Crop response to irrigation with acidic and neutralized, saline mine water

By

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DECLARATION

I hereby certify that this dissertation is my own work, except where duly acknowledged. I also certify that no plagiarism was committed in writing this dissertation.

Signed ________________________

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Abstract

The cessation of mining activities and concurrent abandonment of mines in many South African mining areas has left the state with the responsibility of caring for and rehabilitating ownerless mines, which are prone to flooding and discharge acid mine drainage (AMD) to surrounding environments. In the Witwatersrand Goldfields, AMD arising from abandoned mines is currently being treated by High-Density Sludge (HDS) neutralization and released into surrounding natural water bodies as part of a short-term intervention. Long term management of the water would require the construction of more HDS plants and an additional desalination step, which is estimated to cost the state several billions of Rands in capital costs and R1 billion in annual running costs.

Alternative cost-effective AMD management strategies are being considered and irrigation is one of the strategies being proposed. One of the options being suggested is to irrigate with neutralized AMD, which would eliminate the need for desalination. Another option is to irrigate with untreated AMD, which would eliminate the need to construct treatment plants altogether. There is, however, a concern that the mine waters do not comply with the 1996 South African Water Quality Guidelines for Irrigation, which are generic and outdated. Another concern is that continuous irrigation with the water may have detrimental long-term environmental effects. The South African Water Quality Guidelines for Irrigation have, however, recently been updated to a software-based, risk-based, generic and site-specific decision support system (DSS) that allows users to run long term irrigation simulations.

The aim of this study was to ascertain if acidic and neutralized, saline Goldfield mine water can be used successfully for crop irrigation, using the waters from the Witwatersrand Goldfields, as water quality references. The study also aimed to investigate the role played by crop tolerance and soil type in mitigating the effects of the mine waters on selected crops. An additional aim for this study was to assess the fitness-for-use of mine water for irrigation under site-specific conditions and to investigate the potential use of the South African Water Quality Guidelines for Irrigation decision support system (SAWQI-DSS) in predicting long term effects of irrigating with acidic and saline mine water.

A greenhouse pot trial was undertaken in 2015, in which several crops, selected for their tolerance/sensitivity to acidity and salinity, were planted and irrigated with municipal water as well as with synthetic acidic and neutralized saline mine waters. A red sandy soil loam with theoretically low acid neutralizing capacity, and a vertic soil with a theoretically higher acid neutralizing capacity were used as growth media. Water loss was supplemented to each pot's individual field capacity so that each crop's unique water requirements were met. Crops were initially watered on a weekly basis and then twice a week as crop water requirement increased. Each treatment had three replicates, set up in a completely randomized design on a rotating table. Site-specific fitness-for-use assessments of acidic and neutralized saline mine water for irrigation were performed using the SAWQI-DSS. Long term simulations (45 years) were conducted for irrigation of a salt-sensitive summer crop and a salt tolerant winter crop grown on a sandy loam or clay soil, with the application of different leaching fractions. The field chosen for the simulations received some rainfall.

Most crops irrigated with the mine waters did not show signs of foliar injury. However, crops irrigated with acidic mine water did show symptoms of nutrient imbalances, phytotoxicity and drought stress. Crops grown on the red sandy loam soil, typically showed symptoms of drought and manganese toxicity, whereas those grown on the vertic soil typically showed signs of nutrient imbalances when irrigated with municipal water. Most crops irrigated with acidic mine waters accumulated phytotoxic levels of Al and Mn, and excessive levels of Fe. Accumulation of Al, Fe and Mn was lower in crops irrigated with neutralized mine water, however, crops grown on red sandy loam soil typically accumulated phytotoxic levels of these metals when irrigated with neutralized mine water.

Irrigation with mine waters had no significant effects on the growth and grain yield of most crops grown on the vertic soil. On the other hand, crops grown on the red sandy loam soil had less growth and grain yield. The grain of crops grown on the red sandy loam soil and the vertic soil presented potential health risks associated with Al and Mn toxicity when irrigated with mine waters. However, the Al, Fe and Mn content of this grain did not exceed the tolerance thresholds for livestock, indicating that the grain would be suitable for use as livestock fodder. Fodder safety evaluations indicated that crops grown on the red sandy loam soil, when irrigated with mine waters, are more likely to present potential health risks associated with Al, Fe and Mn zootoxicity in livestock than those grown on the vertic soil, particularly if their foliage is consumed.

Health risk assessments indicated that the grain of these crops would not be safe for consumption by individuals who are vulnerable to Al, Fe and Mn toxicity, particularly the grain of crops that are consumed in large amounts. Grain Al and Mn content of most crops was, however, below zootoxicity thresholds for livestock.

The differences in crop response to irrigation with mine water, particularly the difference between crops grown on the red sandy loam soil and those grown on the vertic soil, can be attributed to the higher CEC and organic matter content of the vertic soil than in the sandy loam soil, which can buffer against the effects of acidity, salinity and render potentially toxic elements less mobile, and therefore, less available for crop uptake. The evaluations indicated that the exceedance of food safety thresholds for humans were more a result of high consumption of the crops and less a reflection of high levels of potentially toxic metals in the crops.

SAWQI-DSS fitness-for use assessments predicted that long term irrigation with acidic saline mine water would have detrimental effects on root zone salinity and crop yield. Root zone salinity was predicted to be higher on the clay soil than on the sandy loam soil. The model used in the SAWQI-DSS accounts for differences in water and solute movements between soil types, as influenced by soil texture. Coarse-textured soils are typically easier to leach than fine-textured soils, hence, the model predicted that sandy loam soils would be less saline. The assessments indicated that increasing leaching fraction would have an influence on rootzone salinity, however, clay soils required a higher leaching fraction to reduce salinity than sandy loam soil. Al, Mn and Fe were predicted to reach the accumulation threshold in less than 100 years, with accumulation being more rapid in sandy loam soil. The assessments also predicted that the salt-tolerant crop would perform better than the salt-sensitive crop. SAWQI-DSS fitness-for use assessments predicted that long term irrigation with neutralized saline mine water would not have detrimental effects on root zone salinity and crop yield.

Irrigation with acidic saline mine water has major cost saving implications, as it means that there would be no need to build mine water treatment plants. Irrigation with neutralized mine water is also a promising alternative for mine water management, as it would eliminate the need to construct desalinization facilities and the running costs associated with the process. This study has demonstrated that crops can be produced successfully through irrigation with mine waters, especially neutralized mine water, which showed positive results regardless of the soil type used. Further studies are, however, required to determine the effects of irrigation with such waters in field conditions for different soil types. In the case of acidic saline mine water, the influence of lime application, irrigation management (i.e. type of irrigation system, irrigation timing, etc.) and leaching on soil and crop responses are required. In the case of the neutralized mine water, the effects of leaching and irrigation management on soil and crops. Further studies to establish relevant health risk assessments with regard to the trace element content of foods, in the South African context, are also required.

The SAWQI-DSS has displayed great potential for use in evaluating long-term effects of irrigating with water that would typically be considered undesirable. The option to introduce site specificity gives users the flexibility to assess the effect that alternative options, for managing the water they have available, will have when used for irrigation. The SAWQI-DSS does, however, have limitations in assessing the fitness-for-use of acidic mine waters as it does not give a comprehensive account of the effects of irrigation water acidity on soil quality, and crop yield and quality. For instance, the fitness-for-use assessments do not indicate the degree of soil acidification or foliar injury associated with the direct effects of irrigation water acidity. Furthermore, the assessments do not indicate how relative yield would be affected by trace element toxicity as it does for Na, Cl, and B. Further studies are therefore required to account for foliar injury resulting from irrigation water acidity, similar to what has been done for foliar injury resulting from irrigation water salinity. There is also a need to incorporate the effects of trace element toxicity on relative yield, similar to what has been done for Na, Cl and B. In cases whereby toxicity thresholds and yield reductions associated with trace element toxicity have not been established, experimental trials should be conducted to fill those knowledge gaps. In addition, the incorporation of health risk assessments associated with trace element accumulation in grain is required.

Chapter 1: Introduction

1.1 Background

Since the establishment of the formal mining industry in the 19th century, South Africa has been subject to widespread mining activities following the discovery of its vast mineral wealth. Although the mining industry has been economically beneficial to the country, mining activities have had a negative impact on the environment (Swart, 2003). The excavation and mineral processing associated with common mining methods, particularly underground mining, leaves a network of tunnels and voids that become flooded with water and generate acid mine drainage (Ochieng et al., 2010). Under normal mining operations, the water is pumped out of the voids and the acid mine drainage (AMD) is treated by neutralization (Durand, 2012). When mining ceases, however, most mines are abandoned and along with this, the responsibility of dewatering and AMD treatment often falls on the state (Swart et al., 2007). As a result, South Africa has been left with thousands of abandoned mines that are prone to flooding, and discharge AMD into surrounding environments, thereby contaminating natural water bodies (Naicker et al., 2003).

Incidents of underground mine flooding and AMD discharge have been reported in several parts of South Africa, including the coal mining areas in Mpumalanga and the copper mining district in O'Kiep (Department of Water Affairs, 2010). It was, however, the chain of events that unfolded in the Witwatersrand Goldfields that brought the mine water problems to mainstream public attention (Oelofse, 2009). The underground mine workings and voids in the Western Basin of the Witwatersrand Goldfields began to flood and discharge water to surface environments. The average decant rate was 15 megalitres per day (ML/day) and reached peaks of 20 ML/day. A few years later the mines in the Eastern and Central Basins were shut down, and all pumping ceased, resulting in an increase in water levels in the underground mine workings. Water levels reportedly rose at a rate of 0.3 to 0.4 metres per day (m/d) (Department of Water Affairs, 2013b). The main concern with these basins flooding and decanting AMD is that they are a threat to natural water systems, as well as tourist/heritage sites. In the Western Basin, mine water decants into Tweelopiespruit, a stream that forms part of the Crocodile River Catchment. In the Central Basin further increases in water levels will cause flooding of the Gold Reef City tourist mine and contaminate groundwater. In the Eastern Basin, flooding will result in the decanting of AMD to the town of Nigel.

Following reports of AMD decanting into areas surrounding the Witwatersrand Goldfields, short-term interventions were put into effect to manage this mine water. The Western Basin was first to be addressed due to the extent of the problem in that region and the water is currently being neutralized and released into the Tweelopiespruit (Department of Water Affairs, 2010). This process was, however, found to be inefficient in dealing with the problem, because the acid mine water is decanting faster than the rate at which it is being treated and released (Department of Water Affairs, 2010).

In addition to being inefficient, the release of neutralized mine water into natural water bodies is not sustainable. The salinity of neutralized mine water, as well as the high concentrations of sulphates it contains, will eventually increase salt loads in the receiving water bodies, rendering them unsuitable for industrial use and human consumption (Department of Water Affairs, 2013a). If this strategy is employed over the long-term, large volumes of fresh water would be required to dilute the salinity (Department of Water Affairs, 2013a). Due to water scarcity and the droughts that have plagued South Africa in recent years, as well as the high cost of the Lesotho Highlands water, releasing additional water to dilute the neutralized mine water is not feasible. Alternatively, the neutralized water will require desalinization through reverse osmosis (RO), however, the process is projected to be very costly, with capital cost estimates amounting to several billion Rands and annual running costs of R1billion (Bobbins, 2015).

Considering the challenges associated with mine water treatment, the research community has been exploring alternative, cost-effective, long-term management strategies to address the mine water problem. One of the strategies being suggested is the use of mine water for crop irrigation. In addition to addressing the mine water problem, this approach could also provide relief for the country’s already strained water resources. Two irrigation options have been presented, the first option is to irrigate crops with the neutralized mine water, which would serve as a good alternative for utilizing the mine water without having to treat it any further. The second option is to irrigate with untreated acid mine water on limed soil, using the soil as a reactor for neutralization. Irrigating with the acid mine water would eliminate the need to build treatment plants as well as the need for sludge waste disposal measures associated with the neutralization process.

The use of untreated acidic mine water is not widely researched, but literature suggests that it is somewhat feasible (Cronce et al., 1980). The concern with untreated acidic mine water is that its characteristic acidity, salinity and high concentrations of phytotoxic elements (particularly Al, Fe and Mn) may make it detrimental to crops and people or animals consuming them. The water may cause foliar injury if applied by overhead irrigation and the water can also create hostile growth conditions by decreasing soil pH, as well as increasing the salinity and concentrations of phytotoxic elements in the soil (Lin et al., 2005). Neutralizing the mine water reduces acidity and drastically reduces the concentrations of Fe and Mn, but salinity often remains higher than the recommended level for the growth of many crops (Jovanovic et al., 1998; Maree et al., 2013). Previous studies with mine water from the coalfields have demonstrated that neutralized mine water may be used for crop irrigation (Jovanovic et al., 1998). However, there is uncertainty as to whether the same will apply for mine water from the goldfields.

Although the quality of mine water suggests that the waters may be detrimental to crop growth, there are factors that can mitigate such effects. One of these factors is crop tolerance to the mine water constituents. Another factor is the interaction between soil and irrigation water constituents. These factors may render the otherwise undesirable mine water less detrimental and more viable for use in crop irrigation. There are, however, some constraints and challenges to using water of this quality for irrigation. One constraint is that acidic mine water might increase the phytoavailability of potentially toxic elements which could render the produce unsafe for human consumption. Another constraint is that the sustainability and long-term environmental effects of the mine water have not been investigated. In addition, the quality of water produced by most mines does not comply with the current South African Water Quality Guidelines for Irrigation, which are presently under review.

This study investigates crop response to acidic and neutralized saline goldmine water and explores the influence of crop tolerance, as well as soil-water interactions on the effect of the mine water. Grain and foliage of selected crops were assessed for food and fodder safety. The investigation was carried out in a glasshouse trial and involved summer and winter crops selected for their reported tolerance or sensitivity to low pH and salinity. In addition, the revised South African Water Quality Guidelines for Irrigation Decision Support System (SAWQI-DSS) was used to run long-term simulations and assess the use of mine water for irrigation under conditions that could not be included in the trials (Du Plessis et al., 2017a).

1.2 Aims

The aim of this study was to investigate crop response to foliar spraying and irrigation with mine water, using the water from the Witwatersrand Goldfields as a water quality reference. The study also aimed to investigate if crops produced by irrigation with mine water would be safe for human and livestock consumption. In addition, the potential use of the SAWQI-DSS in predicting long-term effects of crop irrigation with mine water was also explored.

1.3 Hypotheses

- Crop response to irrigation with mine water will be influenced by soil properties and crop tolerance/sensitivity to water constituents
- Food and fodder safety of crops irrigated with mine waters will be influenced by soil properties and crops propensity to accumulate potentially elements

1.4 Objectives

- Determine the effects of goldfield mine water on selected soil chemical properties
- Determine if wetting the crop canopy with mine water will cause foliar injury
- Investigate the effect of mine water on the growth and yield of selected crops
- Determine if selected elements will accumulate to phytotoxic and zootoxic levels in crops
- Explore the potential use of SAWQI-DSS in modelling the long-term effects of irrigation with mine water emanating from the goldfields

Chapter 2: Literature review

2.1 Mine water history and AMD

South Africa is renowned for its abundance of economically important minerals which account for a significant portion of the world's mineral reserves. The country's geological formations bear 11% of the world's gold reserves and 96 % of the platinum group metals, along with a host of other minerals including diamonds, coal and iron ore (GCIS, 2016). The recognition of South Africa's mineral wealth and subsequent establishment of its mining industry was initiated by the discovery of diamonds in 1867 and propelled by the discovery of gold in 1886 (Chamber of Mines, 2016; GCIS, 2016). Since then, thousands of mines have gone in and out of operation in the mineral-rich parts of the country. The manner in which the minerals are deposited in the rock layers has led to deep and extensive mining activities, as seen in the Witwatersrand Goldfields, where mining has reached depths of 4 km below the surface (Chamber of Mines, 2016).

In South Africa, two types of mining activities take place; surface mining and underground mining (Ochieng et al., 2010). The mining activities include the excavation of mineral-bearing rock, followed by processing of the rock and disposal of waste materials. During mining, disulphide compounds become exposed and in the case of underground mining, tunnels and voids are created (Durand, 2012). The underground tunnels and voids created during the mining process are prone to infiltration by surface or groundwater. Under oxic conditions, disulphide minerals exposed by mining activities react with the water that enters underground tunnels and voids to produce an acidic, sulphate and iron-rich solution. The acidity of the solution then facilitates the dissolution of other metals/metalloids, completing the process of AMD formation.

Under normal operations, the mine water is pumped out of underground workings and treated, which lowers the water table and disrupts groundwater movement (Wolkersdorfer, 2008). When treatment and dewatering activities cease, the water table returns to its former level and the underground workings and voids become flooded, resulting in the discharge of mine water into surface environments. The cessation of treatment and dewatering activities was very prevalent in the earlier years following the establishment of the mining industry, when mining companies would abandon mines. The irresponsible abandonment of mines was the result of a lack of legislative framework to enforce environmental protection and rehabilitation in the mining sector. In 2007, the number of abandoned, ownerless mines had reportedly reached in excess of 5000. In some areas, mines owned and operated by different companies had become interconnected, further complicating the assignment of environmental responsibility (Banks, 2011). Over time, as mines in an area are abandoned, water accumulates in these abandoned mines and begins to discharge into adjacent operational mines. The receiving operational mines then bear the responsibility of pumping and treating the water from the abandoned mines. Often the financial burden of treating and pumping mine water becomes so overwhelming that the remaining mines are also forced to shut down their operations, which results in the discharge of the mine water into surface environments.

In the Witbank Coalfields, AMD had already become a concern by 1998. One case study found that seepage of AMD from backfilled open cast mines and old underground workings was contaminating the Humanspruit. Despite the attempt to contain the AMD by discharging it into pollution reservoirs, high rainfall during rainy seasons overfilled the reservoirs and the water seeped into the stream. In another study, focusing on the Middelburg Colliery, surface subsidence and underground spontaneous combustion were implicated in the flooding of underground mine workings and the generation of AMD. AMD from the abandoned mine discharged into the Blesbokspruit, a part of the Olifants River Catchment. In the Witwatersrand Goldfields, flooding of underground mines reached a peak in 2002 and the water began to discharge into Tweelopiespruit. The contaminated water migrated downstream, impacting environments along its path, which included the Krugersdorp Game Reserve and the Cradle of Human Kind (Department of Water Affairs, 2010).

A common characteristic of water affected by AMD is the low pH, high concentration of sulphates and potentially toxic metals, as well as high salinity. The quality of mine water is highly influenced by the chemical composition of the geological strata in the area, as is demonstrated in the Witwatersrand Basin. The Western and Central Basins of the Witwatersrand produce typical AMD, while the Eastern Basin produces near neutral water with lower sulphate and potentially toxic metal concentrations.

The seemingly better water quality produced in the Eastern Basin is largely attributed to the dolomitic layers that cover it and the ingress of dolomitic water supplied by the dolomitic aquifer in its vicinity. The dolomite increases the pH of the mine water and, in the process, reduces metal and sulphate concentrations (Department of Water Affairs, 2013b). In contrast, there is no ingress of dolomitic water in the Central and Western Basins, which are buried beneath the Black Reef Formation and overlain by a thin layer of dolomite. In the case of the Western Basin, the dolomitic layer has decomposed into an iron-manganese oxide mixture, with little or no acid neutralizing capability. In the Central Basin, the Black Reef Formation is separated from the dolomitic layer by volcanic rock which precludes the interaction between the dolomite and basin's mine water.

The quality of the mine water produced in the Western, Eastern and Central Basins of the Witwatersrand Goldfields is presented in Table 2.1. Due to the inconsistencies in the available data, constituent values from various sources were consolidated and are presented as ranges. The minimum values are 5^{th} percentiles, which represent the best mine water quality and indicate that 5% of the time the water constituents will be at the specified level or lower. The maximum values are 95^{th} percentiles, which represent the poorest mine water quality and indicate that 95% of the time the water constituents will be at the specified level or lower. With regard to pH, the minimum values are the 95th percentiles and the maximum values are 5^{th} percentiles.

Table 2.1: Western, Central and Eastern Basin water quality before treatment

Constituent		Western	Central	Eastern
Aluminium	**(mg/l)**	2 - 54	44 - 193	0.3 – 2
Calcium	**(mg/l)**	419 - 823	483 - 583	421 – 550
Chloride	**(mg/l)**	*40	253 - 260	184 – 260
Iron	**(mg/l)**	662 - 954	108 - 1000	135 - 370
Magnesium	**(mg/l)**	*150	161 - 380	165 - 230
Manganese	**(mg/l)**	56 - 312	20 - 60	4 - 10
Sodium	**(mg/l)**	65 - 243	150 - 185	264 - 325
Sulphate	**(mg/l)**	2366 - 3623	2831 - 5200	1383 - 3275
EC	**(mS/m)**	320 - 442	397 - 730	322 - 450
pH		3.5 – 6	2 - 3	5 - 7

Data sources: Department of Water Affairs (2013b), Table 6.12; Fey et al. (2013), Table1.
*No data, estimated by Fey et al. (2013).

2.2 Mine water management

As part of a short-term intervention, mine water in the Witwatersrand Basins is being neutralized using a method called the High-Density Sludge (HDS) process and discharged into freshwater bodies. During this process, acid mine drainage is fed into a reactor that contains sludge mixed with lime to increase the pH. This step also serves to precipitate some metals such as Al, Fe and Mn (Aubé and Zinck, 1999). The water is then fed into an aeration tank to oxidize Fe into a more stable form, and then fed into a clarifier to separate the solid and liquid phases (Aubé and Eng, 2004). This neutralization process produces a gypsiferous solution, with a lower concentration of potentially toxic metals and higher pH values than the untreated water (Department of Water Affairs, 2010). The process also produces a sludge that is rich in iron, manganese and aluminium oxides, as well as calcium carbonate and needs to be disposed of safely (Department of Water Affairs, 2010).

Although the water produced by HDS is of an improved quality, salinity remains a concern. Hence, this treatment alone is only intended to operate for three to five years. The long-term management strategy requires a supplementary desalinization step, to ensure the production of a potable water quality. A feasibility study conducted by the Department of Water Affairs (2013c), identified reverse osmosis

(RO) as the preferred method for desalinization of the neutralized mine water. The method uses high pressure to force water through a semi-permeable membrane, producing a concentrated brine solution that needs disposal, and purified water that can be used for domestic and industrial purposes.

The appeal of treating mine water by HDS neutralization and RO, to produce potable water, is somewhat overshadowed by the costs that are associated with the establishment and operation of the treatment plants. The capital cost of implementing the long-term management strategy in the Witwatersrand Basins was projected to amount to R10 billion (Bobbins, 2015). If changes in the currency and inflation are taken into consideration, the amount can be expected to increase significantly by the time of implementation. Thus far the Department of Water and Sanitation (DWS) has reportedly spent an estimated R385 million on mine water management and committed R600 million per year towards implementing the long-term solution (Department of Water and Sanitation, 2016a, b). In addition, RO is an energy-intensive process, which raises concerns about the carbon footprint. In the Witwatersrand, the energy that will be required for RO is estimated to range between 2.7 and 3 kW/m^3 treated AMD in the Western Basin, 1.4 and 1.8 kW/m^3 treated AMD in the Central Basin and 1.3 to 2.8 kW/m^3 treated AMD in the Eastern Basin.

Owing to the high cost and energy requirements of treating mine water by HDS neutralization and RO, other cost-effective, energy efficient management options are being considered (Department of Water and Sanitation, 2016a). One of the options that have been suggested for managing mine water, is to use it for irrigation. Irrigating with the acidic water would eliminate the need to build HDS treatment plants, as well as the need for waste disposal measures. If irrigation with the acidic water is found not to be feasible, irrigation with neutralized water would serve as a good alternative for utilizing the mine water without having to treat it any further, thereby saving financial and energy costs of RO.

2.3 Irrigation as a mine water management strategy

The concept of irrigating with mine water in South Africa can be traced back to a study by Du Plessis (1983), in which the potential use of lime treated acid mine water for irrigation was evaluated. Du Plessis (1983) used a chemical equilibrium model to predict the effects of gypsiferous mine water on crop yield as well as soil chemical and physical properties. A reduction in soil solution conductivity (ECe) was noted for all leaching fractions applied in the model (0.05 - 0.5), which suggested the occurrence of gypsum precipitation. Using a salinity-yield relationship, Du Plessis (1983) demonstrated that certain crops could successfully be grown under irrigation with gypsiferous mine water. Du Plessis (1983) did not predict any concerning changes in soil physical properties resulting from the use of the mine water.

Jovanovic et al. (1998) put the theory presented by Du Plessis (1983) to the test in a field screening trial, conducted at a colliery in Mpumalanga. In their study, they irrigated selected crops with lime-treated acid coal mine water and found that crops such as soybean, cowpeas and pearl millet produced satisfactory yields. The successful production of certain crops irrigated with neutralized mine water was attributed to crop tolerance to salinity. Jovanovic et al. (1998) also observed a substantial increase in the pH of the soil irrigated with the lime-treated mine water, suggesting that irrigation with such water can ameliorate acid soils. In other related studies, Annandale et al. (2001); Annandale et al. (2002) further investigated the use of gypsiferous mine water for irrigation by means of field and glasshouse trials, as well as undertaking long-term modelling simulations. The trials indicated that, in addition to having little or no detrimental effect on the growth of most crops, the use of gypsiferous mine water for irrigation could improve the yield of certain dryland crops. Their long-term modelling simulations demonstrated that large volumes of gypsiferous mine water could be utilized, through irrigation, without salts building up to unacceptable levels.

The concept of irrigating with mine water was taken a step further when acidic saline mine water was presented as a candidate for irrigation water. Cronce et al. (1980) explored this concept by applying acid coal mine water to floodplain soil planted with tall fescue and ryegrass. It was observed that the mine water had no adverse effect on the crops' growth and liming the soil significantly improved growth, suggesting that soil properties were influential in mitigating the effects of acid coal mine water.

2.4 Agronomic effects of selected mine water constituents

2.4.1 Acidity

Acidity in agricultural soils and waters is known to have detrimental effects on crop growth and quality. Overhead application of acidic waters on crops has been found to cause foliar injury and yield reductions in several species. Lee et al. (1981) conducted a study in which selected dicotyledonous crops which included beet, Swiss chard, potato, soybean, lucerne, green pea and green pepper and monocotyledonous crops which included barley, wheat, maize, onion, and fescue were subjected to spraying with simulated acid rain at pH 3.0, 3.5 and 4.0 in a greenhouse. In their study, dicotyledonous crops were typically found to be more susceptible to foliar injury by acid rain than monocotyledonous crops. The small grains, oat and wheat, were found to be the least susceptible to foliar injury by acid rain, showing no signs of injury even at the lowest pH (3.0). Beet, Swiss chard, green pepper and soybean were most susceptible to foliar injury by acid rain, showing injury at the highest pH (4.0). Lee et al. (1981) found that for most crops, foliar injury was not associated with decreases in the marketable yield.

Foliar injury by acid rain has been associated with the direct effects of protons and the indirect effect of acidity which can alter the morphology of leaves. According to Evans (1984), changes in proton concentrations in cell membranes cause disruptions in the plasmalemma of leaf cells which induces necrosis. In a study by Da Silva et al. (2005) leaves of plants treated with simulated acid rain at pH 3 developed ruptures in their cuticles and epidermal cells. In a study by Percy and Baker (1987), exposure to acid rain influenced the production and composition of epicuticular wax. They also found that the thickness of the cuticular membrane of dwarf beans and peas decreased when the leaves were treated with simulated acid rain with a pH between 4.2 and 2.6.

