2002).

## 2.2 The Sources of Potassium in Soil: Classical View

The K content in a soil is a reflection of its parent material, degree of weathering, and amount of K added minus losses (Bertsch and Thomas, 1985):

**K Inputs to soil:**

- Plant and animal residues;
- Animal manures;
- Rainfall;
- Irrigation water;
- Fertilizers;
- Aeolian dust.

**K Outputs from soil:**

- Crop removal;
- Leaching to subsoil or groundwater is of little or no consequence;
- Runoff/erosion of topsoil.

Crop removal, irrigation and fertilization are very important factors in cropped soils, whereas for soils under pasture or forest and range, crop removal and fertilization may be of little or no importance. Hence, an indication of the native K status of soils can be obtained from pasture, forest, or range samples, whereas the K status of cropping soils is much more difficult to assess, yet quite important in relation to their K nutrition status (Bertsch and Thomas, 1985).

### 2.2.1 Parent Materials and Mineral Weathering

The amount of K supplied by soils varies due to large differences in soil parent materials and the state of weathering of these materials. Potassium is present in igneous, sedimentary, and metamorphic rocks and comprises about 25g $kg^{-1}$ (2.5%) of the earth's crust (Stewart, 1985). Mineral soils generally range between 0.04 and ≥ 3% K. The most important source of potassium in mineral soils are the primary aluminosilicates, which include the K-feldspars, biotite, and muscovite micas, and the secondary aluminosilicates, comprising the hydrous micas (illite) and the continuum of their weathering products.

According to Ahrens (1965) the K-feldspars comprise approximately 15% of the total lithosphere. The relative importance of K-feldspars in defining the K status of soils in relation to $K^+$ availability is very dependent on the intensity of weathering, time of deposition or exposure and other factors (Bertsch and Thomas, 1985). The most common clay mineral formed is kaolinite. In the weathering of feldspars to kaolinite, potassium, sodium, calcium and silicon are released from the feldspar structure and go into solution. Since the speed of chemical reactions increases with increasing temperature, weathering occurs at a much faster rate in tropical areas than in more temperate ones. Feldspars generally only remain unaltered in very arid climates (Gore, 2008) and quite cold climates (Churchman, 1978).

Micas are primary minerals of the 2:1 phyllosilicate group in the silicate mineral class. The micaceous minerals present in most soils generally range from 8.3% K for the soil micas to 3.3% K for the hydrous micas or illites. The structural differences between the various mica minerals are of great significance in determining the ease of weathering and K release characteristics. Micaceous minerals and their weathering products are the most important sources of plant available $K^+$ in a soil system; however, as with the K-feldspars, the relationships between K supply and crop demand are dependent on the intensity of weathering, time of deposition, and relative composition of the soil mineral suite, rather than parent materials, particularly for more highly weathered soils (Bertsch and Thomas, 1985).

Micas in soil are almost always inherited from the parent material. Micas are thermodynamically unstable in most soil environments. That said, their rates of weathering are often very slow and they may persist for many thousands of years. The weathering of micas produces a variety of secondary products having a range of properties and degrees of disorder. Weathering occurs most rapidly through the loss of interlayer cations and their exchange for cations present in the soil solution. Other changes also occur, however. The layer charge of the secondary products is generally lower than that of the mica parent material, so charge reduction processes must have occurred in conjunction with the loss of interlayer cations (Nater, 2000).

### 2.2.2 K Inputs to the Soil

Of the K removed by plants, some will be returned to the soil in plant residues, leached from plant foliage, or returned in the waste of animals feeding on the vegetation (Syers, 1998).

Applying farmyard manure to cropped land and spreading wood ash were observed to improve crop growth many centuries ago (Johnston, 2003). Wood ash contains about 5% K that is readily available to the plants. Manure is a good source of K for plant growth. The amount of potassium in the manure will depend on the animal, its diet, and the way the excreta is handled. Most of the potassium will be immediately available to the crop, but it must be applied at the correct time (Johnston, 2003). The K in manure is inorganic. Unlike some of the other manure nutrients, there are no transformations required by soil microorganisms to make potassium readily available for plant uptake. K is relatively mobile in coarse textured or organic soils and less mobile in fine textured soils.

The supply of naturally occurring, plant-available potassium in the soil plus the amounts recycled through organic manures and residues is usually too small to achieve economically acceptable yields. Assuring proper nutrition for crop plants generally requires the addition of fertilizers to the soil. The fertilizers are more easily managed and can be applied with greater accuracy than manures. Two materials are available for soil K application: muriate of potash (61% $K_2O$) and sulphate of potash (51% $K_2SO_4$) (McAfee, 2005).

Application of potassium fertilizer will be determined by factors such as soil potassium level, soil type, time of the year and intensity of use of the site. Sandy soils or soils with low cation exchange capacity (CEC) will require light frequent applications of potassium fertilizer as opposed to clayey type soils with high to very high levels of potassium. Soils with high levels of other cations such as calcium, magnesium or sodium will also probably require more frequent, light applications of potassium. As use of the site increases, so should the amount of potassium fertilization. Spring and autumn is the most important times of the year to make potassium fertilizer applications (McAfee, 2005).

Potassium in soluble form is also present in rain and irrigation water, especially in irrigation with wastewaters from agri-industry processes. These wastewaters all have high levels of potassium (from 13-20 mg $L^{-1}$ for municipal wastewater to 10,000 – 200,000 mg $L^{-1}$ for the olive oil processing industry) (Arienzo et al., 2009). The annual amount of potassium which comes into the soil with rainwater ranges from 1 to 10 kg per ha (depends from quantity and location) (Prokoshev, 2005). The aeolian dust suspended in the atmosphere and subsequently deposited on land also contains some potassium. While potassium which comes with irrigation water to the soil could be managed, aeolian dust movement and rainfall are largely controlled by processes related to climate.

### 2.2.3 K Outputs from the Soil

Crops remove large amounts of potassium from soil: from one-fifth (e.g., in cereal grains) to nearly all (e.g., in hay crops) of the potassium taken up by plants may be exported to distant markets, from which it is unlikely to return (Brady and Weil, 2008). Some potassium is lost with eroded soil particles and in runoff water, and some is lost to groundwater by leaching (Brady and Weil, 2008). If clay is abundant in the subsoil, potassium leached from the surface soil may become concentrated there in exchangeable and fixed forms. Erosion of surface soil in extreme cases may cause an appreciable loss of available potassium by the removal of fertilizer particles and of soil particles and organic matter that have high exchangeable potassium content. Because the total content of potassium usually does not vary abruptly with depth, erosion does not alter appreciably the total potassium of the surface soil (Reitemeier, 1957).

## 2.3 Potassium in Clay Minerals

Most of the potassium that is readily available to plants exists as exchangeable ions principally on clay mineral surfaces. As this potassium is removed, it is replaced at various rates depending on the amount and characteristics of the potassium-bearing minerals present in the soil (Rich, 1968).

Soils contain varying amounts of K-bearing minerals constitute a major K reserve. The aluminosilicates are the most abundant K-bearing minerals. They include primary minerals, namely K-feldspars, biotite and muscovite mica. They also include the secondary aluminosilicates, comprising hydrous mica (illite) as well as a continuum of micaceous weathered or inherited products (Bertsch & Thomas 1985), including mixed layer phyllosilicates. The primary soil minerals are inherited from the parent material, whereas the secondary minerals are either inherited from sedimentary rocks or formed in soils during the weathering process (Rangel, 2008).

The ability of the soil to release and fix potassium depends on the minerals present. The more finely divided the mineral particles, the more quickly they will release nutrients from the primary materials. The weathering products of the primary minerals occur predominantly in the fine fraction of the soil. Potassium added to the soil may be fixed by certain clay minerals sometimes so strongly as to be no longer available to the plants (Semb et al., 1959).

### 2.3.1 Clay Minerals

The word “clays” was assigned early to fine grained material in geological formations (Agricola, 1546) or soils (De Serres, 1600). Clays have been identified as mineral species since the beginning of the 19th century for the production of ceramic materials (Brongniart, 1844). Since this pioneer work, the definition of clays has varied. Until recently, the definition of clay minerals was debated. Bailey (1980) restricted the definition of clay to fine-grained phyllosilicates (from the Greek “phyllon”: leaf, and from the Latin “silic”: flint) (Velde and Meunier, 2008).

Clays are historically considered to be formed of < 2 µm particles. The use of the optical microscope for petrographic observations at the end of the 19th century defined the limit of a recognizable crystal and mineral. Crystals whose size was lower than the resolution of the optical microscope, 2 µm, were unidentifiable and called clays. However, the value of the size limit considered to define clays varies according to the particular need of each discipline: 2 µm for, geologists; 1 µm for chemists; and 4 µm for sedimentologists. It is evident that such a definition based on the grain size alone is not convenient for the study of mineral species. Consequently, no size condition will be imposed. Indeed, the size of clay minerals can be much greater than 2 µm: for instance, 50 µm sized kaolinites or illites are frequently observed in diagenetic environments. However surface alteration usually produces new phases almost always of less than 2 µm diameter (Velde and Meunier, 2008).

The formation of clay minerals most commonly occurs under surface (alterites, soils, sediments) or subsurface (diagenesis, hydrothermal alterations) conditions. Difficult to observe without using electronmicroscopy (scanning and transmission), they have been abundantly studied by X-ray diffraction, which is the basic tool for their identification. While the number of their species is relatively small, clay minerals exhibit a great diversity in their composition because of the large compositional ranges of solid solutions and their ability to form polyphased crystals by interstratification (Meunier, 2005).

### 2.3.2 Study Tools

Because clay particles cannot be seen with a microscope, the initial petrographic-mineralogical approach, optical petrographic microscopy, cannot be used. The foundations of the knowledge of clay structures were laid, and the basic mineral names given, in the late nineteenth and first half of the twentieth centuries. However, much imprecision characterized clay mineralogy. In favourable cases, such as samples with only one mineral type present, it was possible to give a general chemical formula and, with the aid of the initial stages of X-ray diffraction in the 1920s – 1930s, establish the structural family of clay samples. However, clays in soils and also sediments are most often found in aggregates containing several different minerals, with millions of grains per gram of sample, and the methods of bulk chemistry of powder diffraction does not permit a sufficiently precise definition of the clay minerals, so that often a mixture of phases was present when one assumed a pure species (Velde, 1992).

As the normal means of identification could not be used, clay mineralogy had to wait for new technology to come to its aid. The new methods refined that of X-ray diffraction, which allows one to determine the phases present rapidly and with precision. Once the phases are known one can proceed to an analysis of the aggregate sample. Chemical methods are still employed, classical as well as those based upon the phenomenon of X-ray fluorescence in macro or micro (electron microprobe) samples, and infrared spectral analysis and thermo-gravimetric analysis are also very useful in determining and defining the specific characteristics of clays (Velde, 1992).

In the past 20 years or so synchrotron-based **X-ray absorption spectroscopy** (XAS) techniques have become generally available for investigating the crystal structures and surface chemistry of clays and clay minerals. XAS is a general term denoting a range of X-ray spectroscopic techniques based on scattering, absorption and emission (fluorescence, auger) of X-rays by matter. It extends diffraction methods by allowing detailed local (short-range) structural information to be obtained but can be regarded mainly as a supplementary technique for clay structure analyses (Gates, 2006).

**X-ray diffraction** (XRD) remains the most important method for identifying soil minerals (Schulze, 1989). XRD deals with distances between atomic planes (Meunier, 2005). Soil minerals are usually studied using the powder diffraction method. A powdered sample, with particles typically < 50µm in diameter, is placed in the diffractometer and irradiated with x-rays. A plot of diffracted x-ray intensity versus twice the diffraction angle – i.e. $2\theta$ – is obtained.

A simple mathematical relationship called Bragg's law is then used to relate the peaks on the x-ray chart with the distances between the diffracting planes of atoms within the crystals (Schulze, 1989).

Once a mineral phase has been identified based on its diffraction peaks, additional information often can be obtained from diffraction line widths. Well-crystallized minerals of sand and silt size give sharp diffraction lines whose widths are determined only by broadening caused by the x-ray diffractometer itself. Clay-sized particles show broader lines caused by diffraction effects from the small size of the particles. The smaller the particles are, the broader the diffraction lines (Schulze, 1989).

The major problem in XRD is that, since clay particles are very small, a coherent domain in a single crystal will also be very small and will not give strong diffraction maxima, so that most of these maxima will be invisible or only faintly visible. There are insufficient atoms present in any one plane to give a satisfactory intensity of diffracted x-rays. This is aggravated by the fact that the clays are found essentially in a two-dimensional form, due to their sheet structure. In addition, if the greatest diameter of a clay particle is 2µm, the smallest is smaller by a factor of 10-20 or more. This reduces the diffraction power of the atomic planes even more in most of the crystallographic directions. As a result, XRD had to wait for a clever mechanism to be devised to reinforce the signal coming from the crystal lattice (Velde, 1992).

**Thermo-gravimetric analysis** determines the differential weight loss associated with energy changes as a sample is heated (Grim, 1968). Heating of clays at a regular rate affects weight loss depending upon the energy of retention of water in or on the clay structures. All clays have at least two, at times three or four, types of water or hydrogen ion in or on their crystallites. The binding energy of these types of water can be used to identify the clay minerals (Velde, 1992). The method is less sensitive than **differential thermal analysis** (Grim, 1968).

**Differential thermal analysis** (DTA) is based upon whether the thermal reaction which occurs as a clay mineral is heated is exothermic or endothermic. Here not only water loss (endothermic reactions for the most part) but also eventual recrystallization and recombinations (exothermic) are observed. The complexity of the full mineral transformations and the problems of kinetics concerning these reactions make interpretation of full DTA diagrams very complex. Such methods are rarely employed in routine investigations; they are left for the more specialised applications of mineral species characterization or certain industrial applications such as ceramics (Velde, 1992).

**Infrared** (IR) **spectral analysis** has been used to characterize clays for some time, and to a lesser extent to identify them. In clay studies IR spectra are produced by passing a multi-wavelength infrared beam through a finely dispersed sample or reflecting it off a powdered sample. This method is somewhat less sensitive to the differences in clay structures and as a result its use as a method of identification, especially in a mixed-phase sample, is difficult. However, the method is useful in identifying certain features of pure phases. An XRD study for identification of clay minerals is usually necessary before this method is used (Velde, 1992).

The development of the **electron microscope** has permitted the precise determination of the shape and size of the particles of the various clay minerals (Grim, 1968). Several derivative methods of analysis are based upon the same principle: the physics of interaction of a beam of electrons with crystalline (or non-crystalline) matter (Velde, 1992).

The **scanning electron microscope** (SEM) uses the flux of secondary and backscattered electrons from the material to form an intensity image of the material bombarded by electron beam. The resulting cathode tube realization indicates the three-dimensional aspect of the sample. This is very useful in the identification of textures and shapes of mineral grain aggregates. The definition or resolution of the image is of the order of 0.01µm (Velde, 1992).

**Transmission electron microscopes** (TEM) are used to see the shapes of crystals in essentially a two-dimensional plane. The clays are deposited on a carbon-coated copper grid (with holes in it so that the clays can be “seen” by the electron beam). The electron beam is absorbed more by the clay than by the carbon film and thus a shadow image of the clay particle is produced. The TEM resolution is greater than that of SEM (µm). Their main use is that of identifying the crystal shapes of clays and their dimension (Velde, 1992).

The newer **high-resolution transmission electron microscopes** (HRTEM) provide a smaller dimension for the study of clay. Transmission micrographic methods give resolutions of less than 2 Å. This allows one to “see” the levels of atomic planes in the clays with ease and in special cases the atoms themselves (Velde, 1992).

The **electron microprobe** is essentially an x-ray fluorescence spectrometer hooked up to an electron microscope. The method is a reliable and reasonably rapid one which can be used to obtain an excellent chemical analysis of a very small quantity of clay material. The method of analysis allows one to use a normal petrographic thin section (thickness 30 µm) to locate the precise environment of clay formation or the precise grains which give rise to new clay minerals. In weathering, for example, it is possible to see what clays form from which minerals.

The resolution of the method is close to that of the petrographic microscope and therefore the old limitations are still present: a single clay particle cannot be designated for analysis as in TEM (Velde, 1992).

**Cation exchange capacity** (CEC) is a measure of the soil's capacity to exchange ions (a charge on a surface). The surface of the clay can be of two sorts, external and internal. The external exchange capacity is largely dependent upon broken bonds and surface growth defects and reflects the average crystalline size but the result is affected by the cation measured. The internal exchange capacity is much more interesting in that it reflects the overall charge imbalance on the layer structure and the absorption capacity of the clays. The exchange capacity is an estimate of both the number of ions adsorbed between the layers of a clay structure and of those adsorbed on the outer surfaces (Velde, 1992).

The tools listed above are those in common use today and can be classified into the zones and scales of interest in clay structures.

1. XRD and SEM are methods used to study the form and structure of crystal aggregates. Information can be derived concerning the crystals by using monomineral samples but always by using aggregates of crystals. Average interplanar distances and the average composition of the atomic planes can be derived from XRD study. The morphology of aggregates is determined by SEM.
2. DTA and TGA studies are concerned with the water molecules in clays. Such studies are done on clay aggregates.
3. TEM investigates the shapes of individual crystals and the compositions of these individual crystals. The observation is looking down on the top of the sheet-like clay grains, that is, the direction of the greatest lateral extension of the crystals.
4. IR methods investigate the relations of individual molecules in the crystals, OH, $H_2O$, Si-O etc. This is then within the crystals but the method is limited to multi-crystalline aggregates.
5. At the same level or below it is the HRTEM analysis methods. Here the atomic layers of the atoms themselves are visible to the investigator's eye via the electron beam.
6. Cation exchange is used to determine the amount of exchange ions which can be fixed on clay structure and the nature and proportions of the various exchangeable cations.

The relations of scale and method are summarized in Figure 3. The sequence indicates that of scale with XRD and SEM (scanning electron microscope) being the largest-scale methods and HRTM giving the smallest-scale view of clay particles (Velde, 1992).

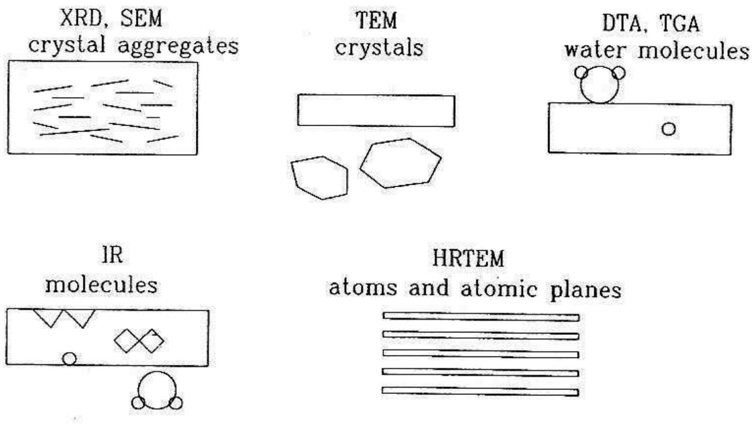


**Figure 3** Uses of different methods of analysis to determine the properties of clays (Velde, 1992)

### 2.3.3 Structure of K-bearing Minerals

Clay minerals, i.e. phyllosilicates, are composed of a combination of two types of layer structures which are coordinations of oxygen or hydroxyl anions with various cations. Two types of sheets occur following the number of anions coordinated with the cations, one of six-fold coordinations (tetrahedra) and the other of eight-fold coordinations (octahedra) (Velde and Meunier, 2008).

Tetrahedra arranged into sheets are common to the structures of all phyllosilicates. Octahedra arranged into sheets are present in the structures of phyllosilicates and in some hydroxide minerals as well. Different combinations of tetrahedral and octahedral sheets give rise to the different clay mineral structures. Figure 4 shows ideal crystal structures based on the closest packing of spheres. The real structures have varying degrees of distortion of this ideal structure (Schulze, 1989).

Phyllosilicates are divided into two groups, 1:1- and 2:1-type minerals, based on the number of tetrahedral and octahedral sheets in the layer structure. The 1:1 layer structure consists of a unit made up of one octahedral and one tetrahedral sheet, with the apical $O^{2-}$ ions of the tetrahedral sheets being shared with (and part of) the octahedral sheet (Figure 5). There are three planes of anions. One plane consists of the basal $O^{2-}$ ions of the tetrahedral sheet, the second consists of $O^{2-}$ ions common to both the tetrahedral and octahedral sheets plus $OH^-$

belonging to the octahedral sheet, and the third consists only of $OH^-$ belonging to the octahedral sheet (Schulze, 1989).

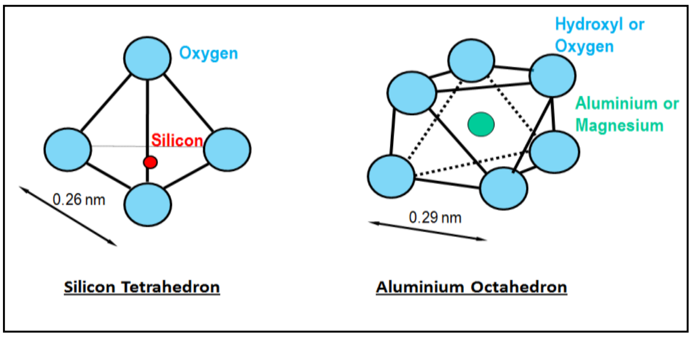


**Figure 4** Types of layer structure of clay minerals (Sivakugan, 2001)

In contrast to the 1:1 minerals, which are represented in soils by only two major minerals (kaolinite and halloysite), the 2:1 minerals are structurally more diverse and are represented by several mineral species. The 2:1 layer structure consists of two tetrahedral sheets bound to either side of an octahedral sheet (Figure 5). There are four planes of anions. The outer two planes consist of the basal oxygen (O's) of the two tetrahedral sheets, while the two inner planes consist of oxygens common to the octahedral sheet and one of the tetrahedral sheets, plus the hydroxyls (OH's) of the octahedral sheet (Schulze, 1989).

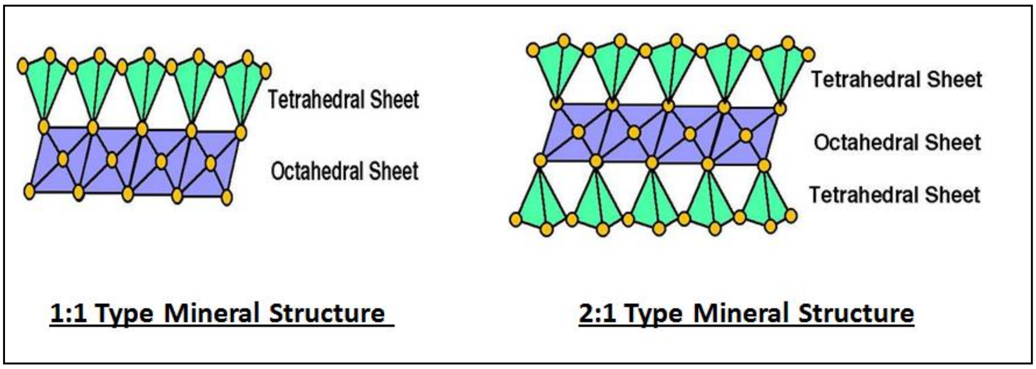


**Figure 5** Structure of 1:1 and 2:1 clay minerals (Sivakugan, 2001)

Many clay materials are composed of more than one clay mineral, and the clay minerals may be mixed in several ways. The mixture may be of discrete clay-mineral particles in which there is no preferred geometric orientation of one particle with respect to its neighbouring clay-mineral particles. Another type of mixing is the interstratification of the layer clay minerals in which the individual layers are of the order of a single or a few aluminosilicate sheets. These mixed-layer structures (MLMs) are a consequence of the fact that the layers of the different layer clay minerals are very similar, all being composed of silica tetrahedral-hexagonal layers and closely packed octahedral layers of oxygens and hydroxyl groups (Grim, 1968).

These minerals are most frequently found in the soil or upper parts of an alteration sequence. Their importance as far as mineral stability and transformation is not well known at present. In some cases, it appears that they are a transition between one structure and another, a sort of intermediate phase while in others their status is less evident. Their importance, though poorly understood, is most likely the key to understanding clay mineral stability in many soils. The most commonly described two-component mixed-layer minerals at Earth's surface are:

- dioctahedral species: illite/smectites (I/S) (Figure 6) and kaolinite/smectites (K/S). They are usually randomly ordered (regular forms of I/S occur in some soils e.g. (Churchman, 1978)) and abundant in soils
- trioctahedral species: biotite-vermiculite, chlorite-vermiculite or smectite (saponite). These MLMs are ordered and sometimes regular. They are formed in weathered rock microsystems (Velde and Meunier, 2008)

For clay minerals, the type of bonding within the crystal structure, the extent and type of disorder within the crystal or at crystal terminations, and crystal size are mineral properties that determine the rate at which weathering occurs and potassium is released. These crystal properties also determine, to a great extent, the exchange properties, including potassium-selectivity and fixation (Rich, 1968).

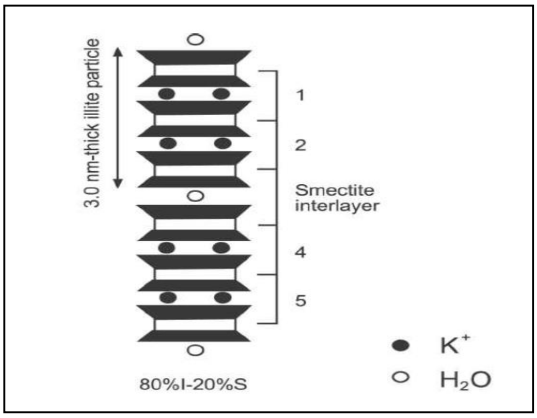


**Figure 6** Structure of an illite-smectite mixed-layer clay (Aldega and Eberl, 2005)

Because of their small size, individual clay mineral crystals are currently observed using transmission electron microscopes (TEM). Most often, clay minerals appear as complex bodies whose origin may be natural (particles, aggregates) or due to artefacts (sedimentation during drying the grid preparation). Because of the difficulty of distinguishing artefacts from natural bodies, definitions are needed for particles, aggregates and natural coalescence:

- Particles. Including twinned crystals, these often exhibit re-entrant angles allowing the boundaries of coalescing crystals to be recognized. These natural particles, contrary to artefacts, cannot be dispersed by chemical or ultrasonic treatment. They result from crystal growth processes on individual crystallites (epitaxy) or on an association of crystallites (coalescence),
- Aggregates are units of higher organization in which crystals and/or particles are bonded together by Coulomb forces or by metal hydroxide or organic matter cements. They result from chemical and/or physical processes in soils.

Schematical representations of epitaxy, aggregation and coalescence are shown in Figure 7.

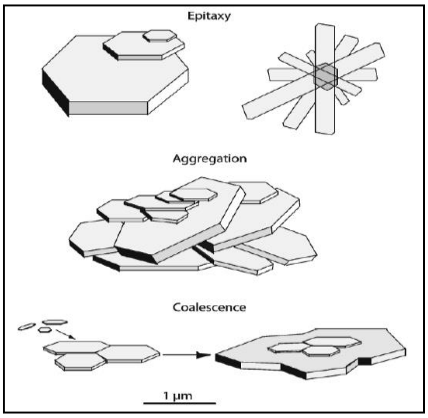


**Figure 7** Main types of particles and aggregates of clay minerals (Velde and Meunier, 2008)

### 2.3.4 Brief Description of K-bearing Minerals

*Micas*

The micas are 2:1 phyllosilicates consisting of unit layers each composed of two Si, Al—O tetrahedral sheets between which is a M—O, OH octahedral sheet, where M consist of $Al^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Mg^{2+}$, and some other cations (Figure 8). Potassium ions occupy positions between the unit layers in facing ditrigonal holes. Micas are classified in two major groups, dioctahedral and trioctahedral. In the dioctahedral group, two out of three octahedral cation positions are occupied, whereas in trioctahedral micas, all three positions are occupied (Rich, 1968).

Mica in soils is usually inherited from the parent rock and is likely to occur in soils derived from various igneous and metamorphic rocks, as well as from sediments derived from them. The most common mica group minerals in soils are three K-containing micas: muscovite, biotite and phlogopite. The tetrahedral sheets of all three are similar, but their octahedral sheets differ. Biotite and phlogopite are trioctahedral, with phlogopite containing $Mg^{2+}$ in the octahedral sites, while biotite contains $Mg^{2+}$ and $Fe^{2+}$. Muscovite is dioctahedral and contains Al in the octahedral sheet (Schulze, 1989).

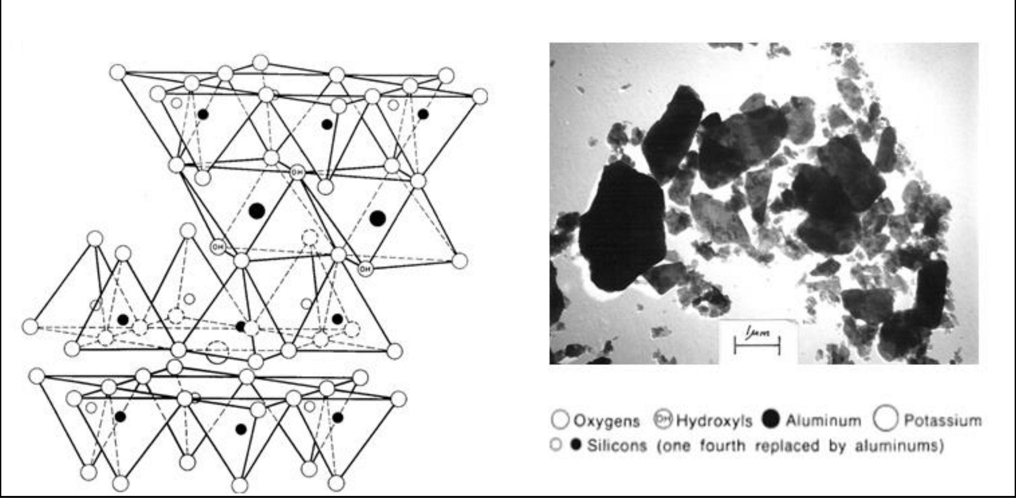


**Figure 8** Diagrammatic sketch of the structure of mica (Grim, 1968) and a transmission electronic micrograph (Churchman, 1986) of an example of this mineral

Mica in the clay fraction of soils and sediments often has poorer crystallinity, lower K content, and higher $H_2O$ content than the macroscopic muscovite that it most closely resembles. This clay-sized mica is often referred to as illite. Glauconite is similar to illite, but contains more Fe and less Al in its octahedral sheet than illite. Both illite and glauconite are poorly defined terms, and much of what has been described as illite or glauconite may be a mixture of minerals rather than one discrete phase (Schulze, 1989).

Micas weather to other minerals, particularly to vermiculites and smectites, and the $K^+$ released during weathering is an important source of K for plants. As a rule, the dioctahedral micas such as muscovite are more resistant to weathering than trioctahedral micas such as biotite and phlogopite. Consequently, muscovite is more likely than biotite or phlogopite to occur in more weathered soils (Schulze, 1989).

Through K release, micas in soils are an important mineral source of K for growing plants. The natural K-supplying power of a soil depends to a considerable extent on the kinds, amounts, and particle size of any mica present and upon factors that affect the release of K by these minerals, such as wetting and drying of the soil (Fanning et al., 1989).

### *Vermiculites*

Expansible layer silicates, the vermiculite and montmorillonite-saponite groups, are particularly important in exchange reactions, because of the very extensive internal exchange surface of these minerals (Rich, 1968). Vermiculite consists of the 2:1 layer structure described for mica, but instead of having a layer charge of ~ 1 per formula unit and $K^+$ in interlayer positions, vermiculite has a layer charge of 0.9 to 0.6 and contains exchangeable cations, primarily Ca and Mg, in the interlayer (Figure 9). The high charge per formula unit gives vermiculites a high CEC and causes them to have a high affinity for weakly hydrated cations such as $K^+$, $NH_4^+$, and $Cs^+$. Fixation of $K^+$ by vermiculites can be significant in soils high in vermiculite (Schulze, 1989) which are held in the interlayer region of the mineral.

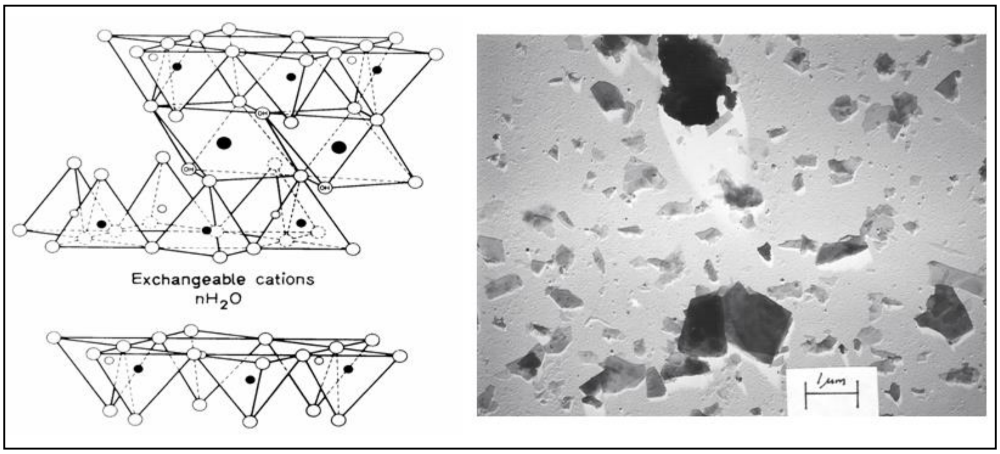


**Figure 9** Diagrammatic sketch of the structure of vermiculite (Grim, 1968) and a transmission electronic micrograph (Churchman, 1986) of an example of this mineral

Vermiculite is known to be widely distributed, and it has the widest particle-size distribution of the secondary phyllosilicates, having been found in all fractions from fine clay to greater than coarse sand (Douglas, 1989). Vermiculites in soils are believed to form almost exclusively from the weathering of micas and chlorites. The dioctahedral vermiculites are the most common in soils, perhaps mirroring the relative stability of muscovite (dioctahedral) over trioctahedral micas. The weathering of micas to vermiculite (or smectites) is believed to occur by replacement of $K^+$ in the interlayer sites with hydrated exchangeable cations. The integrity of the 2:1 layer is preserved, but there is a reduction in the layer charge (Schulze, 1989).

### *Montmorillonite-saponite (Smectites)*

The montmorillonite-saponite (smectites) group is similar to the vermiculite except that the charge density in less [0.25-0.5 per $O_{10}(OH)_2$] (Rich, 1968). As in vermiculite, the interlayer contains exchangeable cations (Figure 10). The dioctahedral smectites are the most common in soils. Their compositions vary between the three end-members montmorillonite, beidellite, and nontronite. In montmorillonite, Mg substitutes for Al in the octahedral sheet to produce the layer charge. In beidellite and nontronite, layer charge is produced in the tetrahedral sheet. Beidellite contains Al in the octahedral sheet, while in nontronite the octahedral sheet contains

Fe. Smectites do not fix $K^+$ as readily as do vermiculites because of their lower layer charge (Schulze, 1989).

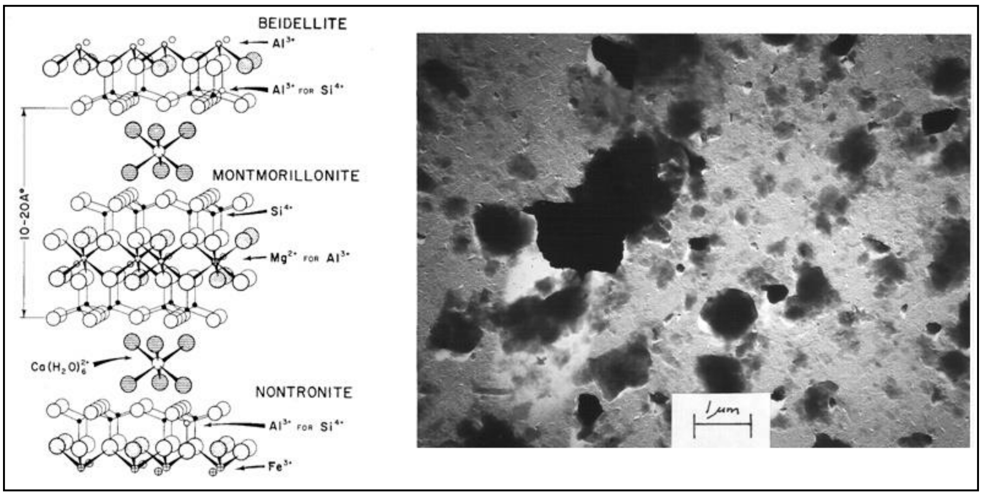


**Figure 10** Diagrammatic sketch of the structure of smectite (Grim, 1968) and a transmission electronic micrograph (Churchman, 1986) of an example of this mineral type

Smectites are important minerals in temperate-region soils because of their high surface area and their adsorptive properties. Smectites shrink upon drying and swell upon wetting. This shrink-swell behaviour is most pronounced in the Vertisol order and in vertic subgroups (Schulze, 1989). The expansive nature and negative charge of smectites cause them to be extremely reactive in soil environments. Smectites in the surface of a soil may be responsible for the adhesive property that helps prevent sheet erosion, while those in the subsurface may adsorb large quantities of $H_2O$, diminish the shear strength, and cause the soil to move downslope (Borchardt, 1989).

### *Illite*

Illite has caused many nomenclature problems for clay mineralogists. Illite was proposed (Grim et al., 1937) as a name for the “mica occurring in argillaceous sediments” (Fanning et al., 1989). The name was derived from the state of Illinois where it was first described. It has been widely used as a name for clay minerals with a ~10 Å *d (001)* spacing which show substantially no expanding-lattice characteristics, i.e. no swelling clay components (Meunier and Velde, 2004). Grim et al. (1937) gave illite a general unit formula which in fact includes both di- and trioctahedral structures. Hence illite is a mineral group by this conception and not a specific mineral. Although this definition is generally accepted by soil scientists, it is not completely satisfying because in other geological situations (diagenesis, supergene and hydrothermal alterations), illite is often considered as a mineral species (Meunier and Velde, 2004).

According to Grim (1968) the illite clay minerals differ from the well-crystallized micas in several possible ways, all of which may be exhibited by a given sample; these are as follows:

1) there is less substitution of $Al^{3+}$ for $Si^{4+}$; in the well-crystallized micas one-fourth of the $Si^{4+}$ are replaced, whereas in the illites frequently only about one-sixth are replaced;
2) there is some randomness in the stacking of the layers in the *c* direction, and the size of the illite particles occurring naturally is very small, of the order of 1 to 2µm or less.

Since then, the illite definition has been progressively improved. In 1982-83 the Clay Minerals Society (USA) Nomenclature Committee (CMS, 1984) made a more precise definition of illite where the mineral illite is:

1 Non-expandable.
2 A dioctahedral mineral.
3 Ionic substitutions occur in both the octahedral and tetrahedral sites of the mica structure.
4 Interlayer substitutions can include not only potassium but also hydronium ($H_3O^+$) ions.
5 Interlayer charge ranges between 0.8 and 0.6.
6 Mineral structure (polytype) is not considered as valid criteria.

More accurate definition was given by (Srodon and Eberl, 1984) who restricted the term “illite” to the non-expanding dioctahedral aluminous, potassium mica-like minerals occurring in the clay-size (< 4µm) fraction of a geological sample (Meunier and Velde, 2004). However, this later definition is not fully satisfying either since it is strictly based on XRD analysis of a given size fraction (Meunier and Velde, 2004) and a particle size criterion (< 4µm) is not acceptable for strict mineral classification purposes (Fanning et al., 1989) even though clay minerals are normally relegated to the clay sized fraction of a geologic material (< 2µm) (Meunier and Velde, 2004).

### *Kaolinite and Halloysite*

Kaolin minerals are composed of Al-based octahedral sheets and Si-substituted tetrahedral sheets in a 1:1 relationship. Kaolinite and halloysite are 1:1-layer- based aluminosilicates with the same ideal composition. Halloysite may be hydrated, in which case there is water between the structural layers. Collectively they are referred to as kaolins. These minerals typically have low surface areas and low cation- and anion-exchange capacities (Dixon, 1989). In contrast to the 2:1 layer silicates, cation exchange in kaolinite and halloysite is at external surfaces only (Rich, 1968). Kaolinite is one of the most widespread clay minerals in soils, especially those of warm, moist climates. Both kaolinite and halloysite are products of acid weathering, but halloysite is formed more rapidly in soils of volcanic origin (Dixon, 1989).

Kaolinite is composed of a tetrahedral and an octahedral sheet, which constitute a single 0.7nm layer in a triclinic unit cell. Two-thirds of the octahedral positions are occupied by Al ions, and the tetrahedral positions are occupied by Si ions. Aluminium ions are arranged in an orderly distribution occupying two rows of sites parallel to the *x*-axis (Figure 11). Every third row of octahedral sites is vacant (Bailey, 1966). Hydroxyl ions make up the surface plane of the octahedral sheet and are one-third of the inner (shared) plane of anions in each 0.7-nm layer. The surface OH’s bond through their H’s to the O plane of the adjacent layer. Halloysite contains the same basic 0.7-nm layer as kaolinite, but the stacking sequence of layers is different in each mineral. Because only two of every three octahedral positions are occupied by Al in the kaolin subgroup members, they are termed dioctahedral (Dixon, 1989).

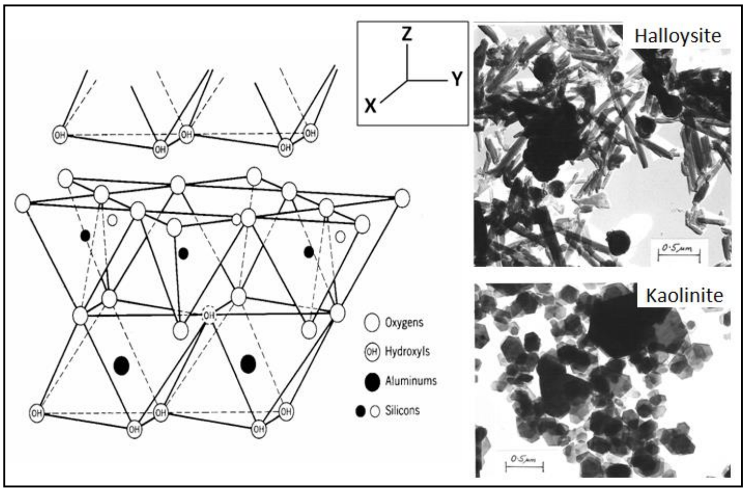


**Figure 11** Diagrammatic sketch of the structure of Kaolinite and Halloysite (Grim, 1968) and transmission electronic micrographs (Churchman, 1986) of examples of these minerals

Halloysite, with two interlayer $H_2O$ molecules per formula unit and 1.0-nm spacing when fully hydrated, is a member of the kaolin subgroup. Structural layers of halloysite exhibit disordered stacking in both *a* and *b* directions (X and Y axes on Figure 11) (Brindley and Robinson, 1946). Due to the disorder of halloysite, the structure of the interlayer $H_2O$ has largely eluded direct investigation, and has been considered rigid like that of ice (Dixon, 1989).

