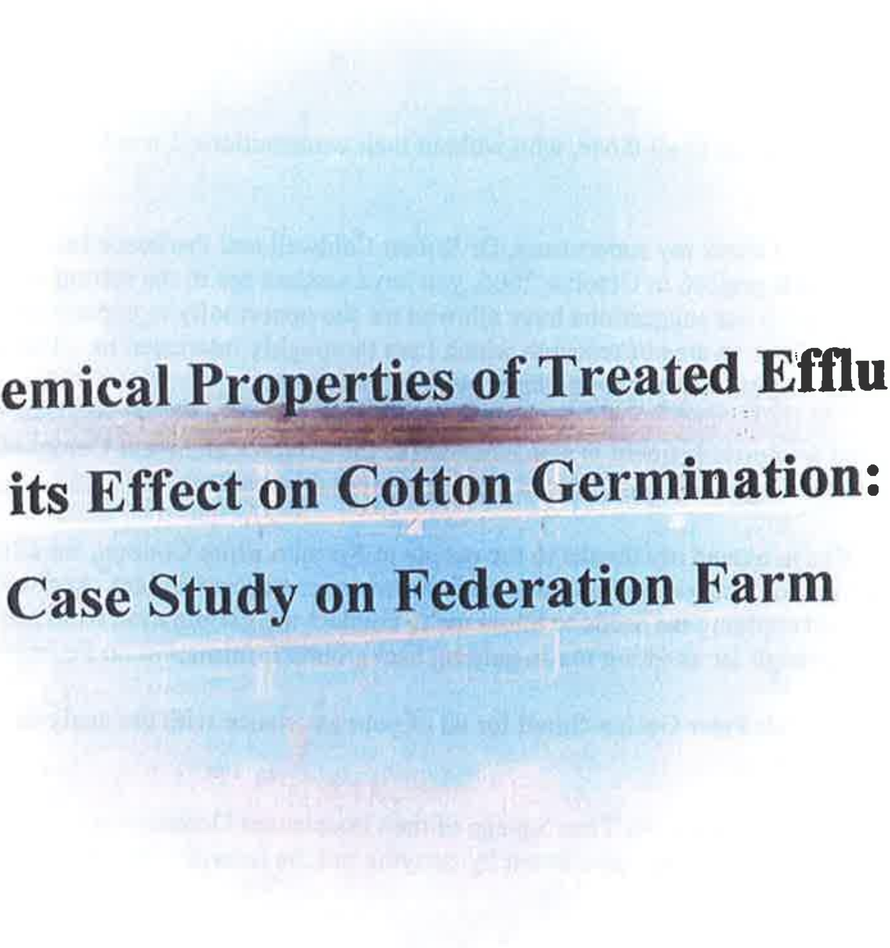

The Chemical Properties of Treated Effluent and its Effect on Cotton Germination: A Case Study on Federation Farm

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ABSTRACT

It has been predicted that in the 21st century water will become as monetarily valuable as oil (Qadir et al., 2003). As a low profit to megalitre user of water agriculture is likely to suffer from water shortages (UNEP, 2002). In order to maintain a steady supply of water a large amount of research has been conducted into alternate sources of water for irrigation. In a number of countries treated effluent is already being used as a source of water for irrigation. While effluent is perceived by many to be a viable source of water for sustainable farming numerous chemicals are present within this treated effluent that can cause illness within crop species (Toze, 2006). This review has examined many of the major contaminants that are present in treated effluent and discussed their affect on crops and the maximum allowable concentrations in both the effluent and the soils.

Keywords: Treated, Effluent, metals, contaminants, Irrigation, Agriculture, pharmaceuticals

I. INTRODUCTION

Water covers 71% of the Earths surface and yet is one of the most limiting factors to the growth and development of human society. A large amount of the earths water (>97%) is located in the salt oceans, and is not suitable for many human uses. Freshwater, which is required by industry, agriculture and the general population, comprises only 2.7% of the earth's water. A majority of this freshwater is tied up in glaciers and polar icecaps, limiting its availability.

Experts have predicted that as the global population continues to increase water will become as valuable as oil during the 21st century (Qadir et al., 2003). It has been estimated (Qadir et al., 2007) that the Earth has a renewable water supply of 7000m^3/capita/year, which is sufficient to sustain the current global population. However because population density and the freshwater resource is not spread evenly across the planet (Figures 1 and 2) (Qadir et al., 2007). Already a number of regions suffer from problems related to water stress and scarcity (Pimentel et al., 1999). Water stress has been defined as <1700m^3 water/person/year, and scarcity is defined as <1000m^3 water/person/year (UNEP 2002). Current prediction (UNEP 2002) estimate that by 2025 approximately two out of every three people will live under water stressed conditions.

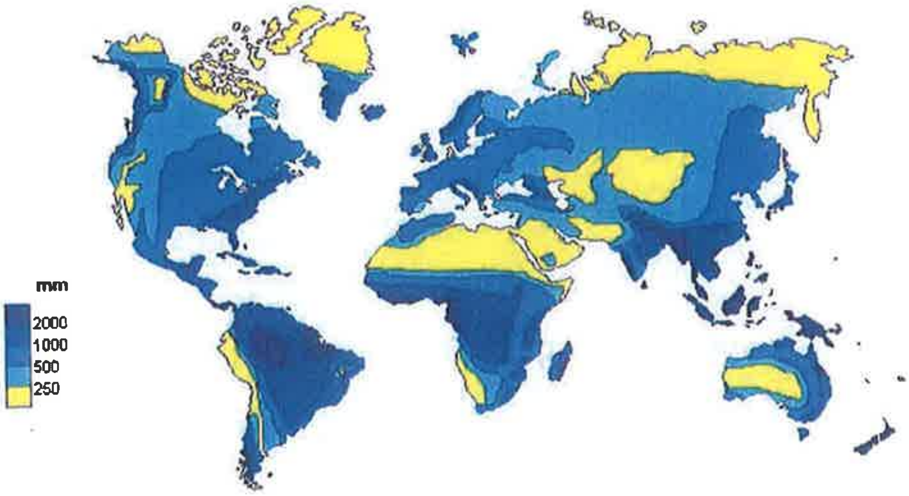


Figure 1. Global rainfall patterns (Source: www.sos.bangor.ac.uk)

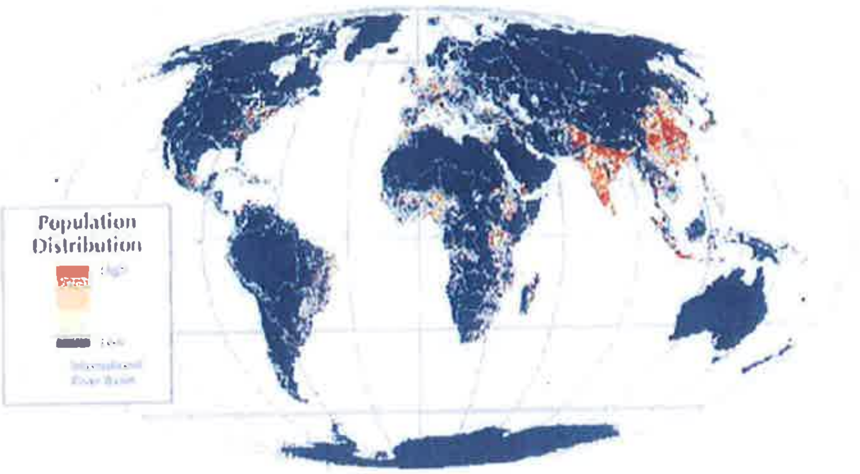


Figure 2. Global population density (Source: www.transboundarywaters.orst.edu)

Globally 75% of the water extracted from the environment is for Agricultural use, 20% for industry and only 5% for domestic use (UNEP 2002). The agriculture: industry: domestic water use ratio varies depending on the region (Figure 3). A large proportion of the agricultural water is used to irrigate fields (Zhang et al., 2007), that represent only 15% of agricultural land, however produce 50% of global agricultural product (UNEP 2002). Freshwater for Agriculture, industry and domestic use is currently obtained from a number of different sources, including surface rivers, rain-fed dams and underground reservoirs.

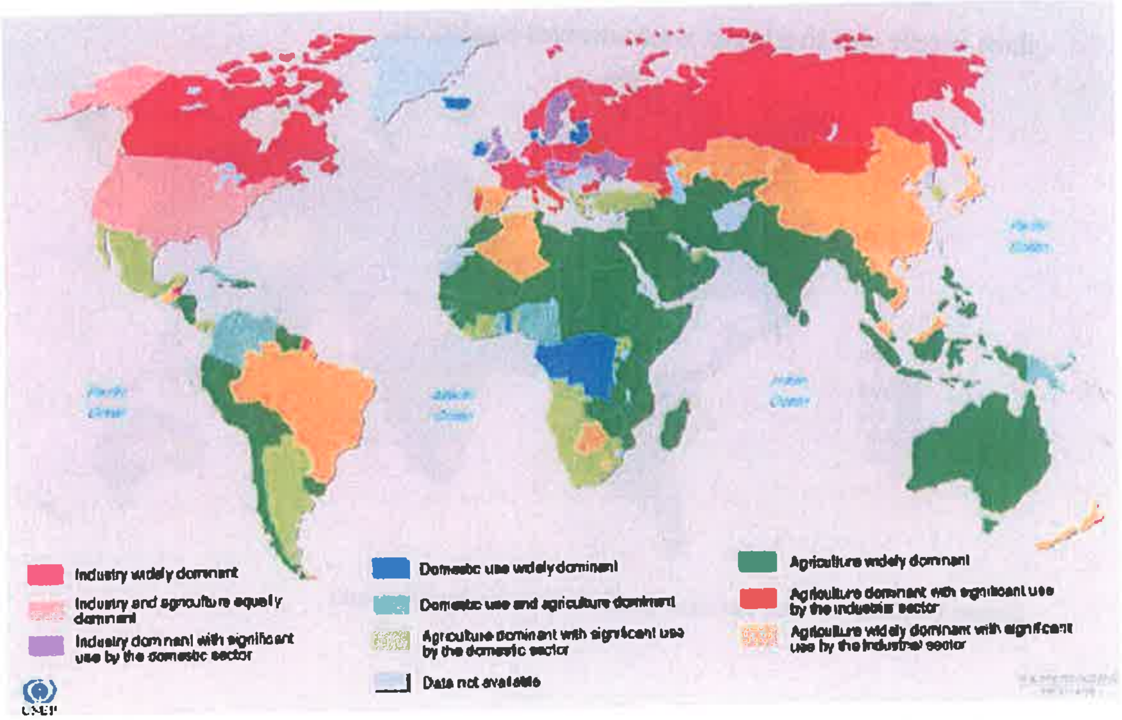


Figure 3. Global water use. Although Agriculture is dominant, a number of other uses, including industry are significant water uses in some regions, particularly Europe and Nth America. (UNEP 2002)

Despite the importance of agriculture it is believed that in the near future it will have its access to freshwater severely restricted (Hellegers & Perry, 2006). The restriction to water will be due to market forces. As water becomes a monetarily valuable resource, low profit/ML users of water, such as agriculture, will be pushed out in favour of higher value/ML industries, such as mining, metal works and domestic use (Hellegers & Perry, 2006).

For agriculture to remain an economically viable industry into the future it needs to find an alternative source of water for irrigation. An alternative water source that has been discussed for manufacturing and other high value industries is desalination ((Wade Miller, 2006). The cost of the desalination process is prohibitive, at approximately $120 /ML for its use as a source of freshwater in agriculture. The major alternate source of freshwater for agricultural production that has been examined is treated effluent (Anderson, 1996).

Effluent is a term for any water discharged from households, agriculture, mining or other industries (Healy, 2001). Effluent contains a wide range of both suspended and dissolved chemicals and compounds (Papaiacovou, 2001). Effluent is a major source of environmental pollution (UNEP 2002). The eutrophication of river systems is a major environmental problem in many regions of the world, particularly in Asia, South America, and areas of Europe (UNEP 2002). Treated Effluent is any effluent that has undergone one or more forms of purification (Wade Miller, 2006). The purification aims to remove harmful chemicals and organisms to reduce the impact the effluent has on the environment (Dinesh, Sickerdick & Liston, 2006). The use of treated effluent to irrigate crops is a system that can both increase the availability of water for agriculture and decrease eutrophication in river systems by removing the effluent and its nutrients.

II. TREATMENT PROCESS

a. Treatment Processes

There are a variety of different treatment processes that wastewater can undergo to remove many of the toxic, or environmentally hazardous compounds (Dinesh et al., 2006). While irrigating untreated wastewater over a soil is considered an effective method of treatment (Asano, Smith & Tchobanoglous, 1990) poses a significant risk to public health (Abdulraheem, 1989) and can damage the soils. This practice is only common in developing nations such as Mexico (Lucho-Constantino et al., 2005a). The wide range of different processes used to treat effluent are broadly split into five categories; preliminary, primary, secondary, advanced/tertiary treatment and disinfection. For agricultural irrigation only up to secondary (with disinfection) is required to meet public health requirements in most developed countries.

i. Preliminary Treatment

In medium-large scale plants preliminary treatment includes coarse screening, grit removal and the comminution of large objects (Ortiz, Raluy & Serra, 2007). In most sewage treatment plants the velocity at which the water moves prevents the settling of organic solids. In many small scale treatment plants the grit removal step is not present in the preliminary treatment (Asano et al., 1990).

ii. Primary Treatment

This step focuses on the removal of materials via sedimentation and the skimming of floating debris. This process removes a large proportion (65%) of the oils and grease in the wastewater (Ortiz et al., 2007), upto 50% of the biological oxygen demand (BOD) and chemical oxygen demand (COD) (Asano et al., 1990) and 50-75% of the suspended solids (Asano et al., 1990).

iii. Secondary Treatment

This process primarily uses aerobic microbes to breakdown and remove biodegradable substances that are either suspended or dissolved in the wastewater (Asano et al., 1990). The different methods of secondary treatment work on the same technique of microbial aerobic decomposition (Feigin, Ravina & Shalhevet, 1991). Secondary treatment can be split into two main categories, high- and low-rate biological systems (Asano et al., 1990).

High-rate biological processes have a relatively small area but a high microbe population and are more commonly used in modern plants than the low-rate systems due to their shorter processing time (Asano et al., 1990). High-rate systems, in combination with primary treatment, remove up to 95% of BOD and suspended solids. The three main high-rate processes are activated sludge (Lin & Kiang, 2003), bio-filter (Asano et al., 1990) and rotating biological contactors (Asano et al., 1990; González, 1996).

Low-rate methods of water treatment are characterised by low concentrations of microbes and long treatment periods (Asano et al., 1990). In low-rate systems the micro-organisms are generally not separated from the liquid as they are in high-rate methods (Asano et al., 1990). The commonly used low-rate methods are aerated lagoons (Asano et al., 1990)and stabilisation ponds (Asano et al., 1990).

iv. Tertiary treatment (advanced treatment) methods

Tertiary treatment methods are often employed when specific compounds within the wastewater, such as nitrogen, heavy metals or phosphorus are required to be removed (Asano et al., 1990). There are a number of different tertiary treatment methods available. The most common form of tertiary treatment is desalination, usually via reverse osmosis. Other forms of treatment include:

Chemical	**Removal Method**
Nitrogen	Simultaneous Nitrification-denitrification (SND) (Zeng et al., 2004) Selective ion exchange (van der Hoek & Klapwijk, 1987) Overland flow (OF) (Taebi & Droste, 2007)

Phosphorus	Chemical precipitation (Morse et al., 1998; Yeoman et al., 1988)
Suspended solids removal	Chemical coagulation (Song et al., 2006) Superfine filtration
Organic and metals removal	Carbon adsorption (Hu et al., 2003; Zhang & Chuang, 2001)
Dissolved solids removal (including salts)	Reverse Osmosis (Asano et al., 1990) Electrodialysis (ED) (Asano et al., 1990) Distillation (Gryta, Tomaszewska & Karakulski, 2006)

Table 1. Methods of Tertiary water treatment.

v. *Disinfection*

There are two common methods for the disinfection of effluent, chlorine disinfection and U.V. disinfection. Chlorine disinfection is the most commonly used method of disinfecting wastewater prior to its release into the environment. The chloride dose usually applied to water is 5-10mg/L. After chlorine has been added it will pass through a series of baffles to give the chlorine time to denature the harmful bacteria. Due to chlorines harmful effect on the environment the water will often undergo a dechlorination process to remove the chlorine before it is passed into the environment.

The other major method of wastewater disinfection is via UV treatment ponds (see figure 4) where the water is slowly passed through a shallow pond. This method takes around 14 days, depending on depth and speed of water flow.

Figure 4. A UV detention pond. The pond is set up in a zig-zag pattern, with gentle slopes that create a set flow rate. The maximum depth of these ponds is usually 1m to ensure that light penetration is 100% and that a significant proportion of the microbes are denatured.

b. Uses of Treated Effluent

i. Environmental flow

Globally treated effluent has a number of end uses. In the majority of developed nations, such as the U.S.A, England and Australia treated effluent is released into the nearest water source, either rivers or oceans. This use of treated effluent is designated as environmental flows. While this release of effluent does help to alleviate the environmental water shortages that are seen in many farming regions, due to over extraction of water from the rivers, it can lead to a number of problems, primarily the eutrophication of the river systems, which leads to algal blooms, including the toxic cyanobacteria known as blue-green algae. These algal blooms often remove a large quantity of the oxygen and sunlight from the river ecosystem, leading to the death of both flora and fauna in the river.

ii. Domestic uses

Treated effluent is used in a number of water scarce and water stressed regions around the world, particularly in the Middle East and Mediterranean countries. Depending on the planned domestic use of the effluent it may undergo tertiary treatments. In a number of water scarce countries such as Australia and Kuwait wastewater is utilised for outdoor use, in gardens, playing fields and golf courses (Abdulraheem, 1989; Asano et al., 1990; Derry, Attwater & Booth, 2006). Water for this sort of application does not undergo any tertiary treatment (Derry et al., 2006).

The use of treated effluent in houses as a source of drinking water has been put forward in many water scarce countries (Papaiacovou, 2001). Public perceptions have limited the use of treated effluent as a source of drinking water (Anderson, 1996; Friedler et al., 2006; Papaiacovou, 2001). Despite the public perception problems a number of governments have installed, or are pursuing recycled water plants, where treated effluent undergoes tertiary treatment (which can include desalination) to produce water of a quality fit for human consumption (Ammary, 2007).

iii. Agricultural irrigation

Agricultural irrigation is currently a major, and growing use of treated effluent (Friedler et al., 2006; Haruvy, 1997). Treated effluent contains a number of nutrients, including nitrogen, phosphorus and potassium, which are essential for crop development (da Fonseca et al., 2007; Herpin et al., 2007). Treated effluent is perceived as suitable for agricultural purposes, and does not suffer negative public perception as the use of treated effluent in town water supplies does (Papaiacovou, 2001). Treated effluent used for irrigation not only reduces the need for fertiliser application due to the presence of nitrogen and phosphorus it also limits the amount of nutrients from the effluent that directly enter the wider environment. This paper aims to examine the validity of the belief that treated effluent is a sustainable method of agriculture.

Despite the environmental and economic benefits of using treated effluent for irrigation there are a number of associated risks (Oswald, 1989). The risks associated with treated effluent irrigation relate to human health concerns due to faecal coliforms in the effluent (Salgot et al., 2006), and to the long term sustainability issues of effluent irrigation. The long term sustainability of effluent irrigation is often affected by a number of harmful metals and chemicals present in treated effluent. Because of the threat to human health, and the quality of the water used, the method of irrigation must be given detailed consideration when using treated effluent.

III. IRRIGATION METHOD

There are a variety of irrigation methods that are currently used in large scale farming. Each different method has a number of advantages and disadvantages. For irrigation with treated effluent a number of factors that are not necessarily normally considered must be examined when selecting a method of irrigation (Christen et al., 2006). The 4 main irrigation methods are flood (Bouman et al., 2007), furrow (Christen et al., 2006), large movement irrigation machines (LMIM's) (Christen et al., 2006) and drip irrigation (Christen et al., 2006).

Due to the high loading of harmful substances found within effluent flood irrigation, which often exceeds good irrigation guidelines (10 000m^3 water/ha/year) (Qadir et al., 2003) is not deemed a suitable method for effluent irrigation. Furrow irrigation is one of the most common methods as it usually allows for the following of good irrigation guidelines. Furrow irrigation systems do not possess the fine tubes and numerous mechanical pumps of other methods. Fine tubing can lead to blockages due to the suspended solids often present within treated effluent.

While LMIM's are used for treated effluent irrigation the pumps and small nozzles can often lead to blockages. The overhead spray system of LMIM's also leads to concerns over food safety due to the presence of faecal coliforms within the water. Drip Irrigation systems face a significant hurdle in their use as a method of effluent irrigation due to their small pipe diameters and nozzles. The small diameter of the system often leads to blockages, preventing water from reach the plants (Christen et al., 2006).

IV. CHEMICAL CONTAMINANTS IN TREATED EFFLUENT

There are a number of different forms of contamination present in treated effluent. Effluent contaminants come in 3 categories biological, chemical and physical. This section is examining what chemical contaminants are present in the water, and the threat that is posed by these contaminants to the sustainability and success of irrigation with treated effluent. In this section the maximum concentrations make the assumption of good irrigation practice ($\leq$ 10 000m^3 water/ha/year) if more than this level of water is applied to the soil then the maximum concentrations need to adjusted downward in accordance. For a list of analytical methods to analyse soil contaminants please see appendix 1.

a. pH

The pH of effluent water is an important chemical property that needs to be monitored. A pH of 6.5-8 is the suitable range for agriculture (Rattan et al., 2005). In most situations this will provide the greatest supply of necessary minerals, while limiting harmful ionic substances entering soil solution. Soil pH is also an important measure to manage the absorption of toxic ions, such as arsenic, iron and lead. The solubility of an ion is a function of the soils pH (see figure 5).

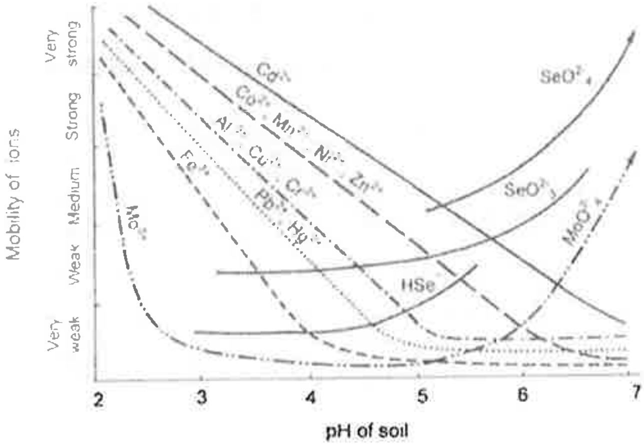


Figure 5. Ionic solubility as a function of pH. Changes in soil pH alter ion mobility. As a pH increases the mobility of cations is decreased, and the mobility of anions increases (Kabata-Pendias & Pendias, 2001).

