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Methods and difficulties of soil solution monitoring under irrigated Vertosols

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Methods and difficulties of soil solution monitoring under irrigated Vertosols

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Abstract

Vertosols, are a heavy clay soil that cover a large part of the world, and are used extensively for irrigated agriculture. They are considered to be quite fertile soils, but development is limited by their physical properties. The dominate clay minerals are smectites which give the soil its distinctive shrink-swell properties. Due to their shrink-swell nature, it has been hypothesised that the cracks serve as preferential flow paths for water and soluble nutrients. Increasing environmental awareness of the impact of nutrient runoff from farms and the rising prices of fertilisers has resulted in farmers wishing to increase the efficiency of their fertiliser use, to do this we need a greater understanding of the movement of nutrients in the soil profile. Over the last 100 years various types of lysimeters have been developed to measure the soil solution. However there are still significant areas of unknown in their impact of on soil hydrology, how effective they are in sampling the soil solution and their effect on the sample collected.
This review aims to summarise and analyse the present understanding of the hydrology and chemical properties of Vertosol soils, assessing the need for monitoring the soil solution under irrigated crops grown on these soils. The methods used for soil solution monitoring are also evaluated and suggestions are made for future research.

Additional keywords: lysimeters, vertisols, monitoring.

Introduction

The broad alluvial valleys of Northern NSW and southern Queensland constitute one of the main agricultural regions of Australia; producing cotton, pasture for stock feed, and cereals. The predominant soils in the region are red and black self-mulching clays (Vertosols), interspersed with Kurosols, Calcarosols and Chromosols . With increasing concern about the water use and environmental impact of growing irrigated crops in Australia (Falivene 2008), the cotton and wheat industries need to develop more efficient and sustainable irrigation and growing practices. One area of significant concern is the movement in the environment of pesticides and fertilisers applied to irrigated crops (Weihermuller *et al.* 2007), and salts leached from the profile in to water ways.

The downward movement of dissolved salts in the soil profile with percolating water, is known as leaching. Leached nutrients may contribute to groundwater contamination in regions with intensive agriculture. Given that large amounts of nutrients may be lost in this way, the potential cost to farmers can also be high. In 2008 due to rises in the price of oil and increased demand fertiliser prices shot up (Economist 2008), in India the price of rock phosphate rose by 707.7% in April 2008 compared to the average for Jan – March 2007

(Jagannathan 2008). In Australia price rises have not been quite so extreme but they are having a significant impact on the return farmers can expect from their crops (Fuller 2008).

Although leaching has been studied extensively on sandy and silty soils, research into deep drainage under irrigated crops grown on shrink-swell clay soils has been neglected until quite recently (Hearn 2000). (Chen *et al.* 2002) showed that shrink-swell clays create preferential flow paths in the soil, which speeds the movement of fertilizers below the root zone. Percolation rates of up to 250 mm per season have been estimated under irrigated crops on the shrink-swell clay soils of Northern NSW and Southern QLD (Hullugalle 2005).

The soil solution is the aqueous liquid (mainly water) found within a soil, this liquid normally contains ions released from mineral particles, organic matter or plant roots and leaves. The soil solution is stored in pore spaces and cracks in the soil matrix and is essential in the supply of nutrients to plants, mainly in the form of inorganic ions (Smethurst 2000). For example, plant access to potassium (K) is related to its ability to diffuse through the soil in the soil solution, a positive response to higher levels of K application can only be seen when there is sufficient soil moisture to allow diffusion into the root zone (Mengel and Von Braunschweig 1972). The behaviour of the soil water is significantly affected by the soil texture class; a predominantly sand profile will have a higher hydraulic conductivity and deep drainage rate than a heavy clay soil (Saxton *et al.* 1986)**.**

Soil solute movement is inherently very hard to monitor, and numerous different methods have been developed. One of the first reports of the use of ceramic cup samplers was by (Briggs and McCall 1904), and there are currently several models on the market. Other methods of measuring soil solute movement include the use of tension plate lysimeters, pan lysimeters, wick samplers, wetting front detectors and resin boxes (Weihermuller *et al.* 2007; Falivene 2008)**.** Ceramic cup samplers have an advantage over these methods in that they are relatively cheap and easy to install and maintain. In spite of this, very little research has been done with them in Australia, particularly on Vertosols. Nevertheless a number of studies under different irrigated crops on different soil types have been conducted worldwide and can be used to direct research into more efficient soil solution monitoring and fertilizer and irrigation practices in Australia.
In spite of the importance of the soil solution there are still large gaps in out understanding of it. (Raine *et al.* 2007) highlighted four key areas where there are significant gaps in our knowledge; (i) the effect of root distribution, evapotranspiration, and soil type on soil wetting patterns, (ii) the accuracy and adequacy of using simple estimates of salt levels to predict effect on crops, (iii) fate of solutes over time in relation to irrigation events, and (iv) effect of soil texture on solute behaviour.

This review aims to summarise and analyse the present understanding of the hydrology and chemical properties of Vertosol soils, assessing the need for monitoring the soil solution under irrigated crops grown on these soils. The methods used for soil solution monitoring are also evaluated and suggestions are made for improving current management practices and opportunities for future research.

Vertosols

Vertosols cover around 335 million hectares worldwide, with roughly half of that area suitable for cropping. Predominantly found in the semi-arid tropics, they form on sediments

that produce smectite rich clays when weathered (e.g. in Sudan), and on extensive basalt plateaus (e.g. India and Ethiopia). They are also prominent in Australia, Texas, and parts of South America (Dudal and Eswaran 1988).

Australia has around 70 million hectares of Vertosols (Dudal and Eswaran 1988), which in arid and semi- arid regions are grazed under native pasture and improved pasture in areas of higher rainfall. In the south and east, particularly northern NSW and southern Qld where irrigation is available, Vertosols are used extensively for cropping. The main summer crops are sorghum (*Sorghum spp.*), maize (*Zea mays*), soybean (*Glycine max*), cotton (*Gossypium hirsutum*), sunflower (*Helianthus annus*), and millet. In the winter wheat (*Triticum avestium),* sunflower (*Helianthus annus*), oats (*Avena satvia)* and barley (*Hordeum vulgare*) are grown either dryland or under irrigation (Connolly *et al.* 2001).

Soils classified as 'Vertosols' under the Australian Soil Classification scheme (Isbell 1996) are equivalent to a 'Vertisol' in the International Soil Classification Scheme (ISCS) and the World Reference Base (WRB) used by the Food and Agriculture Organisation, United Nations. A general definition of a vertosolic soil is a dark montmorillonite-rich clay with characteristic shrink-swell properties. These soils with high clay content, and possesiong cracks of at least 1 cm wide that can reach a depth of 50 cm or more, are also called heavy cracking clay soils.

Mineral composition

Vertosols form on rich, basic parent materials, like basalt. Specific conditions are required to allow the formation of smectite from the parent material, including:

- enough rain to weather the rock, but not leach,
- dry periods to allow the crystallisation of clay minerals,
- and heat to encourage weathering.

This is why these soils are normally found in the arid to semi-arid tropics (Dudal and Eswaran 1988). Vertosols are considered to be dominated by smectite, but kaolinite, illite have also been reported as being abundant (Coulombe *et al.* 1996). In northern NSW, the Namoi Valley has several dominant rock formations, the most notable being the Nandewar Range, to the east of Narrabri. The Nandewar Range is the remains of a large Tertiary basalt shield volcano which has been eroded to about one third of its original size. The basalt intrusion overlies a large sheet of tertiary alluvial sandstone and conglomerate (Young *et al.* 2002). Along the foothills of the Nandewar Range, outcrops of Jurassic Pilliga Sandstone occur over the mudstones of the Purlawaugh Formation (Ward 1999). The basalt and mudstone have eroded to form fine-grained soils as the source of the deep clay profiles around Narrabri. Where sandstone forms the dominant geology, the soils are shallower and coarser-grained forming predominantly sandy profiles, like those of the Pilliga (Young *et al.* 2002).

Physical Properties

The physical properties of Vertosols are considered the main factors limiting their agricultural use, however because of their shrink swell nature they are very hard to measure (Vervoort *et al.* 2003). The shrink-swell nature is caused by smectite clay minerals. The swelling occurs in two stages; the insertion of water between elementary clay layers

increasing interlayer distance, and the division of the initial particles into finer grains (Saiyouri *et al.* 2004) causing the clay to increase in volume, swell. As the clay dries out the clay particles re-crystallise and the interlayer spaces dehydrate forcing the clay minerals closer together again. If the soil dries out sufficiently, the clays become very dense, hard, and often crack open. The cracking is due to the developing tension overcoming the soil's tensile strength. The cracking pattern becomes finer as the soil dries out (Deckers *et al.* 2001) often forming 'granules' on the surface. Cracks can be up to 3cm wide and extend 90cm down the profile. Surface material like organic matter and soil 'granules' often fall down these cracks, giving them the name 'self-mulching' and is the origin of the term 'churning' soils; the name Vertosol is from the Latin 'vertere' to turn. When the clay minerals are re-hydrated the soil swells closing the cracks. This shrink-swell nature can lead to the formation of distinctive micro-relief known as Gilgai, slight mounds and depressions in the soil surface.

When wet, Vertosols develop a slippery surface, and become very sticky and plastic which can make access very difficult. This is one of the main factors limiting their use. There is only a very narrow window of moisture content at which they are trafficable and they are prone to compaction (Radford *et al.* 2000), meaning that agricultural practices have to be very carefully timed.

While Vertosols have a very high water holding capacity, they have very low hydraulic conductivity rates making them prone to flooding (Deckers *et al.* 2001). In a study of the hydraulic properties of Vertosols in eastern Australia (Vervoort *et al.* 2003) showed that below around 40 cm, there was a significant difference in the hydraulic conductivity (Ks) of the soil. They attributed this difference to a combination of over burden pressure and increased Exchangeable Sodium Potential (ESP). The correlation between ESP and Ks was identified by (Quirk and Schofield 1955). Northcote and Skene (1972) and McIntyre (1979) argued that the critical ESP for Australian soil should be 6, not 15 as suggested by the United States Soil Lab in 1954. In the Namoi valley and other areas with deep, heavy clay soil profiles, very little deep drainage has been observed because the profiles are naturally dry and have a low hydraulic conductivity (Deckers *et al.* 2001; Silburn and Montgomery 2004; Vervoort *et al.* 2003). Cores to 6 m under native vegetation show that the profile is essentially dry below 1m, but in areas that have been under irrigation for the last 30 – 50 years, the profile is slowly being saturated. 'Wetting fronts' have now been detected down to 5 m. Currently there is very little water movement out of Vertosols, at least in Australia, but the effect of irrigation on total water content over time still requires attention, if or when these profiles finally reach saturation and begin to drain they have the potential to significantly change the hydrology of the region.

Chemical Properties

The chemical properties of a soil are controlled by a number of factors, primarily the mineral composition, organic carbon content, pH and water content. In a soil system with very low organic carbon content and high content of charged minerals (e.g. a Vertosol), the electrochemical properties of the soil are controlled by the net exchange capacity of the smectite clay minerals (Moody *et al.* 1997). Most soil clays contain abundant smectite associated with small amounts of mica, kaolinite, and an interstratified mineral (Singh and Heffernan 2002).

The high clay content in Vertosols (30-90%) means that they are generally considered to be very fertile soils (Seyers *et al.* 2001), but this preconception may mask a range of deficiencies, e.g. nitrogen deficiency in the tropics. (LeMare 1987) stressed that these soils are classed entirely on their physical properties, not chemical, and therefore require chemical analysis on a site-by-site basis. Studies of chemical properties in Vertosols from various regions have found consistently high CEC values of 30 – 80 cmol(+)/kg, often with high base saturation due to the presence of lime ($CaCO_3$) (Deckers *et al.* 2001)**.** Calcium and magnesium tend to be the dominant cations with potassium and sodium present in lower concentrations. These soils generally do not have natural salinity problems, but they may eventuate following prolonged irrigation with poor quality water.

Fertility/Nutrients

While generally quite fertile, Vertosols are often deficient in certain nutrients due to their parent material or climatic conditions. Managing nutrient deficiency can be difficult because of their shrink-swell nature, making fertilisers prone to loss through volatilisation, by-pass flow and denitrification. Certain nutrient-moisture relationships can be exploited to maximise fertiliser efficiency, particularly in the case of nitrogen fertilisers. The low organic matter content of these soils generally results in low nitrogen content; on average Australian Vertosols have less than 0.1% total nitrogen (Seyers *et al.* 2001). Research by (Dalal and Mayer 1986) showed that under continuous cropping soil nitrogen content decreased linearly over a 25 year period, highlighting the need to replenish nitrogen stores in intensively farmed areas. Deep placing of N-fertilisers and split banding in wet years can decrease losses through volatisation and preferential flow (Van Wambeke 1991). Response to N-fertiliser can also be affected by moisture content (Bennett *et al.* 1989).

After nitrogen, phosphorus is considered the next limiting plant nutrient in most Vertosols, however not much is known about its availability and movement in heavy clay soils. High aluminium levels can decrease phosphorous availability as it replaces Al on exchange sites (Klemmedson and Blaser 1990), and by inhibiting the uptake of P by plants (Klemmedson and Blaser 1990). Furthermore, Phosphorus binds strongly to smaller sediments and colloids on a mass/mass basis, and can be transported on these particles through cracks and preferential flow paths that develop in Vertosols, thus becoming unavailable to shallow root crops. However there is evidence to suggest that upon saturation of the soil profile, P availability is increased as hydrous ferrous oxides, which bind P, are reduced to ferrous form (Willet and Muirhead (1984).
Predicting the amount of fertiliser required to increase yield and the crop response is hindered by the fact that response to fertiliser application varies considerably with region, climate and landform (Read and Warder 1974); (Seyers *et al.* 2001). (Seyers *et al.* 2001) found that application of 50% of the recommended amount of fertiliser on a chambered-bed cropping system had a more significant effect than a 100% application to a flat seedbed system. This may be as a result of changes in phosphorus fixing rates in soil due to the different water content and hydrological balance, as suggested by (Willett and Muirhead 1984).

Potassium (K) is rarely deficient, with exchangeable K values ranging from 1 - 13 $cmol_c/kg$ in most Vertosols. The ability of a soil to fix K is related to the interstratified smectite and micaceous clay content. Though K is fixed by the soil, it is still plant available (Said 1971). The availability of exchangeable K is affected by the soil moisture content, with lower moisture contents decreasing availability (Mengel and Von Braunschweig 1972).