There is a general inverse relation between soil fertility and kaolinite content because kaolinite has neither a significant cation exchange capacity, or useful cations which can be attracted and desorbed by plants. Further it is devoid of potassium, and hence not a reservoir for this precious element. Thus kaolinite is often more of a hindrance to agricultural productivity of a soil than anything else (Velde and Meunier, 2008).

### *Potassium Feldspars*

Feldspars are found in virtually all sediments and soils in quantities that vary with the nature of the parent material and the stage of weathering (Huang, 1989). These are framework silicates consisting of $SiO_4$ and $AlO_4$ tetrahedra linked in all directions through the oxygen of the tetrahedra. Potassium in the potassium-feldspars and sodium, calcium, and other cations in other feldspars, are held in the interstices of the Si, Al—O framework. The negative charge produced by aluminium in tetrahedral coordination is balanced by the positive charge of the cations in the interstices. The formula for the various potassium feldspars is $KAlSi_3O_8$, showing that only one out of four of the tetrahedra contain aluminium (Rich, 1968). The three principal varieties of K-feldspar are: microcline (low temperature origin), orthoclase (medium temperature origin), and sanidine (high temperature origin). Occurrence, weathering processes and distribution of K-feldspar are described earlier in this Chapter.

### *Zeolites*

Zeolite are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess infinite, three-dimensional crystal structures. They are further characterized by their abilities to hydrate and dehydrate reversibly and to exchange some of their constituent cations, both without major change of structure. Along with quartz and feldspars, zeolites are tectosilicates – i.e., they consist of three-dimensional frameworks of $SiO_4^{4-}$ tetrahedra wherein all O’s of each tetrahedron are shared with adjacent tetrahedra. This arrangement reduces the overall O/Si ratio to 2:1, and if each tetrahedron were to contain Si as its central cation, the structure would be electrically neutral, as is quartz ($SiO_2$). In zeolite structures, however, some of the quadrivalent Si is replaced by trivalent Al, giving rise to a deficiency of positive charge in the framework. This charge is balanced by monovalent and divalent cations, principally $Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$, elsewhere in the structure (Ming, 1989). Zeolites can act as ionic sieves with characteristic upper limits on the size of the ion that can permeate these structural channels. An additional feature of the zeolite group is the presence of water molecules within the structural channel (Sparks and Huang, 1985).

Zeolites are present in vugs and cavities of basalts and other traprock formations. Furthermore, zeolites are major constituents in numerous bedded pyroclastics and are some of the most widespread and abundant authigenic silicate minerals in sedimentary rocks (Mumpton and Sheppard, 1972). Zeolite occurrences have been recognized in all ages of sedimentary rocks of pyroclastic origin from late Paleozoic to Holocene. In soils, zeolites may be formed when impeded drainage and soda accumulation maintain a high alkali ion to hydrogen ion activity ratio, e.g. in sodic and saline-sodic soils (Balder and Whittig, 1968; Stitcher, 1972 in Sparks and Huang, 1985).

### *Allophane*

Allophane is not a distinct mineral species but rather a series of minerals that are hydrous aluminosilicates of widely varying chemical composition, characterized by short-range order (van Olphen, 1971 in Sparks and Huang, 1985). Earlier, allophane had been considered an amorphous material (Rich, 1968). Since the 1970's information has been accumulated to indicate that allophane is not amorphous (without form) and that there is some short-range order in the structure of allophane (Wada, 1989). In the literature allophane is often coupled with imogolite (Brigatti et al., 2006; Wada, 1989). Their chemical compositions vary, but remain within the limits necessary to maintain a predominance of Al—O—Si bonds (Wada, 1989). Although these minerals have been found in soils of different origins and environments, they are especially abundant in soils derived from volcanic ash and weathered pumice (Brigatti et al., 2006). These minerals are often considered to be precursor phases to others. The key to the presence of both imogolite and allophane is a continuous humid condition. They are likely to be very important in processes of chemical transfer from surface to lower horizons in acid soils under temperate climate conditions (Velde and Meunier, 2008).

Allophane consist of hollow, irregularly spherical particles with diameters of 3.5 to 5 nm and has a Si/Al ratio typically of 1 : 2 to 1 : 1 (Wada, 1989), but allophanes with Si : Al ratios < 1 : 2 and > 1 : 1 may also occur (Figure 12) (Parfitt and Kimble, 1989 in Wada, 1995). Allophane has a large specific surface area and high chemical reactivity. This mineral is more sensitive to chemical dissolution than crystalline clay minerals (Wada, 1989). The cation exchange capacity of allophanes depends on pH, concentration, and ionic species used to measure CEC (Wada, 1977 in Norrish and Pickering, 1983), but it is usually in the range 20 – 50 cmol$_+$/kg

. Allophane has a definite affinity for K because of its structural configuration. Wada and Haranda (1969) obtained unusually high CEC values for Japanese soil allophanes when determined with K salts. Allophane has high anion sorption capacity and soils containing it retain large amount of phosphate (Norrish and Pickering, 1983).

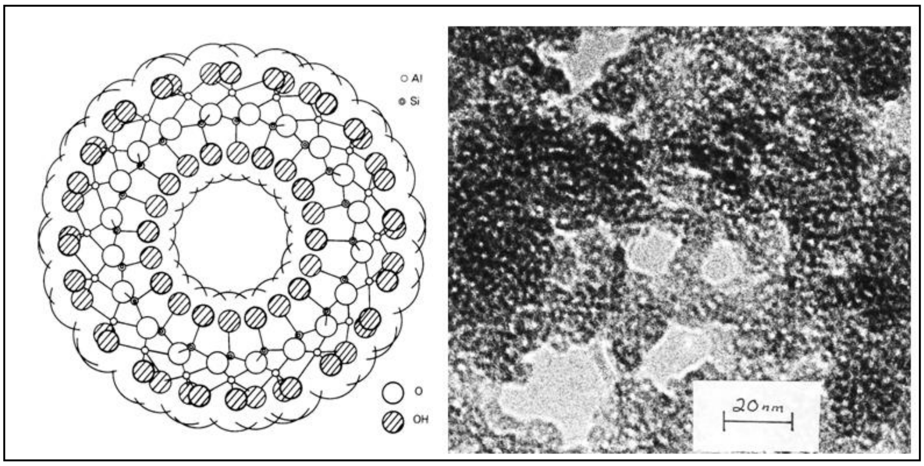


**Figure 12** Diagrammatic sketch of the structure of allophane (Grim, 1968) and a transmission electronic micrograph (Churchman, 1986) of an example of this mineral type

## 2.4 Potassium in Plant-Soil System

Potassium (K) is a key element for plant growth and K fertilizers are widely used in agriculture all over the world (about 28,106 t in 2006–07 according to the FAO). Improving knowledge about the K cycle is considered to be important for a better understanding of the productivity and sustainability of many ecosystems (Tripler et al., 2006) and to design management options that would favour efficient use of K and secure a sustainable future for global K reserves (Öborn et al., 2005 in Barré et al., 2008).

Among major nutrients, K is usually the most abundant in soils. A major proportion of soil K (Figure 13) occurs as structural K in feldspars and interlayer K in micaceous minerals (except in highly weathered soils where these minerals are depleted or absent) (International Potash Institute, 1987; Munson, 1985; Sparks, 1987 in Hinsinger, 2002).

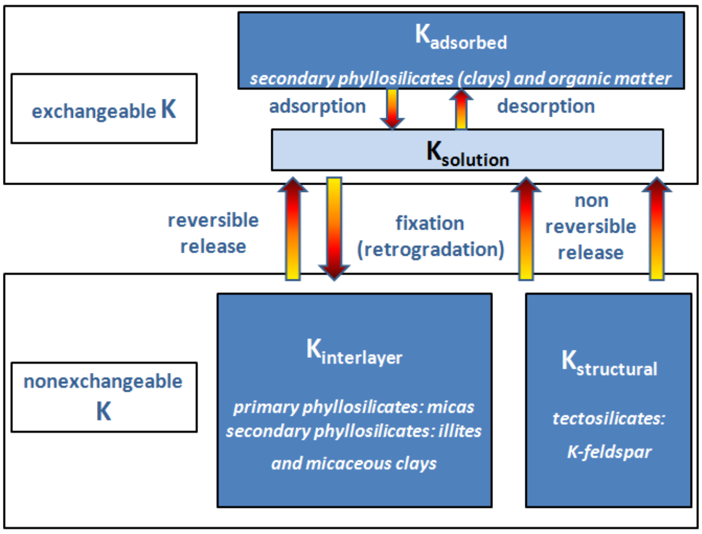


**Figure 13** The various forms of soil K and the chemical processes involved in soil K dynamics (Hinsinger, 2002)

A minor proportion of soil K (usually much less than 1%) is adsorbed on negatively charged soil constituents, namely clay minerals and organic matter. A marginal part is present as free K-ions in the soil solution. Bulk soil solution concentrations usually amount to 100 – 1000 µM (less than 0.01 – 0.1% of total K). The reason for this rather low concentration of K in the soil solution and hence restricted mobility of K in soils, compared to other metal cations such as Na or Ca, is related to its selective adsorption onto some clay minerals (Hinsinger, 2002).

Because of its ionic radius and small hydration energy, K-ions perfectly fit into the interlayer sites of micaceous minerals (micas, illites and mica-derived clays) (Dixon and Weed, 1989). These sites and, to a lesser degree, the sites on the frayed edges of these minerals have thus a considerably larger affinity for K than for other cations, including divalent cations such as Ca or Mg (Figure 14) (Hinsinger, 2002).

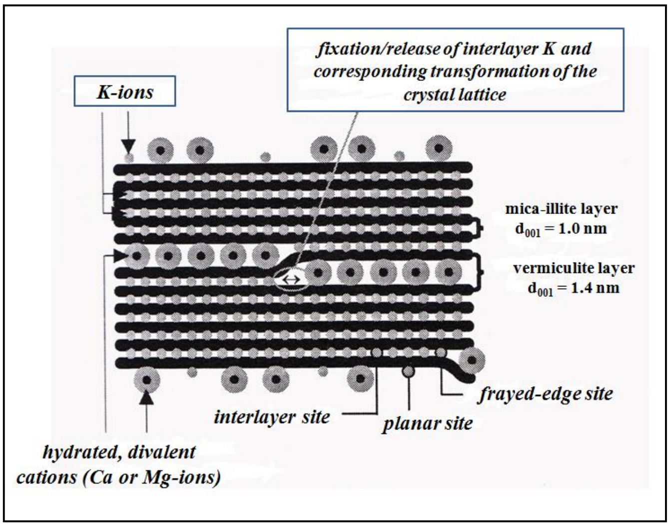


**Figure 14** The various sites of exchange of K-ions in micaceous clay minerals and the transition between mica and vermiculite layer that occurs when interlayer K is exchanged by hydrated divalent cations (Hinsinger, 2002)

Clay minerals also contain sites with larger affinity for divalent cations than for monovalent cations such as K. These sites are located on the planar faces of clay minerals and are thus dominant in clays such as kaolins and smectites. They also occur in organic compounds. K is thus much less strongly held in soils dominated by kaolins (tropical soils), sand or organic matter than in soils dominated by illite-vermiculite clay minerals. Traces of mica-derived clay minerals can dramatically influence the dynamics of soil K as evidenced in tropical soils that are apparently dominated by kaolins (Fontaine et al., 1989). More generally, K dynamics is largely dependent on soil mineralogy which determines both ion exchange and release-fixation processes (International Potash Institute, 1987; Sparks, 1987), i.e., the dynamics of "nonexchangeable K" (Hinsinger, 2002).

The latter is defined as that (often major) portion of soil K which cannot be exchanged by $NH_4$-ions. $NH_4$-ions have the same charge as and similar radius to K-ions and can successfully displace and desorb K only from low K-affinity sites. Readily available K thus comprises soil solution and easily desorbable K-ions. Nonexchangeable K mostly comprises interlayer K (high K-affinity sites) of micaceous minerals and structural K of feldspars (Figure 13), i.e., 90 – 99% of total K in many soils. The release of K from feldspar requires a complete and irreversible dissolution of the mineral and is enhanced under acidic conditions (International Potash Institute, 1987; Sparks, 1987). The release of interlayer K from micaceous minerals can proceed similarly or involve an ion exchange process (Figure 13) leading to an expansion of the phyllosilicate (Figure 14). This reversible release is essentially governed by the concentrations of K and competing cations in the outer solution (Dixon and Weed, 1989; Schneider, 1997; Springob and Richter, 1998). Cations which can be responsible for this release, such as Ca- and Mg-ions, have large hydration energy, contrary to K- or $NH_4$-ions. Therefore, they remain hydrated when exchanging interlayer K-ions and expand the interlayer space (Figure 14), making it possible for the release to proceed further, whereas $NH_4$-ions would block the reaction (Springob, 1999). However, because of the considerable affinity of these interlayer sites for K relative to Ca or Mg, the release can occur only for extremely low concentrations of K in the soil solution (Figure 15), in the micromolar range (Springob, 1999; Springob and Richter, 1998). Conversely, elevated concentrations of K are prone to the reverse reaction of fixation, i.e., the collapse of expanded layers and concomitant increase in nonexchangeable K at the expense of readily available K (Hinsinger, 2002).

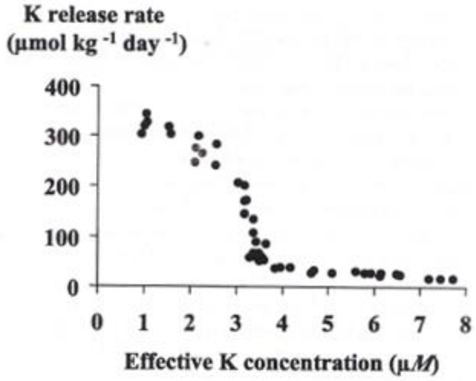


**Figure 15** Effect of solution K concentration on the rate of release of nonexchangeable K from a soil. Adapted from (Springob and Richter, 1998) in (Hinsinger, 2002)

Soil structure plays an important role in determining the quantity of K that is available to plant roots (Marschner, 1995). In friable soil the roots are normally smooth and cylindrical, whereas in compacted soil, where root elongation is impaired, roots become stubby and gnarled (Marschner, 1995; Passioura, 1991). Thus reduced K uptake is common in soils with high compaction or mechanical impedance because of the relatively low mobility of K (Bennie, 1996). Potassium mobility decreases with decreasing water content and at water potentials where water availability is still adequate for normal growth, the K diffusion may be considerably affected (Mengel et al., 2001). Potassium uptake also increases with temperature (Barber, 1995; Nelson, 1968). Schimansky (1981) found that the increase in K uptake with temperature in young barley was greater than for Mg or Ca (Öborn et al., 2005).

Any interpretation of the interaction between plants and their substrate must use clay identification procedures in order to understand the chemical changes and equilibria that occur (Velde and Barré, 2010). A review of clay mineral assemblages in weathering profiles indicates that the upper-most zones (A horizon for the most part) contain species that are not present or less represented in the layers below, the alterite or C horizon. If there is a difference in the A horizon mineralogy, it must be either due to a higher intensity of weathering due to rainwater and clay interaction, or to the influence of the chemistry engendered by plants on clay minerals (Velde and Meunier, 2008)

As it turns out plants strongly affect the chemistry of the soil in which they evolve and in doing so change the chemistry of the clays present. In order to understand the dynamics of the plant systems one must be able to identify the clay minerals and hence estimate their chemistry (Velde and Barré, 2010). Two to one (2:1) clay minerals are known to play a key role in the soil K cycle (Arkcoll et al., 1985; Hinsinger, 2002 in Barré et al., 2008).

However, 2:1 soil clay minerals do not all contain potassium. Indeed, if we consider potassium content as fixed or strongly held, i.e. not exchanged by ambient cations, the most common soil clay types with the 2:1 structure can be classified as follows: (1) illite with high potassium content, (2) mixed layered illite/smectite (I/S) with variable potassium content, (3) smectite with low potassium content, (4) hydroxy-interlayered (HI) clay minerals with very low potassium content (Barré et al., 2007).

Illite is generally assumed to have a rather low capacity to attract and release ambient exchangeable ions such as Ca, Mg, Na but a high potential to accumulate potassium. It is the most potassium-rich of the common soil clay minerals. Smectite normally has low potassium content but a high capacity to accept and release ions. It controls for a large part the amount of exchangeable ions such as Ca, Mg and to a lesser extent K necessary for plant metabolism. Mixed layered minerals (essentially variable mixtures of illite and smectite layers in the same crystallites) have of course intermediate properties depending upon the proportion of each component, illite or smectite, present. Hydroxy-interlayered (HI) are clay minerals whose layers are closed with hydroxy-aluminium. HI has very low ability to accept or release ions and they have very low potassium content. Clay mineral potassium content is therefore strongly linked to illite layer quantity (true illite and illite layers in I/S clay minerals) (Barré et al., 2007).

The mineralogical difference between illite, smectite and HI is to a large extent based on the layer charge. Illite layers have a 0.8–0.9 charge whereas smectite layer charge can range between 0.8 and 0.2. HI (hydroxyl interlayered minerals) are generally described as high charge smectite layer minerals (0.6–0.8) collapsed with hydroxylaluminium. Studies in diagenetic contexts showed that there is a good agreement between the theoretical definition of illite and its identification with X-Ray diffraction techniques (Meunier and Velde, 2004). Basically, it is assumed that illite layers are collapsed with potassium ions and have characteristic X-ray diffraction peaks near 10 Å (d-spacing = 10 Å = 1 nm). The situation is more complex in soils. Indeed, several studies reported that HI minerals could collapse to 10 Å if saturated by potassium ions (April et al., 1986; Egli et al., 2004; Pevear et al., 1984). Reciprocally, illite or even mica layers could reopen in a potassium depletion context (Hinsinger et al., 1992). These studies suggest that soil clay minerals which do not correspond to the mineralogical definition of illite could be identified as illite and vice-versa. In order to avoid these theoretical problems in the present study, we will use the term ‘‘illite-like’’ for the 10 Å mineral identified as illite with XRD techniques (Barré et al., 2007).

Previous studies have shown that total soil potassium content tends to increase with depth because weathering of primary minerals is greater near the surface than at depth (Mohr and van Baren, 1954; Oh and Richter, 2005). On the contrary, the ‘‘exchangeable’’ potassium pool tends to increase in the top of soil profiles (Jobbagy and Jackson, 2004; Mariotti, 1982). Jobbagy and Jackson (2001) proposed that nutrients are ‘‘uplifted’’ in the soil profile through plant activity which induces this increase of ‘‘exchangeable’’ potassium ions on top of soil profiles. Figures 16 and 17 illustrate these two opposite trends. In spite of the potential interest for soil potassium supply, such trends have not been considered for 2:1 clay minerals (Barré et al., 2007).

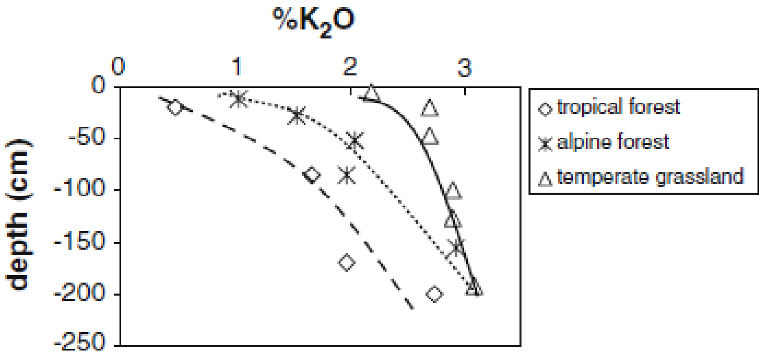


**Figure 16** Total potassium content as a function of depth in various soil profiles. Profiles of tropical forest, alpine forest and temperate grassland were established respectively thanks to data by (Egli et al., 2002; Mohr and van Baren, 1954; Oh and Richter, 2005). Lines are added by visual interpretation (Barré et al., 2007)

Two opposite patterns could be expected for surface soil 2:1 clay minerals. One would be the destabilization of minerals which lose potassium by the formation of less potassic clay minerals through water – rock interaction. In this case, as physical and biological alterations are higher near the surface, one would expect that the ‘illite-like’’ quantity should increase with depth with a minimum at the plant–soil interface. On the contrary, one could consider that 2:1 clay minerals may accept potassium translocated by plants through root absorption at depth and thus acquire an increased potassium content. In this case, ‘‘illite-like’’ layer quantity should follow ‘‘exchangeable’’ potassium distribution with a maximum at the surface and a decrease with depth (Barré et al., 2007).

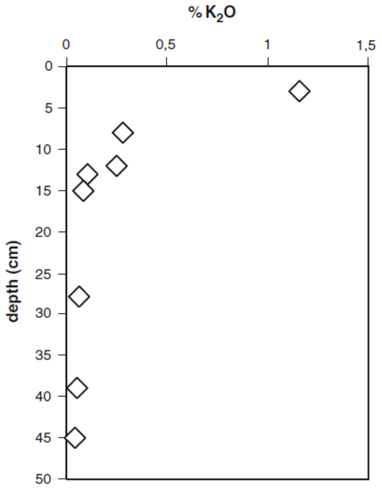


**Figure 17** Exchangeable potassium variation with depth. This figure is adapted from (Mariotti, 1982). The increase of exchangeable potassium near the surface conforms to Jobbagy and Jackson (2004) observations. Adapted from (Barré et al., 2007)

Several studies were conducted in order to investigate general trends of the ‘‘illite-like’’ minerals dynamics in soil. Barré et al. (2007) showed that the impact of potassium translocation should also be taken in consideration for surface soil clay mineral stability in temperate ecosystems. These authors reviewed several sites where an increase of illite layers at the expense of smectite layers in the upper part of soil profiles was observed (Barré et al., 2009).

The increase of illitic layers in surface soils was also clearly observed in the data published by (Ruhe, 1984). In this study, clay mineralogy of samples from 15 sites in the Kansas–Iowa region showed a strong tendency to form illite at the surface and increase from 20 to 50% of the amount of the clays present. In fact, this phenomenon has been described for a long time as Nettleton et al., (1973) observed the formation of illite materials in surface horizons of several dryland soils in the US. It is also interesting to note that a few studies reported the occurrence of illite in the upper part of soils developed on basaltic rocks containing no micaceous phases originally (He et al., 2008; Juang and Uehera, 1968). Indeed, these later studies show that illite might be neosynthesized in soils and do not necessarily derive from primary micaceous minerals (Barré et al., 2009). The references showing an influence of K translocation on surface soil clay mineralogy are summarized in Table 2.

Most of the presented data are only qualitative. This is due to the fact that very few studies attempted to quantify the relative abundance of each clay mineral types in complex soil clay assemblages. More precise quantified data might be available in the future, if soil clay scientists begin to systematically use X-ray diffractogram modelling programs that allow one to quantify the different clay mineral types (Barré et al., 2009).

**Table 2** Summary or the references indicating an effect of K translocation by plants on clay mineralogy in the upper part of soil profile (Barré et al., 2009)

| **References** | **Climatic zone** | **Country** | **Effect of element translocation** |
|---|---|---|---|
| (Oh and Richter, 2005) | Temperate | USA | + |
| (Glenn, 1964) | Temperate | USA | + |
| (Ruhe, 1984) | Temperate | USA | + |
| (Nettleton et al., 1973) | Temperate | USA | + |
| (Juang and Uehera, 1968) | Tropical | USA | + |
| (He et al., 2008) | Tropical | China | + |
| (Mahjoory, 1975) | Temperate | Iran | + |
| (Velde and Peck, 2002) | Temperate | France | + |
| (Spiers et al., 1984) | Temperate | Canada | + |
| (Badraoui et al., 1987) | Temperate | Morocco | + |
| (Kuzila and Lewis, 1993) | Temperate | USA | + |
| (Tice et al., 1996) | Temperate | USA | + |
| (Boettinger and Southard, 1995) | Arid | USA | + |
| de Mecquenem in Barré et al. (2007) | Temperate | France | + |

Clays tend to have exchangeable potassium in increased quantities towards the surface of alteration soil profiles but potassium is none the less a minor component of exchangeable bases.

However, the absolute amount of potassium increases on soil exchange sites. The higher amount of exchange ions present indicates a higher potassium content in the soil materials, silicate clays and organic matter exchangers. This increase has a strong influence on the presence of illitic clay minerals. The increase in potassium seems to be dependent on a return of plant material to the soil profile, either from leaf litter or upper level root masses. Hence plants typically enrich the surface layers of soils with potassium, among other elements. The impact is rather strong when replacement occurs each year by plant litter. Grasses for example enrich soils greatly in potassium while trees do to a lesser extent. Trees on the contrary keep a significant part of the nutrient material (potassium and silica) in their woody parts which remain above ground. Such a prolonged subtraction of alkalis as well as calcium, changes the balance of cations and favours acid soils where $K^+$ and $Ca^{2+}$ are replaced by hydrogen ions (Velde and Meunier, 2008).

If plants are responsible for potassium translocation, what effect can this have on the solids present, i.e. the clay minerals? It is highly probable then that plants control the clay mineralogy in the soil (plant/silicate) interaction horizon by translocation of silica and potassium plus other base cations. Thus the presence of these minerals is to a large extent dependent upon the presence of plants. Climate will dictate the types of plant regime present, and this related to rainfall in particular will determine the balance between translocation and loss through water/clay interaction. Hence it is extremely important to observe the type of plant regime when describing soil (A horizon) mineralogy and hence the type of reaction possible when changing from one plant regime to another (Velde and Meunier, 2008).

## 2.5 Potassium and Wastewater Irrigation

As demand for fresh water intensifies, wastewater is frequently being seen as a valuable resource. An attractive property of reclaimed wastewater is its potential fertilizing capacity. On the other hand, the high concentrations of nutrients in wastewater can be problematic to agriculture and the environment. The reality of challenges facing wastewater irrigation are perhaps best summarized by Part 1 of the Hyderabad Declaration on Wastewater Use in Agriculture, in which water, health, environmental, and agricultural professionals from 27 institutions across 18 countries formally recognized that (i) wastewater (raw, diluted, or treated) is a resource of increasing global importance, particularly in urban and peri-urban agriculture; (ii) with proper management, wastewater use contributes significantly to sustaining livelihoods, food security, and the quality of the environment; and (iii) without proper management, wastewater use poses serious risks to human health and the environment (Hamilton et al., 2007).

Potassium is ubiquitous in wastewaters and in some wastewaters is present at several hundred to several thousand $mgL^{-1}$. The current trend for substitution of sodium hydroxide with potassium hydroxide as a caustic cleaning and disinfection chemical in the operational processes of many industries such as wineries also has the potential to further increase potassium levels in wastewater. Thus, potassium accumulation in soils is seen by industry and regulators as a potential problem because of the effect it might have on salt accumulation and soil structure. These effects at the present are unclear since very few studies exist. The processes that control the fate of potassium in soils deriving from landwaste disposal are complex and many of them are poorly understood, e.g. the rate of potassium release, leaching, as well the long-term plant bioavailability (Arienzo et al., 2009).

A wide variety of wastewaters are produced which contain potassium. These can be from dairy sheds and milk processing factories, piggeries, chicken farms and processing plants, meat processing plants, fellmongeries, fish processing plants, timber processing plants, wool scours, feedlots, vegetable processing plants, wineries, paper and printing operations, textile plants, metal industries, and sewage treatment plants (Hart and Speir, 1992; McLaren and Smith, 1996). Some examples of the potassium contents of these wastes are given in Table 3.

**Table 3** Potassium concentration in municipal and agricultural sewage effluents (Arienzo et al., 2009)

| **Water Source** | **K concentration,** ($mgL^{-1}$) |
|---|---|
| Milk powder/butter factory | 13 |
| Municipal | 13–20 |
| Meat processing | 20–150 |
| Fellmongery | 50 |
| Slaughterhouse | 90 |
| Dairy shed | 220 |
| Winery | 250 |
| Piggery | 500–1000 |
| Lactic/casein whey | 1,660 |
| Cheese whey | 1,680 |
| Palm oil processing | 2,100 |
| Olive oil processing | 10,000–200,000 |

The wide range of chemical, physical, and biological characteristics of these wastes makes it difficult to develop guidelines for their use. The chemical composition not only varies between the various waste streams but also varies with time and with treatment of the individual waste stream. A lot of attention has traditionally been paid to nitrogen, phosphorus and organic matter in wastewater for reuse. These elements can be controlled/treated by typical aerobic and anaerobic treatment processes. The levels of potassium have received less attention and are not reduced during typical treatment processes, in fact the concentration often increases due to evaporation from wastewater treatment and storage ponds (Arienzo et al., 2009).

Apart from the concentration of potassium, the total loading to soil is important, therefore when irrigating crops with wastewater effluent the application of potassium fertilizer should be reduced (Arienzo et al., 2009). Many studies have shown that the overall soil fertility is increased after land application of liquid and solid wastes (Cameron et al., 1997; Keeley and Quin, 1979). Land application of wastewaters can increase the levels of soluble and exchangeable forms of potassium in soil expressed as potassium exchange percentage more rapidly than with conventional inorganic fertilizers. Most of the potassium in wastewater is immediately available (Levy and Torrento, 1995). Because of the equilibrium between the different potassium forms in soil it is possible that application of high potassium wastewaters, (500–20,000 $mgL^{-1}$) can cause a consistent and rapid increase of potassium in solution. This localized increase of potassium concentration in soil will cause the re-entry of potassium in the wedge-zones of hydrated micas, vermiculite and illite (Arienzo et al., 2009).

Soil with a higher clay content (illite) retained potassium in the exchangeable form to a much greater extent than the soil with a low clay content. Smiles and Smith (2004) reported on an irrigation study with piggery effluents in south-eastern Australia. The effluent had pH values of 7.5–8, K levels of 370–650mgL−1, Na concentrations of 140–220mgL−1, potassium adsorption ratio values of 10.2–14.2 and sodium adsorption ratio values of 6.1–8.6. The results showed that electrical conductivity (EC), exchangeable potassium ratios and PAR values in the soils that had been irrigated with the wastewater were greater than their non-irrigated partners. Potassium availability is also strongly affected by the pH of the wastewater as well as by the pH of the receiving soil (Arienzo et al., 2009).

Some studies report that potassium in wastewater reduced water infiltration rates. Peacock (1999) determined the effect of potassium added to irrigation water at a concentration of 120mg $L^{-1}$, on the rate of water infiltration under drip irrigation in a sandy loam soil. The potassium significantly reduced infiltration rates compared to the untreated control, and the drop in the infiltration rate occurred within 2 weeks of the first application of potassium. After 4 weeks the infiltration rate dropped to less than one-fifth that of the untreated control (Arienzo et al., 2009).

The potential for accumulation of potassium in soil from wastewater disposal is high since the element has a low leachability. Potassium ions not adsorbed by plants are absorbed by the soil particles thus minimising the risk of potassium leaching. According to Öborn et al., (2005) disposal of high K wastewater on soil with a low content of selective adsorbing minerals like vermiculite and illite will increase the risk of leaching as well in coarse sandy soil following saturation of the exchange sites of the colloids (Arienzo et al., 2009).

Irrigation with high potassium effluent has been shown to help sustain the overall fertility in soils. In general, the wastewater constitutes a fertilizing mineral and with a high content of organic matter and hence the potassium in wastewater can behave differently to fertilizer potassium. Disposal of high potassium wastewater in soil with a low content of selective adsorbing minerals will create very high concentrations of potassium in solution with potential effects on soil structure and potassium mobility. However, the effect of disposing high potassium effluents on soil structure is still not clear and more research is needed. For sustainable disposal of wastewaters plant tolerance and uptake of potassium must also be known. Further research needs also to focus on the effect of the K/Na ratio in the wastewaters and its effect on potassium availability and leaching in soil and potential increased plant tolerance to salinity (Arienzo et al., 2009).

## 2.6 Effect of Potassium on Structural Stability and Dispersion of the soil

Of the four major cations found in the soil ($Ca^{2+}$, $Mg^{2+}$, $Na^+$ and $K^+$), the effect of exchangeable potassium on soil physical and hydraulic properties is the least clear (Levy and Torrento 1995). Only limited research data exist on the effects of potassium on soil structure stability (Chen et al., 1983; Quirk and Schofield, 1955; Reeve et al., 1954; Rengasamy and Sumner, 1998). The literature shows a broad spectrum of possibilities for the effect of potassium on infiltration, ranging from being similar to sodium (negative effect) to being similar to calcium (positive effect). Potassium, as a monovalent cation, appears to be not as effective as sodium in causing structural problems in soils (Chen *et al.* 1983; Levy and Van der Watt 1990; Rengasamy and Sumner 1998). Similarly, Rengasamy (2002a) found modest differences in flocculation potential between Na and K. Other researchers have reported that this is not the case, and the effect of exchangeable potassium, while not as detrimental as that of Na, is also not clearly beneficial as is Ca addition (Reeve *et al.* 1954). Thus it seems that the research data is inconclusive.

Dispersion of clay particles is one of the major processes responsible for the degradation of soil structure (Chorom *et al.* 1994; Rengasamy 2002a). Dispersion involves the breakdown of associations of the soil clay particles into a heterogeneous collection of individual particles or groups of particles (Churchman e*t al.* 1993). On interaction with water the clay particles with high concentrations of adsorbed monovalent cations are separated from the aggregates to form a dispersive phase. Adsorbed sodium is traditionally considered to be a primary cause for poor soil structural stability. However, there is a knowledge gap in understanding the effect of adsorbed monovalent potassium on soil structure. Recent reports have drawn attention to elevated concentration of potassium in some soils naturally or induced by potassium added as fertilisers and wastewaters with high potassium content (Smiles and Smith 2004; Arienzo *et al.* 2009, 2012; Rengasamy and Marchuk A. 2011). Chen *at al.* (1983) found that the major mechanism by which $K^+$ can cause a reduction in relative hydraulic conductivity is due to dispersion of the fine soil fraction (mostly clay aggregates) and its rearrangement in situ to form a dense network of particles with smaller pores, rather than by massive clay migration (Arienzo *et al.* 2012).

Many of the authors have attributed the diverse response of different soils to increases in exchangeable potassium due to differences in soil clay mineralogy (Shainberg *at al.* 1987; Levy and van der Watt 1990; Churchman *at al.* 1993; Auerswald *at al.* 1996; Arienzo 2009). In the studies where the effect of potassium was grouped with that of sodium, or intermediate between that of sodium and calcium, the soils were mainly illitic (Churchman *et al.* 1993) or kaolinitic-illitic (Geeves *et al.* 1995; Oster 2008; Arienzo *et al.* 2009). When the soils contained mainly smectites with high charge densities the effect of potassium on the hydraulic conductivity was comparable to that of calcium (Boeck et al., 1995). These mixed results from the literature point to more research being required to explore the potential effect of applied $K^+$ on soil dispersive properties and the role played by clay minerals.

## 2.7 Summary

Plant availability of soil K is controlled by dynamic interactions among its different pools. Misunderstanding of these dynamics leads to mismanagement of soil fertility (Wang et al., 2004). Understanding (identification) of the factors and processes involved with K dynamics in soils would help to better evaluate the effects of different management options in different land-use systems (Öborn et al., 2005).

The major readily available source of potassium for plants in soils is from clay minerals (Velde and Barré, 2010) which are key-components in soil systems (Barré et al., 2009). Understanding the mechanisms that involve release and fixation of K in soil is important because soils may contain widely variable pools of K that are potentially mobilized by chemical weathering of soil minerals (Simonsson et al., 2009). Potassium can be extracted from high temperature primary minerals in the water – rock interaction portion of alteration profiles, and deeper plant roots use this as a source of potassium renewal as this rather soluble element is leached out of the plant soil horizons. The potassium is transferred from root zone to plant and plant to soil by leaf and other plant decay mechanisms. Then the potassium is reincorporated into the clays as illite, which contains an anhydrous layer of potassium ions in the 2:1 structures (Velde and Barré, 2010), or as one of its degraded forms.

Officer et al. (2006) specified the importance of 2:1 clay minerals and plant K nutrition by showing a very significant relationship between plant available non-exchangeable K and 2:1 clay mineralogy. Conversely, many authors reported that 2:1 clay minerals can fix potassium ions from the solution. This ability to fix or release K led Barré et al. (2007) to postulate that 2:1 minerals behave as a K reservoir in soils (Barré et al., 2008), which is likely to have a key role for K cycle in soils. Clay minerals could supply short term K plant needs and preserve long term ecosystem productivity by reducing K leaching (Barré et al., 2008).

The research into the fate of potassium in the soil–plant system under wastewater application is limited. Irrigation with high potassium effluent has been shown to help sustain the overall fertility in soils. In general, the wastewater constitutes a fertilizing mineral and additional organic matter potential and hence the potassium in wastewater can behave differently to fertilizer potassium. Disposal of high potassium wastewater in soil with a low content of selective adsorbing minerals will create very high concentrations of potassium in solution with potential effects on soil structure and potassium mobility. However, the effect of disposing high potassium effluents on soil structure is still not clear and more research is needed (Arienzo et al., 2009; Öborn et al., 2005).

**This literature review has summarised the present state of knowledge and research trends on the fate of potassium in soil-plant system. Particular emphasis has been placed on the role of soil clay minerals in the dynamics of different forms of potassium in soil.**

# Chapter 3. Examine the effect of application of potassium on clay minerals (fixation of potassium induced by wetting-drying cycles).

The fixation and release of potassium by phyllosilicate clay minerals in soils are very important processes influencing the availability of K to plants (Hosseinpur and Kalbasi, 2001). The fixation of potassium has been considered to occur because of a good fit of the crystal radius and coordination number of K within an area created by holes in the two adjacent Si-O sheets (Barshad, 1951, 1954). The important forces involved in the interlayer reactions in mineral colloids are electrostatic attractions between the negatively charged layers and the interlayer cations, and expansive forces due to ion hydration (Huang, 2005). The extent of K fixation is related to the kind of clay mineral and its charge density, the degree of hydroxy interlayering, the concentrations of $K^+$ ions and competing cations, and the pH of the ambient solution bathing the clay or soil (Rich, 1968; Sparks and Huang, 1985). Vermiculite, montmorillonite, kaolinite and hydrous mica (illite) vary drastically in their ionic preferences, ion-binding affinities, and types of ion-exchange reactions. Such fundamental differences in these clay minerals account for the varying kinetics of exchange (Sparks, 1987). Beidellites and vermiculites are known to have greater K-fixation capacities than montmorillonite.

One method for studying reactions that occur at the mineral-water interface is to concentrate ions at the interface by drying a clay mineral slurry. The process of fixation of potassium by clay minerals also responds to wetting-drying cycles (WD). These cycles can rearrange clay 2:1 layers into more stable configurations, can substantially alter smectite selectivity for competing exchange cations, and can weather sparingly-soluble K-minerals in the presence of smectite (Eberl et al., 1986). WD is an important mechanism for producing a mixed-layer illite-smectite from smectite at low temperatures in nature by a transformation mechanism. The percentage of illite layers formed by this mechanism is proportional to the number of WD cycles, and to the layer charge of the original smectite. Illite layers form relatively quickly (most in less than 20 WD cycles), and the reaction rate is not affected greatly by changes in solution composition or by temperatures that are typical of near-surface environments. The fixation of K is expected to occur wherever smectite and K-minerals are subjected to the wetting and drying process. This process occurs, for example, in soils, deltas and flood plains. The fixation of K decreases the ability of smectites to swell and decreases their cation exchange capacity (Eberl et al., 1986).

The purpose of the study was to characterise the first step of K-smectite evolution following wetting-drying cycles of Wyoming bentonite. XRD was used for this purpose. My second goal was to develop and verify a procedure of potassium application to be used in further experiments.

# Materials and Methods

## Materials

Wyoming bentonite (SWy-2) from Wyoming, USA was used. The clay was supplied by the Clay Minerals Society as source clay SWy-2-Na-montmorillonite (Wyoming). This clay originates from the Newcastle formation (Cretaceous), Crook County, Wyoming. The chemical composition of the montmorillonite is 62.9% $SiO_2$, 19.6% $Al_2O_3$, 0.09 $TiO_2$, 3.35% $Fe_2O_3$, 0.32% FeO, 0.006% MnO, 3.05% MgO, 1.68% CaO, 1.53% $Na_2O$, 0.53% $K_2O$, 0.111% F, 0.049% $P_2O_5$ and 0.05% S (Clay Minerals Society, 2012).

The formula of the montmorillonite can be expressed as:

$$(Ca_{0.12}Na_{0.32}\ K_{0.05})[Al_{3.01}Fe(III)_{0.41}Mn_{0.01}Mg_{0.54}Ti_{0.02}][Si_{7.98}Al_{0.02}]O_{20}(OH)_4,$$

as calculated from its chemical composition. Its octahedral charge is - 0.53, its tetrahedral charge is - 0.02, and its interlayer charge: - 0.55. Its cation exchange capacity (CEC) is 76.4 $cmol_+/kg$ (Clay Minerals Society, 2012). The clay was used without further purification and pre-treatments.

## Samples preparation

Firstly, raw Wyoming bentonite was separated from the bulk clay sample by sedimentation (Jackson 2005). After the clay fraction (< 2µm) was separated and dried, it was ground, mixed with saturated KCl solution (347 g of KCl per 1L of KCl/DI water solution) and shaken overnight on an orbital shaker. Excess salt was removed using dialysis against deionised water until free of chloride by the method described in Churchman and Weissmann (1995), (Figure 18). Chloride in solution was verified using silver nitrate and dialysis was continued until its addition led to no further white precipitate of silver chloride. Following completion of dialysis, the conductivity of the dialysate was below 10 µS/cm. The WD treatment was conducted at 60° in a drying oven.