The maintenance of an appropriate soil pH (6.5-8) is essential for the long term sustainability of a farm. As the soil pH decreases more cations are released from the soil, increasing there availability often to toxic levels. If the pH of a soil increases into the alkaline region (above pH 8) it can also have deleterious affects on the plant/soil system, by restricting the movement of essential ions.

The pH of treated effluent for irrigation must be carefully monitored. Treated effluent can have a significant impact on a soils pH over the medium to long-term. The current belief is that the pH of irrigation water should not be lower than 6 or higher than 9 (Reid & Sarkis, 2006). A number of countries, including Australia, have imposed stricter guidelines, with a pH range of 6.5-8.5 being the acceptable limit to ensure the long term sustainability of a farm (Reid & Sarkis, 2006). pH of a soil is monitored using a 1:5 soil water extract and a pH probe. The pH of the irrigation water should be measured directly using a pH probe.

b. Salinity and Sodicity

i. Salinity

Salt present in irrigation water is capable of accumulating in the soil profile. Effluent irrigation has the potential to increase the salinity in a field. Correct irrigation practices will, in most cases remove the risk that any salts in the water may pose (Hulugalle et al., 2006). Soil salinity can lead to production losses via osmotic stresses placed on the plant.

The concentration at which salt will affect a plant varies depending on the plant species and a number of soil properties, including structure and location of the water table. Irrigation water with an electrical conductivity (EC) reading >0.2dS/m is considered to have the capacity to affecting a soils long term sustainability (Rengasamy, 2006). Treated effluent commonly has a EC varying between 0.6 – 1.7dS/m (Balks, Bond & Smith, 1998). A soil is considered saline if the EC is >4dS/m however many plants are capable of growing unaffected at this level. The maximum allowable concentration of salt present in a soil varies depending on the tolerance capabilities of a plant. Table 4 lists a number of the major broad-acre crops and their salt tolerance levels.

Crop	50% emergence EC (dS/m)	50% yield reduction EC (dS/m)
Barley	16-24	18
Corn	21-24	5.9
Cotton	15	17
Rice	18	3.6
Sorghum	13	15
Wheat	14-16	13

Table 2. Crop salt tolerance levels. The 50% emergence level is the EC value at which 50% of the seeds will fail to germinate. 50% yield reduction is the EC at which a crops yield will be half that of a salinity free field (Rengasamy, 2006).

ii. Sodicity

Sodicity is related to the excess concentration of sodium (Na) cations in soil in relation to the other cations (Balks et al., 1998). The amount of Na that enters the soil via irrigation water is measured in a relation to calcium and magnesium (Rengasamy, 2006). The value given by this ratio is referred to as the sodium adsorption ratio (SAR) (see figure 11).

$$SAR = (Na^{+}) / ([Ca^{2+}] + [Mg^{2+}])^{½}$$

Figure 6. Sodium Absorbance ratio. This equation determines the level of sodium in water in relation to the other 2 main cations while compensating for the difference in charge.

The exchangeable sodium percentage (ESP) is the measurement used to determine the cation exchange capacity of soil that is occupied by sodium (Balks et al., 1998). The combination of the SAR and salts in effluent usually combine to increase a soils ESP. There is a significant relationship between a soils ESP and its ability to support agriculture (see figure 7) (Rengasamy, 2006).

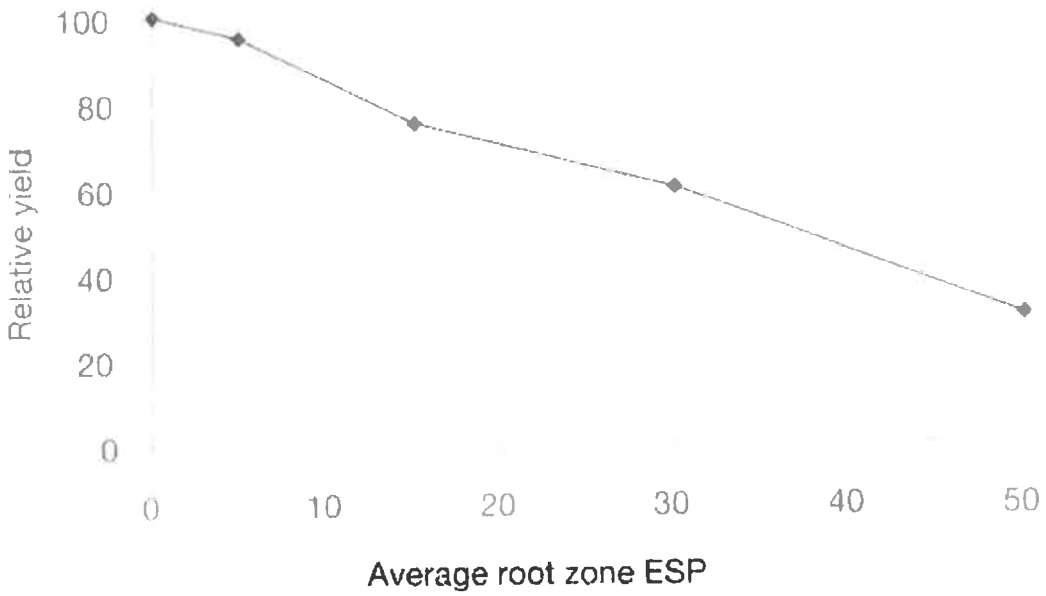
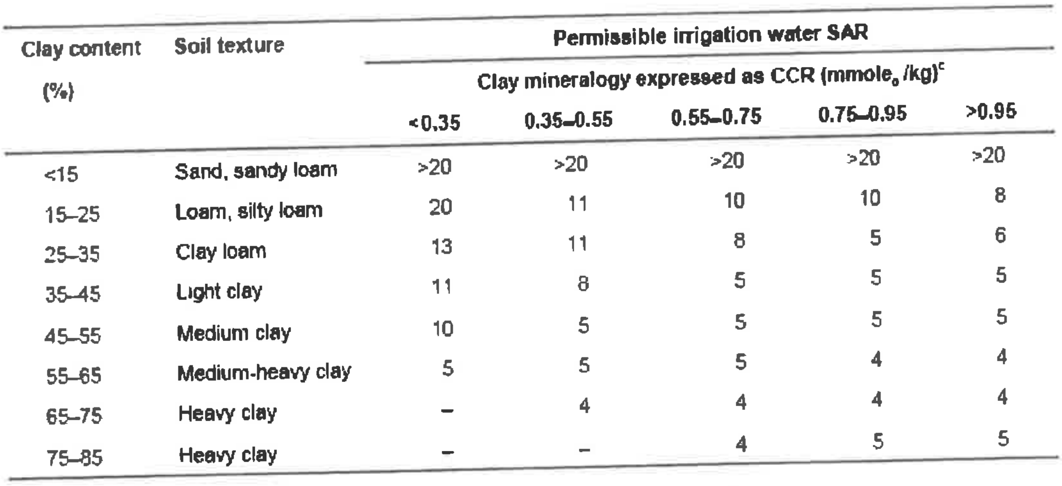


Figure 7. ESP and yield. As the ESP increases in the soil the yield, in relation to an unaffected field, decreases (Kabata-Pendias and Pendias, 2001).

Sodicity leads to a breakdown in soil structure due to dispersive forces, reducing the porosity of the soil (Rengasamy, 2006). The reduced porosity leads to a decrease in soil permeability and soil water content (Balks et al., 1998). As the structure of the soil decreases its ability to sustain plant growth is diminished and in extreme cases this can lead to germination delays, reduced yields and crop failure (Nunes et al., 2007).

To prevent long term damage to a soil structure due to sodium the SAR of irrigation water should be carefully monitored. Due to the mineralogical differences between different soil types, different maximum sodium contents in irrigation waters exist (ARMCANZ, ANZECC & NHMRC, 2000). For the maximum sodium contents permissible in irrigation water see table 5.



Clay content (%)	Soil texture	Permissible irrigation water SAR				
		Clay mineralogy expressed as CCR ($mmole_c$/kg)[c]				
		<0.35	0.35–0.55	0.55–0.75	0.75–0.95	>0.95
<15	Sand, sandy loam	>20	>20	>20	>20	>20
15–25	Loam, silty loam	20	11	10	10	8
25–35	Clay loam	13	11	8	5	6
35–45	Light clay	11	8	5	5	5
45–55	Medium clay	10	5	5	5	5
55–65	Medium-heavy clay	5	5	5	4	4
65–75	Heavy clay	–	4	4	4	4
75–85	Heavy clay	–	–	4	5	5

Table 3. Maximum SAR for irrigation water (ARMCANZ *et al.*, 2000)

c. Metals

i. Copper

Location	Maximum Allowable Concentration (MAC)
Cumulative load limit – shallow root system	140 kg/Ha
Cumulative load limit –Deep root system	250 kg/ha
Long term irrigation water	0.2 ppm
Short term irrigation water	5 ppm

Table 4. Summary of MAC for copper (ARMCANZ *et al., 2000)*

Copper (Cu) is an essential micronutrient for plant growth and development (Boojar & Goodarzi, 2007; Foy, Chaney & White, 1978) and plays an important role in both plant photosynthetic and respiratory electron transport chains. Although copper is an essential micronutrient it can also have a detrimental effect on the growth and development of a plant (Ouzounidou et al., 1995; Wang et al., 2007; Xiong & Wang, 2005), preventing root development, reducing nutrient uptake and causing stunting and chlorosis in plants (Boojar & Goodarzi, 2007; Borkert, Cox & Tucker, 1998; Foy *et al.*, 1978).

Numerous studies have been conducted in an attempt to determine at what level copper concentrations become toxic to plants. The studies have had a number of different findings, and only a general conclusion has been achieved, different species of plants possess significantly different tolerances to copper concentrations within the soil. In one paper (Borkert *et al.*, 1998) the effect of varying copper concentrations on a number of different agricultural crops was tested, the results from this trial indicated that field crops, such as rice, soybeans and corn, had tolerance levels in the range of 130-170 ppm. A different study (Mozaffari, Alva & Chen, 1996) indicates that citrus crops, a perennial species with a deeper root system, has a higher tolerance to copper, with stress due to copper only arising above 250ppm. In the report by ARMCANZ, ANZECC and NHMRC (2000) the maximum loading of copper in soil for agricultural use should not exceed 140 kg/ha. The concentration of copper that should be present in water, including effluent, used for irrigation should not exceed 0.2ppm according to the ARMCANZ *et al.* (2000) report.

ii. Lead

Location	**MAC**
Cumulative load limit (Soil)	100 kg/ha
Long term irrigation water	2.0ppm
Short term irrigation water	5.0ppm

Table 5. Summary of MAC for lead (ARMCANZ *et al., 2000)*

Lead (Pb) is a heavy metal that is toxic to a large number of organisms and plays little to no role in the biological systems of plants or animals **SOURCE**. Lead occurs naturally in soils as a trace element, at mg/Kg^{-1} levels or less (He, Yang & Stoffella, 2005). While a natural baseline of 12-16ppm may have existed prior to human activities (Gough, Severson & Shacklette, 1988) further studies have found that around the world agricultural soils tend to have an average of 32ppm with a 95% Confidence interval of 3 – 189ppm of Pb in the soil profile (Kabata-Pendias & Pendias, 2001).

Lead can be deposited in soils via a number of processes. Before the introduction of lead replacement fuels and unleaded petrol, a major source of Pb in the environment was the Pb expelled from car exhausts as an aerosol, current sources include industrial waste and wastewater. Lead is present in the wastewater of a number of countries at the ppb level. A study conducted by He *et al.* (2005) found that the average daily output of lead from a wastewater plant was 57 ppb. The majority of lead found in wastewater is likely to be from lead pipes, and lead solders used during the building of older system, as well as other miscellaneous sources such as old paints that have entered into the sewage system. While daily amounts of lead produced by treatment plants is relatively small a major problem with irrigating using this water is that the metal readily binds to compounds in the soil and will accumulate within the soils profile (Koeppe, 1977).

While Pb will remain relatively stable within a soil, at high and neutral pH levels, if the soil pH decreases, as is common in many agricultural soils due to farming practices such as over application of nitrogen, then the lead bound to the soil will disassociate and enter into the soils solution (Lepp, 1981). Once in the soil solution Pb can be absorbed by plant roots, however there are a number of natural biochemical defences within most plants to prevent this from occurring (Sinha et al., 2006). These include the accumulation of Pb along the outside of cell walls, primarily in the root system at lower concentrations, as well as accumulation within the cell wall, binding of the Pb to the orthophosphate ions within the cell nucleus, Pb can also be bound, inactivated and/or precipitated from the plant, thus preventing any harmful affects to the plant (Kim, Yang & Lee, 2002; Sinha *et al.*, 2006; Tandler & Solari, 1969).

Lead in the soil at excessive levels can lead to a number of problems with plant growth, including delayed or failed germination and growth suppression (Sinha *et al.*, 2006). These symptoms have been noted in a variety of crops, including Corn, rice, Sunflower, oats as well as legume crops (Carlson et al., 1976; Kastori et al., 1998; Mukherji & Maitra, 1977; Munzuroglu & Geckil, 2002; Sinha et al., 2006; Tomar et al., 2000).

According to Kabata-Pendias and Pendias (2001) upto 500ppm of Pb is acceptable in Agricultural soils before plants begin to show signs of stress. This value has been disputed (Paivoke, 2002) with results from a number of trials indicating that some crops are affected at significantly lower concentrations than the accepted 500ppm. In many countries the level of lead allowable in soil is far lower than 500ppm, however this is due to public health and environmental concerns, not agronomic considerations. While the allowable levels of Pb vary depending on region and country (ranging from 20ppm in Russia to 300 ppm in the EU) a nominal value of 100ppm (100mg/Kg^{-1}) can be used to determine if Pb is present at elevated levels.

If treated effluent is used to irrigate crops Pb concentrations are required to be significantly lower than the maximum allowable concentrations within the soil. This is due to the soils ability to adsorb chemicals, such as Pb, onto its surface. Few countries have produced guidelines for metals within irrigation water, however one of the countries that has produced guidelines covering metal concentrations in irrigation water is Australia, which has set an upper limit of 2ppm of Pb within any water, including effluent, that is being used for long term crop irrigation.

iii. Arsenic

Location	MAC (ppm)
Cumulative load limit (Soil)	20
Long term irrigation water	0.1
Short term irrigation water	2

Table 6. Summary of MAC for arsenic (ARMCANZ *et al., 2000)*

Arsenic (As) is a metalloid compound (McLaughlin, Parker & Clarke, 1999) that is naturally found in soils around the world at relatively low concentrations (McLaughlin *et al.*, 1999). The metal is also commonly found in the groundwater reservoirs of different regions around the world, including the Indian subcontinent, Australia and Central America (Mukherjee et al., 2006; Smith et al., 2003a; Smith, Jankowski & Sammut, 2003b). Many of the towns in these affected regions use this groundwater for both drinking and irrigation purposes and the arsenic will often still be present in the towns effluent unless special treatment methods are applied (Mukherjee et al., 2006). Arsenic is a non-essential element known to have a detrimental effect on the development of plants(Azizur Rahman et al., 2007; McLaughlin et al., 1999).

Plants are severely affected by elevated inorganic arsenate levels within soils, because the chemical properties resemble orthophosphate (McLaughlin *et al.*, 1999). Because A plants root system is designed to readily absorb phosphorus they will also easily absorb the As within the soil (McLaughlin *et al.*, 1999).

Excess arsenic will reduce a plants chlorophyll production (Azizur Rahman *et al.*, 2007) and cause a reduction in the plant root mass (Abedin et al., 2002). The reduction in chlorophyll can lead to a number of visible symptoms including, chlorosis and necrosis of the leaves and stunting. The reduction in root mass also contributes to the plants symptoms by limiting the amount of nutrients available to the plant for growth and production (Abedin *et al.*, 2002; Abedin & Meharg, 2002; Azizur Rahman *et al.*, 2007). High As levels in the soil and/or water can also prevent or delay seed germination (Abedin & Meharg, 2002).

The recommended maximum concentration of arsenic in agricultural soils is 20ppm (Kabata-Pendias & Pendias, 2001). A number of studies have shown <20ppm As can be beneficial to plant production by binding with soil clay particles. The binding displaces orthophosphate molecules, increasing the plant available phosphate in the soil (Duel &

Swoboda, 1972; Kabata-Pendias & Pendias, 2001). According to Australian irrigation guidelines the maximum safe level of As long term use is 0.1 ppm (ARMCANZ et al., 2000)

iv. Manganese

Location	MAC (ppm)
Cumulative load limit (Soil)	<1500
Long term irrigation water	0.2
Short term irrigation water	10

Table 7. Summary of MAC for manganese (ARMCANZ *et al., 2000)*

Manganese (Mn) is an essential micronutrient to plants that is involved in the photosynthetic electron transport chain as part of the enzyme phosphotransferase. Mn is also an essential part of the enzyme arginase, and in some cases can substitute for magnesium in other plant enzymes (Kabata-Pendias & Pendias, 2001).

According to Kabata-Pendias & Pendias (2001) the maximum allowable concentration of manganese in agricultural soils is 1500ppm, however a number of studies indicate that plant toxicity can occur at far lower levels and a number of different factors must be considered when looking for manganese toxicity. The major contributing factors to Mn toxicity are acidic (below pH 5.5) or basic (above pH of 8) soils, anerobic conditions (such as water logging or severe compaction), and iron deficiency. Iron and Mn have an antagonistic relation in the soil, and a ratio of Fe:Mn of 1.5 to 2.5 should be maintained. If the ratio is altered it can cause imbalances in nutrient uptake (Kabata-Pendias & Pendias, 2001).

The application of treated effluent to a field can result in an increase of soil Mn by 2 – 3 times the original levels (Singh & Bhati, 2005). In an attempt to mitigate the chance of Mn toxicity in soils irrigated with treated effluent, a number of countries, including Australia, Canada, United States of America and Israel, have placed an upper limit for magnesium concentration of 0.2ppm has been placed on all waters that are used for long term irrigation (Reid & Sarkis, 2006).

v. Iron

Location	MAC (ppm)
Cumulative load limit (Soil)	Unknown see text
Long term irrigation water	0.2
Short term irrigation water	10

Table 8. Summary of MAC for iron (ARMCANZ *et al., 2000)*

Iron (Fe) is an essential micronutrient for plant growth and development, used in the electron transport chain for photosynthesis and respiration. Iron toxicity is not a common problem in most agricultural enterprises, and will only occur under anaerobic (water logged) conditions (Becker & Asch, 2005). There is no agreement between different studies on the level of Fe required in the soil for Fe toxicity to occur. The range for the minimum Fe content varies from 20 – 500 mg/L^{-1} (Becker & Asch, 2005). Because of the requirement for water logged conditions iron toxicity is normally only seen in the production of lowland rice, which is grown in flooded paddies, and is recognised as one of the most wide-spread disorders of the rice industry (Becker & Asch, 2005). Water logged soils allow for an increase in anaerobic respiration by microbes. One of the reactions that is undertaken by some of these anaerobic microbes is the conversion of the insoluble Fe(III) into the soluble form Fe(II) (Ponnampe, Tianco & Loy, 1967) which allows iron to more easily be absorbed by plant roots.

Although iron toxicity is only commonly seen in the rice industry it is possible for iron toxicity to occur in cotton and other irrigated crops when irrigation scheduling is not properly managed to prevent water logging (Rashid & Ryan, 2004). In plants excessive levels of Fe in the leaves leads to an elevated production of free radicals which damage their cells. The cell damage reduces the plants ability to photosynthesis and leads to reduced yields and a "bronzing" of the leaves (Becker & Asch, 2005). Fe toxicity can lead to a yield loss of 15-30% (Becker & Asch, 2005) however a different study (Audeburt & Sahrawat, 2000), has found that cases of severe Fe toxicity can lead to complete crop failure in rice paddies.

While iron toxicity can be managed with proper irrigation practice, excessive iron in the soil under aerobic conditions can still have a detrimental effect on a plant by preventing the uptake of other nutrients such as manganese (Becker & Asch, 2005; Hell & Stephan, 2003;

Lepp, 1981). To ensure the long term viability of a cropping enterprise the level of Fe in the water applied should not exceed 0..2ppm (ARMCANZ *et al.*, 2000).

vi. *Cadmium*

Location	MAC
Cumulative load limit (Soil)	Arbitrarily 22Kg/ha
Long term irrigation water	0.01
Short term irrigation water	0.05

Table 9. Summary of MAC for cadmium (ARMCANZ *et al., 2000)*

Cadmium (Cd) is a non-essential element to plant growth and production (Satarug et al., 2003) that is found in soils around the world, with its natural content between 0.06 – 1.1ppm. Phosphate fertilisers have a naturally high Cd content (Garrett, 2000), and the application of these fertilisers, along with the application of treated effluent and the application of sewage sludge (Resource Sciences, 1997), have lead to increased soil Cd levels in large parts of the global agricultural industry (Satarug *et al.*, 2003).

In numerous agricultural areas around the world Cd contamination is a major problem (Gouia, Habib Ghorbal & Meyer, 2000). Excess Cd can lead to reduction in photosynthesis, alterations to nitrogen and carbohydrate metabolism and a reduction in sulphate assimilation (Gouia *et al.*, 2000; Resource Sciences, 1997). For Cd toxicity to occur there are 2 main factors which are required; an excess of Cd within the soil profile (Kabata-Pendias & Pendias, 2001; Kirkham, 2006; Resource Sciences, 1997) and a pH below 6, with the greatest level of Cd uptake by plants is seen in the pH range of 4.5-5.5 (Kabata-Pendias & Pendias, 2001; Kirkham, 2006).

The maximum concentration of Cd that may be safely present in a soil has not yet been determined ((ARMCANZ et al., 2000; Kirkham, 2006). WHO guidelines indicate that a concentration of 0.2ppm in a plant is considered dangerous to human health (Hespanhol & Prost, 1994). Many of the studies that have been conducted on the uptake of Cd by plants have failed to look at the properties and nature of the soil, making a reliable estimate of the maximum allowable soil concentrations difficult (Kirkham, 2006). Kabat-Pendias & Pendias (2001) have given a maximum allowable lev el of 22kg/Ha for Cadmium, however this is a figure that has been devised for fields fertilised with sewage sludge. The Cd uptake of plants is heavily dependant on the pH of a soil, and is most mobile in soils with a pH ranging from 4.5 - 5.5. For long term irrigation the water used should not have a Cd concentration that exceeds 0.01ppm, and for short term use it should not exceed 0.05ppm (ARMCANZ et al., 2000).

vii. Molybdenum

Location	MAC (ppm)
Cumulative load limit (Soil)	Cu:Mo >2:1 and Mo should not exceed 20ppm
Long term irrigation water	0.01
Short term irrigation water	0.05

Table 10. Summary of MAC for molybdenum (ARMCANZ *et al., 2000)*

Molybednum (Mo) is an essential micronutrient that is required at extremely low levels for plant growth and development (McBride & Cherney, 2004). While plants require only relatively low levels of Mo for proper growth and function, they will normally absorb Mo in proportion to its levels within the soil (Kabata-Pendias & Pendias, 2001).