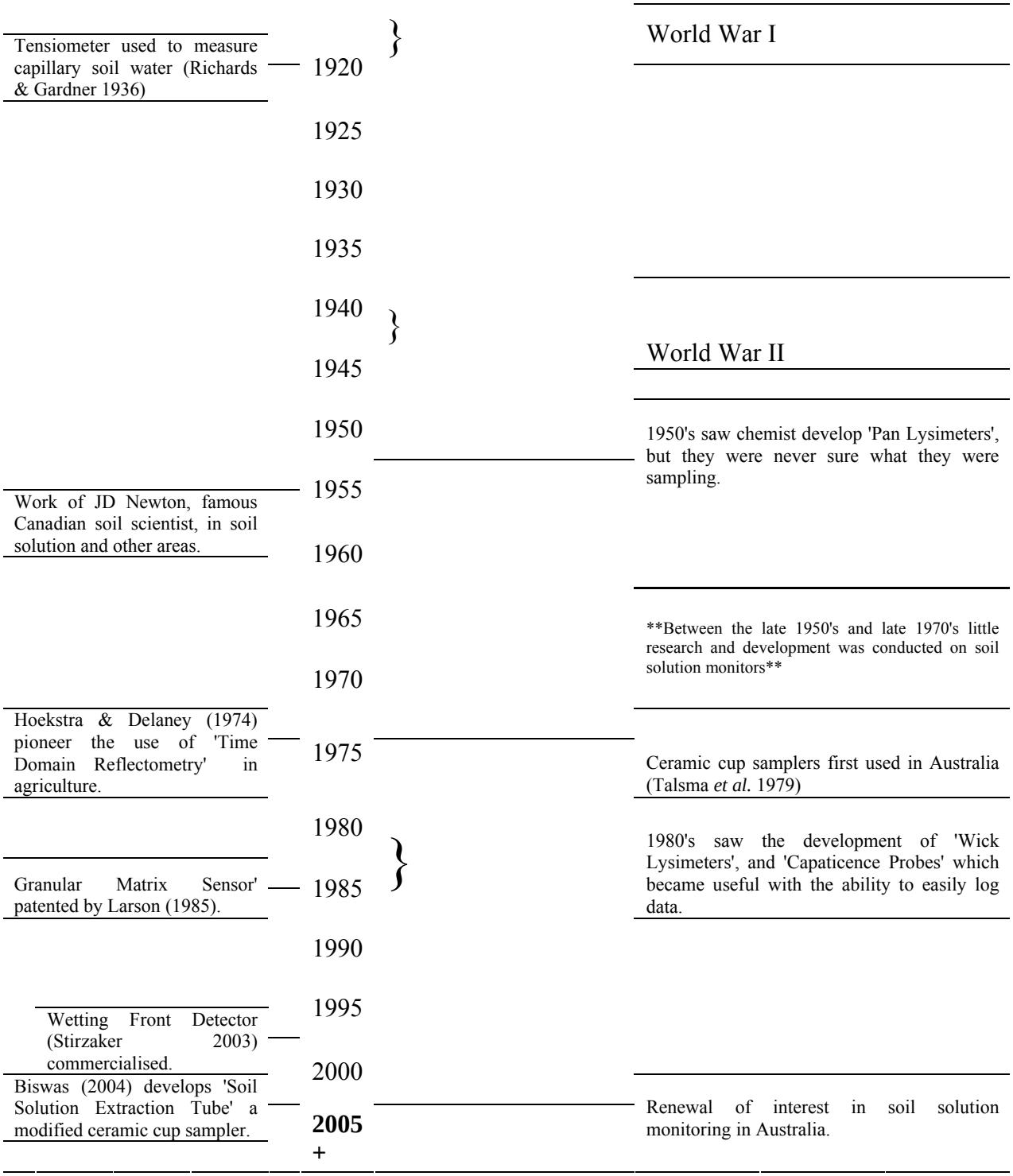
The leaching of P and N from soil into groundwater and surface water systems is a major environmental hazard and can lead to eutrophication in rivers, lakes, dams and estuaries, severely impacting water quality (Kronvang *et al.* 2005; Elrashidi *et al.* 2009). Nutrients and water in agricultural systems need to be used more efficiently and economically for crop production while the adverse environmental effects, associated with the use of fertilisers, are minimized or eliminated (Smethurst 2000). With increasing recognition of the need to limit contamination from non-point sources, like agricultural areas, and the development of management guidelines for catchments and waterways (e.g. EU Water Framework Directive (WISE 2009), and the National Water Quality Management Strategy, Australia (Dept. Environment 2000)) a greater understanding of nutrient movement and behaviour in soil water is required. Instruments such as lysimeters provide the opportunity to track the movement of nutrients in a soil profile over time, and their response to irrigation events and tillage practices.

Lysimeters

Since the late 1800's when people first began to take an interest in the movement of water through the soil, various means of measuring or tracking the soil solution have been developed. The generic term for these instruments is 'Lysimeter' derived from the Greek for dissolved (lysis) and a measure (metron). Table 1 provides a summary of the development of these instruments over the last 100 years. Lysimeters can be divided into two main groups: active and passive. Active lysimeters have suction or a pressure gradient applied to them so that they 'actively' absorb the soil solution, where as passive samplers rely on gravity to direct water into the sampler. Ceramic cup samplers have been around over 100 years (Briggs and McCall 1904) and are one of the most widely used forms of lysimeters because they are relatively cheap, and easy to install and use. Lysimeters come in a range of shapes and size designed for use in different circumstances. Some, like the Wetting Front Detector, was designed to be used by farmers to track the movement of wetting fronts in the profile, and therefore are easy to install and simple in design. Large pan lysimeters, and resin boxes have been developed more for use by researchers, as they require greater time and capital to install and the interpretation of results is more complex because of their design.

Table 1. A summary of the development of soil moisture and solute sampling technology, listing general developments and seminal papers.

Specific Developments	Date	General Developments
Ebermayer (1873) uses a Pan Lysimeter to study the impact of forests on soil.	**Pre 1900**	First references to the use of lysimeters to study water use from the late 17th Century; De la Hire in France, and Van Helmont in the Netherlands (Howell *et al* 1991).
	1900	
Ceramic cup samplers developed (Briggs & McCall 1904)	1905	
	1910	
	1915	



Ceramic Cup Samplers

The principal of the porous cup was first described by (Briggs and McCall 1904) and further developed between 1940 and the early 1970s. They were first introduced into Australia by (Talsma *et al.* 1979)**.** Since then they have been used for a variety of purposes under several different names: porous tubes (Krone *et al.* 1951), deep pressure vacuum lysimeters (Parizek and Lane 1970), vacuum extractor, porous candle, porous cup (Duke and Haise 1973), suction cup (Weihermuller *et al.* 2007) and suction probe. (Biswas *et al.* 2008) propose

standardising the name to Soil Solution Extraction Tube to avoid confusion caused by the various nomenclatures. In this review, the term Soil Solution Extraction Tube (SSET) will be used to describe all forms of ceramic cup samplers, to be consistent with other current Australian literature. SSETs consist of a 'porous cup' (made from ceramic, sintered materials or a membranes) attached to a tube, with a smaller tube inside to extract the sample. The length of the casing and extraction tube varies with different designs. The sample is pulled into the tube when the internal vacuum is greater than the soil deficit pressure. The vacuum is applied to the sampler with a syringe or pump; the optimal pressure is still under debate (Weihermuller *et al.* 2007), but it depends on the volume of water you want needed and the exact process under investigation**.**

Fig. 1. A 40 mm SSET developed by SARDI/Sentec. (SoluSAMPLER^{TM} http://www.hydroterra.com.au/soil_moisture_monitoring.html).

There are 3 different methods of installing the SSET's: (i) vertically, (ii) at 45^{o} angle, and (iii) horizontally from a trench; and they have either continuous or discontinuous operational modes. In continuous mode they are connected to an automated sampler that applies a constant potential gradient based on the pressure in the soil measured by a tensiometer (Weihermuller *et al.* 2007), but this is quite a difficult system to set up and often is impractical in the field (Falivene 2008). More common is the discontinuous mode which involves manually priming the sampler before the irrigation event and then going around and collecting the samples afterwards. Samples can be reliably collected after irrigation, though in heavy clay soils they can become less reliable after the first season (Weaver, *pers. comm*.), as they become clogged with fine clay particles.

There are various advantages and disadvantages of the different types of lysimeters on the market, in terms of ease of use and installation and cost, as summarised in Table 2.

Table 2. Summary of the advantages and disadvantages of the different types of lysimeters

	Sampler						
	SSET	WFD	Lysimeter	Pan Lysimeter	Resin Box	Suction Plate	Wick Sampler
Advantages							
Easy to install and use	X	X					
Cheap and low maintainence	X	X		X	X		X
No priming required		X	X		X		X
Disadvantages							
Expensive			X			X	
Disturbs large soil area		X	X	X		X	X
Difficult to install		X	X		X	X	
May effect flow patterns	X			X	X		

Full-Stop Wetting Front Detector

The 'Full-Stop' or 'Wetting Front Detector' (WFD) was commercialised by Stirzaker (CSIRO) in 2003, and is very simple in design. The detector consists of a plastic funnel with a small collection cup at its base, and a tube extending to the surface which contains a float indicator. The sampler is installed by digging/coring a hole to the required depth then backfilling the funnel and hole with the same soil. The WFD is a form of passive lysimetry that collects a soil solute sample when a wetting front passes the sampler with flow being directed into the funnel. Because it is a passive sampler it is limited to collecting a sample at a matric potential of 0 to -3kPa.

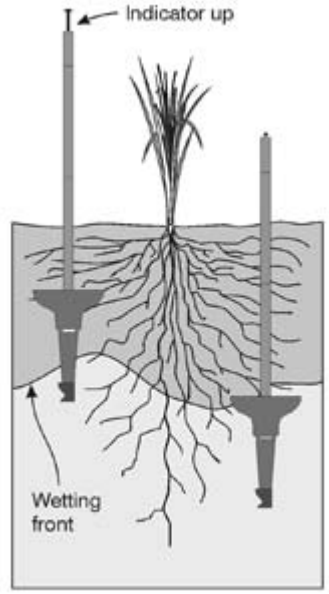


Fig. 2. Wetting Front Detector, showing the indicator raised after a sample has been collected (www.allsun.com.au/FullStop/FullStopIntro.html**).**

The WFD was designed to monitor soil water conditions as an irrigation tool for farmers so they can track the depth to which their irrigation events are penetrating, the small water sample collected (maximum of 5 mL) is sufficient for a farmer to test EC and nitrate concentration with field kits as a rough guide to what is being leached down the soil profile.

Lysimeter

Lysimeters or soil columns consist of containers or vessels of disturbed or undisturbed soil used in mass balance experiments. The surface area and length of the column, fill procedure, lower boundary and location depend on the question to be answered (Weihermuller *et al.* 2007). The choice in soil type (natural or artificial, disturbed or not) is important as it can significantly change flow patterns through the lysimeter. Two main types of Lysimeter exist (i) Free drainage lysimeters (cheaper and easier to install) and (ii) Suction controlled lysimeters (more expensive and difficult to install and use); which can be set up in the field or in controlled conditions in a glasshouse (Messiner *et al.* 2000). Lysimeters are a very labour intensive instrument to install and run, and therefore are not suitable for use by farmers, and are best suited for use by researchers on long term projects.

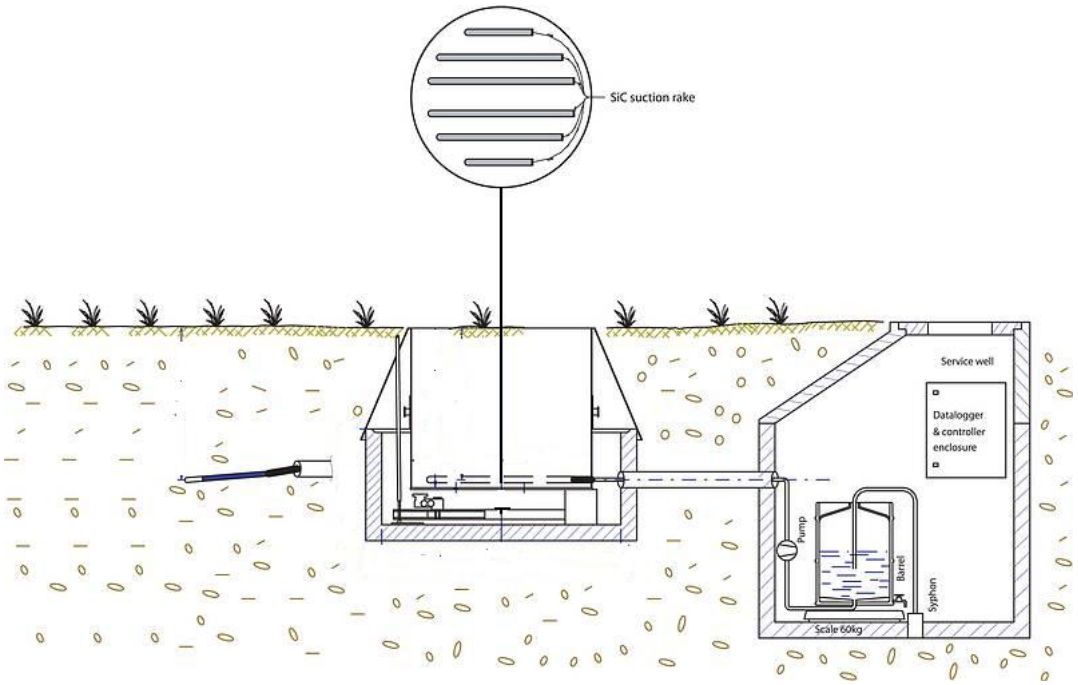


Fig. 3. Schematic diagram of a suction controlled 'Weighing Lysimeter' showing the service well/access area for collecting samples and containing a data logger to record changes in mass, the scales, porous suction rake(inset), pump, and collection jar.
(http://www.ums-muc.de/en/products/lysimeter/hydrolysimeter.html 2009)

The set up of the lysimeters affects what they can be used for, but they are commonly used in studies that look at solute concentration, transport studies, mass balance questions (e.g. salt), as well as for estimating soil water balance parameters. Caution must be taken in interpreting the results as they do not account for lateral flow and solute fluxes, and the vertical boundaries may create fringe effects and preferential flow paths (Schoen *et al.* 1999).

Pan Lysimeter

Pan or Zero-tension lysimeters consist of a 'pan' shaped device filled with a coarse, conductive material to collect freely percolating soil water. They are generally installed horizontally into the profile from a trench; the pan is often around 0.5 m^2. The material used to fill in the pan can create preferential flow towards or away from the pan due to the formation of a saturated horizon above the pan. Because of this efficiencies as low as 10%

have been noted, they appear to be more inclined to work in soils with a lot of macro-pores, and not so well in fine textures soils (Zhu *et al.* 2002).

Resin Box

Resin Boxes are boxes with an open top and bottom containing alternating layers of soil and resin, freely percolating water enters the box, and solutes are absorbed onto the synthetic exchange resins, the type of resin depends on the target compound. The compound can then be extracted in the lab, and the solute mass normalised with the cross sectional area to get solute flux (Weihermuller *et al.* 2007). Because of the way the Resin boxes work, concentrations of solutes cannot be derived, only flux rates. They are generally installed horizontally from a pit to minimise disturbance to the profile above the box (Weihermuller *et al.* 2007).

Suction Plates

Consist of a porous plate inserted into a frame to collect the sample with a tube for extraction; a pressure gradient is generally applied to the plate to collect a sample. (Weihermuller *et al.* 2007) recommend applying a pressure equal to ambient conditions to minimise the disturbance to natural flow. This can be done by using a tensiometer to measure the soil potential and using it to control the pressure applied to the suction plate. Because of their large surface area they may be able to detect preferential flow paths.

Wick Samplers

Several years of testing under field conditions has shown that Wick Samplers (Fig 4) have a lechate collection efficiency (calculated as 'measured drainage' over 'estimated drainage') of ≥ 100% (Zhu *et al.* 2002).

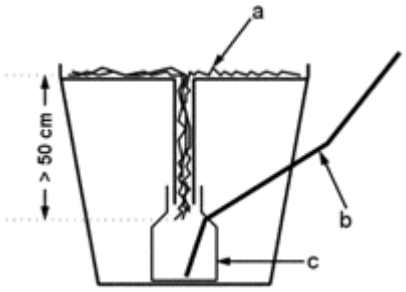


Fig. 4. Sketch of a wick sampler with (a) wick, (b)sampling tube, and (c) sampling bottle (from Brandi-Dohrn *et al* 1996).

The effect of the wick material on sample composition is debated. (Holder *et al.* 1991; Knutson and Selker 1994)**;**(Siemens and Kaupenjohann 2004) found no effect, but (Goyne *et al.* 2000) observed considerable changes in sample composition and properties when using a fibre glass wick. They require further testing before they can be considered reliable, for use in scientific experiments (Weihermuller *et al.* 2007), but overall they provide a compromise in price and associated problems with Pan Lysimeters and Suction Plates.

Problems with the samplers

The main problem with SSETs and other lysimeters is that their influence on the surrounding soil-water regime is unknown. (Hart and Lowery 1997) estimated that in a 'Sparta sand' (mesic, uncoated Typic Quartzipsamment) SSETs have a mean axial sampling radius of ~24 mm, but recognised that this would change significantly with different textured soils. There has been research to suggest that SSET's are biased towards the soil solution in large pores over small pores, so that in a fine textured media, like heavy clays, they become biased towards preferential flow (Hansen and Harris 1975), (Severson and Grigal 1976), and that they change the surrounding natural flow patterns (Hart and Lowery 1997). The area sampled by the SSET is influenced by soil hydraulic properties, ambient water content and extraction time, making the sampling area highly variable in space and time (Weihermuller *et al.* 2007). These problems are common across all types of lysimeters and further research under field and lab conditions needs to be conducted to determine the effects on soil-water flow patterns and the sampling area of the different instruments; before they can be a really useful instrument in the monitoring of salt and nutrient movement in the soil profile.

Another area of concern is the impact of the porous media on the sample composition. (Wolff 1967) was one of the first to show that new cups contaminated deionised water. (Debyle *et al.* 1988) showed under lab conditions, that with use SSET's produced samples with Mg, Na, NO3 and K concentrations that were consistently equal to or greater than, the samples from new cups. Washing with acid, frequently HCl (Wolff 1967; Grover and Lamborn 1970; Debyle *et al.* 1988) is a common practice to clean cups before reuse, and while it appears to re-establish the balance of some cations in the samplers the exact results vary. (Grover and Lamborn 1970) found that Na and K contamination decreased but Ca remained unchanged, while (Debyle *et al.* 1988) found that Ca and Mg contamination decreased and Na, K and NO3 remained variable. (Raulund-Rasmussen 1989) concluded that they were unsuitable in acid-soils because amorphous gibbsite in the ceramic decomposed, releasing Al contaminating samples, but (Hughes and Reynolds 1990) found that with suitable pre-treatment and equilibration they can be used successfully in acid soils.
Unfortunately no information or discussion is provided on the origin of the ceramic and its possible impact on the results, and there appears to be little literature on the effect.
Soil solution samplers are made from a variety of porous materials which are known to absorb different compounds, Table 3 based on the work by (Weihermuller *et al.* 2007) summarises which materials are best suited for the collection of different substances, and the potential artefacts based on current findings.