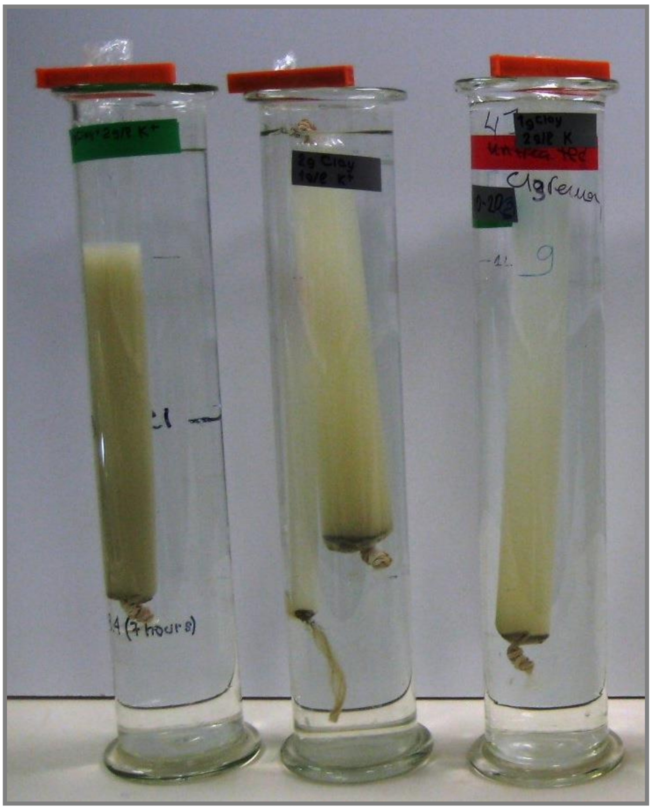


**Figure 18** Removing excess salts using dialysis

## Characterisation Methods

Both the original and potassium treated clays were investigated by powder XRD of oriented and glycerol saturated clay samples. Clay samples were finely ground and backfilled into steel holders for XRD analysis. The XRD patterns for randomly oriented air-dried (AD) and orientated and glycerolated (G) samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer using Fe filtered CoKα radiation, an automatic divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded from 3 to 80° 2θ (for randomly oriented samples) and from 3 to 33° 2θ (for orientated and glycerolated samples) in steps of 0.017° 2θ with a 0.5 second counting time per step for an overall counting time of approximately 30 minutes.

# Results and Discussion

## X-ray diffraction

Diffractograms of original and K treated Wyoming montmorillonite clay are shown in Figure 19. The patterns produced by the < 2 µm fraction of air-dried (AD) original sample showed a sharp *d 001* reflection at 15.0 Å which corresponds to discrete smectite mineral. Potassium treated AD sample of the same fractions showed broad *d 001* peak at 11.8 Å and a small sharp

10.0 Å peak which occurs on the right side shoulder of the 11.8 Å peak. After glycerol saturation the peak at 11.8 Å shifted to 17.8 Å, intensified and became sharper. The illitic 10.0 Å peak after glycerol treatment did not shift and was now located on the left side of the shoulder of the second order smectite peak at 8.9 Å. The quartz mineral is present in all the samples as evident from the peaks appearing at 3.34 Å.

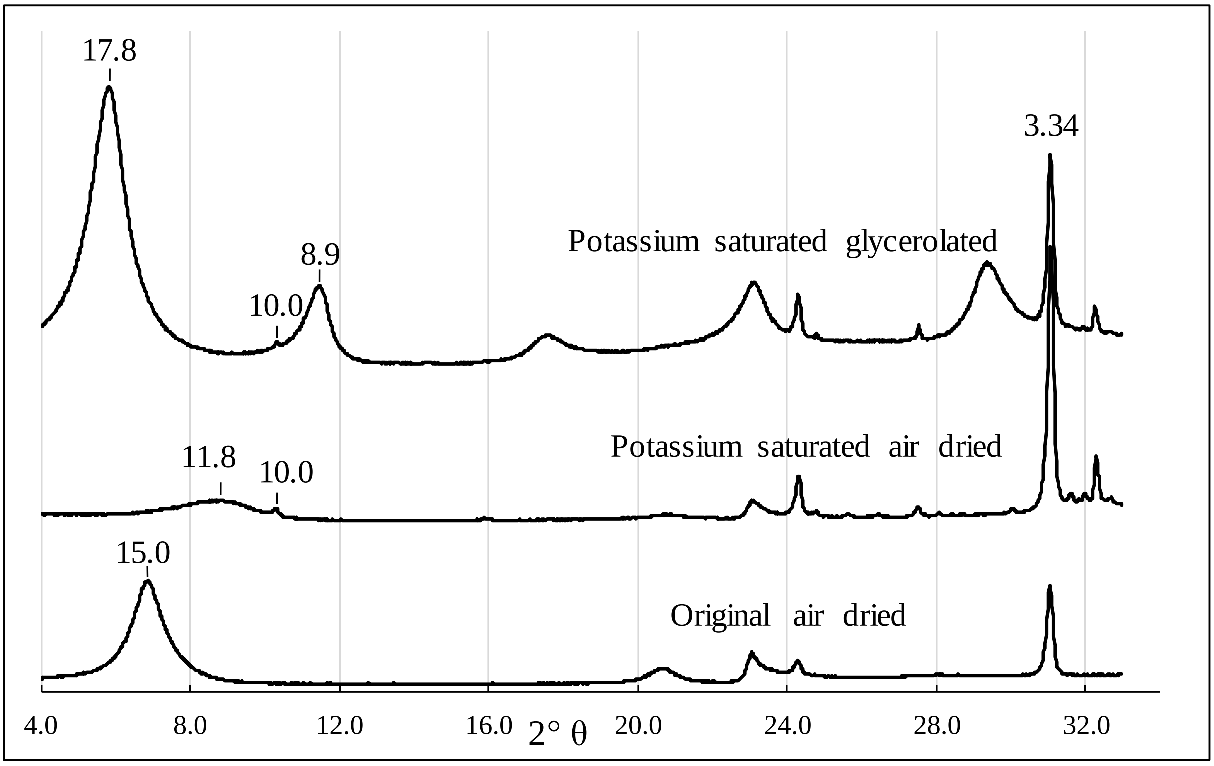


**Figure 19** XRD patterns of clay fraction (< 2 micron) of Wyoming bentonite before and after treatment with potassium

The following pattern of the reaction could be seen from XRD data. After application of potassium and drying, the treated AD sample seems to produce illite-smectite interstratified mineral (11.8 Å in AD sample) and discrete illite (10.0 Å). But glycerolation has shown that potassium was not fixed and interstratified smectite-illite layers in AD conditions re-expanded under glycerol. Smectites expand or contract very readily depending on the nature of the exchangeable cations (Moore and Reynolds 1997). In this experiment, applied potassium, apart from producing some illite, displaced more hydrated interlayer cations such as $Na^+$ or $Ca^+$ in smectite, dehydrated its interlayer space and caused a decrease in the *d 001* spacing of adjacent silicate layers (from 15.0 to 11.8 Å in the AD state), but not a collapse.

Figure 20 shows the XRD pattern of glycerolated Wyoming sample before and after treatment with potassium. The peak position of the *d 001* reflection of both treated and original samples did not change (17.7 Å), but the relative intensity after treatment decreased more than twice

(45% for the treated sample compared to the original 100%) and the full width at half maximum intensity (FWHM) increased from 0.82° 2θ for the original sample to 1.17° 2θ for potassium treated clay. In XRD patterns, the spacing of *d 001*, intensities and full width at half maximum intensity (FWHM) reflect the degree of organization of the smectites (Moore and Reynolds, 1997). In general terms, as the amount of interstratification with illite increases, the first order peak (17.7 Å) and the second order peak (8.87 Å for the original sample) located to the right of the illite peak (9.98 Å in the treated sample) move closer together (8.97 Å in treated sample). It seems that treatment with potassium has transformed smectite into illite and interstratified smectite-illite. However, the retention of the *d 001* peak at 17.7 Å suggests that much of the smectite remained unaltered.

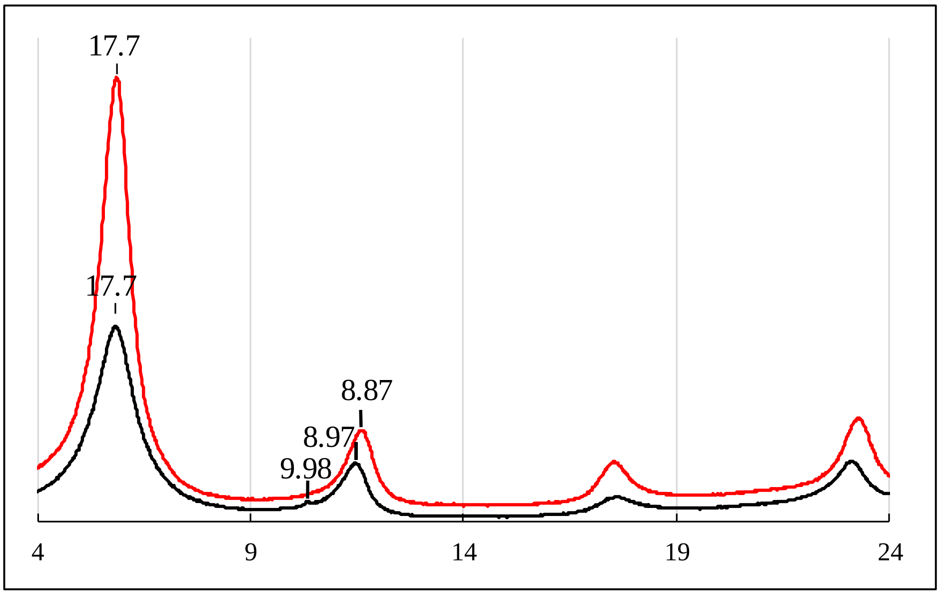


**Figure 20** XRD patterns of glycerolated clay samples (< 2 micron) of Wyoming bentonite before (red) and after treatment (black) with potassium

In order to obtain quantitative information about the nature of the clay modification that occurred, modelling of the XRD profiles was carried out using NEWMOD (Reynolds, 1985) software. As recommended by Moore and Reynolds (1997) the default NEWMOD program settings (such as goniometer radius and sample length) were adjusted with accordance to the parameters of the XRD instrument used for the experimental diffractograms. By modelling the individual clay mineral species in this way we could compare patterns of calculated diffraction profiles with experimental data. As could be seen from simulated diffractograms (Figure 21) with illite content increasing towards the lower patterns, the first order peaks did not shift, but decreased in relative intensity. The second order peaks moved towards the low angle region with increasing illite content in interstratified smectite-illite (Table 4).

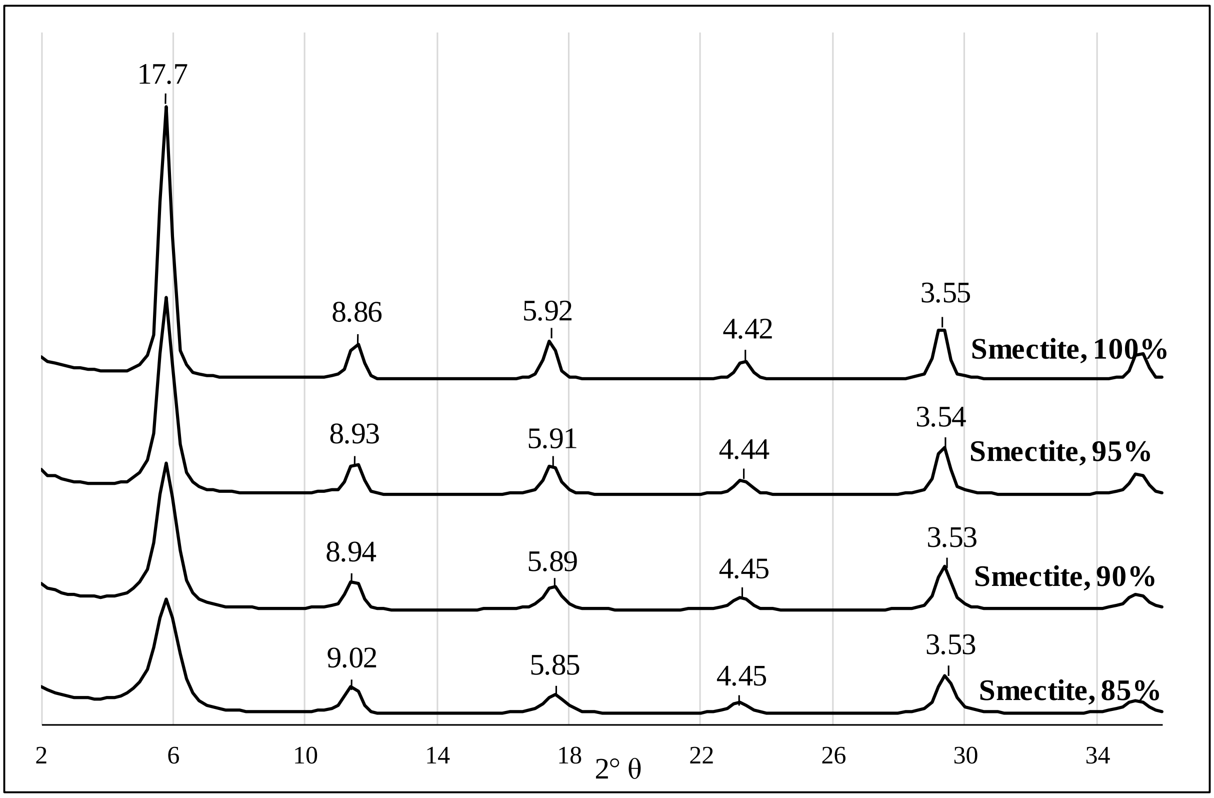


**Figure 21** NEWMOD calculated XRD patterns of pure smectite and interstratified smectite-illite including gradually increased amounts of illite

**Table 4** XRD parameters of simulated diffractograms from Figure 21

| **Mineral** | ***d 001*** | | | ***d 002*** | |
|---|---|---|---|---|---|
| | ***d-spacing, Å*** | ***FWHM, ° 2θ*** | ***Intensity, %*** | ***d-spacing, Å*** | ***FWHM, ° 2θ*** |
| Smectite, 100% | 17.69 | 0.45 | 100 | 8.86 | 0.45 |
| Smectite, 95% | 17.69 | 0.55 | 72 | 8.93 | 0.51 |
| Smectite, 90% | 17.69 | 0.66 | 54 | 8.94 | 0.53 |
| Smectite, 85% | 17.69 | 0.81 | 42 | 9.02 | 0.56 |

By comparing parameters of experimental diffractograms (Figure 20) with those modelled by NEWMOD (Figure 21 and Table 4) it could be concluded that the interstratified smectite-illite phase of the treated sample consisted of approximately 10-15% of illite.

## Conclusion

As could be seen from XRD results the application of potassium solutions to Wyoming smectite with wetting and drying produced randomly interstratified mixed-layered smectite/illite and illite minerals in clay fraction (< 2 µm) even at 60°C. The procedure developed enabled transformation of smectite into mixtures of smectite/illite and illite phases.

This experiment indicates that WD can have major effect on reactions that occur at the mineral-water interface. This process can rearrange clay 2:1 layers into more stable configurations. WD may be an important mechanism for producing smectite-illite at ambient temperatures in nature by a transformation mechanism. Illite layers form relatively quickly by WD (after just one WD cycle) under temperatures that are typical of near-surface environments. Thus, an effect seen in the laboratory also may occur abundantly in nature. Agriculturally, the WD process can free K from sparingly soluble K-minerals, and then store it with varying degrees of availability in expanding clays (Eberl et al., 1986).

# Chapter 4. Cation exchange and related physical properties as influenced by the type of cations in different type clay minerals

Physical and chemical properties of most soils are influenced by their ion-exchange characteristics, including the amount and balance of individual ions present (Rayment and Lyons, 2011). Cation Exchange Capacity is a general indicator of soil/clay storage capacity for available positively-charged plant nutrients such as calcium, magnesium, potassium and sodium. Many empirical results are catalogued in the literature of cation exchange phenomenology, but a clear description of the underlying forces that govern cation selectivity is lacking. Knowledge of these fundamental forces is desirable, because predictive ability would enable the rational management of soils (Teppen and Miller, 2005). According to Jackson (2005), the range and mean values of CEC for natural clays differ when different cations (particularly Ca or K) are used in the exchange reactions (Table 5).

**Table 5** CEC of phyllosilicate minerals, after (Jackson, 2005), mean values in brackets

| **Mineral** | **cmol$_+$/kg** | |
|---|---|---|
| | **CaEC** | **KEC** |
| Kaolinite* | 2.7 – 4.2 (3.5) | 2.3 – 3.6 (2.9) |
| Micas | 6 – 10 (8) | 3 - 6 (5) |
| Vermiculites | 140 – 180 (160±20) | 2 – 7 (5) |
| Smectites | 80 – 140 (110±30) | 80 – 140 (110) |
| Amorphous minerals | 20 – 160 (110) | 20 – 160 (110) |

* data from Lim et al. 1980

An ion exchange reaction is defined as a thermodynamically reversible interaction between the ions originally occupying a fixed number of reactive sites of the insoluble exchanger with the several ionic species in the solution. When a clay mineral is placed in a solution containing several dissolved salts, the whole assembly will in time reach a steady-state condition of ionic distribution between the clay and the solution. It is important to know how this equilibrium distribution depends upon the nature of the exchanger and its physical condition and how it depends on the nature of the solution (Lewis, 1952).

The literature is abundant with reports on cation exchange phenomena in clays resulting from clay-cation interactions. Several authors have developed models to compute selectivity coefficients from the contributions of electrostatic versus specific energies of adsorption as a function of cation valence and hydrated radius (Bergaya et al., 2006). The importance of clay layer charge in cation exchange selectivity has also been reported (Teppen and Miller, 2005).

Recent models also define cation exchange selectivity in terms of polarizability-based electrostatic and covalent interactions (Sposito, 2008).

Recently Marchuk, and Rengasamy (2011) developed the ionicity indices for various cations involved in clay-cation bonds. This new type of index depends on cation valence and the energy required to extract an electron from a cation, but it does not depend on cation size. Table 3 in Marchuk, A. and Rengasamy (2011) shows that the ionicity index is a very good predictor of both clay suspension turbidity and clay particle zeta potential for a wide variety of soil clays. In particular, it predicts observed differences in turbidity, a measure of clay dispersion, with the ordering: Na > K > Mg > Ca (Smith at al., 2015). The degree of ionicity of clay-cation bonds will dictate the ease of cation exchange and hence, the cation exchange capacity of the clays. The present experiment was started with an aim to understand the involvement of the bonding mechanism in exchange reactions.

# Materials and Methods

## Preparation of homoionic samples

The clays examined in this study were obtained from variety of sources and are described in detail in Table 6. The clays were used without any pre-treatment. Firstly, 5 g of each of raw clay sample was dispersed in 200ml of DI water and shaken in an end-over-end shaker for 16 hours. Then clay suspensions were transferred into 500ml measuring cylinders, shaken for 1 minute and left for 8 hours to settle. The observed dispersion for kaolinite and halloysite were low and hence a few drops of 0.1M NaOH were added to each clay sample to increase dispersion.

**Table 6** List of clays

| Nº | Name | Location of clay deposit |
|---|---|---|
| 1 | Kaolinite KGa-1b | Washington county, Georgia, USA |
| 2 | Halloysite | Matauri Bay, Northland, New Zealand |
| 3 | Illite-Cambrian shale IMt-1 | Silver Hill, Montana |
| 4 | Texas MMT* STx-1b | Texas, USA |
| 5 | Otay MMT SCa-3 | Otay, San Diego County, California, USA |
| 6 | Wyoming MMT SWy-2 | Crook County, Wyoming, USA |
| 7 | Arumpo MMT | Arumpo, New South Wales, Australia |
| 8 | Stop 12 Vermiculite | Carl Moss Ranch, Llano County, Texas |

* Montmorillonite

For determinations of exchange capacities for K, Na, Ca and Mg clay samples were prepared by treating a portion of the clay suspension with ≈ 220mL of a 1.0 M solution of the monovalent (K and Na) chlorides and 0.5 M solution of the divalent (Ca and Mg) chlorides. The suspensions were shaken overnight, then centrifuged to remove excess salts. The clay samples were then washed several times with 250mL of 70 vol. % ethanol/water solution to remove soluble cations.

The extraction of the exchangeable cations was carried out by shaking clays with ≈ 250mL of 1 M $NH_4Cl$ solution in a centrifuge bottle overnight, followed by centrifugation and collection of supernatant solution. The procedure was repeated three times. These extractions were combined and the cations (K, Na, Ca and Mg) displaced by $NH_4Cl$ were measured by inductively coupled plasma atomic emission spectrometry (ICP AES). The sum of exchangeable cations is considered as CEC in this report.

## Characterization of samples

### *Mean particle size*

Mean particle size measurements of homoionic samples were performed with dynamic light scattering using a NICOMP 370 Particle Sizer with a fixed 90° scattering and external (optical fibre) angle, and a 632.8-nm wavelength helium-neon laser. The instrument operates in two analysis modes: unimodal (Gaussian) and multi-modal (Nicomp) distributions. The multi-modal analysis was found to be most suitable for the wide distribution of particles found in clay suspensions. Prior to measurements, the samples were diluted to an appropriate concentration so that the intensity of the transmitted laser beam was within the limits required by the instrument and to attain consistent and compatible measurements. All samples were placed in the machine for 5 minutes prior to starting measurements to eliminate temperature differences between the sample and an instrument. The instrument parameters were set as follows: automatic choice of channel width; solid particle mode; the autocorrelator was set to clear after each sample. The following values were recorded: mean particle diameter, standard deviation, chi-squared ($\chi^2$), baseline adjustment, fit error and residual. Results presented here were acquired using intensity-weighted distribution with the Nicomp analysis mode recorded after 60 min.

### *Zeta potential measurements*

The zeta potential ($\zeta$) is related to the surface charge, a property that all materials possess, or acquire, when suspended in a fluid. In terms of soil/clay particles - water interactions it is a function of the surface charge of the particle, adsorbed species on its surface (cations or anions), and the composition and ionic strength of the surrounding solution (Powers *et al.* 2006). Zeta potential is directly related to the total interaction energy between particles and is used to interpret clay dispersion behaviour (Chorom and Rengasamy 1995; Marchuk A. and

Rengasamy 2011; Yong *et al.* 2012). The zeta potential is measured experimentally from the migration rate of suspended particles under the action of an electric field.

The zeta potential of the homoionized samples was measured by laser Doppler velocimetry on a Malvern Zeta Master Particle Electrophoresis Analyser. The intensity for each clay sample was measured prior to the readings to ensure the compatibility of the samples. The zeta potentials (ζ) were calculated as the mean of ten runs, each of which was averaged over 25 individual measurements performed automatically by the instrument.

## Results and Discussion

The exchangeable K, Na, Ca, Mg and CEC for each sample are presented in Table 7.

**Table 7** Experimental cation-exchange capacities

| **Clay** | **pH** | **EC, dS/m** | **Treatment** | **ζ mV** | **Exchangeable cations, cmol$_{+}$/kg** | | | | **Σ of Exch. Cations** |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | **Na** | **K** | **Mg** | **Ca** | |
| Kaolinite KGa-1b | 10.7 | 0.01 | K | -29 | 5.51 | 5.35 | 1.29 | 0.21 | 12.36 |
| | | | Na | -36 | 9.66 | 1.31 | 1.23 | 0.19 | 12.40 |
| | | | Ca | -10 | 5.52 | 1.02 | 1.23 | 4.86 | 12.62 |
| | | | Mg | -20 | 5.43 | 0.95 | 7.28 | 0.18 | 13.84 |
| Halloysite | 9.3 | 0.03 | K | -50 | 6.65 | 1.56 | 0.73 | 0.37 | 9.31 |
| | | | Na | -58 | 6.87 | 0.81 | 0.73 | 0.27 | 8.68 |
| | | | Ca | -39 | 6.70 | 0.74 | 0.74 | 2.55 | 10.73 |
| | | | Mg | -41 | 6.64 | 0.57 | 2.33 | 0.16 | 9.70 |
| Illite-Cambrianshale IMt-1 | 7.3 | 0.04 | K | -44 | 12.45 | 18.85 | 1.64 | 0.21 | 33.15 |
| | | | Na | -47 | 31.80 | 1.76 | 1.56 | 0.18 | 35.31 |
| | | | Ca | -13 | 11.73 | 1.40 | 3.00 | 25.78 | 41.91 |
| | | | Mg | -16 | 11.89 | 1.07 | 23.42 | 0.51 | 36.89 |
| Smectite STx-1b | 9.8 | 0.01 | K | -59 | 13.20 | 98.72 | 1.76 | 0.27 | 113.96 |
| | | | Na | -61 | 96.49 | 1.62 | 1.79 | 0.27 | 100.18 |
| | | | Ca | -34 | 14.17 | 6.10 | 1.81 | 94.51 | 116.59 |
| | | | Mg | -36 | 14.04 | 3.91 | 95.67 | 0.27 | 113.89 |
| Smectite SCa-3 | 10.5 | 0.02 | K | -55 | 9.27 | 122.80 | 1.94 | 0.18 | 134.19 |
| | | | Na | -57 | 132.26 | 2.24 | 2.57 | 0.18 | 137.25 |
| | | | Ca | -35 | 9.70 | 2.39 | 1.78 | 131.49 | 145.37 |
| | | | Mg | -37 | 9.78 | 3.03 | 130.95 | 0.18 | 143.94 |
| Smectite SWy-2 | 7.9 | 0.05 | K | -40 | 6.56 | 97.65 | 1.57 | 0.07 | 105.85 |
| | | | Na | -41 | 97.65 | 0.95 | 2.42 | 0.75 | 101.77 |
| | | | Ca | -15 | 6.73 | 0.58 | 1.25 | 104.69 | 113.24 |
| | | | Mg | -18 | 6.43 | 0.44 | 100.44 | 0.07 | 107.38 |
| Smectite Arumpo | 7.2 | 0.04 | K | -45 | 15.33 | 71.29 | 2.36 | 1.75 | 90.73 |
| | | | Na | -44 | 89.21 | 1.36 | 2.04 | 1.15 | 93.77 |
| | | | Ca | -20 | 8.94 | 1.03 | 0.98 | 93.36 | 104.32 |
| | | | Mg | -18 | 13.08 | 1.09 | 97.01 | 1.09 | 112.26 |
| Stop 12 Vermiculite | 10.4 | 0.01 | K | -50 | 33.04 | 85.44 | 24.23 | 0.61 | 143.33 |
| | | | Na | -52 | 158.54 | 8.43 | 18.37 | 0.68 | 186.03 |
| | | | Ca | -26 | 33.92 | 3.32 | 14.97 | 138.75 | 190.95 |
| | | | Mg | -31 | 35.07 | 4.32 | 154.82 | 0.65 | 194.86 |

Data represent an average of duplicates for all determinations. Values of CEC tend to be high, compared to the reported data in the literature, because of the high pH induced by the addition of NaOH during sample preparation.

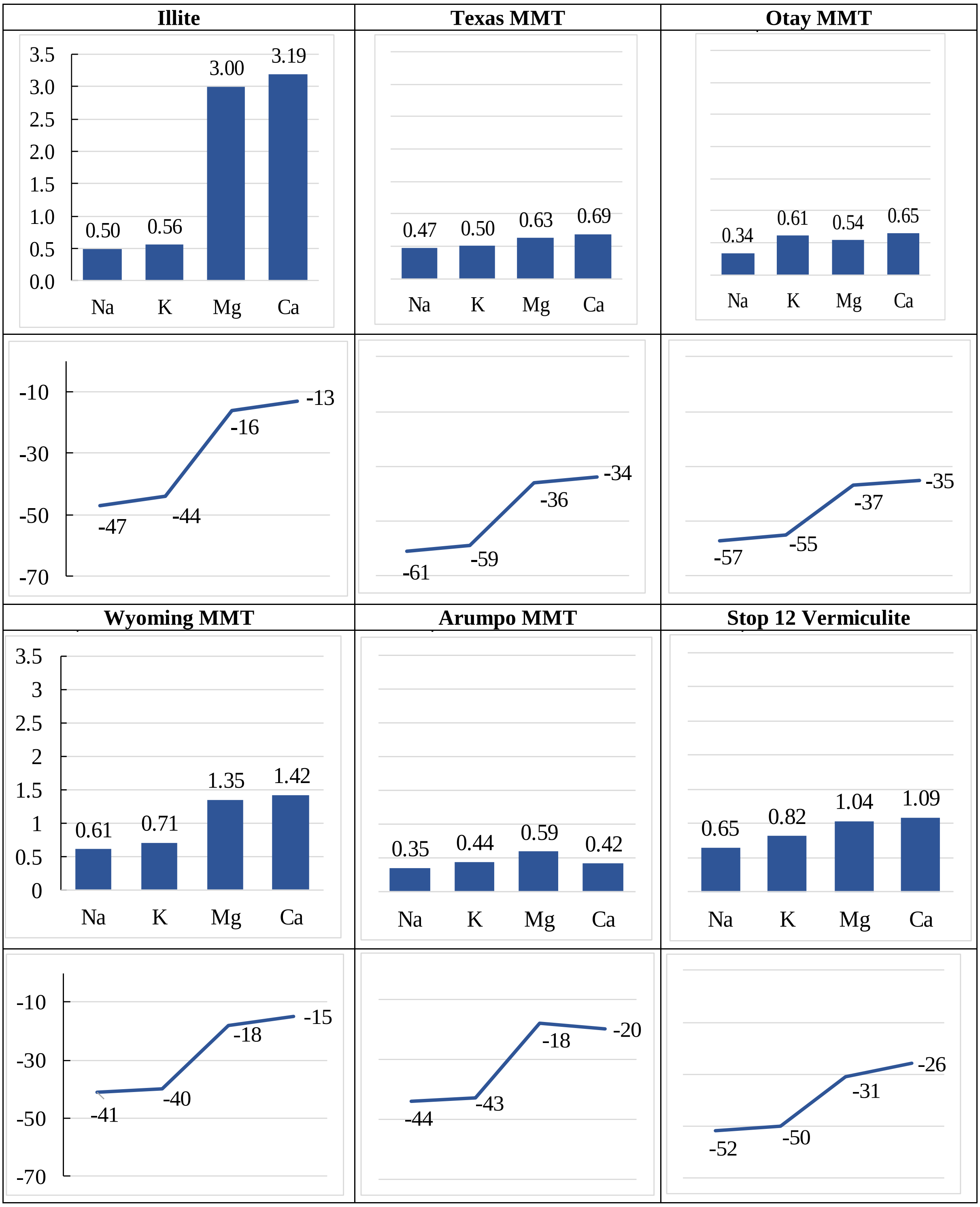


**Figure 22** Mean particle size in µm (upper) and Zeta potential in mV (lower) of investigated homoionic clays

Comparing the CEC of monovalent cationic clays, K-saturated clays have lower CEC's than Na-saturated clays with the exception of halloysite, Wyoming and Texas smectites. The monovalent cations almost always gave lower CECs than divalent ones. However, values from each cation are never vastly different from each other, except in one case (vermiculite).

CEC of K-vermiculite is much lower than that of Na-vermiculite. This is probably because of the great affinity of the vermiculite interlayer for potassium. For the divalent cationic clays, the effect of Ca and Mg is not clear. Ca-saturated clays have higher CEC’s than Mg-saturated clays with the exception of kaolinite, Arumpo smectite and vermiculite.

The changes in particle size after ion adsorption are given as the mean particle size measured. The mean particle size increased in all clay samples in the order Na < K < Mg < Ca. The changes in size observed correlate well with zeta potential data which tended to become less negative in this order.

The ionicity indices of clay-cation bonds are in the order Na > K > Mg > Ca (A. Marchuk and Rengasamy, 2011). The results presented here do not show a similar order for CEC values for homoionic clays. But, when monovalent ions and divalent ions are separately considered, the higher were the ionicity indices, the greater was the CEC. There are exceptions, as mentioned earlier. Differences in the CEC of homoionic clays are attributed to differences in particle size (Figure 22), i.e. lower CECs of monovalent clays corresponded with smaller particles.

# Chapter 5. Influence of the major exchangeable cations on the particle size distribution and dispersive behaviour of soil clays with contrasting mineralogy

In soil/water systems an equilibrium exists between the cations in the soil solution and those on the exchange sites. Hence, the soil will adsorb ions from the soil solution in proportion to its composition and the concentration of the cations in solution. The nature of cations adsorbed on soil surfaces (exchange complex) has the potential to significantly affect the physical and chemical properties of the soils. The purpose of this investigation has been to study the effect of the most common cations ($Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) on the dispersive behaviour of soils with contrasting mineralogy.

## Materials and methods

### Soil used

Four soils from South Australia (Figure 23) were chosen for the study. Selection of these soils was based on the differences in their texture, clay mineralogy, electrical conductivity and pH (Tables 8 and 9). Soil samples were collected from the 0.20–0.40 m depth (where clay content is relatively high and organic matter content is relatively low) by a hand auger, air-dried, crushed, and passed through a 2-mm sieve. Soil particle size distribution, soluble and exchangeable cations, pH and EC are presented in Table 9.

**Table 8** Soil type, location, classification and main clay minerals

| **Soil texture** | **Location** | **Mineralogy** | **Australian classification**[1] |
|---|---|---|---|
| Urrbrae Sandy Loam | Waite Research Institute,<br>34°58’00.41” S; 138°38’03.29” E | Illite, Kaolinite | Red Chromosol |
| McLaren Clay Loam | McLaren Valley,<br>35°15’04.31” S; 138°33’44.9” E | Illite, Kaolinite | Brown Sodosol |
| Claremont Clay | Waite Research Institute,<br>34°58’20.7” S; 138°38’11.87” E | Montmorillonite | Vertosol |
| Keilira Clay | Woolumbool,<br>36°48.726' S; 140°08.638'E | Saponite | Grey Sodosol |

[1] Australian Soil Classification (Isbell 1996)

### Soil analysis

Standard methods were used for the determination of pH and EC (1:5 soil/water) (Rayment and Lyons 2011) and particle size distribution (Gee and Bauder 1986). Mean particle size and zeta potential (ζ) measurements of homoionic soil samples were done as described in Chapter 4.

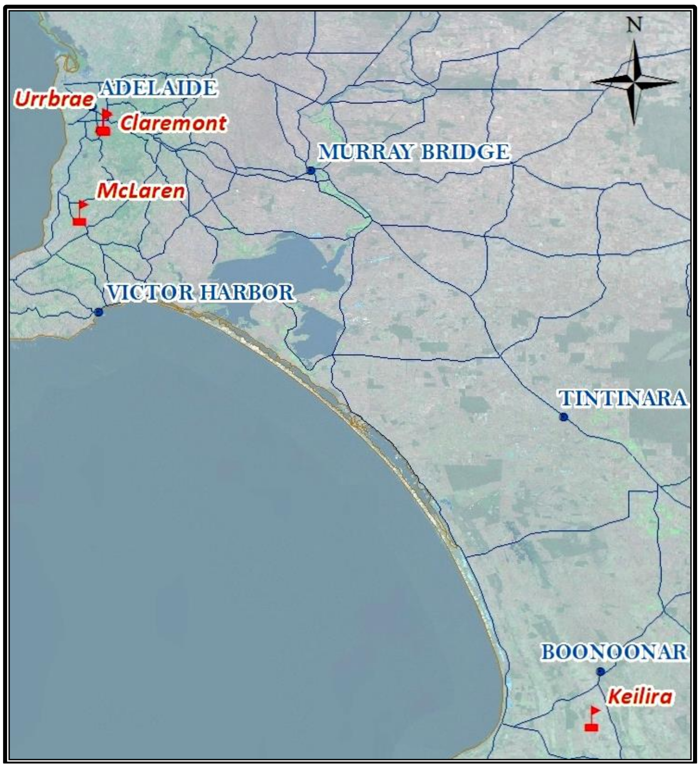


**Figure 23** Soil sites location

**Table 9** Selected physico-chemical properties of soils

| Soil | pH | EC, dS/m | CEC, $\text{cmol}_+/\text{kg}$ | Texture |  |  | Zeta potential, mV |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Clay | Silt | Sand |  |
| Urrbrae | 6.7 | 0.06 | 5.8 | 26 | 34 | 40 | -38 |
| McLaren | 7.3 | 0.14 | 8.8 | 44 | 19 | 37 | -42 |
| Claremont | 8.3 | 0.16 | 30.6 | 63 | 13 | 25 | -19 |
| Keilira | 8.6 | 1.45 | 26.6 | 73 | 11 | 16 | -21 |

## Soil clays preparation for XRD analysis

In order to improve the identification of the mineralogical composition of the soils by XRD analysis, clay fractions were separated by sedimentation (Jackson 2005). Firstly, 5 g of the sieved original soil from each sample was mixed with 150 ml of deionised water and disaggregated by using a RATEK orbital mixer with a speed of 120 rpm for 16 hours. Then soil/water suspensions were transferred into 1 L glass cylinders with addition of deionised water to the required level. The height of the soil/water column (19 cm) was determined by Stokes' Law to give the settling time (16 hours) required for settling particles ≥ 2 µm. The cylinders were then allowed to stand, and after 16 hours of settling the clay fraction (< 2 µm) was isolated from soil by siphoning off the dispersed material. The procedures of adding water, stirring, settling, and siphoning were carried out for a total of 6 times, and the clay suspensions thus obtained were combined. The supernatant suspension containing < 2 µm clay fraction was transferred into a 5 L beaker and oven-dried at 60°C. No additions of dispersing agent or other chemical treatments (such as for organic matter or oxide removal) were applied to the clay samples.

## X-Ray diffraction (XRD) analysis of the clay fraction

Dry clay samples (<2 µm fraction) were finely ground and backfilled into steel holders for XRD analysis. The XRD patterns for randomly oriented air-dried (AD) and orientated, Mg saturated-glycerolated (G) samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer using Fe filtered CoKα radiation, automatic divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector.  The diffraction patterns were recorded from 3 to 80° 2θ (for randomly oriented samples) and from 3 to 33° 2θ (for orientated, Mg saturated-glycerolated samples) in steps of 0.017° 2θ with a 0.5 second counting time per step for an overall counting time of approximately 30 minutes.

XRD data were collected and displayed using CSIRO software XPLOT for Windows (Raven 1990). Mineralogical phase identifications were first made by comparing the measured XRD patterns with the ICDD database of standard diffraction patterns using computer aided search/match algorithms. Quartz structure tolerates no significant atomic substitution and its peak position was used as the internal standard for estimating the accuracy and precision of peak position for the other phases present (Moore and Reynolds 1997). Specific clay mineral identification criteria were based on Brindley and Brown (1980) and Moore and Reynolds (1997). Only peaks for crystalline minerals were considered in these analyses. Information about the dioctahedral/trioctahedral structure of the clay minerals was obtained by examination of the 060 reflections of randomly oriented samples.

## Preparation of homoionic samples

Homoionic forms of soils with $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ adsorbed cations were prepared by treating a 10 g portion of the soils with 200 mL of a 1 M solutions of NaCl and KCl, and 0.5 M of $MgCl_2$ and $CaCl_2$. The suspensions were shaken overnight and centrifuged to remove excess salts.  The homoionized samples were then washed several times with 200 mL of 60 vol. % ethanol/water solution until the electrolyte concentration of each of the homoionic samples was below 0.05 dS/m. The soils were then air dried and 2 g of each soil was redispersed in 100 ml of deionised water (EC< 0.035dS/m) and allowed to settle in 100 ml cylinders for 4 hours. The clay particles (<2 µm) up to a depth of 10 cm in the cylinders were pipetted out and used for measurements of zeta potential and particle size.

The extraction of the exchangeable cations was carried out by shaking 5 g of each homoionized soil samples with ~ 200 mL of 1 M $NH_4Cl$ solution in a centrifuge bottle overnight, followed by centrifugation and collection of supernatant solution. The procedure was repeated three times. These extractions were combined and the cations ($K^+$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) displaced by $NH_4Cl$ were measured by ICP AES.

# Results and discussion

## Mineralogical analysis of investigated soils

The XRD patterns for randomly oriented clay samples (< 0.2 µm) of the soils are shown in Figure 24. Urrbrae and McLaren soils have largely a two-component clay mineral suite of illite and kaolinite dioctahedral types for both soils (060 patterns not shown) in addition to the primary minerals quartz and k-feldspar. The Claremont and Keilira soils were dominated by smectite with small quantities of illite and kaolinite. Quartz and k-feldspar were also present. The analysis of their 060 diffraction area (not shown) revealed that in the case of Claremont soil the smectite is of a dioctahedral type (montmorillonite), whereas the Keilira smectite is of trioctahedral nature (saponite).

## Effect of pH and adsorbing cations on CEC of homoionised soil clays

The pH and CEC values for original and homoionic soil samples are presented in Table 10. Data represent an average of triplicates for all determinations. The pH and CEC of the different homoionic systems varies. Variation in CEC partially could be explained by the presence in the studied soils of clay assemblages with considerable pH dependable variable charge – kaolinite and illite (Chorom and Rengasamy 1995). The other reason is the fact that CEC values for the same soil/clay vary when different cations are used as an exchanger in the cation exchange reactions (Sawhney *et al*. 1959; Jackson 2005; Marchuk S. *et al.* 2012). The distribution of cations (in $cmol_+/kg$ and % of saturation) on exchange sites before and after treatment are presented in Table 11.

Cation exchange is a stoichiometric reaction governed by the laws of mass action. This means that, in general, increased concentration of the replacing cation in the exchanging solution causes greater exchange by that ion on the exchange sites of soil/clay particles.