Another concern with the use of acid saline mine water for irrigation is that such water can acidify soils. The increase in H^+ resulting from soil acidification can have direct and indirect effects on crop growth and yield (Alam et al., 1999). Yan et al. (1992) studied the effect of H^+ activity on root growth of maize and broad beans in solutions with pH between 4.5 (32 µmol/L H^+) and 3.5 (316 µmol/L H^+). In their study, Yan et al. (1992) found that the root growth of maize and broad beans decreased notably as H^+ ion activity increased. The decrease in root growth was attributed to a decrease in net H^+ release by the roots and re-entry of protons into the root cells. It was suggested that these dynamics disturb the regulation of cytoplasmic pH in the root cells.

A study by Fageria and Zimmermann (1998) showed that pH affects the solubility, and therefore the availability, of plant nutrients. In their study, it was found that Ca and Mg uptake decreased as soil pH decreased and uptake of Zn, Mn and Fe increased as soil pH decreased. Acid rain studies also demonstrated that the application of acidic water to soil increases the mobility and phytoavailability of potentially toxic elements. In a study by Nawaz et al. (2013) the application of acidic solutions with pH levels ranging between 2.0 and 3.5 was found to increase the mobilization of Al, Fe and Mn. Mobilization of these metals was found to increase with decreasing pH.

It should be noted that the severity of acidic water effects will vary depending on the ionic composition of the water. For instance, acidic waters that contain hydrolysable cations (Al, Fe and Mn) will have more severe acidity effects on crop growth and quality than acidic waters that are non-saline and contain non-hydrolysable cations (Ca, Na and K). This is because hydrolysable cations can generate more acidity through hydrolysis, oxidation and precipitation reactions.

2.4.2 Al, Fe and Mn

As indicated in section 2.1, mine water from the Witwatersrand Goldfields typically contains high concentrations of Al, Fe and Mn. These metals are known to be detrimental to crop growth if soluble forms of these elements are present in high concentrations, specifically forms that are primarily taken up by crops, which are Al^{3+}, Fe^{2+}, and Mn^{2+} (Dramé et al., 2010; Mukhopadhyay and Sharma, 1991; Poschenrieder et al., 2008). Soils commonly contain high concentrations of the elements. However, these elements are unlikely to cause toxicity when they are in immobile forms or forms that are not easily absorbed by crops, such as amorphous oxides and hydroxides (Barker and Pilbeam, 2015).

The phytoavailability of Al, Mn and Fe is influenced by biogeochemical processes that alter soil pH and redox potential. A decrease in soil pH, particularly below pH 5.5

is known to result in an increase in phytotoxic concentrations of Al^{3+} and Mn^{2+}. However, Al toxicity has been reported in soils with a pH greater than 9.0 (Barker and Pilbeam, 2015; Brautigan et al., 2012). As indicated in the previous section, a decrease in soil pH can also increase Fe concentrations, but in oxidized soils, Fe toxicity is usually not a concern as applied and mobilized Fe^{2+} is often rapidly oxidized to Fe^{3+}, which rapidly precipitates to form sparingly soluble oxides which are not readily taken up by crops (Lindsay, 1995). Fe toxicity is often a problem in waterlogged soils, were conditions are reducing (Khabaz-Saberi et al., 2006).

Aluminium

Al toxicity has been found to reduce the growth of roots and is reported to be responsible for the inhibition of cell division in sensitive crops (Delhaize and Ryan, 1995; Matsumoto, 2000). Lidon and Barreiro (1998) studied the effects of Al toxicity on crop growth by growing maize in solution culture containing Al concentrations of 0, 9, 27 and 81 mg/L. In their study root and shoot biomass production of maize decreased in the solution that contained the highest Al concentration (81 mg/L). The decrease in biomass production was attributed to inhibition of root development, which they related to Al inhibiting cell division in the root apex and Al being adsorbed onto the carboxylic groups of pectin in root cells. In lucerne, high concentrations of Al in the growth medium were found to inhibit root elongation (Yokota and Ojima, 1995). In their study, Yokota and Ojima (1995) placed lucerne seedlings in a rooting solution (pH 5) containing 20 $mmol/m^3$ Al and found that Al can be toxic to roots even in the absence of low pH stress.

Manganese

Excessive concentrations of Mn are often associated with a reduction in the shoot growth of crops. However, the direct physiological effects of Mn toxicity are not well understood. It has been reported that Mn excess decreases photosynthesis and induces oxidative stress in crops (Millaleo et al., 2010). Symptoms of Mn toxicity include leaf chlorosis, necrosis and curling, as well as the appearance of brown necrotic spots on leaves (Mukhopadhyay and Sharma, 1991). Peas grown in solution culture containing 0 to 300 mg/L Mn for 15 days, began to show signs of Mn toxicity at an Mn solution concentration of 100 mg/L (Rezai and Farboodnia, 2008). The toxicity symptoms manifested as leaf chlorosis at a solution concentration of 100 mg/L and progressed to necrotic and brown spots as the concentration increased. In the study by Rezai and Farboodnia (2008), an increase in solution Mn concentration (>25 mg/L) was associated with a decrease in root and shoot growth. It has also been reported that when manganese is present at high concentrations, it is oxidised and deposited in roots, where it reduces water uptake and nutrient absorption (El-Jaoual and Cox, 1998).

Iron

Fe is often not available in excess in most biological systems. Rather, Fe deficiency is often more of a problem than Fe toxicity in crop production. However, Fe toxicity is typically prevalent in soils that are not well aerated, such as waterlogged soils. According to Dramé et al. (2010), Fe can affect crop growth by coating the roots with iron, thereby decreasing nutrient uptake, and by accumulating to toxic concentrations in the crop. High concentrations of Fe in plant tissue can induce the production of toxic reactive oxygen species that damage cells (Becker and Asch, 2005).

In a study by Pinto et al. (2016), oxidative stress induced by iron toxicity was studied by growing rice in solution culture containing 0 – 500 mg/L Fe. Fe toxicity symptoms appeared in crops grown in 250 mg/L Fe solutions, and leaf Fe concentrations were approximately 3000 mg/kg dry mass. Pinto et al. (2016) also found that toxic levels of Fe in the solution increased shoot Fe content, along with hydrogen peroxide and other compounds associated with oxidative stress. De Dorlodot et al. (2005) found that the root surface of rice that was grown in nutrient solutions containing 125 to 500 mg/L of Fe^{2+} became coated with orange-brown deposits, referred to as a root ‘coat’. The root coat contained nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), Al, copper (Cu), Fe, Mn, molybdenum (Mo) and sodium (Na), which made up 38% of the coats dry mass. Fe and P were the most abundant of the elements present in the coat, Fe made up 30 % and P made up 3%, of the 38%. De Dorlodot et al. (2005) suggested that the oxidation of Fe^{2+} outside of the root, resulting in coating, is a response mechanism to prevent accumulation of Fe^{2+} to toxic concentrations in crops. The root coat was associated with a decrease in P, Ca, Mg, Cu, Mn and Mo observed in the shoot of crops that were grown in the 125 mg/L Fe solution. De Dorlodot et al. (2005) also found that the crops started showing symptoms of iron toxicity, which manifested as bronzing of leaves when they were grown in solutions exceeding 250 mg/L Fe.

Al, Fe and Mn interactions

An antagonistic interaction has been reported to take place in the rootzone whereby the presence of one element, hinders the uptake of another (Fageria, 2001). Fe and Mn, for example, have been found to interact such that high concentrations of Fe reduced the uptake of Mn and vice versa (El-Jaoual and Cox, 1998). The antagonistic interaction between certain elements can have a negative effect by inducing deficiency or a positive effect by alleviating toxicity.

An example of the negative and positive effects of the antagonistic interactions between certain elements was demonstrated in a study done by Alam et al. (2002), whereby manganese toxicity was alleviated with iron. In their study, crops grown at the highest Mn concentration (2.5 μmol/L) and lowest Fe concentration (10 μmol/L), showed signs of manganese toxicity and iron deficiency. Fe deficiency was attributed to Fe being replaced by the excess Mn, likely due to the competition between Fe and Mn ions which have similar properties. On the other hand, crops grown at an Fe level of 100 μmol/L and an Mn level of 2.50 μmol/L, did not show signs of Fe deficiency but exhibited reduced symptoms of Mn toxicity. Alam et al. (2002) suggested that the higher availability of Fe created a balance between the Mn and Fe ions, decreasing the effects of Mn toxicity.

Al and Mn have been found to have a synergistic and antagonistic interaction depending on the concentration present in the growth medium. Taylor et al. (1998) studied the combined effects of Al and Mn on crop growth by planting cowpea in solutions containing a combination of Al and Fe at varying concentrations. They found that low concentrations of one element had no effect on the accumulation of the other, but higher concentrations of one decreased the accumulation of the other. Wang et al. (2015) conducted a similar study by growing rice in solution cultures with no Al and others with 200 μmol/L Al, with incremental concentrations of Mn (6.7, 200, 500 and 1000 μmol/L). They found that crops grown without Al had high concentrations of Mn in roots and shoots, whereas the addition of Al decreased shoot Mn concentrations, while root Mn concentrations remained high. This suggested that Al activity decreased the translocation of Mn to the shoots.

In addition to its effect on root growth, Al is known to affect the uptake of other nutrients when available at high concentrations. Al toxicity often manifests in a similar way to symptoms of phosphorus, calcium and iron deficiency (Rout et al., 2001). In a study by Choudhary and Singh (2011), the effect of Al concentration on nutrient uptake in pigeon pea was investigated by growing the crop in nutrient solutions with Al concentrations ranging from 0 to 205 μmol/L Al for 24 hrs. Choudhary and Singh (2011) found that root and shoot Ca and Mg concentration decreased with an increase in Al concentration of the nutrient solution. The decreases in Ca and Mg concentrations were attributed to Al competing with these elements for common binding sites involved in nutrient uptake. In maize, Al was also found to reduce K, Mn and Zn uptake when the crop was grown in solution culture containing 100 μM Al for 14 days.

Assessing zootoxicity of Al, Fe and Mn

The accumulation of Al, Fe and Mn in plants is not only a concern for phytotoxic implications but also poses a health risk to humans and animals if these metals accumulate in crop organs that are used for food or animal feed. Maximum tolerable levels of dietary Fe and Mn intake for selected livestock are provided in Table 2.2. Although aluminium is a potentially toxic element, it is unlikely to be present in excessive levels in fodder. The maximum tolerable level of dietary Al is, therefore, reservedly reported as 1000 mg/kg dry diet for most domestic livestock (NRC, 2005).

Table 2.2: Maximum tolerable levels of dietary Fe and Mn for selected livestock (Chaney, 1989; NRC, 2005).

	Fe	**Mn**
	mg/kg dry diet	
Cattle	40 -1000	1000 - 2000
Sheep	60	1000 - 2000
Poultry	1000	2000
Pigs	3000	400 -1000

It should be noted that the zootoxic effects of hazardous elements are typically dependent on dose and influenced by factors such as body mass and age. Thus, in human nutrition, health risks associated with consuming foods that contain potentially toxic elements are assessed by determining hazard quotients (HQ) or health risk indices (HRI), which account for these factors.

HQ is the ratio between potential exposure to a contaminant and the level at which an adverse effect is unlikely to be observed. It is determined using equation 2.1, where W_{plant} is the dry mass of plant material consumed per day (in kg/day), M_{plant} is the concentration of the potentially toxic element in plant material (in mg/kg), R_fD is the oral reference dose for the potentially toxic element (in mg/kg body mass/day) and B is the body mass of the consumer (in kg)(Chary et al., 2008). An HQ of less than one indicates that there is no obvious health risk if the contaminated food is consumed. An HQ greater than or equal to one indicates that there will be health risks if the contaminated food is consumed.

$$HQ = \frac{W_{plant}\text{ (kg/day)} \times M_{plant}\text{ (mg/kg)}}{R_fD\text{ (mg/kg body mass/day)} \times B\text{ (kg body mass)}} \quad (2.1)$$

HRI is similar to HQ and is calculated as the ratio of the daily intake of metals (DIM) and R_fD using equation 2.2 (Khan et al., 2008). DIM is calculated using equation 2.3, where C_{metal} is the metal concentration in the plants (in mg/kg), C_{factor} is the conversion factor used to convert fresh green vegetable mass to dry mass (in kg dry mass/kg wet mass), D_{food_intake} is the daily vegetable intake (in kg wet mass/ day) and $B_{average\_mass}$ is the average body mass (in kg).

$$HRI = \frac{DIM\text{ (mg/kg body mass/day)}}{R_fD\text{ (mg/kg body mass/day)}} \quad (2.2)$$

$$DIM = \frac{C_{metal}\text{ (mg/kg)} \times C_{factor}\text{ (kg drymass/kg wet mass)} \times D_{food\ intake}\text{(kg wet mass/day)}}{B_{average\_mass}\text{ (kg body mass)}} \quad (2.3)$$

HRI and HQ calculations are useful tools for assessing risks associated with exposure to potentially toxic metals in crops. However, they require an input of oral reference dose values, which are not available for potentially toxic elements such as Al and Fe. As a result, the health risk associated with consuming foods that contain these metals cannot be assessed by determining HQ or HRI. The Joint Food and Agriculture Organization/World Health Organisation has, however, established a provisional tolerable weekly intake of 1 mg/kg body mass (bm) for Al, and a provisional maximum tolerable daily intake (PMTDI) of 0.8 mg/kg bm for Fe (FAO-

WHO, 2011). These provisional reference intakes can be used to assess the health risks associated with Al and Fe intake through consumption of crops irrigated with mine waters.

2.4.3 Salinity

Salinity in irrigation water is commonly caused by high concentrations of dissolved Cl^- or SO_4^{2-} salts, in the form of NaCl, Na_2SO_4 and $CaSO_4$. The different forms of salts have been found to have varying effects on crops. Sulphate salts have been found to be less destructive to crop growth than chloride salts (Yaron et al., 2012). Rogers et al. (1998) compared the effects of sulphate and chloride salinity by growing lucerne in sandy soils at EC levels ranging between 210 and 1720 mS/m, achieved by adding salts in the form of Na_2SO_4 or NaCl. In their study, they found that lucerne was more sensitive to salinity induced by NaCl, than that induced by Na_2SO_4. Rogers et al. (1998) suggested that the difference in crop sensitivity to the two types of salinity was due to Cl^- being absorbed at higher rates than sulphate.

NaCl salinity in irrigation water is often associated with foliar injury, especially when the water is applied through sprinkler irrigation (Maas, 1985). The injury of crops sprinkled with NaCl saline water is associated with the absorption and accumulation of Na^+ and Cl^- in the leaves, which have been found to be toxic at high concentrations. In a study by Maas et al. (1982), the effect of NaCl salinity on foliar injury in crops was investigated. Crops were sprinkled with saline water, prepared by adding NaCl and $CaSO_4$ (9:1) to demineralized water, to achieve ECs of 180, 340 and 650 mS/m. Maas et al. (1982) found that barley, lucerne, sorghum, tomato and potato were susceptible to foliar injury when sprinkled with 15 meq/L (180 mS/m) and 30 meq/L (340 mS/m) NaCl. Leaf analyses showed that Na^+ and Cl^- accumulated over time, leading to foliar injury which appeared as tip and marginal necrosis in some crops and necrotic spotting in other crops.

In a study done by Benes et al. (1996), NaCl accumulation was found to be higher when applied to leaves than when applied to soils. Barley that was grown on non-saline soil but sprinkled with saline water (EC 420 mS/m) developed foliar injury, whereas barley grown on saline soils, with no salinity applied to the leaves, did not develop foliar injury. One of the mechanisms used by crops to mitigate the effects of soil salinity, particularly salinity caused by sodium and/or chloride salt, is by Na^+

and/or Cl^- exclusion. Benes et al. (1996), suggested that the foliar application of NaCl salinity could overcome the aforementioned salinity tolerance mechanism since this mechanism usually operates at the root level. In addition to foliar injury, leaf sprinkling with saline water also reduced the vegetative biomass of barley more than when the saline water was only applied to the soil.

Irrigation with saline water also leads to an accumulation of salts in the soil, which affects water uptake of crops, thereby reducing growth (Volkmar et al., 1998). Maize irrigated with water at three salinities and three Sodium Adsorption Ratios (SAR) showed a decrease in fresh biomass yield as salinity and SAR increased (Abid et al., 2001). It was suspected that the reduction of growth was due to the osmotic effect of the salts. According to Abid et al. (2001), the accumulation of salts in the soil causes changes in the osmotic potential which in turn affects the availability of water to crops. Under such conditions, plants struggle to maintain turgor, resulting in the observed decrease in height and biomass yield.

2.5 Response mechanisms and crop tolerance

Studies have shown that different crops respond differently to stress caused by acidity, salinity and high concentrations of potentially toxic metals in irrigation water and soil (Fageria and Zimmermann, 1998; Maas, 1985). These differences are attributed to genotypic variation between crop species, which exhibit different physiological responses (El-Jaoual and Cox, 1998; Garvin and Carver, 2003). These physiological properties confer tolerance or resistance to crop injury and accumulation of toxic elements, through physical barriers or biochemical response mechanisms (Matsumoto, 2000; Rao et al., 1993).

Resistance to foliar injury and penetration of toxic substances is widely attributed to the leaf structure, particularly the cuticle. The cuticle, among other functions, acts a protective barrier and regulates the flux of ions in leaves (Haynes and Goh, 1977). The surface of the cuticle is covered in a waxy layer that can minimize leaf wetting and thus reduce the rate at which ions are absorbed (Maas, 1985). However, it has been reported that in some species, the amount of wax on the cuticle does not contribute to protection against foliar injury and the absorption of harmful substances. In a study done by Percy and Baker (1987), crop species with the thickest layer of wax were injured the most by simulated acid rain.

Plant leaves have also been found to have pH buffering capabilities. It has been suggested that some plants release acid neutralizing substances when their leaves come into contact with acidic water (Evans, 1984). Certain cations such as Ca^{2+}, interfere with the movement of protons in and out of cells and thereby reduce the damage that is caused by acid water on leaves (Smalley et al., 1993). When crops are exposed to acidity, salinity and/or toxic concentrations of certain elements in the rootzone, they employ response mechanisms such as ion retention/accumulation or exclusion/exudation in organs to mitigate the effects (Delhaize and Ryan, 1995; Rao et al., 1993).

In their study on foliar and root absorption of Na and Cl, Benes et al. (1996) found that maize was highly effective in excluding Na from its leaves when exposed to soil salinity. The same mechanism of Na exclusion was suspected to be used by sorghum grown under salt stress in an experiment by Yang et al. (1990). According to Horiguchi (1987), root retention of toxic ions is not the only way in which crops are able to tolerate high concentrations of ions, and a crops ability to retain Mn is not a sign of tolerance. In a study on crop response to toxic levels of Mn in the growth media, Horiguchi (1987) found that Mn tolerant rice accumulated high levels of Mn in the leaves, without showing signs of toxicity. It was also found that although lucerne retained high concentrations of Mn in the roots, it was still susceptible to toxicity.

In addition to internal responses, crops can also alter the immediate external environment to reduce the effects of stress. According to Delhaize and Ryan (1995), results from a study done on Al tolerance in wheat suggest that excretion of malate from the roots serves as a mechanism for aluminium tolerance. Malates and other organic acids such as citrates bind Al in the form of organic complexes that are not toxic to plants (Jones, 1998). In a study by Pellet et al. (1997), it was found that Al-tolerant wheat genotypes employ multiple exclusion mechanisms to reduce the effects of Al toxicity. In their study, they found that in addition to a malate exudation, the Al-tolerant genotypes also exuded phosphate. Phosphate decreases the mobility, and therefore the availability of Al, through precipitation/sorption reactions that bind the Al. Mugwira et al. (1978) found that Al tolerant crops accumulated less Al in the roots than sensitive crops, but when pH in the growth medium was increased, the difference in Al accumulation between the Al tolerant and sensitive crops decreased.

They interpreted this result as an indicator that Al tolerance in some species might be related to its ability to increase rootzone pH.

2.6 Soil-water-interactions

Soils, like plants, respond differently to irrigation water constituents owing to differences in chemical and physical properties of the various soil types. The fate of water constituents in soil is controlled by the chemical reactions that occur in the soil solution as influenced by the biotic and abiotic components of soils. According to Vries et al. (1989), one of the main processes that contribute to a soil's response to acidity is the exchange between base cations and protons. A soil's ability to exchange cations is referred to as the cation exchange capacity CEC (Essington, 2003). In soils, the main contributors to CEC are clay minerals and organic matter. Typically soils with a higher CEC are more capable of resisting changes in pH due to acidity than soils with a low CEC (Jiang et al., 2016).

In addition to conferring acid buffering capabilities to soils, clay minerals and organic matter play an important role in controlling the mobility of potentially toxic elements. In a study on the effects of acid rain on the mobility of Al, Fe and Mn, Nawaz et al. (2013) compared the mobility of these elements in three soils, two clay soils and a sandy soil. The investigators found these elements were mobilizable in the sandy soil, which they attributed to its low CEC. It has been reported that soil organic matter decreases the mobility and phytoavailability of Al by complexation (Bona et al., 1993). In a study by Wong and Swift (1995), the effect of organic matter on Al^{3+} activity was investigated by adding humic acidic, the main component of organic matter, to two acidic soils with Al^{3+} activities of 38 µmol/L and 11 µmol/L. Addition of humic acid to the soils decreased the Al^{3+} activities to 11 µmol/L and 2 µmol/L. Wong and Swift (1995) concluded that the humic acid decreased Al^{3+} activity by decreasing its solubility and increasing soil selectivity for exchangeable Al.

Another important process in soils that can influence crop growth, particularly in soils irrigated with mine water, is the precipitation of salts. Papadopoulos (1984), investigated the effects of irrigation with sulphate water on soil salinity by applying water that contained 16 or 32 meq/L SO_4^{2-} and 15 or 30 meq/L Ca^{2+}. Papadopoulos (1984) found that Ca^{2+} and SO_4^{2-} concentrations increased to a point whereby they exceeded the solubility of gypsum, resulting in its precipitation. Due to the salts low solubility, gypsum precipitation is a favourable reaction as it minimizes salinity effects (Papadopoulos, 1984).

2.7 Irrigation water quality: fitness-for-use assessments and long-term effects

In light of the contribution water quality makes to crop growth, yield and quality, many countries have developed water quality guidelines with the aim of equipping users with information that will assist them in assessing the fitness-for-use of a given water quality for irrigation purposes. These water quality guidelines are also aimed at advising users on best management practices when using water of a certain quality. The guidelines present information on water constituents that are known contributors to crop yield and have an impact on soil properties, as well as irrigation equipment.

A summary of acceptable ranges for selected water quality constituents, particularly those associated with mine water, are presented in Table 2.3 The South African Water Quality Guidelines provide target values that represent the level at which a given water constituent will not affect sensitive crops. In the Australian and Canadian water quality guidelines, the guideline values presented are referred to as trigger values and they represent the maximum levels that can be tolerated by sensitive crops. The Australian and Canadian guidelines provide values that represent long-term (100 years) and short-term (20 years) irrigation, with the values presented in Table 2.3 representing long-term irrigation. The Na and Cl guideline values presented in the table represent concentrations that are likely to cause foliar damage in sensitive crops if sprinkler irrigation is used.

Table 2.3: Summary of acceptable water quality values and ranges for selected constituents as indicated by the South African, Australian, Canadian and FAO irrigation water quality guidelines.

		South African[1]	Australian[2]	Canadian[3]	FAO[4]
pH		6.5 - 6.8	6.0 - 7	6.4 - 8.9	6.5 - 8.4
EC	**(mS/m)**	40	≤65	50 - 400	70 - 300
Al	**(mg/L)**	5	5	5	5
Fe	**(mg/L)**	5	0.2	5	5
Mn	**(mg/L)**	0.2	0.2	0.2	0.2
Na	**(mg/L)**	70	<115	<115	<117
Cl	**(mg/L)**	100	<175	100	<117

1. Department of Water Affairs (1996)
2. ANZECC (2000)
3. CCME (2008)
4. FAO = Food and agricultural organisation (Ayers and Westcot, 1985)

Although South African Water Quality Guidelines are one of the most widely used tools for assessing water quality, the version that has been most recently used has not been updated since 1996, and had, therefore, become outdated (Du Plessis et al., 2017a). Following an assessment by a panel of experts, mandated by the Department of Water Affairs (now DWS, Department of Water and Sanitation), a resolution was made to revise the guidelines (Du Plessis et al., 2017a). Very recently, the South African Water Quality Guidelines for Irrigation have been updated to a software-based decision support system that can perform generic and site-specific risk-based assessments by (Du Plessis et al., 2017a)

2.7.1 SAWQI-DSS description

This section provides a brief overview of the South African Water Quality Guidelines Decision Support System (SAWQI-DSS) as described by Du Plessis et al. (2017a). SAWQI-DSS is a risk-based site-specific decision support system that caters for the evaluation of fitness-for-use of a specified water quality. SAWQI-DSS software operates on three tiers, however, for the purpose of this study, only Tier 1 and Tier 2 will be discussed, as the third tier is not explicitly included in the DSS. Tier 1 of the SAWQI-DSS, generates generic guidelines similar to the 1996 guidelines. In this tier, minimum user defined input is required, and a conservative water quality assessment is performed. A Tier 1 assessment provides an indication of potential problems that can be encountered if water of a specified quality is used for irrigation. If the assessment does not identify any problems, the specified water is considered fit to irrigate all crops under most circumstances. If the assessment identifies a problem with the specified water, a more comprehensive assessment can be performed in Tier 2.

Tier 2 of the SAWQI-DSS generates site-specific guidelines by accounting for factors such as crop tolerance, soil type, irrigation management and climatic conditions, which can influence the fitness-for-use of water. In this tier, specific selectable input parameters are required and an assessment of the effects of irrigation water quality on specific crops, under specific climatic conditions, with defined irrigation management, on a specific soil texture is performed. A Tier 2 assessment provides an indication of how site-specific management options will influence the fitness-for-use of a specified water quality.

The SAWQI-DSS uses calculation procedures to assess interactions between water quality constituents, soil and crop water uptake. With Tier1 assessments, simplified assumptions are made, and analytical steady state calculations used. The calculation assumes an idealised 4-layer soil in which crop water requirements are met by withdrawing 10% of their water requirement from the bottom layer, 20% from the third layer, 30% from the second layer and 40% from the topmost layer. Furthermore, it is assumed that water is solely applied through sprinkler irrigation (i.e. the dilution effects of rain are not considered) and that the leaching fraction does not deviate from 0.1.

In Tier 2 assessments a simplified version of the Soil Water Balance (SWB) model is used to model interactions between water quality constituents, soil and crop water uptake. The model used in the DSS Tier 2 assessments is less mechanistic than the SWB crop growth model as it uses an FAO crop factor approach to estimate evapotranspiration. As a result, the DSS model does not account for feedback between water or salt stress and crop growth. The DSS model has, however, retained the cascading approach used in the SWB for estimating soil water content and redistribution, and determines water loss as being supply or demand limited.

The incorporation of climatic records, soil properties and irrigation management factors into the DSS allows the user to run site-specific simulations over several seasons and provides probability assessment overviews for specific yield intervals.

The SAWQI-DSS uses a colour coded classification system that categorises water quality into 4 levels of acceptability with implied risk (Table 2.4). When a Tier 1 assessment is conducted, the DSS calculates a single value for a specified parameter. For example, when trace element accumulation in soil is evaluated, the resulting output will be the number of years it will take for the trace elements to accumulate to an unacceptable level.