Table 3: Presents a summary of different soil solutes and the potential artefacts of different sampler material on the sample, different materials are listed with regards to their suitability for sampling different solutes. Adapted from (Weihermuller *et al.* 2007).

Solute	Potential problems	Suitable materials	Less suitable materials	Literature
Aluminium ($Al(OH)_x^{n-x}$)	sorption, precipitation by increase in pH	PA, PE, PTFE	stainless steel, oxide ceramic	Suarez (1986, 1987); Kaupenjohann and David (1996); Goyne et al. (2000)

Ammonium (NH_4^+)	nitrification, N-assimilation	stainless steel, glass, oxide ceramic, nylon, PE, PTFE, PVC		
Lead (Pb^{2+})	sorption, contamination	PA, PE, PTFE	stainless steel, oxide ceramic, PVC	Grossmann et al. (1990); Wenzel and Wieshammer (1995); Wenzel et al. (1997); Rais et al. (2006).
Cadmium (Cd^{2+})	sorption, contamination	PA, PE, PTFE	stainless steel, oxide ceramic, PVC	Grossmann et al. (1990); Wenzel and Wieshammer (1995); Wenzel et al. (1997); Rais et al. (2006).
Iron (Fe^{2+})	precipitation by oxygen contact or increase in pH	glass, Nylon, PE, PTFE, PVC		Suarez (1986, 1987);Schwarz and Miehlich (1993)
Potassium (K^+)	cation exchange	stainless steel, glass, (oxide ceramic), Nylon, PE, PTFE, PVC		Grover and Lamborn (1970)
Calcium (Ca^{2+})	cation exchange, precipitation of carbonate	stainless steel, glass, (oxide ceramic), Nylon, PE, PTFE, PVC		Grover and Lamborn (1970); Schwarz and Miehlich (1993)
Carbonate (H_2CO_3, HCO_3^-, CO_3^{2-})	degassing of CO_2	stainless steel, glass, oxide ceramic, Nylon, PE, PTFE, PVC	glass fibre wicks	Suarez (1986, 1987); Grossmann et al. (1988);Kaupenjohann and David (1996); Goyne et al. (2000)
Copper (Cu^{2+})	sorption, contamination	PA, PE, PTFE	stainless steel, oxide ceramic, PVC	Grossmann et al. (1990); Wenzel and Wieshammer, (1995); Wenzel et al. (1997); Rais et al. (2006).
Magnesium (Mg^{2+})	cation exchange, precipitation of carbonate	stainless steel, glass, (oxide ceramic), Nylon, PE, PTFE, PVC		Grover and Lamborn (1970); Schwarz and Miehlich (1993)
Manganese (Mn^{2+})	precipitation by oxygen contact or pH enrichment	glass, Nylon, PE, PTFE, PVC		Suarez (1986, 1987);Schwarz and Miehlich (1993)
Sodium (Na^+)	cation exchange	stainless steel, glass, (oxide ceramic), Nylon, PE, PTFE, PVC		Grover and Lamborn (1970)

Nickel (Ni^{2+})	sorption, contamination	PA, PE, PTFE	stainless steel, oxide ceramic, PVC	Grossmann et al. (1990)
Nitrate (NO_3^-)	nitrification, N-assimilation	stainless steel, glass, oxide ceramic, Nylon, PE, PTFE, PVC		
Pesticides	sorption, contamination from solvents and flexibilizers, volatilization	glass, stainless steel	oxide ceramic, PE, PVC, (PTFE)	Wood et al. (1981)
Phosphate ($H_xPO_4^{x-3}$)	specific sorption by ligand exchange	stainless steel, glass	oxide ceramic	Hansen and Harris (1975); Bottcher et al. (1984)
Protons (H^+, pH-value)	degassing of CO_2	stainless steel, glass, oxide ceramic, Nylon, PE, PTFE, PVC	specific fibre glass wicks	Suarez (1986, 1987);Grossmann et al. (1988);Kaupenjohann and David (1996); Goyne et al. (2000)
Sulfate (SO_4^{2-})	Sorption	stainless steel, glass, oxide ceramic, Nylon, PE, PTFE, PVC,		
Zinc (Zn^{2+})	sorption, contamination	PA, PE, PTFE	stainless steel, oxide ceramic, PVC	Grossmann et al. (1990);Wenzel and Wieshammer (1995); Wenzel et al. (1997); Rais et al. (2006)

Note: PA: polyamide (e.g. Nylon), PE: polyethylene, PVC: polyvinylchloride, PTFE: polytetrafluoroethylene (e.g. Teflon), glass: borosilica-glass (e.g. Duran).

Sample interpretation

There are various methods of measuring soil EC and solute concentrations, however how representative they are of what the plant actually experiences has been questioned ((Nadler 1995); (Biswas *et al.* 2008)**,** particularly EC. Soil EC is generally measured as soil-paste extract either in deionised water in a 1:2 or 1:5 ratio. By adding deionised water the soil water content is changed to around -1 kPa diluting the concentration of ions in the extracted soil solution so that the EC of the saturated paste extract is less than the field condition. The degree of change is related to the original soil water content (Falivene 2008). As this is the most common method of soil EC testing most threshold values are based on these results (Mass and Hoffman 1977).
(Biswas *et al.* 2008) on sandy loam soils in South Australia found a 2:1 ratio (equation 1) between the salinity of soil water extracts (ECsw) and saturated paste extract (ECe), a 1:5 H_2O ratio, (standard soil salinity testing method).

$$ECsw = 2.1 \times ECe \quad \ldots (1)$$

This relationship held true for the Riverland irrigated soils, but needs further testing for heavier texture and duplex soils.

Field studies using Lysimeters

Weaver *et al* (2004) used SSET's to study the movement of nutrients and estimate deep drainage, using the chloride mass balance method, under irrigated Vertosols. Three trial sites were set up in the Namoi Valley, and were monitored over a three year period from 2000 to 2003. Each site replicated three planting treatments (i) cotton-wheat standing stubble (no tillage), (ii) continuous cotton no tillage, (iii) continuous cotton with conventional tillage, and the samplers were installed at 60, 90 and 120 cm depths and sampled at frequent intervals in the cotton seasons.
Across all sites it was found that minimum tillage and cotton-wheat rotations facilitated higher deep drainage rates, than continuous cotton with conventional tillage. The greatest drainage rates were under cotton-wheat rotations with an average value of 65 mm/year, with the lowest under continuous cotton with conventional tillage averaging 20 mm/year. The leaching fraction defined as the percent drainage past 120 cm relative to the total water inputs, was found at all sites were < 10%. Knowing which crop rotations maximise the deep drainage will be beneficial in improving root zone soil quality and yield, though Weaver *et al* (2004) recognised that more field data on rates of deep drainage is required for different land management systems and options.

(Biswas *et al.* 2008) looked at problems with root zone salinity in drip irrigated vineyards, stone and fruit orchards. As water availability has decreased in most Australian agricultural areas over the last decade, grape growers have become more efficient in their practices, planting fewer vines and aiming for grape quality over quantity. This has meant that in areas of poor irrigation water quality (high EC) they now face problems of root zone salinity. It is necessary to have accurate measurements of root zone salinity to determine EC patterns through the season and threshold values for the crops. Most growers and researchers use the thresholds set out by (Mass and Hoffman 1977), but vine growth Australia has not been strongly impacted above these levels. To monitor the root zone salinity Biswas et al. developed modified SSET's for colleting soil pore water. The samplers were installed in nests of three at 30, 60, 90 cm depth with in 15 cm of the dripper in a vineyard in South Australia.
Initial results from the study, which is ongoing, found that at 30 cm values well above the Mass and Hoffman (1977) thresholds (3.6 dS/cm) were observed consistently with out any obvious impact on the vines. After a summer storm EC spiked at 11.9 dS/cm as salts in the surrounding profile were mobilised. These values gradually decreased over winter with irrigation and rainfall events that gradually leached salts down the profile. Patterns of ECsw from the 60 and 90 cm samplers suggest that the salt is moving below the root zone but not yet being leached from the profile. (Biswas *et al.* 2008) concluded that with increased irrigation efficiency monitoring and management of root zone salinity is very important, especially in areas of poor irrigation water quality, to avoid loss of crop value due to high salt content. The SSETs are a cheap and simple to use tool that allows growers to monitor the salinity and make decisions about when to apply leaching irrigations.

Fine *et al*. (2002) used lysimeters to study the organic carbon (OC) leached from under *Eucalyptus spp.* irrigated with secondary effluent. The hypothesis was that delayed transport times would be sufficient to enable biological degradation to eliminate OC from leachate. They tested the hypotheses by building lysimeters in 200 L drums, packed with sand or one of two clayey soils, which were either planted or not. They found that to a certain extent the soil was able to reduce the OC content of lechate, but at higher application rates the system

appeared to become over loaded and dissolved organic carbon (DOC) and Total organic Carbon (TOC) levels begin to increase again (Fine *et al.* 2002).

Chertkov and Ravina (2002) used lysimeters to study the generalisation of an earlier proposed model describing the hydraulic conductivity of a Vertosol. The cracks in swelling clay soils at high enough water contents can be presented as the superposition of interblock- and interaggregate- crack networks. For the vertical hydraulic conductivity the generalisation is based on the results relative to the geometrical and hydraulic properties of capillary crack networks (Chertkov and Ravina 2002). The contribution of interblock-capillary cracks to the hydraulic conductivity of a soil, changes with depth. The numerical estimates indicated that capillary cracks of both types, contribute essentially and prevailing to the hydraulic conductivity at sufficiently small pressure heads. The validation of the model is based on a comparison between two independent estimates of the summary of hydraulic conductivities of the soil matrix, and interaggregate capillary cracks. The results of the comparison validate the model showing that it is in agreement with the available data from the lysimeter experiment.

Conclusion

The last few years has seen dramatic rises in food and fertiliser prices partially caused by high oil prices but also due to increased demand for protein and cereals from developing nations. This, coupled with increased environmental awareness of consumers has put pressure on farmers to increase yields, while minimising their environmental impact. The leaching of nutrients from the soil into ground and surface water systems is a major environmental hazard and can lead to eutrophication in rivers, lakes, dams and estuaries, severely impacting water quality (Kronvang *et al.* 2005); (Elrashidi *et al.* 2009). With the introduction of legislation that requires the reduction in pollution from non-point sources, like agricultural areas, e.g. EU Water Framework Directive (WISE 2009), and the National Water Quality Management Strategy, Australia (Dept. Environment 2000) it is becoming more essential to develop greater efficiency in the use of fertilisers both environmentally and economically.

Vertosols soils cover a large area of the world and are used predominantly for intensive, irrigated agriculture. The impact of water on the structure of swelling clays has been extensively studied, but limited work has been done on the hydrology of Vertosols and the effect of irrigation on nutrient movement because of the difficulty in measuring the soil solution.

Lysimeters enable the monitoring of the soil solution, but as scientific instruments there are still large areas that require extensive research before they can be used reliably to test scientific hypotheses. Some of the major knowledge gaps that need research include (i) the impact of lysimeters on the surrounding soil hydrology, (ii) the impact of the sampler material on the sample collected and (iii) their representation of the bulk solution via the sample collected, spatially and temporally

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Monitoring nutrients in the soil solution of an irrigated Vertosol near Narrabri, Australia.

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Abstract

With rising costs and increased environmental awareness, agricultural industries need to develop more sustainable irrigation and growing practices. The ability to monitor the soil solution is key in developing better management practices, but so far there has been little research conducted on Vertosols. Ceramic cup samplers were installed in an irrigated Vertosol near Narrabri, under a cotton and wheat crop to assess their effectiveness in a heavy clay soil at different 3 depths, and the impact of irrigation rates on the concentration of ammonium, nitrate and phosphorus in the root zone of the crops. Samples were collected from the samplers approximately 90% of the time, but under drier conditions appeared to be affected by poor soil-cup contact caused by cracking in the clay profile. The replication of samplers (9) under cotton was insufficient to quantify the root zone variation, so the values found can only be used as indicators of the conditions in the root zone. Greater replication under the wheat (36 samplers) quantified the root zone variation. The trends observed varied considerably for each of the nutrients studied (PO_4-P, NO_3 and NH_4). Phosphorus and nitrate concentrations decreased over time, while ammonium showed no significant difference over time. Two irrigation treatments were studied on the wheat plots and phosphorus concentrations where greatest under Treatment 1, where as nitrate concentrations were greatest under Treatment 2. The ammonium concentrations under wheat fluctuated with depth for irrigation treatments 1 and 2.

A lab experiment was also run to determine the amount of soluble ortho-phosphate absorbed by Australian made cups during soil-water sample collection. Past research in Europe and the United States has shown that ceramic cup samplers can absorb large amounts of ortho-phosphate from the soil-water sample. The results indicate that Australian made ceramic cups do not absorb significant amounts of ortho-phosphate from the solution.

Key words: Ceramic cup samplers, Vertosols, monitoring, phosphorus, sorption.

Introduction

The broad alluvial valleys of Northern NSW and southern Queensland constitute one of the main agricultural regions of Australia; producing cotton, pasture for stock feed, and cereals. The predominant soils in the region are red and black self-mulching clays (Vertosols), interspersed with Kurosols, Calcarosols and Chromosols. With rising capital costs, and public concern about water use and the environmental impacts of growing irrigated crops in Australia (Falivene 2008), the cotton and grain industries need to develop more efficient and sustainable irrigation and growing practices. Because of the need to limit contamination from non-point sources, like agricultural areas *(*Weihermuller *et al.* 2007*)*, and the development of management guidelines for catchments and waterways (e.g. the National Water Quality Management Strategy, Australia) a greater understanding of nutrient movement and behaviour in soil water is required. Instruments such as lysimeters and other forms of water monitoring provide the opportunity to track the movement of nutrients in a soil profile over time, and their response to irrigation events and tillage practices.

The soil solution is the aqueous liquid (mainly water) found within a soil, containing ions released from clay minerals, organic matter or plant roots and leaves as well as added fertilisers. The soil solution is stored in pore spaces and cracks in the soil matrix and is essential in the supply of nutrients to plants, mainly in the form of inorganic ions (Smethurst 2000). For example, plant access to potassium (K) is related to the ability of K^+ ions to diffuse through the soil in the soil solution. A positive response to higher levels of K application can only be seen when there is sufficient soil moisture to allow diffusion into the root zone (Mengel and Von Braunschweig 1972). The downward movement of dissolved salts in the soil profile with percolating water is known as leaching and may contribute to groundwater contamination in regions with intensive agriculture.

The behaviour of the soil water is significantly affected by the soil texture class; a predominantly sand profile will have a higher hydraulic conductivity and deep drainage rate than a heavy clay soil (Saxton *et al.* 1986). Although leaching has been studied extensively on sandy and silty soils, research into deep drainage under irrigated crops grown on shrink-swell clay soils has been neglected until quite recently (Hearn 2000). Chen *et al.* (2002) showed that shrink-swell clays create preferential flow paths in the soil, which speed the

movement of fertilisers below the root zone. Percolation rates of up to 250 mm per season have been estimated under irrigated crops on the shrink-swell clay soils of Northern NSW and Southern QLD (Hullugalle 2005).

The leaching of phosphorus and nitrogen from soil into groundwater and surface water systems is a major environmental hazard and can lead to eutrophication in rivers, lakes, dams and estuaries, severely impacting water quality (Kronvang et al. 2005; Elrashidi et al. 2009). Nutrients and water in agricultural systems need to be used more efficiently and economically for crop production while the adverse environmental effects, associated with the use of fertilisers, are minimized or eliminated (Smethurst 2000). Given that large amounts of nutrients may be lost in this way, the potential cost to farmers can also be high. In 2008 due to rises in the price of oil and higher agricultural demand, fertiliser prices dramatically increased (Economist 2008). The price of rock phosphate in India rose by 708% in April 2008 compared to the average for January – March 2007 (Jagannathan 2008). In Australia price rises have not been quite so extreme but they are having a significant impact on the economic return farmers can expect from their crops (Fuller 2008).