In natural soils Mo concentration is estimated to be at an average concentration of 3ppm (Kabata-Pendias & Pendias, 2001), however the application of effluent and/or sewage sludge, as well as mine tailings and other wastes, can increase the levels of Mo in soils. Unlike other micronutrients Mo availability increases as soil pH increases (Kabata-Pendias & Pendias, 2001). Although Mo is readily soluble and thus easily absorbed by plants cases of Mo toxicity are very rare (Kabata-Pendias & Pendias, 2001). Molybdenum levels in plant tissues are important as it can become toxic to livestock at levels lower than plant toxic levels (Kabata-Pendias & Pendias, 2001). Ruminant animals are especially effected (McBride & Cherney, 2004) where levels of only 5ppm can cause illness in the animals (ARMCANZ *et al.*, 2000).

Molybdenum and copper levels in the soil have a direct effect on each others availability and should exist in a ratio Cu:Mo of greater than 2. However levels > 20ppm of Mo in the soils is considered excessive (Kabata-Pendias & Pendias, 2001). For long term irrigation the water should not contain Mo in excess of 0.01ppm (ARMCANZ *et al.*, 2000) to ensure the safety of animals that eat the crops produced on these fields, as Mo toxicity can be seen in animals at 1.5-5ppm (Kabata-Pendias & Pendias, 2001) while many plants, including legumes, can accumulate as much as 500ppm Mo.

viii. *Aluminium*

Location	MAC (ppm)
Cumulative load limit (Soil)	Based on pH
Long term irrigation water	5
Short term irrigation water	20

Table 11. Summary of MAC for aluminium (ARMCANZ *et al., 2000)*

Aluminium (Al) availability to plants, and thus its toxicity, is directly tied to the soils pH (Peterson & Girling, 1981). Because aluminium is a major component in most clays Al toxicity is possible to occur in most soils around the world when pH conditions are favourable for the release of Al ions into the soil solution.

Because of the nature of an acid soil it is usual that Al is not the only limiting factor, and because of this it is difficult to isolate symptoms of aluminium toxicity (Peterson & Girling, 1981). There is a reasonable relationship between Al toxicity and plant root length (Moore, Kronstad & Metzger, 1976) that can be used to determine the extent of Al toxicity. The main control method to prevent Al toxicity is the monitoring of soil pH rather than the levels of soils Al concentration. As long as a soil is kept above a pH of 6.5 (ARMCANZ *et al.*, 2000; Peterson & Girling, 1981) the risk of Al toxicity is minimal. To reduce the risk of Al toxicity if a soil does becomes acidic ARMCANZ *et al.* (2000) places a trigger value of 5ppm Al in water used to irrigate crops.

ix. *Zinc*

Location	MAC
Cumulative load limit (Soil)	313 kg/ha
Long term irrigation water	2 ppm
Short term irrigation water	5 ppm

Table 12. Summary of MAC for zinc (ARMCANZ *et al., 2000)*

Zinc (Zn) is an essential element for plant growth (Kabata-Pendias & Pendias, 2001) however there is debate over whether it is passively or actively absorbed by plants (Collins, 1981). Zinc toxicity is rare in nature, however in agricultural systems it is reported relatively often, especially in the presence of acidic (Bucher & Schenk, 2000), or sludge amended soils (Collins, 1981; Dong et al., 2006). Symptoms of Zn toxicity are similar to those of other metals, including bronzing of the leaves, stunting and chlorosis (Collins, 1981; Dong *et al.*, 2006). In comparison to other heavy metals Zn is not considered highly phototoxic (Kabata-Pendias & Pendias, 2001). Excessive Zn in a plant is known to inhibit the fixation of CO_2, however it is not known if this is a direct or indirect factor of the excessive Zn (Collins, 1981). Zinc is also known to affect the plants respiration and its non-cyclic electron transport chain (Collins, 1981).

Studies have found that elevated levels of Zn are present in town effluent (Chague-Goff, Rosen & Eser, 1999), and to ensure the long term viability of farming land a safe upper limit of 2ppm of Zn in irrigation water has been set, and in cases of short term irrigation an upper limit of 5ppm (ARMCANZ et al., 2000). Zinc affects plant growth at different concentrations depending on the plant species, soil acidity and form of Zn in the soil. The exact form in which Zn is absorbed by a plant has not been precisely defined however it is predominately absorbed in aqueous solution, in either the form Zn or Zn^{2+} (Kabata-Pendias & Pendias, 2001). The maximum concentration of Zn that should be present in an agricultural soil is given as 313 kg/ha^{-1} (ARMCANZ et al., 2000), although the maximum safe concentration of Zn in a soil does depend on the soil properties (Kabata-Pendias & Pendias, 2001) specifically on the soil pH. Zinc availability and soil pH have an inverse relation, as the pH decrease the Zn availability will increase (Bucher & Schenk, 2000).

x. *Lithium*

Location	MAC (ppm)
Cumulative load limit (Soil)	See Text
Long-term irrigation water	2.5 (0.75 for citrus)
Short-term irrigation water	2.5 (0.75 for citrus)

Table 13. Summary of MAC for lithium (ARMCANZ *et al., 2000)*

Lithium (Li) is a highly reactive element, and as such is not found in nature in its pure form (Kszos, Beuchamp & Stewart, 2003). In nature lithium is found in stable minerals and salts. Lithium has a number of uses in households where it is commonly found in batteries, oils and a number of different pharmaceuticals (Kszos et al., 2003). Lithium has been detected in treated effluent for a number of years (Kszos & Stewart, 2003; Waly et al., 1987).

Lithium water soluble, and is readily available to plants (Kabata-Pendias & Pendias, 2001). Excess lithium damages plant tissue, and has an effect on the growing tips of the roots (Kabata-Pendias & Pendias, 2001) which can prevent further development of the plant. Lithium also has a number of non-specific symptoms such as chlorotic and necrotic spots on the plants leaves. Studies have found that Li affects a number of species; citrus species appear to be the most susceptible plants to Li toxicity, however other crops, such as corn (Kabata-Pendias & Pendias, 2001) have also exhibited symptoms when exposed to excess amounts of Li in their environment.

According to the ARMCANZ *et al.* report (2000) the maximum acceptable concentration for lithium in water used for irrigation of crops is 2.5ppm for both long and short term irrigation, however if the irrigation water is to be applied to a citrus crop the level of Li should not exceed 0.075ppm. ARMCANZ *et al.* (2000) has not produced a maximum allowable concentration of Li within the soil profile. The national academy of science (1972), cited in (Waly et al., 1987), have published a maximum allowable concentration for lithium within the soil, of 0.04 ppm, however this value appears to be in contradiction with the allowable concentration in irrigation water, this value may either be outdated or it may have been misreferenced. It is possible that the value given is for the maximum available concentration of Li, which is usually far smaller than the amount of Li present in a soil (Waly et al., 1987).

xi. Beryllium

Location	MAC (ppm)
Cumulative load limit (Soil)	10
Long-term irrigation water	0.1
Short-term irrigation water	0.5

Table 14. Summary of MAC for beryllium (ARMCANZ *et al., 2000)*

Beryllium (Be) is a relatively rare element in nature that is found bound to organic matter and as inorganic salts (Kaplan et al., 1990). Because of the ease with which Be binds to organic matter it is commonly found with coal and fossil fuel deposits, and the combustion of these is a major source of the Be released into the environment (Kabata-Pendias &

Pendias, 2001; Kaplan et al., 1990). Beryllium is also present in other substances, specifically from household chemicals that contain petroleum derived products.

While there are no generally accepted methods for extracting available Be from the soil (Kabata-Pendias & Pendias, 2001; Kaplan et al., 1990) studies have shown that an addition of 2ppm Be to acidic soils can cause phytotoxicity in plants, however the same level of Be added to a alkaline soil will not induce a phytotoxic effect (Kaplan et al., 1990). The difference in the results from these experiments indicated that Be toxicity is driven by a low pH, and that the addition of lime or gypsum to a soil will lower the risk of Be toxicity (Kaplan et al., 1990)

The maximum level of Be in irrigation water, for long term applications, should be 0.1ppm, and at no point should Be concentrations exceed 0.5ppm (ARMCANZ et al., 2000). In soils the level of Be that is naturally present ranges from less than 1ppm up to approximately 7ppm. Levels of Be above 15ppm are considered to be contaminated (Kabata-Pendias & Pendias, 2001) however the effect of Be on plants is dependent on the form that the Be is present in, when bound to organic matter in the surface layers Be is not toxic to the plants, however as a salt beryllium is soluble, and therefore, readily available to plants (Kaplan et al., 1990). In agricultural soils, particularly soils with a low pH, 10ppm Be should be considered high and a possible threat to long term production.

d. Non-Metals

i. *Boron*

Tolerance	Concentration of Boron in Water (ppm)	Crop
Highly Sensitive	<0.5	Blackberry, lemon
Sensitive	0.5 – 1	Peach, cherry, plum, grape, cowpea, onion, garlic, sweet potato, wheat, barley, sunflower, mung bean, sesame, lupin, strawberry, artichoke, Kidney beans, lime beans
Moderately sensitive	1 – 2	Capsicum, pea, carrot, radish, potato, cucumber
Moderately Tolerant	2 – 4	Lttuce, Cabbage, celery, turnip, bluegrass, oat, corn, obacco, mustard, clover, squash
Tolerant	4 – 6	Sorghum, tomato, alfalfa, purple vetch, parsley, red beet
Highly Tolerant	6 – 15	Asparagus, Cotton

Table 15 . Boron tolerance in different plants (Sourced from (Westcot & Ayers, 1985)

Boron (B) is an essential micronutrient required at low concentrations for plant growth and development (Kabata-Pendias & Pendias, 2001), in high concentration it is a highly toxic element that can significantly effect a crops yield (Lucho-Constantino et al., 2005b). A major source of anthropogenic B contamination is treated effluent. When applied to fields B can become locked in the soils, leading to its accumulation over time, and is capable of reaching levels toxic to plants. In wastewater up to 40% of the B is derived from detergents (Kabata-Pendias & Pendias, 2001) where it is used as a whitening agent. Symptoms of B toxicity in plants varies depeding on the species, however the symptoms are primarily seen in the leaves, where B accumulates. Symptoms include dark green, wilted leaves and necrotic edges typically on the older leaves in the plant (Choi et al., 2006; Nable, Banuelos & Paull, 1997).

Boron toxicity in plants can be caused via direct application of toxic levels of B with irrigation water, fertiliser or other applications, or via a build up of B contained within the soil profile (Nable et al., 1997). The maximum concentration of B that should be present within irrigation water, including treated effluent, is dependent on the crop that is being grown (see table 15). Due to the varying techniques used to extract B no specific MAC has been determined. Boron toxicity has been demonstrated at 13ppm extractable B (Choi et al., 2006).

ii. Fluoride

Location	MAC (ppm)
Cumulative load limit (Soil)	500
Long term irrigation water	1
Short term irrigation water	2

Table 16. Summary of MAC for fluoride (ARMCANZ *et al., 2000)*

Fluoride (F) is a halogenic element that has few stable mineral forms (Arnesen, 1998). There are a number of anthropogenic sources of F that contribute to its build up in the soils, the primary sources include coal combustion and metal smelting plants, particularly Al smelters (Arnesen, 1998; Facanha & Okorokova-Facanha, 2002; Manoharan et al., 2007). Fluoride compounds also enters the environment through the addition of F to drinking water (in the forms NaF; Na_2SiF_6 and H_2SiF_6) as well as from a number of products found through the house, particularly products to do with dental care, such as toothpaste, and a number of different pharmaceuticals (Weinstein & Davidson, 2004). These sources of F commonly enter the environment via sewage, and because of this the amount of F in effluent used for irrigation needs to be monitored (Weinstein & Davidson, 2004).

As the fluoride compounds break down the F is released into the environment, where it had been assumed until recently it posed little to no threat as F strongly adsorbs to most soil particles at neutral pH (Manoharan et al., 2007; Stevens et al., 2000; Weinstein & Davidson, 2004). Recent studies however have shown that as the pH of soils decrease F is released from the soil and forms mineral complexes with aluminium. A number of these AlF_x complexes have been described as effective analogs of inorganic phosphate, allowing them to bind with a number of phosphate sites within the plant (Manoharan et al., 2007). While the AlF_x complex's can bind with the phosphate sites, they cannot perform the same function, leading to AlF_x toxicity which will result in phosphate deficiency (Facanha & Okorokova-Facanha, 2002; Manoharan et al., 2007). As well as reducing the ability of a plant to absorb phosphorus, F in soil solution can also inhibit the solubility of potassium, manganese and other minerals which can lead to mineral deficiencies within organisms.

The recommendation in the ARMCANZ *et al.* (2000) report is for a concentration of no greater than 1ppm F for long term, or 2ppm F for short term irrigation use. The maximum allowable concentration of F within a soil is unclear as studies examining its toxic effects are still uncertain, however to reduce the risk of F toxicity, or F induced nutrient problems in crops, the pH of the soil should be maintained at a neutral pH (6.5-7.5), and soils with F levels greater than 500ppm should be considered to have excessive amounts of F, with normal soils ranging from 150 – 400ppm (Kabata-Pendias & Pendias, 2001).

e. Macro-nutrients

iii. Nitrogen

Nitrogen (N) is an essential macro-nutrient for plant growth and development however excessive nitrogen in the soil can be toxic to plants. The presence of N in effluent is a benefit to farmers as it is able to substitute for some of the fertilisers, reducing the cost of production (Herpin et al., 2007). While this added nitrogen is of benefit to farmers it is important that the levels of N being added is closely monitored in order to prevent over fertilisation of the soil, leading to N toxicity (da Fonseca et al., 2007).

A study conducted by Hullugale *et al.* (2006) showed that in a common cotton – wheat rotation irrigated with treated effluent not all the nitrogen was used by plants and leached into the subsoil. Other studies (Herpin et al., 2007) have shown that effluent cannot provide all the N required by plants and that N fertiliser needs to be added for optimal growth. Excess nitrogen in the soil can lead to an increase in microbial activity which increases the breakdown of organic carbon within the soil, decreasing soil structural stability and reducing the soils pH buffering capacity (Myrold, 2005).

To prevent plant toxicity, and maintain stable soil structure nitrogen in the water should not exceed 5ppm for long term irrigation, or 125ppm for short term irrigation, however these values can alter depending on the soil quality at the site (ARMCANZ et al., 2000). Excess nitrogen in the soil is measured via the amount of N passing below the root zone (Hulugalle et al., 2006).

iv. Phosphorus

Phosphorus (P) is a major nutrient that is required for the growth and development of plants (ARMCANZ et al., 2000). P usually occurs in nature as the soluble phosphate (PO^{4-}) molecules. Because P is adsorbed strongly onto most soils (ARMCANZ et al., 2000) and the high P requirements of plants cases of P toxicity are rare. Guidelines for a MAC for phosphorus look at phosphorus in terms of water ecosystems, where it can lead to algal blooms. If treated effluent is to be stored on farm it should have a P concentration less than 0.05ppm to ensure no algal blooms occur in the water storage (ARMCANZ et al., 2000).

v. Potassium

Potassium (K) is a nutrient that is required by plants in high concentration for healthy growth. Potassium is required in plants at a 1:4 ratio with nitrogen (Bennett, 1993). Potassium toxicity is rarely seen (Bennett, 1993). Excess K in the soil, rather than leading to potassium toxicity is usually seen in the form of calcium or magnesium deficiency within the plant. Because K is a necessary element, and it is rarely toxic no guidelines have been established for its concentration in irrigation water (Salgot *et al.*, 2006).

1. Surfactants

Surfactants (surface active agents) are the major chemicals present in soaps and detergents (Kloepper-Sams et al., 1996) and are organic molecules that consist of a hydrophobic and hydrophyllic groups (Wiel-Shafran et al., 2006). Because most surfactants are used in washing the majority of these chemicals end up in effluent, and in most treatment plants they are not completely removed from the water (Toze, 2006). Surfactants are one of the most abundant organic chemicals in effluent (Wiel-Shafran *et al.*, 2006).

The surfactant molecules tend to accumulate at the solid: liquid and air: liquid interfaces which increases the distance between water molecules (Weber, Khan & Hollender, 2006). The increased distance between the water molecules reduces the capillary action of the soil, and this reduces a soils water holding capacity (Salgot et al., 2006). Although most surfactants in use today are biodegradable (Wiel-Shafran et al., 2006) their accumulation in the soil can still be a problem due to binding with soils increasing the time for the chemicals to break-down (Wiel-Shafran et al., 2006).

In a recent study (Wiel-Shafran et al., 2006) surfactants were found in influent (sewage entering a plant) at an average rate of 5.4ppm, with fluctuations between 0 and 10ppm. These results are similar to the results of a previous study (Dehenau, Mathijs & Hopping, 1986) who found the rates of surfactants to be 0-4.8ppm. While wastewater treatment plants (WWTP) remove a large proportion of surfactants from the water there are still some remaining (Dehenau et al., 1986). In the effluent leaving WWTP's surfactants are not at concentrations capable of causing direct damage to the crops (>250ppm) (Garland et al., 2004; Wiel-Shafran et al., 2006). Surfactants in effluent are a concern because of their ability to alter a soils capacity to retain water. To prevent damage to the soil total surfactants in the water should not exceed 0.5ppm (Salgot et al., 2006). Concentration limits for surfactants in soils has not been determined as the effect is variable depending on soil properties (Salgot et al., 2006).

i.Pharmaceutically active compounds

There are a large number of pharmaceutically active compounds (PhAC's) in use today (Toze, 2006). Many of the PhAC's enter sewage systems relatively unaltered (Kanda et al., 2003) however most WWTP are capable of removing a large proportion of the PhAC's that are present in the effluent before it leaves the plant (Brun et al., 2006; Toze, 2006). Studies conducted have shown that, although plants are affected by a number of PhAC's present after effluent has been treated, the concentrations required are in excess of 1ppm, whereas the concentrations of the most common PhAC's, leaving a WWTP are found at the nanogram/litre level (parts per trillion) (Brun *et al.*, 2006; Yu, Bouwer & Coelhan, 2006). Because of the low concentration that PhAC's in treated effluent its affect on crops has been largely considered inconsequential (Brun *et al.*, 2006; Toze, 2006).

One groups of PhAC's which need to be considered as having potentially delitereous affects on crop production is the antiseptic (antibiotic) group of chemicals. Although these chemical will not directly affect a plants growth and development they are capable of altering the balance of microbes in the soil, and specifically reducing the level of vesicular-arbuscular mychorriza (VAM) which are essential for plant growth.

b. Anticeptics

90% of antibiotics are excreted from the human body unchanged (Watkinson, Murby & Costanzo, 2007) and are not completely removed by WWTP's are (Yang, Cha & Carlson, 2005). While antibiotic compounds do not directly affect plant growth, they can contribute to growth problems by limiting the growth of the symbiotic vesicular-arbuscular mycorrhiza (VAM) which assist plants in extracting nutrients from the soil (Azaizeh et al., 1995).

The major antibiotics that been identified in treated effluent, and their median concentations, are ciprofloxacin ($0.5\mu g/L^{-1}$), sulphamethoxazole ($0.27\mu g/L^{-1}$), triclosan ($.25\mu g/L^{-1}$), Chlorophene ($0.2\mu g/L^{-1}$), lincomycin ($0.05\mu g/L^{-1}$) and trimethoprim ($0.05\mu g/L^{-1}$) (Watkinson et al., 2007). Other antibiotics have also been found in effluent include naladixic acid, enrofloxacin and roxithromycin (Watkinson et al., 2007; Yu et al., 2006). Concerns over these, and other antibiotic compounds is relatively recent, as with many other PhAC's, and as such no specific guidelines have been determined (Ammary, 2007). Studies have shown that PhAC's generally are dangerous to plants above 1ppm concentrations

A value of 0.001mg/L has been proposed as the MAC for PhAC's in treated wastewater (Salgot *et al.*, 2006). Due to the high cost of monitoring it is unlike that government bodies would undertake regular analysis of the effluent (Salgot *et al.*, 2006). The measurement of antiseptic compounds from effluent in the soil is difficult due to natural antibiotic agents excreted by plants. The common method for determining if there is an adverse affect is to determine the microbial activity of the soil.

V. CONCLUSION

As the Earth's population continues to grow newer alternate sources of water will continue to be exploited. Agriculture as the primary consumer of water is continuing to look for new, cheap and readily available sources of water. Treated effluent is seen by many as a safe and ready alternative to assist alleviate the demand on limited freshwater supplies in many countries.

The use of effluent is quickly being taken up, in many areas without considering the long term implications of this water source. This review has identified a considerable number of chemicals present in treated effluent which are capable of affecting the long term sustainability of the agricultural industry.

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The Chemical Properties of Treated Effluent and its Effect on Cotton Germination: A Case Study on Federation Farm

Abstract

Federation Farm near the township of Narrabri in Northern New South Wales is a property that uses treated effluent to irrigate its crops. The farm primarily grows a cotton rotation, with wheat and legume crops. Recent observations have been made concerning delays in germination times by scientists involved in the operations on Federation Farm. This report has examined these observations with respect to the treated effluent used to irrigate Federation Farm. It aimed to determine if the effluent was directly responsible for the germination delays, and what chemical risk factors are present in the effluent that could cause the observed germination delay. The experiment conducted a germination trial using the cotton variety Sicot 71BR seeds from the CSIRO as well as using analytical techniques to examine the effluent for barium, calcium, copper, iron, magnesium, manganese, nitrate, orthophosphate, potassium, sodium, strontium and zinc.

The results of the germination trial indicated that the treated effluent did cause statistically significant delays in the germination time of the cotton seed. The delays in germination of the seeds germinated were in comparison to the water from the Namoi River, the source of irrigation water for other farms in the region. The chemical analysis of the water showed elevated levels of calcium sodium, strontium and zinc in comparison to the Namoi River.

While a number of elements were found at elevated levels in the effluent, only sodium and iron which were found at levels of 200 mg L^{-1} and 0.4 mg L^{-1} respectively were at levels that are considered hazardous. These levels may not only be affecting the germination of the seed, but also could have detrimental affects on the long term sustainability of Federation Farm. A full sample set collected on the 24th of February 2007 from the irrigation canal on Federation Farm also showed significantly lower rates of germination than all other replicates, however this was not seen repeated in other samples collected from within the farms dam, this indicates that a substance, undetected by this analysis such as a herbicide, may have been added to the canal prior to sampling.