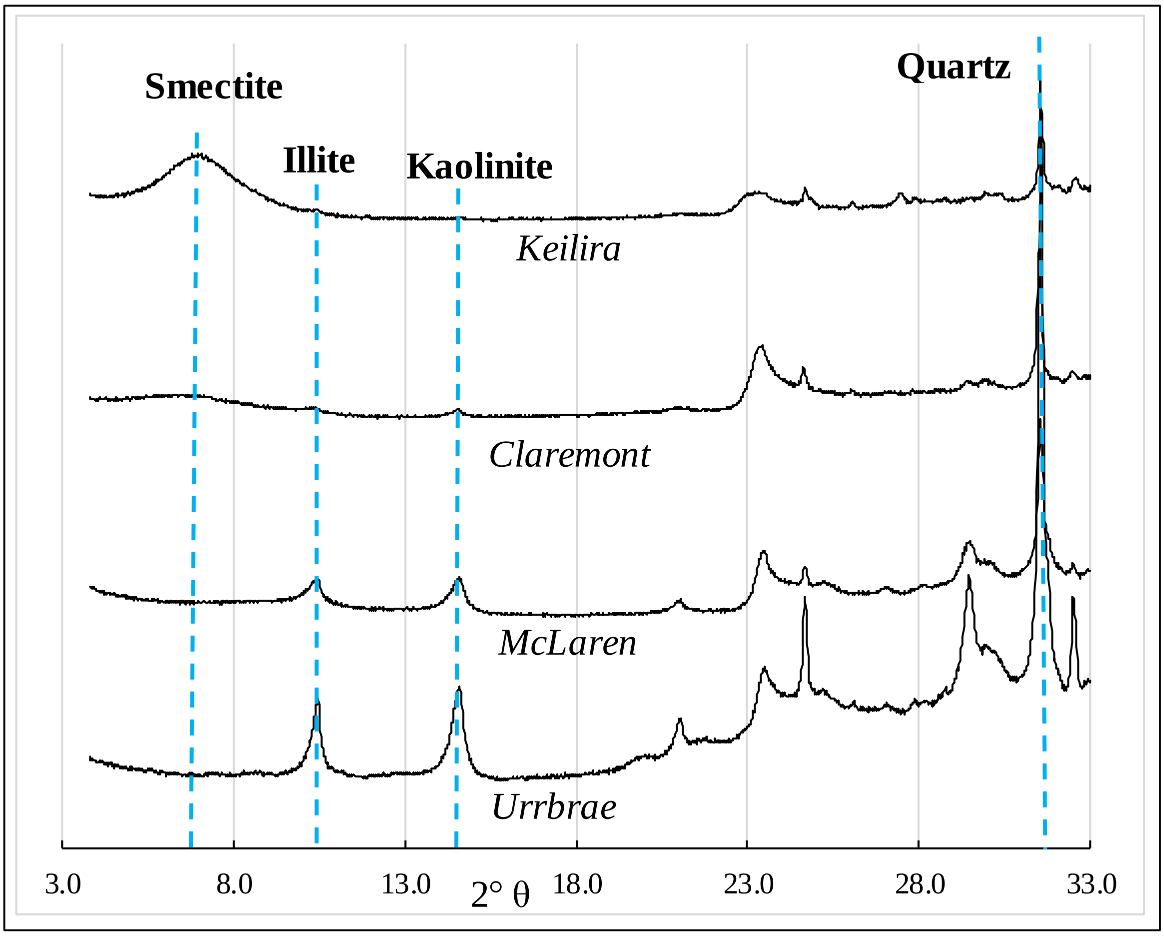


**Figure 24** XRD patterns of clay fractions for investigated soils

**Table 10** pH and CEC (in cmol+/kg) of original and homoionic samples

| Soil | Measurement | Original | Na | K | Mg | Ca |
|---|---|---|---|---|---|---|
| Urrbrae | pH | 6.7 | 7.9 | 7.9 | 7.3 | 6.8 |
| | CEC | 5.8 | 6.7 | 6.5 | 7.3 | 7.0 |
| McLaren | pH | 7.3 | 9.2 | 8.2 | 7.4 | 7.3 |
| | CEC | 8.8 | 14.6 | 10.0 | 10.1 | 11.1 |
| Claremont | pH | 8.3 | 10.9 | 10.6 | 9.8 | 9.0 |
| | CEC | 30.6 | 36.8 | 46.5 | 49.4 | 32.4 |
| Keilira | pH | 8.6 | 11.0 | 10.8 | 10.0 | 9.1 |
| | CEC | 26.6 | 35.2 | 32.0 | 35.6 | 27.2 |

Results for the kaolinitic/illitic Urrbrae and McLaren soils (Table 11) show that all cation-saturated samples were nearly homoionic with concentration of desired cations more than 95% with one exception: in McLaren soil Na could only saturate the exchange complex to 91%. A different tendency was observed in the smectitic Claremont and Keilira soils. Only saturation with Ca produced homoionic species with 97.6 and 94.9% of saturation respectively for Claremont and Keilira soils. Mg could only occupy 81.5 and 69.9% of exchange sites for the same soils. Potassium ions saturated Claremont soil by 76% and Keilira by 46.1% and the results for Na were 61 and 48.8% respectively.

**Table 11** Cationic composition of exchange complex for original and treated soils (in cmol$_+$/kg and % of saturation)

| **Soil ID** | **Ca** | **Mg** | **Na** | **K** | **Ca** | **Mg** | **Na** | **K** |
|---|---|---|---|---|---|---|---|---|
| | **cmol$_+$/kg** | | | | **% saturation** | | | |
| Urrbrae original | 4.31 | 0.86 | 0.12 | 0.51 | 74.3 | 14.8 | 2.1 | 8.8 |
| Urrbrae Na treated | 0.06 | 0.03 | 6.48 | 0.11 | 0.9 | 0.5 | 96.9 | 1.7 |
| Urrbrae K treated | 0.03 | 0.02 | 0.11 | 6.36 | 0.4 | 0.3 | 1.7 | 97.5 |
| Urrbrae Ca treated | 6.72 | 0.03 | 0.12 | 0.11 | 96.4 | 0.4 | 1.7 | 1.5 |
| Urrbrae Mg treated | 0.03 | 6.98 | 0.13 | 0.15 | 0.3 | 95.8 | 1.7 | 2.1 |
| | | | | | | | | |
| McLaren original | 4.74 | 2.74 | 0.71 | 0.60 | 53.9 | 31.2 | 8.1 | 6.8 |
| McLaren Na treated | 0.18 | 0.10 | 13.25 | 1.09 | 1.2 | 0.7 | 90.6 | 7.5 |
| McLaren K treated | 0.26 | 0.09 | 0.12 | 9.48 | 2.6 | 0.9 | 1.2 | 95.3 |
| McLaren Ca treated | 10.68 | 0.19 | 0.13 | 0.15 | 95.9 | 1.7 | 1.1 | 1.3 |
| McLaren Mg treated | 0.12 | 10.08 | 0.14 | 0.07 | 1.1 | 96.9 | 1.3 | 0.7 |
| | | | | | | | | |
| Claremont original | 21.37 | 7.44 | 0.26 | 1.48 | 70.0 | 24.4 | 0.9 | 4.8 |
| Claremont Na treated | 13.24 | 0.91 | 22.44 | 0.18 | 36.0 | 2.5 | 61.0 | 0.5 |
| Claremont K treated | 10.15 | 0.78 | 0.24 | 35.38 | 21.8 | 1.7 | 0.5 | 76.0 |
| Claremont Ca treated | 31.61 | 0.21 | 0.20 | 0.39 | 97.6 | 0.6 | 0.6 | 1.2 |
| Claremont Mg treated | 8.78 | 40.23 | 0.16 | 0.19 | 17.8 | 81.5 | 0.3 | 0.4 |
| | | | | | | | | |
| Keilira original | 10.70 | 9.44 | 5.34 | 1.07 | 40.3 | 35.6 | 20.1 | 4.0 |
| Keilira Na treated | 14.94 | 2.92 | 17.14 | 0.12 | 42.6 | 8.3 | 48.8 | 0.3 |
| Keilira K treated | 14.32 | 2.71 | 0.19 | 14.75 | 44.8 | 8.5 | 0.6 | 46.1 |
| Keilira Ca treated | 25.85 | 1.07 | 0.17 | 0.15 | 94.9 | 3.9 | 0.6 | 0.5 |
| Keilira Mg treated | 10.36 | 24.85 | 0.22 | 0.12 | 29.1 | 69.9 | 0.6 | 0.3 |

These differences in response to homoionic treatments of the soils reflect the differences in their clay mineralogy. The main structural difference between kaolinite/illite and smectite in terms of cation adsorptions is that kaolinite and illite adsorb cations on their outer surfaces, whereas in case of smectites the exchange complex is located both on the outer and also the inner surfaces (interlayer exchange sites). For smectites the interlayer exchange sites have much larger capacities and also divalent cations tend to concentrate on interlayer rather than on external surfaces (Churchman *et al.* 1993). Smectites expand or contract very readily depending on the nature of the exchangeable cations (Moore and Reynolds 1997). Cations which are easily hydrated, such as sodium, readily induce expansion of smectites. By contrast, anhydrous monovalent potassium cations, when entering the inner exchange complex, could induce contraction, or even collapse of the interlayer space around the edges of particles, locking exchangeable divalent cations inside the interlayers of clay particles. We demonstrate this effect using XRD diffractograms of homoionic Keilira samples (Figure 25).

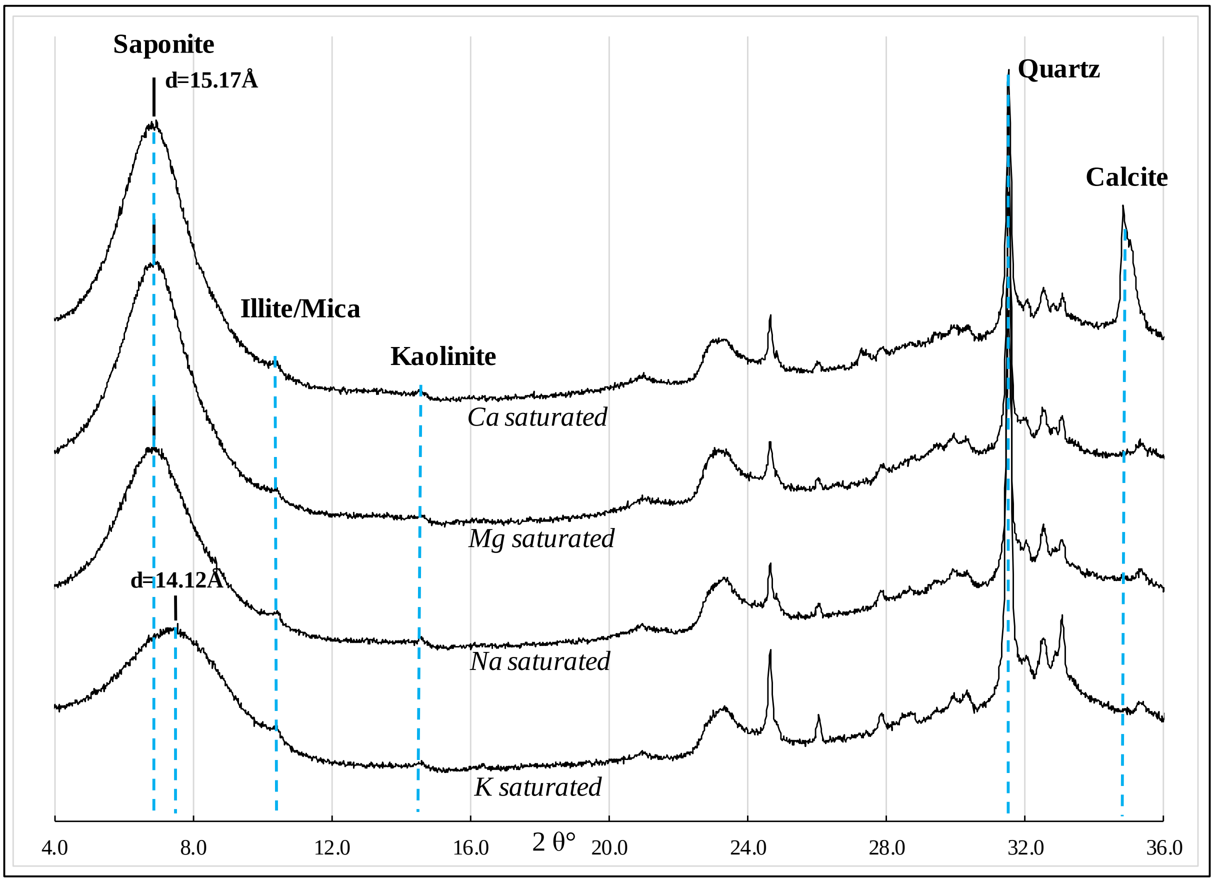


**Figure 25** XRD of homoionic Keilira samples

The variation of the basal spacings of smectites as a function of water adsorption has been studied by a number of workers (e.g., Hendricks *et al.* 1940; Mooney *et al.* 1952; Zettlemoyer *et al.* 1955; Fripiat *et al.* 1965; Keren and Shainberg 1975). These works indicate that the variation of basal spacings depends chiefly on the chemical difference among interlayer cations, especially between monovalent and divalent cations. $Ca^{2+}$ and $Na^{+}$ are usually found in smectites as interlayer cations, $Ca^{2+}$ having two layers of molecular water and giving rise to a basal spacing *d* of about ~ 15.2 Å, and $Na^{+}$ having one layer of molecular water and giving rise to a basal spacing of about ~ 12.6 Å (see, e.g., Keren and Shainberg 1975). Glaeser and Mering (1954) pointed out that these ions tend to occur in a "demixed state," that is, some interlayer regions are occupied mainly by $Ca^{2+}$ and others mainly by $Na^{+}$.

Keilira $Ca^{2+}$, $Mg^{2+}$ and $Na^{+}$ saturated samples have 001 *d*-spacing at ~15.20 Å – typical for smectite saturated with divalent cations which has double water layer. The $K^{+}$ – homoionised sample having saturated exchangeable sites for only 46% of its capacity has a *d*-spacing at ~14.10 Å. This could be due to: a) the collapse of part of the smectite layers and their transformation into an interstratified smectite-illite phase (Eberl and Hower 1977; Velde and Barré 2010 among many others), where in this scenario potassium became a part of mineral structure; b) potassium cations having saturated a part of the smectite interlayer space dehydrated, but did not collapse it. In the second scenario potassium is available for exchange reaction (Velde and Barré 2010). Considering that the CEC of the K$^+$ homoionised sample is slightly lower than Na$^+$ and Mg$^{2+}$ samples both reactions could occur: part of the smectitic layer became interstratified and another part just dehydrated, decreasing the interlayer space.

## Effect of homoionic treatments on particle size and zeta potential of soil clays

The results of mean particle size (MPS) and zeta potential measurements show that for all soil clays studied the samples with monovalent homoionic species have smaller MPS and higher negative zeta potential values (Figure 26). The homoionic clays treated with divalent cations showed larger MPS and lower negative zeta potentials. The MPS increased in all clay samples in the order Na < K < Mg < Ca with the exception of the Urrbrae Ca-saturated sample which had a smaller MPS than its Mg-saturated sample. The changes in size observed are reflected in the zeta potential data, with samples having smaller sizes giving higher negative zeta potentials.

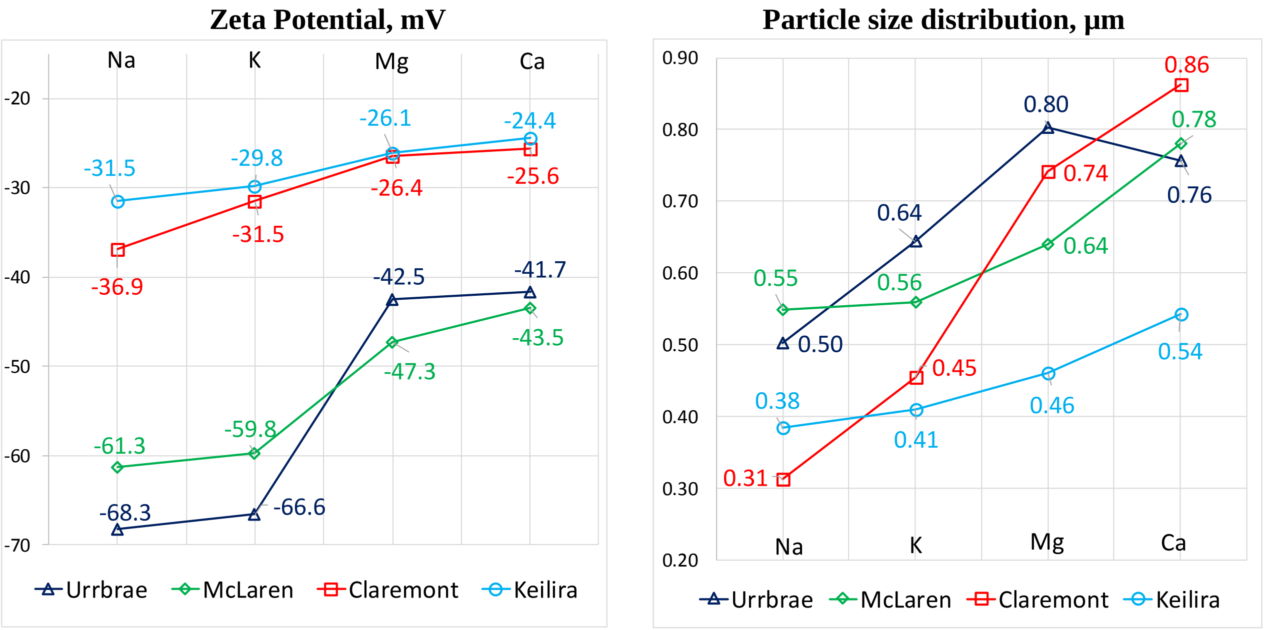


**Figure 26** Zeta potential and mean particle size measurements for studied soils

The zeta potential is directly related to the total interaction energy between particles. Yong and Sethi (1977) studied clay dispersibility using refiltration experiments. Measurements of refiltration rate relative to zeta potential provided information on the dispersibility of the clay studied. The results showed that the higher the refiltration rate, the more flocculated the clay and *vice versa.* Yong *et al.* (2012) categorized zeta potential values in terms of dispersion behaviour of clays (Figure 27). The illustration shows that as the zeta potential decreases, the degree of dispersibility increases. Chorom and Rengasamy (1995) came to the same conclusion. In our experiment all soil clays saturated with monovalent cations gave higher negative zeta potential values than those saturated with $Ca^{2+}$ or $Mg^{2+}$. The potassium saturated samples have larger MPS and higher (less negative) zeta potential values than those saturated with sodium. In view of the findings of Chorom and Rengasamy (1995) and Yong *et al.* (2012) I can conclude that exchangeable potassium has a lower dispersive potential than exchangeable sodium. Both monovalent cations, when present on the outer exchange sites of clays, have a greater ability to promote dispersion than their divalent counterparts.

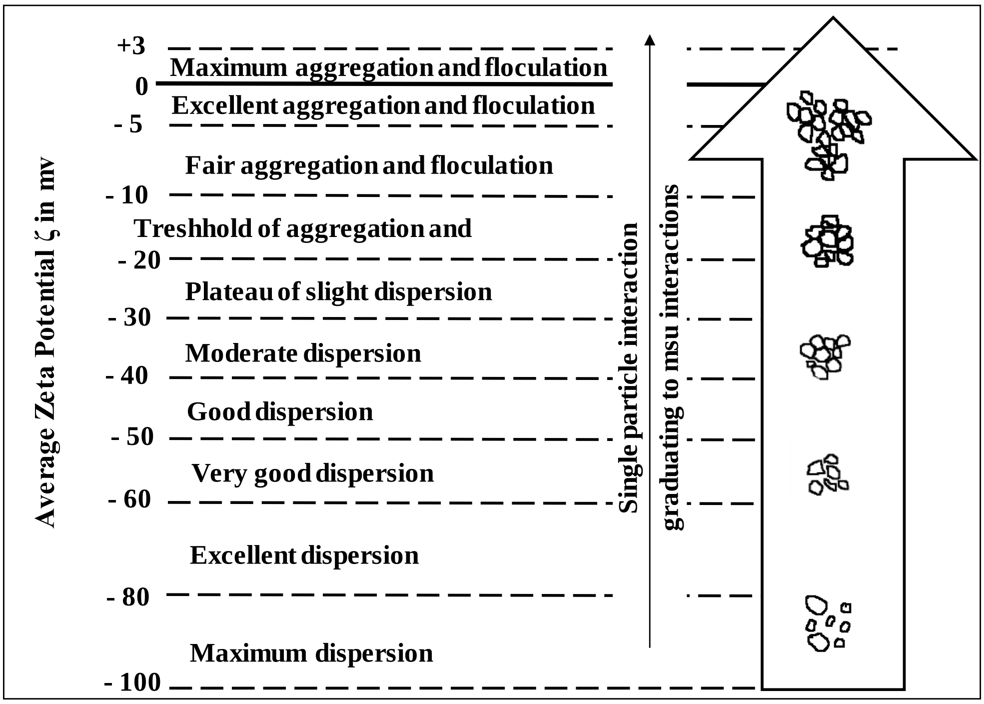


**Figure 27** Interpretation of presence of microstructures from ranges of average zeta potential (after Yong *et al.* (2012)

Clay particles of smaller size would be expected to disperse more easily, but their charge characteristics, as indicated by zeta potentials, also affect ease of dispersion. My findings show that smectitic Claremont and Keilira samples homoionized with monovalent cations have smaller MPS but lower negative values of zeta potential than illite/kaolinite Urrbrae and McLaren soil clays and lower dispersion potential. Dispersion/flocculation phenomena are governed by the attractive and repulsive forces in the electrical double layer at the surface of charged colloids (Chorom and Rengasamy 1995). The balance between these forces is determined by factors such as exchangeable cation and ionic strength of the soil solution (Rengasamy and Olsson 1991).

Of the attractive forces, van der Waals forces account for most attractive effects (Churchman *et al.* 1993) though they are strongly inversely related to particle separation (Crooks 1999). Since van der Waals forces are additive in polyatomic systems, their strength is directly related to the number of atoms and to their closeness of approach. Hence, they are likely to be enhanced by large surface areas and by flat particles which fit closely together. Particles with low surface areas, and/or irregular surfaces which prevent close approach will generate low attractive forces of the van der Waals type (Churchman *et al.* 1993).

Kaolinite, illite and smectite are the most common clay minerals in soils. Typically, kaolinites have large particles, low specific surface areas and a low CEC, while smectites have small particles, high specific surface areas and high CEC's. For most illites, these properties are intermediate between those for kaolinites and smectites. The shapes of their particles also contrast. Kaolinites have flat, relatively thick and generally regular (hexagonal) platy particles, while smectites have thin flakes. Illites also have platy particles which cover a range of thicknesses and which often have irregular surfaces (Churchman *et al.* 1993). Many illites consist of relatively thick particles with little flexibility (Greene *et al.* 1978). In contrast, smectite particles can be very thin and highly flexible (Emerson 1983). Electron micrographs show that illite crystals may have irregular surfaces (Greene *et al.* 1978). In particular, their planar surfaces can be terraced (Quirk 1978). These features mean that contact between illite particles is less intimate than that between the flexible thin flakes in smectites. Both these morphological factors and a lower effective layer charge mean that edge-to-face attraction between illite particles is usually weaker than between those of smectites (Churchman *at al.* 1993). In general, these differing morphologies of smectite, illite and kaolinite lead to differing packing of their tactoids, so that they form clay aggregates that differ in their stability (Fig. 28). The differences in the organisation of clay particles of different clay minerals and their electric charge reflects their differences in interactions with water in soil solution and consequently in their dispersive behaviour (Lado and Ben-Hur 2004).

Tessier *at al.* (1992) studied the changes in clays microstructure under different wetting regimes. They noticed that illite and smectite clays have different pore size distributions and, consequently, very different solid phase structures. For illite, a single wetting was enough to bring about a breakdown of the structure so that the arrangement of the particles was affected and a significant fraction of the pore volume was occupied by air. For smectite, under direct wetting with water, the structure was like a sponge, without a complete dispersion of the particles. The system would appear to be like a continuous network of particles arranged face to face, limiting the pores and without any real continuity with each other. At higher resolution the layers appear to be stacked in parallel, or practically parallel, ensembles. The pore size was of the order of 1 µm for illite to 10 nm for smectite. Tessier and co-workers concluded that in the case of illite the loss of cohesion was related to two factors: a) 90% of the porosity of the sample was occupied by air; b) the large size interparticle pores results from the stacking of rigid particles. Therefore, some free water (at atmospheric pressure) in contact with the illite can very quickly migrate to the pores by capillarity. An overpressure of air should result and lead to the disintegration of the illite and produce slaking. The interlayer spaces in illites are closed and the particles are flat and very rigid and the interparticle contact surface is very limited. This results in very weak overall interparticle cohesion forces, even if they are locally very strong.

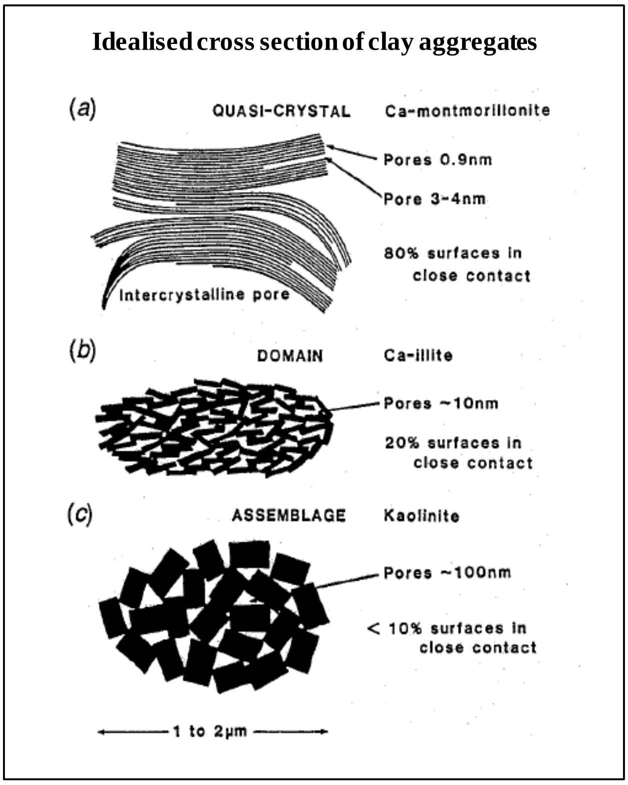


**Figure 28** Schematic structure of clay aggregates (after Oades and Waters 1991)

With smectite, the structure is very different. As the size of the pores before wetting was small (1-2 nm), the hydraulic conductivity was low and the water can migrate only very slowly in the material. Moreover, because there is only a small amount of air, it can escape without producing an overpressure. As the smectite clay layers are stacked face to face, their surfaces overlap over large surface areas. Thus there is extensive continuity of the solid phase through the hydrated interlayer spaces. These two aspects of the structure of smectites lead to very strong cohesion and low hydraulic conductivities (Tessier *at al.* 1992).

Taking into account all morphological and structural differences between smectite and illite microstructures it can be deduced that smectitic soils having smaller particles possess better organization of aggregates than illite. For smectites, when interacting with water, the attractive forces of the van der Waals type overcome repulsive forces which reflect in better cohesion and lesser dispersivity than illitic minerals. Particle size distribution and zeta potential data presented in Figure 26 support this finding. Illitic soils are more dispersive than soils with dominant smectitic clays. In this experiment I have shown that zeta potential could effectively reflect soil clay dispersive properties. But to appropriately understand the meaning of zeta potential we should have prior knowledge of the mineralogy of the soil studied.

# Chapter 6. Potassium status of Urrbrae soil. Laboratory and field study using traditional analytical methods, XRD and TEM

In the first, a field based study, I investigated the variability of the clay fraction of one of the South Australia most common soils – a Chromosol, with depth and under different vegetation regimes. In the second, laboratory study, I evaluated the influence of exchangeable K+ on the dispersive behaviour of the clay fraction of the Chromosol using traditional analytical methods, XRD and TEM.

In the second study I have used the Urrbrae soil material from a laboratory controlled experiment conducted by A. Marchuk (2013) and reported in her PhD thesis. A. Marchuk in her study concentrated on the behaviour of Urrbrae soil as a whole, while my study was focused on clay fractions of Urrbrae soil. I studied the influence of exchangeable $K^+$, compared with exchangeable $Na^+$, $Ca^{2+}$ and $Mg^{2+}$, on the dispersive behaviour of Urrbrae soil clays.

## Materials and methods

### Selection of study site and soil

Red Brown Earth soil was taken from six soil profiles in the Permanent Rotation Trial at the Waite Agricultural Research Institute. Profiles were chosen under different vegetation regimes: cereal crops (cultivated site), grazing, vineyard, soil under a coniferous tree, soil under a deciduous tree and uncultivated soil. The soil sampling sites were located within 50 m of each other (Figure 29 and Table 12), which gave a unique opportunity to explore the short distance variability of soil clays.

The Waite Agricultural Research Institute at Urrbrae, about 7 km from the centre of Adelaide, was established in 1925. The climate is typically Mediterranean with a mean annual rainfall of 626 mm, of which 487 mm falls in the growing season (April-October). Mean annual maximum and minimum temperatures are 21° and 12°C, respectively. The fine sandy loam found on this site is a prime example of a red-brown earth (Stace et al., 1968) Urrbrae series (Litchfield, 1951) defined as a Red Chromosol (Isbell, 1996), with illite and kaolin being the main clay minerals (Norrish and Pickering, 1977). The topography of the area is a plain with gentle slopes.

The Urrbrae series of red-brown earths may be regarded as an automorphic soil developed under well-drained conditions under the regional climate beneath the scarp of the range. The low proportion of coarse sand and relatively high proportions of fine sand and silt reflects the dominance of the argillaceous or finely siliceous material of the adjacent Pre-Cambrian strata and indicates the uniform nature of the original parent material through the profile. The reddish surface colour is presumably an expression of the mineral content, the organic matter being depleted through cultivation or sheet erosion (Litchfield, 1951).

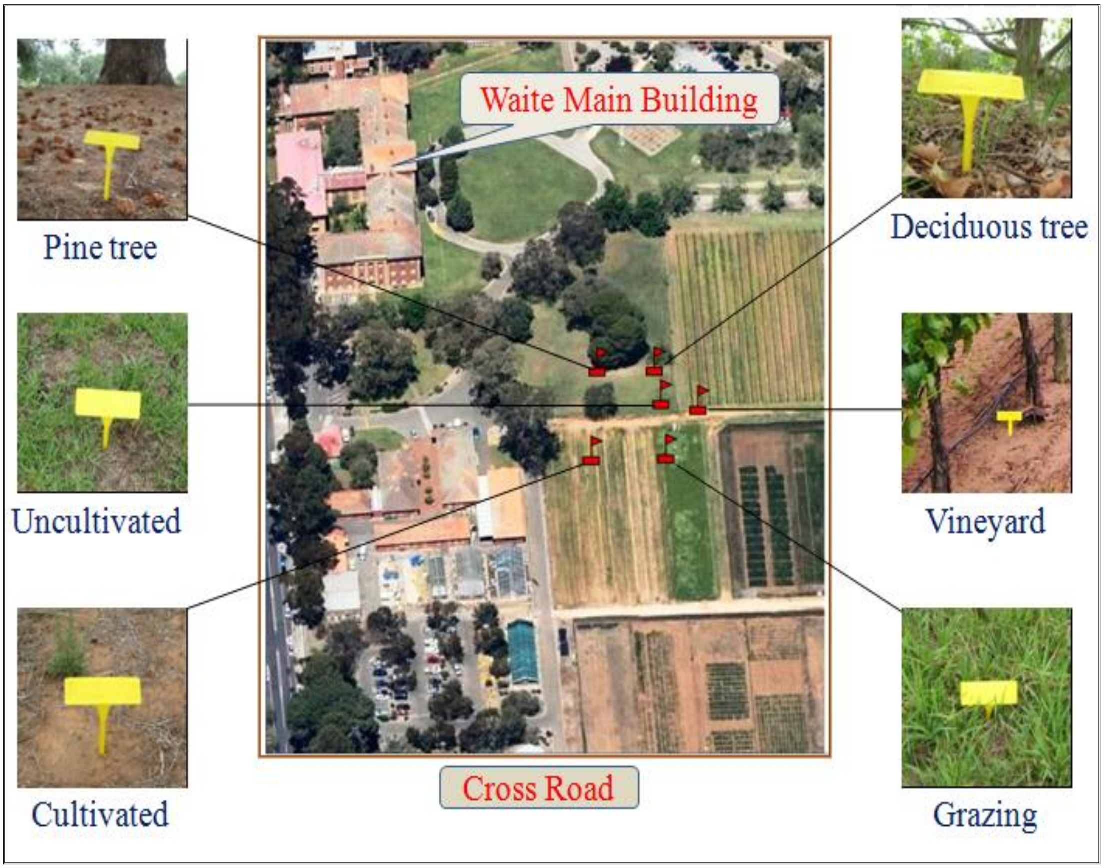


**Figure 29** Study sites

**Table 12** Location, elevation and climate condition of soil sampling sites

| Soil sampling sites | Latitude (°S) | Longitude (°E) | Elevation (m) | Mean annual temperature | Annual rainfall |
|---|---|---|---|---|---|
| Cultivated, cereal crops | 34.966938 | 138.634416 | 109 | Max 21°C<br>Min 12° C | 626 mm |
| Cultivated, grazing | 34.966916 | 138.634152 | 108 | | |
| Uncultivated | 34.967187 | 138.634195 | 110 | | |
| Cultivated, vineyard | 34.967146 | 138.634067 | 109 | | |
| Uncultivated, pine tree | 34.967281 | 138.634347 | 112 | | |
| Uncultivated, deciduous tree | 34.967301 | 138.634205 | 111 | | |

## Soil sampling and preparation

Soil samples were collected and geo-referenced using a Garmin eTrex GPS device with 5 m accuracy in November 2010. At each site, soil was taken with a hand auger from the following depths: 0 – 10, 10 – 20, 20 – 30, 30 – 40, and 40 - 50 cm (where possible) in polyethylene bags. Samples were first air-dried, ground and sieved to < 2 mm.

## Clay fractioning

The soil was fractionated in water following the procedure summarised in Figure 30. The height of the soil/water column (19 cm) was calculated according to settling time (16 hours) by means of Stokes' Law (Jackson, 2005) to ensure that particles in suspension were all < 2 μm.

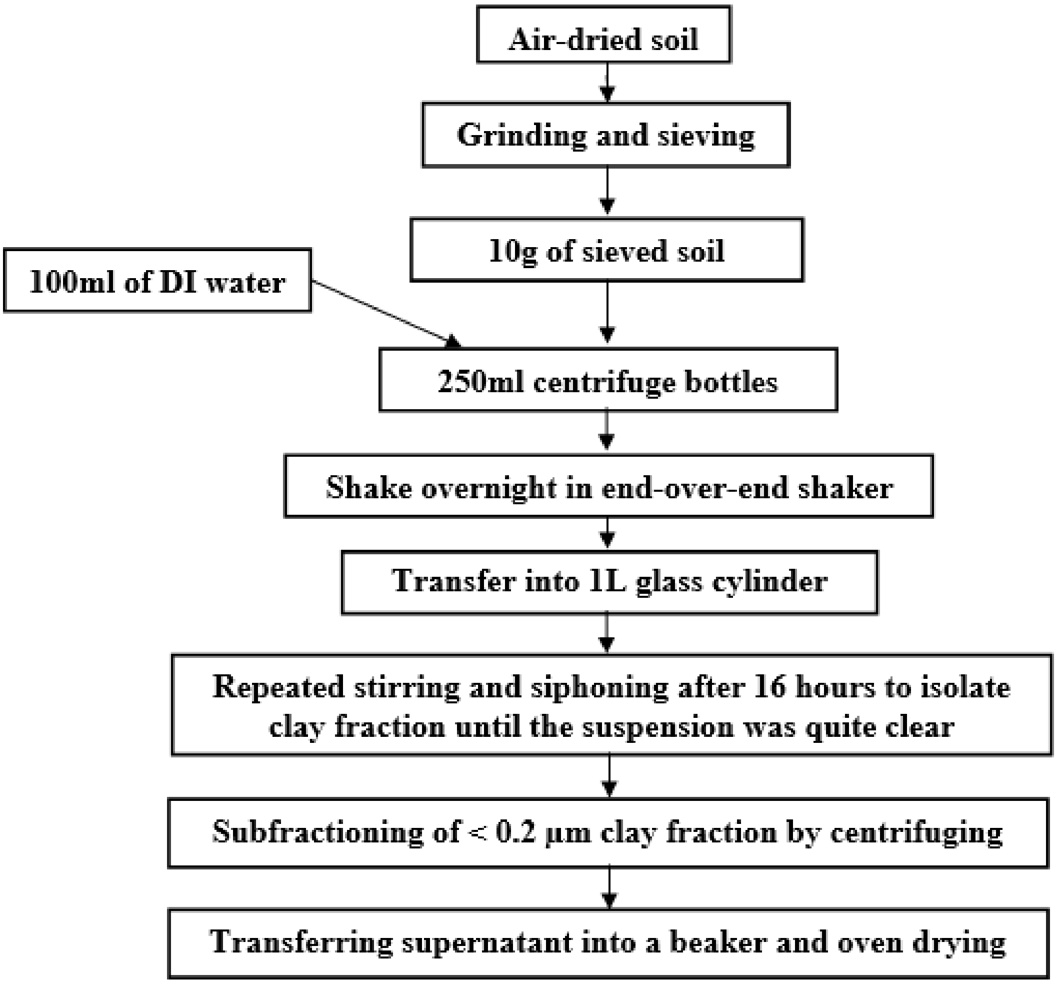


**Figure 30** Fractionation procedure

**Figure 31** Settling of soil/water suspension of Urrbrae soil from cultivated (cereal) site for different depths, from the left: 0-10 cm, 10-20 cm, 20-30 cm and 30-40 cm

The cylinders were then allowed to stand (Figure 31), and after 16 hours of settling the clay (< 2 µm) fraction was isolated from soil by siphoning of the dispersed material. No chemical treatments were applied to the raw samples in order to preserve all forms of potassium and other chemical elements in soil in their initial states. The procedures of adding water, stirring, allowing settling and siphoning were carried out for a total of 6 times, and the clay suspensions thus obtained were combined. The bulk clay fraction was divided into fine (< 0.2 µm) and coarse (0.2-2 µm) clay subfractions using a Beckman J2-21M centrifuge equipped with the JS-7.5 swinging bucket rotor. The supernatant containing 0.2 µm clay fraction (Fig. 33, B) was poured in a beaker and oven-dried at 60ºC (Figures 32 and 33).

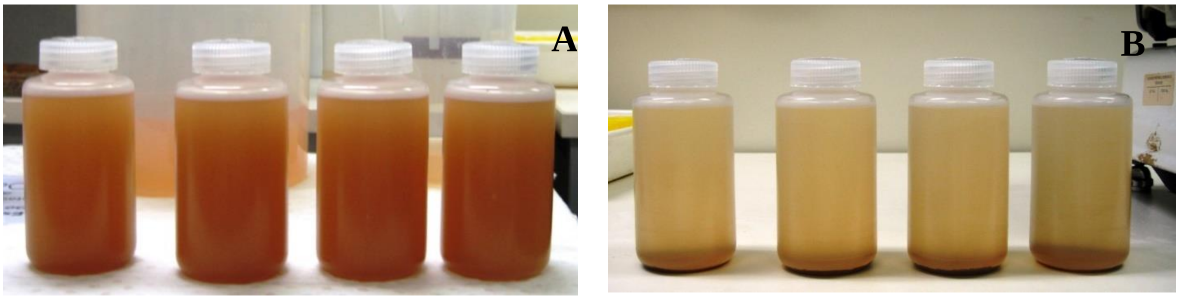
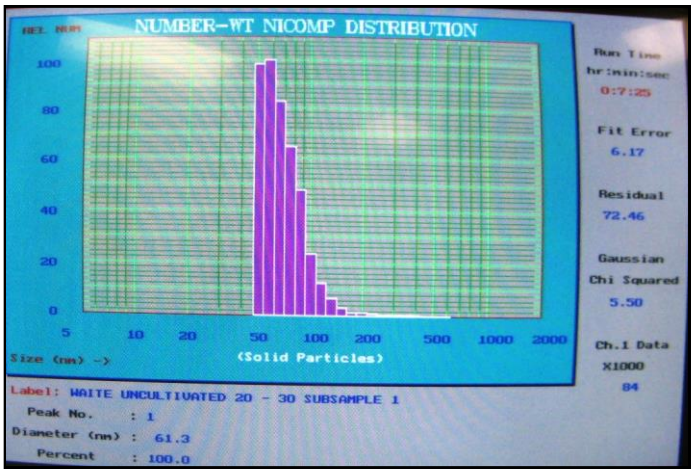


**Figure 32** Clay fractionation: A - Bulk clay fraction before centrifugation. B - Suspended < 0.2 µm clay fraction (supernatant) after centrifugation

The particle size distribution of the remaining supernatant was also examined using a Nicomp Submicron Particle-Sizer, Model 370 which analyses particles using dynamic light scattering. The average particle size and size distribution was determined by a number-based so-called 'Nicomp' (non-Gaussian) fit to raw data which had been collected over 7-8 min at 20 °C at an angle of 90° (Figure 34).

**Figure 33** Drying of supernatant in oven



```
Run Time
hr:min:sec
0:7:25

Fit Error
6.17

Residual
72.46

Gaussian
Chi Squared
5.50

Ch.1 Data
X1000
84

Label: WAITE UNCULTIVATED 20 - 30 SUBSAMPLE 1
  Peak No.      : 1
Diameter (nm) :  61.3
   Percent      : 100.0
```

**Figure 34** Snapshot of particle size distribution data (in nm) for < 0.2 µm clay fraction obtained using a Nicomp Particle-Sizer

## X-Ray diffraction (XRD) analysis

The protocol for XRD analysis was described in previous experiment (Chapter 5).

## Transmission electron microscopy (TEM)

Transmission electron microscopy was undertaken to determine the mineralogy and composition of the clay samples. Among the tools available for the study of very small particles, transmission electron microscopy (TEM) is perfectly adapted to the characterization of soil fine particles (Elsass *et al.* 2008). Samples were prepared by dispersing a small amount (10-15 mg) of material in similar amount of deionised water by ultrasonic treatment. A drop of the remaining slurry was allowed to dry on a carbon-coated cellulose film supported by a 200 mesh copper grid.

High-resolution imaging and chemical analyses were performed using a Philips CM200 Transmission Electron Microscope (Figure 35)) fitted with an EDAX r-TEM system to perform energy-dispersive x-ray spectroscopy (EDS). The TEM was operated at 120 kV and a beam current of 20 µA. High resolution imaging was conducted at magnifications between 50,000x and 350,000x.