Table 2.4: Description of the SAWQI-DSS fitness-for-use categories (Du Plessis et al., 2017a)

Fitness-for-use category	**Description**
Ideal	A water quality that would not normally impair the fitness of the water for its intended use
Acceptable	A water quality that would exhibit some impairment to the fitness of the water for its intended use
Tolerable	A water quality that would exhibit increasingly unacceptable impairment to the fitness of the water for its intended use
Unacceptable	A water quality that would exhibit unacceptable impairment to the fitness of the water for its intended use

A Tier 2 assessment produces results in the form of percentages. The system calculates 10 or more annual mean values which are used to determine the percentage of time a value will fall into a specified fitness-for-use category. For both Tier 1 and Tier 2, water quality is evaluated according to its effect on soil quality, crop yield and quality, as well as irrigation equipment. The DSS shows great potential for use in assessing water quality for irrigation and being site-specific means, it will provide less conservative and more pragmatic results.

The aim of this study is to assess the use of mine water for irrigation. Due to the large volumes of water required by crops and the dynamic nature of mine water quality, it was decided that synthetic mine water would be used. Synthesizing the mine water allowed for the close monitoring and adjustment of the mine water quality and eliminated the need to frequently collect mine water from mine sites. The experimental procedures and findings of this study are presented in the chapters that follow. Chapter 3 provides a description of the materials and methods used to synthesize mine water, study the effects of mine water on selected soil chemical properties, study crop responses crop responses and assess the fitness-for-use of mine water using SAWQI. In Chapter 4, the effects of mine water irrigation on selected soil chemical properties are presented. Chapter 5 presents the results and discusses the effects of mine water irrigation on crop quality. In Chapter 6, the effects of irrigation with mine water on crop production and yield are discussed. Chapter 7 presents the results of the food and fodder safety evaluations. Chapter 8 presents fitness-for-use assessments for long term irrigation with mine waters, followed by a conclusion of the investigation.

Chapter 3: Materials and methods

3.1 Mine water synthesis

Following feasibility studies by the DWS, it was suggested that the Western Basin be used as the main site for pilot studies to explore alternative methods for managing mine water. In this regard, the aim of this experiment was to synthesize acidic and neutralized mine water based on the Western Basin mine water quality. Since the main concerns with the mine water from the Western Basin are the acidity, salinity and high concentrations Fe and Mn; the main objective was to obtain pH, EC, Mn and Fe values similar to those detected in the Western Basin mine water.

Due to the inconsistencies in mine water quality data from the Western Basin, synthetic mine water was designed based on estimated data by Maree et al. (2013), statistically analysed historic data by Fey et al. (2013) and Department of Water Affairs (2013b). The data from all the aforementioned sources was combined to establish a range within which the synthetic mine waters should reside as shown in Table 3.1.

Table 3.1: Target water quality range for synthetic acidic and neutralized mine water.

Constituent		Acidic	Neutralized
Al	(mg/L)	2-54	0
Ca		419 - 823	≥ 420
Cl		37 - 65	37 – 65
Fe		625 - 954	0.02 - 4.59
Mg		147 - 345	140 - 340
Mn		56 - 312	4.57 - 19.04
Na		50 - 243	50 - 243
SO_4^{2-}		2574 - 4800	2300 - 2700
EC	**(mS/m)**	417 - 548	< 425
pH		2.6 - 3.5	6.5 - 9.5

Mine water from the Western Basin is dominated by sulphates, thus the majority of salts used to generate the synthetic mine waters were sulphate salts. The following salts were used; $FeSO_4.7H_2O$, $MnSO_4.7H_2O$, $MgSO_4.7H_2O$, Na_2SO_4, $Al_2(SO_4)_3.18H_2O$, KCl and $CaCl_2$. The amount of salt required to obtain the desired concentration of each element or ion was calculated using equation 3.1. Details on the procedure are provided in Appendix A.

$$\frac{\text{mg salt}}{\text{L of water}} = \frac{\text{mg ion}}{\text{L water}} \times \frac{\text{mg/mmol salt}}{\text{mg/mmol ion}} \times \frac{\text{mmols of salt}}{\text{mmols ion}} \quad (3.1)$$

The mine waters were synthesized by adding the calculated amounts $FeSO_4.7H_2O$, $MnSO_4.7H_2O$, $MgSO_4.7H_2O$, Na_2SO_4, $Al_2(SO_4)_3.18H_2O$, KCl and $CaCl_2$ to a saturated gypsum solution.

3.2 Crop irrigation with synthetic acidic and neutralized waters

Using acidic mine water for irrigation can create hostile conditions for crop growth through soil acidification, salinization and excessive loading and mobilization of Al, Fe and Mn in the soil. The water may also cause foliar injury and damage the harvestable parts of crops if applied by sprinkler irrigation. There are, however, factors that can influence the extent to which such water qualities will have an effect on crop growth. These factors include agronomic practices, crop tolerance and soil chemical properties. In this study, the focus will be on crop tolerance and soil chemical properties.

Experimental site

A pot experiment was conducted in a glasshouse at the UP Hatfield Experimental Farm in 2015. Plastic pots (260 mm diameter, 240 mm height) were filled with 10 kg of soil. Two types of soil were used, a vertic soil and a red sandy loam soil. Vertic soil was selected due to its theoretical acid neutralizing capabilities which are attributed to its relatively high clay content, and therefore, high expected CEC. Vertic soil is also typically more alkaline and often naturally contains free carbonate (Virmani et al., 1982). For comparison, a red sandy loam soil was also selected to represent highly leached soils with low pH and low nutrient status, similar to many reclaimed soils. The vertic soil consisted of 48% clay (<0.002 mm), 15% silt (0.002−0.05 mm) and 36% sand (0.05−2.00 mm). The red sandy loam (RSL) soil consisted of 18% clay, 8. % silt and 74% sand. Chemical properties of the two soils prior to fertilization are indicated in Table 3.2.

Table 3.2: Chemical properties of the soils

Property	Red Sandy Loam Soil	Vertic Soil
pH_{KCl}	3.5	6.5
EC_e (mS/m)	163	105
Ca^a (mg/kg)	57	2576
Mg^a	10	1662
Na^a	0.4	69
K^a	17	115
P^b	61	0.9
Al^c	129	72
Fe^c	21	67
Mn^c	180	49
CEC (cmol/kg)	15	35
Organic Matter (%)	0.2	2.4

[a] Ammonium acetate extractable, [b]Bray 1,[c]EDTA extractable.

Different fertilizer rates were applied to the two soils based on the soil nutrient status as indicated in Table 3.2. Since the vertic soil was only deficient in phosphorus, an ammonium phosphate fertilizer was opted for, instead of a Ca or K phosphate fertilizer, to meet both N and P requirements. Fertilizer was applied at a rate of 200 mg/kg P and 90 mg/kg N in the form of $NH_4H_2PO_4$, and thoroughly mixed into the vertic soil. On the red sandy loam soil, fertilizer was applied at the rate of 90 mg/kg N in the form of $(NH_4)_2SO_4$ and 30 mg/kg K in the form of KCl, and thoroughly mixed into the soil. N was administered in the form of ammonium in the red sandy loam soil as this was the form in which it was administered in the vertic soil.

Lime, in the form of $Ca(OH)_2$, was applied to the red sandy loam soil to raise the pH_{KCl} of the soil from 3.5 to 6.5, the lime requirement was determined experimentally according to the method described by Kissel et al. (2005). The vertic soil was not limed. The pots were lined with geotextile fabric, to limit soil loss. Crops were irrigated to field capacity. Field capacity was determined prior to planting by over irrigating pots containing soil, allowing the pots to drain and then weighing the pots. The weight of the pots, after drainage, was taken as the field capacity. There was no leaching fraction applied to the soils. The intention was to allow salinity to build-up in the soils to simulate conditions where the crops only receive the amount of water they require, as this was a single season experiment.

Treatments

Summer and winter crops, chosen for their reported tolerance or sensitivity to pH and salinity (Table 3.3) were planted in June 2015. Three water qualities were used for irrigation; municipal water (control), synthetic acid mine water and synthetic neutralized mine water. An attempt was made to plant summer crops in the summer season, however, the crops grown on the vertic soil suffered from phosphorus deficiency as indicated by purpling of the leaves and confirmed by means of a Pbray 1 test. This was despite phosphorus being administered along with other nutrients in the form of a nutrient solution. The experiment was terminated, and it was resolved that instead of nutrients being administered in the form of a nutrient solution, they would be applied directly to soils in the mineral form and mixed into the soil. The amount of phosphorus added to the vertic soil was doubled to account for P sorption by the soil.

Due to time constraints, the summer crops were grown at the same time as the winter crops. Although glasshouse temperatures were not always optimum for all crops, conditions were cool enough to meet the growth requirements for winter crops (minimum temperatures ranged between 7 and 17^{o}C) and warm enough to meet the growth requirements for summer crops (maximum temperatures ranged between 26 and 38^{o}C). Summer crops were replanted in the same soils that were used in the failed trials. Using soils that had already been “treated” with the waters was intended to simulate the conditions that would have prevailed in summer, with regards to the loading of water constituents, since evapotranspiration rate is higher in summer thus more water is required for the irrigation of summer crops.

Summer crops were represented by maize (*Zea mays* cv ‘PAN 6Q-345CB’), lucerne (*Medicago sativa* cv ‘Super Aurora’) and sorghum (*Sorghum bicolor* cv ‘NS 5511’). Winter crops were represented by barley (*Hordeum vulgare* cv ‘Puma’), stooling rye (*Secale cereale* cv ‘Agri Blue’) and field peas (*Pisum sativum* var ‘Greenfeast’). Crops were irrigated to field capacity once a week after emergence, then irrigation frequency was increased as their water demand increased with growth. For each irrigation, the pots were weighed to determine the amount of water lost. Irrigation water was applied to the soil surface using a beaker and crop leaves were sprayed with the corresponding water quality, to ascertain if leaf scorching would be a problem. Crops were grown until they began to senesce.

Table 3.3: Crop acid/salt tolerance

	Acid Tolerance		**Salt Tolerance**		**Reference**
	Threshold Soil pH (H_2O)	**Rating**	**Threshold EC_e (mS/m)**	**Rating**	
Barley (*Hordeum vulgare)*	5.5	MT	800	T	Ayers and Westcot (1985); Fageria et al. (2010)
Lucerne (*Medicago sativa)*	6	S	200	S	Ayers and Westcot (1985); Fageria et al. (2010)
Maize (*Zea mays*)	5	T	170	S	Ayers and Westcot (1985); Fageria et al. (2010)
Peas (*Pisum sativum)*	6	S	340	S	Halley and Soffe (2011); Maas and Grattan (1999)
Rye (*Secale cereale*)	4.9	T	1140	T	Jayasundara et al. (1997); Maas and Grattan (1999)
Sorghum (*Sorghum bicolor*)	5.5	MT	680	T	Ayers and Westcot (1985); Fageria et al. (2010)

MT = Moderately tolerant
T = Tolerant
MS = Moderately sensitive
S = Sensitive

Visual analysis for leaf burn and other stress symptoms

Crops were visually assessed for symptoms of stress and foliar injury. If there were noticeable symptoms of stress, control crops were checked for similar symptoms. If the control crops did not display similar symptoms, the symptom was attributed to the water quality. Images of crops showing signs of leaf burn were analysed using CompuEye to estimate the area of the crop that was affected by scorching (Bakr, 2005). CompuEye has a colour detection system that enables the selection of the "symptom" colour which can then be used to detect the total area with similar colour, thus providing an estimate of the area affected. Parts of the crops that were injured were photographed and the symptom area ratio of the crop was calculated as the total area affected divided by the total area scanned and converted into percentages. An example of the image analysis is presented in Figure 3.1. The red area in Figure 3.1b is the area detected as having symptoms.

Figure 3.1: Example of lucerne crop Image (a) before and (b) after analysis with CompuEye

Crop growth measurements and sample preparation

Crop dry mass was determined by sampling the foliage (stem and leaves), oven drying the samples at 70°C for 48 hours, and then weighing the samples. In preparation for plant chemical analyses, fresh leaves were collected from the crops and washed according to a modified version of the method outlined by (Kalra, 1997). The leaves were then oven dried at 70°C for 24 hours and milled in preparation for analysis. Seeds were also oven dried at 70°C for 24 hours and milled in preparation for analysis. Soils were collected from the pots at the end of the trial, air dried for 2 weeks and sieved in preparation for analysis.

Chemical analysis

Chemical analyses of the crops and soils were carried out at the University of Pretoria Soil Science laboratory. Soils were analysed to determine pH (in KCl), saturated paste electrical conductivity (ECe), as well as Al, Mn and Fe concentrations before planting and at the end of the trial. These constituents were identified as being of main concern with regards to the quality of the mine waters, for irrigation. Al, Mn and Fe concentrations were determined by EDTA extraction according to a modified version of the method described by Kučak and Blanuša (1999), whereby 10 g of soil and 30 ml of 0.02 M EDTA were used. Leaves and seeds (grain) were also analysed to determine Al, Fe and Mn content using the nitrate microwave digestion method prescribed by Wu et al. (1997).

Food safety assessments

Health risks associated with Al and Fe intake through the consumption of crops irrigation with synthetic mine waters were assessed by comparing provisional tolerable intakes with estimated dietary intakes. Health risks associated with Mn intake through consumption of crops irrigated with synthetic mine waters was assessed by calculating the hazard quotient (HQ) as indicated in equation 3.2.

$$HQ = \frac{W_{plant}\text{ (kg/day)} \times M_{plant}\text{ (mg/kg)}}{R_fD\text{ (mg/kg body mass/day)} \times B\text{ (kg body mass)}} \qquad (3.2)$$

Infants and children have been identified as individuals that are most vulnerable to trace element toxicity (Khan et al., 2008; Krewski et al., 2007; Mertz, 1998). For the purpose of this study, human health risks associated with consuming crops irrigated with mine waters was assessed for children aged between 1 and 2, based on available anthropometric data from South African surveys. It was assumed that if the crops do not pose a health risk for children aged between 1 and 2, then they would likely be safe for consumption by older ‘healthy’ individuals. Details on the approach used to derive the values for dietary intakes and hazard quotients are presented in Appendix B.

Statistical analysis

The pots were split between two rotating tables with summer crops on one table and winter crops on the other. There were three water treatments; two mine water treatments (acidic and neutralized) and municipal tap water. There were two soil types and six crop species used. Each water treatment was replicated three times in a completely randomized design. Data for crop height, crop dry mass, soil pH, soil ECe, as well as soil and plant Al, Fe and Mn content was analysed using the analysis of variance procedure in the statistical analysis software (SAS) (Littell, 1996). Treatment means were compared using Tukey's Studentized Range (HSD) test and the least significant difference (LSD) at a significance level of α=0.05.

3.3 Assessment of fitness-for-use of mine water using the SAWQI-DSS

A review of the available data indicated that the acidic mine water is non-compliant with the 1996 South African Water Quality Guidelines for irrigation. It was, therefore, expected that the Tier 1 SAWQI-DSS assessment would present the water as unacceptable for use and that a Tier 2 assessment would be required.

For the tier 2 assessment, 45 years of irrigation with acidic and neutralized mine water was simulated, using synthetic acidic and neutralized saline water qualities prepared in section 3.1 as input values. Two soils were evaluated, a sandy soil and a clay soil. The site-specific input data for the simulations are provided in Table 3.4. Maize was selected to represent salt-sensitive crops and barley was selected to represent salt-tolerant crops. The following leaching requirements were evaluated: 15 %, 35%, 45% and 65%. Measured trace element concentrations of the vertic and red sandy loam soils used in the pot trials were included as input values for the initial trace element concentration of the soils used in the assessments. The sandy soil represented the red sandy loam and the clay soil represented the vertic soil.

Table 3.4: Input values for selected site-specific parameters of the Tier 2 assessment

Irrigation system	Overhead
Irrigation Timing	30 % depletion to FC
Weather Station	PTA-Univ-Proefplaas
Soil depth	1 m
Initial salt content	Low

The results of the procedures described in this chapter will be presented in the coming chapters. The next chapter will discuss the effects of mine water irrigation on selected soil chemical properties.

Chapter 4: Effect of mine water irrigation on selected soil chemical properties

In this chapter, the effects of mine water quality on soil pH, ECe, and soil Al, Fe and Mn content were investigated. These constituents of concern were selected based on assessments made with the South African Water Quality Guidelines for Irrigation (Department of Water Affairs, 1996).

Investigations were carried out in a glasshouse pot trial, whereby two soil types were used as crop growth media, red sandy loam (RSL) soil and a vertic soil. These soils were selected for their differences in soil properties. The red sandy loam soil represents soils with low clay content and, therefore, low CEC. The red sandy loam soil also had low initial pH (3.5 in KCl) and theoretically low acid neutralizing capacity, similar to most rehabilitated or reclaimed soils. Vertic soil was selected due to its relatively high 2:1 clay content and, therefore, high expected CEC. This soil, therefore, has high theoretical acid neutralizing capabilities and potential to reduce the phyto-availability of potentially toxic metals.

Three water qualities were used for irrigation; synthetic acidic saline mine water (henceforth referred to as acidic mine water), synthetic neutralized saline mine water (henceforth referred to as neutralized mine water) and municipal water, which served as a control. The quality of the three irrigation waters is provided in the table below:

Table 4.1: Irrigation water quality

Constituent		Acidic Mine Water	Neutralized Mine Water	Municipal Water
Al	**(mg/L)**	6	0	0
Ca		675	743	19
Cl		48	48	35
Fe		715	3	1
Mg		221	196	12
Mn		165	11	0.2
Na		65	61	21
SO_4^{2-}		4574	2316	38
EC	**(mS/m)**	475	276	31
pH		3	6.5	7.4

4.1 Effect of mine water irrigation on soil pH

The pH of the soils at the end of the trial is presented in Figure 4.1. Due to the composition of the irrigation waters, soil pH was measured in KCl instead of water as it was important to account for soluble acidity and exchangeable acidity. Soluble acidity refers to active H^+ in the soil solution and can be measured directly by equilibrating soil with water. Exchangeable acidity refers to H^+ and hydrolysable cations (Al^{3+}, Fe^{2+} and Mn^{2+}) bound to the exchange complex, which cannot be measured directly by equilibrating soil and water.

To measure exchangeable acidity, non-hydrolysable cations, such as the K^+ from KCl, are required to displace the H^+ and hydrolysable cations from the exchange complex. Once in solution, hydrolysable cations hydrolyse and release H^+. Since salinity influences H^+ activity, differences in salinity between treatments affects pH measurements in water. By using 1M KCl, which has an EC of 10000 mS/m, the salinity of the soil solution is rendered negligible and this creates a standard salinity background.

Figure 4.1 indicates that there was a slight decrease in the pH of both soils even when irrigated with neutralized mine water and municipal water. This is likely due to the application of ammonium-based fertilizer which acidifies soils by generating protons when ammonium is oxidized. The acidity generated by crops during nutrient uptake also likely contributed to the decrease in pH (Houmani et al., 2015; Sparks, 2003). The results show that irrigation with synthetic acidic saline mine water decreased the pH of all the soils, whereas irrigation with synthetic neutralized saline mine water had no significant effect on the pH of the soils. There was no significant difference in pH between the red sandy loam soil and the vertic soil irrigated with acidic mine water. This was unexpected considering the vertic soil had a higher CEC and, therefore, a higher theoretical pH buffering capacity than the red sandy loam soil.

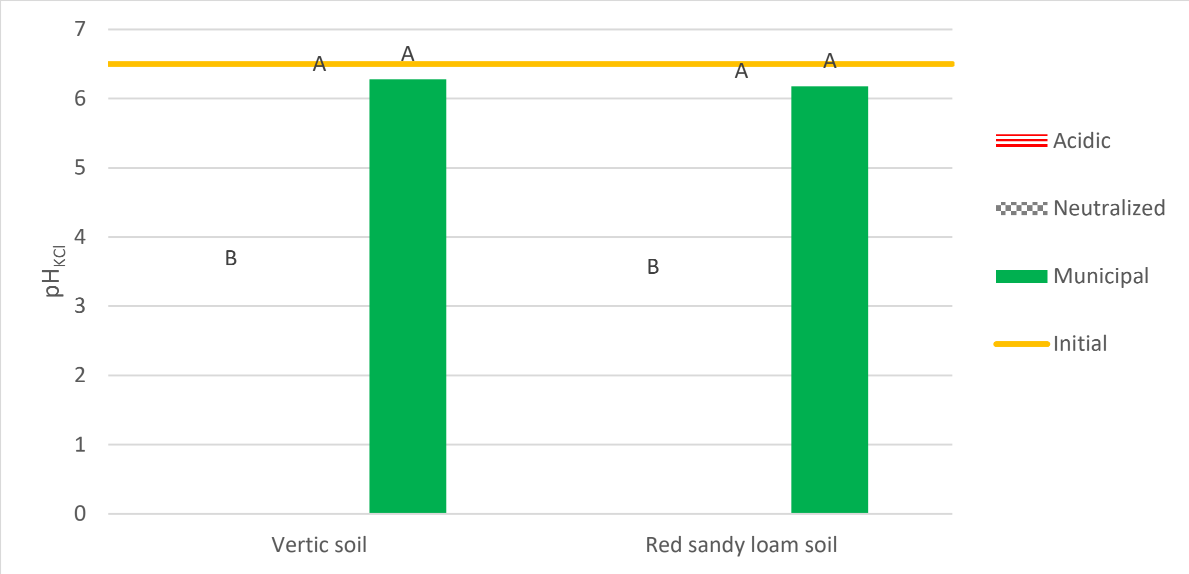

Figure 4.1: Soil pH of a vertic and a red sandy loam soil as influenced by irrigation water quality.

Means with similar letters are not significantly different.

The decrease in pH of vertic soil irrigated with synthetic acidic mine water suggested that the water was able to overcome the soil's acid buffering capacity after just one season of irrigation. Due to the soil's high clay content, CEC and higher organic matter content in comparison to the red sandy loam soil, the unexpected decrease in the vertic soil's pH sparked interest and prompted further investigation. The approach taken to probe the decrease in the vertic soil's pH was to determine the soil's acid buffering/neutralizing capacity and compare this to an estimate the acid generating potential of the acidic mine water.

4.1.1 Acid buffering in vertic soil

The acid buffering/neutralization capacity of the vertic soil was determined by means of an equilibration and titration experiment (Essington, 2003; Sparks, 2003). During the procedure, an H_2SO_4 solution with a pH of 3, similar to the pH of the synthetic acidic saline mine water, was prepared. The principle behind this was to react the soil with a large excess of acidic solution with similar acidity as the mine water to determine, in theory, how much acid is needed (per mass of soil) to overcome the soil's ability to buffer against acidification. After 24 hours the pH of this soil and the acid suspension was measured and, as it had not decreased to the same pH as the unreacted H_2SO_4 solution (pH 3), another known volume of the H_2SO_4 solution was added to the mixture and equilibrated once again for 24 hours. This was repeated until the pH of the suspension reached 3 and remained stable, indicating the soil's buffer against acidification was depleted.

Once the pH of the suspension had stabilized, the solution was separated from the soil by centrifugation and membrane filtration (0.1 µm filter). A 20 mL aliquot of the supernatant solution was taken and titrated with 0.01 M NaOH, to determine the concentration of protons, using phenolphthalein as an indicator. The concentration of protons in the unreacted H_2SO_4 solution was also determined by back titrating the solution with 0.01 M NaOH, using phenolphthalein as an indicator.

The vertic soil's acid buffering/neutralization capacity (q, in mmol/kg) was then calculated using Equation 4.1, where V_l is the total volume of H_2SO_4 solution that was reacted with soil (in L), C_{in} is the concentration of protons in the unreacted H_2SO_4 solution (in mmol/L), C_{eq} is the concentration of protons remaining in the soil solution at equilibrium (in mmol/L) and m is the mass of soil used (in kg).

$$q = (V_l \times (C_{in} - C_{eq})) / m \qquad (4.1)$$

The initial concentration of protons in the solution (C_{in}), was determined using equation 4.2, where V_{NaOH_1} is the volume of NaOH (in L) needed to neutralise the acidity of a known volume of unreacted H_2SO_4 solution (pH 3), C_{NaOH} was the concentration of the NaOH used for titration (in mmol/L) and V_{H2SO4} is the aliquot of unreacted H_2SO_4 (pH 3) used for the back titration (in L), which was 0.02 l.

$$C_{in} = V_{NaOH\_1} \times C_{NaOH} / V_{H2SO4} \qquad (4.2)$$

The concentration of protons remaining in solution at equilibrium (C_{eq}) was back titrated using the same approach (equation 4.3), where V_{NaOH_2} was the volume of NaOH needed to neutralise the acidity of solution that reacted with the soil, C_{NaOH} is the concentration of the NaOH used for titration (in mmol/L) and V_{al} is the aliquot of the solution that reacted with the soil (in L).

$$C_{eq} = V_{NaOH\_2} \times C_{NaOH} / V_{al} \qquad (4.3)$$

The input values used in the calculations are presented in the table below:

Table 4.2: Results of the vertic soil titration experiments

	$V_{NaOH\_1\ or\ 2}$ (L)	C_{NaOH} (mmol/L)	V_{H2SO4} or V_al (L)	C_{in} or C_{eq} (mmol/L)
C_{in}	0.003	10	0.02	1.5
C_{eq}	0.0015	10	0.02	0.75

Using values presented in Table 4.2, vertic soil buffering/neutralizing capacity was calculated as follows:

q (mmol/kg) = [1L (1.5 mmol/L – 0.75 mmol/L)]/ 0.002 kg

= 375 mmol/kg

This means the soil, in theory, can neutralise 375 mmol of H^+ per kilogram of soil. The acid buffering/neutralization capacity acted as a theoretical upper limit as there was good contact between soil and solution and sufficient time was allowed for reaction during this experiment. In the pots, however, the solution to soil ratio was lower and not all the surfaces reacted with the acid in the irrigation water due to preferential flow paths. Therefore, buffering capacity is expected to be lower in the pots.

4.1.2 Acid generating potential of acidic mine water

Since soil pH gives a measure of H^+ activity, it was important to get a quantitative account of the acidity (H^+) generated by the acidic mine water constituents when applied to the vertic soil. It was assumed that there would be two sources of acidity in the acidic mine water. The primary source of acidity is the H^+ activity, which is reflected by pH. The secondary source of acidity was assumed to be Al, Fe and Mn that participate in acid generating reactions. In any given solution, these metals will be present in different forms, or species. These forms/species are often dictated by pH, as demonstrated by the predominance diagrams for metal speciation presented in Figure 4.2. Such diagrams indicate the metal species that will be dominant in a solution, i.e. make up more than 50% of the metal's total concentration. Redox conditions may also dictate metal speciation in solution, however, in this case, pH was assumed to be the dominant driving force.