In the Namoi valley cotton is often grown in rotation with wheat. Farmers experience and research has shown that this is the most economically profitable and a highly beneficial rotation (Hulugalle *et al* 2005), having a positive impact on soil structure and quality as shown by the enhanced ability to retain water. This is particularly true if combined with no-tillage practices (Hulugalle *et al* 2005) with the deeper rooting wheat meant to utilise nutrients leached below the cotton root zone (Weaver *et al.* 2003).

Soil solute movement is inherently difficult to monitor, and numerous different methods have been developed. One of the first reports of the use of ceramic cup samplers was by (Briggs and McCall 1904), and there are currently several models commercially available. Other methods of measuring soil solute movement include the use of tension plate lysimeters, pan lysimeters, wick samplers, wetting front detectors and resin boxes (Weihermuller *et al.* 2007; Falivene 2008). Ceramic cup samplers have an advantage over these methods in that they are relatively cheap and easy to install and maintain. In spite of this, very little research has been conducted with them in Australia, particularly on Vertosols. Nevertheless a number of studies under different irrigated crops on different soil types have been conducted worldwide

and can be used to direct research into more efficient soil solution monitoring and fertilizer and irrigation practices in Australia.

In spite of the importance of the soil solution for crop growth and soil management, there are still large gaps in out understanding of it. Raine *et al*. (2007) highlighted four key areas where there are significant gaps in our knowledge; (i) the effect of root distribution, evapotranspiration, and soil type on soil wetting patterns, (ii) the accuracy and adequacy of using simple estimates of salt levels to predict effect on crops, (iii) fate of solutes over time in relation to irrigation events, and (iv) effect of soil texture on solute behaviour.

This project has four main aims based on the use of ceramic cup samplers under an irrigated crop.

1. To determine the rate of phosphorus adsorption by new Australian ceramic cups.
2. To establish the effectiveness of ceramic cup samplers to sample and access the soil solution in clay soils.
3. To estimate the concentrations of major nutrients in the root zone solution of a cotton and wheat crop.
4. To quantify the variation of major nutrients in the root zone solution over time after irrigation of a cotton and wheat crop, using ceramic cup samplers.

It was hypothesised that in the field three main factors would influence the concentration of nutrients in the soil solution at any given time. The three factors are irrigation level (i.e. amount of water applied to the field), the depth to which the samplers were installed, and time. It was thought that time would be highly significant as the crop grew and external conditions changed influencing the soil solution's composition.

Materials and Methods

Ceramic cup samplers

Two types of ceramic cup samplers were used in this research; commercially available ceramic cup SoluSAMPLERS^{TM} (Fig. 1) and purpose-built samplers following the guidelines provided by (Deery *et al* 2006). Information from Tim Weaver (*pers. comm*.) about his

experience with using purpose-built samplers, and previous experience with the Sentek produced samplers led to a few modifications of the design proposed by Deery *et al* (2006).

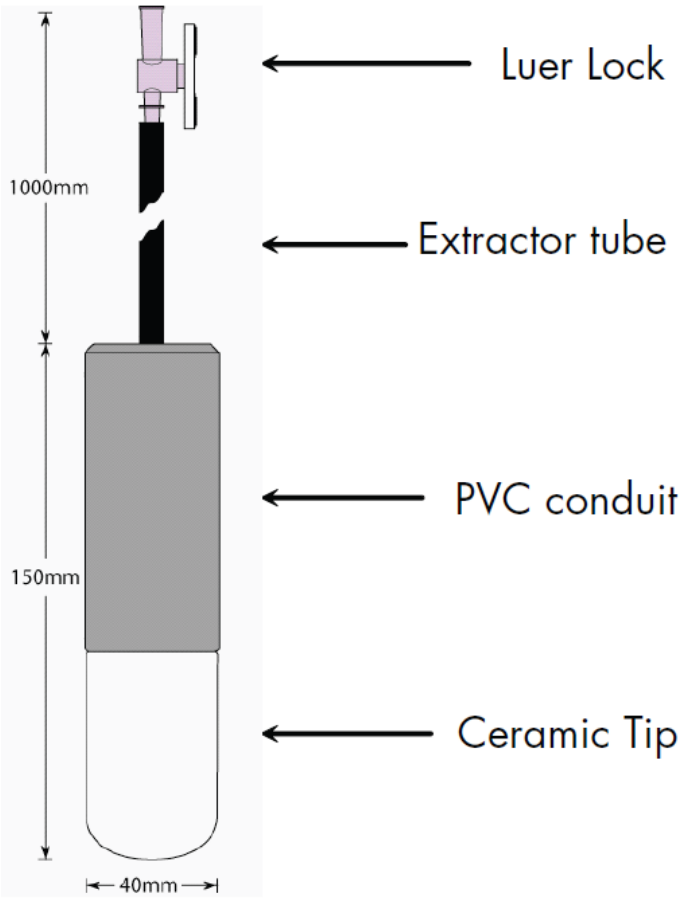

Fig. 1: Diagram and approximate proportions of a ceramic cup SoluSAMPLER. The ceramic tip and PVC conduit are buried in the soil, and the extractor tube is used to apply the vacuum and extract the water sample (Biswas *et al* 2007).

The samplers were installed in the middle of the cotton and wheat beds. The wheat beds were approximately 2m wide with 6 'lines' of wheat, the samplers were installed in the middle of these lines (Fig. 2.).

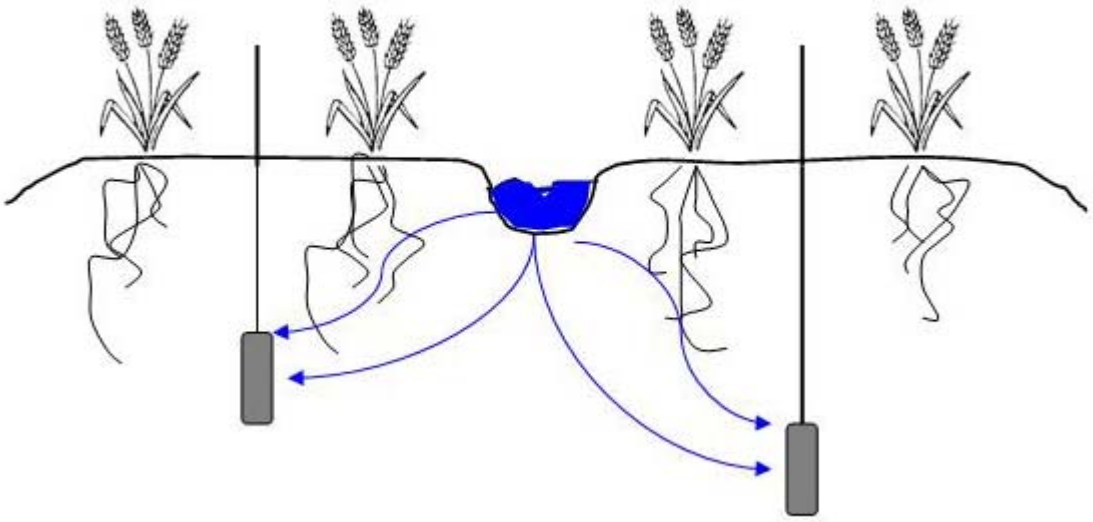

Fig. 2. Sketch of the samplers installed in the wheat bed, and a simplified flow path of water from the irrigation furrow to the sampler.

The samplers extract the soil water by creating a pressure gradient between the ceramic cup and the surrounding soil Fig. 3. is a simplified representation of the zone of influence of the suction cup and the response of the surrounding soil solution. Soil water is drawn into the cup, till it is full or the pressure gradient no longer exists, and is then held in the cup till the sample is extracted by syringe. Approximately a 60 kPa vacuum can be applied by extracting three 50 mL syringes of 'air' from the samplers after they are installed in the soil. Care has to be taken during installation to ensure good soil – ceramic cup contact otherwise the samplers do not hold their vacuum.

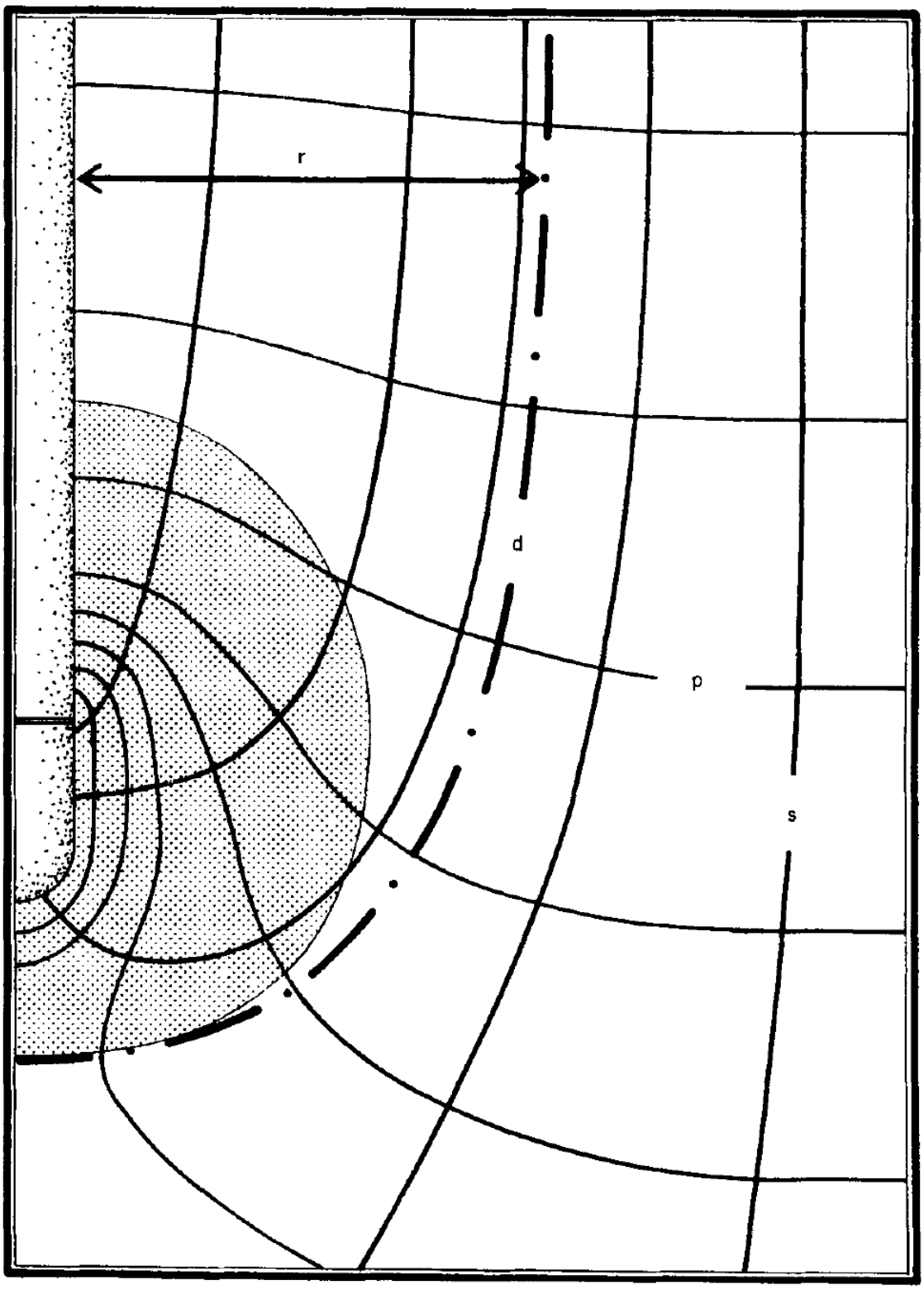

Fig. 3. Potential field linesaround a suction cup in a homognous soil, where r - radius of the recharge area, d - dividing stream line, p - iso-potential line, s- stream line and the dotted field is the area from which the sample is taken (**Grossman and Udluft 1991)**.

Phosphorus sorption experiment

A phosphorus sorption experiment was set up following the procedure described by (Bottcher et al 1984**).** Five ceramic cup samplers were examined, including two of the Sentek 'SoluSamplers', and three purpose-built samplers. A standard ortho-phosphate solution of 5 ± 0.1 mg L^{-1} concentration as phosphorus was made by dissolving 0.10985 g of KH_2PO_4 in deionised water and diluting to 5 L. The apparatus used in this experiment (Fig. 4) consisted of five 1-L graduated measuring cylinders, a 60 mL plastic syringe and plastic 50 mL sample tubes.

The samplers were not pre-treated with an acid-wash as suggested by (Bottcher et al 1984**)** so as to mimic the condition of the samplers in the field. All the samplers were in an air-dry condition before being suspended in the measuring cylinders. The tip was suspended at the 100mL mark to enable absorption from all sides of the cup. After the samplers were placed in the 1-L measuring cylinders they were filled to the 1-L mark with the 5 mg L-1 ortho-phosphate solution. The samples were left for 15 minutes before 60 kPa suction was applied; 50 mL samples were then collected after half an hour from the samplers, from within the measuring cylinder and a sample of the stock solution.

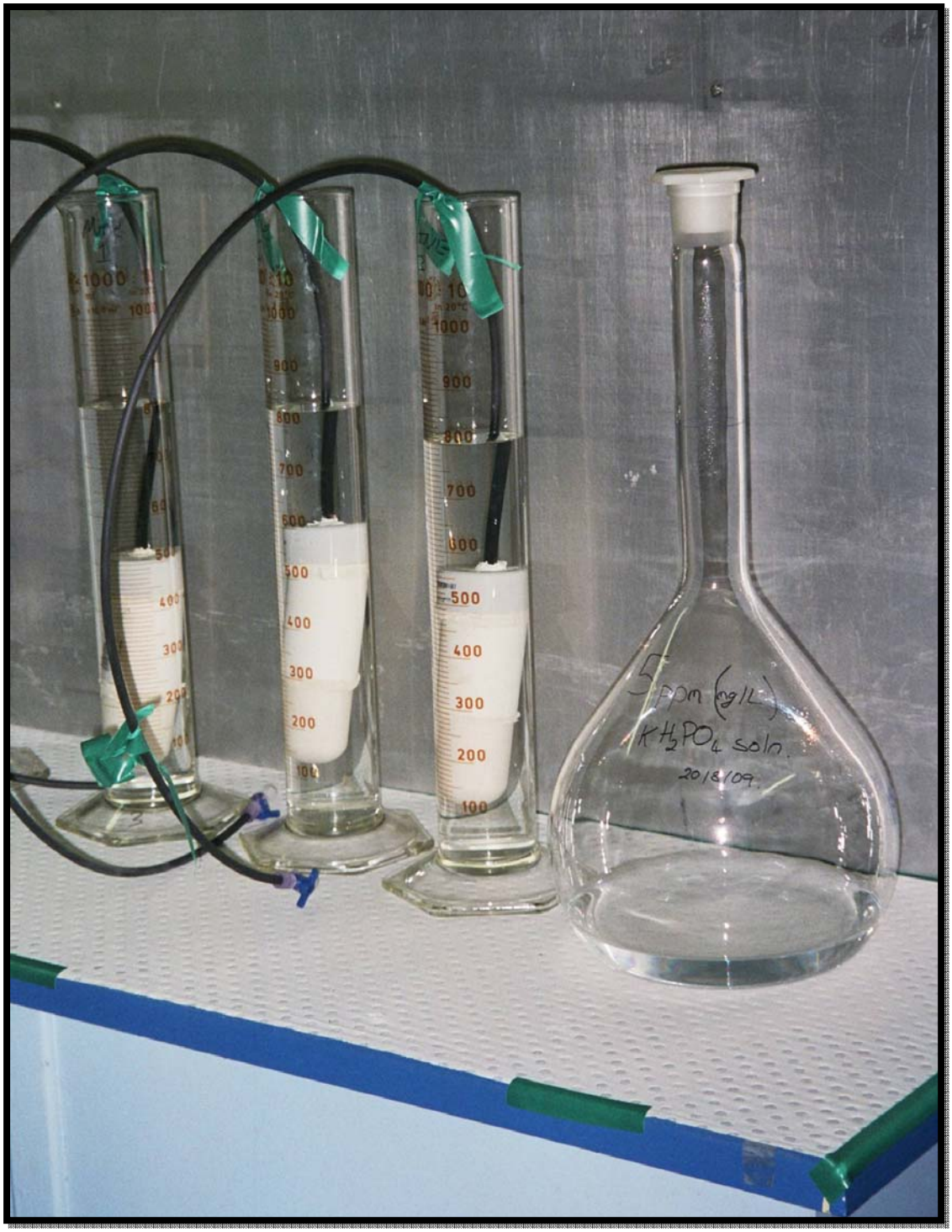

Fig 4: Determining rates of PO4-P absorption by ceramic cups in the lab.