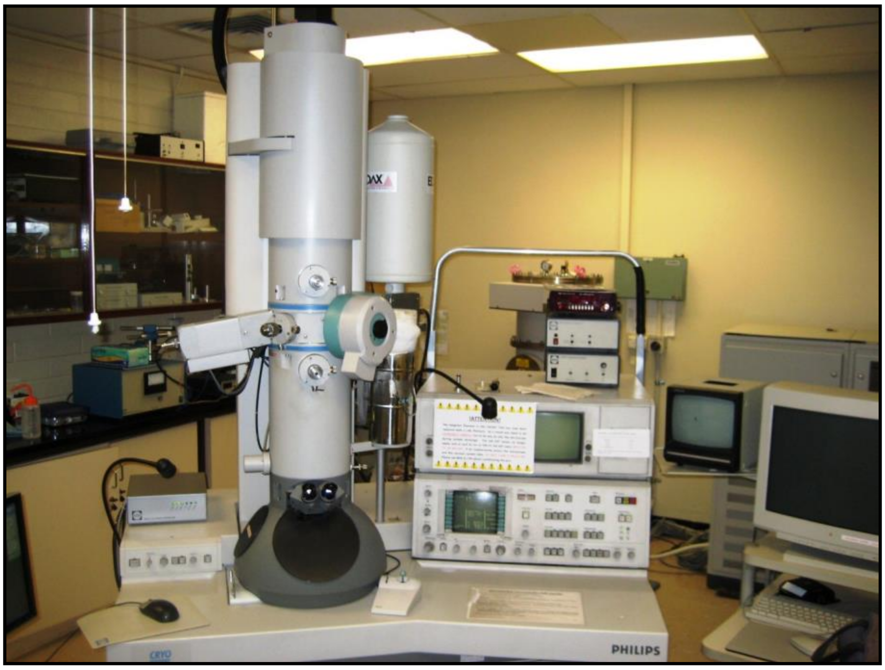


**Figure 35** Philips CM200 Transmission Electron Microscope

# Results and discussion

## Soil Analysis

Soils from 6 locations, each under different types of vegetation, were analysed for the determination of pH, EC and soluble potassium content (Rayment and Lyons, 2011). The results of soil analysis (Table 13 and 14) has shown that investigated sites differ in pH, EC and soluble potassium content. Figures 36 - 38 illustrates the spatial distribution of the pH, EC and soluble $K^+$ within sampling depths. Soluble potassium content particularly varied considerably, mostly in the top two horizons.

**Table 13** Variation of analysed soil properties with depth

| **Depth** | **Cultivated** | **Grazing** | **Uncultivated** | **Wine** | **Pine** | **Tree** |
|---|---|---|---|---|---|---|
| **pH** | | | | | | |
| **0 – 10** | 5.5 | 7.4 | 6.0 | 7.0 | 6.7 | 7.5 |
| **10 – 20** | 5.5 | 7.2 | 6.3 | 7.3 | 6.8 | 8.1 |
| **20 – 30** | 6.1 | 7.2 | 6.5 | 7.4 | 7.4 | 8.4 |
| **30 – 40** | 6.4 | 7.2 | 6.7 | 7.4 | 7.8 | 8.5 |
| **EC, dS/m** | | | | | | |
| **0 – 10** | 0.18 | 0.19 | 0.07 | 0.06 | 0.21 | 0.12 |
| **10 – 20** | 0.09 | 0.08 | 0.03 | 0.04 | 0.31 | 0.1 |
| **20 – 30** | 0.08 | 0.04 | 0.03 | 0.03 | 0.30 | 0.08 |
| **30 – 40** | 0.09 | 0.04 | 0.04 | 0.03 | 0.24 | 0.06 |
| **$K^+$, ppm** | | | | | | |
| **0 – 10** | 9 | 40 | 7 | 2 | 18 | 15 |
| **10 – 20** | 7 | 12 | 3 | 1 | 13 | 11 |
| **20 – 30** | 5 | 6 | 1 | 1 | 7 | 8 |
| **30 – 40** | 5 | 3 | 1 | 1 | 3 | 5 |

**Table 14** Summary statistics of analysed soil properties

| **Statistics** | **pH** | **EC, dS/m** | **$K^+$, ppm** |
|---|---|---|---|
| **Minimum** | 5.5 | 0.03 | 1 |
| **Maximum** | 8.5 | 0.31 | 40 |
| **Mean** | 6.99 | 0.11 | 7.52 |
| **Standard Error** | 0.16 | 0.02 | 1.65 |
| **Standard Deviation** | 0.79 | 0.08 | 8.23 |
| **Coefficient of variation, %** | 11 | 73 | 109 |

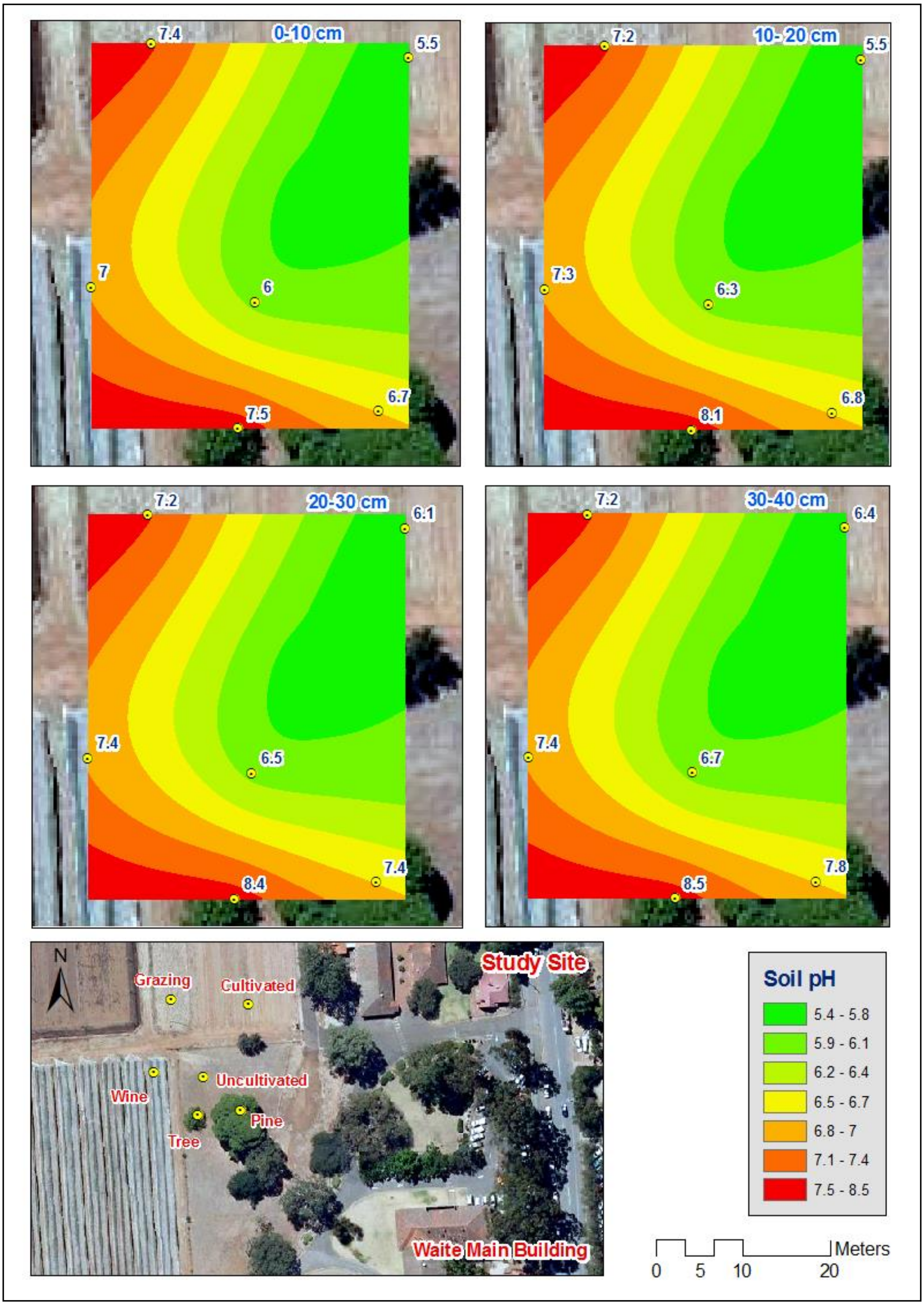


**Figure 36** Spatial variability of soil pH

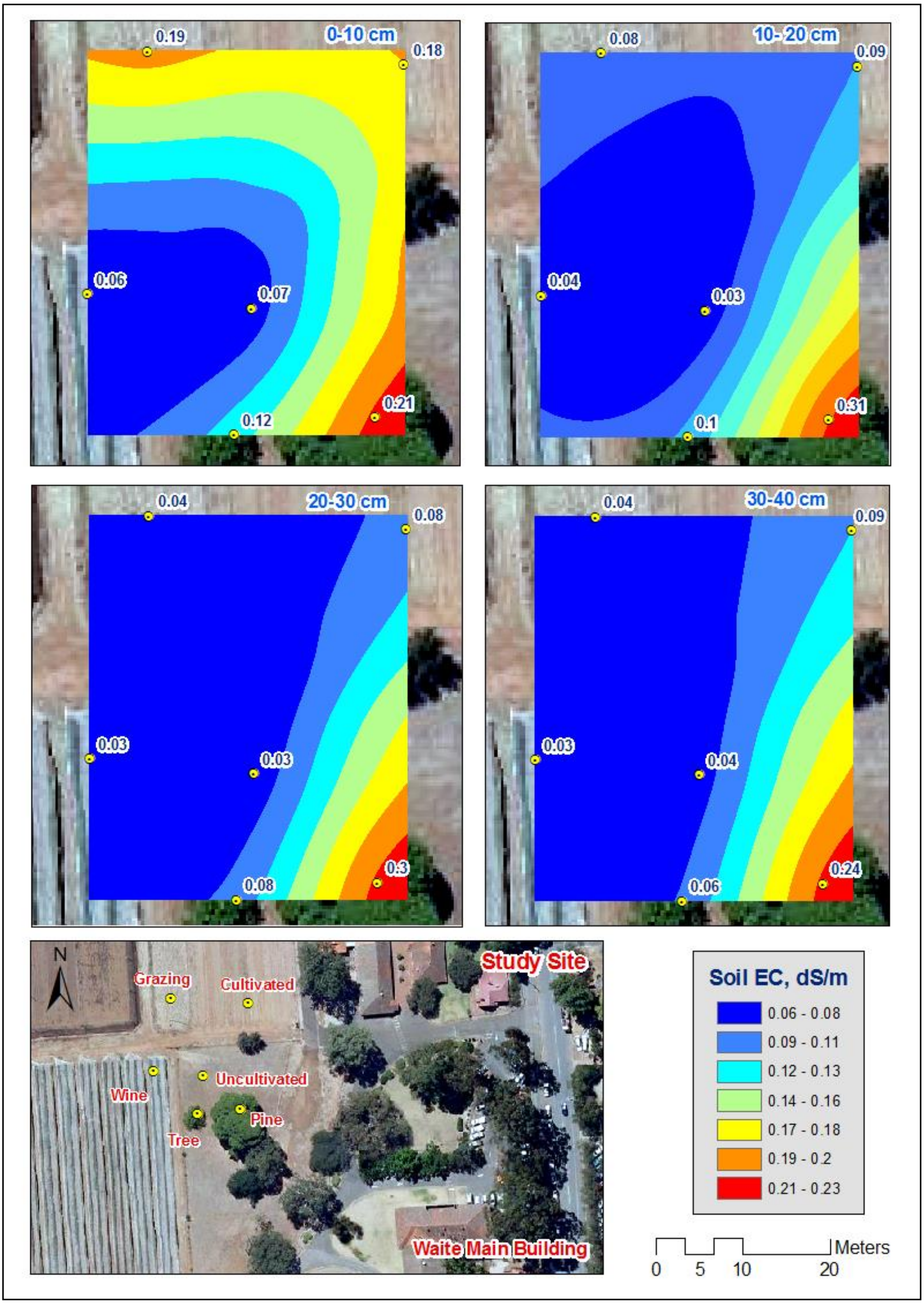


**Figure 37** Spatial variability of soil EC

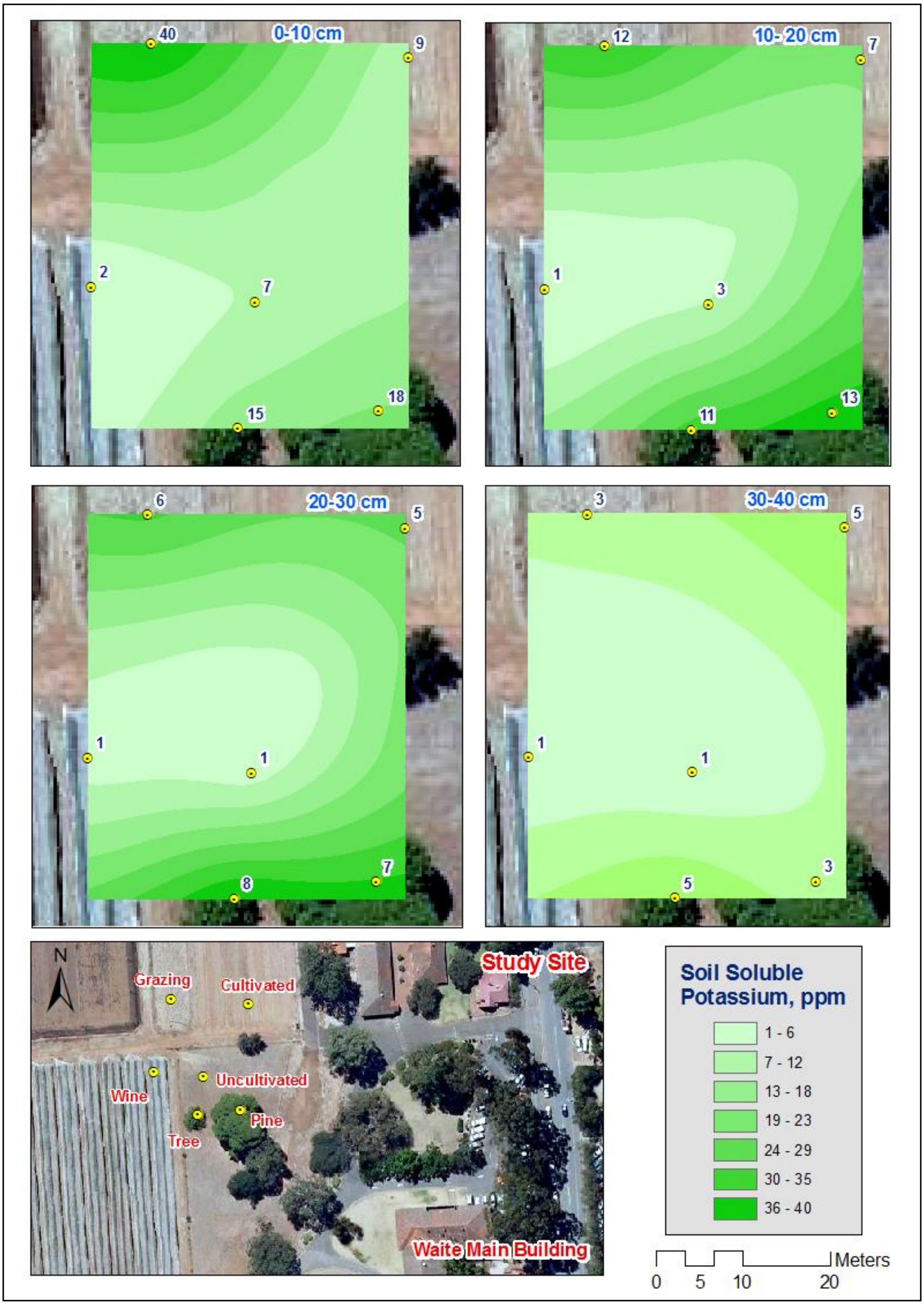


**Figure 38** Spatial variability of soil soluble potassium

# Mineralogical determination of clay fractions by XRD

## Previous study

In 1951 Radoslovich conducted survey “Soil Colloids of Several Adelaide Red-Brown Earths”. Up to the present date this is the most comprehensive existing mineralogical report on Urrbrae soil. The closest pit examined is from the north-west part of arboretum of Waite institute (Figure 39). The results of this survey are presented in table 15.

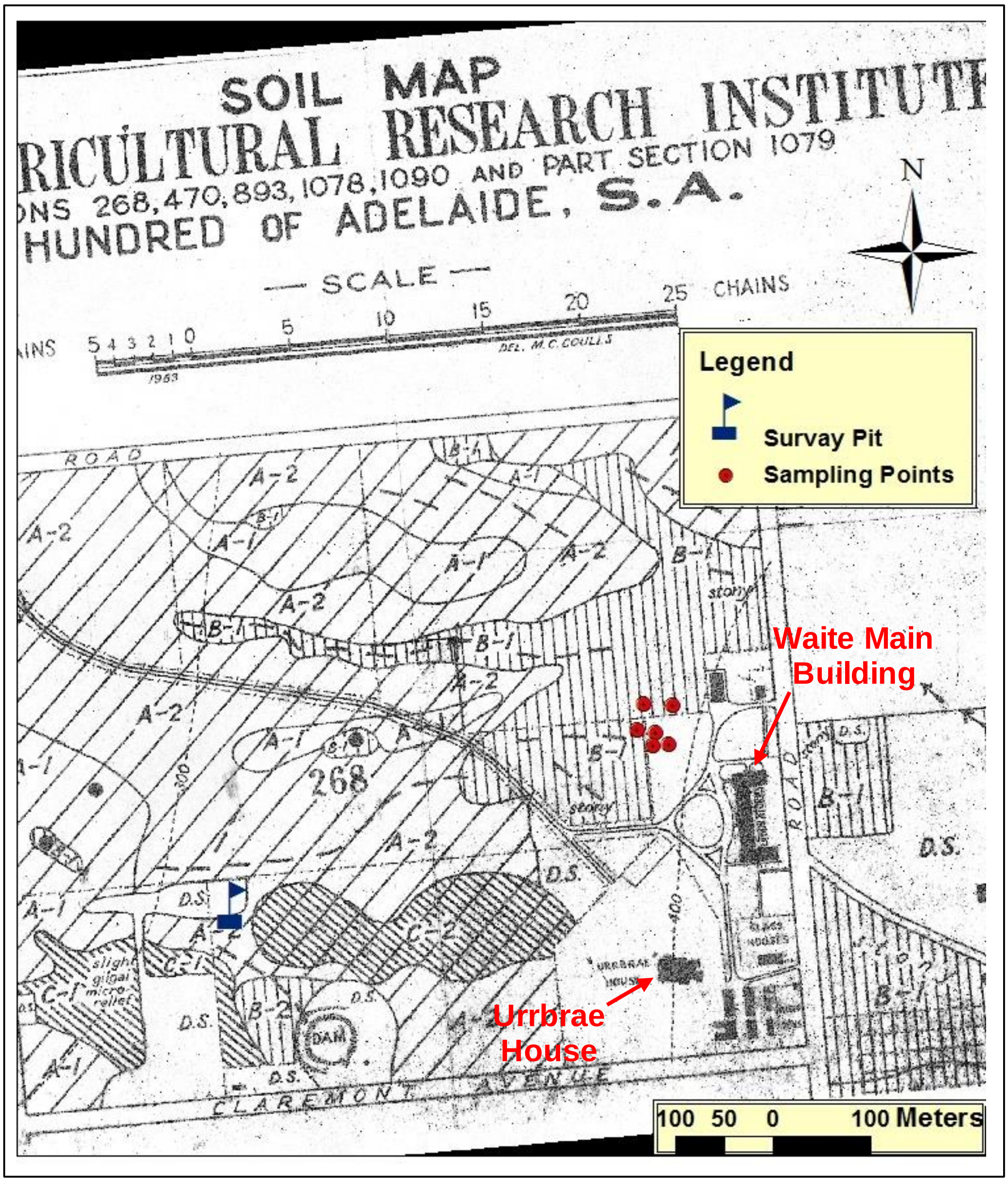


**Figure 39** Location of survey pit and experimental soil sites on map of W.H. Litchfield, 1951

According to Radoslovich’s (1951) survey, in clay mineral composition Urrbrae soil colloids are basically mixtures of illite and kaolinite. A moderate amount of chlorite is present in some cases and is apparently alluvial in origin. Montmorillonite is definitely present (in fairly small amounts, probably < 10% of the clay fraction) in a few horizons. There is also evidence of components of rather indefinite structure and spacing in some cases. These have been termed “mica-montmorillonite intermediates”, but they have not been positively identified as any definite clay mineral types. The montmorillonite found in these soils could occur mainly in these phases.

**Table 15** X-Ray Crystallograph Analysis of the Colloidal Fraction of the Waite Institute Profile Pit (in Litchfield, 1951) based on survey of Radoslovich, 1951

| **Depth** | **0-18 cm** | **18-33 cm** | **33-75 cm** | **88-113 cm** | **113-173 cm** |
|---|---|---|---|---|---|
| **Horizon** | **$A_1$** | **$A_2$** | **$B_1$** | **$B_2C$** | **$B_3C$** |
| **Minerals present** | Illite<br>Kaolinite<br>Quartz<br>Ferric oxide<br>Chlorite (weak)<br>Mica-MMT* (some evidence) | Illite<br>Kaolinite<br>Quartz<br>Ferric oxide<br>Mica-MMT (some evidence) | Kaolinite<br>Illite<br>Ferric oxide (fairly intense, stronger)<br>Quartz (weak)<br>Mica-MMT (some evidence)<br>Chlorite (very weak) | Kaolinite<br>Illite<br>Chlorite (stronger)<br>Quartz<br>Ferric oxide<br>Calcite<br>MMT (weak) | Kaolinite<br>Illite<br>Chlorite (strong)<br>Quartz<br>Ferric oxide<br>Mica-MMT (stronger)<br>Goethite (?)<br>Gibbsite (?) |

* Montmorillonite

## Mineralogical analysis of clay fraction

Similar XRD patterns were acquired from all six profiles (Figures 40). The XRD traces of < 2 μm clay fractions obtained for the randomly orientated, air-dried (AD) samples show diffraction peaks typical of clay minerals, with additional reflections that were attributed to the primary minerals quartz (4.26, 3.34 Å) and K-feldspar (3.24 Å). The rational 00l reflections series appeared at ~10.0, ~5.00, and ~3.34 Å, and at ~7.2 and ~3.6 Å corresponding to discrete illite/mica and kaolinite phases, respectively. The positions of these peaks were not affected by glycerol treatment (Figure 41). The samples from cultivated and grazing profiles contain traces of vermiculite and vermiculite-illite. Given the problems of proper identification of vermiculite phases (Brindley and Brown 1980) and the small amount possibly present, no further attempt was made to identify these minerals. The position of the 060 reflection is useful in distinguishing between dioctahedral and trioctahedral species (Figure 42). A peak at $d$ = 1.49 Å was attributed to kaolinite, which is dioctahedral (Grim 1968); a peak at $d$ = 1.54 Å was attributed to quartz. A peak at d~1.50 Å overlapped with the kaolinite 060 peak indicated an illite/mica with a dioctahedral structure.

In order to achieve a better insight on the detailed structural aspects of clay mineral assemblages of studied clays semiquantitative assessment was performed. The semiquantitative clay mineral proportions were estimated from the glycerolated patterns. Expansion with glycerol is diagnostic for swelling clays, including smectites and vermiculites.

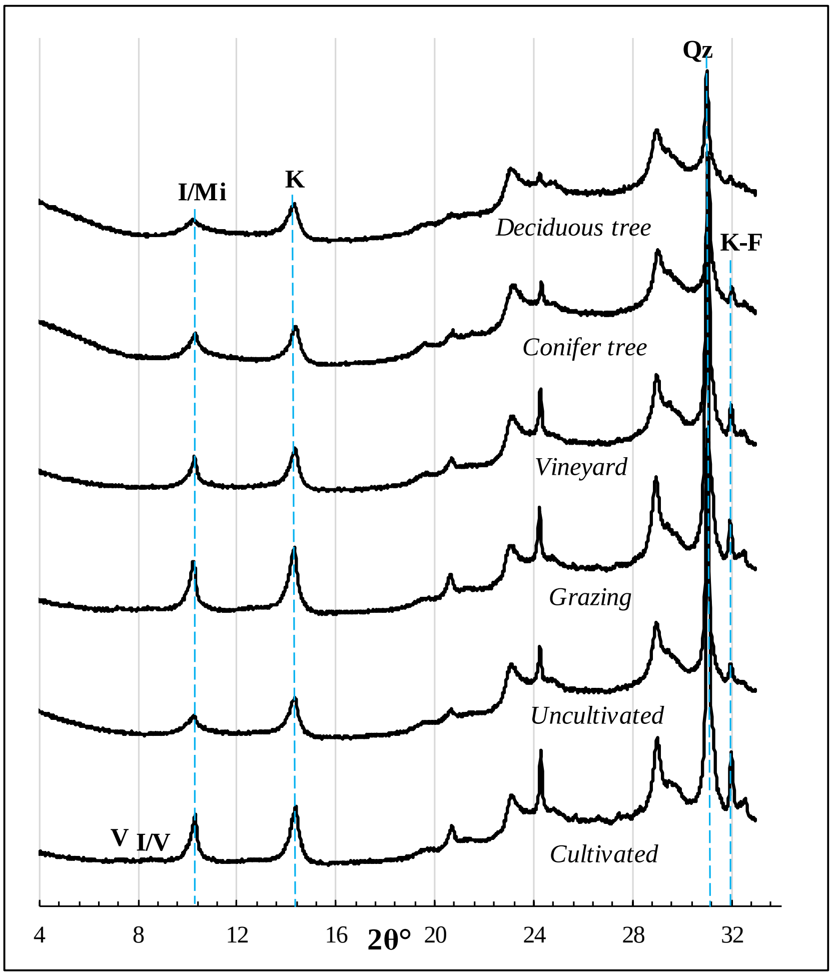


**Figure 40** XRD patterns of Urrbrae soil clay under different vegetation regime. V, vermiculite (*d*~14.2 Å); I/V, illite-vermiculite (*d*~12.1 Å); I/Mi, illite/mica (*d*~10.0 Å); K, kaolinite (*d*~7.2 Å); Q, quartz (*d*=3.43 Å); K-F, K –feldspar (*d*=3.24 Å), Co Kα radiation

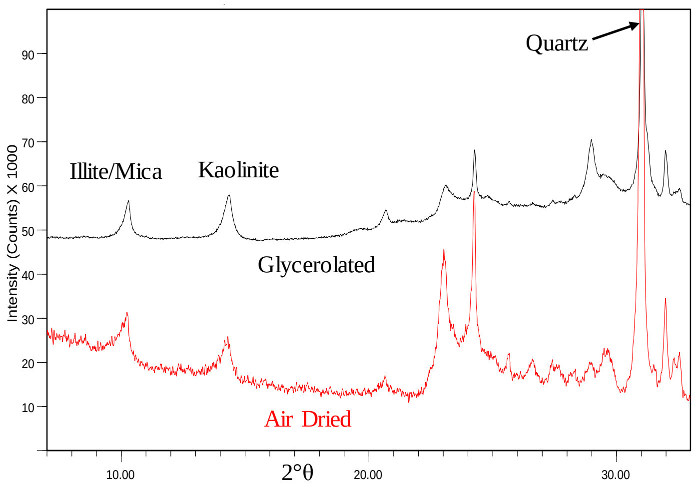


**Figure 41** Air dried and glycerolated XRD patterns of cultivated profile

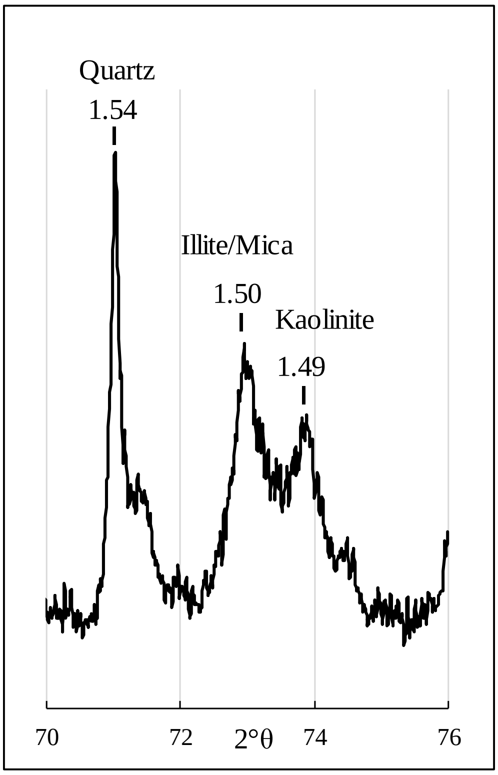


**Figure 42** 060 region of XRD traces for cultivated profile

The integrated areas were multiplied by weighting factors (Biscaye, 1965) and normalized to 100%. Weighting factors used are 0.6 for illite, 1.1 for kaolinite, 3.1 for quartz and 0.7 for potassium feldspar (P. Self, personal communication). Weighting factors vary in detail with operators and XRD machines used, P. Self has worked them out for his system. The results for all 6 profiles (20-30 cm depth) are presented in Table 16.

**Table 16** Quantitative estimation of clay phases

| **Mineral** | **Cultivated** | **Grazing** | **Uncultivated** | **Wine** | **Coniferous tree** | **Deciduous tree** |
|---|---|---|---|---|---|---|
| **Illite** | 37% | 39% | 35% | 35% | 49% | 45% |
| **Kaolinite** | 26% | 27% | 29% | 24% | 29% | 33% |
| **Quartz** | 21% | 22% | 24% | 25% | 15% | 15% |
| **Feldspar** | 16% | 12% | 12% | 17% | 7% | 7% |

Illite and kaolinite were the most abundant clay minerals in all profiles ranging from 49 to 35 % and from 33 to 24 % respectively. The clay assemblages under both coniferous and deciduous trees had the highest content of illite and kaolinite. In order to identify variability of clay assembledges with depth, XRD patterns of cultivated profile for 3 depths were quantified (Figure 43). We observed a gradual increase with depth in illite and kaolinite mineral content at the expenses of quartz and k-feldspar.

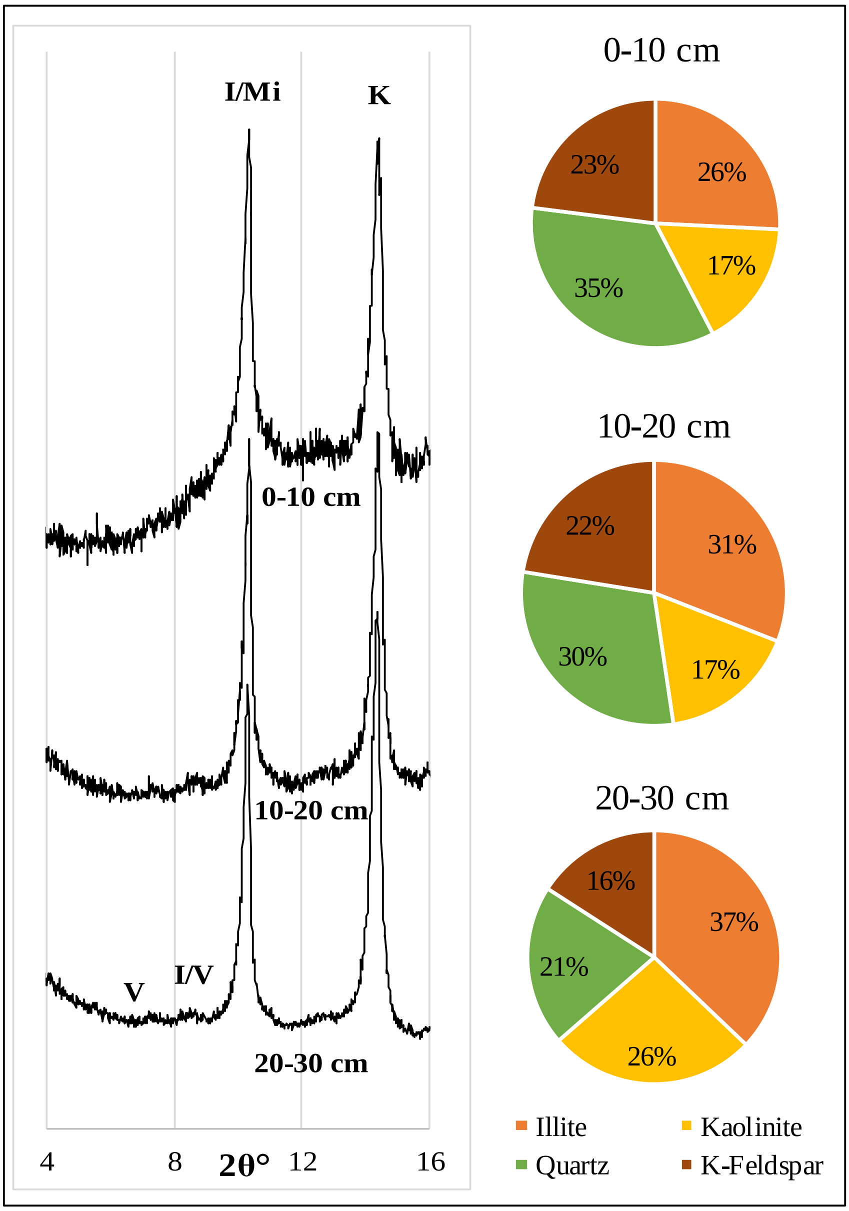


**Figure 43** Variation of clay assembledges with depth for samples from cultivated profile

The results of mineralogical analysis of Urrbrae soil clays from 6 sites with different vegetation regime correspond well with the study of Radoslovich (1951). Both horizontal and vertical variability in clay-mineralogical composition of the studied soil clays were found to be qualitatively homogeneous.

The study was an attempt to clarify the relationship between the clay minerals and different plants. The main part of the work comprised a study of the X-ray diffraction basal peak reflection of clay minerals in Urrbrae soil. These particular reflections are of interest since they characterise the potassium status of particular soil. Even with a range of land treatments Urrbrae soil shows only minor changes in its XRD diagrams. The samples taken from soil under cereal crops and grazing show the presence of vermiculite and mixed layered illite-vermiculite phases, which were not present in clay from uncultivated soil. These minerals derive from Illite which has been completely (in the case of vermiculite) and partially (for illite-vermiculite) depleted of potassium. It is a quite difficult for plants to remove enough K from Illite to show mineral changes. Urrbrae soil does not give a strong XRD effect for the removal of K. The results from XRD alone are not enough to characterise the potassium status of a particular soil.

## The behaviour of Urrbrae soil clay under different rates of potassium application

XRD data analysis of 6 soil profiles from different vegetation regimes has shown variation only in the amount of clay mineral present, with mineralogical composition being the same for all soils: illite, kaolinite, quartz and k-feldspar. During the clay separation procedure, I have noticed that clays from different sampling sites and depth showed varying levels of dispersion. In Chapter 5 I have shown that zeta potential could reflect the dispersive behaviour of soil/clay. Table 17 presents zeta potential measurements for all soil clays studied. Taking into account that the clay mineralogy for all soils was similar, variation in zeta potential could reflect differences in the distribution of exchangeable cations and as a result differences in surface charge.

**Table 17** Zeta potential (mV) for studied soils

| Depth | Cultivated | Grazing | Uncultivated | Wine | Pine | Tree |
|---|---|---|---|---|---|---|
| **0 – 10** | -25 | -40 | -43 | -37 | -38 | -30 |
| **10 – 20** | -29 | -45 | -40 | -46 | -30 | -27 |
| **20 – 30** | -31 | -43 | -41 | -51 | -34 | -27 |
| **30 – 40** | -27 | -44 | -38 | -51 | -40 | -28 |

A. Marchuk in her PhD study (2013) used the same Urrbrae soil from cultivated plots. In laboratory controlled leaching experiments she applied solutions with different amount of potassium. Her results have shown that, as amount of applied potassium increased, the hydraulic conductivity decreased and dispersibility, expressed as turbidity, increased. In this experiment, cation ratio of structural stability index (CROSS) (Rengasamy and Marchuk, A., 2011) was used as the indication of different potassium rates. The cationic composition of solutions applied is given in Table 18. Application of potassium simulated the effects of disposal of common fruit-based wastewaters on this soil, which is a soil type that is widespread in the agricultural regions of South Australia. For my study I have used two treated soils: with

CROSS 6 and 15 solutions applied. For comparison, I have used untreated soil from the same plot. The soil samples after treatment were dried and the clay fraction extracted.

**Table 18.** Cationic composition of treatment solutions expressed as CROSS. After Marchuk A., (2013)

| Treatment | Cations in treatment solutions (mmol$_c$/L) | | | | CROSS |
|---|---|---|---|---|---|
| | **$K^+$** | **$Na^+$** | **$Ca^{2+}$** | **$Mg^{2+}$** | **mol$^{0.5}$m$^{-1.5}$** |
| **1** | 20 | 3.2 | 5.4 | 10 | 6.0 |
| **2** | 30 | 3.2 | 5.4 | 10 | 8.4 |
| **3** | 42 | 3.2 | 5.4 | 10 | 11.2 |
| **4** | 60 | 3.2 | 5.4 | 10 | 15.4 |

## Mineralogical analysis of original and treated clays

The XRD patterns of the < 0.2 µm fractions for original and treated soil clays (‘fine clays’) are shown in Figure 44. As one of the aims of this experiment was to assess the effect of application of solutions with different potassium concentrations on clay minerals, we were particularly interested in establishing the clay mineralogy of the studied soils, and identifying differences in the original clay as well as mineralogical changes after treatment.

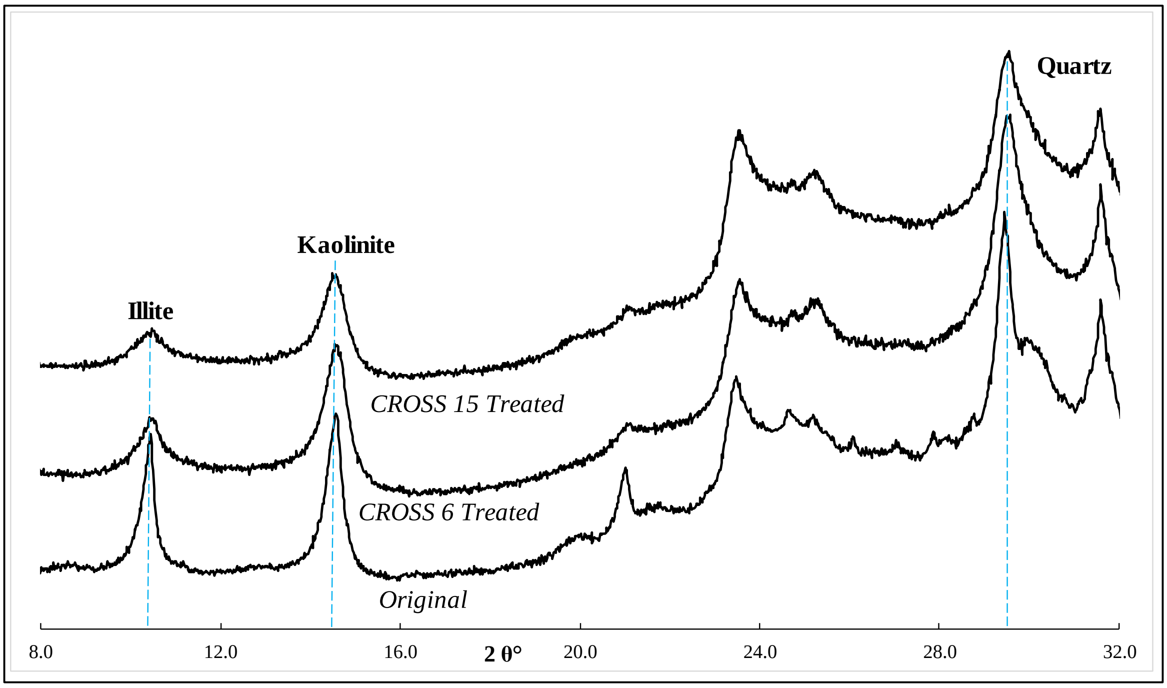


**Figure 44** XRD of Urrbrae soil clays (< 0.2 micron): original and after treatments

The XRD patterns of < 0.2 µm fraction obtained for the orientated, Mg-saturated glycerolated states show diffraction peaks typical of clay minerals, with additional reflections that are attributed to quartz (4.26, 3.34 Å). The rational 001 reflections series at 9.98, 4.99, and 3.34 Å, and at 7.17 and 3.58 Å correspond to discrete illite and kaolinite phases, respectively.

Quantitative assessment of the identified clay phases and their relative abundance are given in Table 19. From the comparison of diffractograms of original and treated soils we could observe a gradual symmetrical broadening of the illite peak with increasing solution concentration (from CROSS 6 to CROSS 15). The broadening of XRD peaks could be due to interlayering and/or a decrease in the size of the diffraction domain (small grain size) (Moore and Reynolds 1997). In our case, as we did not detect expandable clay minerals in any samples, so broadening of XRD peak means a decrease in the grain size of the illitic mineral phase (Velde and Barré 2010).

**Table 19** Quantitative analysis of clay < 0.2 micron fraction

| **Sample** | **Illite** | **Kaolinite** | **Quartz** |
|---|---|---|---|
| Original | 46 | 46 | 8 |
| Treated with CROSS 6 | 45 | 47 | 6 |
| Treated with CROSS 15 | 46 | 47 | 7 |

In order to separate the contribution of various phases to the diffracted intensity Lanson (1992, 1997) developed a decomposition program for X-ray profiles of clay minerals. This decomposition program can fit the experimental XRD pattern with elementary curves that are related to the different phases present in the soil clays. The position and full width at half maximum intensity (FWHM) of these elementary curves should let us identify each associated phase by comparison with simulated patterns (Lanson and Besson 1992). Peak position indicates, for the most part, compositional changes, while FWHM indicates the relative number of layers coherently diffracting in the crystallites. Peak area can be used to indicate the relative proportions of the different clay phases within the same soil/clay type and to quantify modifications in the clay assemblages (in our example – before and after treatments) (Velde *et al*. 2003). Any phase identified with this method will be characterized by a mean value for all these parameters, with the mean values actually representing a population. The major use of decomposition is to identify the peaks present and to compare their relative areas in order to identify changes in mineral abundance and mineral type. This can be done for similar materials which have been subjected to different chemical changes (Velde and Barré 2010).