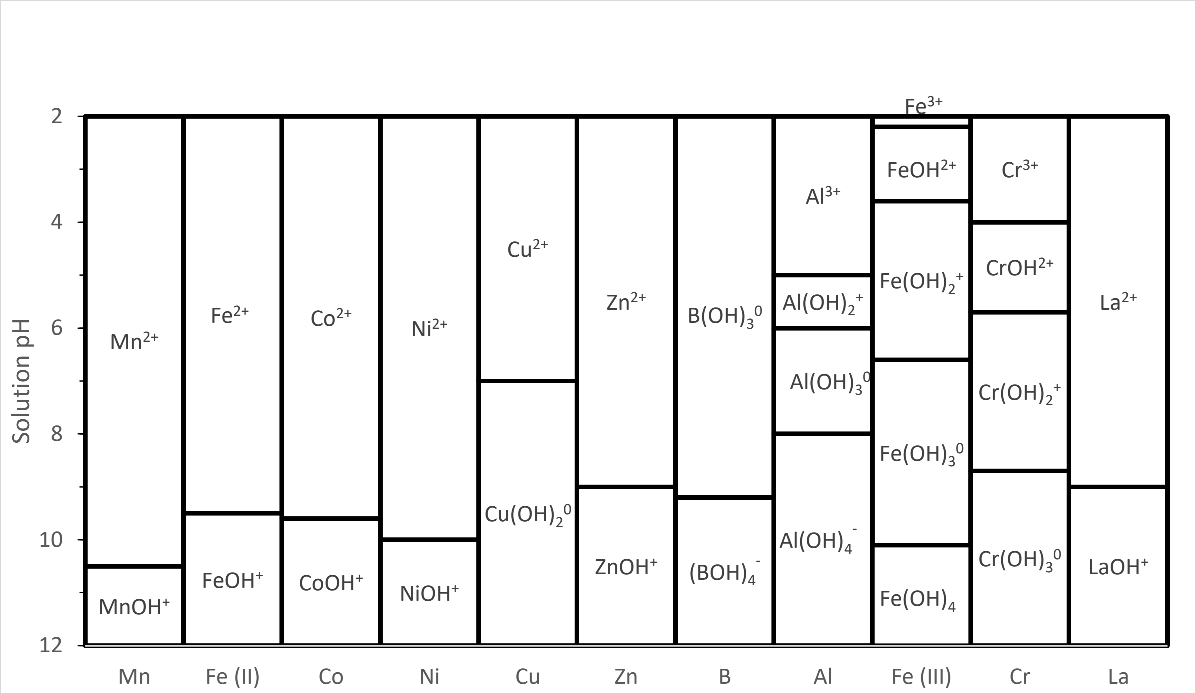

Figure 4.2: Predominance diagrams for metal speciation as a function of pH according to Essington (2003).

According to the predominance diagram, the dominant Al species in the acidic mine water would be Al^{3+} and in soil, at pH 6.5 the dominant Al species would be $Al(OH)_3^0$. This implies that most Al^{3+} applied through the water would likely undergo hydrolysis and precipitation as summarized in Equation 4.4, thereby generating H^+.

$$Al^{3+} + 3\ H_2O \rightarrow Al\ (OH)_3 + 3\ H^+ \qquad (4.4)$$

Mn would predominantly be present as Mn^{2+} in the acidic mine water, however, when the water is applied on an aerated soil the Mn^{2+} would likely become oxidised and precipitate as MnO_2, resulting in net acid generation (Equation 4.5).

$$Mn^{2+} + 0.5\ O_2 + H_2O \rightarrow MnOOH + 2\ H^+ \qquad (4.5)$$

In the acidic mine water, the dominant Fe species will likely be Fe^{2+}. When the water is applied on aerated soil, Fe^{2+} would likely be oxidised to Fe^{3+}, Fe^{3+} will likely undergo hydrolysis and precipitate as FeOOH, which is predicted to be dominant at soil pH 6.5. The oxidation Fe^{2+} and subsequent hydrolysis of Fe^{3+} generate protons as is summarised in Equation 4.6.

$Fe^{2+} + 0.5\ O_2 + 2\ H_2O \rightarrow \alpha\text{-}FeOOH + 3\ H^+$ (4.6)

The $NH_4H_2PO_4$ applied to the soil as N and P fertilizer also contributed to soil acidification, through nitrification, as indicated in Equation 4.7.

$NH_4^+ + 1.5\ O_2 \rightarrow NO_3^- + 4\ H^+$ (4.7)

PHREEQC (Parkhurst, 2017) was used to determine the acid generating potential of the synthetic acidic saline mine water when applied to vertic soil. The model was programmed to concentrate the synthetic acidic saline mine water by removing specified moles of water from the solution, simulating evaporation. A command for the model to provide H^+ molality and activity was also included. This procedure simulated evaporation along with various other acid generating reactions that are likely to occur in solution, including hydrolysis, cation oxidation and precipitation. The model assumes that evaporation and evapotranspiration have the same effect. Both processes concentrate solutions. However, during evapotranspiration, plant roots contribute to ion exchange. It was assumed that the equilibrium phases of the acidity generating reactions of Al, Mn and Fe would be gibbsite, birnessite and goethite, respectively as indicated in equations 4.4 - 4.6.

The acid generating potential (AGP) of the acidic mine water was calculated from the output generated by PHREEQC according to Equation 4.8, where H^+_{input} is the amount of protons generated through irrigation with acidic mine water (in mol/kg water), m_{water} is the total amount of irrigation water applied (in kg) and m_{soil} is the mass of soil. In the pot trials, an average total of 20L (equivalent to 20 kg) of water was applied to 10 kg of soil.

$AGP = (H^+_{input} \times m_{water})/m_{soil}$ (4.8)

$= 82$ mmol H^+/kg water x 20 kg water/ 10kg soil

$= 162.5$ mmol H^+/kg soil

A comparison between the acid buffering/neutralizing capacity of the vertic soil and the acid generating potential of the acidic mine water indicates that the acid generating potential of acidic mine water accounted for 43% of the vertic soil's acid buffering/neutralizing capacity (Table 4.3). This means that if the water generated all the acidity it can generate, 43% of the soil's acid buffering capacity would have been used up. For further exploration, the active and exchangeable acidity (KCl acidity) of the vertic soil at the end of the trial was also measured and it was found to account for only 9% of the soil's acid buffering capacity.

Table 4.3: Comparison between estimated acid buffering capacity of the vertic soil, acid generating potential of acidic mine water and KCl acidity of the vertic soil after irrigation.

	mmol/kg
Acid buffering/neutralizing capacity (q)	370
Acid generating potential	162
KCl exchangeable acidity	35

These results indicate that the vertic soil's acid buffering/neutralizing capacity was not exhausted and suggests that there may have been other processes that contributed to the sharp decrease in pH.

It has been reported that aluminium and iron oxide precipitates can coat the surfaces of clay minerals and alter some of their chemical properties. In a study by Sakurai et al. (1990), the precipitation of aluminium hydroxides and their subsequent coating of montmorillonite clay particles were found to cause a decrease in the CEC. The decrease in CEC was attributed to the addition of positive charges of oxides to the clay particles which results in charge neutralization.

A decrease in soil CEC is likely to decrease the soils ability to buffer against acidity. In passive AMD treatment plants using limestone as a neutralizing agent, the oxidation of ferrous iron to ferric iron has been found to result in the limestone being coated with ferric oxide precipitates (Gazea et al., 1996). The process reportedly reduces the dissolution of limestone and, therefore, the production of acid-neutralizing alkalinity. In the case of limestone armouring, a more soluble alkaline mineral is coated with an appreciably less soluble mineral. This would be expected to result in a more pronounced effect than that of Al and/or Fe oxides coating clay mineral surfaces.

Other factors that may have contributed to the sharp decrease in pH may be the dissolution of clay minerals which, in the case of the vertic soil, produces Al^{3+}. When the Al^{3+} is hydrolysed H^+ ions are produced, generating acidity. The formation of

Hydroxy-Interlayer-Smectite (HIS) may also have contributed to the sharp decrease in pH. The hydroxy layer of HIS forms between two clay minerals, which decreases the layer charge of the clay mineral, and results in a decrease in CEC and hence buffer capacity (Sparks, 2003). In addition, it should be noted that water applied to pots probably did not react with all the soil surfaces, and the water may have established a preferred flow path. As a result, some parts of the soils may have been subject to more acidification than other parts, whereas in the equilibration experiment all the soil surface were reacted with the acidic solution. Due to the complex dynamics of soil chemical reactions, the exact cause for the rapid decrease in the vertic soil pH could not be identified within the scope of this study.

4.2 Effect of mine water irrigation on soil salinity

Soil salinity was determined by measuring saturated paste electrical conductivity (ECe). The intention was to isolate salts with the highest solubility, as they have the most significant impact on crop growth, due to osmotic and specific ion effects. To ascertain if the amount of water used to make the saturated paste was sufficient to dissolve all the highly soluble salts that may have formed, the dissolution potential (DP) of the salts (in mg/kg soil) was determined and compared to the theoretical amount of salt that was loaded through irrigation (in mg/kg soil). That is the amount of salts that can be dissolved from the soils taking into consideration the specific solution to soil ratio used to prepare saturated paste extracts.

The results of the above exercise indicate that the amounts of highly soluble salts loaded through irrigation (in mg/kg soil) were lower than the dissolution potential of these salts (Table 4.4). This means that the volume of water used to make the saturated paste was able to dissolve all the highly soluble salts. Calculations used to derive the values in Table 4.4 are presented in Appendix C.

Table 4.4: Comparison between the dissolution potential of the salts and the amount of salts loaded by the mine waters.

		Na_2SO4	$MgSO_4.7H_2O$
		mg/kg	
Vertic	**DP**	156111	200000
	Salt loaded by acidic water	392	4370
	Salt loaded by neutralized water	373	3875
Red Sandy Loam	**DP**	76636	98182
	Salt loaded by acidic water	201	2241
	Salt loaded by neutralized water	271	2816

4.2.1 The effects of irrigating with mine waters on ECe

ECe measurements show that irrigation with mine waters significantly increased the salinity of both the vertic and the red sandy loam soil (Figure 4.3). Soils irrigated with acidic mine water were significantly more saline than those irrigated with neutralized mine water. This was expected, given that the acidic water was more saline than the neutralized mine water. In addition, the ECe of soils irrigated with synthetic mine waters exceeded the tolerance threshold of moderately salt sensitive crops and fell within the tolerance range of moderately tolerant crops. This suggests that irrigation with such waters is likely to restrict the types of crops that can subsequently be grown, at least in the short term.

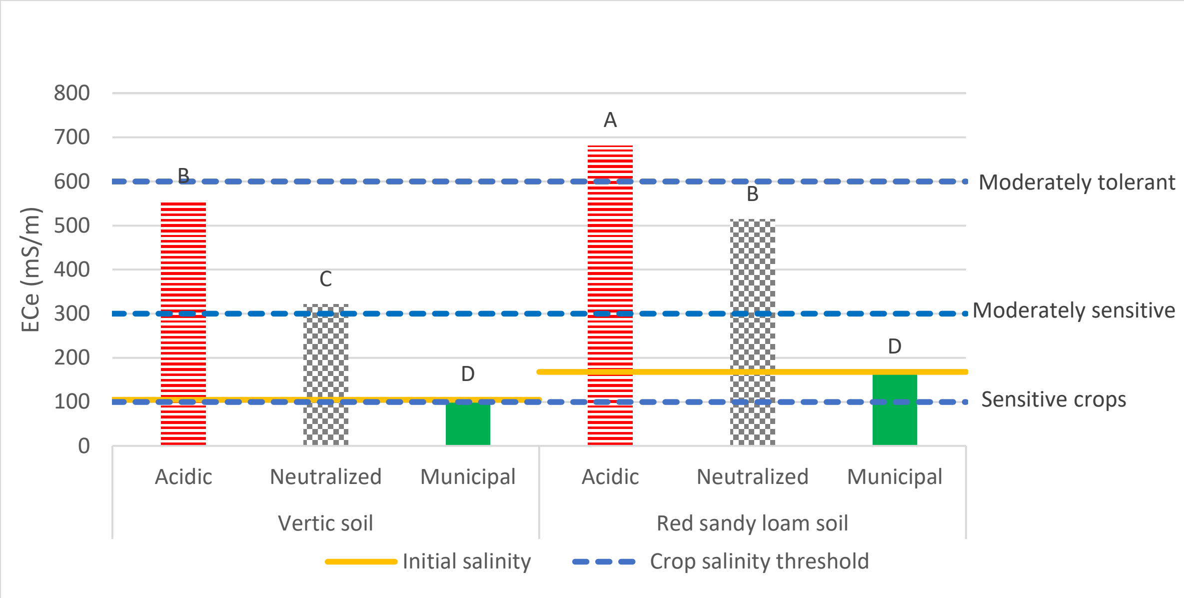

Figure 4.3: Soil salinity as influenced by irrigation with mine waters on a vertic and red sandy loam soil.

Means with similar letters are not significantly different.

The salinity of the red sandy loam soil was significantly higher than that of the vertic soil when irrigated with synthetic mine waters. This suggests that the vertic soil had higher salinity buffering capabilities than did the red sandy loam soil. To get an estimate of the salt buffering capabilities of the soils, the percentage of salts removed from the soluble pool of salts, by precipitation/exchange reactions, was estimated (Equation 4.9).

% Salt removed = [(Salt Input – (Final soil salt content-Initial soil salt content)) /Salt Input]*100 (4.9)

Table 4.5 shows that over 70% of the salts that were loaded by irrigation with mine waters, were removed from the soluble salt pool in both the vertic and red sandy loam soils This 'loss' of soluble salts can mostly be attributed to precipitation of insoluble and sparingly soluble compounds. The amount of soluble salts removed in the vertic soil was 3 % more salt than that removed in the red sandy loam soil. This difference could be attributed to the vertic soil having a higher CEC, and therefore, sorbing more of the soluble salt forming ions than the red sandy loam soil. The amount of soluble salts removed in soils irrigated with neutralized mine water was 4% more than that removed in soils irrigated with acidic mine water. This suggests that the acidic mine water interfered with the salt buffering efficiency of the soils. It is also likely that the difference in salinity between the vertic and red sandy loam soil is due to the vertic soil having a higher saturation percentage than the red sandy loam soil. Thusly, the vertic soil has a higher water content at saturation than the red sandy loam soil, resulting in the salts being more concentrated in the red sandy loam soil.

Table 4.5: Percentage of salts removed from the soluble salt pool of the vertic and red sandy loam soils after a season of irrigation with mine waters.

Treatment	% Salt removed from vertic soil	% Salt removed from red sandy loam soil
Acidic mine water	75	72
Neutralized mine water	78	76

4.3 Al, Fe and Mn content of soils as influenced by synthetic mine water irrigation

Al, Fe and Mn content of soils were determined by EDTA extraction. The portion of Al, Fe and Mn that was EDTA extractable was considered as being phytoavailable, particularly in acidic conditions. It should, however, be noted that availability does not necessarily translate to accessibility. EDTA mostly extracts organically bound metals. Mass balance calculations were also performed, to get an account of the metal distribution in the soils and crops (see Appendix D for details).

4.3.1 Al, Fe and Mn content of the red sandy loam soil

Al, Fe and Mn content were higher in soils irrigated with acidic mine water than in those irrigated with the other waters (Figure 4.4). Soils irrigated with acidic mine water contained significantly higher levels of phytoavailable Fe at the end of the trial than what was in the soils initially. This indicates that there was an accumulation of Fe in the soils as a result of the high Fe content in the irrigation water. The mass balance calculations indicate that the phytoavailable Fe that accumulated in the soils only accounted for 18% of the Fe that was available (i.e. initial soil Fe and applied

Fe). The remainder of the available Fe was either taken by crops or transformed into forms that are not extractable by EDTA. According to the mass balance, only 2% the Fe that was removed from the EDTA extractable pool was taken up by crops. This indicates that most of the available Fe was transformed into unavailable forms, likely through precipitation as the liming material reacted with the soil.

There was no increase in the levels of phytoavailable Al and Mn in red sandy loam soils, even those irrigated with mine waters. Instead, levels of these elements were substantially lower at the end of the trial than they were initially. This is contrary to what was expected, particularly in soils that were irrigated with acidic mine water, given that this water contained excessive levels of Al and Mn. The mass balance calculations indicated that crop uptake only accounted for a small fraction of the decrease in Al (less than 10%). Mn uptake by crops was more substantial (between 28% and 38%), however, it was not the main contributor to the decrease in Mn. The observed decrease in Al and Mn content can, therefore, mainly be attributed to soil chemical processes, likely precipitation resulting from the soils reacting with the applied lime.

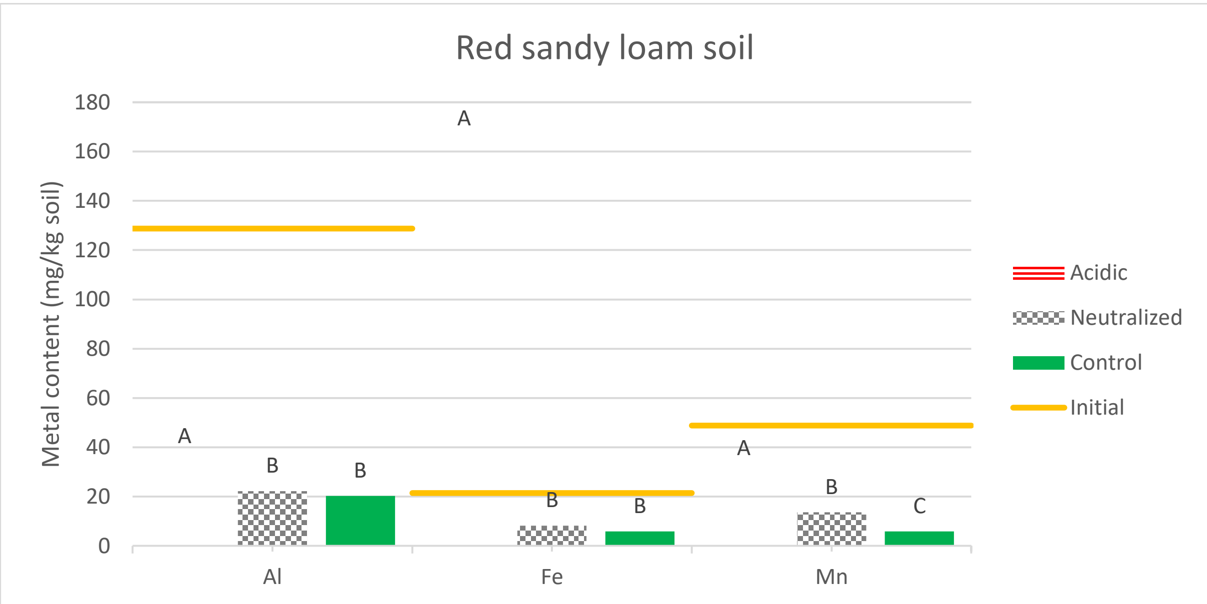

Figure 4.4: Al, Fe and Mn content of a red sandy loam soil as influenced by irrigation water quality.

Means with similar letters are not significantly different.

4.3.2 Al, Fe and Mn content of the vertic soil

Al and Fe content was significantly higher in the vertic soil irrigated with acidic mine water, than in those irrigated with neutralized mine water and municipal water. This is due to the acidic mine water containing higher concentrations of these elements than the other waters. Although Al content was relatively high in soils irrigated with acidic mine water, the Al content at the end of the trial was lower than it was initially. This indicates that there was no accumulation of phytoavailable Al. There was, however, an accumulation of phytoavailable Fe in soils irrigated with the acidic mine water, similar to what was observed in red sandy loam soil.

Mn content was significantly higher in soils irrigated with neutralized mine water than in soils irrigated with the other waters. Mass balances indicated that crop Mn uptake in soils irrigated with neutralized mine water only accounted for 2% of the phytoavailable Mn. This suggests that although the Mn content of soils irrigated with neutralized mine water was relatively high, the Mn was in a form that is not readily accessible to crops. It is likely that the Mn that was detected in soils was in the organically bound fraction which is extractable by EDTA but is not readily accessible by crops. Although the Mn content of soils irrigated with neutralized mine water was higher than that of soils irrigated with the other waters, the Mn content of these soils was lower at the end of the trial than it was initially, indicating that there was no accumulation of phytoavailable Mn.

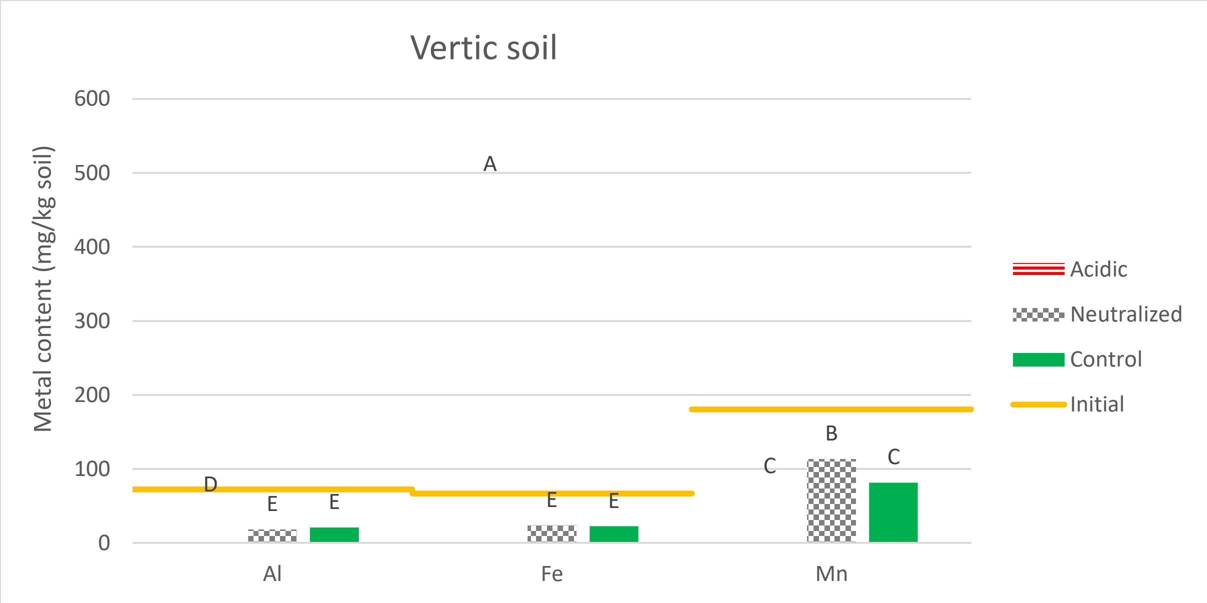

Figure 4.5: Al, Fe and Mn content of a vertic soil as influenced by irrigation water quality.

Means with similar letters are not significantly different.

4.3.3 The red sandy loam soil vs the vertic soil

The vertic soil typically contained higher concentrations of Al, Fe and Mn than red sandy loam soil at the end of the trial. An estimated account of the distribution of these metals indicates that in the vertic soil irrigated with acidic water, more than 50% of the available Al remained in the EDTA extractable pool. On the other hand, only 25% of the available Al remained in the EDTA extractable pool of the red sandy loam soils irrigated with the same water. In both soils, less than 15% of the Al that was removed from the EDTA extractable pool was taken up by crops. However, Al content was higher in crops grown on red sandy loam soil than in vertic soil. This indicates that, although the vertic soil irrigated with acidic mine water contained much higher levels of Al than the red sandy loam soil, the Al in the vertic soil was contained in forms that are not readily accessible by crops. Similar trends were observed in soils irrigated with neutralized and municipal water.

In the vertic soil irrigated with neutralized mine water and municipal water, 45-55% of the available Mn remained in the EDTA extractable pool. Of the portion that was removed from the EDTA extractable pool, less than 15% was taken up by crops. In red sandy loam soils, 12-20% of Mn remained in the EDTA extractable pool. Of the portion that was removed from the EDTA extractable pool, more than 45% was removed by plants and crops grown on red sandy loam soils contained higher levels of Mn than those grown on the vertic soil. This suggests that although the vertic soil irrigated with neutralized mine water and contained more Mn than red sandy loam soils irrigated with the same water, the Mn in the vertic soil was contained in forms that are not readily accessible by crops.

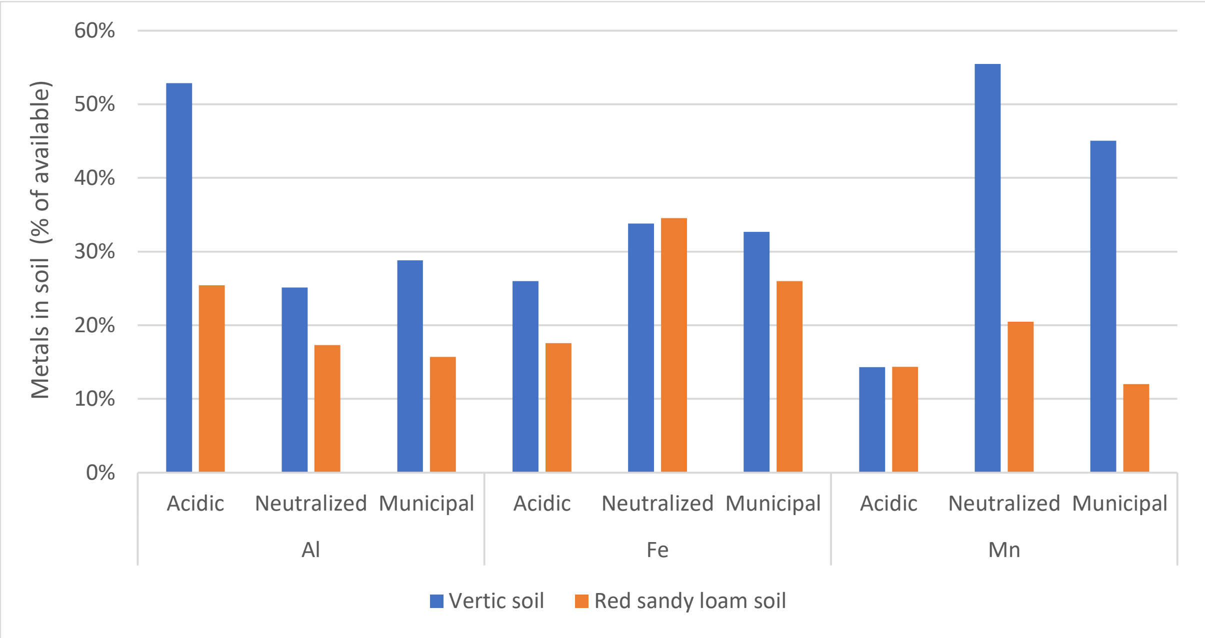

Figure 4.6: EDTA extractable metals in soils at the end of the trial, as a percentage of the theoretical total available.

Chapter 5: Effect of mine water irrigation on crop quality

In this chapter, the quality of crops irrigated with synthetic mine waters was assessed. Crops were analysed for foliar injury and other visual symptoms of stress. Foliage was chemically analysed to determine if Al, Fe and Mn had accumulated to phytotoxic levels. These elements were chosen as they were present in the mine waters at levels higher than what is recommended by the South African Water Quality Guidelines for Irrigation. Grain and foliage of forage crops were assessed for food and fodder safety. Fodder safety assessments were conducted for pigs, poultry, cattle, and sheep.

5.1 Foliar Injury and Other Visual Symptoms of Stress

5.1.1 Red Sandy Loam Soil

Peas, maize, rye, barley and sorghum grown on the red sandy loam soil showed no signs of foliar injury when irrigated and sprayed with mine waters (Figure 5.1 and Figure 5.2.). However, other symptoms of stress were observed in crops irrigated with acidic mine water. Pea and barley leaves developed brown spots and completely lost turgidity and withered when irrigated with acidic mine water. Rye exhibited leaf rolling and a pale green colour. The leaves of sorghum and maize were also rolled, with a pale green colour and the overall growth of the crops was stunted. The emergence of lucerne irrigated with acidic mine water was completely inhibited. Crops irrigated with neutralized mine water did not show any symptoms of stress.

The symptoms of water stress observed in crops irrigated with acidic mine water could be attributed to acidification and/or salinization of their soils, which has been found to affect water uptake and growth by interfering with root growth. An increase in the H^+ ion activity and Al^{3+} concentration, typical of acid soils, has been found to decrease root growth (Mariano and Keltjens, 2005; Yan et al., 1992). In a study by Islam et al. (1980), crops grown in nutrient solutions with pH levels ranging between 3.5 and 8.5 suffered from root injury at the lowest pH (3.5). This led to a decrease in root elongation and lateral growth.