At the conclusion of the study it was determined that the treated effluent used to irrigate Federation Farm was responsible for delays in germination on the property. While the germination analysis did see delays they were not as significant as those on the property, indicating that there might be other factors involved.

Keywords: Treated effluent, irrigation, wastewater, recycled, cotton, sodicity, germination.

Introduction

Water is one of the most important resources on Earth. Its quality is environmentally and economically important. Globally there are a large number of different users vying for this limited resource. Current global supplies of freshwater are estimated at 7000 m^3 per person per year, well above the general consumption rate of 2500 -2000 m^3 per person per year, and well in excess of the 1000 m^3 per person per year that is defined by the U.N. as the level for water scarcity (UNEP, 2002).

Although current global freshwater supplies are adequate, water scarcity, and more commonly water stress (1700 – 1000 m^3/person/year) can already be seen in a number of regions across the globe. Water stress is a result of the uneven distribution of both the human population (Figure 1) and rainfall. Water is economically important to a country as it is not only used for domestic purposes, but also in mining, textiles, manufacturing and agricultural enterprises (Qadir *et al.* 2003).

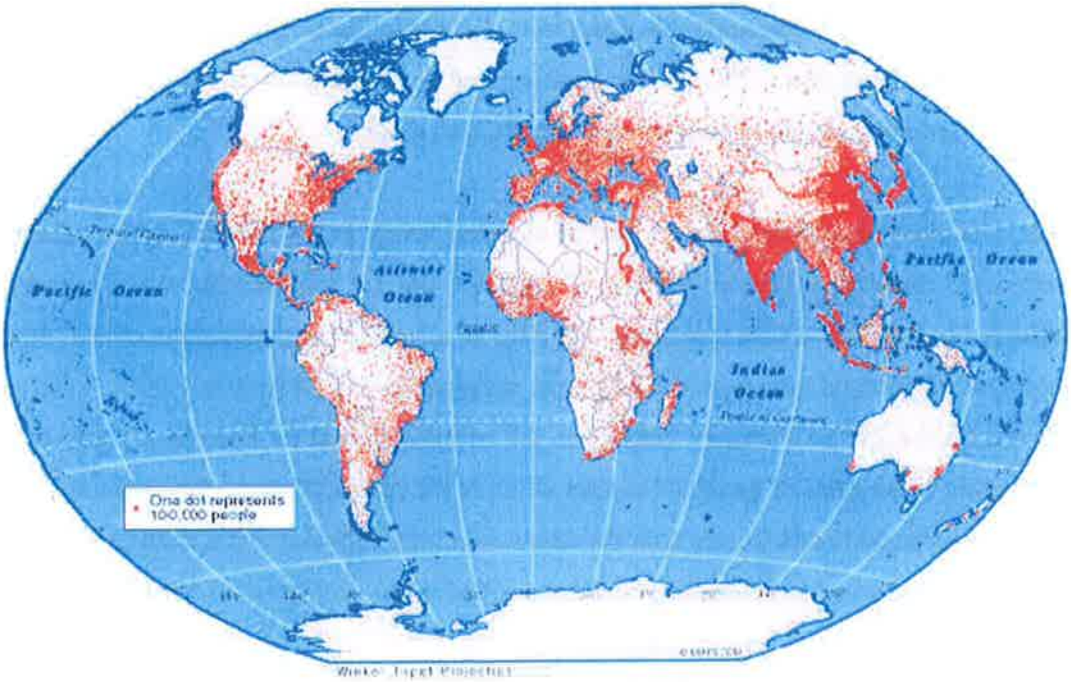
World Population Distribution, 1998

Figure 1. Global Population Distributions (Countywatch 2007)

In recent years as population growth has continued to increase and fears of reduced rainfall due to global warming are considered, a number of economists have turned their attention to modelling supply and demand for water. These models look at the future availability of water, in relation to the supply and cost of the resource across the different industries (Berrittella *et al.* 2007).

The models looking at the cost/production relations show agricultural enterprises will be the most hit by water shortages. This is the result of lower dollar returns per ML expended that is seen in agricultural systems in comparison with other industries such as mining and manufacturing (Hellegers and Perry 2006). The lower returns per ML will see agriculture, in the short – medium term, becoming non-competitive in the emerging water market and unable to pay the increasing cost of water. While supply and demand in the long term will turn agriculture back into a profitable industry as demand of food and fibres outstrips supply, in the medium to short term it will loose ground to other industries, unable to remain profitable with high water costs (Berrittella, 2007).

Water in Australia is important to a number of sectors, domestic, mining, agriculture and manufacturing. As the decreasing availability of water increases in countries such as Australia, agriculture struggles to gain enough water to allow for a sustainable level of production.

Currently 75% of water extracted from the environment around the world is done so for agricultural use (UNEP, 2002). It is this resource that researchers believe will start to diminish as quality water availability decreases (Berrittella, 2007). As more demand is placed on the resource it is likely that the less intensive agriculture sectors (non-hydroponic) will begin to suffer water shortages because of the inability to afford the price increases that will occur as a result of supply and demand (Berrittella, 2007).

In global agriculture production irrigation plays an extremely significant role, both in terms of financial benefits to farmers and food production. While irrigated land equates to only 15% of the worlds cultivated cropland it produce about 50% of the worlds agricultural produce, including food crops, such as rice and maize, and fibre crops such as cotton (UNEP 2002).

While globally irrigation is important to food supplies, it is also of economic importance to Australia with the irrigation industry in 2004-2005 worth $9.1 billion. The Australian cotton crop was grown on approximately 300 000 ha, with 81% of the crop irrigated in the 2004-2005 season (Treewin 2005a) was valued at approximately $1 billion annually (Treewin 2005b). The Australian cotton crop represents almost 12% of the total value of the Australian irrigation industry.

Commonly water for irrigation in Australia is obtained from three sources (Anderson 1996); surface water (such as river systems), groundwater (aquifers) and rainfall/rain fed dams such as those on farms that harvest the water that falls on the property and store it for later use. In Australia the majority of water for irrigated farming comes from river systems, with limitations placed on the percentage of rainfall that a farmer may harvest from his property. Australian rivers generally are of high quality, with low salt concentrations (Anderson 1996). Within Australia another major source of water is that obtained from bores that draw water up from underground aquifers /artesian basins. Water from underground sources generally contains higher levels of cations than river water, making it less suitable for irrigation purposes.

In regions such as Australia, the Middle East and sections of South America water shortages are already impacting the availability of this resource for agricultural production (Wade Miller 2006). In recent years two main alternate sources of water have been put forward to augment its supply in these regions. The alternate sources are desalination and treated effluent/recycled water.

Desalination plants that remove salt from seawater have been constructed in a number of countries, and their use is gaining popularity (Wade Miller 2006). Desalinated water is seen as a suitable source of water for domestic use and some industries, however its cost, of which 50 – 75% is represented by energy requirements, is put at approximately $US100 per ML (Priel *et al.* 2006). The cost of desalination makes it unsuitable as a source of water for irrigation, which requires significant quantities of water for relatively low returns. In many cases fields will require over 4 ML per ha per season and in crops such as cotton water requirements are about 7ML per ha per season. At the current cost of producing desalinated water this would force farmers to pay more than $US700 per ha per season, which would force food and fibre prices to unsustainable levels.

In contrast to desalination, which is seen by domestic users as the more palatable alternative, effluent, once treated is significantly cheaper per megalitre. Effluent can be recycled in two forms, the first is known as treated effluent, where the effluent undergoes a binary or tertiary treatment process. The second form of recycled effluent in known as recycled water, and involves further processing of the effluent by reverse osmosis and other methods. Compared to recycled water treated effluent is relatively cheap and quick to produce. Treated effluent undergoes some treatment processes; removing the solid particles, a portion of the nutrients and disinfecting the water, for example via UV light however chemical treatments are also used. The cost difference is significant, with treated effluent only costing 20% of what desalinated water costs (Priel *et al.* 2006) making it a more economically viably solution.

Using treated effluent to irrigate crops has environmental as well as economic advantages. The use of treated effluent in irrigation, rather than the release of the effluent into river systems, reduces the impact that the effluent will have on the natural ecosystems. The release of effluent into the environment can lead to significant problems, primarily increasing the nutrient loading of river systems (Donnelly *et al.* 1999). The increased nutrient levels in the river systems can lead to a rapid development of algal blooms.

In Australia in the early 1990's one of the major river systems, the Murray-Darling River, was experiencing a number of large (often over 1 km) algal blooms, including toxic cyanobacteria (commonly known as blue-green algae). The cause of these blooms was examined, and found to be due to the levels of nutrients within the river systems, particularly the phosphorus and nitrogen levels (Donnelly *et al.* 1999). The report provided to the NSW government indicated that the increased nutrient levels within the waters of the river system were primarily from waste-water treatment plants (WWTP) along the river, run by local councils. Narrabri council, located in Northern NSW, was identified as a significant contributor to the nutrient problems in the river systems.

In 1995 in response to restrictions and taxes imposed by the state government on all councils, Narrabri shire council began work on Federation Farm. Federation Farm is a 303 ha site located approximately 14 km northwest of the Narrabri township. The farm has been set up as a combined irrigation and dryland cropping enterprise. The 130 ha of irrigated land on the property use treated effluent from the Narrabri WWTP to irrigate the crops. The farm began operations in the year 2000, and grows a cotton rotation, which includes wheat, a legume crop such as chick peas and a fallow period.

The use of the treated effluent on the property has allowed the council to halt the release of the treated effluent into the river systems, thus improving the quality of the river system, and removing the need to pay extra costs that would have been imposed by the government for the release of effluent into the river. Using treated effluent to irrigate crops is seen as an extremely efficient way to improve river health, and maximise the use of the nutrients within the water. While treated effluent does contain nutrients that are essential for plant development, such as nitrogen, phosphorus and potassium in significant quantities (Al-A'ama and Nakhla 1995; Anderson 1996; Rutkowski *et al.* 2007), the effluent may also contain micronutrients and heavy metals in concentrations capable of causing problems to the growth and development of the crops (Hermle *et al.* 2006; Salgot *et al.* 2006).

In recent seasons scientists involved in operations on Federation Farm have noted an increased time to germination as compared to other properties in the region. The reason for this delayed germination is not known, and has been speculated that the treated effluent used to irrigate the crops may be directly linked to the delays. This paper has been conducted under the assumption that the germination delays experienced on Federation Farm are directly related to the contaminants found in the treated effluent used as irrigation water on the property.

This experiment aims to determine if the water is directly responsible for the delays in germination on the Federation Farm, using both chemical analysis of the waters, and germination trials.

Materials and Methods

Materials

All solutions were prepared using ultra pure water from a Barnstead Nanopure II purifier (referred to as NP water)

The following solutions were prepared for use in determination of orthophosphate and nitrate using flow injection analysis:

Orthophosphate

- Ammonium molybdate - Ammonium molybdite (5.00 g) was dissolved in conc. HCl (17.5 mL)and then diluted in a 500 mL volumetric flask with NP water

- Stannous chloride - Hydrazinium sulphate (1.00 g) and AR grade stannous chloride (0.100 g) dissolved in conc. H_2SO_4 (14 mL) and then diluted with NP water in a 500 mL volumetric flask

- Orthophosphate stock solution - Potassium dihydrogen phosphate (0.4393 g) was dissolved in 1000 mL of NP water to produce a 100 mg PO_4^- per L stock solution.

Nitrate

- Ammonium chloride buffer pH 8.5 - Ammonium chloride (85 g) was dissolved in NP water (500 mL), solution was left to reach room temperature and then ammonia was added (approximately 12 mL) to reach a pH of 8.5. Solution was mixed and diluted to 1000 mL with NP water.

- Sulphanilamide reagent - Sulphanilamide (5.00 g) was dissolved in NP water (250 mL). Concentrated HCl (25 mL) was then added and the solution carefully mixed. Solution was then diluted to 500 mL with NP water.

- NED reagent - N-(1-napthyl)-ethylene diamine dihydrochloride (0.500 g) was dissolved in NP water (250 mL). After dilution the solution was made up to 500 mL with NP water.

- Nitrate stock solution - Sodium nitrate (6.068 g) was dissolved in NP water to 1000 mL, to equal 1mg NO_3^- per mL

The following solutions were prepared for use in atomic absorbance analyses:

- 0.1M EDTA - Disodium salt dehydrate (EDTA) (37.22 g) was dissolved in NP water (1000 mL).

- 0.1M sodium chloride - NaCl (5.845 g) was dissolved in NP water (1000 mL).

Stock solutions of the elements analysed using atomic absorbance spectroscopy were obtained commercially or prepared using AR grade reagents.

Method

Location and Sampling

As the experiment was conducted on Federation Farm all sampling points were chosen with respect to this property and its water source. For the experiments there were six different sampling locations, located in different areas, five were related to the WWTP and Federation Farm water supply, and the sixth water source was from the Namoi River, where the majority of farms in the region collect their irrigation water.

Sites

1. Namoi River

Figure 2. Namoi River sampling location

The sampling point was selected due to the relatively constant flow through this section of the river, and the ease of access, being on public, rather than private land. The samples were collected to provide a base point for comparison for the water used on Federation Farm.

2. Town water

The second sampling point was the bore that supplies the Narrabri town water. This sampling point will enable an analysis of the water used by the town. This sampling point will allow the study to determine if the germination is affected by the bore water, or if it is affected by the substances added by the town.

3. Wastewater Treatment Plant

Figure 3. WWTP, Narrabri

Sampling point three was the endpoint of the Narrabri WWTP, after all treatments, including ultraviolet disinfection has been completed.

4. Federation Farm dam inlet

Figure 4. Federation Farm dam inlet

Sampling point four is the point at which the treated effluent enters the dam on the property. This sampling point was at the exit to the pipe. This point allows for a comparison of the effluent at Federation Farm in relation to the WWTP, to determine if the approximately 10Km transport between the two locations is contributing to the contamination of the water supply on Federation Farm.

5. Federation Farm dam

Figure 5. *Federation Farm dam.*

Sampling point five was from a randomly selected point within Federation Farm dam. The water storage site on Federation Farm is a two cell dam, with a maximum holding capacity of 450ML, This sampling point was selected to provide information on the water once it has been stored, to determine if dilutions are occurring due to rainfall, and the quality of water applied to crops on Federation Farm.

6. Irrigation Canal

Figure 6. Irrigation canal on Federation Farm

The final sampling site selected was the irrigation canal as the water was passing to the fields. This final point allowed an accurate measure of the exact quality of the water that was applied to the crops. The water in the canal was pumped directly from the dam into the canal, and was then passed via piping into the field farrows.

Sampling method

Sampling was conducted at two different time periods. The first sample set was taken during summer (24th – 25th of February), and a second sample set was collected during winter (16th of July). Samples were collected in acid washed 1L amber borosilicate bottles. At each sampling site and sampling time, three replicates were collected, giving a total of 36 samples. The replication in the sampling was conducted in order to remove any discrepancies that may occur due to the collection of a single sample. Sampling across time (the two seasons) was conducted to try and determine if there is any difference in the substances present in the water during different seasons.

Preliminary analysis

Field pH and electrical conductivity (EC) were analysed at each sampling site and sampling time.

Qualitative analysis

Prior to the water samples being quantitatively analysed, a preliminary qualitative inductively coupled plasma analysis was conducted on six of the samples. The samples analysed were the Namoi River, Town water and WWTP from the summer set, and the WWTP, town water and Namoi River from the winter samples. This preliminary analysis allowed for the determination of the major elements present within the water sources. We would like to acknowledge the assistance of Mr Tom Savage of the School of Geosciences at the University of Sydney for carrying out the inductively coupled plasma analyses.

Quantitative Analysis

Following the preliminary inductively coupled plasma analyses more extensive quantitative analyses were conducted on the elements that were identified as being present. Analyses were conducted using two different systems, flow injection analyses and atomic absorbance spectroscopy (AAS). Each of the identified elements was analysed using the most suitable method.

Flow injection analysis (FIA)

Nitrate and orthophosphate were analysed using a FOSS FIAstar 5000 Analyser combined with a 5027 autosampler and SoFIA software. Water samples were analysed without further treatment or dilution.

Orthophosphate

For the analysis of orthophosphate via FIA the appropriate analytical cassette was selected and inserted into the instrument and the filters were set to 720 nm for the measuring wavelength and 1000 nm for the reference wavelength. Two reagents were produced, ammonium molybdate and stannous chloride. 1 mL of the stock solution was then diluted to 100 mL with NP water to create an interim standard of 1 mg PO_4^-/L^{-1}. The Interim standard was then used to create a standard range, to produce a standard curve. The range consisted of 0, 50, 100, 200 and 400 µg PO_4^-/L^{-1}. This standard curve was then used by the SoFIA software to analyse the results obtained from the samples and determine the concentration of orthophosphate within the samples.

Nitrate

For the analysis of nitrate via FIA the appropriate cassette was selected and placed into the instrument and filters set to 540 and 720 nm for analysis and reference wavelengths respectively.

The three reagents, ammonium chloride (pH 8.5), sulphanilamide and NED were placed in the FIAstar for the analysis. Using the stock solution a series of standards were created to produce a standard curve, the range consisted of 0, 5, 10, 20, 50 and 100 mg/L.

Atomic Absorbance Spectroscopy (AAS)

The analysis of barium, calcium, copper, iron, magnesium, manganese, potassium, sodium, strontium and zinc were conducted using flame AAS. To conduct these analyses a Varian SpectroAAS FS instrument was used. The standard curves created varied depending on two factors, the range of detection by the Varian SpectroAAS and the expected concentrations in the samples.

Barium

Barium was analysed using a nitrous oxide/acetylene flame. The standards for barium were created by taking 10 mL of the barium stock solution and diluting to 100 mL in a volumetric flask with NP water to create a 100 µg Ba/mL standard. Using this standard solution a standard curve of 0, 5, 10, 15, 20, 25 mg Ba/mL was developed. The standard curve (Figure A.1) was then used to determine the concentration of barium present at the varying locations.

Calcium

Calcium was analysed using an air/acetylene flame. The calcium analysis was conducted following the method described in the Varian AAS manual. A standard curve (Figure A.2) was developed, using the concentrations 0, 2, 4, 6, 8 and 10 µg Ca/mL and this was used to determine the concentration of calcium within the samples collected. Prior to their analysis samples were diluted in a 1:5 mixture with NP water.

Copper

Copper was analysed using an air/acetylene flame. The copper analysis was conducted following the method described in the Varian AAS manual. A standard curve (FigureA.3) was developed using the points 0, 2, 4, 6, 8, 10 µg Cu/mL, and this was used to determine the concentration of copper within the samples collected. No dilution of the samples was necessary prior to analysis.

Iron

Iron was analysed in an air/acetylene flame. The iron analysis was conducted following the method described in the Varian AAS manual. A standard curve (Figure A.4) was developed using the concentrations 0, 2, 4, 6, 8 and 10 µg Fe/mL, and this was used to determine the concentration of iron within the samples collected. No dilution of the samples was necessary prior to analysis.

Magnesium

Magnesium was analysed using an air/acetylene flame. The magnesium analysis was conducted following the method described in the Varian AAS manual. A standard curve (Figure A.5) was developed using the points 0, 2.5, 5.0, 7.5, 10.0, 12.5 µg Mg/mL, and this was used to determine the concentration of magnesium within the samples collected. Prior to analysis the samples were prepared by taking 0.3 mL of the aliquot, adding 5 mL of 0.1M EDTA to each sample and then diluting to 25 mL in a volumetric flask with NP water.

Manganese

Manganese was analysed in an air/acetylene flame. The manganese analysis was conducted following the method described in the Varian AAS manual. A standard curve (Figure A.6) was developed using the concentrations 0. 0.8, 1.6, 2.4, 3.2, 4.0 µg Mn/mL, and this was used to determine the concentration of manganese within the samples collected. No dilution of the samples was conducted prior to the analysis.

Potassium

Potassium was analysed using an air/acetylene flame. The potassium analysis was conducted following the method described in the Varian AAS manual. A standard curve (Figure A.7) was developed using the concentrations 0, 0.2, 0.4, 0.6, 0.8 and 1.0 µg K/mL, and this was used to determine the concentration of potassium within the samples collected. Prior to analysis the samples were prepared by taking 1.0 mL of the aliquot, adding 2.0 mL of 0.1M NaCl to each sample and then diluting to 25 mL in a volumetric flask with NP water.

Sodium

Sodium was analysed using an air/acetylene flame. The sodium analysis was conducted following the method described in the Varian AAS manual. All standards and samples for sodium were prepared in sterilised plastic screw cap tubes to prevent contamination. The standard curve was developed using the concentrations 0, 0.1, 0.2, 0.3, 0.4 and 0.5 µg Na/mL (Figure A.8) to determine the sodium concentrations within the collected samples. Prior to analysis the samples were prepared by diluting 0.1 mL of sample to a final volume of 20 mL with NP water.

Strontium

Strontium was analysed using a nitrous oxide/acetylene flame. The strontium analysis was conducted using the following procedure; a standard solution of 100 μg/mL was produced by diluting 10mL of the stock solution to 100mL. The standard solution was used to create a standard curve using the concentrations 0, 2, 4, 6, 8 and 10 μg Sr/mL (Figure A.9), which was then used to determine the unknown strontium concentrations within the samples. No dilution of the samples was necessary prior to their analysis.

Zinc

Zinc was analysed using an air/acetylene flame. The zinc analysis was conducted following the method described in the Varian AAS manual. A standard curve (Figure A.10) was developed using the point 0, 0.4, 0.8, 1.2, 1.6 and 2.0 μg Zn/mL and this was used to determine the concentration of zinc within the samples collected. No dilution prior to analysis was necessary.

Germination trial

A germination trial was conducted to determine if the water was having a direct impact on the time to germination for the cotton crops on Federation Farm. The trial was conducted using the variety Sicot 71BR, developed by the CSIRO and distributed by Cotton Seed Distributors®, the same variety used in the previous season on the property. The experiment was set up as a completely randomised design, with two factors, test site and season. The trial was conducted using an incubation chamber with a constant temperature of 25°C.

Each site had three replicates created; one replication consisted of 100 Sicot 71BR seeds in a sterile plastic tray 210w x 310L x 20d (mm). Inside the tray a sheet of filter was placed (200 x 300mm) and then moistened with approximately 200 mL of the test sample. The seeds were then randomly placed on the filter paper, a second sheet of filter paper was then placed over the top to cover the samples and this was then moistened with a further 200 mL of the sample. The tray was then covered with a fitted lid to prevent desiccation of the filter paper. This process was repeated three times for each of the 12 samples (size test sites times two seasons) and a further two control groups were created (two groups times three trays) using NP water as the control agent.