From all of the clay phases identified (Figure 44) only illite has potassium in its structure and its potential to release and uptake $K^+$ from soil water solution could lead to mineralogical changes of the whole mineral assemblage of a particular soil clay fraction (Reitemeier 1951; Velde and Barré 2010). In our further investigations kaolinite was not considered, because it has a very low cation exchange capacity and little or no potassium in its mineral structure. The decomposition procedure (Lanson 1992, 1997) was applied essentially on the illite 001 reflection region. As recommended by Lanson and Besson (1992), the XRD patterns were decomposed by progressively increasing the number of elementary curves, in order to obtain a good fit with the smallest number of curves. The decomposed patterns for original clay and after the treatments are shown in Figure 45. For the illite phase two peaks are normally present. The narrower 10 Å peak indicates the presence of fully anhydrous interlayer potassium ions, and this phase is called illite (WCI or well crystallized illite). The wider peak at 10.1 Å in general represents the small grained illite material (PCI or poorly crystalized illite), usually of less than 6 units layers thickness (Lanson and Velde 1992; Lanson and Besson 1992; Lanson, 1997).

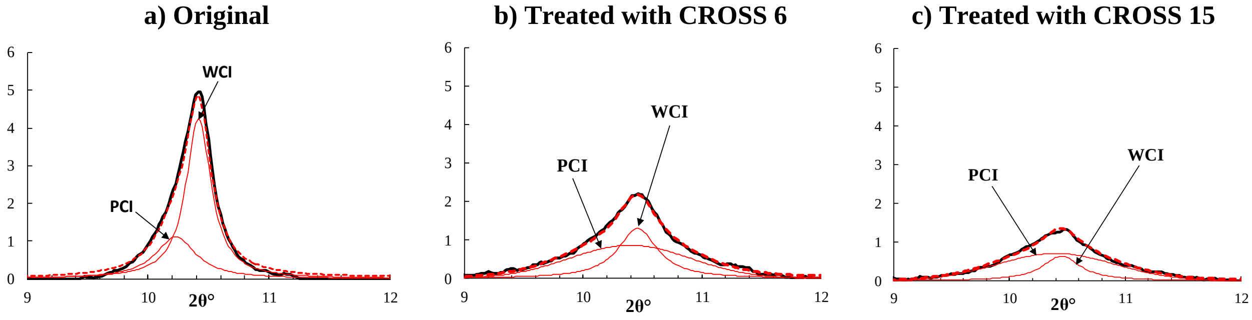


**Figure 45** The decomposed patterns of illite phase for original and treated samples

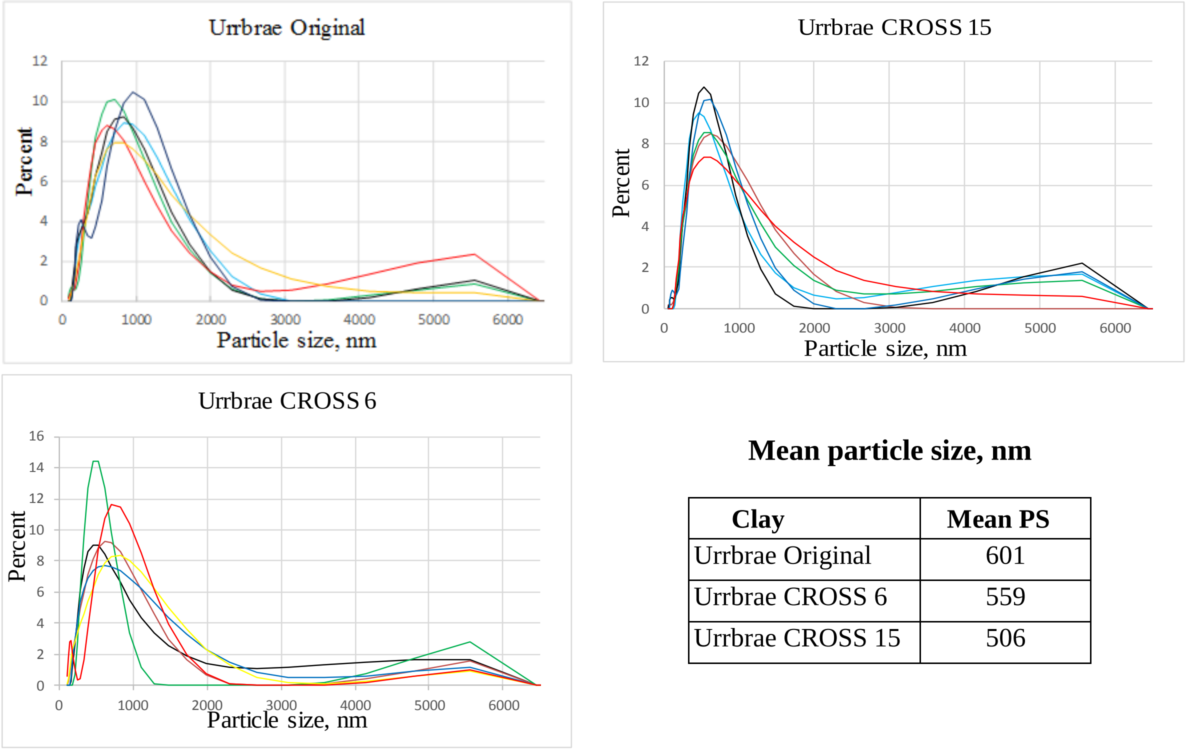
The decomposition of the XRD diagram for the original sample produced 2 basic peaks with maximum intensities at *d* = 10.12 and 9.98 Å (Figure 45a and Table 20). By its position and sharpness, the curve near 9.98 Å was attributed to a mica-like phase (or well-crystallized illite, WCI). The band near 10.1 Å was typical of an illitic mineral (PCI), which was thought to have a finer grain size than the WCI. This is indicated by a broader peak, with a width at half height near 0.41° 2θ against 0.25° 2θ for the WCI phase.

**Table 20** Tabulated decomposition parameters for studied clay samples

| **Sample** | **Phase** | ***d*-sp (Å)** | **FWHM (2° θ)** | **Area** | **%** |
|---|---|---|---|---|---|
| Original | WCI | 9.98 | 0.25 | 98082 | 71 |
| | PCI | 10.1 | 0.41 | 41576 | 30 |
| CROSS 6 | WCI | 9.98 | 0.4 | 47864 | 42 |
| | PCI | 10.0 | 1.2 | 64951 | 58 |
| CROSS 15 | WCI | 9.98 | 0.4 | 23416 | 31 |
| | PCI | 10.0 | 1.2 | 53243 | 70 |

The same illitic phases were identified in treated clays (Figures 45b, 45c and Table 20). The WCI peaks after treatment with CROSS 6 and CROSS 15 solution were constant in peak position (9.98 Å) and FWHM (0.4° 2θ) but the peak area (relative amount of WCI) gradually decreased after the treatment was performed more than twice. The PCI peaks after treatments shifted slightly towards the lower d-spacing (from 10.12 to 10.0 Å) and increased in relative area from 30 % for original sample to 58 and 70% for samples treated with CROSS 6 and CROSS 15 solution respectively. FWHM has changed from 0.41 to 1.2° 2θ after the treatments inferring a decrease in grain size which characterizes the transformation from WCI to PCI (Righi *et al.* 1995; Velde 2001; Barré *et al*. 2008). It seems that an application of potassium rich solution changed the grain size of the illite phase of Urrbrae soil.

Particle size distribution of the studied clays was verified using Zetasizer Nano Malvern® instrument. The Zetasizer system determines the size by first measuring the Brownian motion of the particles in a sample using Dynamic Light Scattering (DLS) and then interpreting a size from this using established theories. According to Pieri *et al*. (2006) and Sandler *et al*. (2015) laser-determined grains of < ~5 µm are equivalent to the clay fraction determined by sedimentation (< ~2 µm). The results obtained are presented in Figure 46. On a graph, each curve represents the particle size distribution for a single run. Each clay sample was run 6 times, each run consisted of an average value of 15 measurements. As could be seen from Figure 46, particle size gradually decreased with increasing amount of potassium applied. The Zetasizer Nano measurements support the XRD data results.



**Mean particle size, nm**

| Clay | Mean PS |
|---|---|
| Urrbrae Original | 601 |
| Urrbrae CROSS 6 | 559 |
| Urrbrae CROSS 15 | 506 |

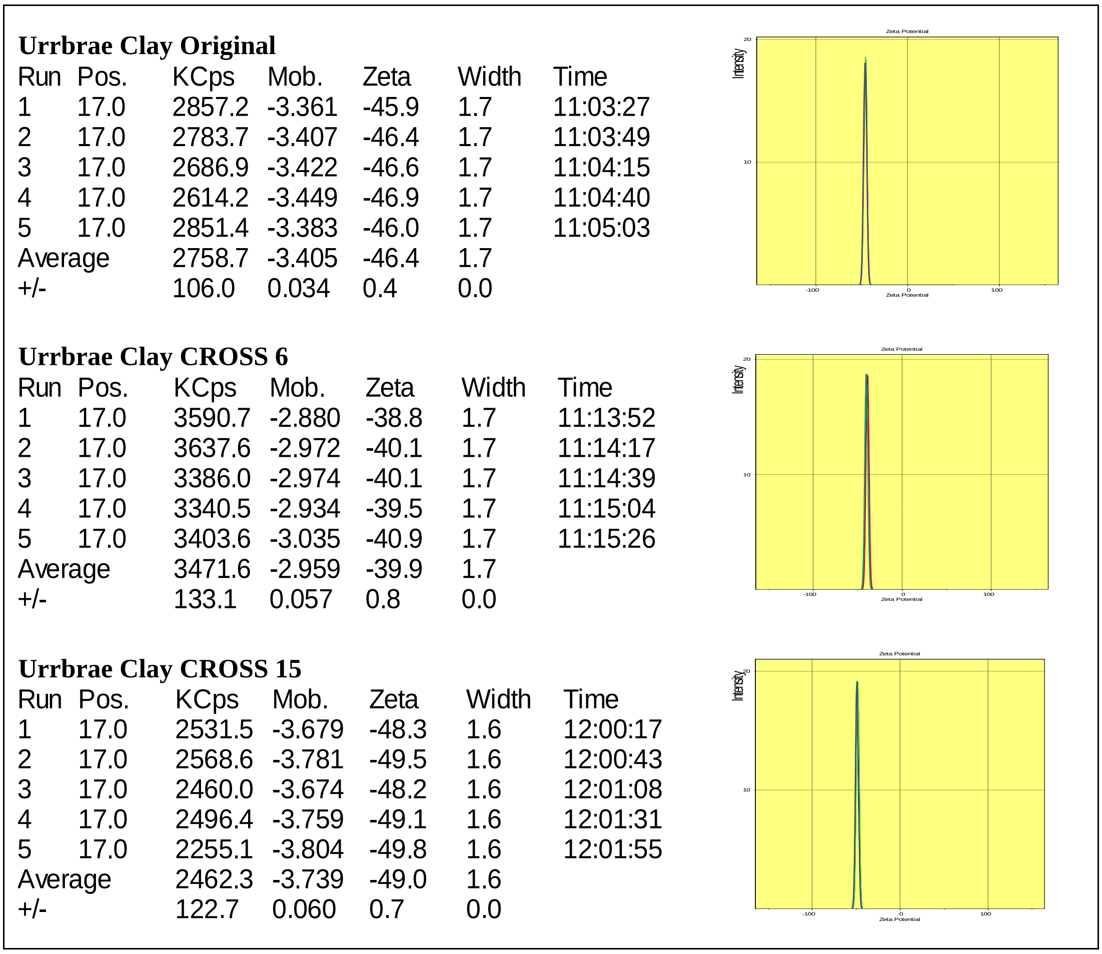
**Figure 46** Particle size distribution (%) and mean particle size (nm) for the studied clays

## Clay chemical properties

Selected chemical characteristics and particle size distributions of the studied clays before and after treatment are given in Table 21 and Figure 47, respectively. Data represent an average of triplicates for all determinations. The original untreated clay has the highest pH, EC and CEC. After each treatment pH gradually decreased. Exchangeable potassium increased after each treatment, as expected.

**Table 21** Analysed chemical properties of clays

| Soils ID | pH | EC, dS/m | Soluble, mg/l | | | | Exchangeable, cmol$_{+}$/kg | | | | CEC cmol$_{+}$/kg |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | Na | K | Ca | Mg | Na | K | |
| **Original** | 7.2 | 0.86 | 14.27 | 0.89 | 152.20 | 20.72 | 14.83 | 1.27 | 3.27 | 3.35 | 22.7 |
| **CROSS 6** | 6.8 | 0.26 | 1.17 | 1.66 | 31.87 | 26.20 | 4.66 | 8.42 | 0.95 | 4.75 | 18.8 |
| **CROSS 15** | 6.6 | 0.31 | 0.93 | 0.97 | 36.43 | 40.68 | 6.13 | 4.59 | 1.30 | 9.97 | 19.0 |



```
Urrbrae Clay Original
Run  Pos.     KCps    Mob.    Zeta    Width   Time
1    17.0     2857.2  -3.361  -45.9   1.7     11:03:27
2    17.0     2783.7  -3.407  -46.4   1.7     11:03:49
3    17.0     2686.9  -3.422  -46.6   1.7     11:04:15
4    17.0     2614.2  -3.449  -46.9   1.7     11:04:40
5    17.0     2851.4  -3.383  -46.0   1.7     11:05:03
Average       2758.7  -3.405  -46.4   1.7
+/-           106.0   0.034   0.4     0.0

Urrbrae Clay CROSS 6
Run  Pos.     KCps    Mob.    Zeta    Width   Time
1    17.0     3590.7  -2.880  -38.8   1.7     11:13:52
2    17.0     3637.6  -2.972  -40.1   1.7     11:14:17
3    17.0     3386.0  -2.974  -40.1   1.7     11:14:39
4    17.0     3340.5  -2.934  -39.5   1.7     11:15:04
5    17.0     3403.6  -3.035  -40.9   1.7     11:15:26
Average       3471.6  -2.959  -39.9   1.7
+/-           133.1   0.057   0.8     0.0

Urrbrae Clay CROSS 15
Run  Pos.     KCps    Mob.    Zeta    Width   Time
1    17.0     2531.5  -3.679  -48.3   1.6     12:00:17
2    17.0     2568.6  -3.781  -49.5   1.6     12:00:43
3    17.0     2460.0  -3.674  -48.2   1.6     12:01:08
4    17.0     2496.4  -3.759  -49.1   1.6     12:01:31
5    17.0     2255.1  -3.804  -49.8   1.6     12:01:55
Average       2462.3  -3.739  -49.0   1.6
+/-           122.7   0.060   0.7     0.0
```

**Figure 47** Zeta potential measurement as it shown on Malvern Zeta master instrument

A decrease in CEC after treatments could partially be explained by the presence in studied soils of clay minerals – kaolinite and illite - with substantial pH dependable variable charge (Chorom and Rengasamy 1995). The second factor is a fixation of potassium by illite. The most important K-bearing minerals are K-feldspar (3-12% K) and mica (biotite, 5-8% K; muscovite, 6-9% K). Weathering of primary K-bearing minerals is associated with the release of $K^+$. The minerals formed during the weathering of micas correspond with the following sequence (Schroeder, 1976): mica (~10% K) → hydromicas (6 to 8% K) → illite (4 to 6 % K). The illite in soil clays certainly have the capacity to fix potassium. As potassium becomes fixed by clay minerals, the cation exchange capacity decreases.

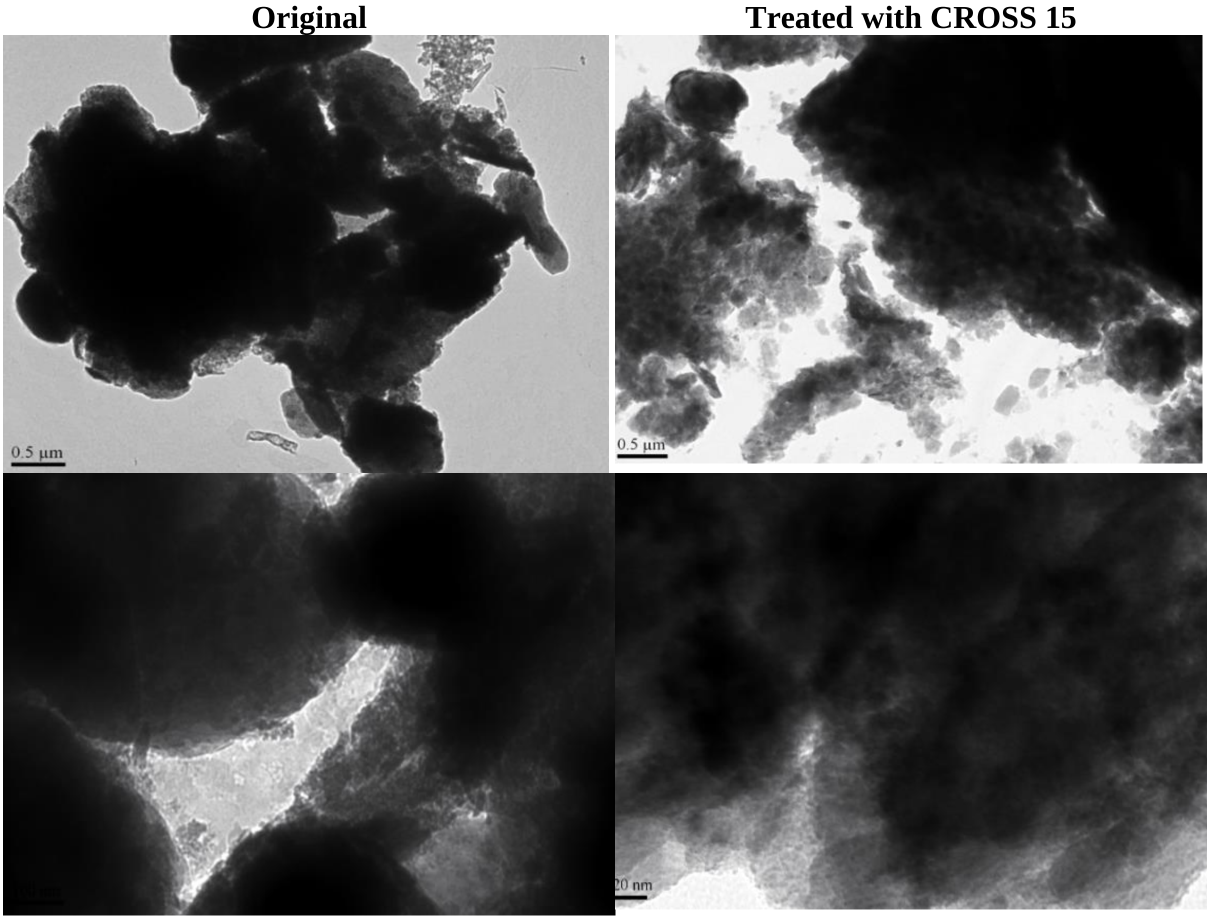
In the case of the Urrbrae soil we are dealing with illitic/kaolinitic soil with exchange complexes located on the outer surface of phyllosilicates. As a monovalent cation, applied potassium exchanges with monovalent sodium first. As we could see from the data presented in Table 22, after CROSS 6 treatment, the $Ca^+$ and $Mg^+$ cations occupied 70% of exchangeable sites (before treatment – 71%). Potassium displaced sodium, changing Na/K ratio from 0.93 to 0.2. However, the potassium dispersive potential is lower than that of sodium and we observe an increase in zeta potential (from – 46.4 to -39.9). This increase reaches a maximum when all available exchange sites previously occupied by sodium are now occupied by potassium. As the exchange reaction continues and the concentration of potassium increases (CROSS values increase) potassium cations now displace magnesium (first) and then calcium cations. In doing so, “dispersive” potasium cations displace “floculating” magnesium and calcium cations. And we observed, a steady decrease in zeta potential (till -49.0) occurred until exchange reactions reached their equilibrium.

**Table 22** Zeta potential and cationic composition in % of studied clays

| Clay ID | Zeta potential, mV | Exchangeable cations, % base saturation | | | | Ca + Mg, % | Na + K, % |
|---|---|---|---|---|---|---|---|
| | | Ca | Mg | Na | K | | |
| Original | -46.4 | 65% | 6% | 14% | 15% | 71 | 29 |
| Treated CROSS 6 | -39.9 | 25% | 45% | 5% | 25% | 70 | 30 |
| Treated CROSS 15 | -49.0 | 32% | 24% | 7% | 37% | 56 | 44 |

## TEM Study

The nature of clay particle associations for original and CROSS 15 treated soils were also examined by transmission electron microscopy (TEM). TEM observations of the effect of applied potassium in a CROSS 15 solution on clay fabric are presented in Figure 48. The untreated clay particles show discrete, rounded clay aggregates (the boundary between particles is clear). Potassium enrichment resulted in formation of a dense continuous network of very fine clay particles with a cloud-like appearance. And at higher magnification the differences – the dispersive effects of adsorbed $K^+$- are seen. The TEM image of a treated sample shows that the clay particles dispersed and have formed a rougher surface. By contrast the original sample shows that the clay particles are flocculated and have formed a coarser granular structure.



**Original** **Treated with CROSS 15**

**Figure 48** TEM images of Urrbrae Clay fraction (<0.2 micron) before and after application of CROSS 15 solution

Results obtained in this experiment show how application of potassium could change soil physical and chemical properties. There is an indication that at low levels of potassium soil structure may not be affected. TEM and XRD methods could compliment a better understanding of the processes occuring in soil.

# Chapter 7. Possible effects of irrigation with wastewater on the mineralogy of some Australian clayey soils: laboratory study

## Statement of Authorship

| | | | |
|---|---|---|---|
| Title of Paper | Possible effects of irrigation with wastewater on the clay mineralogy of some Australian clayey soils: laboratory study | | |
| Publication Status | ☐ Published<br>☐ Submitted for Publication | ☑ Accepted for Publication<br>☐ Unpublished and Unsubmitted work written in manuscript style | |
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### Principal Author

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| Name of Principal Author (Candidate) | Serhiy Marchuk | | |
| Contribution to the Paper | Performed all analysis, interpreted data, wrote manuscript and acted as corresponding author | | |
| Overall percentage (%) | 70% | | |
| Certification: | This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper. | | |
| Signature | | Date | 17/11/2015 |

### Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

the candidate's stated contribution to the publication is accurate (as detailed above);

permission is granted for the candidate in include the publication in the thesis; and

the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

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| Name of Co-Author | Jock Churchman | | |
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| Signature | | Date | 17/11/2015 |

Please cut and paste additional co-author panels here as required.

# Abstract

Potassium is common in a wide variety of wastewaters and in some wastewaters is present at several hundred to several thousand mgL$^{-1}$. Potassium is taken up by expandable clays leading to its fixation and illitisation of smectitic and vermiculitic layers. Hence the addition of wastewaters to soils may lead to mineralogical changes in the soils that affect their physico-chemical properties.

Winery wastewater was equilibrated with some clayey soils from Southern Australia. XRD patterns and chemical composition of clays extracted from untreated and treated soils were determined. In 3 of the 4 soils, shifts in peak positions occurred towards more illitic components along with increases in K and sometimes also Mg and Na contents of soil clays. Peak decomposition showed trends towards the formation of interstratifications of illite with smectite at the expense of smectite and an alteration of poorly-crystallised illite into its more well-ordered forms. The results show that illitisation may occur as a result of the addition of K-rich wastewaters to clayey soils.

# Introduction

As demand for fresh water intensifies, wastewater is frequently being seen as a valuable resource for irrigation. An attractive property of reclaimed wastewater is its potential fertilizing capacity. On the other hand, the high concentrations of nutrients in wastewater can be problematic to agriculture and the environment (Hamilton et al. 2007).

Potassium is ubiquitous in wastewaters and in some wastewaters is present at several hundred to several thousand mgL-1. A wide variety of wastewaters contain potassium (Table 23). Potassium accumulation in soils is seen by industry and regulators as a potential problem because of the effects it might have on salt accumulation and soil structure. These effects are unclear at present because there have been very few relevant studies (Arienzo et al. 2009).

Potassium ions are strongly retained by expandable clay minerals such as smectites and vermiculites (Volk 1934; Levine and Joffe 1947; Reitemeier 1951; Barshad 1954; Mortland *et al.* 1956**;** Richards and Mclean 1963; Sparks and Huang 1985, amongst many others). Smectites and vermiculites are common components of many soils where they occur as single mineral phases or in interstratifications with layers of other minerals such as illite/mica and kaolinite (Norrish and Pickering 1983). The uptake of $K^+$ by these minerals often leads to its 'fixation' within the interlayer region of the expandable layers.

**Table 23** Potassium and sodium concentration in municipal and agricultural wastewater (Arienzo et al., 2009)

| **Water Source** | **K concentration, (mgL-1)** | **Na concentration (mg L−1)** |
|---|---|---|
| Cheese whey | 1,680 | n.d.* |
| Lactic/casein whey | 1,660 | n.d. |
| Slaughterhouse | 90 | n.d. |
| Fellmongery | 50 | n.d. |
| Meat processing | 20–150 | 50-250 |
| Dairy shed | 220 | 50 |
| Piggery | 500–1000 | 320 |
| Winery | 250 | 130 |
| Olive oil processing | 10,000–200,000 | 160-400 |
| Palm oil processing | 2,100 | 80-120 |

* not determined

Smectite íllitization has been well observed and documented in diagenetic series, hydrothermal environments, in bentonite beds, or in a contrast metamorphism context (see Lanson and Champion, 1991 and Meunier and Velde, 2004 for a summary). But this transformation in upper soil horizons of soils occurs under completely different environmental conditions – under lower temperature and pressure. In terms of our investigation we define illitisation as a pedogenetic process, resulting in the fixation (reversible or partially reversible) of applied potassium in the interlayer space of expandable minerals. This newly formed illite or illite-like mineral phase is likely to be different from native illite already present in the profile. Illitisation in soils can occur in a short time interval (Barré at al. 2008). Hence it is likely that the application of potassium rich wastewaters to soils may lead to mineralogical changes in the soils that affect their physico-chemical properties.

Powder X-ray diffraction remains the standard technique of clay mineral identification (Środoń 2006; Barré *et al.* 2007a). Recent progress in X-ray diffraction techniques and X-ray data processing give us the ability to deal with complex overlapping reflections with a variety of computer-based programs, including Rietveld analysis, whole pattern fitting and decomposition, allowing us to observe even subtle modifications in clay minerals (Barré *et al.* 2007b). Because the clay fractions in soils are complex mixtures of different clay mineral phases, including mixed-layer minerals, their characterisation is generally a difficult task. These mixtures exhibit complex XRD reflections combining several poorly resolved maxima (Righi and Elsass 1996). Significant recent progress in understanding of the illite-smectite fundamental particles and interpretation of diffractograms (Lanson 1997; Moore and Reynolds 1997) that has occurred in the past decades, has allowed mineralogists to numerically analyse complex reflection groups which are commonly present in the X-ray diffraction diffractograms of soils (Barré *et al.* 2007a).

Given the fact that the quality of X-ray diffraction equipment has also made great advances in the last three decades, we can now study un-treated soil clay samples. In particular, it has been found that the destruction of organic matter can significantly change the observed clay mineralogy of prairie type soil clay materials (Velde 2001). We can now observe the clay minerals actually present in the soil, with their properties which are important for plant-soil interactions (Barré *et al.* 2007a). Some recent studies by Li *et al.* (2003), Barré *et al.* (2007a, b, 2008) and Velde and Barré (2010) demonstrated that K fixation or release in a soil clay fraction dominated by 2:1 clay minerals could be observed and quantified through X-ray diffraction measurements.

Until now, no attempt has been made to quantify the changes in clay minerals induced by wastewater irrigation. The aim of this work was to determine whether irrigation with wastewater high in potassium could change the clay mineral assemblage of soils and hence how it could influence soil properties that are important for irrigation.

## Materials and methods

### Soil and wastewater used

Four soils were used in this laboratory study, namely Barossa (SA) Red Brown Earth, Charlton (Vic.) Red Sodosol, Claremont series Black Vertosol, Waite Research Institute (Adelaide, SA) and Renmark (SA) Grey Vertosol.  Soil samples were collected from the 0.20–0.40m depth (where clay content is relatively high and organic matter content is low) by a hand auger, air-dried, and sieved to 2mm. Location, coordinates, soil particle size distribution (Gee and Bauder 1986), soluble and exchangeable cations (Rayment and Lyons 2011), and clay mineralogy are presented in Table 24. These soils were selected because of the range that they represent in their texture, clay mineralogy, EC, and pH. The wastewater used was from a Barossa Valley winery (Table 25).

### Experimental design

100 g of each soil was fully saturated with an appropriate volume of wastewater and allowed to equilibrate for 48 hours at room temperature. Then soils were placed into an oven and dried at 60° C for 48 hours. The procedure was repeated 6 times in order to simulate the irrigation

cycle over one season. The chemical and physical properties of treated soils were analysed and compared with original soils.

**Table 24** Selected physical and chemical properties, main clay minerals, classification, and location of the soils used

| Soil properties | Units | Soil | | | |
|---|---|---|---|---|---|
| | | **Red Brown Earth[1]** | **Red Sodosol[1]** | **Black Vertosol[1] Claremont series** | **Grey Vertosol[1]** |
| Depth | cm | 20-40 | 20-40 | 20-40 | 20-40 |
| pH (1:5 soil/water) | | 7.8 | 8.0 | 7.8 | 5.4 |
| EC (1:5 soil/water) | dS/m | 0.11 | 0.06 | 0.15 | 6.39 |
| CEC | cmol$_+$/kg | 21.5 | 30.7 | 32.0 | 30.0 |
| Texture | | Clay | Clay | Clay | Clay |
| Particle size distribution, % | Clay | 43 | 63 | 56 | 63 |
| | Silt | 14 | 12 | 17 | 20 |
| | Sand | 44 | 25 | 28 | 18 |
| Dominant Clay Minerals | | Illite, Kaolinite | Illite, Kaolinite | Smectite | Smectite |
| Location in Australia | | Greenock, Barossa Valley, SA | Near Charlton, Vic | Waite Institute, Adelaide, SA | Pike River, near Renmark, SA |
| Coordinates | | 34°27’49.67”S<br>138°56’08.72”E | 36°15’34.39”S<br>143°19’13.63”E | 34°58’20.64”S<br>138°38’12.26”E | 34°13’37.68”S<br>140°46’46.65”E |

[1] Australian Soil Classification (Isbell, 1996)

**Table 25** Chemical characteristics of the wastewater used in this study

| pH | EC, dS/m | Soluble cations, mg/L | | | |
|---|---|---|---|---|---|
| | | $K^+$ | $Na^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
| 8.4 | 0.865 | 250 | 42 | 36 | 7 |

## Soil clay preparation

In order to improve the identification of the mineralogical composition of the soils by XRD analysis, clay fractions were separated by sedimentation (Jackson 2005). Firstly, 5 g of the sieved soil from each sample was mixed with 150 ml of deionised water and disaggregated by using a RATEK orbital mixer with a speed of 120 rpm for 16 hours. Then soil/water suspensions were transferred into 1 L glass cylinders with addition of deionised water to the required level. The height of the soil/water column (19 cm) was calculated by means of Stokes’ Law to give the settling time (at 16 hours) required for settling particles ≥ 2 μm. The cylinders were then allowed to stand, and after 16 hours of settling the clay fraction (< 2 μm) was isolated from soil by siphoning off the dispersed material. The procedures of adding water, stirring, allowing settling, and siphoning were carried out for a total of 6 times, and the clay suspensions thus obtained were combined. The suspensions containing < 2 μm clay fraction were transferred into a 5 L beakers and oven-dried at 60ºC. No addition of dispersing agents or chemical treatments (such as for organic matter or oxide removal) were made to the clay samples, because we wanted to specifically investigate the soil clays as they would respond to cations in wastewater in their natural state. Such factors as cation exchange capacity and potassium fixation can only be understood in the context of the natural sample (Velde and Peck 2002).

## X-Ray diffraction (XRD) analysis of the silt and clay fractions

Dry clay samples (<2 µm fraction) were finely ground and backfilled into steel holders for XRD analysis. The XRD patterns for randomly oriented air-dried (AD) and orientated, Mg saturated-glycerolated (G) samples were recorded with a PANalytical X'Pert Pro Multi-purpose diffractometer using Fe filtered CoKα radiation, automatic divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded from 3 to 80° 2θ (for randomly oriented samples) and from 3 to 33° 2θ (for orientated, Mg saturated-glycerolated samples) in steps of 0.017° 2θ with a 0.5 second counting time per step for an overall counting time of approximately 30 minutes.

XRD data were collected and displayed using CSIRO software XPLOT for Windows (Raven 1990). Mineralogical phase identifications were first made by comparing the XRD patterns with the ICDD database of standard diffraction patterns using computer aided search/match algorithms. Specific clay mineral identification criteria were based on Brindley and Brown (1980) and Moore and Reynolds (1997). Only reflections for crystalline minerals were considered in these analyses. Information about the dioctahedral/trioctahedral structure of the clay minerals was obtained by examination of the 060 reflections of randomly oriented samples. The XRD diffraction patterns were recorded as intensity-position counts and hence could be treated numerically using curve decomposition methods given in Lanson and Besson (1992) and Lanson (1997). Simulated diagrams made with the NEWMOD program of Reynolds (1985) were also used to help interpretation of experimental XRD diagrams.

## XRD pattern decomposition to obtain the clay mineral assemblages

Because of the coexistence of several clay minerals in the same sample, X-ray diffraction patterns most often contain partially overlapping peaks representative of mixed-layered illite/smectite, vermiculite, illite, mica, and occasionally chlorite. The separation of the contributions from these different phases is essential for soil clay characterization (Lanson and Velde 1992). The problem of overlapping XRD peaks occurs over the whole angular range. The complex peak located between 4° and 10° 2° θ CoKα appears to be the most interesting: 1) because of its high intensity; 2) because of the presence there of reflections due to all the illitic and smectitic phases and only these phases; 3) and because of the availability of some critical information (e.g., broad coherent scattering domain size) (Lanson and Besson 1992). It was only near 4° to 10° 2° θ that areas were considered due to the greater intensities of these peaks and to fewer problems of interference of the other phases with higher order I/S reflections. Also, the effect of the coherent scattering domain size (CSDS) on pattern width and position is greater here, which gives additional information concerning the changes in clay assemblages (Lanson and Champion 1991).

Lanson (1992) developed a decomposition program for X-ray profiles of clay minerals that enables the separation of the individual contributions of various phases to the diffracted intensity. This decomposition program can fit the experimental XRD pattern with elementary curves that are related to the different phases present in the soil clays. The position and full width at half maximum intensity (FWHM) of these elementary curves should let us identify each associated phase by comparison with simulated patterns (Lanson and Besson 1992). By running a large series of tests, Lanson (1990) demonstrated that the standard deviation on curve characteristics is induced mostly by the experimental equipment and that the calculated characteristics are representative of the sample studied (Righi and Elsass 1996).

Prior to decomposition, digitized XRD data were treated using a 4-point smoothing routine and a background stripping in the low-angle region (4 – 10° 2θ) using the default options of Decomp software (Lanson 1997). As recommended by Lanson and Besson (1992), the XRD patterns were decomposed by progressively increasing the number of elementary curves, in order to obtain a good fit with the smallest number of curves. Each elementary curve corresponds to a clay mineral population simulated using NEWMOD software (Reynolds, 1985). The quality of fit is evaluated visually and assumed to be good when the fitted profile, which is the sum of all the elementary peaks, is located within the noise of the smoothed experimental data over complete angular range fitted (Lanson and Velde, 1992). In the decomposition process, FWHM (in 2° θ) and intensity are obtained and are used to determine peak areas which are compared on a scale of 100% for the total of the peak areas investigated (Velde and Peck 2002).

The major use of decomposition is to identify the peaks present and to compare their relative areas in order to identify changes in mineral abundance and mineral type. This can be done for similar materials which have been subjected to different chemical changes (Lanson and Velde 1992; Velde 1995; Velde and Barré 2010).

## Interpretation of the decomposed XRD patterns

According to Barré et al. (2007a) the different peaks obtained from the decomposition were attributed to clay mineral populations based on the observations of Moore and Reynolds (1997), Righi and Elsass (1996) and Velde (2001).

Illite-mica was identified by a single asymmetric peak near 10 Å. The presence of an asymmetric diffraction peak near *d* = 10 Å was always part of the initial observations on illites made using XRD techniques. The asymmetry is caused by the presence of both poorly crystallized illite and well crystallized illite components in the diffraction spectra and also, at times, I/Sm mixed layer minerals (Meunier and Velde, 2004). According to Gharrabi et al. (1998) the poorly crystallized illite (PCI of Lanson) would be a highly illitic phase with some (< 5%) smectite layers, while the well-crystallized illite (WCI) would be pure illite. As pointed out Lanson (1997), when using Decomp, the separation of two peaks, one associated with PCI and the other with a WCI, does not imply the actual existence of two distinct illitic phases. Both peaks may be related to the same illite phase, and are then a simplified way of describing a complex population of illite crystallites (Lanson and Velde 1992). Even though such an asymmetric peak fit is artificial, various elementary peaks may be easier to interpret than by use of an asymmetry coefficient (Lanson, 1997). The PCI peak has a greater width at half-height than that for WCI (about 0.9° vs 0.4° 2θ), and a 10.3 – 10.5 Å spacing whereas WCI has a spacing near 10.0 Å. The WCI and PCI peaks did not change position significantly with glycol or glycerol treatment. In the 5 Å region they form one band at *d* = 5.01 Å (Figure 49), using the simulation methods of Reynolds (1985) for micas of different coherent domain sizes (Velde and Peck, 2002).

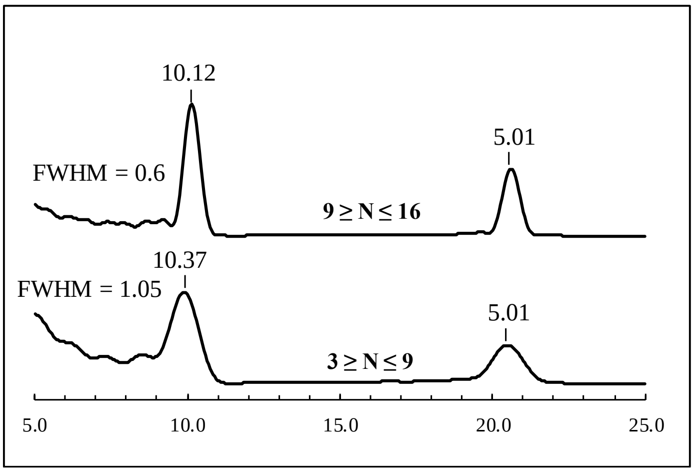


**Figure 49** Calculated X-ray powder diffraction patterns of illite with different domain size (N) using NEWMOD (Reynolds, 1985). N denote coherent domain size. Cobalt Kα radiation

The peaks with spacings ranging from *d* = 11.5 to 15 Å in AD state were attributed to illite-smectite mixed layer minerals. These peaks show widths of 1.5 to 2° 2θ. Such peaks are well modelled by a disordered arrangement of bi-hydrated smectite layers (15.2 Å spacing) and un-hydrated illite layers (10 Å) using the program "NEWMOD" (Moore and Reynolds 1997). Figure 50 shows NEWMOD (Reynolds, 1985) calculated patterns for random (R0) and ordered (R1) illite-smectite interstratified minerals with different Illite/smectite content and their peak positions have been assumed to depend on the proportion of illite and smectite layers. Most soil clay minerals have a disordered, or non-ordered, succession of layers of the different components (Velde and Barré, 2010). In the majority of cases peaks for mixed-layered smectite-illite phases will have a position *d* between 10 and 15.2 Å. Figure 51 indicates the change in peak position for changes in the content of illite relative to smectite (after Velde and Barré 2010). Calculations were made using the NEWMOD (Reynolds, 1985) program.

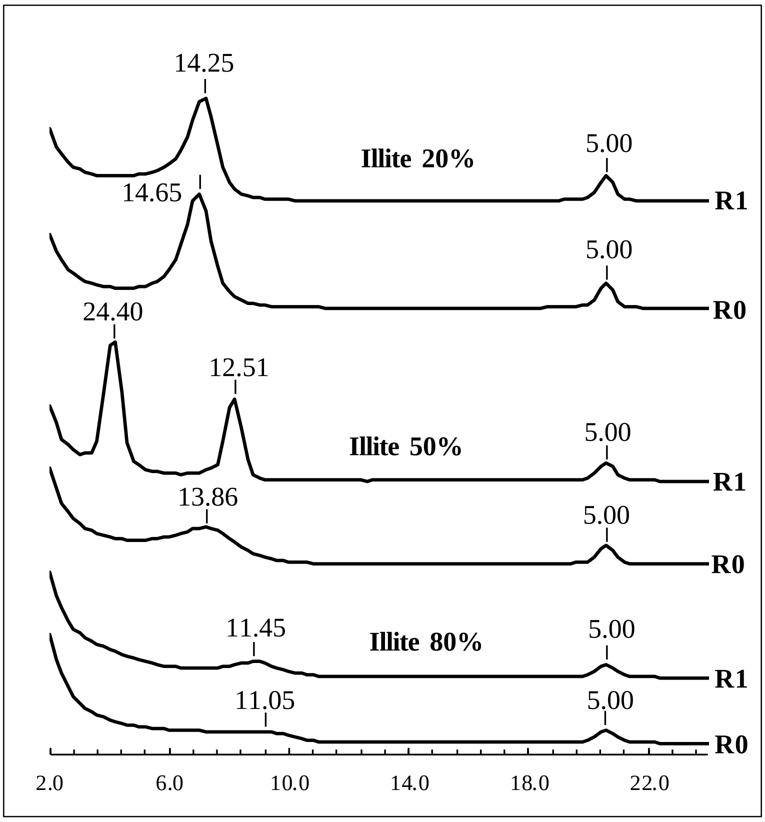


**Figure 50** Calculated X-ray powder diffraction patterns of mixed-layer illite/smectite (I/S) with different expandability and Reichweite (R) ordering using NEWMOD (Reynolds, 1985). Cobalt Kα radiation

This method is not precise near the illite end-member (<10% smectite) composition, as shown by Lanson and Velde (1992) because the I-S peak position varies only slightly for <10% smectite content. However, this method is used in the present study as a simple approach to an as yet unsolved problem of accurate identification of mineral composition of illite-smectite phases in the very low expandable phase range. The method has the merit of being internally consistent, i.e. band shifts indicate relative change (Gharrabi and Velde, 1995).