Mariano and Keltjens (2005) found that exposing maize to nutrient solution concentrations of 100 μM Al, inhibited elongation of its roots. Similar responses to acidity and aluminium toxicity have been observed in sorghum and barley, whereby soil or solution pH resulted in a decrease in root growth (Bona et al., 1993; Tan et al., 1992). It is therefore probable the symptoms of water stress observed in soils irrigated with acidic mine water are in part due to the effects of acidity and aluminium from the water.

In a review of plant response to salinity, Volkmar et al. (1998) indicated that an increase in soil solution salinity decreases crop ability to absorb water. According to Volkmar et al. (1998), when salts accumulate in soil solution they cause a decrease in the water energy gradient which affects the movement of water through the root membranes. Papadopoulos (1984) found that irrigation with high sulphate water (32 meq/L) decreased the growth and yield of tomatoes. The decrease in growth was attributed to the accumulation of salts, which increased the soil solution EC. It was thought that the accumulation of salts decreased the solute potential of the soil solution which affected water uptake in the crops. In this study, irrigation with acidic mine water significantly increased the ECe of the red sandy loam soil, to an ECe of 681 mS/m. It is, therefore, likely the osmotic effects described above, contributed to the symptoms of water stress observed in crops irrigated with acidic mine water,

The exact mechanism by which water uptake in crops grown on red sandy loam soil was affected by irrigation with acidic mine water in this study remains unclear. It is likely that a combination of acidity, aluminium toxicity and salinity effects are responsible for the symptoms of water stress observed in crops irrigated with acidic mine water. However, it is apparent that irrigation with acidic mine water on this type of soil may decrease water uptake in crops regardless of their relative tolerance to acidity and salinity.

The brown spots observed in barley and peas irrigated with acidic mine water are often associated with manganese toxicity (El-Jaoual and Cox, 1998). In this study, foliar analyses indicated that crops irrigated with acidic mine water contained phytotoxic levels of Mn (section 5.2), therefore, the brown spots can be attributed to manganese toxicity.

Figure 5.1: Images of barley (a), stooling rye (b) and peas (c) irrigated with synthetic mine waters and municipal water on a red sandy loam soil.

Figure 5.2: Images of (a) sorghum, (b) maize and (c) lucerne irrigated with synthetic mine waters and municipal water, on a red sandy loam soil.

5.1.2 Vertic Soil

Peas, maize, rye, barley and sorghum grown on the vertic soil showed no signs of foliar injury when irrigated and sprayed with mine waters (Figure 5.3, Figure 6.2.a and b). Lucerne showed signs of foliar injury when sprayed and irrigated with acidic mine water but showed no signs of foliar injury when irrigated with neutralized mine water (Figure 6.2 c). Image analyses estimated that irrigation with acidic mine water injured an average of 15% of the leaf surface of lucerne. In addition to injury, lucerne leaves developed white spots around their margins. Some of the leaves also developed a reddish/purple tint on the margins and interveinal chlorosis was evident. Maize leaves and sorghum stems also developed reddish-purple pigmentation with acidic mine water irrigation.

Table 5.1: Percentage foliar injury caused by irrigating and spraying lucerne leaves with acidic, neutralized and municipal water on a vertic soil

	Total area scanned	**Total area injured**	**% Foliar injury**
	cm^2		
Acidic	840	128	15
Neutralized	837	0	0
Municipal	842	0	0

Acidity and salinity in irrigation water have been found to cause foliar injury when applied to crop leaves, particularly in susceptible crops. Lee et al. (1981) studied foliar injury induced by acid rain in several crops which included maize, barley, lucerne and peas, by sprinkling the crops with simulated sulphuric acid rain with pH 3, 3.5 and 4. In their study, they found that lucerne and peas sprinkled with acid rain of pH 3.0 and 3.5 were susceptible to foliar injury. Maize leaves were only injured by acid rain with pH 3.0, while barley showed no signs of acid rain injury at all studied pH levels.

In a study by Maas et al. (1982) foliar injury in crops sprinkled with saline water was investigated by sprinkling crops with 15 and 30 meq/L NaCl solution. Lucerne, barley and sorghum showed symptoms of marginal necrosis when irrigated with both concentrations, however, symptoms remained minor. Foliar injury was attributed to the accumulation of Na^+ and Cl^-, which are toxic when present at high concentrations.

In this study, however, foliar injury was only observed in lucerne irrigated with acidic mine water and cannot be exclusively attributed to either direct or indirect effects of mine water constituents because the crops were sprayed and irrigated with acidic mine water. Direct effects refer to actual scorching, caused either by the acidity or specific ions (Na/Cl) and indirect effects refer to factors such as deficiencies or toxicities caused by water constituents. Nonetheless, it can be concluded that of all the crops considered in this study, lucerne was the most susceptible to foliar injury when irrigated with acidic mine water.

The development of white spots on the leaf margins, as observed in lucerne, is often symptomatic K deficiency. Marginal necrosis of lucerne leaves, has also been found to be a symptom of Mn toxicity (El-Jaoual and Cox, 1998). The appearance of reddish-purple tint in leaves and stems, as observed in the summer crops, is symptomatic of phosphorus deficiency (Ouellette and Dessureaux, 1958; Stevens et al., 2002). These symptoms of stress may be attributed to nutrient imbalances caused by foliar and soil application of the acidic mine water. The presence of high concentrations of Al, particularly in acidic soils, is known to cause phosphorus deficiency through reactions that form aluminium phosphates, which are immobile forms of phosphorus that are not easily transported through the plant (Clarkson, 1966). Fe and Mn have been found to have an antagonistic interaction with K. High concentrations of Fe and Mn in the growth medium often decrease K uptake in crops (Fageria, 2001). Marginal necrosis of lucerne leaves has also been found to be a symptom of Mn toxicity.

5.1.3 The red sandy loam soil vs the vertic soil

Crops grown on the red sandy loam soil, particularly those irrigated with acidic mine water, showed more severe signs of stress than those grown on the vertic soil. The crops grown on the red sandy loam soils were shorter than those grown on the vertic soil and showed symptoms of water stress, as well as phytotoxicity/nutrient imbalances. Crops grown on vertic soil only showed symptoms of phytotoxicity/nutrient imbalances.

Figure 5.3: Images of (a) barley, stooling (b) rye and (c) peas irrigated with synthetic mine waters and municipal water on a vertic soil.

Figure 5.4: Images of (a) sorghum, (b) maize and (c) lucerne irrigated with synthetic mine waters and municipal water, on a vertic soil.

5.2 Mine water effects on Al, Fe and Mn accumulation in crop foliage

5.2.1 Foliar Al, Fe and Mn content of crops grown on red sandy loam soil

Crops irrigated with acidic mine water typically had a higher foliar content of Al, Fe and Mn than those irrigated with the other waters. Crops irrigated with neutralized mine water typically had lower Al and Fe content than those irrigated with municipal water. The opposite was observed for Mn content, whereby crops irrigated with neutralized mine water had a higher Mn content than those irrigated with municipal water.

Crops irrigated with acidic mine water accumulated Al at levels associated with phytotoxicity (Figure 5.5). Maize, lucerne and peas also accumulated phytotoxic levels of Al in their foliage when irrigated with municipal water, indicating that despite the addition of liming material, there was still some phytoavailable Al. It is likely that the reaction between the soil and the liming material was not rapid enough, resulting in excessive uptake and accumulation of mobile Al for some time until the soil had equilibrated with the liming material. Accumulation of Al in the crops typically followed the order; peas>lucerne>maize> sorghum>barley>stooling rye.

Fe content was within the sufficiency range for all crops and irrigation water qualities considered (Figure 5.6). Fe content was excessively high in most considered crops irrigated with acidic mine water. This suggests that irrigation with acidic mine water increased the phyto-availability of Fe and facilitated the accumulation of excessive amounts of Fe in crops. Accumulation of Fe in the foliage of the crops typically followed the order; maize> peas> lucerne> sorghum> barley> stooling rye.

Mn content was within the sufficiency range for all crops, with all irrigation water qualities considered. All considered crops grown on the red sandy loam soil accumulated phytotoxic levels of Mn when irrigated with mine waters (Figure 5.7). This reflects the high levels of Mn present in the waters. Foliar Mn content in peas and stooling rye irrigated with municipal water also exceeded reported phytotoxicity thresholds. These results indicate that Mn was highly available in the red sandy loam soil and readily accessible to plants.

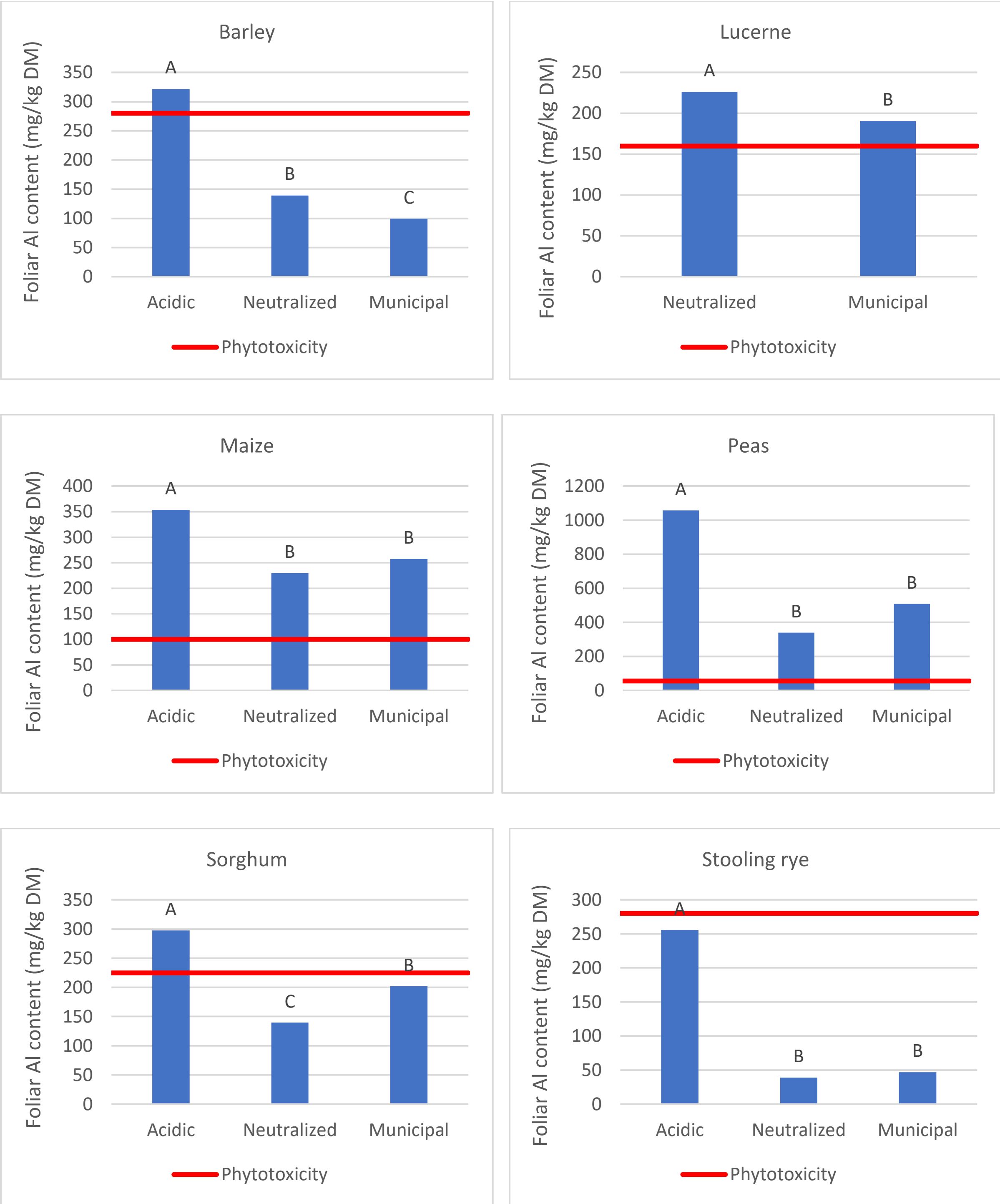

Figure 5.5: Al content in foliage, as influenced by irrigation with synthetic mine waters on sandy loam soil.[1]

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

[1]The phytotoxicity threshold for rye is based on the reported phytotoxicity threshold for wheat.

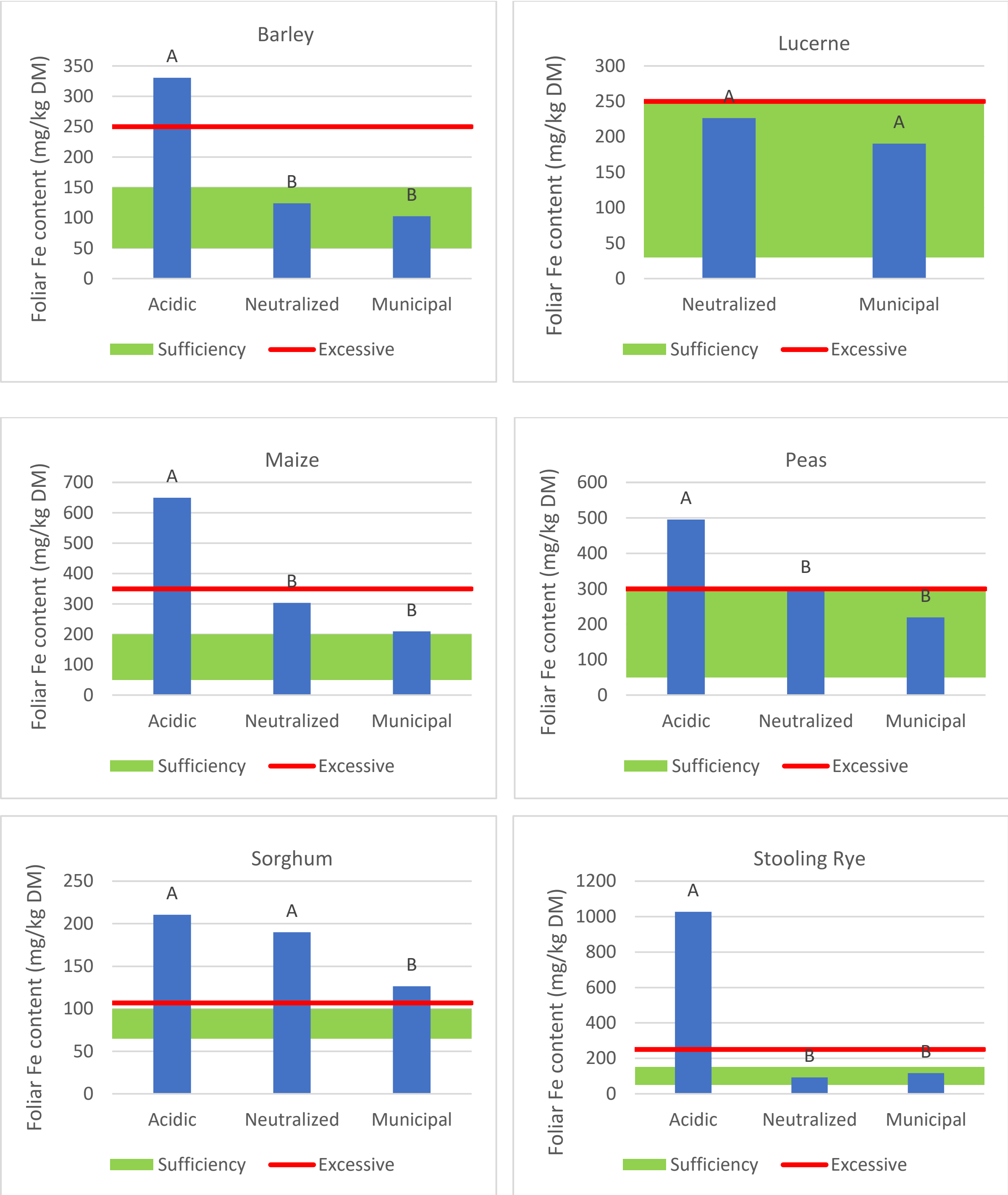

Figure 5.6: Fe content in foliage, as influenced by irrigation with synthetic mine waters on sandy loam soil.

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

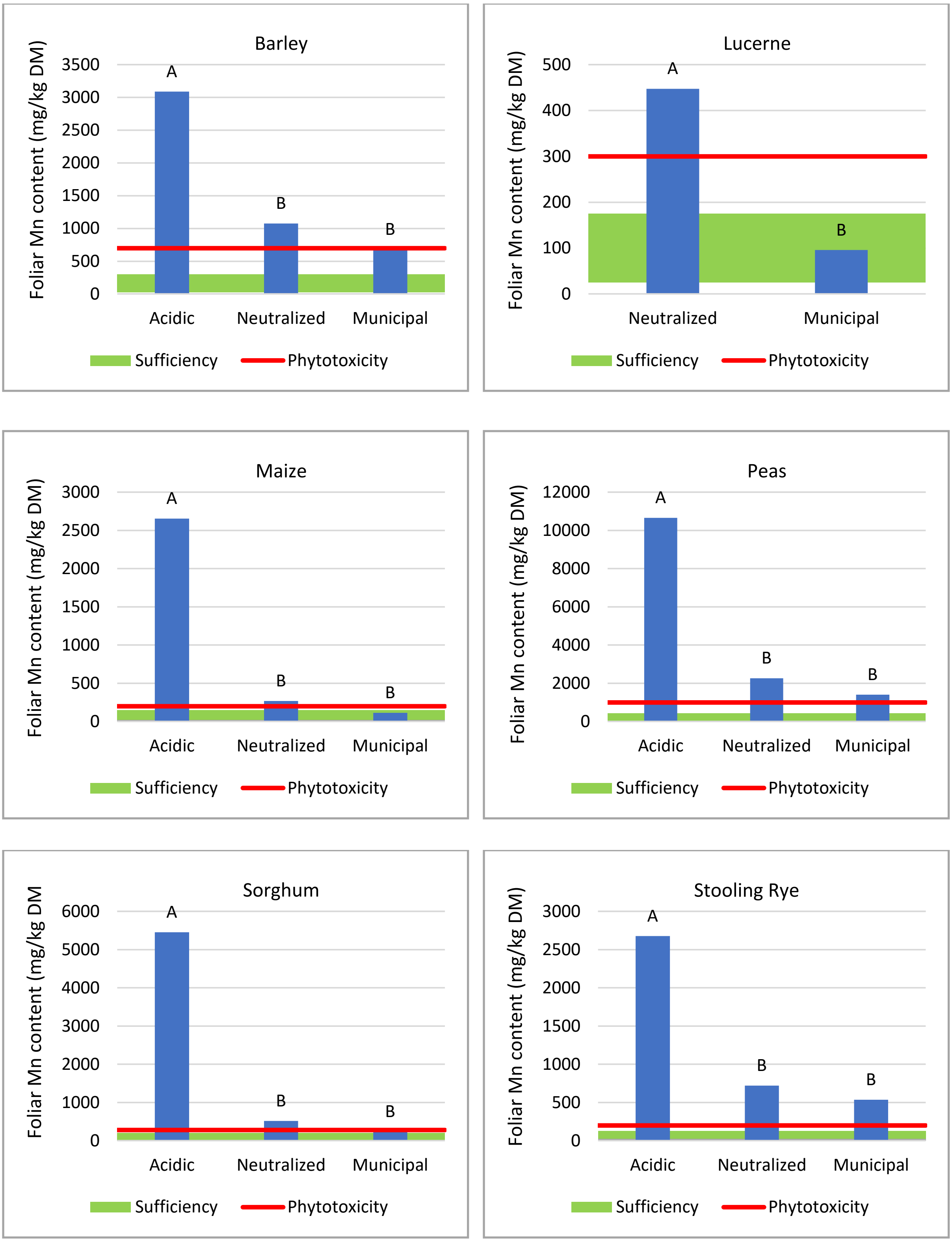

Figure 5.7: Mn content in foliage, as influenced by irrigation with synthetic mine waters on sandy loam soil.

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

5.2.2 Foliar Al, Fe and Mn content of crops grown on a vertic soil

Crops irrigated with acidic mine water typically had a higher foliar content of Al, Fe and Mn than those irrigated with the other waters. In peas, however, foliar Fe content was lower in plants irrigated with mine waters than those irrigated with municipal water. The lowest Fe content was observed in peas irrigated with neutralized mine water. The low foliar Fe content in peas irrigated with mine waters suggests that mine water constituents had a more significant influence on iron uptake in peas than in other crops. Iron and manganese have been found to have an antagonistic interaction, such as was observed by Moosavi and Ronaghi (2011), who found that soil and foliar application of Mn significantly decreased the Fe concentration in soybean. It is likely that the peas grown in this study were more sensitive to the antagonism between Mn and Fe than the other crops, thus, the relatively high concentrations of Mn in the mine waters decreased Fe uptake.

Figure 5.8 indicates that maize and peas accumulated Al levels associated with phytotoxicity when irrigated with acidic mine water. According to Mossor-Pietraszewska (2001), foliar uptake of Al is typically low. However, Zhang et al. (2010) found that leaf wetting with acidic solutions increases foliar Al uptake and induces phytotoxicity. It is, therefore, likely that elevated levels of Al in the leaves of crops irrigated with acidic mine water were a result of soil and foliar uptake of the element.

Figure 5.9 indicates that the foliar Fe content of all studied crops was within the sufficiency range. Maize and sorghum irrigated with acidic mine water contained excessive levels of Fe, these levels are likely to result in phytotoxicity.

Crops irrigated with acidic mine water accumulated phytotoxic levels of Mn, with exception to barley (Figure 5.10). Accumulation of Mn in the leaves of the considered crops followed the same order as that observed in red sandy loam soil.

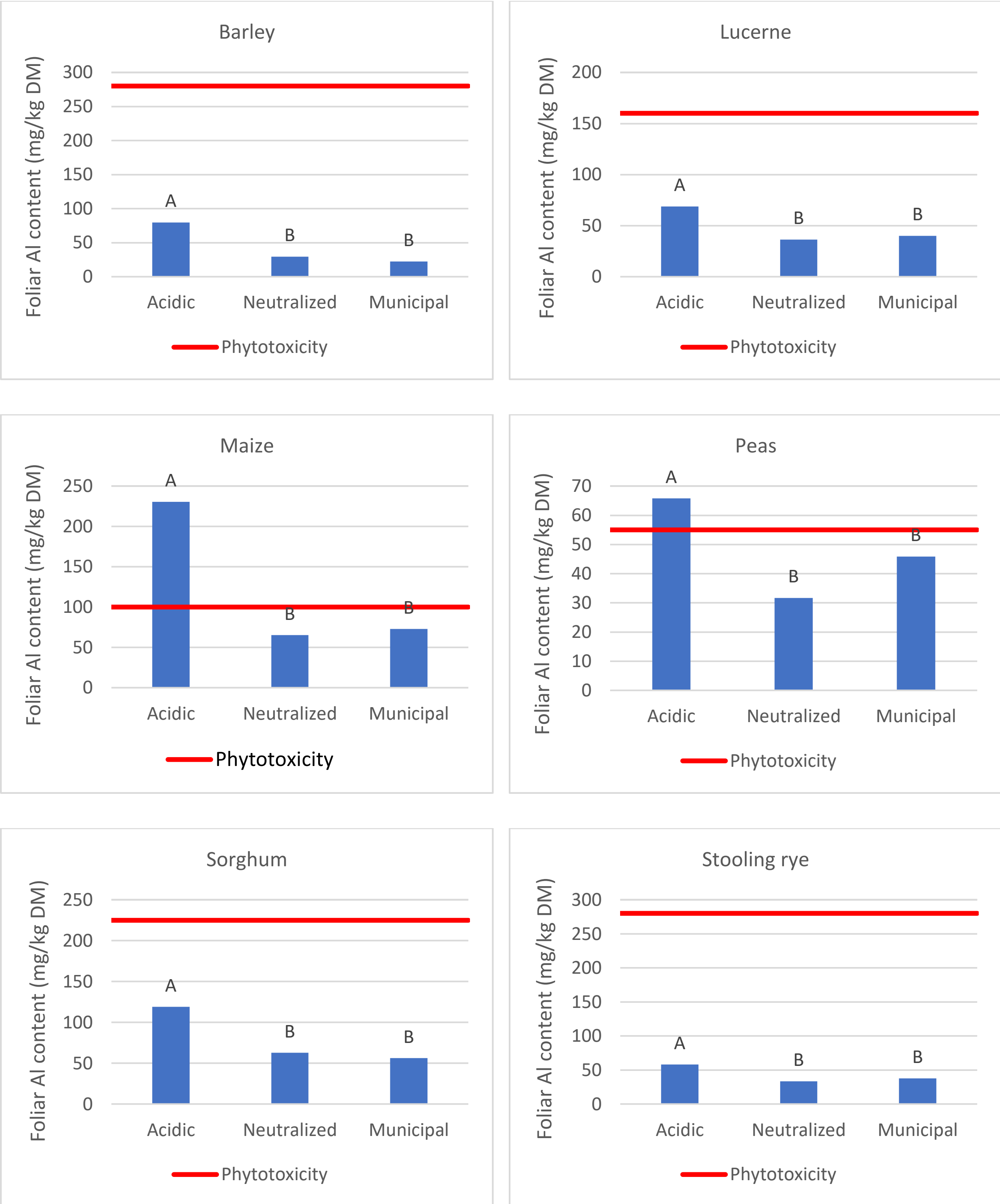

Figure 5.8: Al content in foliage, as influenced by irrigation with synthetic mine waters on vertic soil.

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

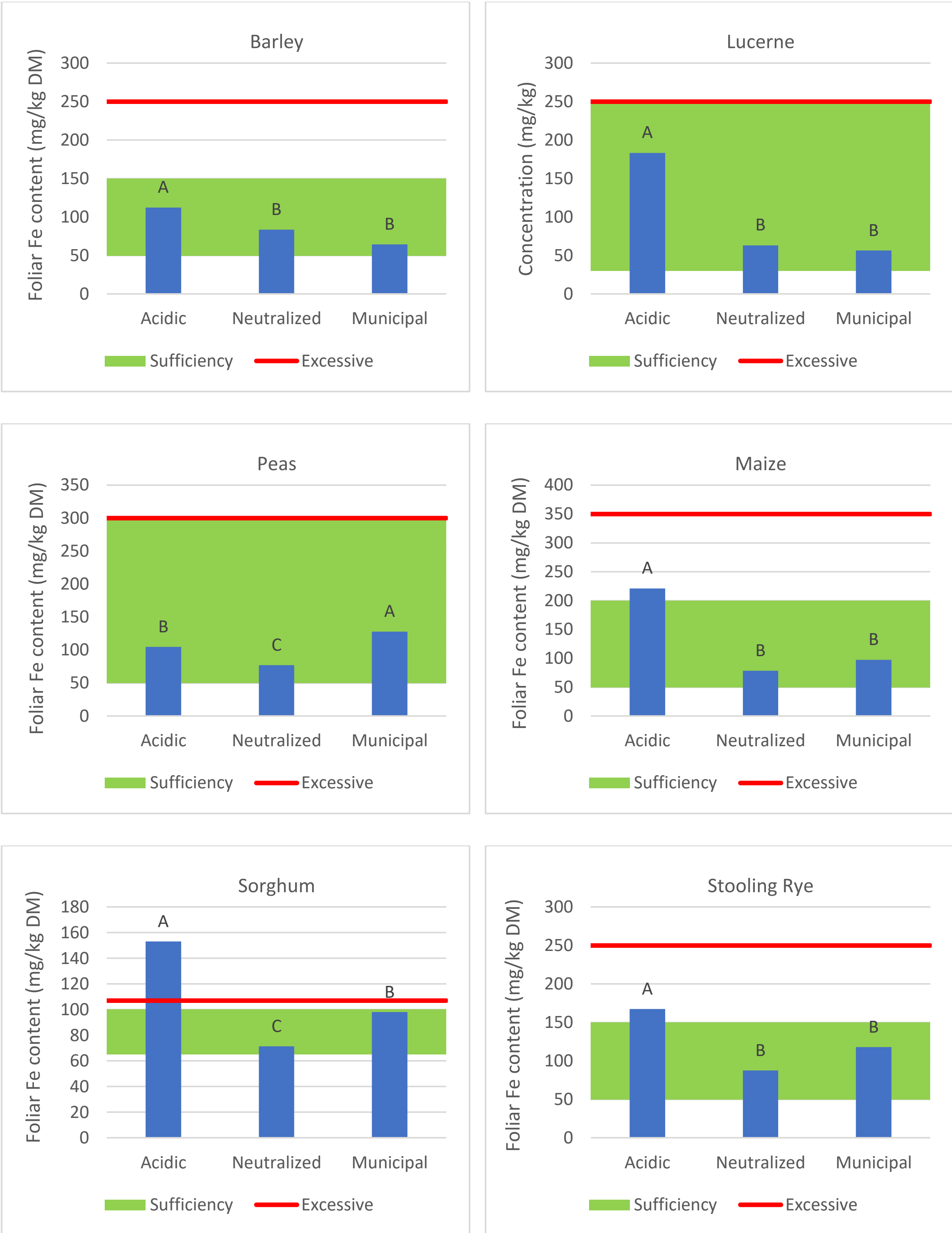

Figure 5.9: Fe content in foliage, as influenced by irrigation with synthetic mine waters on vertic soil.