Three more samples were collected approximately 12 hour intervals; time of each sampling was recorded. The measuring cylinders were topped up to 1L after each sample was collected. After, the fourth set of samples were collected, the stock solution was drained off and the samplers were left to drip dry for 9 hrs. The measuring cylinders were rinsed and

then refilled with deionised water and 60 kPa suction applied to the cups. After 1 hr samples were collected from each of the samplers and measuring cylinders.

Description of field study area

Located in central northern NSW in the Namoi Valley, Narrabri is an important regional centre servicing a large and highly productive agricultural district. The Namoi valley supports large cotton, wheat and livestock enterprises. Located roughly in the middle of the Namoi Valley on the flood plain, Narrabri has a semi-tropical climate with hot summers and cooler winters (Fig. 5.). Average temperatures range from 27^{o}C in the summer to 11.6^{o}C during winter. Precipitation occurs throughout the year with the summer months being distinctly wetter. The average annual rainfall is 644 mm (BOM 2009), but actual annual rainfall varies considerably.

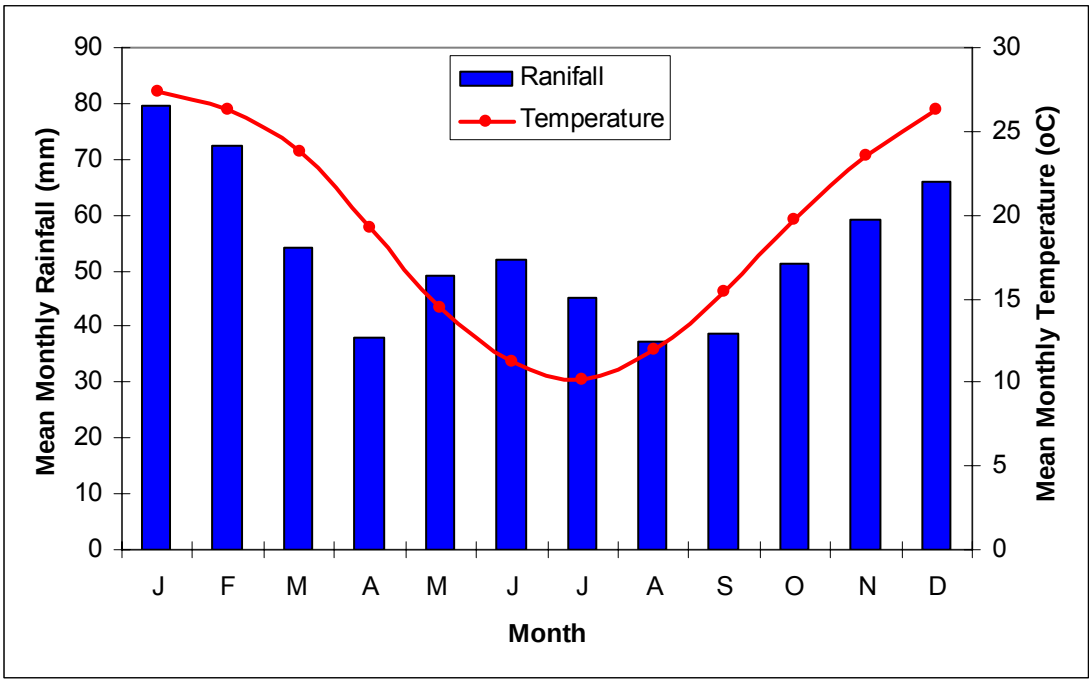

Fig. 5.: Climate statistics for Narrabri, showing average monthly temperature and rainfall (BOM 2009)

Two neighbouring properties were used for this study, the 'Australian Cotton Research Institute' (ACRI) and 'Auscott – Namoi Valley', both located approximately 30 km west of Narrabri.

Field sampling and experimental design

Cotton

'SoluSAMPLER^{TM}' ceramic cup samplers were used to obtain soil water samples from an irrigated cotton crop at different depths. The cotton plots were located at the Australian Cotton Research Institute (ACRI), Narrabri, NSW, and were established as part of a larger experiment to examine the impact of irrigation rates on cotton yield (Appendix 1). Three replicated plots receiving 'normal' flood irrigation treatments were chosen for our experiment, representing the industry standard for flood irrigation, occurring about every 10 days. All fertiliser treatments applied to the crop occurred before the samplers were installed, Table 1 describes the fertilisers applied and when the samples were collected.

Table 1 - Description of the rates of fertiliser applied to the cotton crop throughout the growing season, dates of irrigation, and sampling.

Date	Actions
12-Sep-08	200 kg ha-1 of Anhydrous ammonia
28-Sep-08	100 kg ha-1 of Superphosphate
15-Jan-09	Installed samplers
27-Jan-09	1 kg ha-1 of salt
29-Jan-09	Irrigation
30-Jan-09	Collected samples
31-Jan-09	Collected samples
9-Feb-09	Irrigation
10-Feb-09	Collected samples
11-Feb-09	Last samples collected

Nine ceramic cup samplers were installed in three replicate plots (A, B and C) at the depths 0.25, 0.50 and 0.75 m on the 15th of January, 2009. Samplers 1, 4 and 7 were installed at

0.25 m, samplers 2, 5, 8 were installed at 0.50 m and samplers 3, 6, and 9 were installed at 0.75 m depth.

Each plot consisted of 16 rows of cotton, with the samplers installed in a group in the fourth row from the plot's edge, 10 m from the end of the furrows to minimise edge effects. The soil solution samples were collected 24 hrs after irrigation and at the end of the approximately ten day period between irrigations (vacuum was applied to the samplers and they were then left for 10 days before the sample was collected).

Wheat

The wheat plots under study were located on the Auscott – Namoi Valley property 'Togo'. The field was flood irrigated as part of a larger experiment being conducted to investigate irrigation rates and grain yield (Appendix 2). Auscott Togo was used for the wheat field experiments as a winter wheat crop was not sown at ACRI in 2009. Two different irrigation treatments were investigated on two replicated blocks:

1 – Initial irrigation ('wetting up') followed by scheduled irrigation events when soil water deficit is 50 mm.

2 – Initial irrigation ('wetting-up') followed by scheduled irrigation events when soil water deficit is 90 mm.

The initial irrigation was an event known as 'watering-up the field', which thoroughly wets the upper 1m or so of the soil profile, and was applied uniformly to the whole field. Samples were collected 0 days (02/07/09 am), 0.5 day (02/07/09 pm), 1 days (03/07/09) and 2 days (04/07/09) after the first irrigation event. Then followed a 62 day gap with no irrigation and 41 mm of rain, Treatment 1 reached a soil deficit of at least 50 mm, and was then irrigated over two days on the 8th and 9th of September 2009. Table 2 lists the date the samplers were installed and samples collected, and fertiliser applied to the wheat crop. At the time of sampling no herbicides, pesticides or fungicides had been applied.

Table 2: Fertiliser treatment applied to the wheat crop at Auscott - Namoi Valley.

Date	Action
30-Jun-09	Installed the samplers
1-Jul-09	Initial 'watering up' irrigation
2-Jul-09	Collected samples am and pm (Day 0 & 0.5)
3-Jul-09	Collected samples am (Day 1)
4-Jul-09	Collected samples am (Day 2)
27-Aug-09	25 kg/ha of Urea
8-Sep-09	Treatment 1 irrigated
9-Sep-09	Treatment 1 irrigated
10-Sep-09	Samples collected pm (Day 64)
11-Sep-09	Samples collected am & pm (Day 65 & 65.5)

Sample preparation and storage

Polycarbonate sample tubes were used to collect the water samples. After recording the volume, all samples were frozen and stored at below -4°C and transported back to the University of Sydney for analysis. Before analysis all the water samples were filtered through 0.2 micron cellulose acetate filters (Millipore) to remove any suspended solids.

Soil samples

Soil grab samples were collected from the auger holes when the samplers were being installed, at 0.25, 0.50, and 0.75 m for cotton and 0.30, 0.60 and 0.90 m for wheat. Soil grab samples were collected and stored in plastic sealing lunch bags. The soil samples were

analysed for pH (1:5 soil water extract) and EC (1:5 soil water extract) using a HORIBA probe, and particle size composition with a MasterSizer 2000 (Malvern Instruments Ltd.).

Water sample analysis

Nutrient analysis was conducted by flow-injection analysis absorption spectrophotometry (FOSS FIASTAR 5000) to determine the concentrations of ortho-phosphate (PO_4-P), nitrate (NO_3-N), and ammonium (NH_4-N) in the water samples. All analyses were conducted according to the manufacturer's protocols. For each nutrient an initial run of three randomly selected samples was used to determine the range of the calibration curve and the sample loop required.

Statistical analysis

A two-sided Student's T-test was used to analyse the phosphorus sorption data, testing the hypotheses:

Ho: $\mu = 5.52$ mg L^{-1}

Hn: $\mu \neq 5.52$ mg L^{-1}

Sampling of the field experiments (cotton and wheat) was conducted over time and it was assumed that the data would show some correlation with time. An autocorrelation analysis was performed on the residuals of the nutrient data (cotton and wheat). The Autocorrelation Function (AFC) and Partial Autocorrelation Function (PACF) plots of the residuals showed a trend of significant and not significant terms that does not fit any AR, MR or ARMA model (e.g**.** Fig. 5.). In view of the fact that the results from the autocorrelation were inconclusive a REML test was run on the data to try and account for any correlation with time. The model was run using a 3-factorial fixed model with the random model 'Sampler**.**Depth / time'. The term 'Sampler**.**Depth' identifies each individual sampler that was collecting data over time term: ('/time').

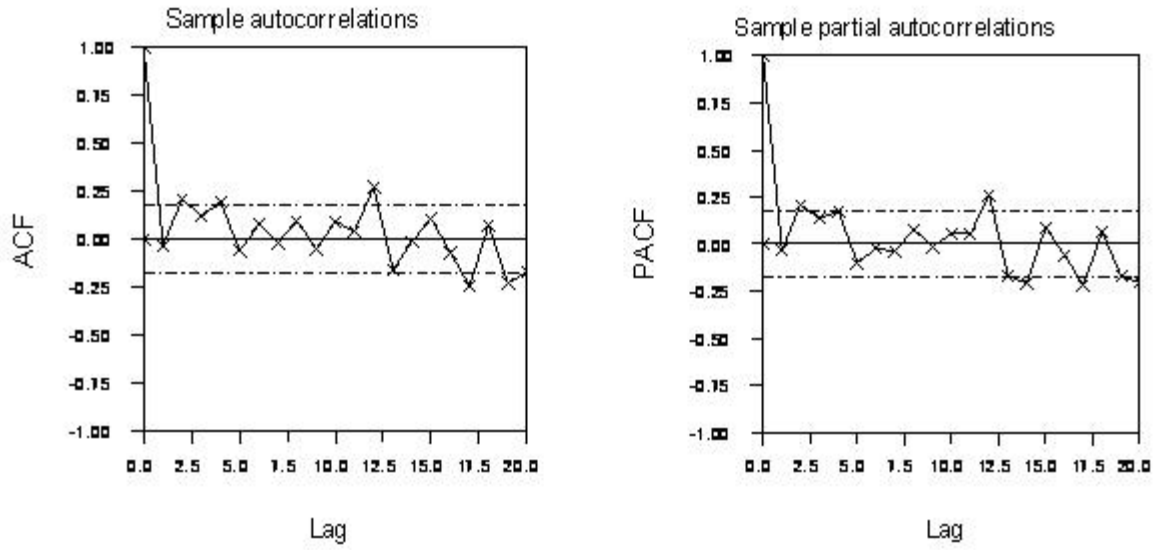

Fig. 5. The PACF and ACF plots of the residuals for wheat ortho-phosphate, as an example of the plots derived for the phosphorus, nitrate, and ammonium data from the cotton and wheat fields. Other plots are in Appendix 3.

The output consistently came up with the result 'terms aliased', and the correlation failed. The 'aliased' term is believed to be caused by unequal replication of the number of data values obtained from each sampler. Based on the results of the two tests we concluded that there was no significant correlation with time and the data can be considered to be independent. As the data could be assumed to be independent, the rest of the analysis was completed with an unbalanced-ANOVA test. ANOVA was chosen over continuing with REML for the analysis for ease of interpretation of the results. Unbalanced- ANOVA and REML as estimators of variance are recognised as being statistically equal (Wulff 2008).

Results

Phosphorus sorption

The phosphorus concentrations in the individual samplers and measuring cylinders at each sampling event (time = 0, 14, 22, 36 hrs) were not significantly different to the standard solution ($P > 0.05$). Table 3 shows the phosphorus concentration data for each ceramic cup

sampler, and the concentrations observed in each measuring cylinder. The standard solution had a concentration of 5.52 ($\sigma \pm 0.183$) mg L^{-1}.

Table 3: The concentration of phosphorus as ortho-phosphate observed in each sampler and measuring cylinder during the adsorption and desorption tests as mg L^{-1}. The volume of inflow (mL) of standard solution through the cup is also given

	Adsorption				**Desorption**
	Time in hours *(Vol. of inflow (mL))*				after 9 hours
	0 *(60)*	14 *(120)*	22 *(180)*	36 *(240)*	
Sampler 1	5.33	5.27	5.20	4.82	1.19
Cylinder 1	*5.41*	*5.60*	*5.20*	*5.11*	*0.00*
Sampler 2	5.01	5.53	5.29	5.13	0.89
Cylinder 2	*5.50*	*5.54*	*5.84*	*5.20*	*0.00*
Sampler 3	4.83	4.71	4.82	4.90	0.69
Cylinder 3	*5.60*	*5.43*	*5.11*	*5.06*	*0.00*
Sampler 4	5.08	4.77	4.88	4.81	2.93
Cylinder 4	*5.74*	*5.74*	*5.10*	*5.03*	*0.00*
Sampler 5	6.15	5.59	5.00	4.83	1.05
Cylinder 5	*5.36*	*4.85*	*4.82*	*4.77*	*0.00*

NB. Sampler 1 was suspended in cylinder 1, sampler 2 in Cylinder 2 etc.

The response of each sampler and measuring cylinder over time was also tested, only the mean phosphorus concentration (4.95 mg L^{-1}) in Cylinder 5 was significantly less than the standard solution 5.518 mg L^{-1} ($P = 0.013$) at the end of the 36 hour period.

The overall mean P-concentration of all the Samplers over the four time periods is significantly ($P < 0.001$) less than the standard solution, as is the over all mean P-concentration in the measuring cylinders ($P = 0.004$).

There was a significant difference ($P = 0.014$) between the deionised water (P concentration of 0.0001 mg L^{-1}) and the concentration of phosphorus observed in the samplers ($\mu = 1.35$ mg L^{-1}) when they were flushed with deionised water. There was no significant difference between the contents of the measuring cups and deionised water ($P > 0.05$).

Soil

The particle size data from the ACRI cotton plot shows a decreasing trend in clay content across the plots (south to north) from A to C but no trend with depth; with clay content values ranging from 52.4% to 37.1%. The wheat field at Auscott shows a trend of slightly increasing clay content with depth but no trend across the field. Across all the wheat plots the clay contents ranged from 57.7% to 40.2%. The ACRI site had a larger sand percentage (16.6% - mean across all depths) than Auscott (8.4% - mean across all depths).

Table 4: Particle size data showing the mean % of clay, silt and sand content, and the pH and EC (μS cm^{-1}) derived from the cotton soil grab samples.

Depth	Soil	Plot		
(m)	Characteristic	A	B	C
	Clay (%)	52.4	45.8	42.9
	Silt (%)	35.3	38.6	45.4
0.25	Sand (%)	12.3	14.3	12.3
	pH	8.9	8.9	8.9
	EC (mS cm^{-1})	0.11	0.11	0.12
	Clay (%)	47.4	37.1	38.5
	Silt (%)	36.8	35.4	44.9
0.50	Sand (%)	15.9	27.6	16.6
	pH	8.7	8.8	8.7
	EC (mS cm^{-1})	0.09	0.08	0.08
	Clay (%)	41.3	40.3	39.8
	Silt (%)	33.6	39.9	51.7
0.75	Sand (%)	22.5	19.8	8.6
	pH	7.8	8.5	8.7
	EC (mS cm^{-1})	0.09	0.09	0.07

The pH of the soil at ACRI ranged from neutral (7.8) to basic (8.9) with no distinct trend (Table 4). The pH of the wheat fields at Auscott was very consistent across all depths with a mean of 9.3 and a range of just +/- 0.5 (Table 5). There was a distinct trend for the pH to

increase with depth, though the difference between 0.3 and 0.9cms decreased as from south to north across the field.

Table 5 - Particle Size data showing % of clay, silt and sand content, and the pH and EC (μS cm^{-1}) derived from the wheat soil grab samples.