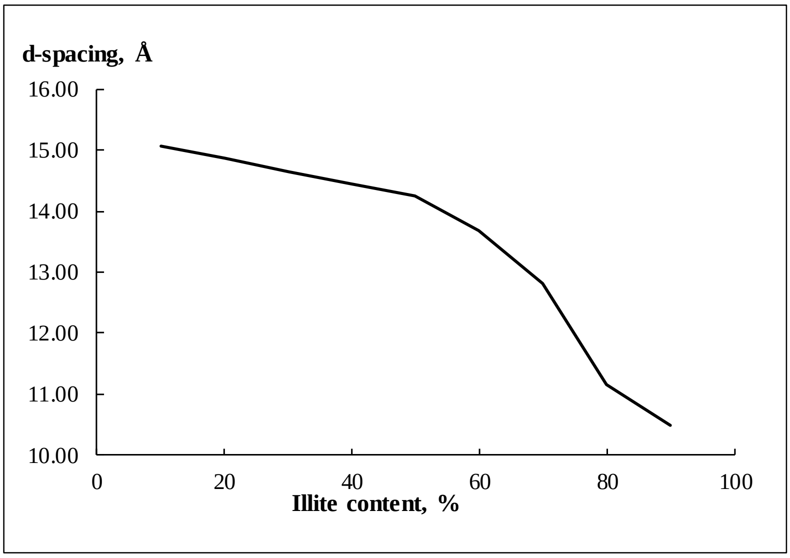


**Figure 51** Relations of peak position in Å and illite content in randomly (R0) interstratified illite-smectite minerals. Calculations were made using NEWMOD (Reynolds, 1985) for randomly oriented XRD patterns in air dried state. Cobalt Kα radiation (After Velde and Barre, 2010)

In order to compare the illite–smectite relations of the sample under different treatments Barré et al. (2007b) used a unique parameter devised from the values calculated by the decomposition program so as to compare them globally and easily. We used the centre of gravity (cg) of the X-ray patterns, a position whose calculation allows all the modifications observed in the X-ray pattern (peak area modifications as well as peak position shifts) to be taken into account. The cg position could be easily calculated as follows:

$$cg = \Sigma\ (ai*posi/\Sigma ai)$$

where ai is the area (FWHM x intensity) of the peak i and posi is the position (d-spacing) of the peak i in Å.

The X coordinate of the centre of gravity of the diffractograms (2θ° or d-spacing axis) could be considered as indicator of the observed modification in clay mineral composition. An increase of the quantity of illitic phases in the clay assemblage should decrease the X-coordinate value (in Å) of the centre of gravity whereas an increase of smectitic or HI vermiculite layers should increase this value (Barré et al. 2007a).

## Spontaneous dispersion and turbidity measurements

Spontaneous dispersion was assessed by a modification of the method described by Rengasamy (2002b) and Marchuk, A. (2013). Firstly, soluble salts were removed from all soil samples using dialysis against deionised water until free of chloride by the method described in Churchman and Weissmann (1995). Chloride in solution was verified using silver nitrate and dialysis was continued until its addition lead to no further white precipitate of silver chloride. Following completion of dialysis, the conductivity of the dialysate was below 50 µS/cm and soil samples were dried at room temperature.

For dispersion measurement original and treated dry soil samples (20g) were placed into 250 ml transparent measuring cylinders and 200 ml of distilled water was added slowly down the sides of the cylinders, taking care to avoid disturbance of the soil. After approximately 5 hr, any particles which had dispersed from the soils were gently stirred into suspension and left to stand for 2 hours. 50 ml of suspensions were pipetted out from 10 cm depth for turbidity measurements. After turbidity measurement the samples were air-dried and weighted.

To quantify the amount of < 2µm particles dispersed, measurements were made on a Hach 2100N Laboratory Turbidimeter at 25°C and recorded in Nephelometric Turbidity Units (NTU). A standard suspension of Formazin was used to calibrate the instrument. The 2100N is equipped with a stable halogen-filled, tungsten filament lamp to meet the reporting requirements of EPA Method 180.1(ASTM 1976,Eaton and Franson 2005). The method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher is the turbidity.

## Determination of chemical composition of the clay fraction

The chemical composition of the clay fraction was measured by inductively coupled plasma mass spectrometry (ICP-MS) (ELAN 6000, Perkin Elmer) after acidic digestion in a microwave oven (Multiwave, 3000 Anton Paar). Prior to digestion soluble and exchangeable cations were extracted using 1M $NH_4Cl$. After extraction samples were dried in an oven at 105°C for 48 hours and finely ground. Samples were weighed to 0.2±0.001g and 9ml of 37% HCl and 3ml of 70% HNO3 added to each sample, using a Dispensette®. Samples were microwave digested using a Multiwave 3000 microwave oven for 40 minutes at 1200W. After digestion the samples were filtered using 0.45 µm PVDF syringe filters and made up to 50ml volume using analytical grade water. Each sample run was replicated three times. After being digested the samples were analysed by ICP-MS. With the ICP-MS analysis seven standards were run first to ensure that the readings were correct. This analysis allowed us to determine mineral Al, Fe, Ca, Mg, K, Na and Mn concentrations of the clay fraction.

# Results and discussion

## Soil chemical properties

The chemical composition of the wastewater used for treatment (Table 25) indicates that, of the four major cations, potassium was the most abundant, with sodium second. Usually, salinity in wastewater relates to $Na^+$ concentrations, but in winery wastewater $K^+$ tends to be the dominant major cation (Arienzo at al. 2012).

Selected chemical characteristics of the soils before and after treatment are given in Table 26. The original Renmark Grey Vertosol had the highest EC and lowest pH compared to the Barossa, Charlton and Waite Claremont soils. The effect of treatments on soil pH was not consistent. Soil salinity, measured as electrical conductivity in 1:5 soil/water solution, increased significantly for all soils after wastewater treatment. This increase was expected as we applied saline wastewater (EC=0.865 dS/m, Table 25) during the experiment. The exchangeable potassium pool for all soils after the treatment was 2.5 times greater than in the original samples.

**Table 26** Selected soil properties

| **Soil** | **pH** | **EC, (dS/m)** | **K sol mg/l** | **Exchangeable cations, ($cmol_+/kg$)** | | | | **CEC, ($cmol_+/kg$)** |
|---|---|---|---|---|---|---|---|---|
| | | | | **Ca** | **Mg** | **Na** | **K** | |
| Barossa original | 7.8 | 0.11 | 2.1 | 15.1 | 4.8 | 1.0 | 0.6 | 21.5 |
| Barossa treated | 7.5 | 0.39 | 9.9 | 15.0 | 4.4 | 1.2 | 1.5 | 22.0 |
| Charlton original | 8.0 | 0.06 | 5.2 | 15.6 | 13.0 | 0.7 | 1.5 | 30.7 |
| Charlton treated | 8.1 | 0.33 | 14.9 | 15.6 | 11.6 | 1.3 | 3.8 | 32.3 |
| Claremont original | 7.8 | 0.15 | 2.1 | 22.3 | 8.0 | 0.1 | 1.0 | 31.4 |
| Claremont treated | 8.5 | 0.35 | 14.5 | 22.9 | 5.8 | 0.5 | 2.8 | 32.0 |
| Renmark original* | 5.4 | 6.39 | 15.3 | 13.5 | 9.1 | 6.7 | 0.8 | 30.0 |
| Renmark treated* | 6.9 | 7.95 | 71.0 | 17.2 | 9.9 | 6.3 | 1.9 | 35.3 |

* Renmark soil was not included in further investigation (see Mineralogical Analysis section for the explanation)

CEC for Barossa and Charlton soils increased slightly after the treatment. Table 27 shows the chemical properties of clay fractions of investigated soils. Increase in CEC after wastewater treatment partially could be explained by the presence in studied soil clays assembledges with pH dependable variable charge. The relative importance of variable charge in the overall CEC is negligible in smectite and important in illite and kaolinite (Chorom and Rengasamy, 1995; Velde and Barré, 2010). Both Barossa and Charlton soil have illite and kaolinite as dominant clay minerals. In contrast, in Claremont soil, the main constituent of clay fraction is smectite and calcite (Table 29). The other reason of the rise in CEC is the increase in organic carbon after the treatment (Table 27).

**Table 27** Selected properties of clay fraction (< 2μm) of investigated soils

| Soil | pH | EC, (dS/m) | OC*, % | Exchangeable cations, (cmol+/kg) | | | | CEC, (cmol+/kg) |
|---|---|---|---|---|---|---|---|---|
| | | | | Ca | Mg | Na | K | |
| Barossa original | 6.0 | 1.35 | 1.23 | 24.1 | 8.1 | 3.0 | 2.7 | 37.8 |
| Barossa treated | 7.8 | 0.89 | 1.59 | 30.3 | 5.0 | 3.0 | 4.8 | 43.0 |
| Charlton original | 6.8 | 0.43 | 0.49 | 21.9 | 18.7 | 1.3 | 3.6 | 45.5 |
| Charlton treated | 8.1 | 0.89 | 0.66 | 34.1 | 6.9 | 3.4 | 8.7 | 53.2 |
| Claremont original | 8.0 | 0.44 | 1.99 | 49.8 | 10.3 | 1.3 | 2.8 | 64.2 |
| Claremont treated | 8.6 | 0.59 | 2.38 | 47.7 | 1.2 | 2.9 | 5.0 | 56.8 |

* Organic carbon

## Effect of wastewater application on dispersive behaviour of soils

Dispersible clay is widely considered as a measure of soil structural stability (Sumner, 1993). The change in dispersive behaviour of studied soil after wastewater treatment was evaluated by the means of zeta potential and turbidity measurements. The results are given in Table 28 and Figure 52.

**Table 28** Dispersive properties of studied soils

| Soil | Turbidity, NTU | Dispersed clay, g | Dispersed clay, %* | Zeta potential, mV |
|---|---|---|---|---|
| Barossa original | 1965 | 0.33 | 1.64% | -52.6 |
| Barossa treated | 1478 | 0.29 | 1.46% | -36.5 |
| Charlton original | 1667 | 0.29 | 1.44% | -43.2 |
| Charlton treated | 1078 | 0.21 | 1.05% | -28.2 |
| Claremont original | 614 | 0.15 | 0.74% | -25.7 |
| Claremont treated | 487 | 0.09 | 0.46% | -25.2 |

* % of total weight (20 g) of a sample

For all soils turbidity and zeta potential decreased after treatment. As a result, the amount of dispersed clay decreased as well. Claremont soil behaved differently from Barossa and Charlton reflecting differences in its mineralogy. We can conclude that for the studied soils the risk of soil dispersion associated with used winery wastewater for irrigation is reduced in the presence of K.

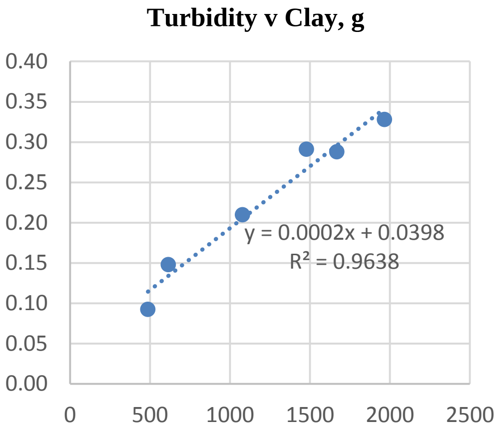


**Figure 52** Relation between turbidity and amount of dispersed clay

## Mineralogical Analysis

The XRD patterns of the <2 µm fractions of original and treated soil clays are shown in Figure 53. As one of the aims of this paper is to assess the effect of application of wastewater irrigation on clay mineral assemblages, we were particularly interested in establishing the clay mineralogy of the studied soils, identifying differences in initial mineralogy as well as mineralogical change after treatment. The XRD pattern of Renmark Grey Vertosol soil clay did not change in intensity and shape of reflections, nor in peak positions after treatment in the low-angle region (4 – 10° 2θ) and was excluded from further mineralogical investigation.

### *Qualitative Description of Experimental XRD Patterns*

#### Barossa Red Brown Earth

The XRD patterns of <2 µm fractions obtained for the air-dried (AD) and glycerolated (G) states show diffraction peaks typical of clay minerals, with additional reflections that are attributed to quartz (4.26, and 3.34 Å). Figure 54 illustrates a peak shift after glycerolation from ~ 15.2 Å in the AD state to ~ 18 Å, indicating the presence of smectite. Peaks near 10 Å occurred for both AD and G states; this indicates the presence of a mica/illite mineral. A peak near 7 Å could denote 002 from chlorite or 001 from kaolinite. The pattern for the Mg-saturated glycerolated state did not show any chlorite present (in ~ 14.2 Å region). Thus XRD evidence suggests that kaolinite is present.

The untreated randomly oriented material was also scanned up to 80° 2θ. The position of the 060 reflection is useful in distinguishing between dioctahedral and trioctahedral species (Figure 54, inset). A peak at d=1.49 Å was attributed to kaolinite, which is dioctahedral (Grim 1968); a peak at d=1.54 Å was attributed to quartz.

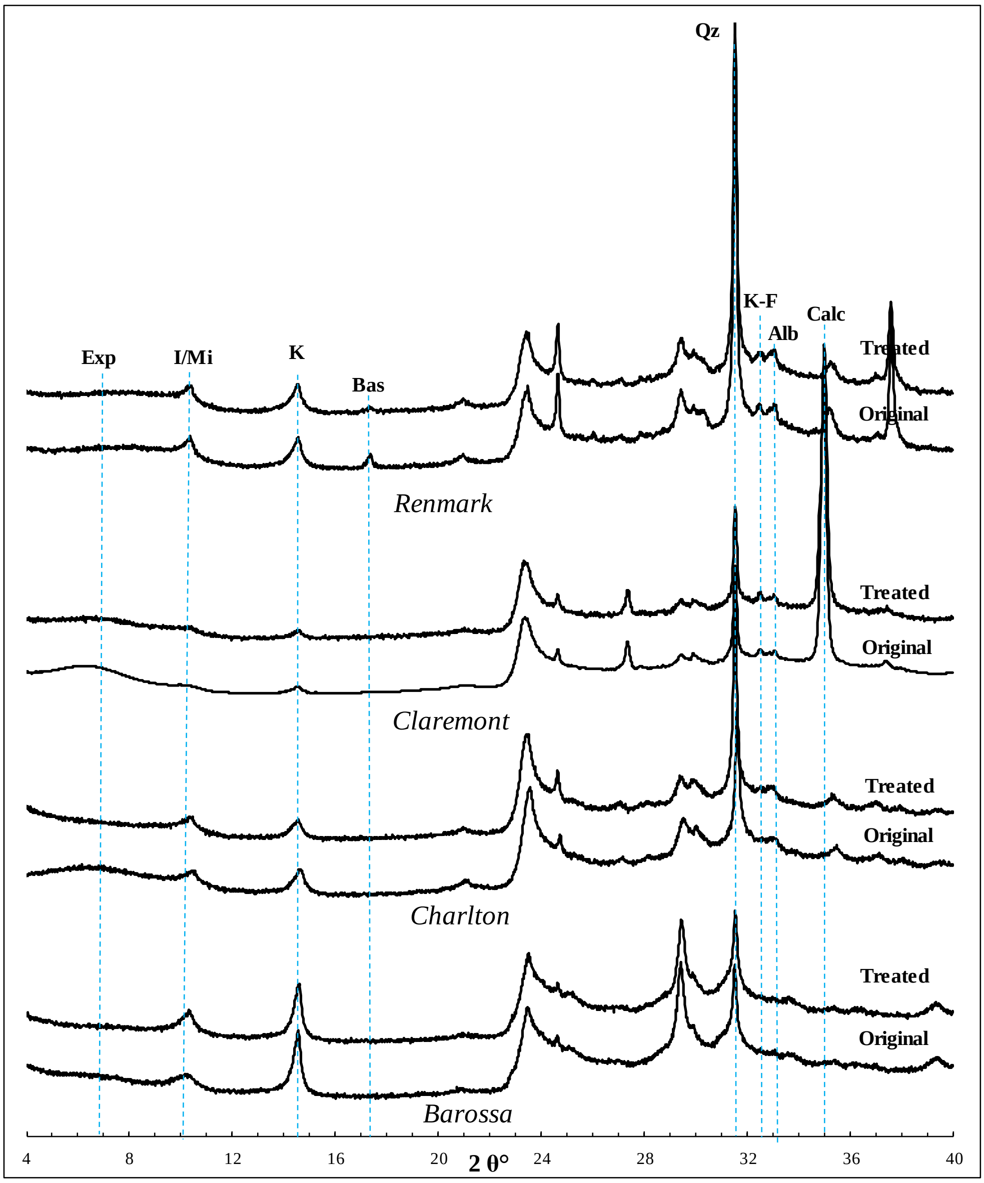


**Figure 53** XRD patterns of air-dried fractions before (lower patterns) and after wastewater treatment (upper patterns). Exp, expandable (d~15.2 Å); I/Mi, illite/mica (d~10.0 Å); K, kaolinite (d=14.2 Å); Bas, bassanite (d=6.03 Å); Q, quartz (d=3.43 Å); K-F, K-feldspar

A broad peak at d~1.50 Å overlapped with the kaolinite 060 peak indicating a smectite with a dioctahedral structure, i.e. montmorillonite. A sharp peak at d~1.53 Å was attributed to a trioctahedral mica/illite phase. These minerals are relatively rare in soil (Fordham 1990; Churchman and Lowe 2012). According to Walker (1950) XRD patterns of trioctahedral micas showed strong, sharp, first-order basal reflections at 10 Å and medium to strong 060 reflections at 1.53 Å. Trioctahedral mica has been reported in soils of the Barossa region in studies by Fordham (1990) and Stace et al. (1968).

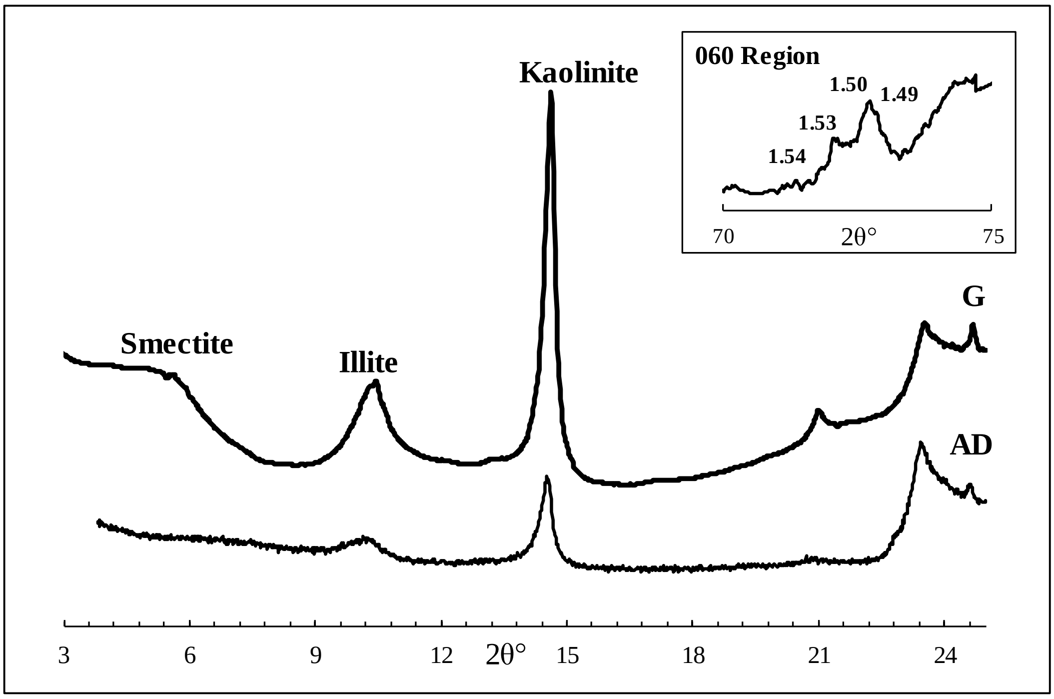


**Figure 54** XRD patterns of Barossa clay assemblage air-dried (AD) and glycerolated (G).

### *Charlton Red Sodosol*

The diffraction pattern of the air-dried clay fraction (Figure 55) has 001 peaks at ~15.2, ~10 and ~7Å. When the Mg-saturated sample was treated with glycerol, the major change was a shift of ~15.2 Å peak to ~18 Å. This indicates the presence of a smectite. The other clay minerals are mica/illite (~10 Å) and kaolinite (~7 Å), with additional reflections that are attributed to quartz (4.26, and 3.34 Å). All clay minerals are dioctahedral as indicated by the 060 reflection, so the smectite present is likely to be a montmorillonite (Figure 55, inset).

### *Claremont Black Vertosol*

More varied XRD diagrams were obtained for the Waite Claremont series soil clay (Figure 56). The results obtained for the AD and G states show diffraction peaks typical of a smectite (~15.2 Å AD and ~18.0 Å G), Illite/mica (~10 Å), and kaolinite (~7 Å), with additional reflections that are attributed to quartz (4.26, 3.34, and 1.82 Å), and feldspars (3.92, 3.25 and 3.20 Å). The Claremont clay may also contain a small amount of vermiculite (or possibly chlorite). The vermiculite/chlorite 001 peak occurs on the shoulder of the glycerolated montmorillonite 001 peak at ~14.2Å (Figure 56). Given the problems of proper identification of vermiculite/chlorite phases and the small amount possibly present, no further attempt was made to identify these materials. A strong 060 reflection at 1.49–1.52 Å (Figure 56, inset) indicates the occurrence of dioctahedral mineral phases.

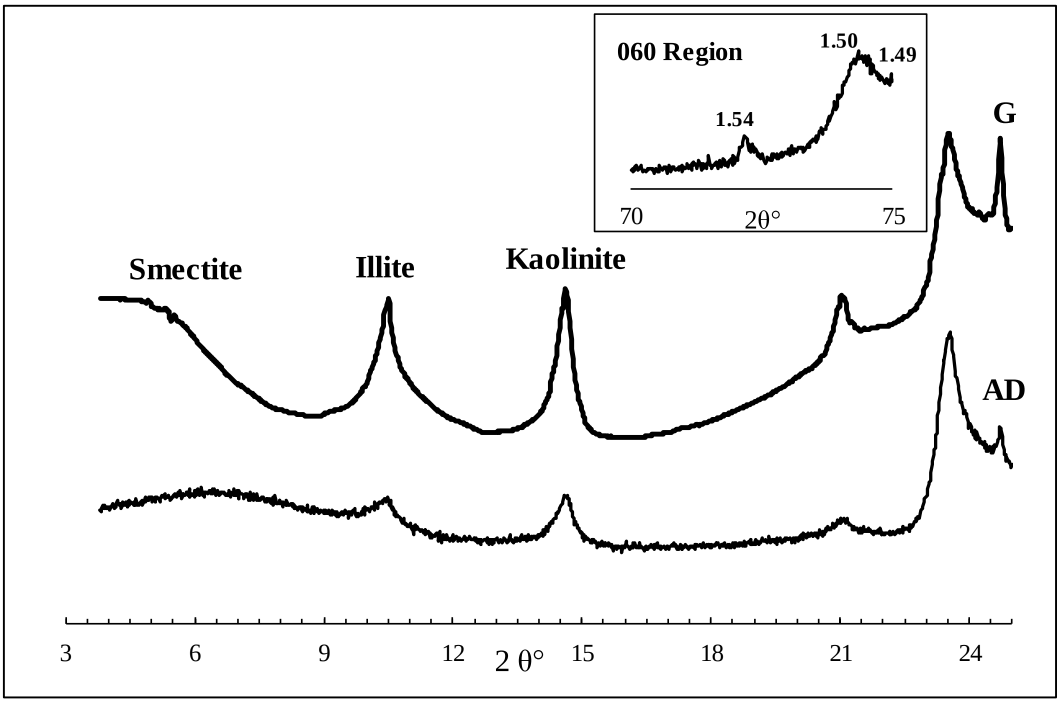


**Figure 55** XRD patterns of Charlton clay assemblage air-dried (AD) and glycerolated (G)

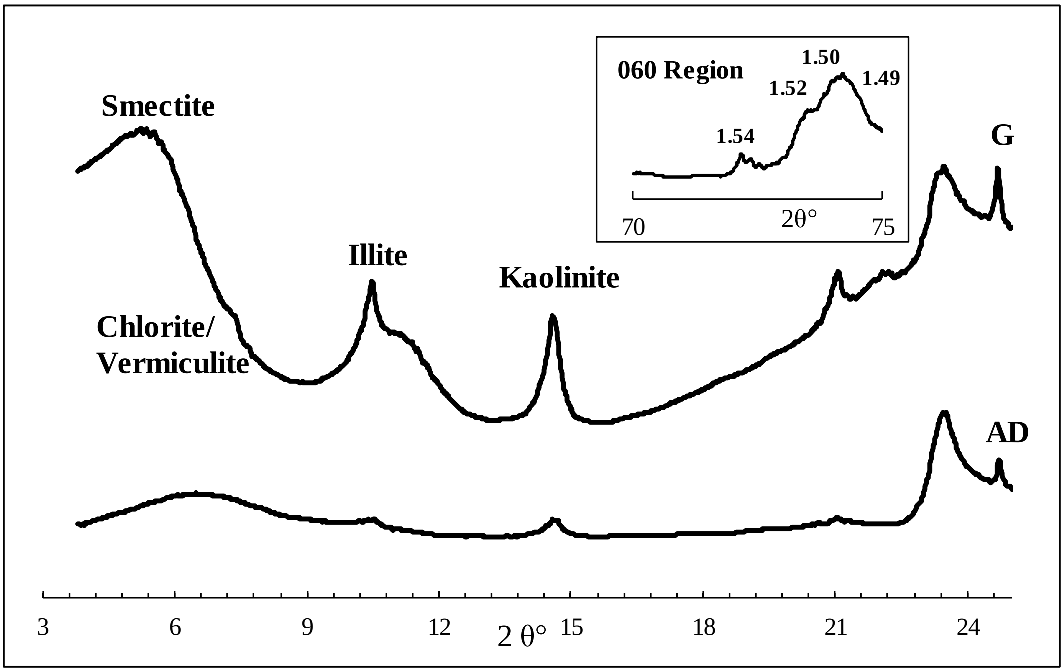


**Figure 56** XRD patterns of Claremont clay assemblage air-dried (AD) and glycerolated (G).

### *Mineralogical Composition of the Clay Fractions*

Semi-quantitative measurements of the identified minerals (Figures 54 – 56) and their relative abundance in the clay fraction of the studied soils before treatment (original) are given in Table 29. Kaolinite was present in all clays investigated, but its proportion and peak position did not change after wastewater treatment (Figure 53). The kaolinite peaks were not affected by glycerol treatment indicating that there is no interstratification with smectite layers in kaolinitic materials. No detailed analysis was made of the kaolinite diffraction peaks in our investigation. We also ignored calcite present in Claremont clay for the same reason.

**Table 29** Mineralogical composition of clays from XRD analysis

| **Clay** | **Sm[1]** | **Chl/V** | **I/Mi** | **Ka** | **Qz** | **Ct** | **KF** | **Alb** |
|---|---|---|---|---|---|---|---|---|
| | **~15.2** | **~14.2** | **~10** | **~7** | **~3.3** | **~3.04** | **~3.24** | **~3.92** |
| Barossa | ** | - | *** | **** | ** | - | - | - |
| Charlton | ** | - | *** | ** | ** | - | - | - |
| Waite Claremont | *** | * | ** | ** | ** | *** | * | * |

[1] Where: Smectite = Sm, Chlorite/Vermiculite = Cl/V, Illite/Mica = I/Mi, Kaolin = Ka, Quartz = Qz, Potassium Feldspar (microcline) = KF, Albite = Alb, Calcite = Ct
Approximate d-spacing in Å used for identification of mineral species (spacings given for air-dried state).
Codes used to indicate amount are: Abundant (*****) >~60%, Major (****) ~40-60%, present (***) ~20-40%, minor (**) ~5-20%, trace (*) <~5%

In our investigation we have focussed on the clay mineral phases which take part in potassium release and fixation processes. They are: illite, illite/smectite mixed-layer minerals, smectite and vermiculite. Diffractograms for the glycerolated Waite Claremont Soil showed a trace of a vermiculite/chlorite phase. To our knowledge, chlorite does not fix potassium, but vermiculite is well known for its ability to uptake potassium in its mineral structure even in a wet state. Our preliminary decomposition analysis has revealed that the relative proportion of the d (001) peak area for vermiculite/chlorite comprises only 0.04% of that of smectite d (001) (result not shown). Considering the quantity of vermiculite/chlorite detected, the contribution of this component alone in terms of potassium fixation (if it occurred) would be insignificant, compared to the capacity of the illite/smectite phases present in clay fraction of Waite Claremont soil. For this reason, we omitted vermiculite/chlorite from further analysis.

Some soil clay minerals have a disordered succession of layers of the different components of 2:1 phases present. As a result, the 001 XRD peaks in the AD state will have a position between 10 and 15.2 Å from which the smectitic component moves to a higher d-spacing (~18 Å) under glycerol treatment. But the glycerol treatment over-rides the potential compositional information for a portion of the smectite-illite/illite-smectite inter-layered minerals (Velde and Barré 2010). Since we are particularly interested in mineral changes induced by potassium rich wastewater, the peak position of the illite-smectite minerals is a very significant index of changes in the mineralogical composition of soil. As pointed out Velde and Barré (2010) the proper assessment and identification of illite-smectites as well as smectite-illites should be done in the air-dried state.

## Decomposition of XRD patterns

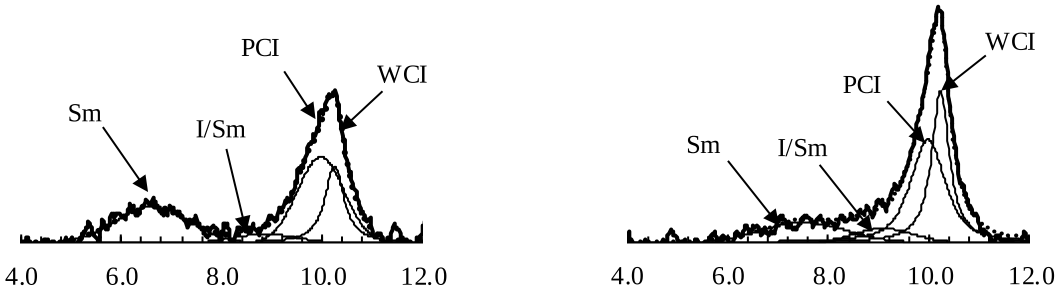
The XRD patterns of air-dried clay showed the greatest variations as a function of wastewater application and will form the core of the discussion which follows. The decomposition procedure was applied essentially in the 4 – 10° 2θ region where the major 001 clay mineral reflections are located (Figures 57 – 59).

According to Velde *at el.* (2003) the decomposition of the XRD spectra can give information concerning the peak position, peak intensity and peak width of individual clay mineral components of a multiphase sample. Peak position indicates, for the most part, compositional changes, either in mica/illite population (see Gharrabi and Velde 1995) or in the proportion of layers within the illite-smectite components of the mixed-layer phases (see Moore and Reynolds 1997). Peak width indicates, for the most part, the relative number of layers coherently diffracting in the crystallites. Peak area can be used to indicate the relative proportions of the different clay phases within the same soil/clay type and to quantify modifications in the clay assemblages (in our example – before and after treatments).

### *Barossa Red Brown Earth*

The decomposition of the XRD diagram for the air dried Barossa original sample produced 4 basic peaks with maximum intensities at d = 15.51, 11.59, 10.29 and 10.02 Å (Figure 57a). Each of these peaks should be related to a distinct mineral "phase". A clay "phase" is not associated with a unique homogeneous material but represents a population of particles whose structural characteristics (smectite/illite content, nature, number and position of the atoms in the structure) can vary within a discrete range. Each of the "phases" identified with this decomposition method will be characterized by its mean value for each of these parameters (Lanson and Champion 1991). The same initial parameters in the decomposition procedure were assumed for all clay samples.

By its position and sharpness, the maximum at 10.02 Å (Figure 57a) was attributed to a mica-like phase (or well-crystallized illite, WCI). The band near 10.29 Å was typical of an illitic mineral (PCI), which was thought to have a finer grain size than the mica. This is indicated by a broader peak, with a width at half height near 1.10° 2θ. An interstratified mineral was identified by the band near 11.59 Å. This band was displaced by the glycerol treatment. Using the NEWMOD based calculation of relations between peak position and smectite content in mixed layer illite-smectites (Figure 51) it was assumed to be an illite-smectite mixed-layer phase with 76% of illite. The curve near 15.51 Å is that of a dominantly smectitic mineral. Figure 57b shows the decomposed patterns of Barossa clay fraction after wastewater application. Four basic curves with maximum intensities at d = 13.67, 11.29, 10.29 and 10.04 Å were attributed to two interstratified illite-smectite (with 58 and 78% of illite according to Figure 51), illite (PCI) and mica (WCI) respectively.



**(a) Barossa original**

**(b) Barossa after treatment**

| Phase | d-sp (Å) | FWHM | Area | % | CG (Å) |
|---|---|---|---|---|---|
| **Sm** | 15.51 | 1.7 | 15522 | 28 | 4.38 |
| **I/Sm** | 11.59 | 1.5 | 3359 | 6 | 0.71 |
| **PCI** | 10.29 | 1.1 | 23445 | 43 | 4.39 |
| **WCI** | 10.02 | 0.45 | 12622 | 23 | 2.30 |
| | | | Σ | 100 | 11.78 |

| Phase | d-sp (Å) | FWHM | Area | % | CG (Å) |
|---|---|---|---|---|---|
| **Sm/I** | 13.67 | 1.97 | 11992 | 15 | 2.08 |
| **I/Sm** | 11.29 | 1.36 | 5841 | 7 | 0.84 |
| **PCI** | 10.29 | 0.82 | 32962 | 42 | 4.30 |
| **WCI** | 10.04 | 0.42 | 28102 | 36 | 3.58 |
| | | | Σ | 100 | 10.79 |

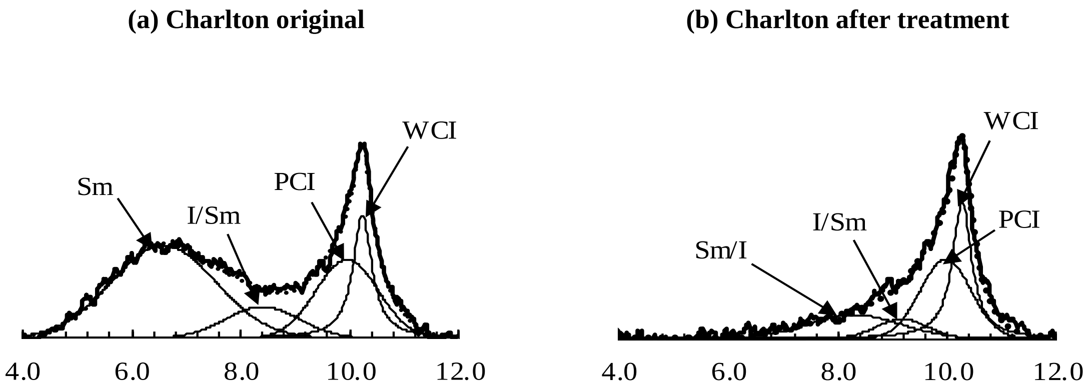
**Figure 57** Decomposition results for Barossa soil clay before and after application of wastewater. The darker pattern represents experimental data and dotted line pattern represents best fit computed data

The WCI peaks before and after treatment for Barossa soil clay were constant in peak position (10.02 and 10.04 Å respectively) and FWHM (0.45 and 0.42° 2θ) but the peak area (relative amount of WCI) increased after the treatment from 23 to 36%. The PCI peak position and relative area did not change (~ 10.3 Å and 43 %), but FWHM decreased from 1.10 to 0.82° 2θ after treatment inferring an increase in grain size which characterizes the transformation from PCI to WCI (Righi et al. 1995; Velde, 2001; Barré et al. 2008). In contrast, the smectitic phases decreased in relative peak areas (from 34 to 22% combined) with a move of peak positions to the higher angle.

### *Charlton Red Sodosol*

The decomposition of the XRD diagram for the air dried Charlton original sample produced 4 basic peaks with maximum intensities at d = 15.59, 12.21, 10.32 and 10.03 Å which were attributed to smectite, illite-smectite (72 % of illite, Fig. 3), PCI and WCI respectively (Figure

58a). Figure 58b shows the decomposed patterns of Charlton clay fraction after wastewater application: 4 basic curves with maximum intensities at d = 12.78, 11.19, 10.29, and 10.00 Å which were attributed to two illite-smectite mixed-layer phases with illite contents of 70 and 79 %, PCI and WCI respectively.


**(a) Charlton original**

**(b) Charlton after treatment**

| Phase | d-sp (Å) | FWHM | Area | % | CG (Å) |
|---|---|---|---|---|---|
| **Sm** | 15.59 | 2.25 | 53576 | 48 | 7.40 |
| **I/Sm** | 12.21 | 1.6 | 12869 | 11 | 1.39 |
| **PCI** | 10.32 | 1.35 | 27116 | 24 | 2.48 |
| **WCI** | 10.03 | 0.42 | 19324 | 17 | 1.72 |
|  |  |  | Σ | 100 | 12.99 |

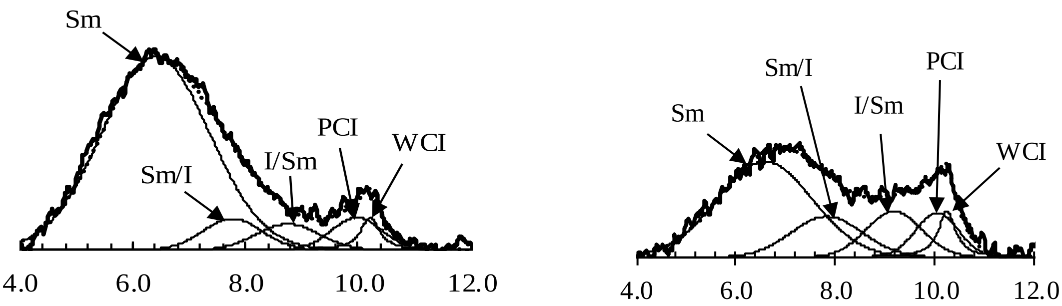
| Phase | d-sp (Å) | FWHM | Area | % | CG (Å) |
|---|---|---|---|---|---|
| **Sm/I** | 12.78 | 2.00 | 11854 | 20 | 2.52 |
| **I-Sm** | 11.19 | 1.10 | 5360 | 9 | 1.00 |
| **PCI** | 10.29 | 1.10 | 21926 | 36 | 3.75 |
| **WCI** | 10.00 | 0.42 | 21078 | 35 | 3.50 |
|  |  |  | Σ | 100 | 10.76 |

**Figure 58** Decomposition results for Charlton Red Sodosol soil clay before and after application of wastewater

Similar changes after wastewater application occurred in the Charlton soil clay (Figure 58b) as in the sample from the Barossa (Figure 57b). The WCI peak position (~10.0 Å) and the FWHM (0.42° 2θ) did not change upon wastewater application, but its relative peak area increased from 17 to 35%. For the PCI phase the peak position changed slightly towards a higher 2θ angle from 10.32 to 10.29 Å, the relative peak area increased from 24 to 36% and the FWHM decreased from 1.35 to 1.10° 2θ indicating more ordered illitic or mica-like structures with a larger grain size. Moreover, the smectitic peaks shifted to a higher 2θ angle after treatment (smectite from 15.59 to 12.78 Å and illite-smectite from 12.21 to 11.19 Å), indicating transformation into mixed-layered illite-smectite with decrease in relative peak area (from 59 to 29% combined).

### *Waite Claremont Vertosol*

The major clay phases present in the original sample are WCI (10.05 Å), PCI (10.30 Å), smectite (16.02 Å), and two interstratified illite-smectites (13.20 Å, I= 64% and 11.73 Å, I=76%, Figure 59a). The decomposition of wastewater treated sample (Figure 59b) also produced 5 basic curves which were attributed to WCI (10.04 Å), PCI (10.23 Å) smectite (15.58 Å), and two illite-smectites (13.12 Å, I= 64% and 11.19 Å, I=79%).


**(a) Claremont original**

**(b) Claremont after treatment**

| Phase | d-sp (Å) | FWHM | Area | % | CG (Å) |
|---|---|---|---|---|---|
| **Sm** | 16.02 | 2.25 | 108290 | 78 | 12.42 |
| **Sm/I** | 13.2 | 1.23 | 9584 | 7 | 0.91 |
| **I/S** | 11.73 | 1.31 | 8524 | 6 | 0.72 |
| **PCI** | 10.3 | 1.05 | 8531 | 6 | 0.63 |
| **WCI** | 10.05 | 0.4 | 4742 | 3 | 0.34 |
|  |  |  | Σ | 100 | 15.01 |

| Phase | d-sp (Å) | FWHM | Area | % | CG (Å) |
|---|---|---|---|---|---|
| **Sm** | 15.58 | 2.26 | 47880 | 52 | 8.04 |
| **Sm/I** | 13.12 | 1.68 | 15256 | 16 | 2.16 |
| **I/S** | 11.19 | 1.32 | 13412 | 14 | 1.62 |
| **PCI** | 10.23 | 1.02 | 10025 | 11 | 1.10 |
| **WCI** | 10.04 | 0.42 | 6257 | 7 | 0.68 |
|  |  |  | Σ | 100 | 13.59 |

**Figure 59** Decomposition results for Waite Claremont Vertosol soil clay before and after application of wastewater

Because of the dominance of smectite in the clay fraction of Waite Claremont soil, application of wastewater induced more complex mineralogical modifications. WCI peak position (10.05 Å) and FWHM (0.4° 2θ) did not change with increasing relative peak area (from 3 to 7%). Peak position for PCI moved towards higher 2θ angles (from 10.30 to 10.23 Å), FWHM decreased slightly (from 1.05 to 1.02° 2θ) with increase in relative peak area (from 6 to 11%). The smectitic phases decreased in relative peak areas (from 91 to 82% combined) with a move of peak positions to the higher 2θ° angle.