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

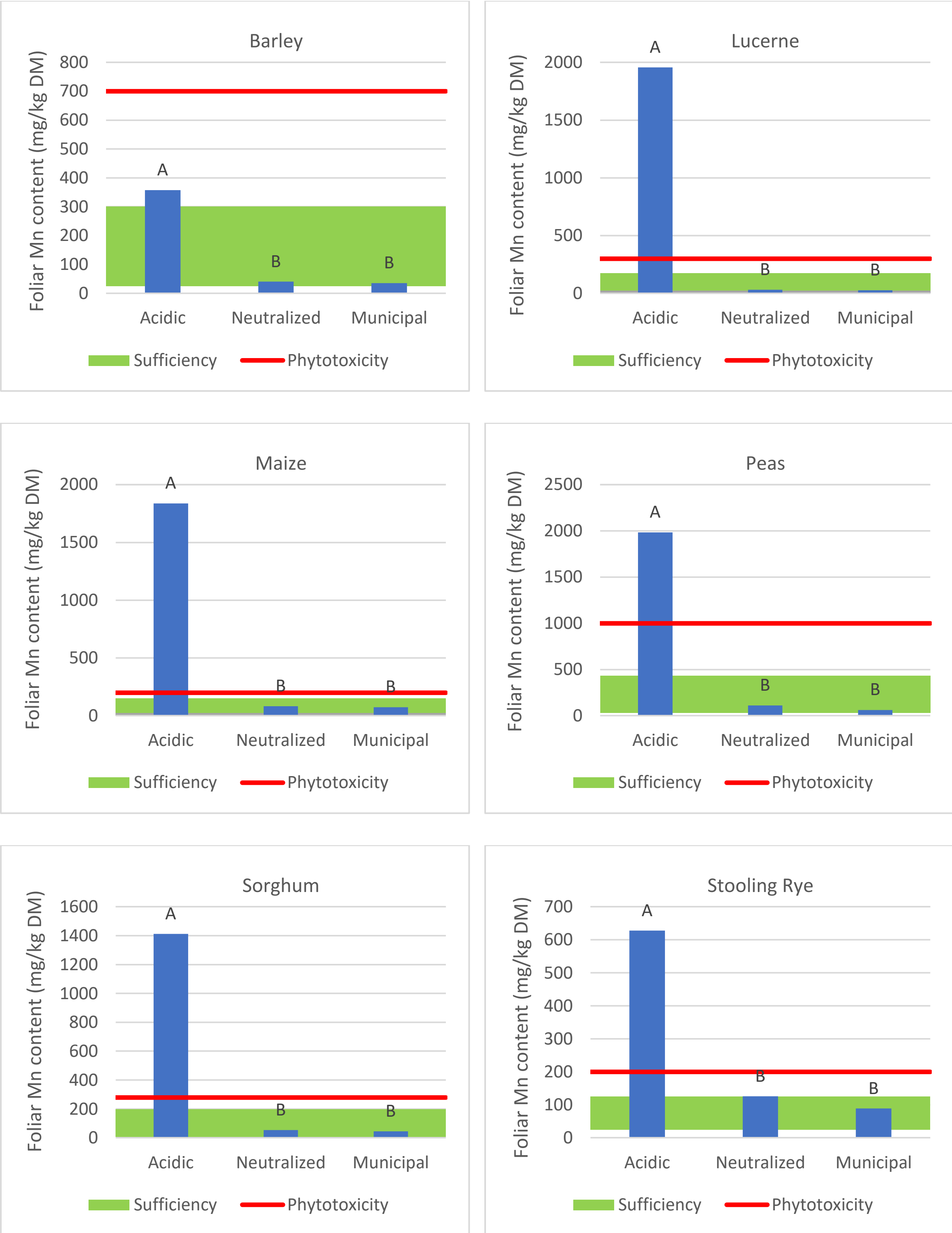

Figure 5.10: Mn content in foliage, as influenced by irrigation with synthetic mine waters on vertic soil.

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

5.2.3 The red sandy loam soil vs the vertic soil

Crops grown on red sandy loam soil displayed similar patterns of trace element uptake as crops that were grown on the vertic soil, however, foliar Al and Mn content was substantially higher in crops grown on the sandy loam soil. There are two possible explanations for these observed differences, the first could be that in the earlier stage of growth, crops grown on sandy loam soil were exposed to parts of the soil that had not yet been neutralized by the liming material applied on the soil. Consequently, the crops could have absorbed the free Al^{3+} and Mn^{2+} that was present in the soil.

Furthermore, crops are known to generate acidity in the rhizosphere, during nutrient acquisition (Zhou et al., 2009). This generation of acidity may have dissolved some of the Al and Mn compounds that had precipitated during acid neutralization, making Al and Mn more available for uptake. If this was the case, irrigation with acidic mine water likely exacerbated the dissolution of Al and Mn in the red sandy loam soil resulting in the excessive concentrations of these elements in the crops, as observed.

Another reason for the observed differences between crops grown on vertic soil and those grown on sandy loam soil could be that the vertic soil was able to sequester the trace elements more effectively than the sandy loam soil. It is likely that the vertic soil was able to complex and/or sorb more of the applied trace elements, owing to its higher CEC and organic matter content.

Chapter 6: Effect of irrigating with mine water on crop growth and yield

In this chapter, the effect of irrigation with mine waters on top dry matter (TDM) and grain yield of selected summer and winter crops was investigated. Since lucerne and stooling rye are forage crops and are not grown to the reproductive stage, there will be no grain yield data presented for these crops.

6.1 Dry matter production of crops as influenced by irrigation water quality

6.1.1 Dry matter production of crops grown on the red sandy loam soil

Irrigation with acidic mine water, on red sandy loam (RSL) soil, significantly reduced dry matter production in all studied crops with exception to stooling rye (Figure 6.1). Irrigation with acidic mine water completely inhibited the growth of lucerne. Irrigation with synthetic neutralized saline mine water, on red sandy loam soil, had no significant effect on the growth of all studied crops, with exception to maize.

The decrease in the top dry matter of crops irrigated with acidic mine water is likely due to the combined effects of acidity and salinity in soils, as well as the accumulation to phytotoxic levels of Al, Fe and Mn in crops. Soil analyses indicate that irrigation with acidic mine water acidified and salinized the red sandy loam soil (pH_{KCl} 3.2 and ECe 681 mS/m). Foliar analyses indicate that there was an accumulation to phytotoxic levels of Al, Fe and Mn in the crops (see section 5.2). Given that maize, lucerne and peas are salt sensitive crops, it was expected that their growth would also be adversely affected by irrigation with the neutralised mine water. However, the water had no adverse effect on these crops, suggesting that acidity (and likely the accumulation of toxic elements) was the main growth limiting factor for these crops when irrigated with acidic mine water, at least in the short term.

6.1.2 Dry matter production of crops grown on vertic soil

Irrigation with synthetic mine waters, on the vertic soil, had no significant effect on the dry matter production of all crops considered, except for sorghum (Figure 6.1). The top dry matter of sorghum increased when the crop was irrigated with synthetic neutralized mine water.

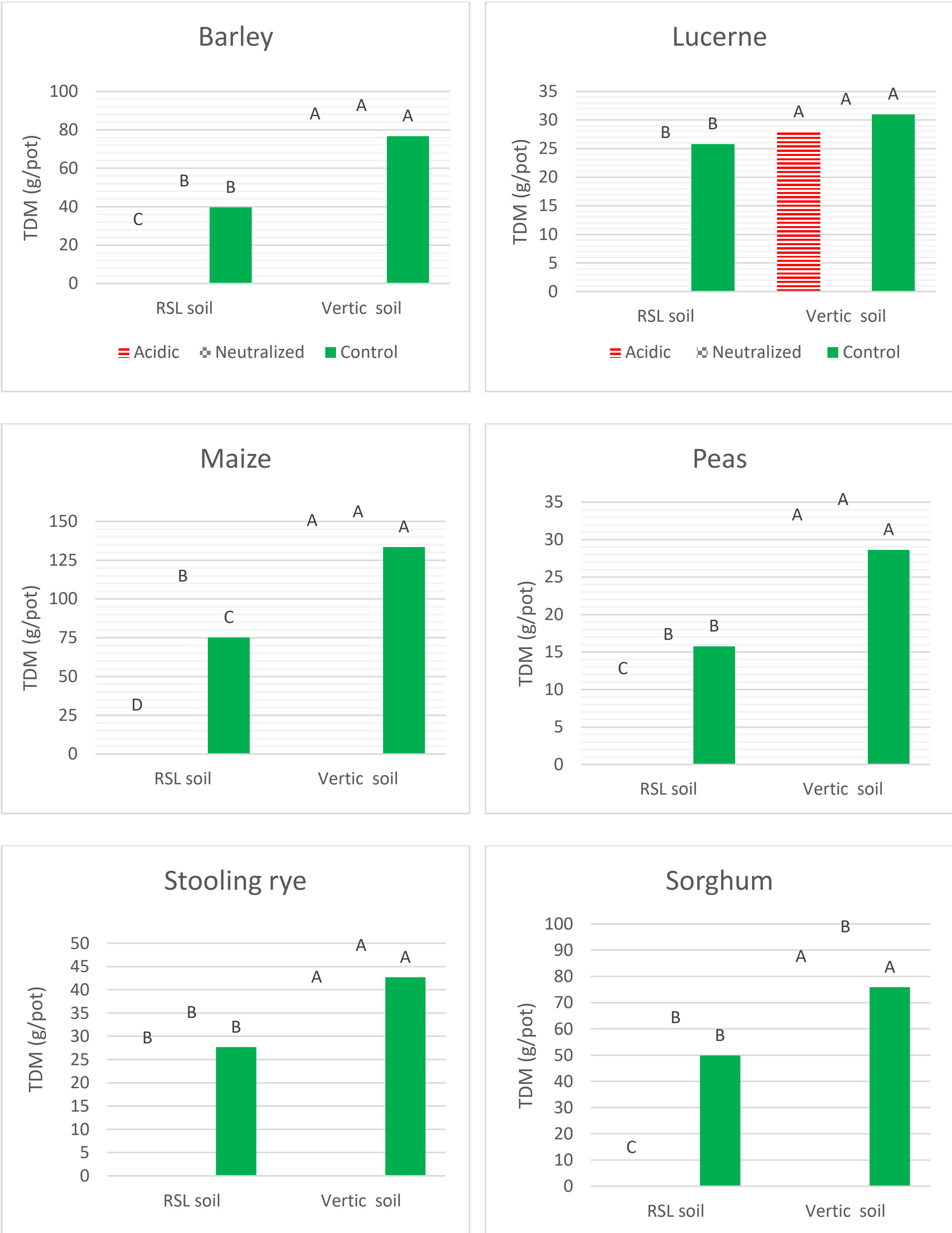

Figure 6.1: Top dry mass of crops as influenced by irrigation water quality.

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

Soil analyses indicate that irrigation with acidic mine water acidified and salinized vertic soil to pH_{KCl} 3.3 and ECe 555 mS/m, respectively. This was above the acidity and salinity tolerance thresholds of the acid and salt sensitive crops, peas and lucerne. However, the dry matter production of these crops was not significantly affected by irrigation with acidic mine water. This suggests that the vertic soil may have mitigated the effects of the acidic mine water constituents. Soils with high CEC are reported as having ameliorative effects against toxic concentrations of elements such as Al and Mn, as well as having an ample acid buffering capacity (Sparks, 2003). A high CEC may also confer salinity buffering capabilities to soils by facilitating the sorbtion of salt-forming ions or ionic compounds.

6.1.3 The red sandy loam soil vs the vertic soil

Crops grown on the vertic soil produced more dry matter than those grown on the red sandy loam soil. These differences were also noted in crops irrigated with municipal water, which was not expected. The differences in dry matter production between crops grown on the red sandy loam soil and those grown on the vertic soil were likely due to the effects of acidity in the red sandy loam soil. It is probable that the red sandy loam soil had not equilibrated with the liming material in the earlier stages of crop growth, resulting in impaired growth.

Foliar analyses also indicate that some of the crops grown on the red sandy loam soil accumulated phytotoxic levels of Al and/or Mn even when irrigated with municipal water (see section 5.2). This suggests that Al, Fe and Mn were likely more phytoavailable or more accessible in red sandy loam soil than in the vertic soil, which is also likely a result of an incomplete reaction between the soil and the liming material in the earlier stages of crop growth.

6.2 Grain yield of crops as influenced by irrigation water quality

6.2.1 Grain yield of crops grown on red sandy loam soil

The grain yield of crops is presented in (Figure 6.2). Irrigation with acidic mine water on red sandy loam soil significantly decreased the yield of peas and barley, and completely inhibited the reproductive growth of maize and sorghum. Irrigation with neutralized mine water had no significant effect on grain yield of maize, peas and sorghum, however, it increased the grain yield of barley.

The decrease in the grain yield of crops irrigated with acidic mine water was likely due to the red sandy loam soil having a low acid buffering capacity. It is probable that the lime applied to the soils was ineffective in neutralizing the acidity input since lime was only applied to raise the pH of the already acidic soil to 6.5, whilst applied acidity was not accounted for. Based on the acid generating potential of the water, an additional 3.2 g of $Ca(OH)_2$ should have been added to the soil to account for applied acidity (see Appendix E for calculations).

Maize and sorghum irrigated with acidic mine water did not reach the reproductive stage, hence, these crops did not produce grain. This could be due to the crops being grown on soils that had previously been irrigated with the acidic mine waters. Crops are known to be more susceptible to phytotoxicity in the earlier stages of growth. It is, therefore, likely that the loading of salts, Al, Fe and Mn on soils that already contained these constituents, adversely affected the crops in their earlier growth stages.

6.2.2 Grain yield of crops grown on vertic soil

Irrigation with mine waters significantly increased the grain yield of barley and peas. In these crops, irrigation with neutralized mine water produced the most grain, whereas irrigation with municipal water produced the least grain. In maize and sorghum, grain yield increased with neutralized mine water irrigation and decreased with acidic mine water irrigation. Similar to what was observed with TDM, the grain yield of crops grown on the vertic soil was typically higher than that of crops grown on the red sandy loam soil, regardless of irrigation water quality.

The low yields observed in crops irrigated with municipal water may have been a result of overpopulation in the pots. Pots were not completely thinned out during the experiment as there was a concern that completely thinning out the pots may result in the loss of data if some of the remaining plants are lost due to non-treatment related issues. The presence of more than one plant in a pot likely resulted in competition for nutrients and other resources. Since the mine waters contained higher concentrations of Ca, Mg, S, Fe and Mn than the municipal water, irrigation with mine waters may have minimized the competition for nutrients, thereby increasing yield.

As discussed in section 6.2.1, maize and sorghum were grown on soils that had previously been irrigated with acidic mine water. It is therefore likely that this 'preloading' of mine water constituents adversely affected the growth of these crops in the earlier stages, resulting in reduced yields.

Figure 6.2: Grain yield of crops as influenced by irrigation water quality.

Means of the same crop with similar letters are not significantly different at $P \leq 0.05$.

6.2.3 The red sandy loam soil vs the vertic soil

There were differences in growth and yield between crops grown on the vertic soil and those grown on the red sandy loam soil, with crops grown on the vertic soil producing more dry matter and having higher grain yield than those grown on the red sandy loam soil. This is likely due to the initial soil condition (pH an Al content) in the vertic soil being more conducive to crop growth than in the red sandy loam soil. This part of the study demonstrated that irrigating with acidic mine waters may have severe effects on crops grown on soils with low CEC, clay content and organic matter, particularly if there is no leaching fraction to mitigate salt accumulation or lime applied to the soils to counteract the acidity of the water. Such soils will likely require high lime application rates, especially if they are already acidified.

This part of the study also demonstrated that soils can mitigate the effects of potentially phytotoxic mine water constituents. This was especially notable with the maize and sorghum which produced grain when grown on the vertic soil irrigated with acidic mine water but did not produce grain when grown on red sandy loam soil and irrigated with the same water. In the next chapter, the food and fodder safety evaluation of crops irrigated with mine waters is presented.

Chapter 7: Food and fodder safety evaluation of crops irrigated with synthetic mine waters

The previous section indicated that crops irrigated with Al, Fe and Mn rich mine waters can accumulate phytotoxic levels of the metal. The accumulation of these metals in forage crops poses a health risk to livestock, furthermore, if these metals accumulate in the grain produced by crops they pose a health risk to both livestock and humans consuming this grain. In this chapter, the health risks associated with consuming foods that contain potentially toxic elements were assessed by determining the hazard quotients (HQ). HQ is calculated using the oral reference doses published by the United States Environmental Protection Agency (EPA). Since there is no established oral reference dose for Al and Fe in the list published by the EPA, a hazard quotient cannot be calculated for these elements. As a result, food safety assessments for Al and Fe are determined by estimating the dietary intake (see Appendix B for details) and comparing that to provisional tolerable intakes. In livestock nutrition maximum tolerable levels of dietary Al, Fe and Mn intake for selected livestock have been developed.

7.1.1 Food safety evaluation of crops grown on a red sandy loam soil

Crops irrigated with acidic mine water contained significantly higher Al, Fe and Mn in their grain than those irrigated the other mine waters (Table 7.1). There was no significant difference in grain Al, Fe and Mn content between crops irrigated with municipal water and those irrigated with neutralized mine water.

Table 7.1: Al, Fe and Mn content in the grain of crops grown on red sandy loam soil, as influenced by irrigation water quality.

Crop	Water Quality	Al	Fe	Mn
			(mg/kg dry mass)	
Barley	Acidic	40^{A}	186^{A}	523^{A}
	Neutralized	15^{B}	52^{B}	95^{B}
	Municipal	18^{B}	62^{B}	46^{B}
Peas	Acidic	28^{A}	99^{A}	1285^{A}
	Neutralized	7^{B}	48^{B}	157^{B}

Crop	Water Quality	Al	Fe	Mn
			(mg/kg dry mass)	
	Municipal	7^{B}	54^{B}	111^{B}
Maize	Acidic	-	-	-
	Neutralized	7^{B}	36^{B}	4^{B}
	Municipal	9^{B}	32^{B}	2^{B}
Sorghum	Acidic	-	-	-
	Neutralized	12^{B}	52^{B}	37^{A}
	Municipal	14^{B}	55^{B}	19^{B}

Means of the same crop in the same column with similar letters are not significantly different at $P \leq 0.05$.

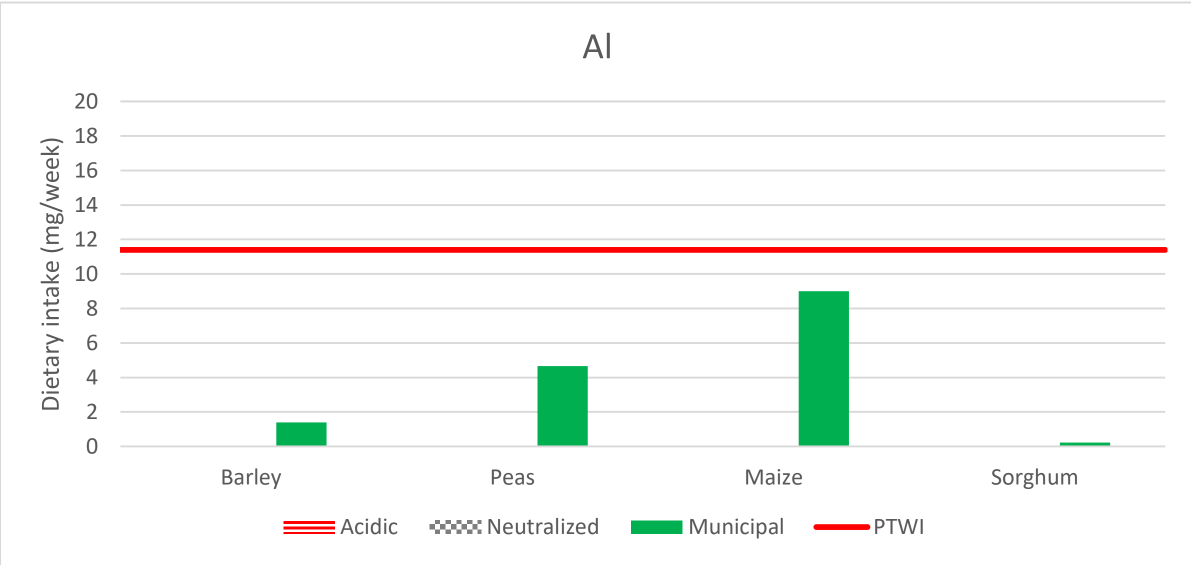

Figure 7.1: Food safety assessment of Al content in the grain of crops grown on red sandy loam soil, as influenced by irrigation water quality.

The estimated dietary intake of Fe was below the PMTDI in all crops, regardless of irrigation water quality (Figure 7.2). This indicates that crops irrigated with mine waters are unlikely to pose a health risk associated with Fe toxicity.

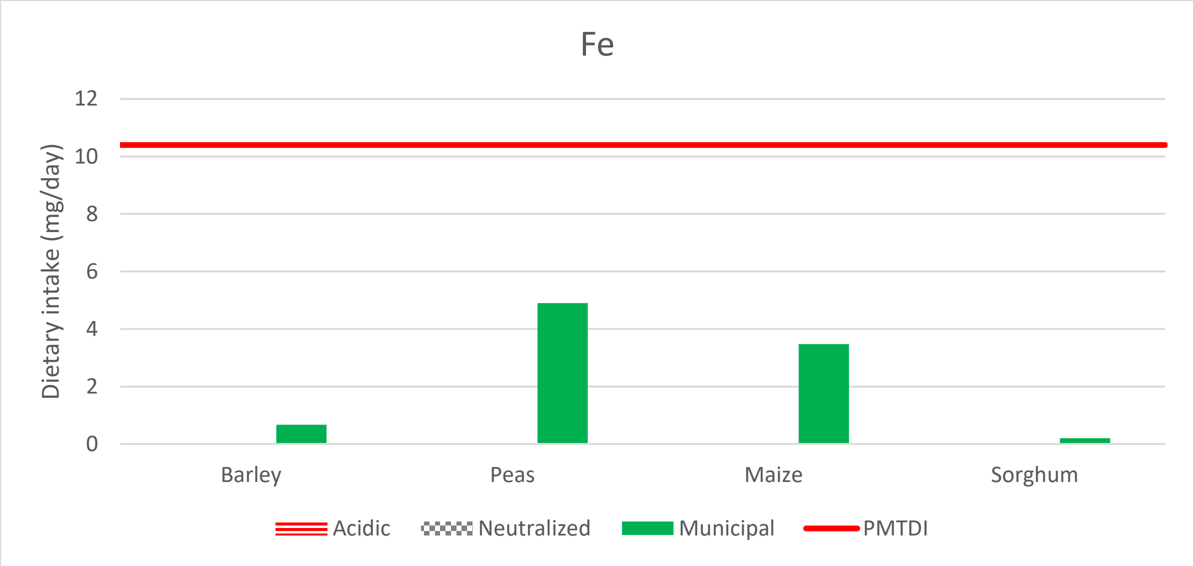

Figure 7.2: Food safety assessment of Fe content in the grain of crops grown on a red sandy loam soil, as influenced by irrigation water quality.

Estimated Mn intake through pea consumption exceeded the hazard quotient threshold, regardless of irrigation water quality (Figure 7.3). Barley grain Mn content exceeded the hazard quotient when irrigated with acidic mine water. However, grain Mn content of the crop was below the hazard quotient when irrigated with the other water qualities. The grain of maize and sorghum irrigated with neutralized mine water and municipal mine water did not present the risk of Al, Fe, or Mn-related toxicity in humans.

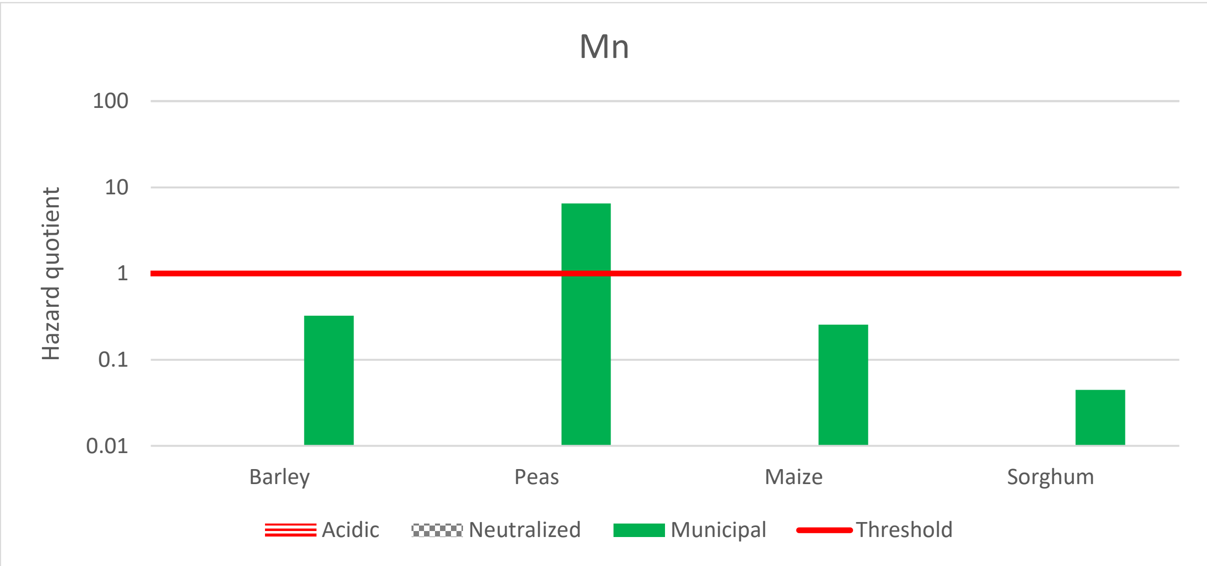

Figure 7.3: Food safety assessment of Mn content in the grain of crops grown on a red sandy loam soil, as influenced by irrigation water quality.