		Wheat Plot			
		Treatment 1		Treatment 2	
Depth (m)	**Soil Characteristic**	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0.3	Clay (%)	45.6	43.6	49.4	48.4
	Silt (%)	47.6	44.4	41.6	42.9
	Sand (%)	6.8	12.1	8.0	8.8
	pH	9.2	9.3	9.1	9.3
	EC (mS cm-1)	0.3	0.3	0.4	0.3
0.6	Clay (%)	45.5	45.9	50.7	49.8
	Silt (%)	43.0	43.8	44.0	41.4
	Sand (%)	11.0	9.5	5.5	8.8
	pH	9.3	9.4	9.3	9.4
	EC (mS cm-1)	0.4	0.6	0.4	0.4
0.9	Clay (%)	50.0	47.5	52.9	54.1
	Silt (%)	42.6	43.3	41.0	39.3
	Sand (%)	7.4	9.2	7.2	6.7
	pH	9.5	9.4	9.4	9.4
	EC (mS cm-1)	0.5	0.7	0.5	0.5

Both sites had quite a large variation in EC values, the cotton had a surface mean of 0.11 mS cm^{-1} and decreased 0.08 mS cm^{-1} with depth (Table 4). The wheat plots had a mean EC of 0.4 mS cm^{-1} with a range of ± 0.42 mS cm^{-1} (Table 5). The mean EC values for each wheat plot showed a definite trend for increasing salinity with depth.

Analysis of the cotton soil solution samples.

Analysis of the water samples collected over the summer under from under the irrigated wheat showed considerable variation in the concentrations of nutrients between replicates and sampling events. The ortho-phosphate concentrations ranged from below the limit of quantification (<LOQ) to 5788 mg L^{-1} (Fig. 6).

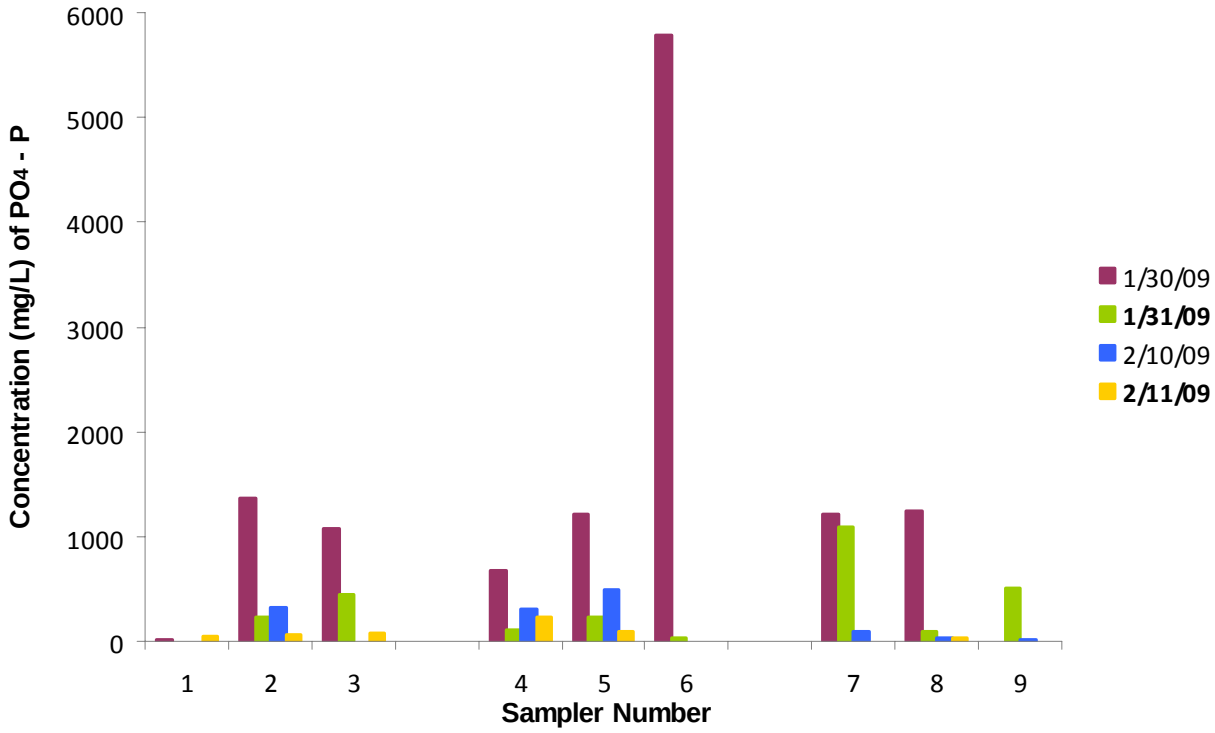

Fig. 6. Plot of the orthophosphate (PO_4-P) concentration in each sample collected from the different depths at each sampling event. The gaps indicate the different plots A, B and C (from left to right). The dates in bold indicate 24 hr samples, the others are 10 day samples. Samplers 1, 4 and 7 were installed at 0.25 m, samplers 2, 5, and 8 were installed at 0.50 m and samplers 3, 6, and 9 were installed at 0.75 m.

Statistical analysis of the data by unbalanced ANOVA showed no significant relationship ($P > 0.05$) between the treatment (depths installed at) or blocking effect (different plots) and the results.

Nitrate concentrations in the water samples collected from under irrigated cotton ranged from below the limit of quantification (<LOQ) to 157 mg L^{-1} (Fig. 7). Statistical analysis of the data by ANOVA showed no significant relationship ($P > 0.05$) between the treatment (depths installed at) or blocking effect (different plots) and the results.

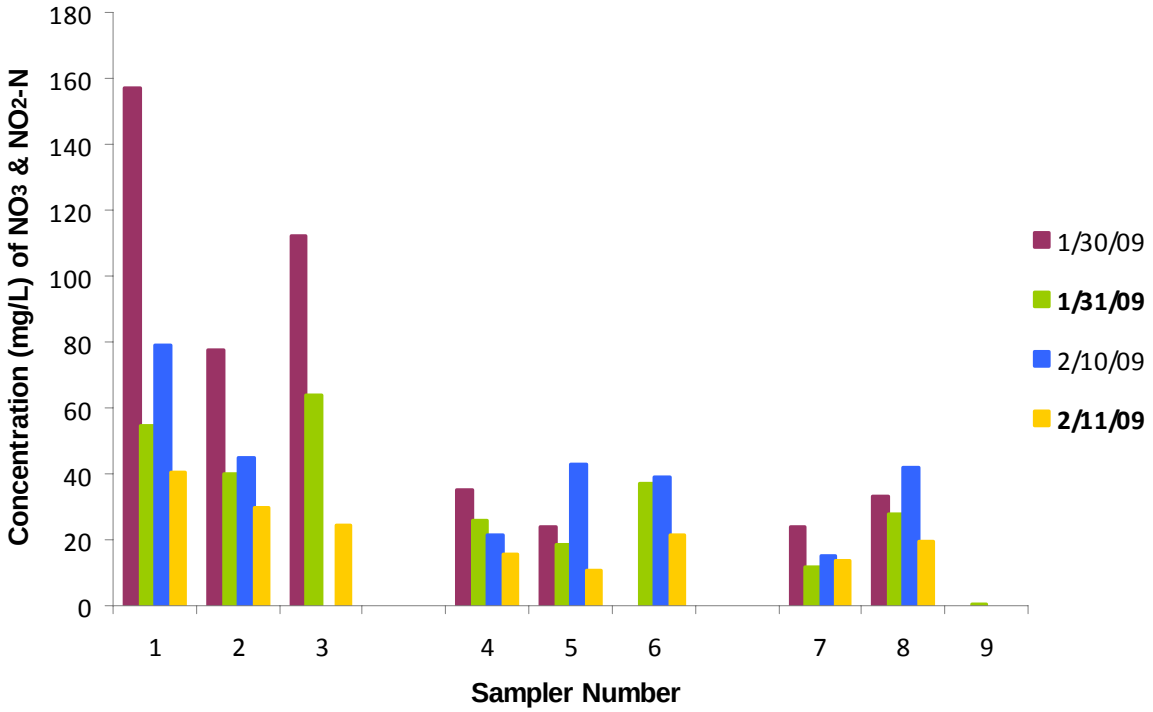

Fig 7: Plot of the nitrate plus nitrite (NO_3^- and NO_2^-) concentration in each sample collected from the different depths at each sampling event. The gaps indicate the different plots A, B and C (from left to right). The dates in bold indicate 24 hr samples, the others are 10 day samples. Samplers 1, 4 and 7 were installed at 0.25 m, samplers 2, 5, and 8 were installed at 0.50 m and samplers 3, 6, and 9 were installed at 0.75 m.

The water analyses showed considerable variation in the concentrations of nutrients between replicates and sampling events. Nitrate concentrations under cotton ranged from below the limit of quantification (<LOQ) to 1300 mg L^{-1} (Fig. 8). Analysis of the data by Analysis of Variance (ANOVA) showed no statistically significant relationship ($P > 0.05$) between the treatments (depths installed at) or blocking effect (different plots).

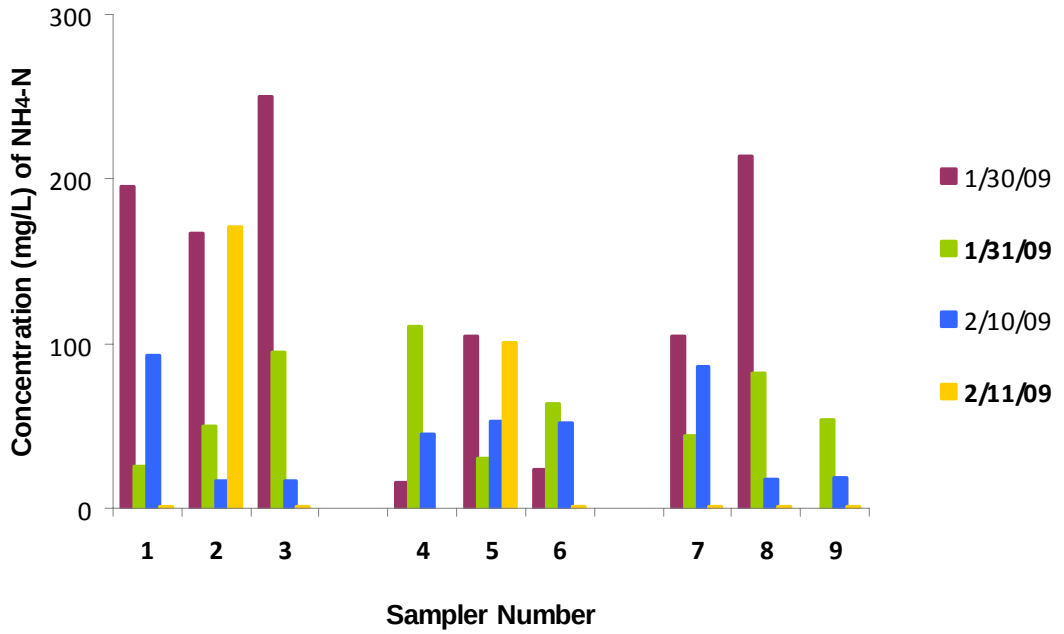

Fig. 8: Plot of the Ammonia (NH4 - N) concentration in each sample collected from the different depths under cotton at each sampling event. The gaps indicate the different plots A, B and C (from left to right). The dates in bold indicate 24 hr samples, the others are 10 day samples. Samplers 1, 4 and 7 were installed at 0.25 m, samplers 2, 5, and 8 were installed at 0.50 m and samplers 3, 6, and 9 were installed at 0.75 m.

Analysis of the wheat soil solution samples

The phosphorus data was log transformed to meet ANOVA's assumptions of normal distribution and equal variance. Analysis of the data using a 3-way factorial unbalanced ANOVA showed no significant interaction ($P > 0.05$) between any combination of the factors irrigation treatment, depth installed, and time. The factors time and treatment were significant on their own. Post-hoc testing of the means showed that the mean at time 0 is significantly larger than the rest of the means (Fig. 9).

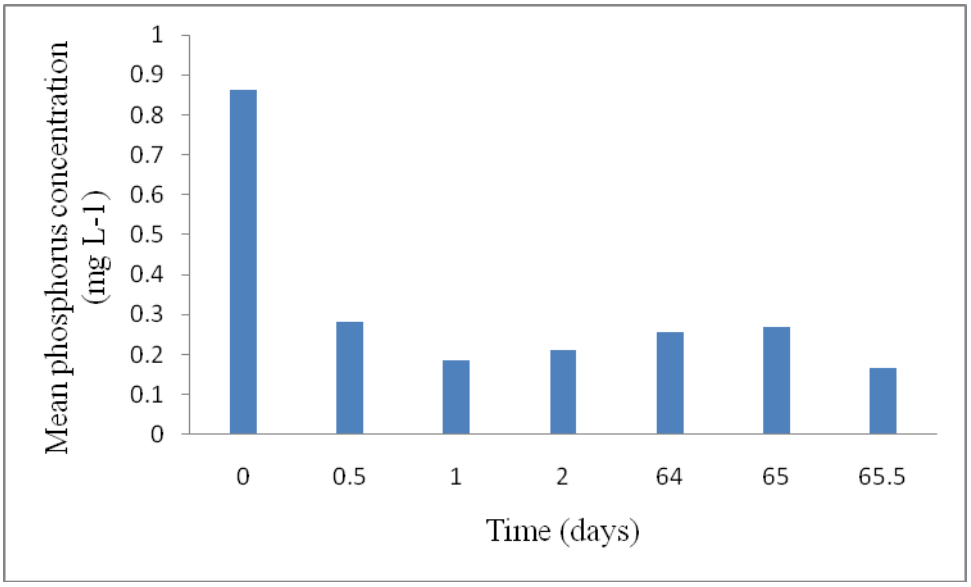

Fig. 9. Mean phosphate concentration (mg L^{-1}) for each time period (number of days).

Comparison of the means for the factor treatment showed that the mean for Treatment 1 was significantly greater than for Treatment 2 (Fig.10).

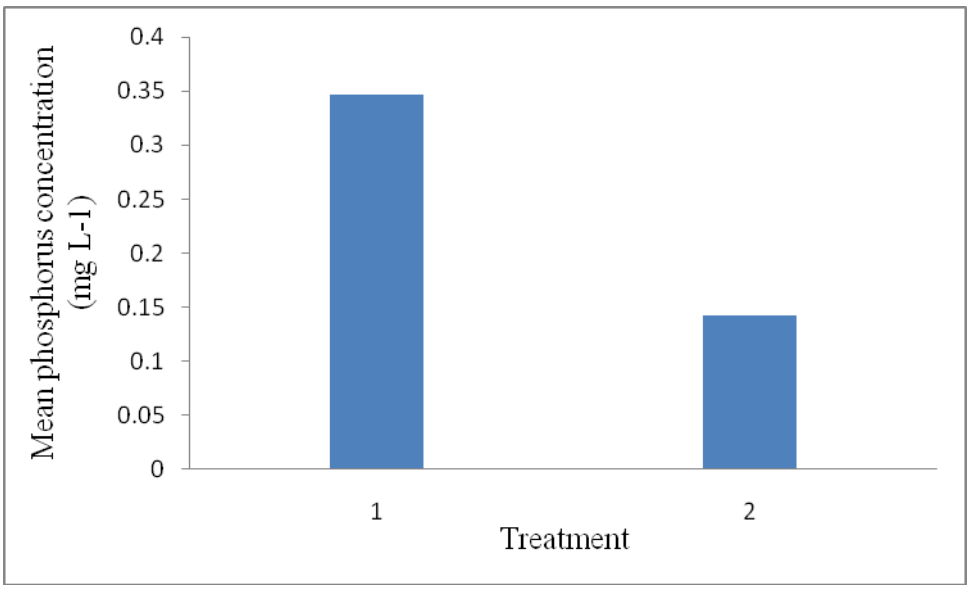

Fig. 10. Back transformed mean phosphorus concentration for irrigation Treatment 1 and 2, across depth and time.

The nitrate data was square root transformed to meet the assumptions of normality and equal variance. Statistical analysis found no significant interaction between the different factors treatment, time and depth ($P > 0.05$). The unbalanced ANOVA indicated that, like the phosphorus data, the factors treatment and time were significant on their own. Post hoc

testing of the means showed that Treatment 2 had a significantly higher mean than Treatment 1 (Fig.11).