After the trays were prepared they were randomly placed in the germination chamber and left for 18 hours. At the 18th hour the number of germinated seeds was counted in each tray. The trays were then placed back in the chamber, and the number of germinated seeds counted every two hours until all had stabilised.

Statistical Analysis

All analyses were conducted in Genstat® version 10. The results from the FIA and AAS were analysed in a general analysis of variance, with a treatment structure of season times test site. The values obtained were then analysed in respect to the difference in the individual experimental unit means against the least significant difference value.

The germination analysis was conducted as a linear mixed model. To enable the experiment to be conducted the data was stacked in the following way:

Table 1. Sample of stacked data for germination analysis

Location	Season	T/C	Time	Response	Unit
Control	NP	C	1	1	1
Control	NP	C	1	1	2
Control	NP	C	1	3	3
River	summer	T	1	0	4
River	summer	T	1	0	5
River	summer	T	1	0	6
Town	summer	T	1	1	7

The Response represented the number of seeds to have germinated, the T/C is a factor determining whether the results are a control or treatment, time was a factor that stated which of the 18 time samples this set came from, and the Unit number represents each individual replication at each time point, so that the same tray was analysed as 1, 2, 3 etc in each time period.

After the data was stacked the results were analysed using a linear mixed model, run as an AR1 with the following parameters:

Y-Variate = Response
Fixed model = (T_C / [Location x Season]) x Time
Random model = Unit . Time

This model allowed for a comparison of the germination results at each time point between both the seasons and the test sites. The results obtained were then analysed, comparing the difference in means to the LSD to determine which treatments were significantly different from the others.

Results

Electrical conductivity and pH

The pH and EC were measured at the six different sites both during the summer and winter sampling. The results collected (Figure 7) indicate no significant difference between the seasons at the varying locations for either the water pH or EC.

The river had a neutral pH of 7.3, in comparison to the slightly alkaline pH (8.5) of the treated effluent used for irrigation on Federation Farm. While pH does not exhibit any significant changes, the EC of the waters is significantly greater on Federation Farm than in the Namoi River. The EC of the treated effluent, at the point of application to the field remains relatively stable from the point at which it enters the farm, and is approximately twice the level found in the Namoi River.

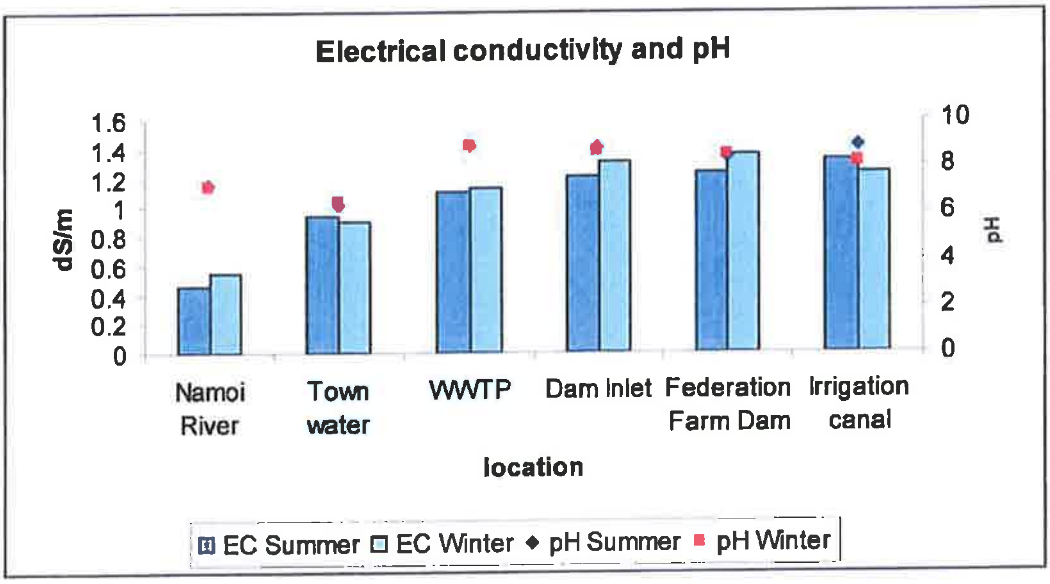

Figure 7. *Field conductivity and pH*

ICP qualitative analysis

The inductively coupled plasma analysis indicated that 12 elements were present within the water samples tested (Table 3.1). Following this preliminary analysis the quantitative analyses were conducted.

Table 2. Results from inductively coupled plasma analysis positive indicates that element was found in 1 of the 6 samples tested.

Silver	negative	**Cobalt**	negative	**Molybdenum**	negative	**Selenium**	negative
Aluminium	negative	**Chromium**	negative	**Sodium**	Positive	**silicon**	Positive
Arsenic	negative	**Copper**	Positive	**Nickel**	negative	**Tin**	negative
Gold	negative	**Iron**	Positive	**Phosphorus**	Positive	**Strontium**	Positive
Boron	negative	**Mercury**	negative	**Lead**	negative	**Tellurium**	negative
Barium	Positive	**Potassium**	Positive	**Palladium**	negative	**Titanium**	negative
Beryllium	negative	**Lanthium**	negative	**Platinum**	negative	**Vanadium**	negative
Bismuth	negative	**Lithium**	negative	**Rubidium**	negative	**Tungsten**	negative
Calcium	Positive	**Magnesium**	Positive	**Sulphur**	Positive	**Zinc**	Positive
Cadmium	negative	**Manganese**	Positive	**Antinomy**	negative	**Zirconium**	Negative

Barium

The quantitative analyses conducted on all samples indicated no barium was present in at any test site.

Calcium

The results from the calcium analysis indicate elevated levels in the treated effluent used for irrigation on Federation Farm in relation to the Namoi River. The greatest peak was in the town water, indicating that calcium levels in the effluent are related to the source of the water, rather than the towns' activities (Figure 8).

Statistically there is a significant difference (<0.05) within the samples, and a difference can be seen between the two seasons. Further analysis of the results indicates that the treated effluent used on Federation Farm contains significantly higher levels of calcium in the water than the irrigation water removed from the river. Results also indicate that the treated effluent contains significantly lower levels of calcium than the town's water supply.

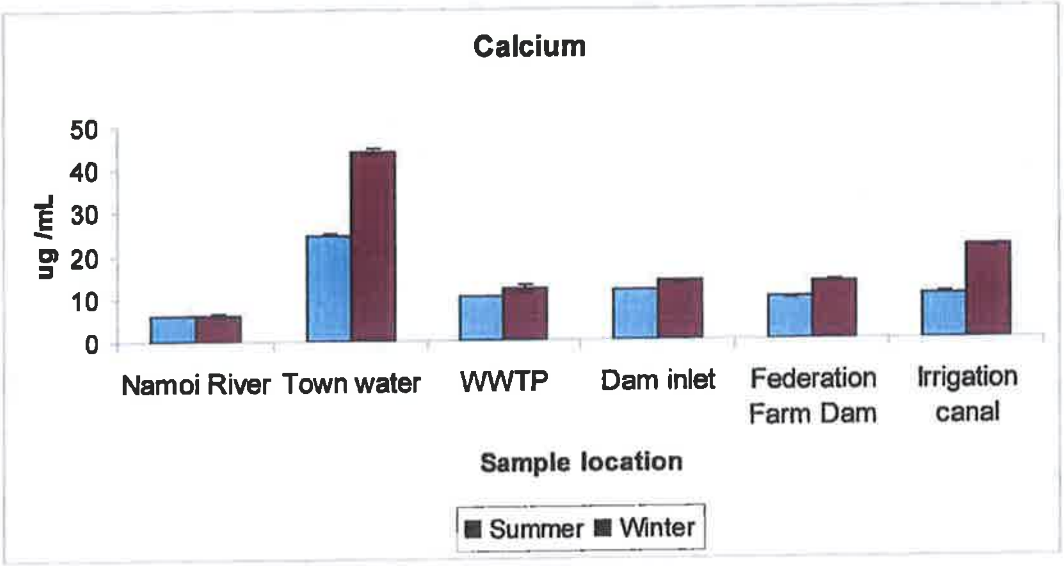

Figure 8. Calcium levels present at the test sites

Copper

There were no obvious trends for increases, or decreases in the copper level between the effluent and the Namoi River, or between the winter and summer seasons (Figure 9). Statistically however there is significant difference between the varying samples and seasons. The town water possesses significantly higher levels of copper than all other sources of water, in the summer sample. Examining the results of the statistical analysis the Namoi River possesses copper levels that are not statistically different from the irrigation water on Federation Farm.

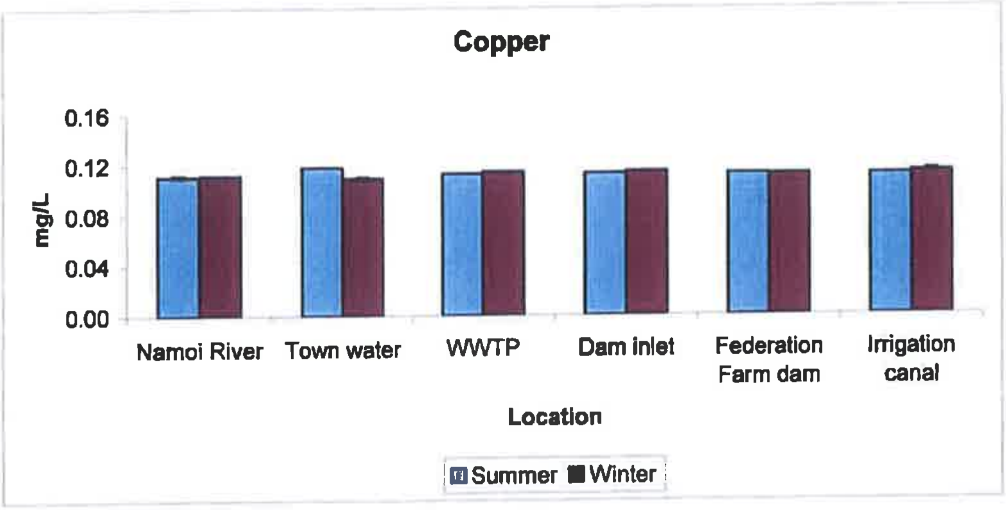

Figure 9. Copper levels present at test sites

Iron

The iron levels present in the samples was not significantly different during the summer period, however clear increases were seen during the winter period in the on farm samples (Figure 10). Statistically the iron levels in the winter samples from the dam inlet through to the irrigation canal were significantly higher than all other samples, while no statistical difference existed between the summer period samples.

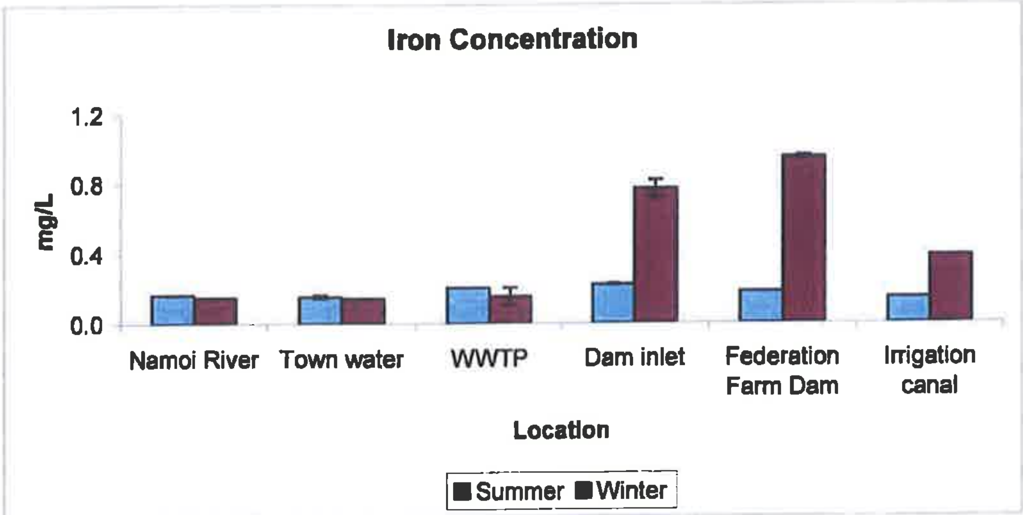

Figure 10. *Iron levels present at test sites*

Magnesium

The magnesium levels present in the river were not greatly different, during the summer months, than the water that was used for irrigation on Federation Farm, however during the winter period there was significant increase in the magnesium levels from the Namoi River (Figure 11). This increase during the winter period was visible in a number of samples. Statistically there was a significant interaction between the season and the location of the sampling in determining differences in the levels of magnesium in the water. Statistical analysis indicated that the levels of magnesium in the river during the summer months were not statistically different from the water used to irrigate Federation Farm, however during the winter sampling magnesium levels were found to be significantly higher than the samples collected from Federation Farm, and the winter samples on Federation Farm have significantly higher levels than the summer samples from the Namoi River

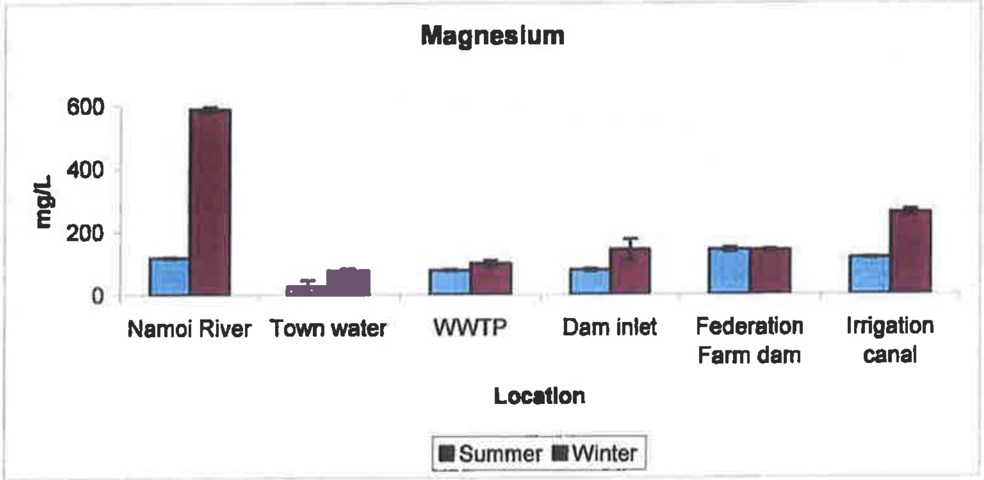

***Figure 11.** Magnesium levels present at test site*

Manganese

The manganese levels were relatively constant across all the sites, with low levels being maintained both in the Namoi River and the treated effluent that is used for irrigation (Figure 12). Statistically there is no difference between the different sample sites, however levels in the winter samples were statistically higher than the summer samples from the same test site, however they were also not statistically different from the other winter sample sites.

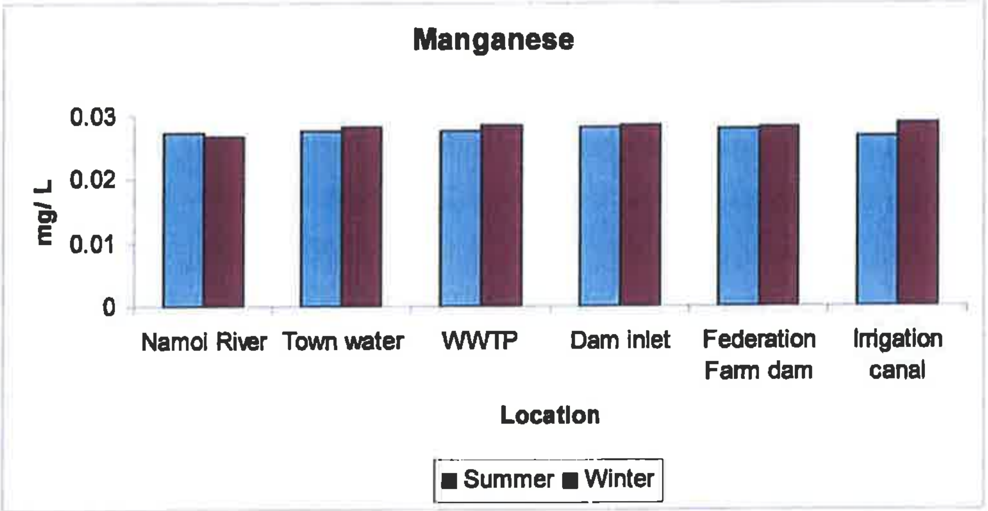

***Figure 12.** Manganese levels present at test sites*

Nitrate

The nitrate values obtained show an increased level in the treated effluent used to irrigate Federation Farm when compared with the nitrate levels in the Namoi River (Figure 13). Statistically there is a significant difference between most samples. Federation Farm dam had no statistical difference with the dam inlet however was statistically lower than the water in the Irrigation canal. Statistically no difference was seen between the Namoi River and the town water samples.

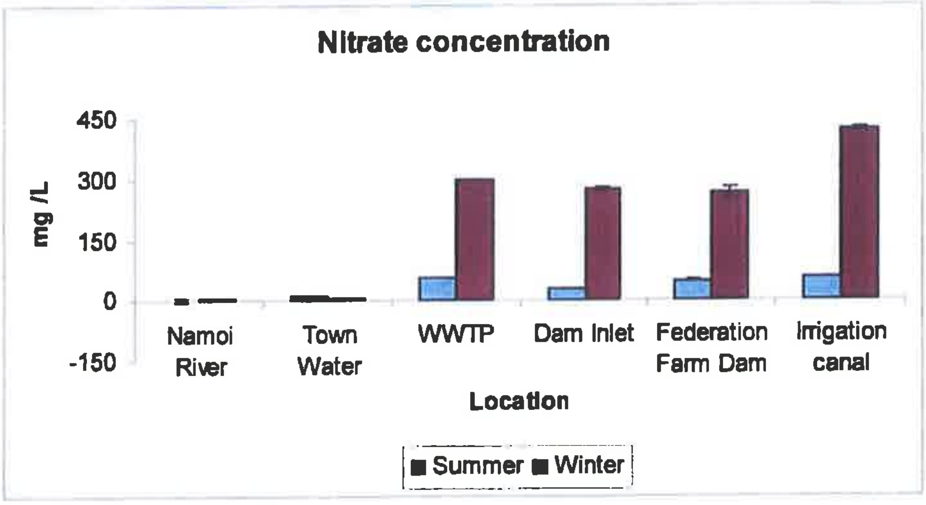

Figure 13. Nitrate levels present at test sites

Orthophosphate

Orthophosphate levels were significantly higher in the treated effluent than in the Namoi River samples (Figure 14). Analysis indicated a significant interaction between the season and the site in determining the significance of the different samples. Results indicate that the summer period had the most significant variation, with the winter months having more stable orthophosphate levels flowing from the WWTP through to the irrigation canal. The Namoi River and Town water have levels of orthophosphate that are relatively similar, with no significant difference between the in three of the four possible interactions; the only significant difference noted was between the River and the Town Water during the summer period.

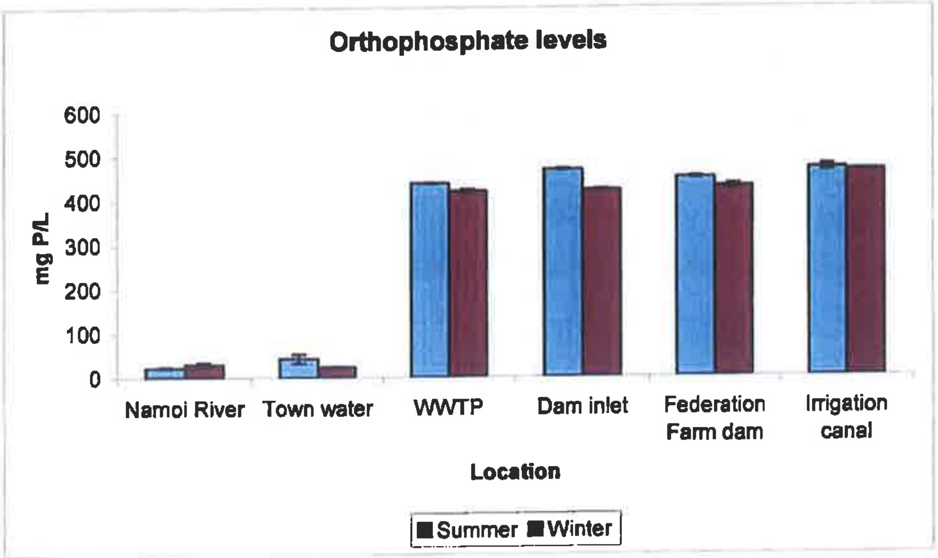

***Figure 14.* Orthophosphate levels present at test sites**

Potassium

There was significant variation between the sample locations. Statistically there was significant interaction between the test site and the season in determining the difference in potassium concentrations between the different samples. There is a constant fluctuation within the samples (Figure 15) statistically there is significant differences between all samples, except in the cases of the WWTP summer test and the irrigation canal, both in summer and winter.

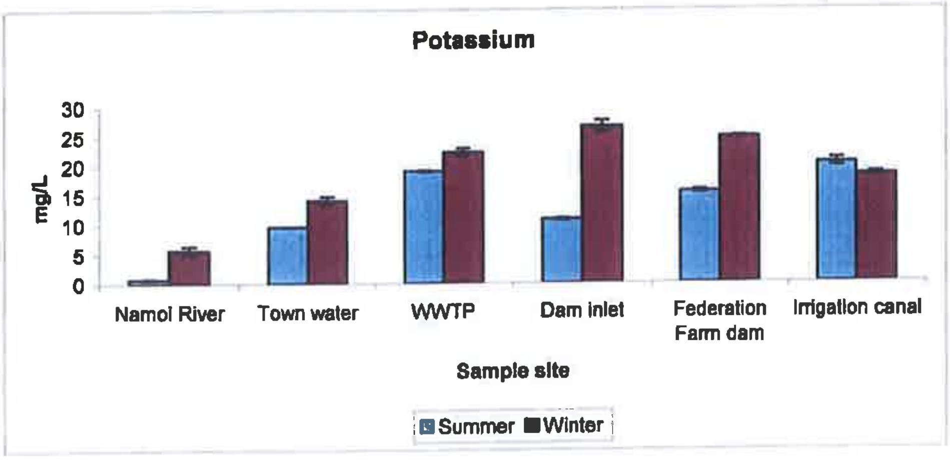

***Figure 15.* Potassium levels present at test sites**

Sodium

Statistical analysis of the sodium levels indicates a significant interaction is present between the test sites and the season, in relation to sodium levels. Statistically the winter results possessed less variation, with no difference present between the WWTP, dam inlet and Federation Farm dam. Analysis indicated that the Namoi River had less sodium in the water than the other test sites. Analysis indicated that the town water possesses levels of sodium relatively lower than the water used for irrigation on Federation Farm (Figure 16).