7.1.2 Food safety evaluation of crops grown on a vertic soil

A summary of grain Al, Fe and Mn content of crops is presented in Table 7.2. Crops irrigated with acidic mine water had significantly higher Al, Fe and Mn in their grain than those irrigated with the other waters, with exception to peas. Al, Fe and Mn in the grain of crops irrigated with neutralized mine water was not significantly different from that of crops irrigated with municipal water.

Table 7.2: Al, Fe and Mn content in the grain of crops grown on vertic soil, as influenced by irrigation water quality.

Crop	Water Quality	Al	Fe	Mn
			(mg/kg dry mass)	
Barley	Acidic	25^{A}	111^{A}	59^{A}
	Neutralized	10^{B}	97^{B}	30^{B}
	Municipal	9^{B}	83^{B}	32^{B}
Peas	Acidic	15^{A}	47^{A}	124^{A}
	Neutralized	4^{B}	40^{B}	15^{B}
	Municipal	7^{B}	51^{A}	12^{B}
Maize	Acidic	13^{A}	32^{A}	11^{A}
	Neutralized	3^{B}	20^{B}	2^{B}
	Municipal	3^{B}	16^{B}	0^{B}
Sorghum	Acidic	11^{A}	56^{A}	36^{A}
	Neutralized	7^{B}	30^{B}	7^{B}
	Municipal	7^{B}	39^{B}	8^{B}

Means of the same crop in the same column with similar letters are not significantly different at $P \leq 0.05$.

Figure 7.4 indicates that the estimated dietary intake of Al was higher for maize and peas than barley and sorghum. However, only maize irrigated with acidic mine water exceeded the provisional tolerable weekly intake (PTWI) for humans. Table 7.1 indicates that the Al content in maize grain was lower than that of peas. This means that exceedance of the PTWI was not necessarily due to maize having high concentrations Al, but rather due to the higher consumption of maize in comparison to the other considered crops.

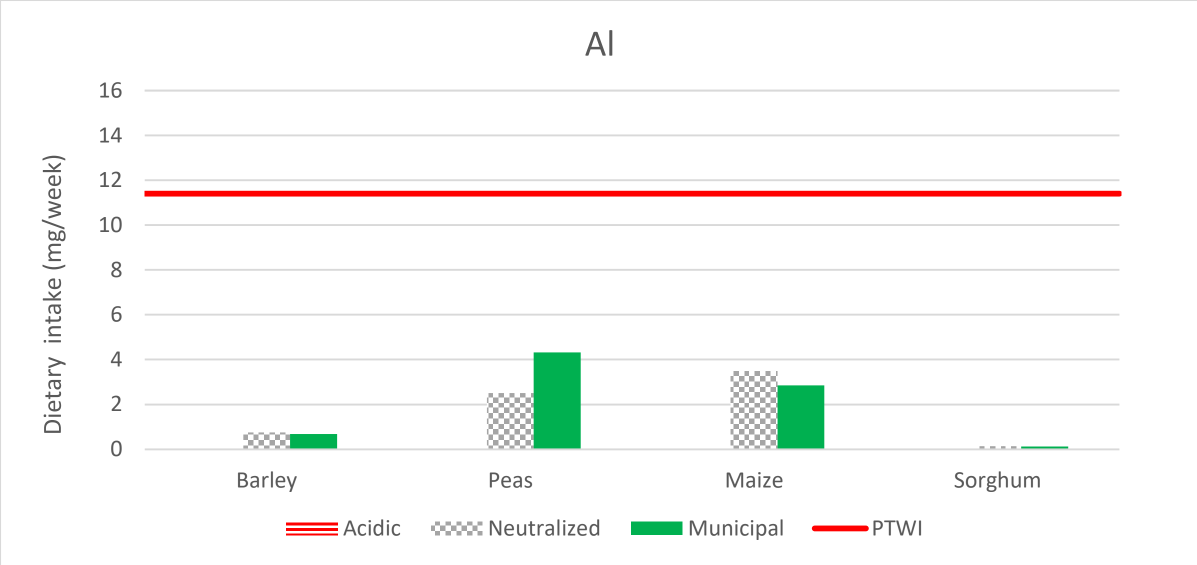

Figure 7.4: Food safety assessment of Al content in the grain crops grown on a vertic soil, as influenced by irrigation water quality.

Dietary Fe intake was below the provisional maximum tolerable daily intake (PMTDI) for all crops and all irrigation water qualities (Figure 7.5). This indicates that consumption of crops grown on soils with high CEC and theoretically high metal retention capacity are unlikely to pose health risks associated with iron toxicity when irrigated with mine waters.

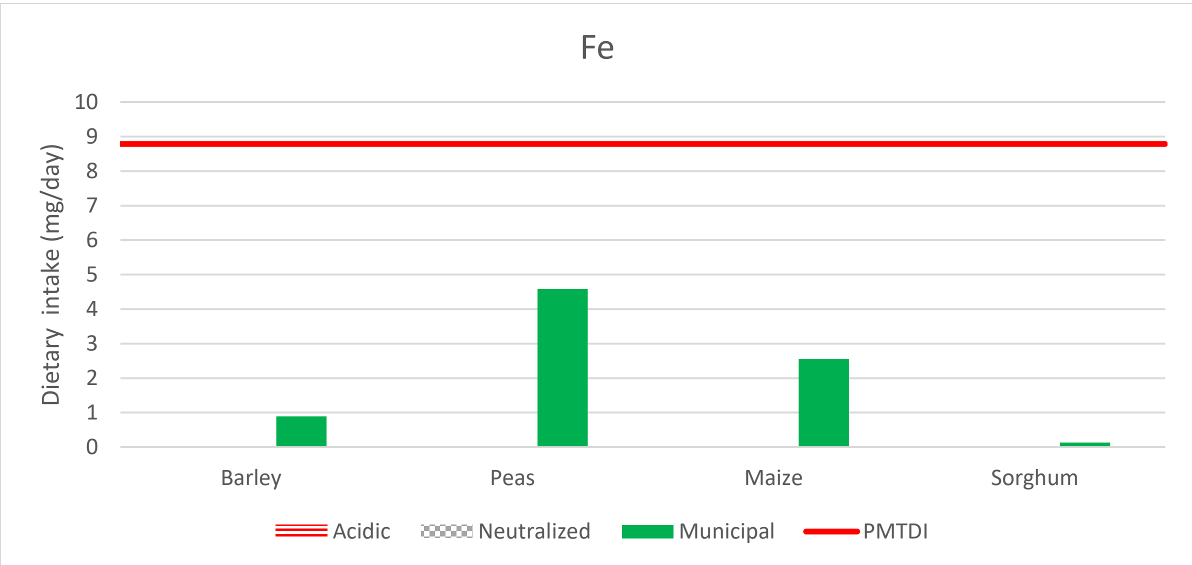

Figure 7.5: Food safety assessment of Fe content in the grain of crops grown on a vertic soil, as influenced by irrigation water quality.

Mn content in maize and peas irrigated with acidic mine water exceeded the hazard quotient threshold (Figure 7.6). These results indicate that the consumption of crops irrigated with acidic mine water may present the risk of Mn toxicity in vulnerable individuals. Grain Fe and Mn content were below zoo toxicity thresholds for sheep, pigs, cattle and chicken.

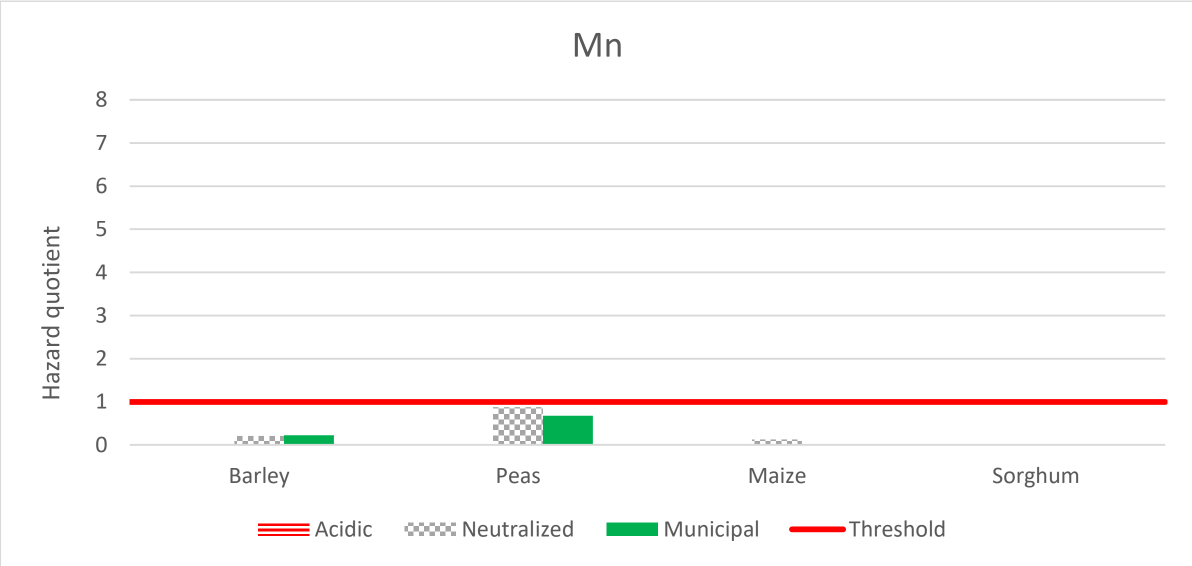

Figure 7.6: Food safety assessment of Mn content in the grain crops grown on a vertic soil, as influenced by irrigation water quality.

7.1.3 Fodder safety evaluation of crops grown on a red sandy loam soil

Al content in the grain of all considered crops grown on the red sandy loam soil was below the zootoxicity threshold for cattle, sheep, poultry and swine, with all irrigation waters considered (Figure 7.7 and 7.8).

Fe content in the grain of all considered crops was below the zootoxicity threshold for cattle, sheep, poultry and swine, with all irrigation waters considered (Figure 7.9 and 7.10). However, the foliar Fe content of stooling rye irrigated with acidic mine water exceeded the zootoxicity threshold of cattle, sheep and poultry.

Mn in the grain of all considered crops was below the zootoxicity threshold of all crops with exception to peas (Figure 7.11 and 7.12). Peas irrigated with acid mine water exceeded the zootoxicity threshold for swine. The Mn content in the foliage of crops irrigated with acid mine water exceeded the zootoxicity threshold for all considered livestock. The foliar Mn content of peas irrigated with neutralized and municipal water also exceeded the zootoxicity threshold for cattle, sheep and poultry.

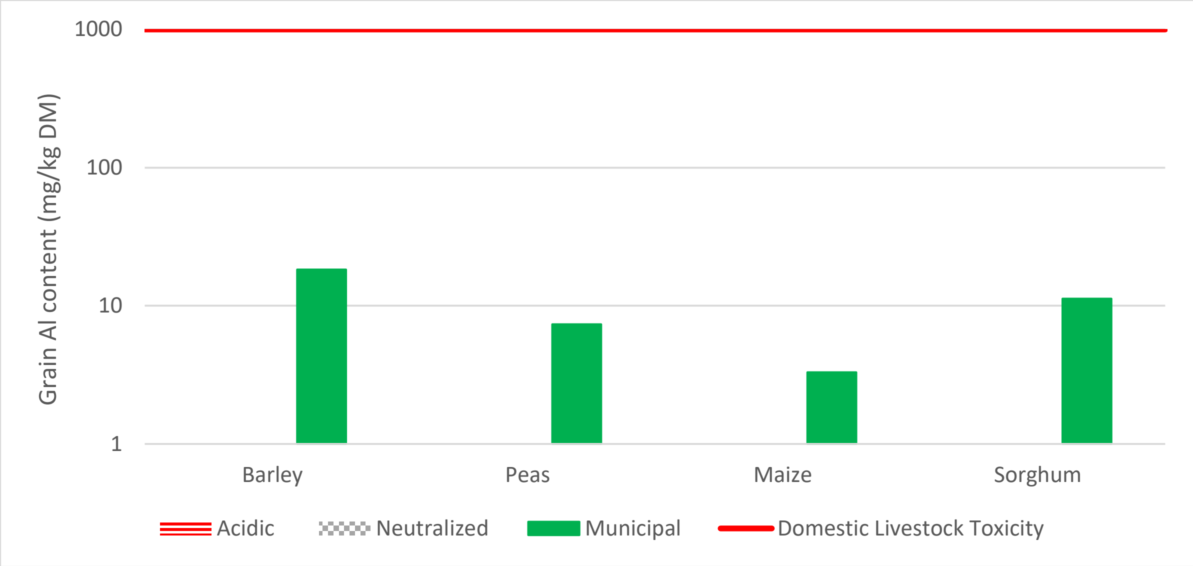

Figure 7.7: Fodder safety evaluation of Al content in the grain of crops grown on a red sandy soil, as influenced by irrigation water quality.

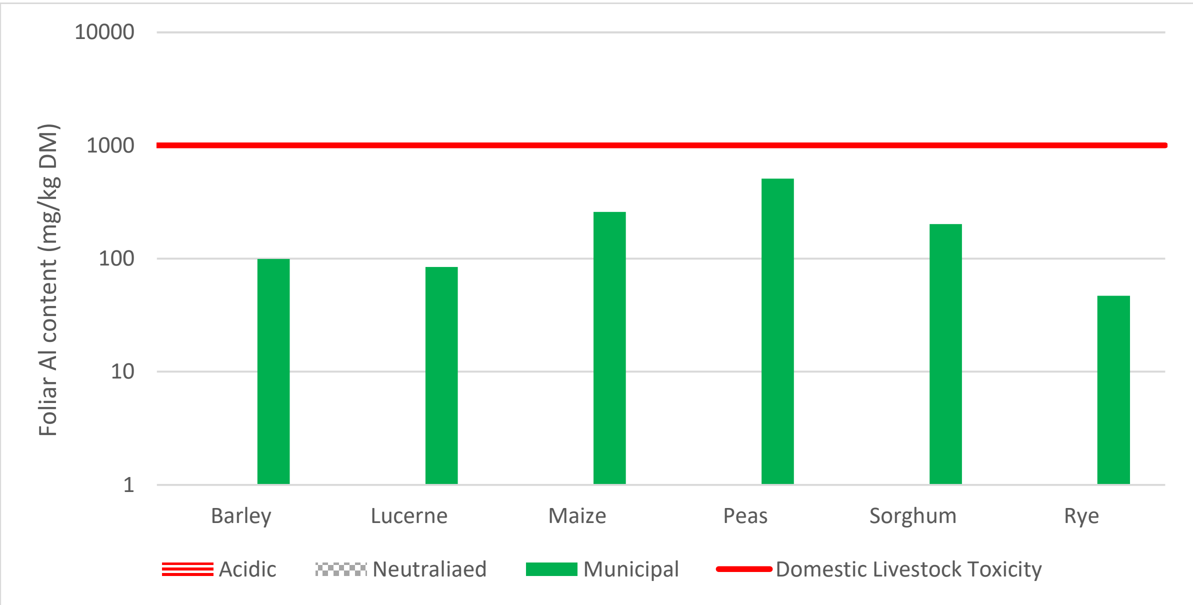

Figure 7.8: Fodder safety evaluation of Al content in the foliage of crops grown on a red sandy soil, as influenced by irrigation water quality.

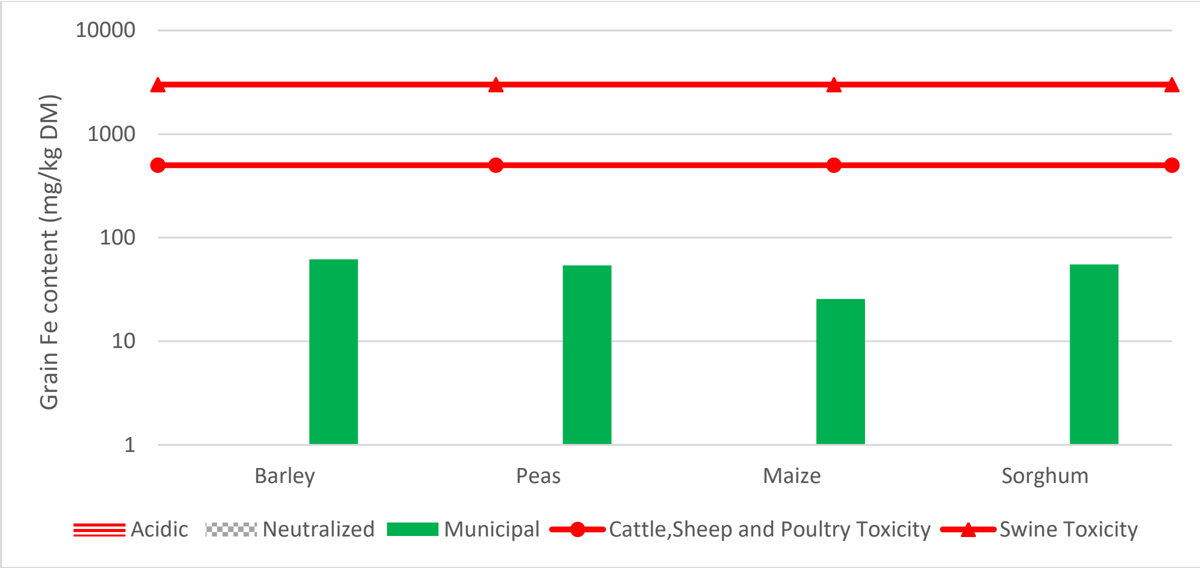

Figure 7.9: Fodder safety evaluation of Fe content in the grain of crops grown on a red sandy loam soil, as influenced by irrigation water quality.

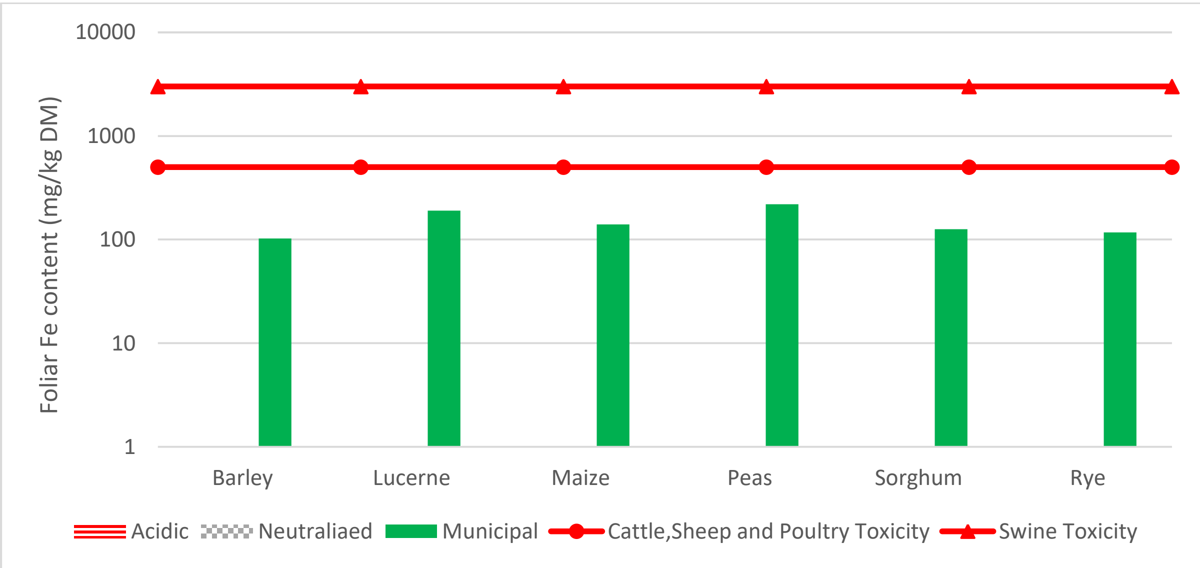

Figure 7.10: Fodder safety evaluation of Fe content in the foliage of crops grown on a red sandy loam soil, as influenced by irrigation water quality.

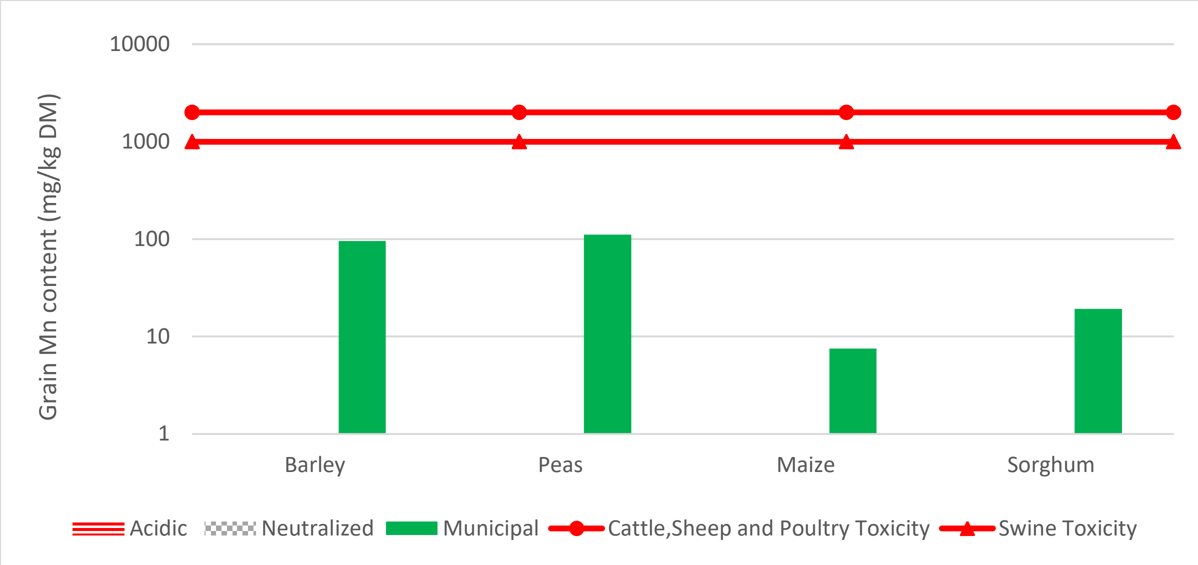

Figure 7.11: Fodder safety evaluation of Mn content in the grain of crops grown on a red sandy soil, as influenced by irrigation water quality.

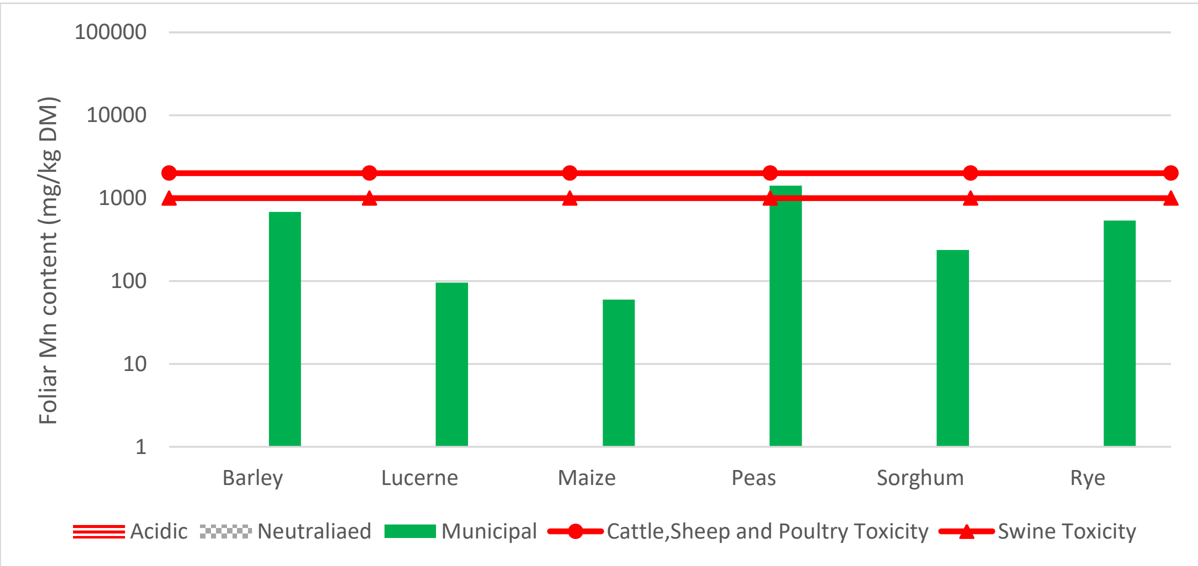

Figure 7.12: Fodder safety evaluation of Mn content in the foliage of crops grown on a red sandy loam soil, as influenced by irrigation water quality.

7.1.4 Fodder safety evaluation of crops grown on a vertic soil

Al and Fe content in the grain and foliage of all considered crops grown on the vertic soil was below the zootoxicity threshold for cattle, sheep, poultry and swine, with all irrigation waters considered (Figure 7.13 - 7.16).

The Mn content in the grain of all considered crops was below the zootoxicity threshold of all the considered livestock (Figure 7.17 and 7.18). On the other hand, the Mn content in the foliage of lucerne, maize and peas exceeded the zootoxicity threshold for all considered livestock. The Mn content in sorghum foliage exceeded the zootoxicity threshold for cattle, sheep and poultry, but was below the zootoxicity threshold for swine.

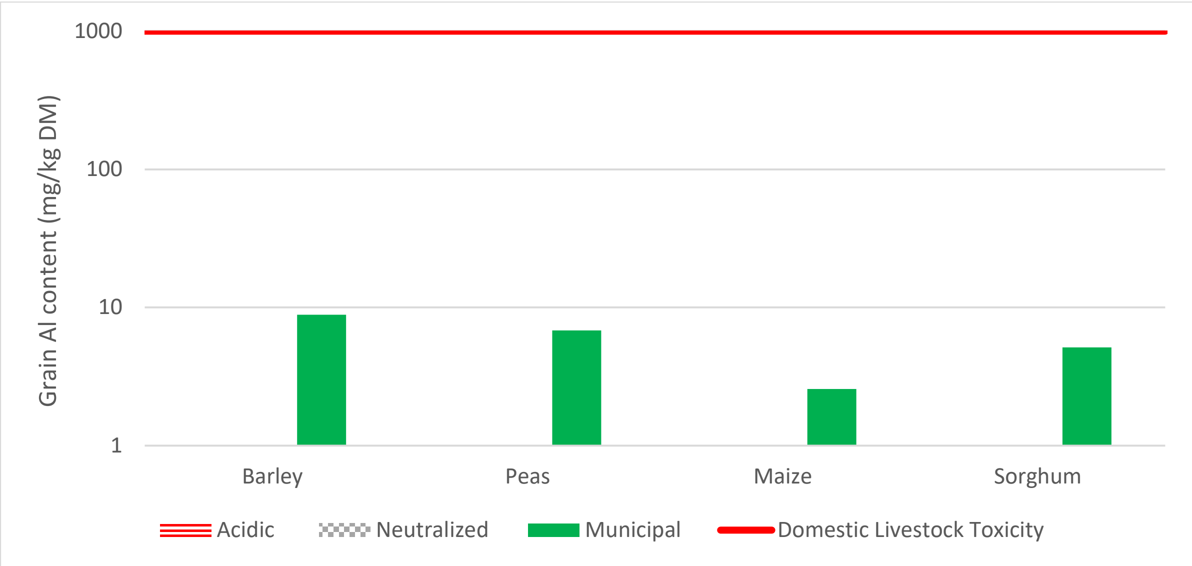

Figure 7.13: Fodder safety evaluation of Al content in the grain of crops grown on a vertic soil, as influenced by irrigation water quality.