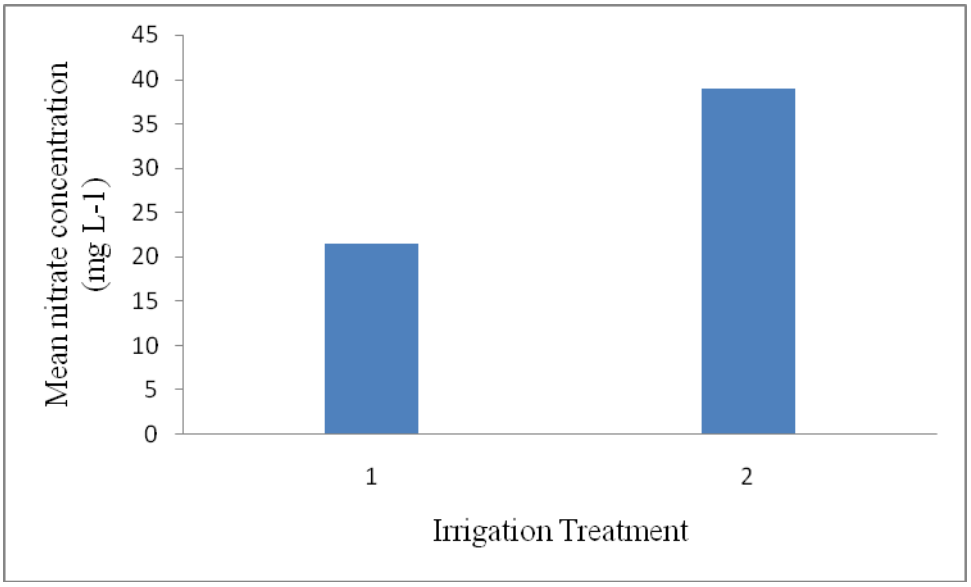

Fig. 11. Back transformed mean nitrate concentration for irrigation Treatments 1 and 2, across depth and time.

The nitrate concentration at 'time 0' is significantly less than the time periods 0.5 to 2, and greater than time 64 to 65.5. The mean concentrations at Time = 64, 65, & 65.5 are significantly lower than time = 0, 0.5, 1, or 2 (Fig. 12**.**).

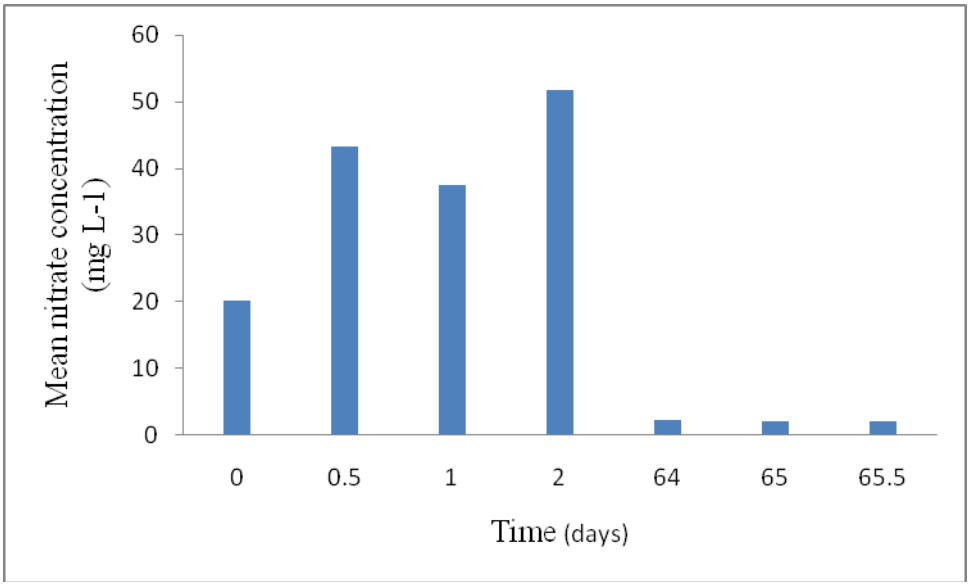

Fig. 12. Back transformed mean nitrate concentration (mg L^{-1}) for each time period (number of days).

The ammonium data was square root transformed to meet the assumptions of normality, equal variance and normal distribution. Concentrations under the irrigated wheat showed a significant interaction between the factors depth and treatment (P = 0.009). The concentrations of NH_4 in Treatment 1 were fairly constant with depth while Treatment 2 changed significantly with depth (Fig.13). There was no significant variation in ammonium concentrations at 0.30 m between the treatments, but Treatment 2 at 0.60 m is significantly lower than treatment 1 and at 0.90 m is significantly greater than Treatment 1.

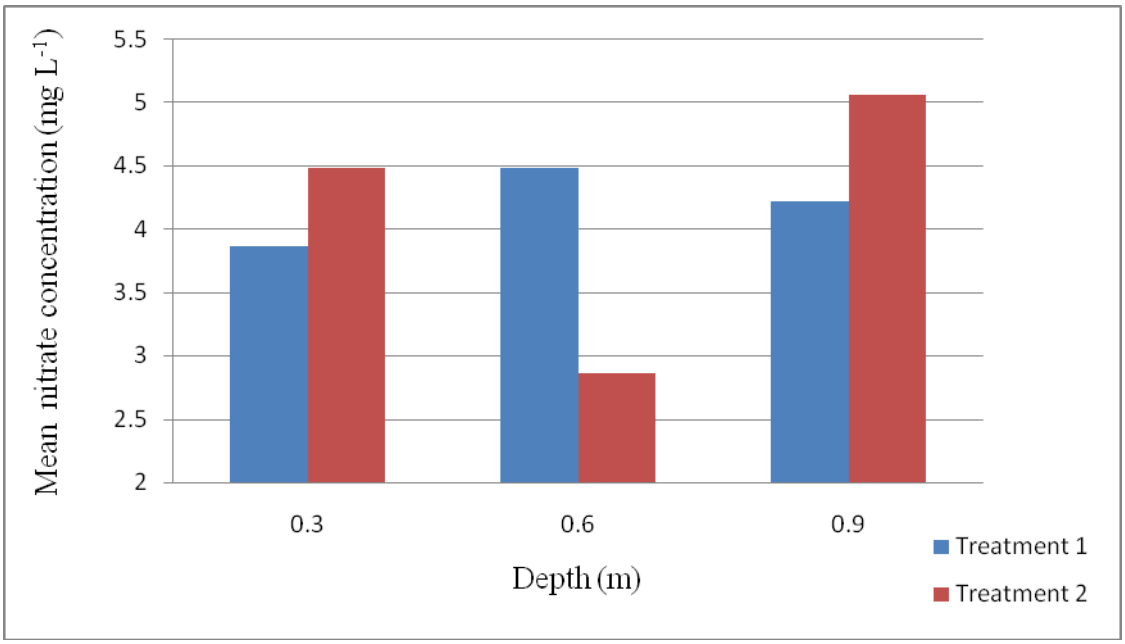

Fig. 13. Back transformed mean ammonium concentrations at each depth for irrigation Treatments 1 and 2.

Discussion

Efficacy of ceramic cup samplers

Ceramic cup samplers have been developed primarily on sandy to loamy soils (Biswas *et al.* 2008) but their suitability for use on clayey soils was uncertain due to limited research into the impact of clay content on soil wetting patterns, solute behaviour and effect of fine grained soil on the ceramic cup (Raine *et al.* 2007). Practically speaking, this experiment showed that the samplers can work in irrigated Vertosols (heavy clay) soils, as samples were collected from 85% to 95% of samplers, at each sampling event (for cotton and wheat). The times that

samples were not collected the sampler appeared to have lost its vacuum. This was likely caused by poor soil – ceramic cup contact because of shrinking and swelling of the soil with changing soil moisture content. As such, the use of the samplers on Vertosolic soils under dryland (non-irrigated) crops would probably be significantly less reliable. Over the different sampling periods, six of the thrity-six samplers never worked. Of the samplers that did work, the volume collected varied significantly with each sampling event and there was no apparent trend with depth, but a slight tendency to collect the greatest volume (50 mL +) 24 hours after irrigation (Time = 1 day and 65 days).

A noticeable result from the cotton and wheat field experiments was the considerable difference in the mean concentration of the nutrients phosphorus and ammonium; the nitrate levels were very similar (Table 6). The differences observed can be partially explained by the different fertiliser treatments (Table 1 & 2) applied to the crops with the cotton receiving 10 times the amount of kgN ha^{-1} applied to wheat. No ammonium based fertiliser was applied to the wheat plots, the observed concentrations are most likely residual from the cotton crop grown the previous season. The concentrations of nutrients measured under cotton are high enough to be of serious concern if they are leached from the profile into local water ways. They exceed the ANZECC (Australian and New Zealand Environment and Conservation Council) guidelines of acceptable nutrient levels in freshwater systems. The concentrations observed under wheat did not exceed the ANZECC guidelines.

Table 6. Overall mean nutrient concentration for each depth sampled in the cotton and wheat fields.

	Mean nutrient concentration (mg/L) for all depths and times.			
	Depth (m)	Phosphorus	Nitrate	Ammonia
Cotton	0.25	303.5	41.1	436.7
	0.50	450.5	34.2	239.7
	0.75	652.3	24.7	14.2
Wheat	0.30	0.9231	27.1	0.1575
	0.60	0.4225	35.9	0.1973
	0.90	1.1104	41.2	0.2966

Phosphorus sorption

A serious concern with the use of porous material, particularly ceramic, to extract soil water is the possible impact of the material on the sample composition (Shaffer et al 1979; Bottecher et al 1984; Weihermuller 2007). Zimmerman et al (1978) found that ceramic cups adsorbed 57% of PO_4 and 4% of NO_3 from a solution passed through the cup. Research by Grover and Lamborn (1970) suggested that a mild acid wash of the cups would reduce the rate of phosphorus absorption and the theory was not verified with newer ceramic cups till Bottecher et al (1984) who found that acid washing significantly increases the rate of phosphorus adsorption and decrease the rate of desorption from ceramic cups. Wihermuller *et al.* (2007) listed ceramic as a material unsuitable for sampling phosphorus due to sorption to the material. All prior research into the rates of phosphorus sorption to ceramic material has been conducted in Europe or the United States.

It was hypothesised that new (unused) ceramic cups made in Australia from clays with different properties, would exhibit different phosphorus sorption properties. The experiment followed the methodology outlined by Bottecher et al (1984), but no cups were acid washed. There was no significant adsorption of phosphorus by the ceramic cups at each time period, but the over all mean was significantly different from the standard solution. The ceramic cups are absorbing some phosphorus from the solution but at such a low rate that it can only be detected over several days. The percentage of phosphorus adsorbed by each sampler decreased over the 4 time periods from 4.3% to 2.7%, values considerably lower than the 57% observed by Zimmerman et al (1978). Flushing the cups with deionised water desorbed a significant amount of phosphorus over a 9 hour period indicating that any equilibrium reached by the cups is quickly reversed. Ceramic cups produced in Australia do absorb some phosphorus from the solution being sampled but at rates significantly lower than those found by researchers abroad. The percentage absorbed showed a linear trend ($R^2 = 0.92$) which could be used to correct the data for percentage absorbed by the cups at a given time period. Solving the linear equation (1) for y = 0 indicates that the cups should reach equilibrium after 72 hours, if it is assumed that one time period (x) is equal to 9 hours.

$$y = -0.5708x + 4.9776 \qquad \ldots(1)$$

Impact of the soil on the samplers

The soil at both properties was identified as a Vertosol, or vertic profile, with clay content over 35% and displaying characteristic shrink-swell properties. The change in clay content has the potential to influence the nutrient concentration of the samples collected by changing both the hydraulic conductivity of the soil and the ion exchange capacity (Vervoort *et al* 2003). Raine *et al* (2007) listed the effect of soil texture on solute behaviour as a significant gap in our understanding of the behaviour of the soil solution. After irrigation events it is believed that infiltrating water moves rapidly down the profile through macro-pores and preferential flow paths created by roots and soil organisms, like worms (Grossman and Udluft 1991) and ceramic cup samplers are biased towards this flow. It has been widely argued that ceramic cup samplers with high potential gradients are biased towards sampling from the macro-pores (Hansen and Harris 1975; Severson and Grigal 1976). Grossman and Udluft (1991) argue that as the potential gradient is exerted evenly on the surrounding soil, water movement occurs in all pores, so under stationary conditions, there is no reason to assume suction cups would be biased towards larger pores. Hart and Lowery (1997) estimated a mean axial sampling radius of 24 mm around a ceramic cup in a 'Sparta' sand but recognised that this would vary significantly with soil type. Germann (1972) argued that the extent of the potential field disturbance could extend up to 1m from the sampler**.**

Dry, vertic clay profiles can form cracks several cm wide and 20 to 50 cm deep, which potentially could create large preferential flow paths down the profile during flood irrigation. In theory this would mean that the first samples collected by the samplers post-irrigation would be more representative of the irrigation water quality than the soil solution. The first samples collected after irrigation (time = 0) for phosphorus had a significantly higher concentration (0.85 mg L^{-1}) than any other time period (Fig. 9). As no phosphate based fertiliser had been applied to the field since the cotton crop the previous season, and the irrigation water had a mean phosphorus concentration of 0.0002 mg L^{-1} (data supplied by B. Stevens of Auscott). The phosphorus concentrations in the samples at 'time 0', must originate from some interaction with phosphorus in the soil, seeming to support the argument that the samplers are not entirely biased towards preferential flow.

Cotton

The water analyses showed considerable variation in the concentrations of nutrients between replicates and sampling events with concentration ranging from 0 (<LOQ) to 5788 mg/L and 1300 mg/L (for phosphate and ammonium respectively). Statistical analysis of the cotton data showed no significant interaction or trend in the phosphorus, ammonium and nitrate data, the number of samplers and replicates used in the trial was insufficient to quantify the root zone variation. Because variation in the data was too large to detect any significant trends in the data, the mean values for each depth can only be used as indicators of the conditions in the root zone of a cotton crop.

For nitrate and ammonia there appears to be a decrease in concentration with depth where as phosphorus concentrations appear to increase with depth (Table 6). The leaching of nutrients, particularly phosphorus from the upper soil to ground and surface water systems can contribute significantly to eutrophication (Kronvang *et al.* 2005; Elrashidi *et al.* 2009). The ANZECC guidelines for aquatic ecosystems recommend that phosphate levels be kept in the range 20 - 50 μg/L. The observed soil water values exceed this level (3.03×10^5 to 6.52×10^5 μg/L), if the increasing concentration with depth are indicative of leaching, the cotton crop could be contributing significant levels of phosphorus to local water ways. Unfortunately not much is known about the availability and movement of phosphorus in heavy clay soils (Klemmedson and Blaser 1990).

The ANZECC guidelines recommend that nitrate levels should not exceed 500 μg/L and ammonia 13 - 20 μg/L in aquatic ecosystems. Vertosols because of their low organic matter content are generally deficient in nitrogen, so that it needs to be applied in the form of fertiliser, the mode of application will influence its behaviour in the profile (Van Wambeke 1991). The soil water concentrations are at least an order of magnitude higher (see Table 6 - 1 mg/L = 1000 μg/L) than the ANZECC guidelines. Recent work by Weaver *et. al.* (2003) and Hulugalle (2005) has shown that leaching does occur on Vertosols, and rates of up to 117mm a year of deep drainage have been observed near Narrabri. If the leachate is substantial and it contains concentrations similar to those observed in this trial, the cotton industry could be a major non-point source polluter of the local aquatic ecosystems. The fact that nitrate and ammonia concentrations decrease with depth indicate that the possibility that the concentrations leached from the profile may be considerably less and that there is active

uptake by plant roots. Samplers need to be installed below the root zone, i.e. at 120 cm (Weaver *et. al.* 2003), and in tail drains, to monitor the concentration of nutrients being leached or transported in runoff.

Wheat

The replication of samplers and treatments under the wheat plots was sufficient to account for the with-in field and treatment variation, with significant trends and interactions detected in the data. The wheat trial was used to study the three factors expected to impact on the soil solution: irrigation treatment, depth and time. The irrigation treatment was meant to be a comparison between irrigating at 50 mm and 90 mm soil water deficit. However, significant rainfall this season meant that only the 50 mm deficit received irrigation after the initial watering up of the field.