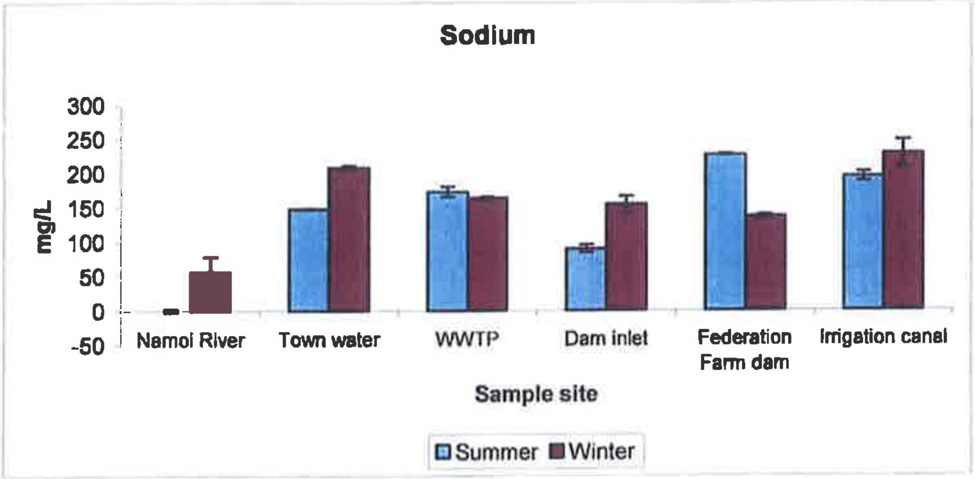

Figure 16. *Sodium levels present at test sites*

Strontium

Strontium was found at relatively low levels through all the samples (Figure 17). The highest levels of Sr were found in the irrigation canal winter samples set, however no statistical difference was present between the irrigation canal and the Namoi Rivers winter values. The statistical analysis indicates that there was a significant interaction between test site and season. The variation between samples indicates that the sample time and test site affects the levels of strontium found within the water. Levels found at the Dam inlet and Federation Farm dam test sites indicated that at these points there was no significant difference in strontium concentrations at these sites; however a significant increase in comparison to the Namoi River was noted.

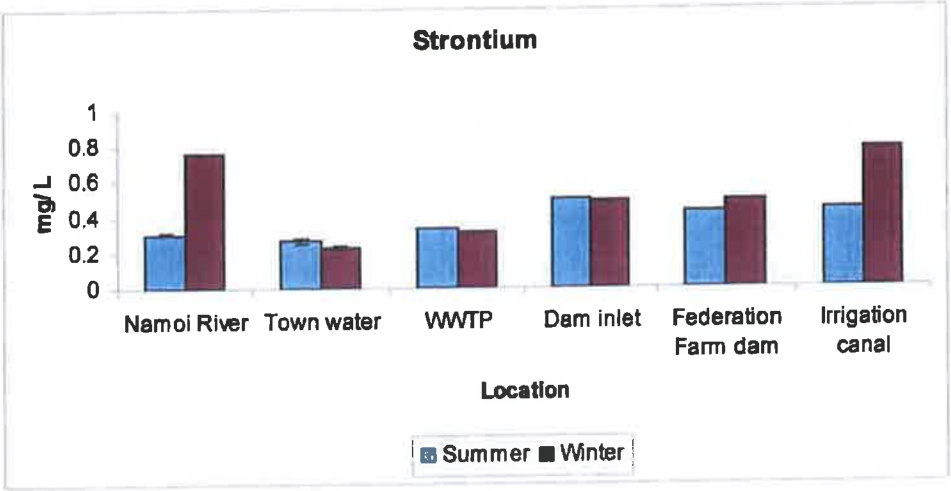

Figure 17. Strontium levels present at test sites

Zinc

There was no statistical variation with the levels of zinc found at the different test sites, with the exception of the summer values found in Federation Farm dam and the irrigation canal. All significant variation was due to the high levels of zinc found at these two locations (Figure 18).

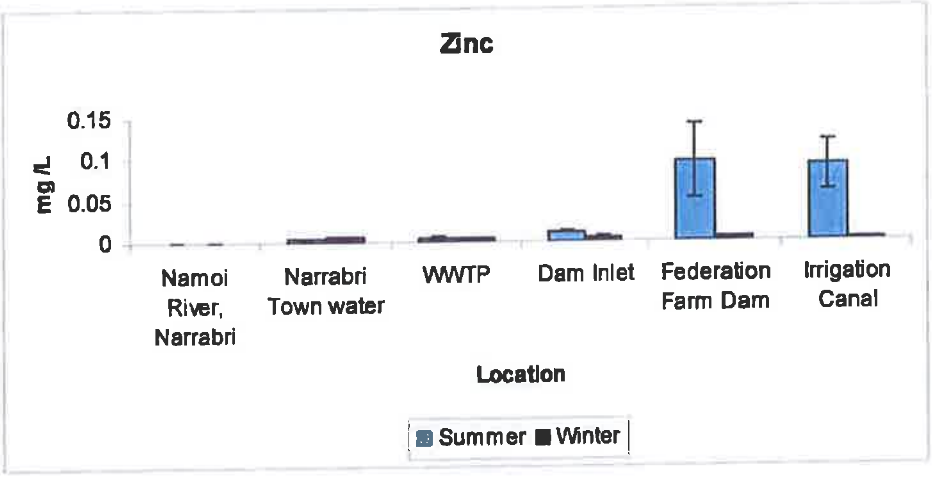

Figure 18. Zinc levels present at test sites

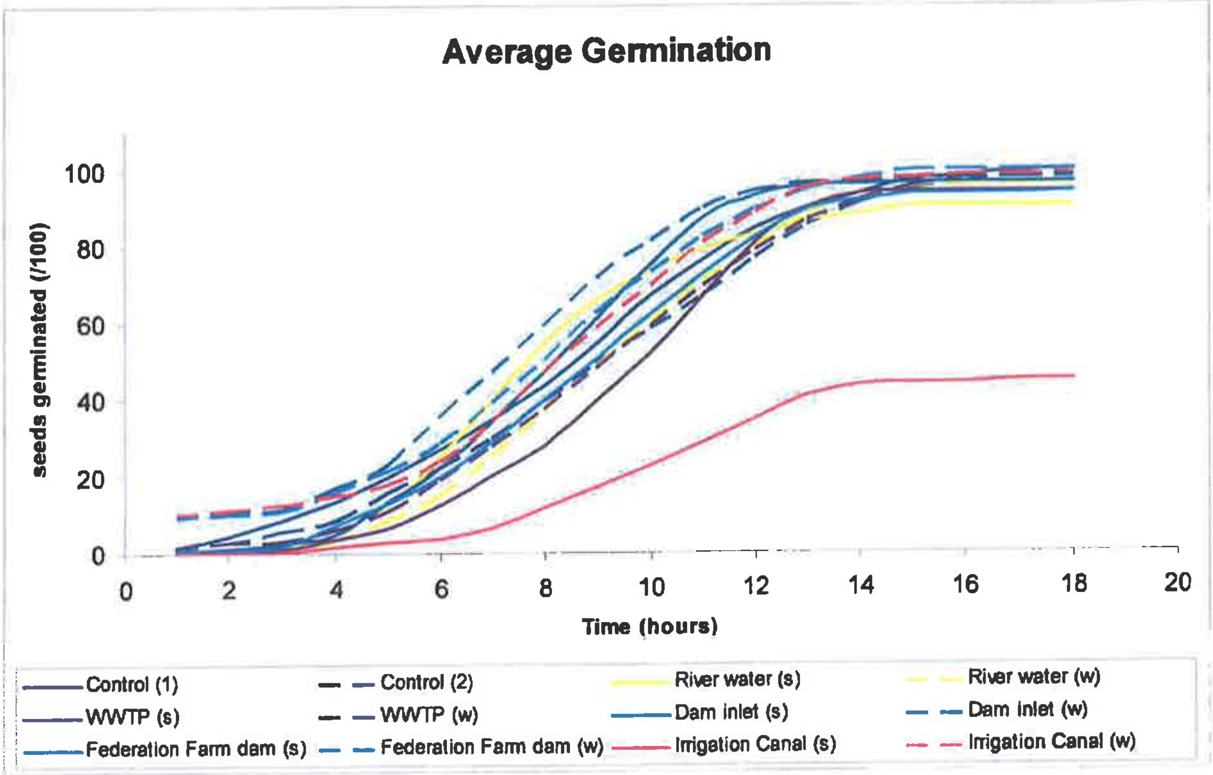

Figure 19. *Average results obtained from the germination trial. Non-averaged results can be found in appendix A.23.*

The germination results were gathered based on the number of seeds (out of 100) that had germinated at a given point in time. The final results show a fairly common trend; however statistical analysis revealed that there were significant differences between a number of the samples. The analysis also revealed a significant interaction occurring between the sample, time and season significant.

The germination values for the *"Canal (summer)"* sample were significantly lower than the other test sites from 22 hours onwards. Both summer and winter samples from the Dam inlet test site reached maximum germination at a significantly faster rate than the Namoi River and the control groups. Other noted factors were that the Namoi River reached its maximum rate of germination at an earlier time point (26 hours) than other water samples. The WWTP samples have a significantly lower germination rate through to the 46th hour when compared to the Namoi River and the Control samples.

Examination of the analytical results for the 34 hour mark, the median point for germination, in relation to pressure and temperature (Wanjura *et al.* 1973), indicated significant differences between a number of the water types times season (appendix table A.1). The *"Irrigation canal (summer)"* sample (—) possessed a significantly lower germination percentage than all other samples. Germination from the Namoi River, both the summer and winter season samples, possessed a greater rate of germination when compared to the majority of samples, including the WWTP and the irrigation canal. The WWTP, both seasons, had results that were either lower, or not significantly different from all other samples, with the exception of the *"Irrigation canal (summer)"* sample. Germination from the water samples taken from Federation Farm dam are significantly higher than the control, however the summer samples have a significantly lower germination numbers compared to the summer and winter samples from the Namoi River, and the *"Federation Farm dam (winter)"* has no significant difference to the Namoi River.

Discussion

The treated effluent used to irrigate Federation Farm has a number of chemical factors that are significantly different from the water in the Namoi River which is used as irrigation water by the majority of farms in the Narrabri region. The results obtained from the experiments indicate not only the presence of possibly toxic chemicals, but also elevated levels of nutrients, potassium, nitrate and phosphorus. The levels of these nutrients were significantly higher in the treated effluent than in the river. The toxic chemicals, such as zinc, strontium, copper and manganese were also found in the treated effluent.

The germination trial that was conducted showed a fairly common trend from all the different test sites (Figure 19./Appendix A.23). The analysis that was conducted, a Linear Mixed Model, is not a perfect design, as the model does not account for correlation between the time points. The linear mixed models works on the assumption that a seed can "un-germinate" from one time point (e.g. 20 hours) to the next (22 hours), which is clearly not possible. While linear mixed models are not an ideal model, it is the most suitable model for this form of experiment available at present.

The statistical examination of the results indicated that there was significant difference in germination rates between the different sites. The summer samples from the irrigation canal showed significantly lower rates of germination, with all three samples cutting out at below 60%. This indicated that there was an inhibitor in the water that significantly affected germination. The inhibitor was not identified in this study. The results may have been caused by a herbicide used to control weeds growing in the canal, such as glyphosate.

The germination rates for the samples from the Federation Farm dam, WWTP and irrigation canal were all lower than that of the Namoi River, indicating that the water is a factor in the germination delays that are being experienced on Federation Farm. While the germination rate is lower than that of the tests on the Namoi River samples, the delays are not as significant as what has been noted on the farm, with delays only in the order of hours, rather than days.

The results obtained from the germination trial do indicate that the chemical constituents of the treated effluent are partially responsible for the delay in germination on Federation Farm; however the results also show that the delay is not as significant as what has been noted. Analysis of the

AAS and FIA results indicated the presence of a number of chemicals in the water at levels which could be detrimental to the germination of the cotton plants.

A number of studies that have been conducted examine the benefits of using treated effluent for farm irrigation have examined the nutrients present within the effluent (Al-A'ama and Nakhla 1995; Wang *et al.* 2007). The treated effluent used on Federation Farm contains significantly elevated levels of the three macro nutrients essential to plant growth and development, these results are similar to those of other international studies (Gori *et al.* 2004; Rutkowski *et al.* 2007). Nitrate levels in the effluent are significantly higher than the levels found in the Namoi River, with values about 400 times greater. In the results there is a large discrepancy between the summer and winter samples at all locations, this is however due to the degradation of the sample due to the long storage time, which makes comparisons between the summer and winter periods difficult. The level of nitrate within the effluent (using winter results as they were tested within 10 days of sampling) was 422 μg/mL, or 422 kg/ML. An average cotton crop grown in Australia requires 7 ML water per Ha per season. If 7 ML was to be applied to the crop then each season 2.95t per Ha of nitrate would be applied to the fields from the treated effluent.

Based on the amount of water applied to an average cotton crop (7 ML) the nitrate within the water supplies the crop with 695 kg per ha of N in a season An average Australian cotton crop requires ca.180 kg per ha of nitrogen in a growing season (Rochester *et al.* 2001). This indicates that the effluent provides significantly more N than required by the plants for optimal growth. In practice the farm still needs to apply N fertilisers to ensure optimal yields, this would indicate that the nitrates within the effluent are not being fully utilised by the crops. The utilisation problems may be related to either the rapid leaching of the nitrate from the soil, or the irrigation times not matching the plants nitrogen demand. According to Australian standards for wastewater re-use the levels of nitrogen in the effluent should not exceed 5 mg/L (5 μg/mL) (ANZECC *et al.* 2000), however these levels are for environmental reasons, rather than as a limit for plant health. The level of N in the water needs to be closely monitored as it can lead to contamination of ground water. While the N may be leaching below the root zone, it may also be volatilised once applied to the fields and further research could be conducted in this area to determine the fate of the N within the treated effluent after it is applied to the cropping system.

The orthophosphate levels found in the treated effluent were significantly greater than the levels seen in the Namoi River and the town water supply. Due to the properties of phosphorus it is considered to be the most inaccessible and immobile nutrient required by plants (Gatiboni *et al.* 2007). The orthophosphate level present in the treated effluent remains relatively stable between the WWTP and the irrigation canal, at ca.420 μg/L (ca.140 μg P/L), which is approximately three times the 50 μg/L long-term trigger value (LTV) for phosphorus (ANZECC *et al.* 2000). The trigger value for phosphorus, as with nitrogen is designed for factors other than crop health. The LTV has been designed for safe operation of farming systems, aiming to maintain low levels of algal contamination of dams, canals and farm irrigation equipment. The soils on Federation Farm are vertisols (Hulugalle *et al.* 2006), with high clay percentages, and high CEC capable of adsorbing significant quantities of P. The farm has not had need to add P fertilisers to maintain yield, while this may be due to the natural levels found in the soils. The application of the P with the irrigation water will also contribute to maintaining soil P levels, thus reducing costs to the farm.

The potassium (K) levels in the treated effluent are significantly higher than in the Namoi River. The results indicate that the towns' water supply is relatively high in K (ca.12 mg/L). Potassium levels in the treated effluent, following the WWTP is seen to fluctuate, during the summer months there is a significant drop between the WWTP and the dam inlet, the reason for this is uncertain but could be due to sampling error. The fluctuation in K within the treated effluent could be due to interactions with the soils of the property. Potassium is the second most abundant nutrient in plants and is taken up in quantities similar to N. There are no limitations to the amount of K that can be applied safely to fields (ANZECC *et al.* 2000). An average cotton crop (1800 kg lint/Ha) will remove between 27 and 58 kg K per Ha. The treated effluent on Federation Farm has, as an average value, 18 mg K per L, or 126 kg of K added per hectare per season (7 ML of irrigation water/Ha). The levels of K in a soil should not exceed 10% of CEC or plants may begin to experience deficiencies in other minerals such as magnesium. Because the level of potassium being added to the soil is between two and five times what is removed, the level of K in the soil should be closely monitored and precautions taken to ensure that K does not exceed the 10% CEC limit.

Nutrient levels in the treated effluent give a number of positive factors to its use for irrigation, these have been examined in a number of studies at other locations (Barton *et al.* 2005; Gori *et al.* 2004; Oyama *et al.* 2005). The majority of these studies have been conducted on farms that had only recently started operations, and have not looked at other chemicals in the effluent that may cause problems in the long-term on the property.

The preliminary analysis indicated a significantly increased salt level in the treated effluent (1.2 dS/m) when compared to the Namoi River (0.5 dS/m). The results obtained indicate that, although the levels are increased they would not affect a cotton crop, which has a relatively high tolerance to salt, with 50% emergence problems being noted only for values higher than 15 dS/m (Rengasamy 2006). The field analysis also indicated an increased pH in the effluent, however the pH is not high enough to be causing any significant damage or lead to the germination problems that have been noted on Federation Farm in the crops that are commonly grown on the property.

The preliminary analysis conducted via inductively coupled plasma indicated a number of elements present in the effluent, other than N, P and K. Further quantitative analysis indicated that while copper, zinc and manganese were present, the levels at which they were found were not sufficient to be having negative affects on the crops, even in a long term (>20 years) irrigation system. The preliminary inductively coupled plasma analysis also indicated that barium was present however the quantitative analysis failed to find barium in any of the samples collected.

Calcium in the effluent was found to be present at levels significantly higher than in the Namoi River, however calcium is not seen as a toxic element and it has no published LTV. Magnesium was also found at the test sites. During summer the values from Federation Farm were not significantly different from the summer values of the Namoi River. The samples collected during winter show significant variation between the test sites, and in comparison to the summer values. The variation may be due to seasonal affects on the concentration of magnesium; however the significant increase at the Namoi River test site is likely due to contamination of the water source at the time of sampling. As with calcium there is no published LTV for magnesium in irrigation water.

Sodium levels in the treated effluent were significantly higher than in the Namoi River. Levels were also generally lower than those from the town water supply, indicating that the town water source played a significant role in the level of sodium to be found in the treated effluent. The variation in the sodium level between the different test sites from the WWTP to the irrigation canal may be due to a number of factors, including fluctuations in the salt levels within the effluent from the WWTP at different times of the day and dilution due to rainfalls. The significant increase in salt levels that can be seen from the Federation Farm storage dam to the irrigation canal in the summer sampling is an anomaly, and there is no clear reason, other than contamination that this would have occurred.

Sodium levels in the treated effluent used to irrigate Federation Farm, are (averaged out) 185 mg/L, indicating that the water is suitable for the major crops grown in Australia (see Table 3.), including cotton. These published levels, while indicating what will not affect a crops growth, may not be suitable in determining if the levels can affect the germination of the crop. It is possible that significantly lower levels may lead to the delays that have been seen in the germination of the crops on Federation Farm, and sodium does need to be considered as an issue to the long term sustainability of cropping on the property as the sodium within the water can rapidly build up in the soil, adsorbing to the particles.

Table 3. Sodium sensitivity in crops (sourced from ANZECC et al., 2000)

Sensitive (<115mg/L)	Moderately sensitive (115 – 230mg/L)	Moderately tolerant (230 – 460mg/L)	Tolerant (>460mg/L)
Almond	Pepper	Barley	Cauliflower
Apricot	Potato	Maize	Cotton
Citrus	Tomato	Cucumber	Sugar beet
Plum		Lucerne	Sunflower
Grape		Safflower	
		Sesame	
		Sorghum	

The main controlling factor in the adsorbance of sodium onto soils is the sodium adsorbance ratio (SAR). The sodium adsorbance ratio is an equation based on the concentrations of sodium, calcium and magnesium cations (Figure 20). The SAR has been devised to ascertain a value to be compared with a maximum safe level that can be present in irrigation water to maintain soil structure, and long term sustainability on farms.

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{[(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})/2]^{0.5}}$$

Figure 20. Equation to determine the sodium adsorbance ratio (ANZECC et al. 2000).

The sodium adsorbance ratio for the effluent used on Federation Farm (Figure 21) is higher than the acceptable SAR value of 10, determined by a soils clay content and mineralogy (ANZECC *et al.* 2000). The SAR value indicates that the continuous irrigation of Federation Farm with this treated effluent will lead to a degradation of the soil. The SAR, while indicating what may become a long term systemic problem on Federation Farm, is unlikely to chemically affect the germination time of the seeds, however by affecting the structure of the soil, increasing dispersion and slaking, it might be able to cause physical hindrances to a plants development.

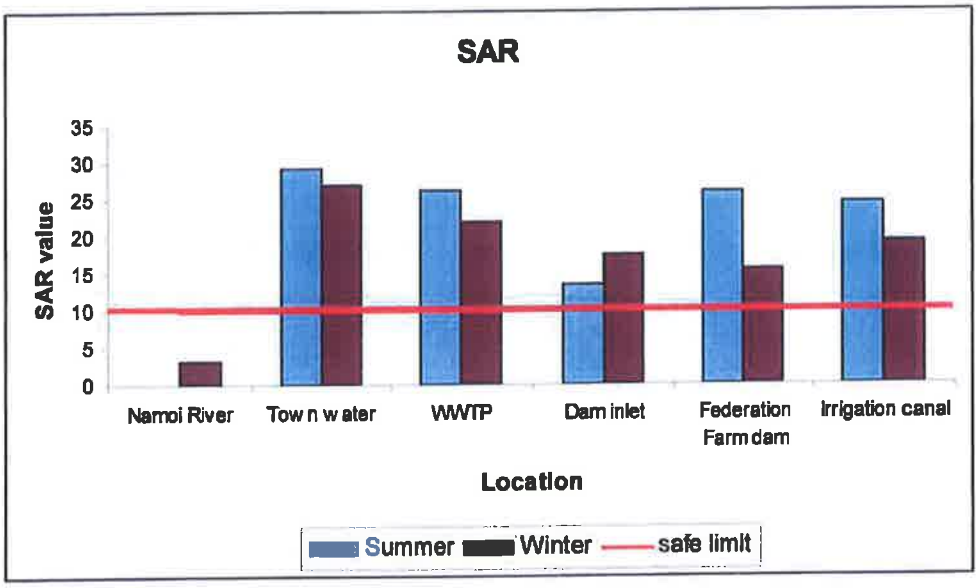

Figure 21. SAR for test sites.

Levels of iron that were found in the treated effluent were similar to the Namoi River during the summer sampling period, however the levels of iron on Federation Farm in winter were significantly greater than the other test sites/times. The level of iron present in the effluent is of concern in crops that are heavily irrigated. While iron is an abundant mineral, and an essential micronutrient for crop development, it can have a toxic effect (Becker and Asch 2005). There have been no reports of iron toxicity under normal conditions, however under water logged conditions, such as after a prolonged irrigation, or in rice paddies, iron can be reduced from Fe^{3+} to Fe^{2+}, which is toxic and easily absorbed by plants (Ponnampe *et al.* 1967). The treated effluent used on Federation Farm exceeds the LTV for iron of 0.2 mg/L and could lead to toxicity problems under water logged conditions. Because iron levels in the irrigation water are higher than the safe limits irrigation should be carefully applied. Caution should especially be taken during the germination phase when plants are highly susceptible to toxins to ensure that the field does not experience water logged conditions.