## Elemental content of clay fraction

Total chemical analyses of clay fractions after removal of exchangeable bases are given in Table 30. Data in this study are reported on a mgg$^{-1}$ basis. In each soil clay under study the content of potassium increased considerably after treatment: for Barossa, + 12%, Charlton, + 15% and Claremont, + 16%. There is no noticeable relationship between Al, Fe, Ca, Mg, Na and K contents. Mg and Na content for Charlton clay increased after treatment (for 10 and 53% respectively) and those for Barossa clay increased to lesser extents. We can conclude that clay K content modification occurred independent by Al, Fe, and Ca contents. The modification observed through decomposition of X-ray data are in a good agreement with variations of mineral clay K concentration: increase in K content after treatment reflects in growth of illitic component of clay assemblages.

**Table 30** Chemical composition of clay fractions, mg/g

| **Sample ID** | **Ca** | **Mg** | **Na** | **K** | **Al** | **Fe** | **Mn** |
|---|---|---|---|---|---|---|---|
| **Barossa Original** | 2.73 | 9.02 | 0.82 | 9.21 | 88.73 | 41.55 | 0.14 |
| **Barossa WW** | 2.90 | 9.61 | 0.98 | 10.33 | 88.13 | 42.37 | 0.14 |
| **Charlton Original** | 2.61 | 7.48 | 0.71 | 12.32 | 78.07 | 38.65 | 0.24 |
| **Charlton WW** | 2.86 | 8.20 | 1.09 | 14.15 | 79.20 | 38.43 | 0.29 |
| **Claremont Original** | 44.64 | 12.40 | 0.67 | 8.84 | 56.19 | 36.15 | 0.36 |
| **Claremont WW** | 43.74 | 12.35 | 0.65 | 10.22 | 54.13 | 35.63 | 0.42 |

### Clay mineral modification through wastewater treatment: Summary

For all clays under study, the relative peak areas for illitic phases (PCI and WCI) increased compared to the smectite peaks after treatment. Furthermore, smectite and smectite/illite peak positions shifted to higher 2θ angles and as a result, a portion of the initial phases became either an illite-rich inter-layered mineral or illite (Velde and Barré 2010).

The measurement of the center of gravity of X-coordinates allows a numerical comparison of the diffractograms before and after wastewater treatment, summarising modification of clay assemblages. According to Moore and Reynolds (1997), the centre of gravity should depend to a large extent on the anhydrous K layer content of the whole clay assemblage and may therefore give an approximation of the K content (Barré at al. 2007b). In all clays studied cg value decreased after treatment – meaning an increase in the quantity of illitic layers at the expense of the expandable smectitic phases.

The present data suggest that illite content, as a phase or as a part of interlayer mineral assemblage increased after wastewater treatment. Our results are similar to the study of Arienzo at al. (2012). They investigated the relative effects of $Na^+$ and $K^+$ on soil structural stability. When they treated soil with solutions of different amounts of potassium (9 treatments), in each case they reported an increase in illite content with simultaneous decrease in smectite in clay fraction.

## Conclusion

Characterisation of the effect of wastewater treatment on clay fraction either by decomposition of XRD diagrams or chemical analysis of the mineral content of studied clays gave consistent results. Hence, it appeared that decomposition of XRD patterns gave a realistic analysis of complex clay assemblages. Many soils contain clay minerals with smectitic layers, often in insterstratifications with illite and also kaolinite (Norrish and Pickering 1983; Velde 2001; Churchman and Lowe 2012). The dynamic of illitisation can be monitored by XRD both qualitatively and quantitatively. Although this study was not performed under field conditions, it suggests that illitisation is likely to occur in interactions of many real soils upon their irrigation with wastewaters rich with potassium. 2:1 clay minerals play a vital role in the potassium cycle in soil. They are capable of sequestering potassium from the soil solutions. Moreover, the sequestered potassium becomes a source of potassium for plant growth.

# Chapter 8. Potassium induced dispersion: a field study

For this study I have chosen 74 dispersive soils from different areas of Australia. The main criteria for selection were: visual assessment of the intensity of soil dispersion after 48 hours (Rengasamy 2002b) and turbidity, measured as nephelometric turbidity units (NTU). In Australia, soil with exchangeable sodium percentage (ESP) > 6% is considered to be dispersive. Out of 74 soils 17 showed high dispersion levels but ESP < 5% (in fact the highest ESP value was 4.2%).

These soils varied in cropping history, management, and physical and chemical properties, except they all had exchangeable $K^+/Na^+$ ratios > 1 (Figure 60 and Table 31). There is little systematic information in the literature on the effects of exchangeable $K^+$ on soil structure and a need to examine its effect on soil/clay dispersive behaviour using exchangeable ratios, rather than solution ratios. I intentionally have chosen these dispersive soils with high levels of exchangeable potassium relative to sodium in order to quantify its effect. The main objectives of this study were: a) determine the relative importance of various physical and chemical properties of potassium rich soils on their dispersive behaviour; b) quantification of the effects of potassium induced dispersion in soils.

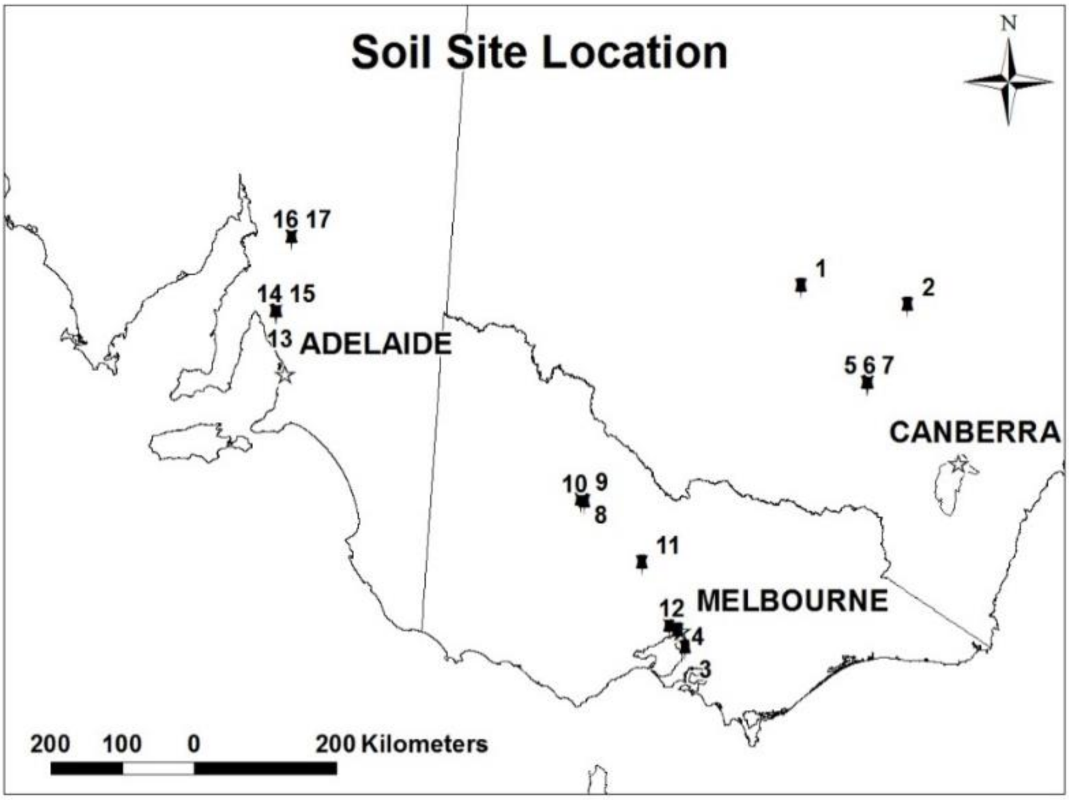


**Figure 60** Soil sites locations

**Table 31** Soil sites characteristics

| **Id** | **Location** | **Land use and horizon** | **Soil[1]** | **Texture class** | **Elevation m** | **Rain Fall, mm $y^{-1}$** |
|---|---|---|---|---|---|---|
| **1** | Lake Cargelligo, Vic | Agriculture, A hor. | Dermosol | Loam | 37 | 961 |
| **2** | Forbes, NSW | Agriculture, A hor. | Kandosol | Silty loam | 19 | 683 |
| **3** | Melbourne, Vic | Recreation, A hor. | Sodosol | Clay | 37 | 572 |
| **4** | Kew East, Vic | Recreation, A hor. | Sodosol | Clay loam | 298 | 645 |
| **5** | Temora, NSW | Agriculture, Plot 2, B hor. | Kandosol | Sandy loam | 199 | 431 |
| **6** | Temora, NSW | Agriculture, Plot 32, B hor. | Kandosol | Loam | 199 | 429 |
| **7** | Temora, NSW | Agriculture, Plot 33, B hor. | Kandosol | Loam | 199 | 411 |
| **8** | Charlton, Vic | Agriculture, A hor. | Chromosol | Clay | 480 | 686 |
| **9** | Charlton, Vic | Agriculture, B hor. | Chromosol | Clay | 480 | 653 |
| **10** | Charlton, Vic | Agriculture, B hor. | Chromosol | Clay | 470 | 653 |
| **11** | Sutton Grange, Vic | Recreation, B hor. | Sodosol | Clay | 65 | 357 |
| **12** | West Essendon, Vic | Recreation, B hor. | Rudosol | Clay | 64 | 357 |
| **13** | Balaklava, SA | Agriculture, A2 hor. | Chromosol | Clay | 64 | 423 |
| **14** | Balaklava, SA | Agriculture, A1 hor. | Chromosol | Clay loam | 64 | 423 |
| **15** | Balaklava, SA | Agriculture, A2 hor. | Chromosol | Clay | 64 | 423 |
| **16** | Jamestown, SA | Agriculture, A1 hor. | Chromosol | Loam | 408 | 477 |
| **17** | Jamestown, SA | Agriculture, A2 hor. | Chromosol | Clay loam | 408 | 477 |

[1] Australian Soil Classification (Isbell, 1996)

## Mineralogical analysis of soil clay fractions

As I pointed out previously, one of the reasons for different response of soils to application of potassium (as a fertiliser or in irrigation water) was attributed to differences in their mineralogy (Levy and van der Watt 1990; Churchman et al. 1993; Arienzo et al. 2009). I examined 17 chosen soils for their mineralogy. The XRD patterns of the <2 μm fractions of investigated soils are shown in Figure 61. The samples 5, 6 and 7; 8 and 9; 13, 14 and 15; 16 and 17 represent the same sampling sites, but different plots or horizons (Table 31). Their XRD patterns are identical in each case and only one XRD diffractogram is presented from the same site.

All samples revealed the reflections of illite (d = 9.9 – 10.0 Å), kaolinite (d = 7.1 – 7.2 Å) and quartz (d = 2.34 Å). The majority of clays have also varying amount of primary minerals – potassium feldspar (d = 2.24 Å) and albite (d = 2.2 Å). Sample 3 was dominated by chlorite (d = 14.2 Å). Expandable minerals (smectite and vermiculite) with some interstratified phases were also present. Illite and kaolinite were the dominant clay phases in general. 3 samples from Temora, NSW (samples 5, 6 and 7) contained trioctahedral illite (the 060 reflections not shown). The rest of the soils studied contained clays with a dioctahedral structure. The results of quantitative mineralogical analyses are presented in Table 32.

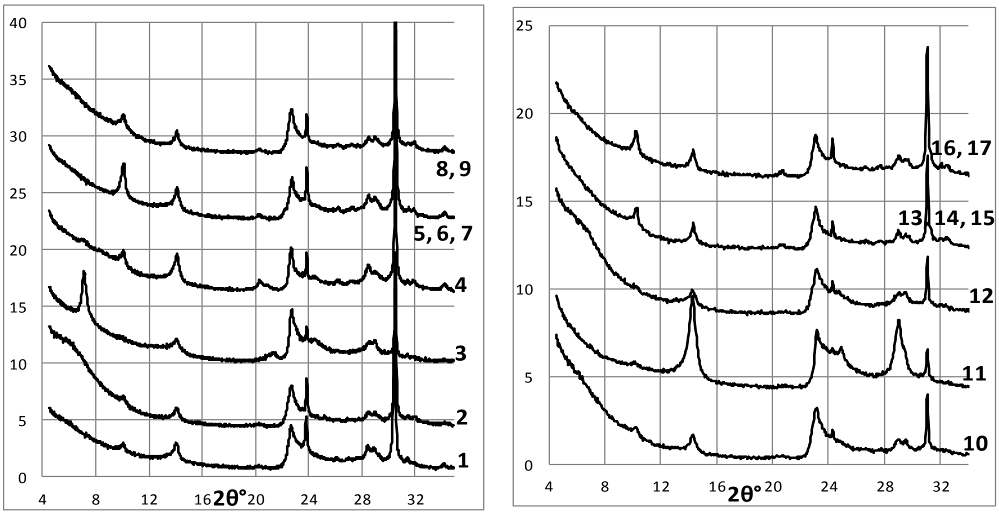


**Figure 61** Experimental XRD patterns obtained for the < 2 micron fraction of the studied soils

As shown by XRD analysis, all samples, except sample 3, have illite/kaolinite as dominant clay minerals. Sample 3 was composed of 49% chlorite with illite (10%) and kaolinite (21%) also present. Only sample 2 had over 10% of expandable minerals.

**Table 32** Quantitative analysis of clay fractions, %

| **Soil ID** | **Sm[1] and Sm/I** | **V and V/I** | **Chl** | **I** | **K** | **Quartz** | **KF** | **Alb** |
|---|---|---|---|---|---|---|---|---|
| | 16.2-15.2[2] | 14.0 | 14.2 | 9.9-10.0 | 7.1-7.2 | 3.34 | 3.24 | 3.2 |
| **1** | 1 | - | - | 16 | 29 | 36 | 17 | - |
| **2** | 13 | - | - | 14 | 17 | 30 | 13 | 13 |
| **3** | - | - | 49 | 10 | 21 | 12 | 9 | - |
| **4** | - | 2 | - | 25 | 37 | 22 | 5 | 7 |
| **5** | - | - | - | 46 | 20 | 20 | 7 | 6 |
| **6** | - | - | - | 41 | 21 | 23 | 8 | 7 |
| **7** | - | - | - | 48 | 21 | 22 | 4 | 5 |
| **8** | 1 | - | - | 38 | 17 | 22 | 11 | 11 |
| **9** | 5 | - | - | 33 | 19 | 16 | 10 | 16 |
| **10** | 2 | - | - | 37 | 36 | 25 | - | - |
| **11** | - | - | - | 4 | 87 | 9 | - | - |
| **12** | 9 | - | - | 6 | 38 | 16 | 19 | 12 |
| **13** | 1 | - | - | 41 | 16 | 14 | 14 | 14 |
| **14** | <0.5 | - | - | 25 | 21 | 18 | 19 | 17 |
| **15** | <0.5 | - | - | 45 | 13 | 24 | 6 | 12 |
| **16** | - | - | - | 38 | 20 | 22 | 9 | 11 |
| **17** | 1 | - | - | 31 | 23 | 12 | 21 | 13 |

[1] Where: Smectite = Sm, Vermiculate = V, Chlorite = Chl, Illite = I, Kaolin = Ka, Quartz = Qz, Potassium Feldspar (microcline) = KF, Albite = Alb

[2] Approximate d-spacing in Å used for identification of mineral species (spacings given for air-dried state)

All soils have in common that they were all composed of clay minerals in which exchangeable cations are almost entirely located on outer surfaces of clay particles. Dispersion of clay minerals related to their structure, composition and particularly the nature of the exposed outer surface, because it is these surfaces which interact with the water and nutrients (Wilson 2014).

## Soils properties

The results of soil physico-chemical analysis (Table 33) have shown that investigated soils differ in pH, EC, organic carbon, texture and CEC. As previously indicated, all the studied soils were predominantly illitic/kaolinitic. However, in spite of their similar mineralogy, the dispersive behaviour of these soils is quite variable (coefficient of variation, CV = 18% for turbidity, 67% for CEC and 42% for clay content), suggesting that other soil properties were also affecting dispersion.

**Table 33** Selected soil properties

| Soil | K/Na[1] | pH | EC, dS/m | Organic C% | Turbidity NTU | Level of dispersion | PSD[2], % | | | CEC, (cmol$_+$/kg) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Clay | Silt | Sand | |
| **1** | 28.17 | 4.9 | 0.19 | 0.75 | 3970 | Very high | 22 | 14 | 64 | 7.0 |
| **2** | 2.00 | 7.9 | 0.29 | 0.90 | 2580 | High | 44 | 9 | 47 | 21.6 |
| **3** | 18.05 | 5.0 | 0.18 | 2.48 | 3480 | Very high | 40 | 22 | 38 | 7.0 |
| **4** | 4.28 | 6.1 | 0.12 | 2.43 | 1860 | Medium | 30 | 26 | 44 | 9.5 |
| **5** | 9.58 | 5.4 | 0.04 | 0.49 | 3240 | Very high | 18 | 10 | 72.5 | 2.9 |
| **6** | 9.94 | 5.1 | 0.04 | 0.46 | 3510 | Very high | 21 | 16 | 63 | 2.7 |
| **7** | 10.28 | 5.0 | 0.04 | 0.49 | 3260 | High | 22 | 14 | 64 | 2.9 |
| **8** | 6.83 | 6.7 | 0.07 | 1.16 | 2890 | High | 39 | 13 | 49 | 11.7 |
| **9** | 1.79 | 8.1 | 0.06 | 0.40 | 2820 | High | 73 | 10 | 18 | 24.9 |
| **10** | 1.12 | 8.8 | 0.16 | 0.56 | 2130 | Medium | 65 | 6 | 29 | 29.1 |
| **11** | 6.50 | 6.3 | 0.10 | 0.91 | 2970 | High | 58 | 6 | 37 | 5.7 |
| **12** | 1.42 | 7.7 | 0.19 | 0.95 | 2560 | High | 43 | 16 | 41 | 17.5 |
| **13** | 7.44 | 9.0 | 0.10 | 1.27 | 2810 | High | 53 | 16 | 32 | 12.8 |
| **14** | 7.77 | 8.5 | 0.13 | 0.69 | 3300 | High | 33 | 27 | 41 | 15.3 |
| **15** | 1.65 | 8.9 | 0.14 | 1.19 | 2780 | High | 48 | 20 | 32 | 20.5 |
| **16** | 15.83 | 5.6 | 0.15 | 0.70 | 3510 | High | 23 | 24 | 53 | 6.4 |
| **17** | 10.21 | 6.0 | 0.15 | 1.19 | 2870 | High | 33 | 22 | 46 | 8.8 |

These 17 soils were further analysed for a range of properties (Table 34) in order to find out the key soil properties and/or indexes which would assist in prediction and assessment of soil dispersion, induced, I hypothesise, by elevated levels of exchangeable potassium relative to sodium. The results of linear regression analysis are presented in Table 35. Dispersion characteristics, expressed as turbidity and zeta potential, were used as dependent variables. CEC, exchangeable cation ratio (ECR), exchangeable sodium percentage (ESP), exchangeable potassium percentage (EPP), clay content and water dispersible clay (WDC) content were then used as independent variables in regression analysis.

The ECR, the ESP and the EPP were calculated as:

$$\text{ECR \%} = [(\text{Na} + 0.56\text{K}) / [\text{exch}\ (\text{Na}+\text{K}+\text{Ca}+\text{Mg})] \times 100 \qquad (1)$$

$$\text{ESP \%} = (\text{Na})/[\text{exch } (\text{Na}+\text{K}+\text{Ca}+\text{Mg})] \times 100 \tag{2}$$

$$\text{EPP \%} = (\text{K})/[\text{exch } (\text{Na}+\text{K}+\text{Ca}+\text{Mg})] \times 100 \tag{3}$$

In the ECR formula the measured difference between the dispersive effect of $K^+$ and that of $Na^+$ was taken into account by multiplying the values for exchangeable K by 0.56 (Rengasamy and Marchuk A. 2011). WDC is considered a good indicator of soil structural stability and has been used to study structural stability of saline and sodic soils (see Nelson et al. 1998).

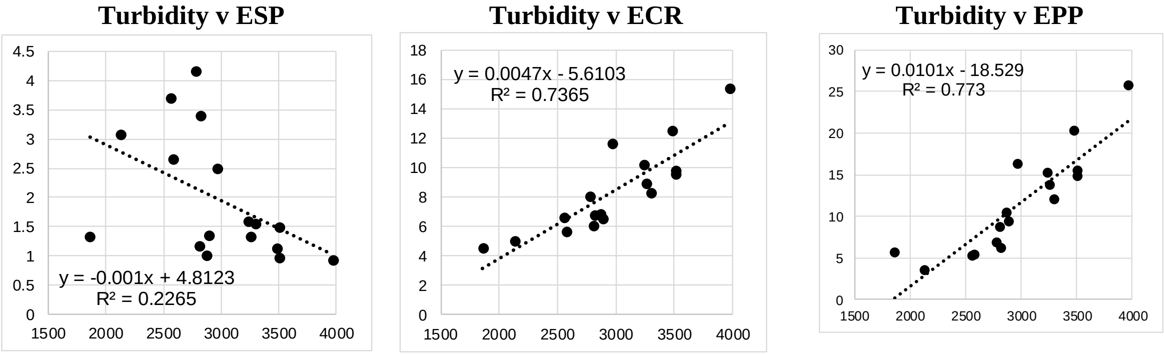
**Table 34 Zeta potential, exchangeable cations, CEC, ECR, ESP, EPP and WDC of selected soils**

| **Soil ID** | **Zeta** | **Exchangeable cations, cmol$_+$/kg** | | | | **CEC** | **ECR** | **ESP** | **EPP** | **WDC** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **mV** | **Ca** | **Mg** | **Na** | **K** | **cmol$_+$/kg** | **%** | **%** | **%** | **%** |
| **1** | -51.6 | 3.58 | 1.51 | 0.06 | 1.80 | 7.0 | 15.43 | 0.92 | 25.71 | 10 |
| **2** | -39.7 | 13.49 | 6.35 | 0.58 | 1.15 | 21.6 | 5.66 | 2.67 | 5.32 | 27 |
| **3** | -40.4 | 3.98 | 1.49 | 0.08 | 1.42 | 7.0 | 12.53 | 1.13 | 20.29 | 21 |
| **4** | -37.7 | 6.73 | 2.14 | 0.13 | 0.54 | 9.5 | 4.53 | 1.33 | 5.68 | 35 |
| **5** | -44.6 | 2.17 | 0.22 | 0.05 | 0.44 | 2.9 | 10.19 | 1.60 | 15.17 | 13 |
| **6** | -46.8 | 2.02 | 0.24 | 0.04 | 0.40 | 2.7 | 9.78 | 1.49 | 14.81 | 17 |
| **7** | -49.0 | 2.22 | 0.25 | 0.04 | 0.40 | 2.9 | 8.95 | 1.33 | 13.79 | 18 |
| **8** | -37.4 | 7.75 | 2.74 | 0.16 | 1.09 | 11.7 | 6.57 | 1.36 | 9.32 | 23 |
| **9** | -38.3 | 11.25 | 11.25 | 0.85 | 1.52 | 24.9 | 6.82 | 3.41 | 6.10 | 45 |
| **10** | -37.5 | 19.75 | 7.44 | 0.90 | 1.00 | 29.1 | 5.02 | 3.08 | 3.44 | 38 |
| **11** | -37.9 | 1.54 | 3.10 | 0.14 | 0.93 | 5.7 | 11.64 | 2.51 | 16.32 | 33 |
| **12** | -36.1 | 8.25 | 7.67 | 0.65 | 0.92 | 17.5 | 6.66 | 3.71 | 5.26 | 30 |
| **13** | -38.0 | 9.25 | 2.28 | 0.15 | 1.12 | 12.8 | 6.08 | 1.18 | 8.75 | 40 |
| **14** | -42.9 | 11.25 | 1.95 | 0.24 | 1.84 | 15.3 | 8.31 | 1.55 | 12.03 | 19 |
| **15** | -37.1 | 13.50 | 4.69 | 0.86 | 1.41 | 20.5 | 8.05 | 4.18 | 6.88 | 26 |
| **16** | -47.8 | 4.18 | 1.20 | 0.06 | 0.99 | 6.4 | 9.61 | 0.97 | 15.47 | 13 |
| **17** | -36.7 | 5.75 | 2.05 | 0.09 | 0.92 | 8.8 | 6.84 | 1.02 | 10.45 | 22 |

Turbidity was highly related to ECR and EPP; increasing ECR and EPP leading to increased turbidity. Figure 62 demonstrates ECR and EPP as superior to ESP as an index to predict soil structural deterioration when sodium is low on soil clay exchange sites. Importantly, the modification of ESP to create ECR has incorporated the Na factor of the function as Na is clearly common and a well-documented issue in the Australian landscape. The extent of soil clay dispersion in investigated soils was influenced by $K^+$ rather than $Na^+$ on the exchange sites, confirming earlier reports on the effects of $K^+$ on soil structural changes (Marchuk A. and Rengasamy 2011; Rengasamy and Marchuk A. 2011).

**Table 35** Results of linear regression analysis ($R^2$)

| Properties | Text Clay | WDC | CEC | ECR | ESP | EPP |
|---|---|---|---|---|---|---|
| Turbidity | 0.267 | 0.566 | 0.349 | 0.736 | 0.226 | 0.773 |
| Zeta | 0.489 | 0.561 | 0.327 | 0.433 | 0.274 | 0.524 |


Turbidity v ESP

Turbidity v ECR

Turbidity v EPP

**Figure 62** Relationships between turbidity against exchangeable sodium percentage, exchangeable cation ratio and exchangeable potassium percentage

For the whole soil dataset EPP was a better predictor of dispersion than ECR (Figure 62). But EPP considers only potassium as a dispersive cation in the same way as ESP considers only sodium. I have shown that potassium could also induce dispersion, although to a lesser extent than sodium. Hence, the most useful index should reflect the combined effects of potassium and sodium as dispersive agents. In soil data presented K/Na ratio varied from 1.12 to 28.17. I suggesting that EPP would be a better predictor than ECR for soils with higher K/Na ratio and vice versa. I separated the 17 soils into two groups, according to K/Na ratio; one group with K/Na ratio ≥ 7 and other group with K/Na ratio < 7 (Tables 36 and 37).

**Table 36** Soils with K/Na ratio ≥ 7

| Soil ID | K/Na ratio | Turbidity | ECR | EPP |
|---|---|---|---|---|
| 1 | **30.0** | 3970 | 15.43 | 25.71 |
| 3 | **17.8** | 3480 | 12.53 | 20.29 |
| 5 | **8.8** | 3240 | 10.19 | 15.17 |
| 6 | **10.0** | 3510 | 9.78 | 14.81 |
| 7 | **10.0** | 3260 | 8.95 | 13.79 |
| 8 | **7.0** | 2890 | 6.57 | 9.32 |
| 11 | **7.0** | 2970 | 11.64 | 16.32 |
| 13 | **7.5** | 2810 | 6.08 | 8.75 |
| 14 | **7.7** | 3300 | 8.31 | 12.03 |
| 16 | **16.5** | 3510 | 9.61 | 15.47 |
| 17 | **10.2** | 2870 | 6.84 | 10.45 |

For the soils with K/Na ratio ≥ 7, EPP is a better predictor than ECR (Figure 63). But for the soils with K/Na ratio < 7, ECR correlates much better with turbidity data (Figure 64).

Considering that soils from Table 36 represent extreme cases with enormously high K/Na ratios and it is likely that soils similar to those from Table 37 are more common, we think that ECR is generally a better, more objective indicator of soil dispersibility.

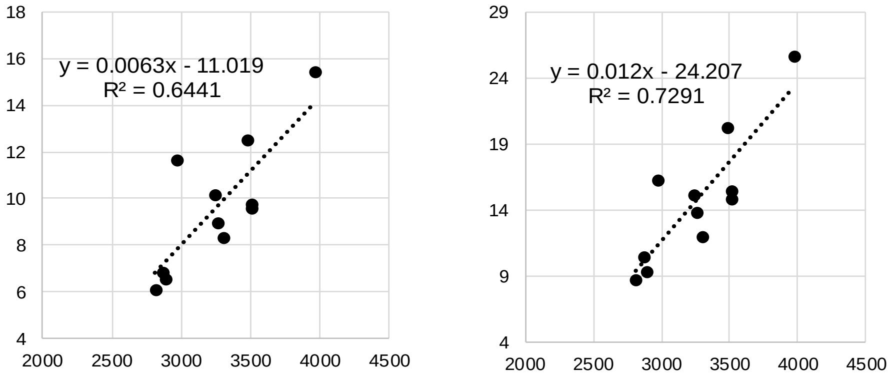


**Figure 63** Turbidity v ECR and EPP for soils with K/Na ratio ≥ 7

**Table 37.** Soils with K/Na ratio < 7

| Soil ID | K/Na ratio | Turbidity | ECR | EPP |
|---|---|---|---|---|
| 2 | **2.0** | 2580 | 5.66 | 5.32 |
| 4 | **4.2** | 1860 | 4.53 | 5.68 |
| 9 | **1.8** | 2820 | 6.82 | 6.10 |
| 10 | **1.1** | 2130 | 5.02 | 3.44 |
| 12 | **1.4** | 2560 | 6.66 | 5.26 |
| 15 | **1.6** | 2780 | 8.05 | 6.88 |

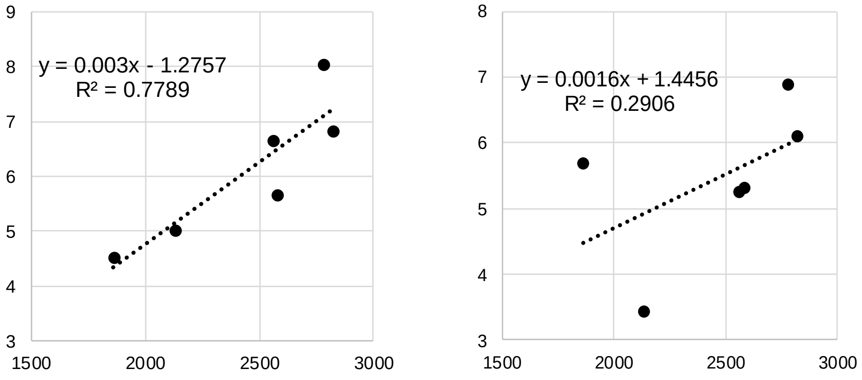
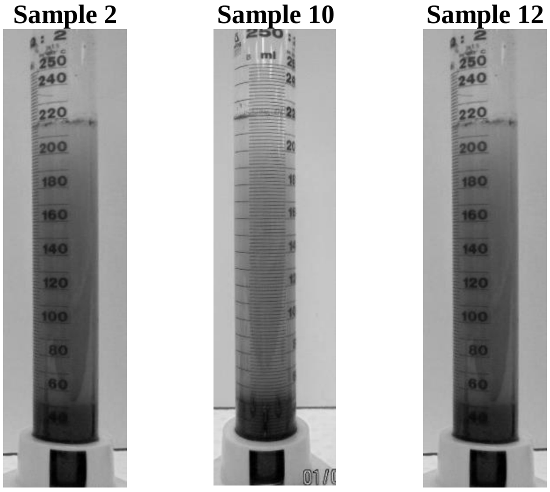


**Figure 64** Turbidity v ECR and EPP for soils with K/Na ratio < 7

Another important issue is a critical or threshold value of EPP (as an analogue for ESP ≥ 6 for dispersive soils). In our dataset we observed dispersion even under such small EPP values as 3.44 %. Figure 65 shows results of dispersion tests on samples 2, 10 and 12 with the lowest EPP values (Table 34).



**Sample 2** **Sample 10** **Sample 12**

**EPP = 5.32%; NTU = 2580** **EPP = 3.44%; NTU = 2130** **EPP = 5.26%; NTU = 2560**

**Figure 65** Dispersion test for the samples 2, 10 and 12

## Conclusion

Exchangeable potassium can cause dispersion of soil even if it’s present in relatively small amount (EPP < 4%). This occurs particularly in soils with dominant illite/kaolinite mineralogy. Exchangeable Cation Ratio, as an indicator of soil dispersion, reflects the combined effects of potassium and sodium as dispersive agents. The ECR is a relatively new index and its applicability in predicting dispersion must be further clarified.

# Chapter 9. General Discussion

This thesis examines various aspects of potassium both inherent in soils and added to soils, as commonly occurs with wastewaters from agricultural industries. It studies both the fate of added K in soil clays and also the effect of potassium as an exchangeable ion on the behaviour of soils and soil clays. It examines the mechanism by which potassium becomes incorporated in soil clay minerals, changing their nature and also the relative behaviour of the $K^+$ cation in relation to other cations in soils, particularly $Na^+$ and the common divalent cations, $Ca^{2+}$ and $Mg^{2+}$.

In Chapter 3, experiments with application of potassium to a pure smectitic mineral, Wyoming montmorillonite, show that wetting and drying, which are often experienced in soils in the Australian environment, when carried out repeatedly, as may occur within a season or from year to year, at realistic surface temperatures, brings about changes in the structure of the clay mineral. The result is that potassium becomes sequestered between the layers of the mineral. The mineral becomes more illitic, step-wise through an interstratification of K-rich illite layers and K-depleted smectite layers. This is the reverse of the weathering that occurs by transformation of micaceous minerals to give first illite, then expanded layer silicates such as vermiculite and smectites. This chapter establishes a mechanism for the uptake and retention of potassium added to soils in, e.g. wastewaters.

Chapter 4 concentrates on the charges on mineral layers as they are determined by displacement by index cations of the mixed suite of cations commonly found in natural clays, to give measures of their cation exchange capacities CEC. It asks the fundamental question about the effect of the nature of the displacing cations on the charge measured. A variety of clay minerals have their CECs determined using the common cations, K, Na, Ca and Mg. It is shown that, generally, differences between the CECs determined using the different cations were relatively minor, indeed, tended to follow similar trends with the different index cations. These trends were related to both the particle sizes resulting from different saturating cations and also their surface charges as given by zeta potentials. The major outstanding difference between CECs measured by different index cations occurred when $K^+$ was used to measure the CEC of a vermiculite, the mineral with the highest layer charge among the set studied.

In Chapter 5, the study of four soils with contrasting mineralogies in relation to their tendencies to disperse with the common cations in soils, namely Na, K, Ca and Mg, were shown to reflect a combination of surface charges, as given by zeta potential, particle sizes and also aspects of particle shape that reflected their mineralogies. There was a consistent effect of the cations, with Na saturation leading to the strongest tendency to disperse, relatively closely followed by K and generally, Mg and Ca were considerable less dispersive as exchangeable cations. Soils with dominantly kaolinite, illite and smectite mineralogies were studied. It was only through a knowledge of their mineralogies and their attendant shapes that the tendencies of particles to disperse and/or flocculate could be understood in relation to the forces of association and dissociation in double layer interactions. In particular, blocky kaolinite particles formed weak associations by van der Waals attractive interactions. At the other extreme, smectites with generally thinner, more extensive and flexible particles, showed close fits together and therefore stronger associations by van der Waals attractions.

Chapter 6 examined the effects of potassium as it was inherently contained within an illite-kaolinite soil of a type that is common in South Australia and also examined the effects of additions of $K^+$ to such a soil. An illite in such a soil is typically partially depleted of structural potassium, reflecting previous land-use to some extent. It was shown that this type of soil, in which smectite was not a significant component could nonetheless re- incorporate potassium into its structure. Newly-developed computer programs for the decomposition of X-ray diffraction patterns into their component separate phases, including at the subtle level of distinguishing poorly-crystallised and well-crystallised forms of the same mineral type (in this case, illite), enabled identification of the formation of a newly-formed poorly crystallised illite that results from the addition of extra potassium. The formation of this phase is shown to accompany a decrease in particle size, a decrease in CEC, a lower zeta potential and the apparent formation of fine particles as seen in electron micrographs. In general, this chapter shows that there is a dynamic in the structural content of potassium in soils regardless of whether they contain smectites. The effect with illites are more subtle than those with smectites that were noted more clearly in Chapters 3-5 (and in Chapters 7 and 8).

In Chapter 7, a laboratory study carried out with real wastewaters examined their effects upon disposal on a number of Australian soils with mixed clay mineralogies. In particular, these soils each had smectitic layers in interstratifications with other layers, particularly illite. Interstratified phases in which smectites appear along with other types of layers are common in Australian soils. Using a recently-developed peak decomposition procedure, it was shown that potassium in wastewaters became incorporated in the interlayers in the structures of the soil clays involved and the mineralogical changes reflected those in the chemical composition of the soils. The net effect was sequestration of some of the added potassium into the structures of the clays so that they become potentially available to plants as nutrients.

Chapter 8 specifically examined the effects of potassium on dispersion, especially when potassium content on exchange sites is high relative to sodium, normally regarded as the principal cation responsible for dispersion in the Australian landscape. A wide range of dispersive soils were studied; generally, these had an illite-kaolinite clay mineral composition. When exchangeable content of $K^+$ was particularly high in relation to that of $Na^+$, an index exchangeable potassium percentage, EPP that is exactly analogous to exchangeable sodium percentage ESP for sodium gave a good prediction of turbidity. However, when potassium and sodium contents were more comparable, exchangeable cation ratio ECR gave a closer relationship with measures of turbidity. ECR incorporates measured differences between the relative dispersion effects of $Na^+$ and $K^+$ and is recommended as an objective index of soil dispersibility that accounts for the effects of both potassium and sodium exchangeable ions as clay dispersion in soils.

# Chapter 10. Conclusions, Limitations of the study, and Recommendation for further research

## Conclusions

The nature of cations adsorbed on soil/clay surfaces (exchange complex) has the potential to significantly affect the physical and chemical properties of the soils and clays. The changes in the adsorbed complex can result in considerable changes in the average size of particles and dispersive/flocculating properties of clays (Chapters 4 and 5). In general, the mean particle size increased in all clay samples in the order Na < K < Mg < Ca. The changes in size observed are reflected in the zeta potential measurements, with samples having smaller sizes giving higher negative zeta potentials. These relationships were independent of the type of clay studied.

The main part of the field study on the effect of vegetation on potassium status of Urrbrae Chromosol comprised a study of the X-ray diffraction basal peak reflections of clay minerals from different profiles and depths (Chapter 6). The analysis presented here demonstrates that even with a range of vegetation regimes Urrbrae soil shows only minor changes in its XRD diagrams, and hence in clay mineral composition. The general trend observed: the growth in illite and kaolinite content at the expense of quartz and feldspar with increasing depth.

In spite of the beneficial effects of potassium as a major plant nutrient, as a monovalent cation it can cause dispersion but to a lesser extent than sodium (Chapters 5 and 6). Potassium cations also could increase soil hydraulic conductivity to some extent when applied to a soil with high sodium content by substituting the $Na^+$ on exchange sites (Chapter 6). I have shown this on Urrbrae soil – an illitic/kaolinitic soil with all exchangeble cations located on the outer surfaces of phyllosilicates. In this case, when potassium cations substitute sodium on the exchange sites, we observe an increase in soil permeability and hydraulic conductivity due to the lower dispersive potential of potassium compared to sodium. But when exchangeable potassium substitutes magnesium or calcium it induces a dispersion of Urrbrae soil, a decrease of clay mean particle size, and as a result, reduction in soil permeability. Illitic and illitic-kaolinitic soils are more prone to dispersion than soils with dominant smectitic clay. This is due to their differences in clay microstructure and fabric when interacting with water (Chapters 5 and 8). I have also proposed the use of Exchangeable Cation Ratio as an indicator of soil dispersion because it reflects the combined effects of potassium and sodium as dispersive agents (Chapter 8).

The application of potassium rich wastewaters to soils may lead to mineralogical changes in the soils that affect their physico-chemical properties. This process is very much dependent on soil clay mineralogy. In an experiment described in Chapter 7, illitic/kaolinitic and smectitic soils changed their clay composition after treatment with wastewater. The results showed trends towards the formation of interstratifications of illite with smectite at the expense of smectite and an alteration of poorly-crystallised illite into its more well-ordered forms. Mineralogical changes gave consistent results, whether monitored by decomposition of XRD diagrams or by chemical analysis of the mineral content of the clays.

The results show that illitisation may occur as a consequence of the addition of K-rich wastewaters to clayey soils. Our results support the view of 2:1 clay minerals as a potassium reservoir and specify the role of each of the 2:1 clay mineral populations in the potassium cycle in soil. Many soils contain clay minerals with smectitic layers, often in insterstratifications with illite and also kaolinite. The dynamics of illitisation can be monitored by XRD both qualitatively and quantitatively. Although this study was not performed under field conditions, it suggests that illitisation is likely to occur in interactions of many real soils upon their irrigation with wastewaters rich with potassium.

The use of mineralogy to explain the potassium dynamics in soil was quite effective. The recent advances in XRD-pattern treatment by specific computer programms such as Decomp and NEWMOD permit the identification of complex clay mineral assemblages and the characterization of their transformation. In my research I have shown that zeta potential and turbidity measurements could effectively reflect soil clay dispersive properties. However, to correctly understand the significance of zeta potential we should have prior knowledge of the mineralogy of the soils studied. TEM and XRD methods could assist in providing a better understanding of the processes occurring in soil.

## Limitations of the study and Recommendations for further research

The research undertaken during the completion of this thesis highlighted several future research opportunities.

Some of the opportunities for future research arise from the limitations of the study to 1) clay fractions only of soils, 2) laboratory studies rather than field studies, and 3) the shortcomings of the available indices for predicting dispersion from the composition of exchangeable cations.

In my study of potassium dynamics in soil I have concentrated on clay fractions. The recent works of Murashkina et al. (2007) and Najafi-Ghiri and Abtahi (2013) indicate that silt and sand fractions of soil could also contribute significantly to the potassium fixation and release. Further research is required to assess the contribution of different soil fractions to the potassium cycle in soil.

The experiment with wastewater treatment of soil was carried out in laboratory condition, but it suggests that illitisation could occur in interactions of many real soils upon their irrigation with wastewaters rich with potassium. Detailed soil and mineralogical studies need to be conducted on a field with a range of irrigated soils.

Finally, the application of Exchangeable Cation Ratio in assessing soil dispersion does not take into account the effects of $Mg^{2+}$, or the concept of threshold cation concentrations in understanding the dispersive behaviour of soils. Future iterations should continue to explore the combined effect of exchangeable cations on the dispersive behaviour of agricultural soils.

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