The mean nitrate concentration for the soil solution under Treatment 2 was significantly larger than Treatment 1 **(**Fig. 11**.).** However phosphorus was the opposite, with Treatment 1 having significantly higher mean concentrations (Fig. 9.). It was expected that Treatment 1, with its higher irrigation rate (irrigate when soil water deficit ≥ 50 mm), would have lower mean concentrations than Treatment 2 due to leaching of nutrients from the profile. Over time the mean phosphorus concentration at 'time 0' was significantly greater than at any of the following times (Fig. 10.). The mean concentration of nitrate in the soil solution decreased significantly between the first sampling event and the second 62 days later, Barraclough (1986) detected a similar trend under a winter wheat crop, and calculated that the crop could take up as much as 2.75 kg ha^{-1} day^{-1} of N. There was a significant difference in nitrate concentrations over time in spite of the application of urea between irrigations. Urea breaks down into ammonium initially before it is oxidised to nitrate by soil organisms, indicating that nitrate levels were extremely low before the urea was applied, or insufficient time had elapsed to allow the ammonium to be oxidised to nitrate. Leaching and crop uptake probably played a key role in the observed nitrate changes. The phosphorus concentrations need further study and testing as, while not much is known about phosphorus movement in heavy clay soils (Klemmedson and Blaker 1990), some research suggests that saturating the profile should increase phosphorus mobility, as hydrous oxides that bind phosphorus are reduced to ferrous form (Willet and Muirhead 1984), resulting in leaching down the profile**.**

The ammonium data had a significant interaction between treatments 1 and 2, and depth (Fig. 13.). The lack of significant change in concentration of ammonium between the first and second sampling trip may be attributed the application of urea in between irrigations maintaining ammonium concentrations in the soil solution over time. The mean concentration of ammonium remained constant with depth under Treatment 1 but fluctuated significantly under Treatment 2 (Fig. 13.). There does not appear to be any logical explanation for the variation, if the trend was caused by a soil property, the oxidation of ammonium to nitrate by soil organisms or uptake by the roots you would expect to see the trend reflected in Treatment 1, but it follows an almost inverse trend. The oxidation of ammonium to nitrate requires oxygen, and the rate of oxidation generally decreases with depth as oxygen becomes limiting, potentially explaining the high concentration at 0.9 m for Treatment 2. Except this then raises the question of why Treatment 1 at 0.9 m is not significantly larger than at 0.3 and 0.6 m. The trend in Treatment 2 may be an artefact of analytical error or part of a larger trend or variation in the field that the replication of samplers was unable to detect. Further field trials with greater replication and analysis of the soil are needed to determine what is occurring.

Unlike the concentrations observed under cotton, the mean nutrient concentrations observed under wheat (Table 6) are well with in the ANZECC guidelines for aquatic ecosystems and any nutrients leached from the profile are unlikely to be in concentrations that would have a negative impact on local water ways. Water quality data from several bores and dams around Auscott, supplied by the manager, had extremely low (~ 0.2 $\mu g\ L^{-1}$) mean concentrations of nitrogen and phosphorus suggesting that there is little or no leaching from the fields into the local groundwater. The high quality irrigation water at Auscott contrasts with data collected from the head and tail ditches of the cotton field which exceeded the ANZECC guidelines.

Conclusion

This experiment has demonstrated that ceramic cup samplers can be used in a heavy clay soil, but the shrink-swell properties of Vertosols profiles may compromise their effectiveness by causing poor soil – ceramic cup contact. There is considerable disparity in concentrations of nutrients measured in the irrigation water versus the concentrations measured in the soil

solution samples. Therefore, it is likely that the samples collected from the soil solution give some indication of the composition of water in soil pores and available to plant roots as nutrients, and are not biased towards sampling preferential flow. The material used to make ceramic cup samplers in Australia does not appear to absorb significant amount of phosphorus from the soil solution, and are expected to have little impact on other major nutrients, but they require further testing to assess their impact on other nutrients. Therefore they can be used to reliably monitor the movement of nutrients in the profile and aid with the development of better management practices.

Soil solution samples where collected from under a cotton and wheat crop and analysed for ammonium, nitrate, and phosphorus. The results showed considerable temporal and spatial variation in the soil solution with the observed trends varying for each nutrient. The nine samplers installed under the cotton where insufficient to explain the variation and no significant results were obtained. The greater replication in the wheat field experiment, with thirty-six samplers, explained some of the variation in the data. Mean phosphorus and nitrate concentrations were very low (ranged from 0.15 to 1.11 mg L^{-1}). Nitrate concentrations where higher (mean of 35 mg L^{-1}). There was still a large amount of unexplained variation indicating that further replication and research is required. Further research into the gaps in our understanding of the soil solution, the impact of soil type and root distribution on wetting patterns and the role soil type and clay minerals play in the availability of nutrients, may help explain the observed variation.

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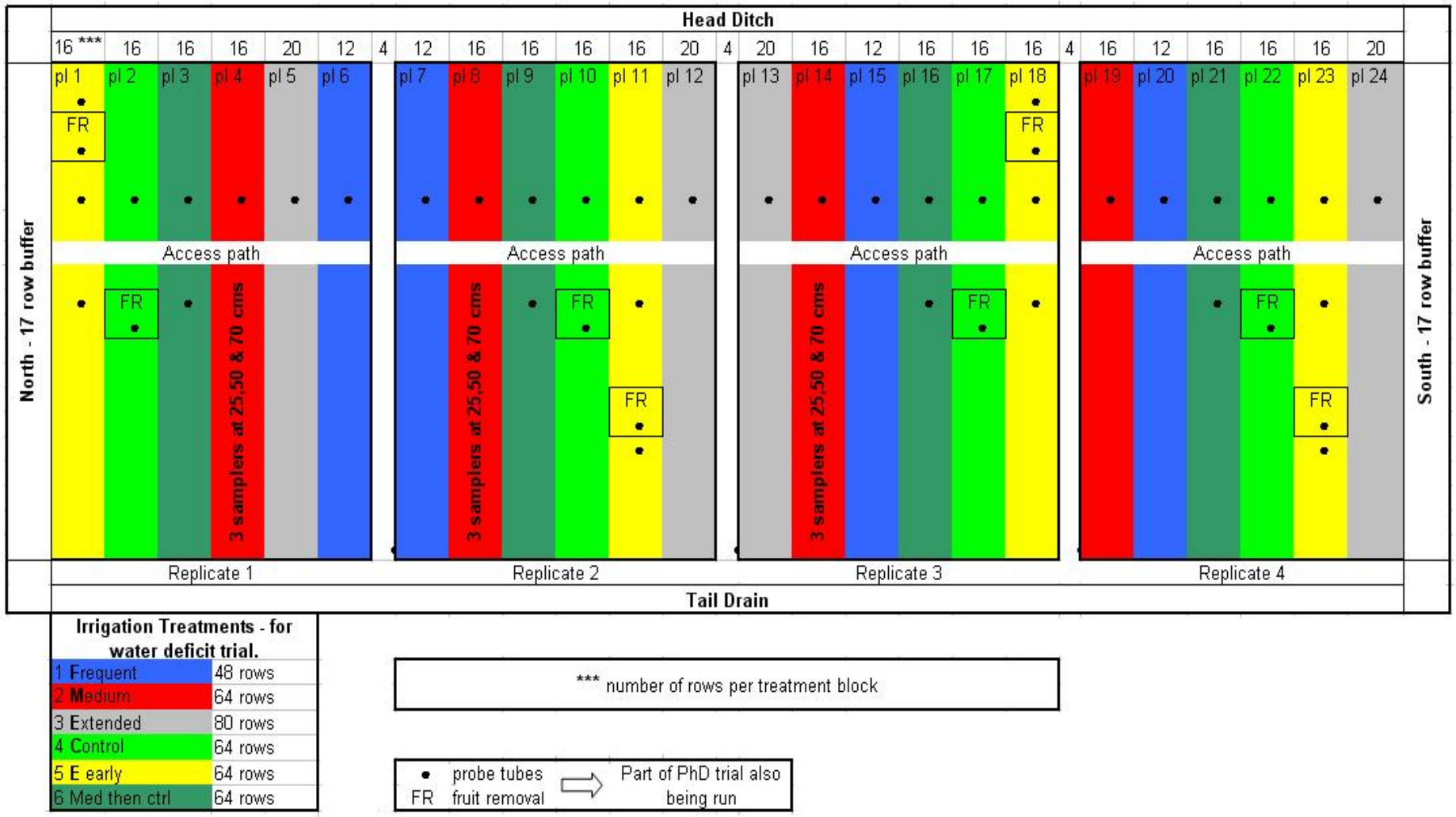
Appendix 1: Layout of the Cotton field.

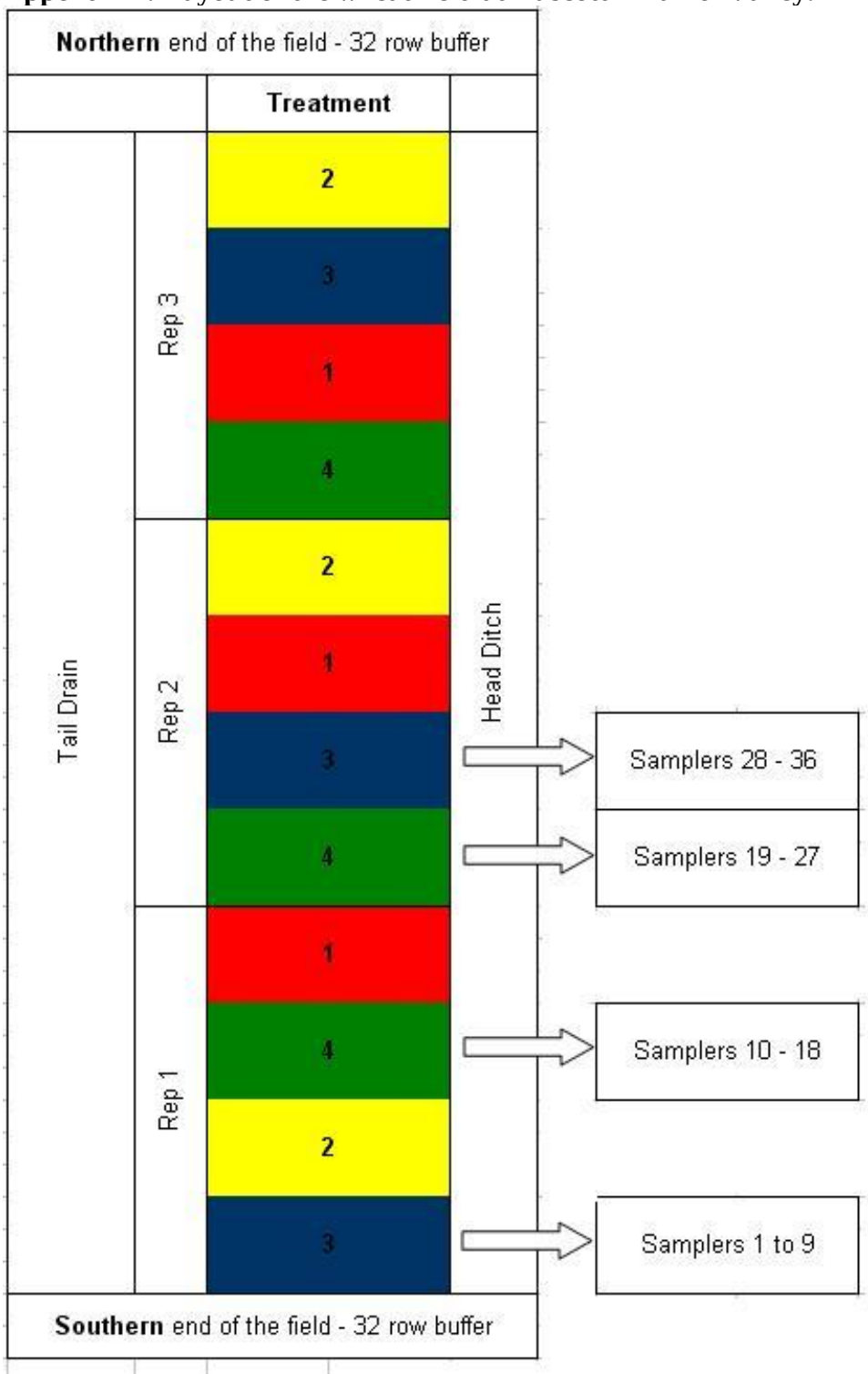


Irrigation Treatments - for water deficit trial.	
1 Frequent	48 rows
2 Medium	64 rows
3 Extended	80 rows
4 Control	64 rows
5 E early	64 rows
6 Med then ctrl	64 rows

*** number of rows per treatment block

• probe tubes
FR fruit removal
⇨ Part of PhD trial also being run

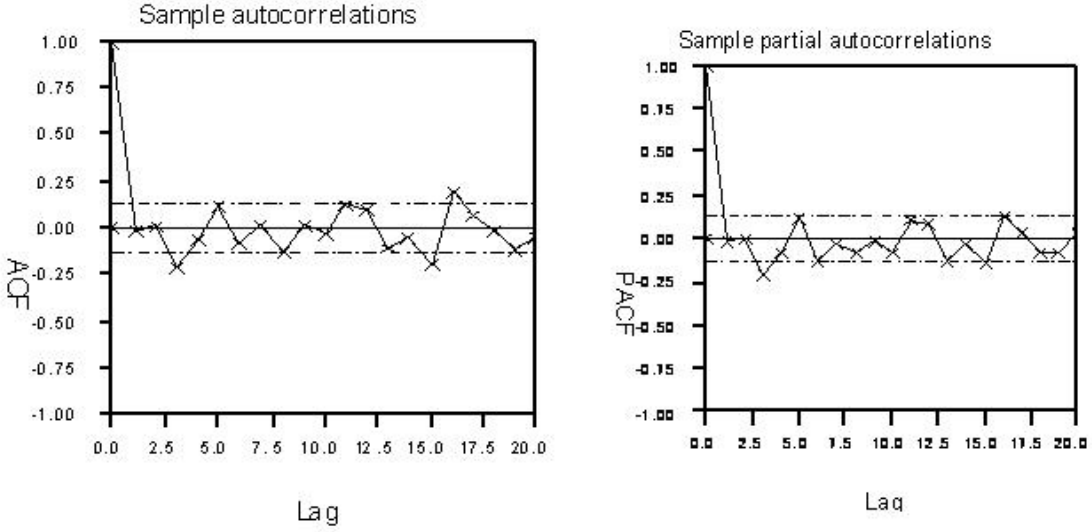
Appendix 2: Layout of the wheat field at Auscott – Namoi Valley.



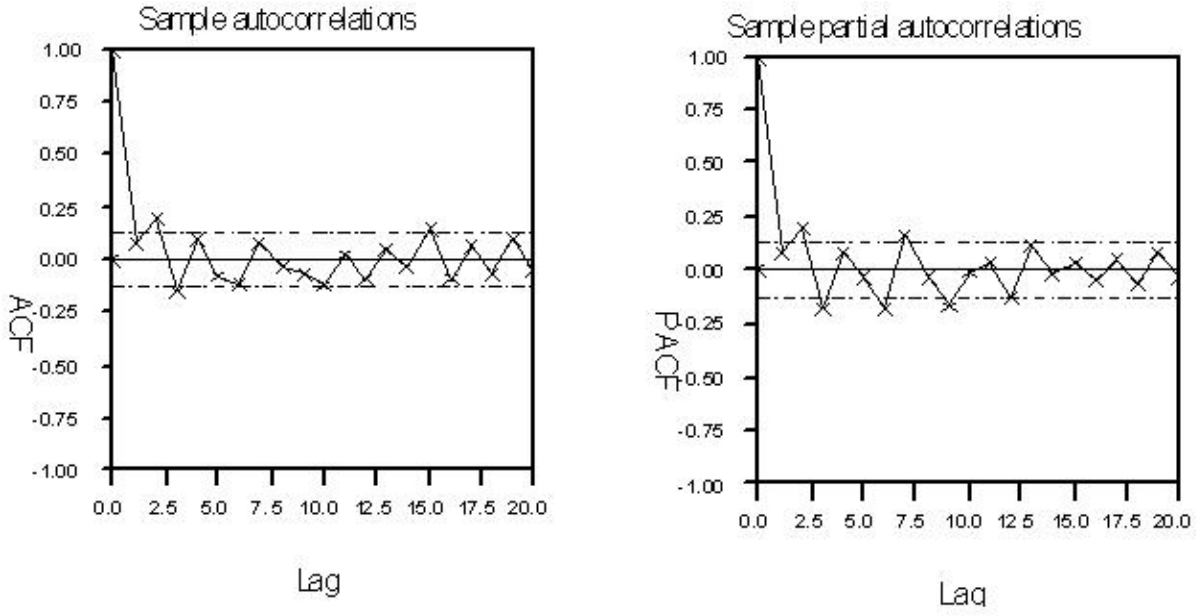
Treatment		*Irrigation Treatment*
1		Waterup then 50mm deficit
2		Waterup then 90mm deficit
3		Waterup then on dryness
4		Waterup then nothing

* each treatment plot is 54 rows wide or 27 beds. There are 2 rows per bed.

Appendix 3:



PACF and ACF plots of the residuals for ammonium (NH4-N)



PACF and ACF plots of the residuals for Nitrate (NO_3-N)