Levels of Strontium in the Federation Farm are relatively low; however they are still higher than the levels found in the Namoi River. Because of the relative rarity of strontium there have been no published LTV values for this element. Studies have examined the effect of strontium on the growth of plants (Kozhevnikova *et al.* 2007; Lasztity 2003) and these studies have found that strontium can affect growth of plants, but only at relatively high concentrations(>3mg/L) that are not reached in the samples tested.

As previously mention a number of trials similar in scope to this one has been conducted on other properties (Al-A'ama and Nakhla 1995; Barton *et al.* 2005; Gori *et al.* 2004; Oyama *et al.* 2005). These trials have examined the quality of the effluent, primarily in terms of nutrient content, but they have also examined possible contaminants. A study conducted in India (Rattan *et al.* 2005) examined the long term build-up of metals within the soil profile, and found a number of minerals, including lead and zinc had built up in the soil, with zinc present at levels that were considered hazardous to crop growth. In comparison to the effluent that is used to irrigate Federation Farm the water used on this property in India had significantly higher zinc levels as well as lead, which was not present in the treated effluent used on Federation Farm.

One of the main contaminants that has been found in studies conducted around the globe is boron (Choi *et al.* 2006; Nable *et al.* 1997). In the study conducted on Federation Farm the effluent was, according to the preliminary analysis, free of any boron contamination. The lack of boron was unexpected as it is commonly used in a number of household products such as washing powders. In comparison to effluent used in a number of other trials the effluent used on Federation Farm is relatively clear of contaminations (da Fonseca *et al.* 2007; Heidarpour *et al.* 2007; Wang *et al.* 2007). However as the germination trial has shown the content of the treated effluent did cause a statistically significant increase in the time to germination indicating that the contaminants present in the effluent are having a negative effect.

Further research could be conducted on Federation Farm to analyse the soil-water interactions to determine if this is the most important factor in the germination delays that have been noted on Federation Farm. The research should work on a similar model to this report, focusing on a germination trial, comparing Federation Farm soils to other farms in the region, using the water sourced from the Namoi River, other farm dams and the treated effluent. The research should also consist of a quantitative analysis of the elements present within the soil. Another study that could be conducted on the property would be to study the fate of the nitrate that is applied to the fields, as previously discussed earlier in this section.

Conclusion

The results from this experiment show that the effluent used for irrigation on Federation Farm does contain a number of potential contaminants, including zinc, iron, manganese and strontium, however only iron and sodium are at levels that could be of concern to the long term farming plan. The germination trial indicated that the treated effluent produced by the Narrabri waste-water treatment plant does have a significant impact on the germination of cotton seeds, when compared to water from the Namoi River.

While the study did find evidence that the treated effluent can cause delays in the germination of the crop, proving the hypothesis, the delays that were found in the germination trial were not as significant as those that have been noted on Federation Farm. The results indicate that the water itself is only one factor in the germination problems and that further research should be conducted on the property examining the soil-water interactions.

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Appendix

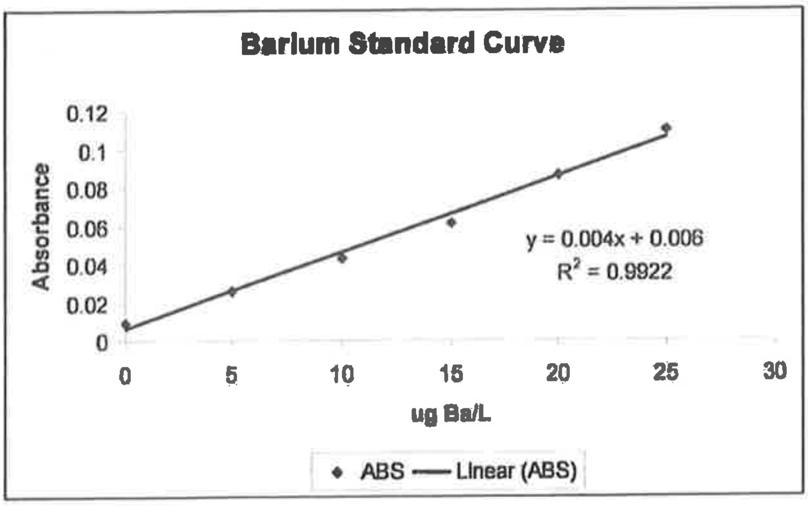


Figure A.1. Barium standard curve.

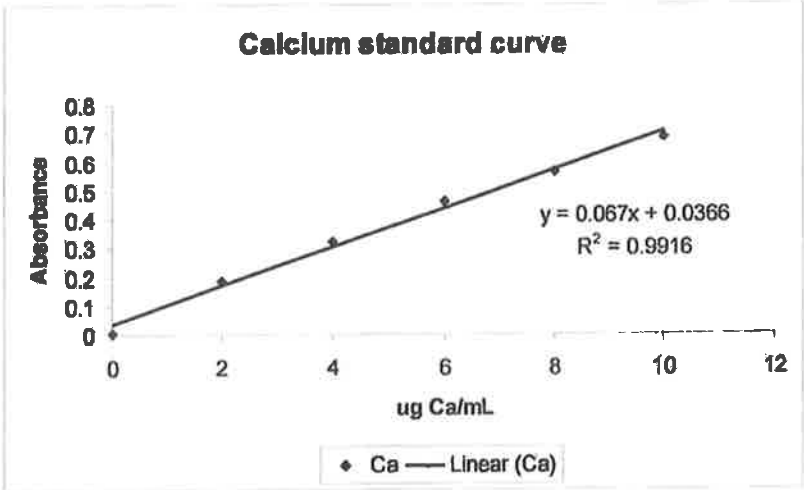


Figure A.2. Calcium standard curve.

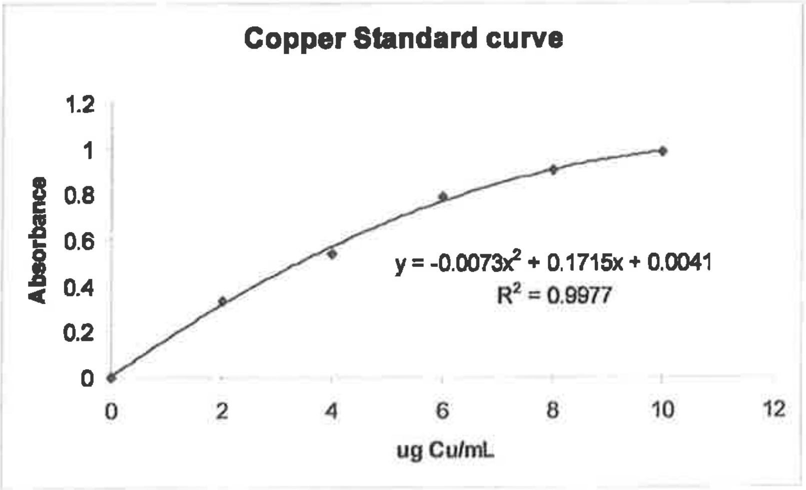


Figure A.3. Copper standard curve.

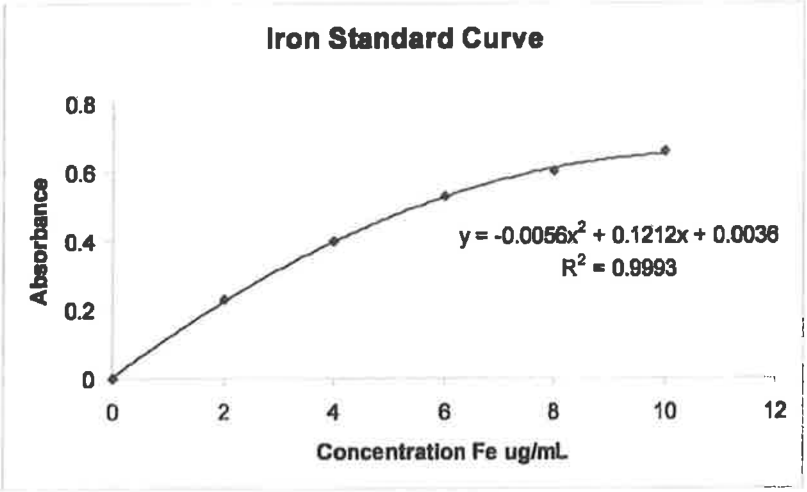


Figure A.4. Iron standard curve

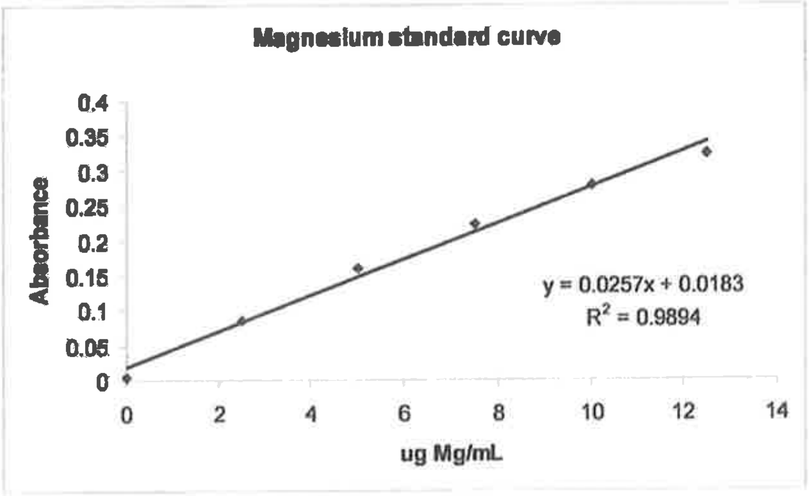


Figure A.5. Magnesium standard curve

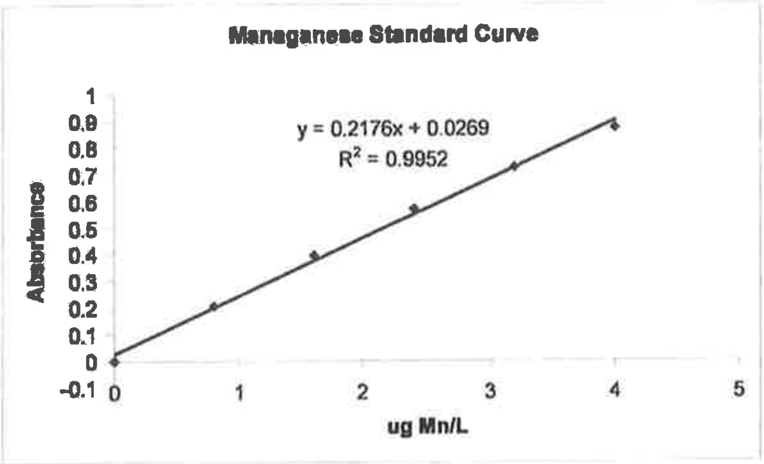


Figure A.6. Manganese standard curve

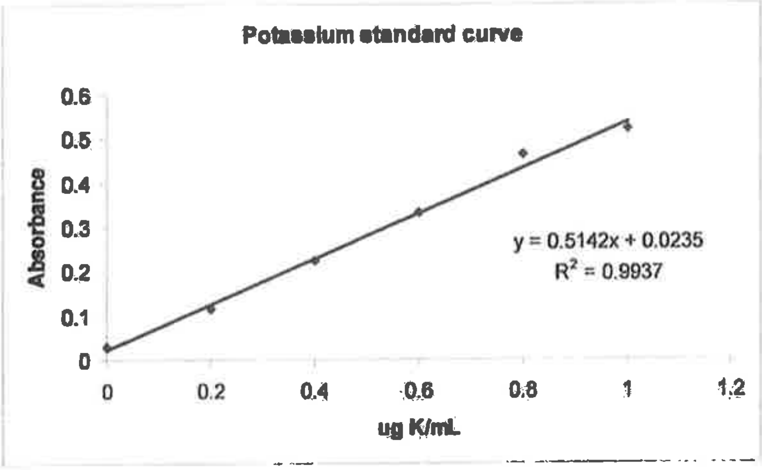


Figure A.7. Potassium standard curve

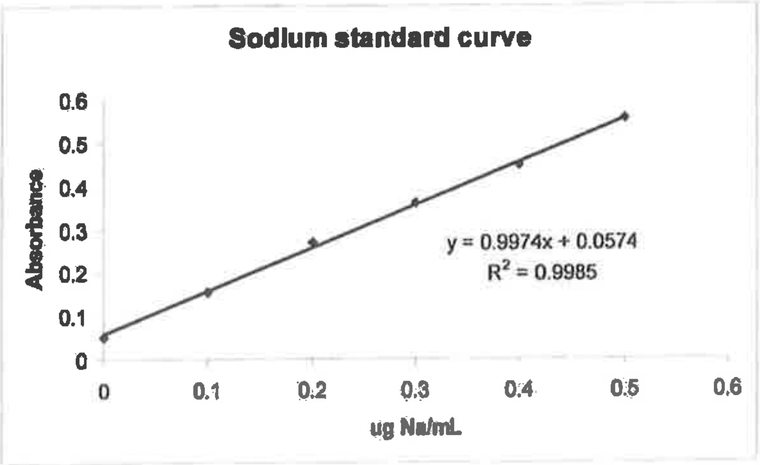


Figure A.8. Sodium standard curve

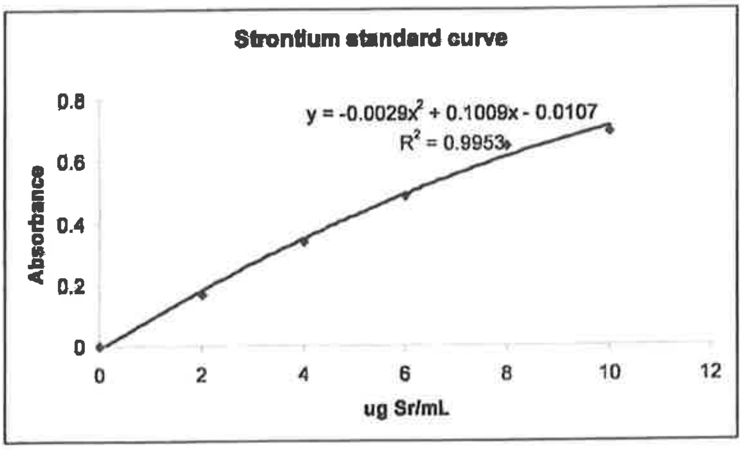


Figure A.9. Strontium standard curve

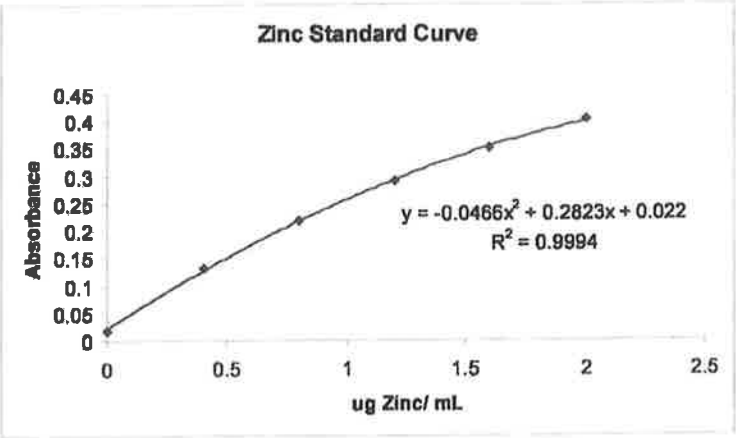
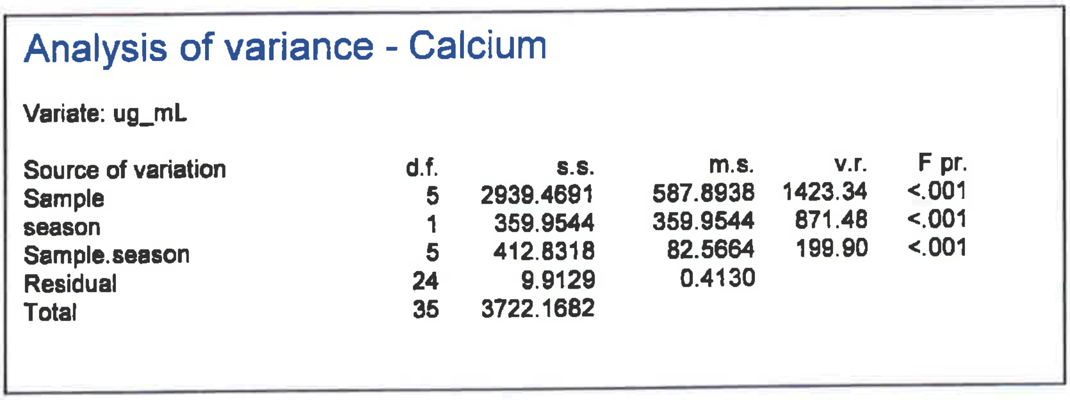


Figure A.10. Zinc standard curve

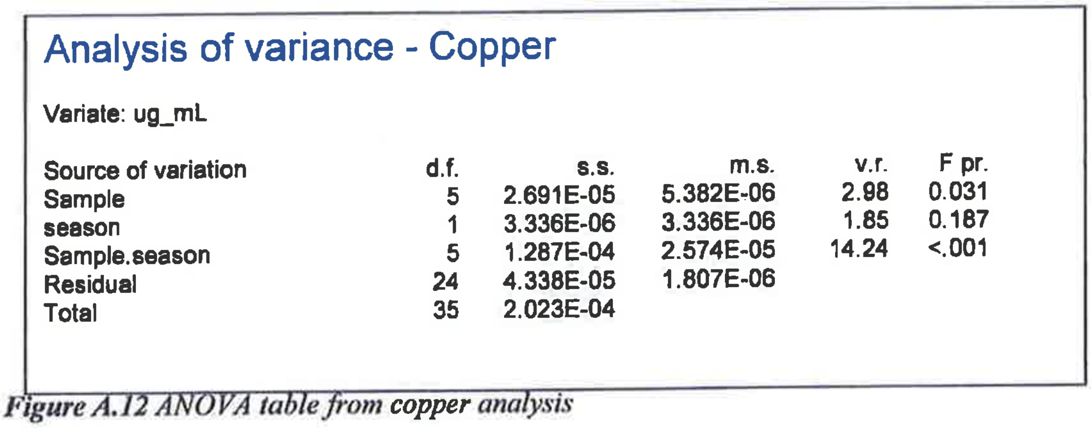


Analysis of variance - Calcium

```
Variate: ug_mL

Source of variation     d.f.        s.s.        m.s.      v.r.   F pr.
Sample                     5   2939.4691    587.8938   1423.34   <.001
season                     1    359.9544    359.9544    871.48   <.001
Sample.season              5    412.8318     82.5664    199.90   <.001
Residual                  24      9.9129      0.4130
Total                     35   3722.1682
```

Figure A.11 ANOVA table for calcium analysis.

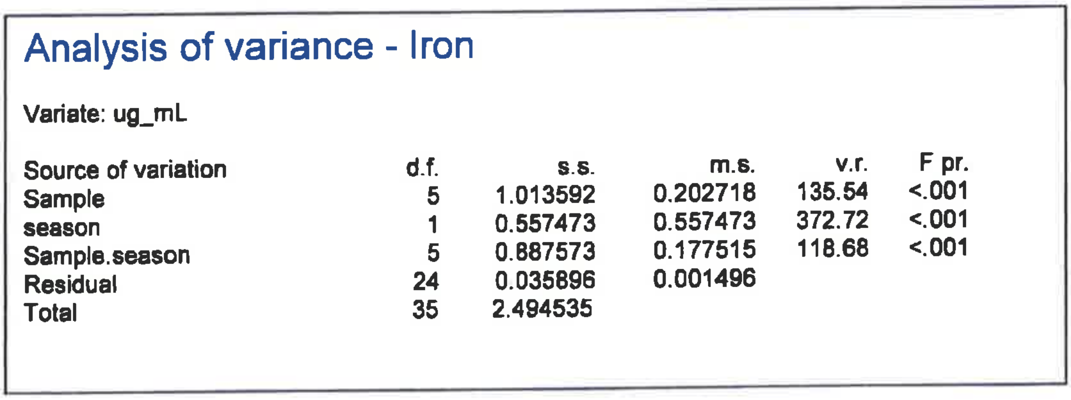


Analysis of variance - Copper

```
Variate: ug_mL

Source of variation     d.f.        s.s.        m.s.      v.r.   F pr.
Sample                     5   2.691E-05   5.382E-06      2.98   0.031
season                     1   3.336E-06   3.336E-06      1.85   0.187
Sample.season              5   1.287E-04   2.574E-05     14.24   <.001
Residual                  24   4.338E-05   1.807E-06
Total                     35   2.023E-04
```

Figure A.12 ANOVA table from copper analysis

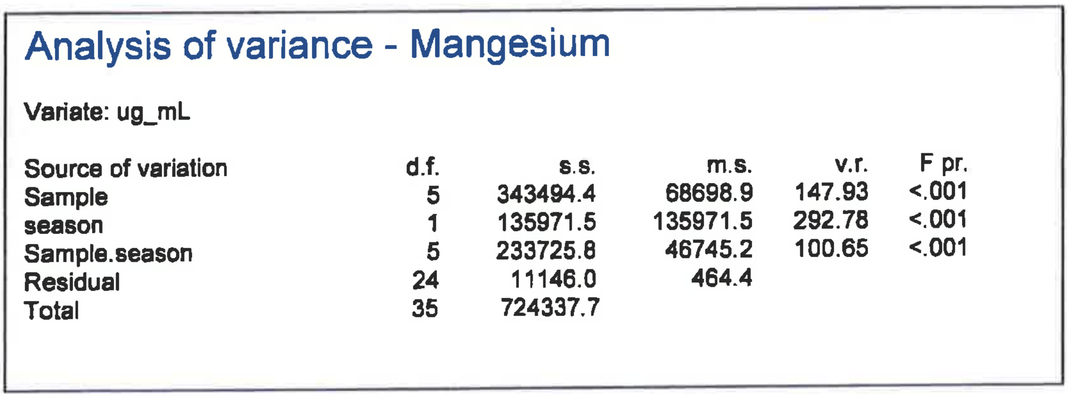


Analysis of variance - Iron

```
Variate: ug_mL

Source of variation     d.f.        s.s.        m.s.      v.r.   F pr.
Sample                     5    1.013592    0.202718    135.54   <.001
season                     1    0.557473    0.557473    372.72   <.001
Sample.season              5    0.887573    0.177515    118.68   <.001
Residual                  24    0.035896    0.001496
Total                     35    2.494535
```

Figure A.13 ANOVA table from Iron analysis

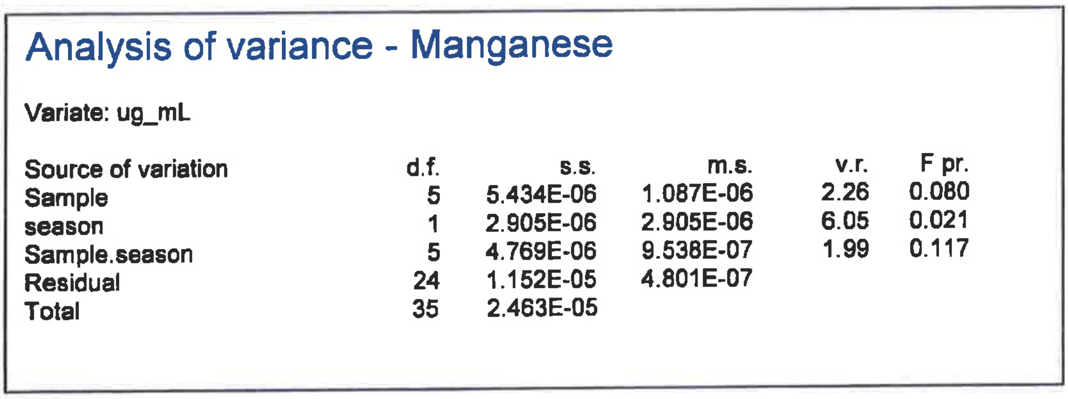


```
Analysis of variance - Mangesium

Variate: ug_mL

Source of variation        d.f.        s.s.        m.s.      v.r.    F pr.
Sample                        5    343494.4     68698.9    147.93    <.001
season                        1    135971.5    135971.5    292.78    <.001
Sample.season                 5    233725.8     46745.2    100.65    <.001
Residual                     24     11146.0       464.4
Total                        35    724337.7
```

Figure A.14 ANOVA table from magnesium analysis

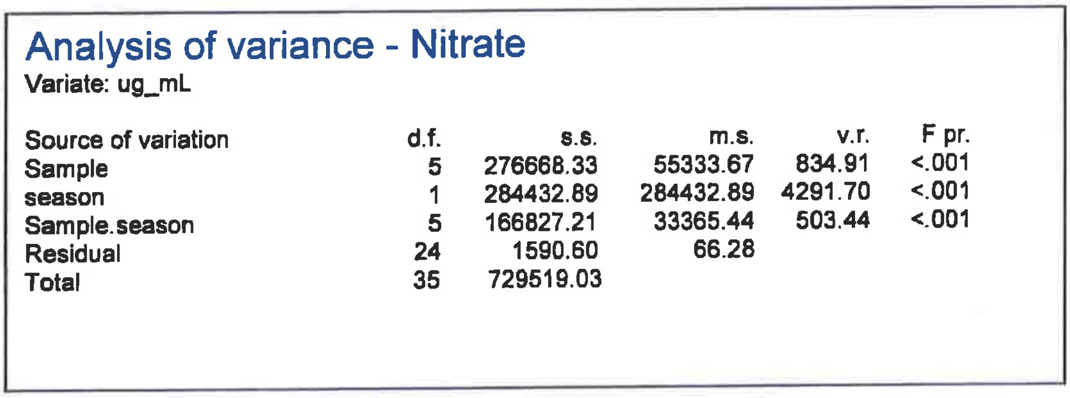


```
Analysis of variance - Manganese

Variate: ug_mL

Source of variation        d.f.        s.s.        m.s.      v.r.    F pr.
Sample                        5   5.434E-06   1.087E-06      2.26    0.080
season                        1   2.905E-06   2.905E-06      6.05    0.021
Sample.season                 5   4.769E-06   9.538E-07      1.99    0.117
Residual                     24   1.152E-05   4.801E-07
Total                        35   2.463E-05
```

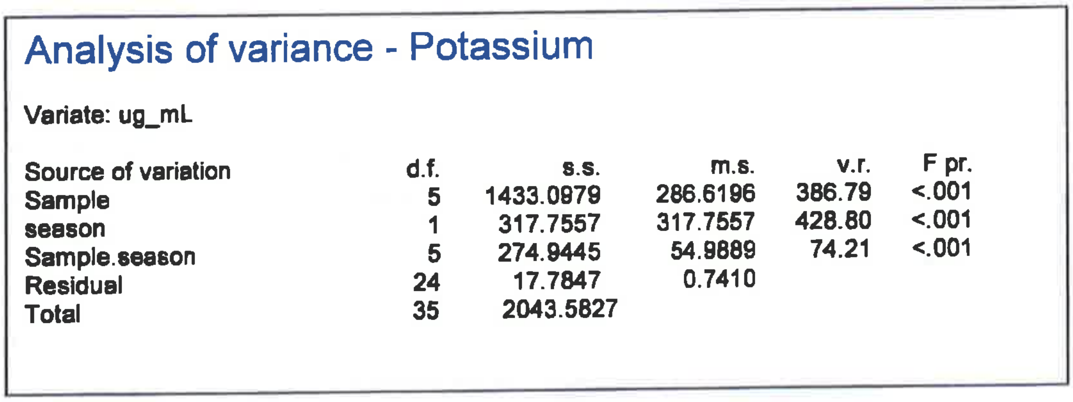
Figure A.15 ANOVA table from manganese analysis



```
Analysis of variance - Nitrate
Variate: ug_mL

Source of variation        d.f.        s.s.        m.s.      v.r.    F pr.
Sample                        5   276668.33    55333.67    834.91    <.001
season                        1   284432.89   284432.89   4291.70    <.001
Sample.season                 5   166827.21    33365.44    503.44    <.001
Residual                     24     1590.60       66.28
Total                        35   729519.03
```

Figure A.16 ANOVA table from Nitrate analysis

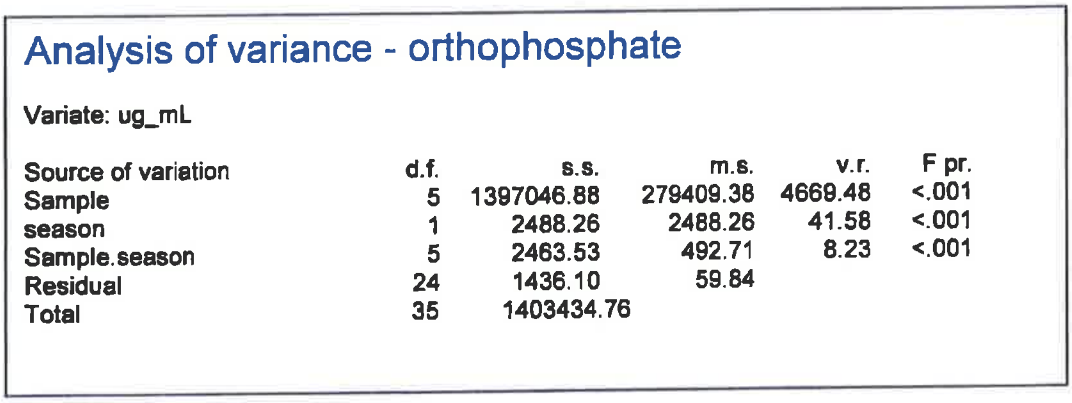


Analysis of variance - Potassium

```
Variate: ug_mL

Source of variation          d.f.        s.s.        m.s.      v.r.   F pr.
Sample                          5   1433.0979    286.6196    386.79   <.001
season                          1    317.7557    317.7557    428.80   <.001
Sample.season                   5    274.9445     54.9889     74.21   <.001
Residual                       24     17.7847      0.7410
Total                          35   2043.5827
```

Figure A.17 ANOVA from potassium analysis

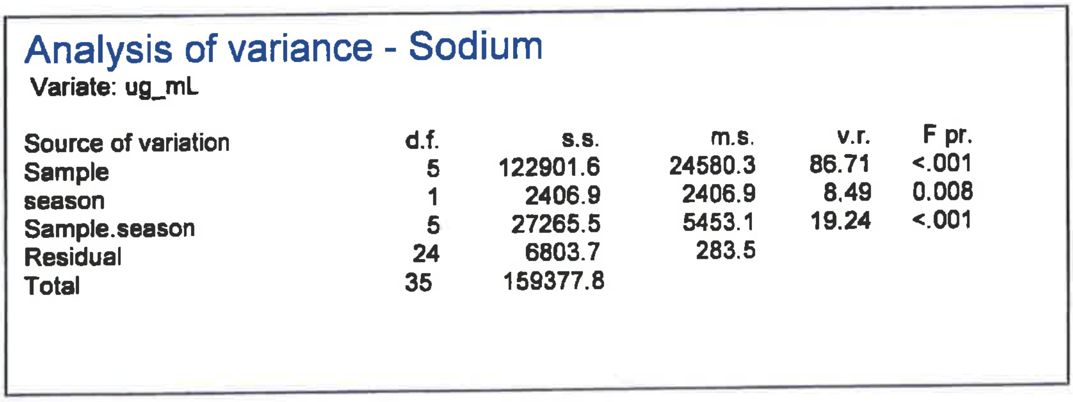


Analysis of variance - orthophosphate

```
Variate: ug_mL

Source of variation          d.f.         s.s.         m.s.      v.r.   F pr.
Sample                          5   1397046.88    279409.38   4669.48   <.001
season                          1      2488.26      2488.26     41.58   <.001
Sample.season                   5      2463.53       492.71      8.23   <.001
Residual                       24      1436.10        59.84
Total                          35   1403434.76
```

Figure A.18 ANOVA from orthophosphate analysis

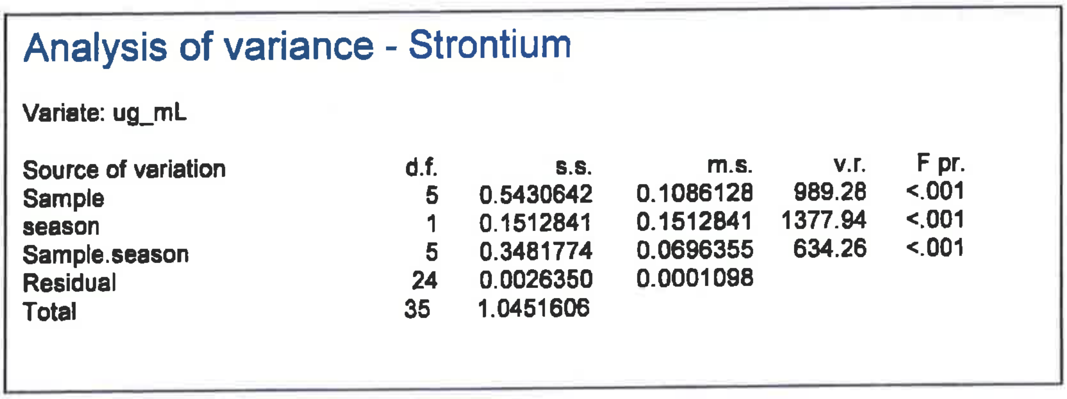


Analysis of variance - Sodium

```
Variate: ug_mL

Source of variation          d.f.        s.s.       m.s.     v.r.   F pr.
Sample                          5    122901.6    24580.3    86.71   <.001
season                          1      2406.9     2406.9     8.49   0.008
Sample.season                   5     27265.5     5453.1    19.24   <.001
Residual                       24      6803.7      283.5
Total                          35    159377.8
```

Figure A.19 ANOVA from sodium analysis

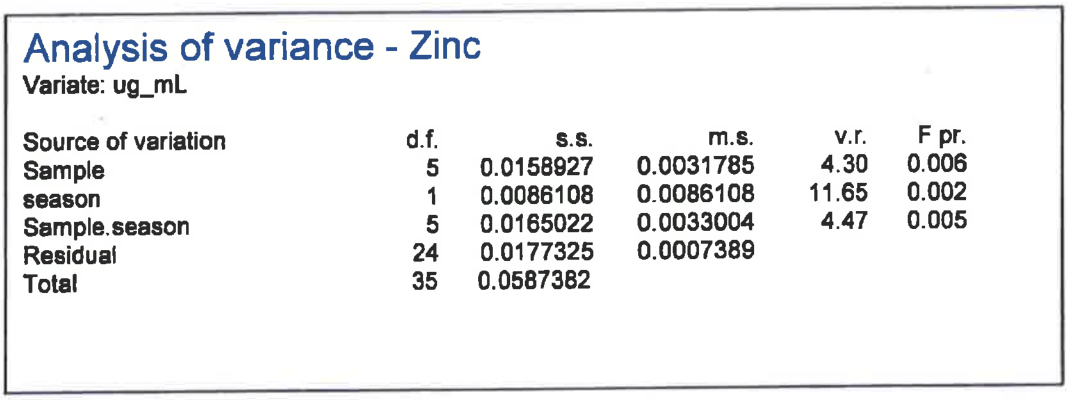


```
Analysis of variance - Strontium

Variate: ug_mL

Source of variation      d.f.        s.s.        m.s.     v.r.   F pr.
Sample                      5   0.5430642   0.1086128   989.28   <.001
season                      1   0.1512841   0.1512841  1377.94   <.001
Sample.season               5   0.3481774   0.0696355   634.26   <.001
Residual                   24   0.0026350   0.0001098
Total                      35   1.0451606
```

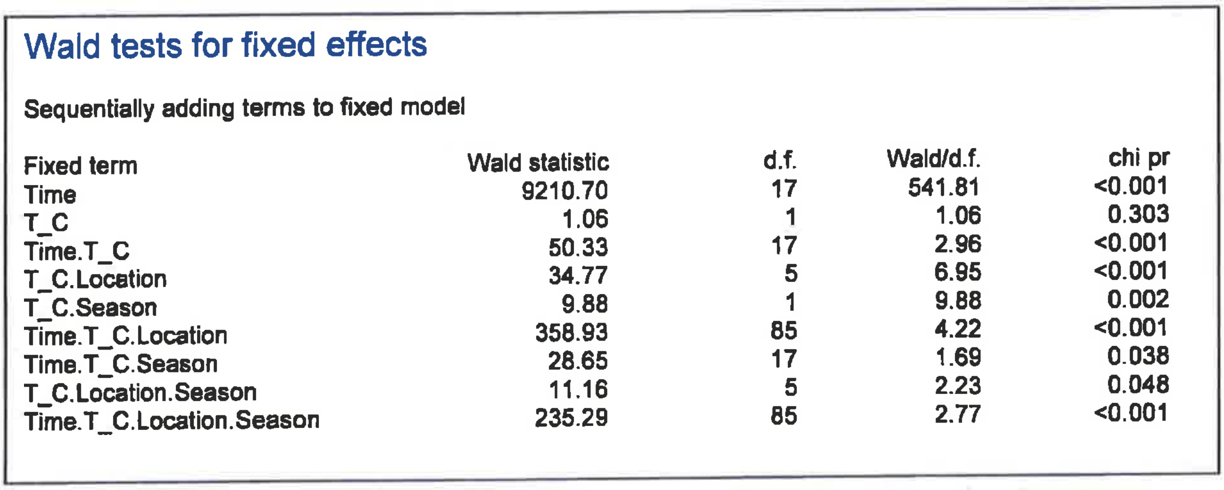
Figure A.20 ANOVA from strontium analysis



```
Analysis of variance - Zinc
Variate: ug_mL

Source of variation      d.f.        s.s.        m.s.     v.r.   F pr.
Sample                      5   0.0158927   0.0031785     4.30   0.006
season                      1   0.0086108   0.0086108    11.65   0.002
Sample.season               5   0.0165022   0.0033004     4.47   0.005
Residual                   24   0.0177325   0.0007389
Total                      35   0.0587382
```

Figure A.21 ANOVA from zinc analysis



```
Wald tests for fixed effects

Sequentially adding terms to fixed model

Fixed term                         Wald statistic      d.f.     Wald/d.f.     chi pr
Time                                      9210.70        17        541.81     <0.001
T_C                                          1.06         1          1.06      0.303
Time.T_C                                    50.33        17          2.96     <0.001
T_C.Location                                34.77         5          6.95     <0.001
T_C.Season                                   9.88         1          9.88      0.002
Time.T_C.Location                          358.93        85          4.22     <0.001
Time.T_C.Season                             28.65        17          1.69      0.038
T_C.Location.Season                         11.16         5          2.23      0.048
Time.T_C.Location.Season                   235.29        85          2.77     <0.001
```

Figure A.22 REML output from genstat LINEAR MIXED MODEL analysis of seed germinations

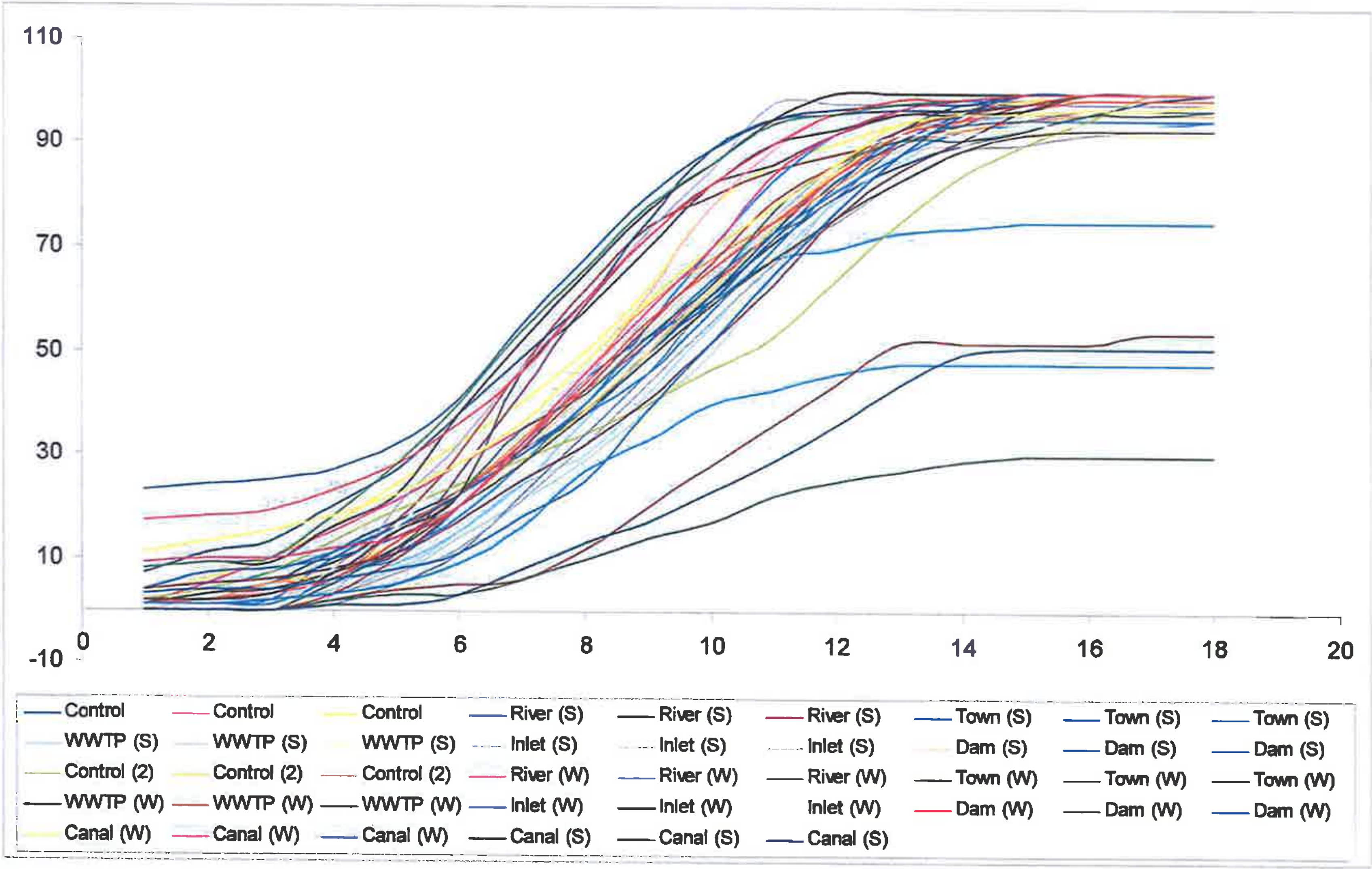


Figure A.23. Germination results for each replicate.

	Control	Namoi R. (summer)	Town water (summer)	WWTP (summer)	Dam inlet (summer)	Federation Farm dam (summer)	Irrigation canal (summer)	Namoi R. (winter)	Town water (winter)	WWTP (winter)	Dam inlet (winter)	Federation Farm dam (winter)	Irrigation canal (winter)
Control	0	*	*	*	*	*	*	*	*	*	*	*	*
Namoi R. (summer)	**-14.1663**	0	*	*	*	*	*	*	*	*	*	*	*
Town water (summer)	0.5	**14.6663**	0	*	*	*	*	*	*	*	*	*	*
WWTP (summer)	**12.5**	**26.6663**	12	0	*	*	*	*	*	*	*	*	*
Dam Inlet (summer)	-9.1663	5	-9.6663	**-21.6663**	0	*	*	*	*	*	*	*	*
Federation Farm dam (summer)	1.4997	**15.666**	0.9997	-11.0003	10.666	0		*	*	*	*	*	*
Irrigation Canal (summer)	**35.1667**	**49.333**	**34.6667**	**22.6667**	**44.333**	**33.667**	0	*	*	*	*	*	*
Namoi R. (winter)	3.5	**17.6663**	3	-9	**12.6663**	2.0003	**-31.6667**	0	*	*	*	*	*
Town water (winter)	**-13.8333**	0.333	**-14.3333**	**-26.3333**	-4.667	**-15.333**	**-49**	-17.3333	0	*	*	*	*
WWTP (winter)	3.8334	**17.9997**	3.3334	-8.6666	**12.9997**	2.3337	**-31.3333**	0.3334	**17.6667**	0		*	*
Dam Inlet (winter)	**-19.5**	-5.3337	-20	**-32**	-10.3337	**-20.9997**	**-54.6667**	-23	-5.6667	**-23.3334**	0	*	*
Federation Farm dam (winter)	**-10.8333**	3.333	-11.3333	**-23.3333**	-1.667	-12.333	**-46**	**-14.3333**	3	**-14.6667**	8.6667	0	*
Irrigation Canal (winter)	1.8367	**16.003**	1.3367	-10.6633	11.003	0.337	-33.33	-1.6633	**15.67**	-1.9967	21.3367	**12.67**	0

***TABLE A.1** Germination analysis at 34th hour. The **BOLD** figures represent statistically significant differences, comparing the differences in the means to the associated LSD.*