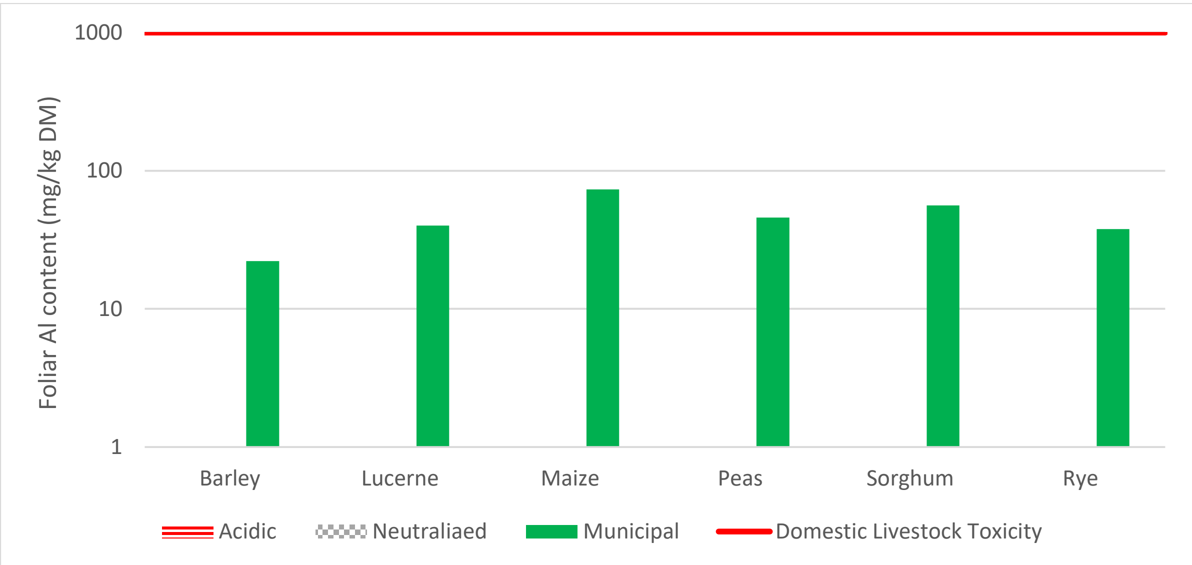

Figure 7.14: Fodder safety evaluation of Al content in the foliage of crops grown on a vertic soil, as influenced by irrigation water quality.

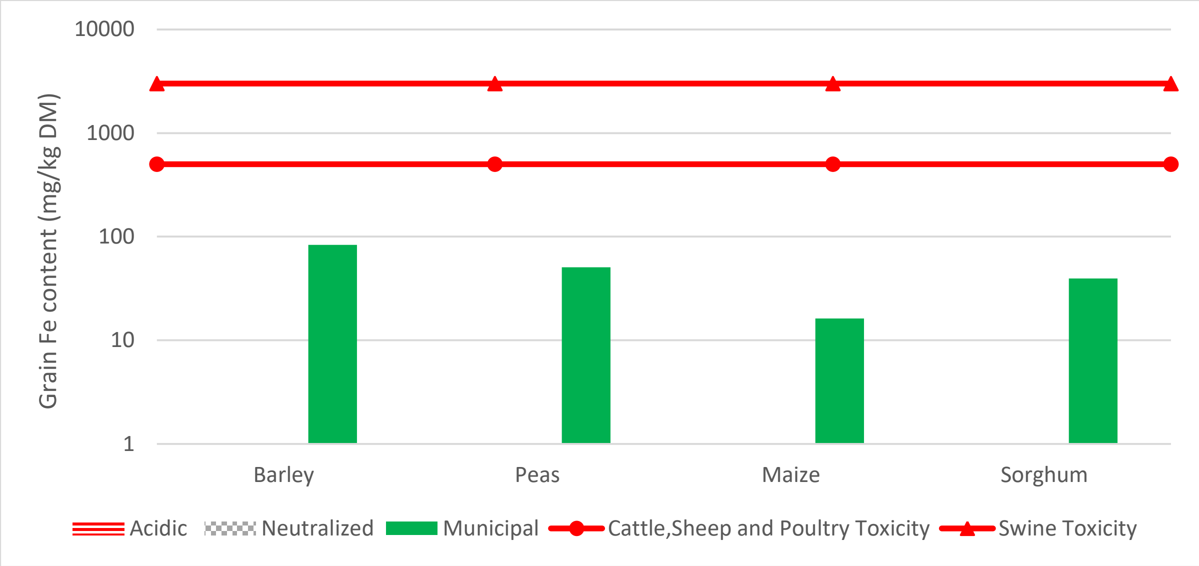

Figure 7.15: Fodder safety evaluation of Fe content in the grain of crops grown on a vertic soil, as influenced by irrigation water quality.

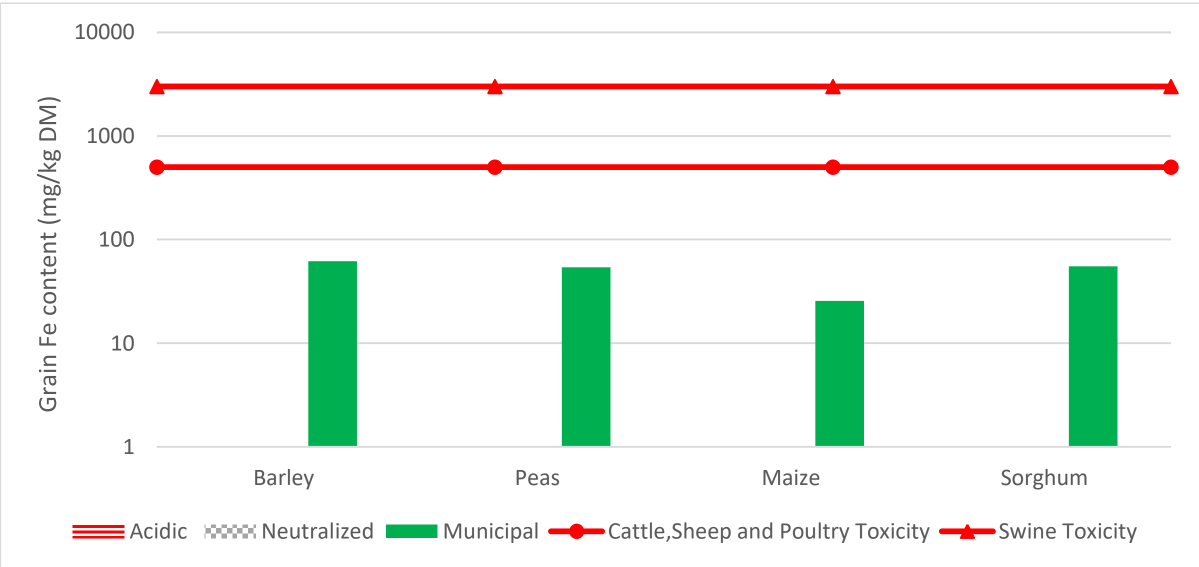

Figure 7.16: Fodder safety evaluation of Fe content in the foliage of crops grown on a vertic soil, as influenced by irrigation water quality.

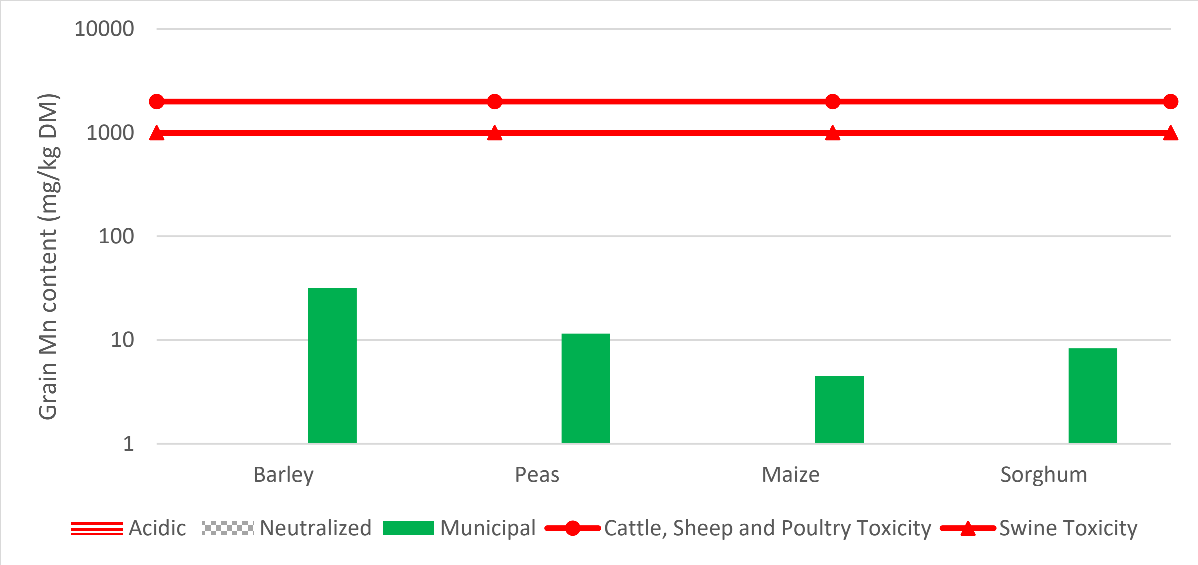

Figure 7.17: Fodder safety evaluation of Mn content in the grain of crops grown on a vertic soil, as influenced by irrigation water quality.

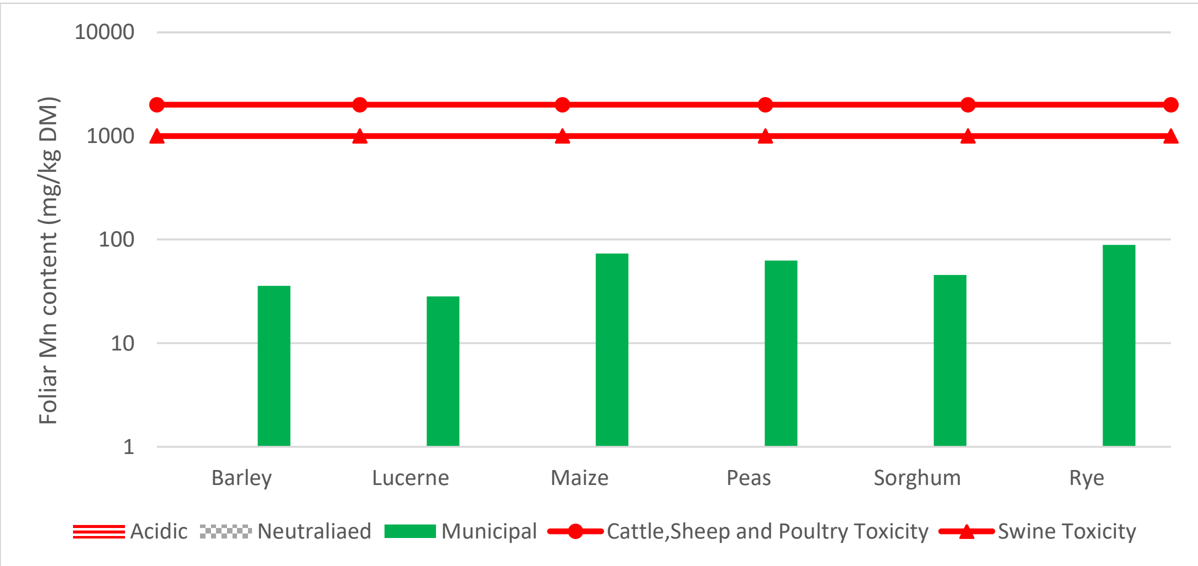

Figure 7.18: Fodder safety evaluation of Mn content in the foliage of crops grown on a vertic soil, as influenced by irrigation water quality.

7.1.5 The red sandy loam soil vs the vertic soil

Crops grown on the red sandy loam soil and the vertic soil presented potential health risks associated with Al and Mn toxicity when irrigated with mine waters. The evaluations indicated that the exceedance of food safety thresholds for humans were more a result of high consumption of the crops and less a reflection of high levels of potentially toxic metals in the crops. Therefore, crops that are typically consumed in large amounts or frequently, such as peas and maize are more likely to cause Al and Mn toxicity than those that are consumed less. Fodder safety evaluations indicated that crops grown on the red sandy loam soil, when irrigated with mine waters, are more likely to presents potential health risks associated with Al, Fe and Mn zootoxicity in livestock than those grown on the vertic soil, particularly if their foliage is consumed. All grain produced by crops grown on vertic soil and irrigated with mine water contained Al, Fe and Mn levels that are below the zootoxicity thresholds for all considered livestock.

Chapter 8: Assessing fitness-for-use of mine water using SAWQI-DSS

In this chapter, the fitness-for-use of the mine waters used in this study for irrigation were assessed using the Decision Support System (DSS) software component of the updated South African Water Quality Guidelines for Irrigation (SAWQI). SAWQI-DSS assesses irrigation water quality based on the effects of water constituents on soil quality, crop yield and quality, as well as irrigation equipment (Du Plessis et al., 2017a). Soil quality effects are assessed based on the influence of water constituents on soil salinity, soil permeability, dissolved carbon loading and trace element accumulation. Crop yield and quality is assessed based on water constituent effects on root zone effects, leaf scorching when wetted, contribution to nutrient removal, microbial contamination and crop damage by atrazine. The effects of water constituents on irrigation systems are also assessed.

For the purposes of this study, fitness for use assessments were focused on the effects of water constituents on soil salinity, soil permeability, trace element accumulation and relative crop yield. The tier 1 assessment indicated that irrigating with mine waters is unlikely to cause leaf scorching and unlikely to affect soil hydraulic conductivity, therefore, these parameters are not included in this assessment. SAWQI-DSS makes the following predictions:

- The percentage of time root zone salinity will fall within a fitness-for-use category,
- The percentage of time surface infiltrability (SI) will fall within a fitness-for-use category,
- The number of years it will take for trace elements to reach the accumulation threshold in soil,
    - The simulation was performed for aluminium (Al), iron (Fe) and manganese (Mn) as these elements were identified as being of concern, especially in the acidic mine water that was used in this study,
- The percentage of time yield will fall within a relative crop yield category as affected by soil salinity.

Fitness-for-use assessments of mine waters were performed for maize (*Zea Mays*) and barley (*Hordeum vulgare*) irrigation on sandy and clay soil. The influence of leaching application was also evaluated. It should be noted that in the SAWQI-DSS, a distinction is made between leaching requirement and leaching fraction (Du Plessis et al., 2017b). Leaching requirement is described as, “the leaching that is required to achieve a desired outcome”, and leaching fraction as, “the degree of leaching that actually took place”. As a result, leaching is presented as the effective leaching fraction in the results. The following leaching requirements were evaluated: 15%, 35%, 45% and 65%. This resulted in leaching fractions of 8.9, 9.2, 9.8, 10.6 and 11.5 % being simulated for the clay soil. In the sandy loam soil leaching fractions of 10.9, 11.3, 12.1, 13.1 and 14.3 were simulated. A summary of the input parameters is provided in Table 8.1.

Table 8.1: Input values for selected site-specific parameters of the Tier 2 assessment

Irrigation system	Overhead
Irrigation Timing	30% depletion to FC
Weather Station	PTA-Univ-Proefplaas
Soil depth	1 m
Initial salt content	Low
Salt-sensitive crop	Maize
Salt tolerant crop	Barley

8.1 Long-term simulation of maize irrigation with acidic saline mine water

8.1.1 Root zone salinity

Sandy loam soil

Irrigation with acidic mine water on a sandy loam soil resulted in root zone salinity that was acceptable 5% of the time, unacceptable 25% of the time and tolerable 70% of the time, at the lowest leaching fraction (10.3%) (Figure 8.1). As the leaching fraction increased from 10.3% to 11.5%, the percentage of time root zone salinity would be unacceptable increased, while the percentage of time root zone salinity would be tolerable decreased. When the leaching fraction increased further from

11.5% to 39.2% the opposite was observed, root zone salinity became more tolerable and less unacceptable.

The increase in root zone salinity, as effective leaching fraction increased from 10.3% to 11.5% is attributed to an increase in salt loading. The decrease in root zone salinity, as leaching fraction increased further, can be attributed to leaching and gypsum precipitation, to a degree. In the SAWQI-DSS, solute modelling is based on the salt routine by Robbins (1991), and since acidic mine water contains high concentrations of Ca and SO_4, gypsum is precipitated by the model and root zone salinity decreases (Du Plessis et al., 2017b). Therefore, as leaching fraction is increased past a certain level, the root zone becomes saturated with dissolved solutes, resulting in salt precipitation.

These results indicate that application of a leaching fraction on a sandy loam soil may decrease salinity effects resulting from irrigation with the acidic saline mine waters used in this study.

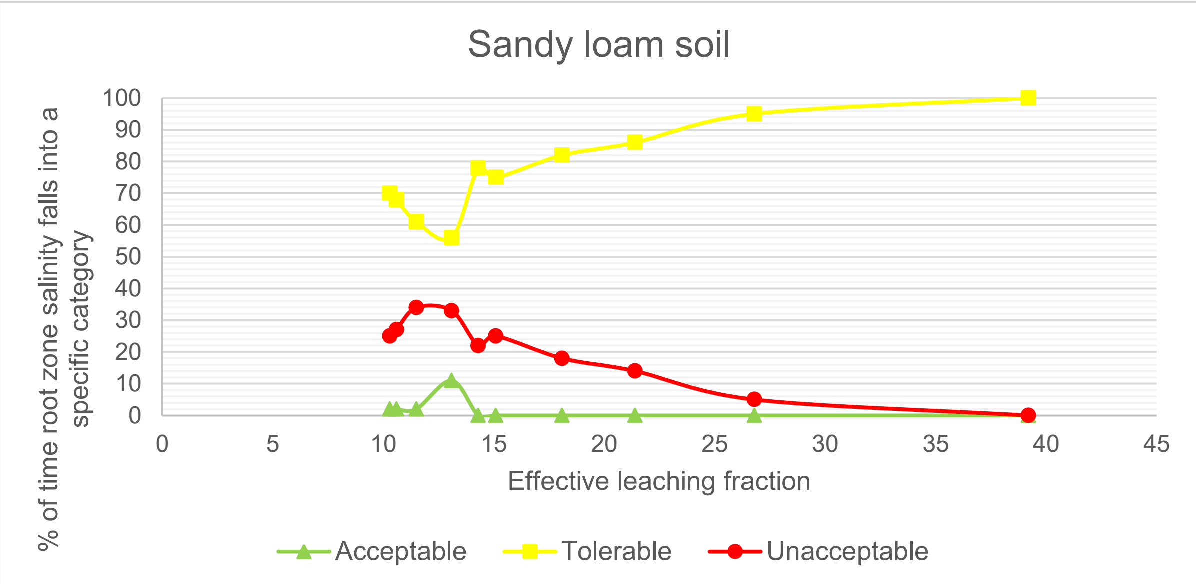

Figure 8.1: Percentage of time root zone salinity of the sandy loam soil was within a specific fitness-for-use category following maize irrigation with acidic mine water for a range of effective leaching fractions.[1]

[1] Acceptable = 200 - 400 mS/m, Tolerable = 400 – 800 mS/m, Unacceptable = >800 mS/m)

Clay soil

The effects of long-term irrigation (45 years) with acidic mine water on root zone salinity are presented in Figure 8.2. Irrigation with acidic saline mine water on a clay soil resulted in root zone salinity that is acceptable 2% of the time, unacceptable 43% of the time and tolerable 55% of the time at the lowest leaching fraction (8.3%). As the leaching fraction increased from 8.3% to 17.4%, the percentage of time root zone salinity would be unacceptable increased, while the percentage of time root zone salinity would be tolerable decreased. When the leaching fraction increased from 17.4% to 34.4% the opposite was observed, that is, the percentage of time root zone salinity would be unacceptable decreased, and the percentage of time root zone salinity would be tolerable increased.

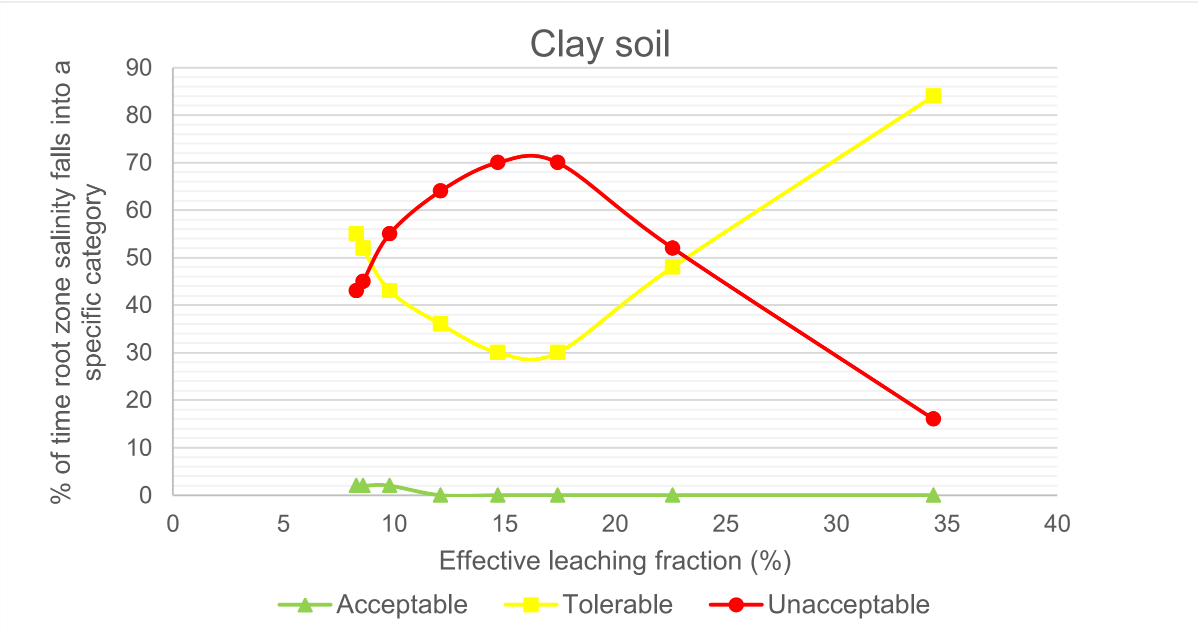

Figure 8.2: Percentage of time root zone salinity of the clay soil was within a specific fitness-for-use category following maize irrigation with acidic mine water for a range of effective leaching fractions.[1]

Similar to what was observed in the sandy loam soil, the increase in root zone salinity, as effective leaching fraction increased from 9.8% to 17.4%, can be

[1] Acceptable = 200 - 400 mS/m, Tolerable = 400 - 800 mS/m, Unacceptable = >800 mS/m)

attributed to an increase in salt loading. The decrease in root zone salinity, as leaching fraction increased further, can be attributed to leaching. In contrast to what was observed in the sandy loam soil, the percentage of time rootzone salinity was in in the unacceptable fitness-for-use category was higher than the percentage of time rootzone salinity was in the acceptable fitness-for-use category. This is due to vertic soil being difficult to leach and therefore accumulating salts to a higher degree than the sandy loam soil.

The fitness-for-use assessments suggest that irrigation with acidic mine water on sandy loam soil will typically result in lower root zone salinity than irrigation with the same water quality on a clay soil if equal leaching is applied. The differences in root zone salinity, between clay and sandy loam soil, can be attributed to the model used to simulate solute transport and reactions in the SAWQI-DSS. This model assigns a drainage factor and drainage rate to each soil type, which dictates how slow or fast water moves through soils in a day and thus how rapidly solutes are leached or accumulate (Du Plessis et al., 2017b). Since water moves slower in a clay soil than in a sandy loam soil, there is less leaching and more accumulation of salts in clay soil than in sandy loam soil. In addition, the simulation was performed for a field that receives rain, which contributes to the leaching. Since sands hold less water than clay effective leaching is higher in the sandy loam soil than in the clay soil.

8.1.2 Relative yield as influenced by soil salinity

Sandy loam soil

The relative yield of maize irrigated with acidic mine water on a sandy loam soil, was unacceptable 98% of the time and acceptable 2% of the time when irrigated with acidic saline mine water with a leaching fraction of 8.3% (Figure 8.4-a). As the effective leaching fraction increased from 11.5% the percentage of time yield was unacceptable increased to 100% and the percentage of time yield was acceptable decreased to zero.

These results are contrary to what was observed for root-zone salinity. The SAWQI-DSS crop growth model estimates the effect of salinity on yield based on the yield response curve by Maas and Hoffman (1977). This yield response curve takes into account crop tolerance to salinity. Maize is a salt-sensitive crop, therefore, improving root zone salinity only slightly may translate to an improvement in yield based on the response curve. Furthermore, it could be that relative yield improved as effective leaching increased to 13%, but remained below 70% relative yield, which is considered unacceptable.

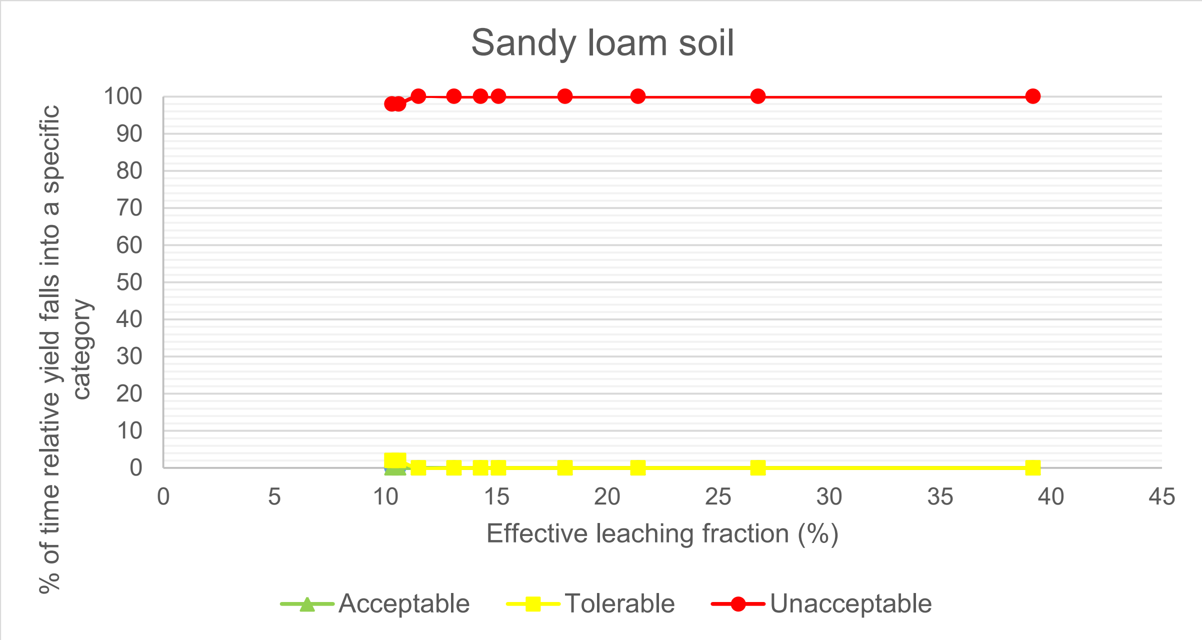

Figure 8.3: Percentage of time relative yield of maize irrigated with acidic mine water was within a specific fitness-for-use category, as influenced by sandy loam soil rootzone salinity for a range of effective leaching fractions.[1]*Figure 8.3*

Clay soil

The relative yield of maize irrigated with acidic mine water, on a clay soil, was unacceptable 98% of the time and acceptable 2% of the time at a leaching fraction of 8.3% (Figure 8.4). As the effective leaching fraction increased to 22.6% the percentage of time yield was unacceptable to 100% and decreased the percentage of time yield was acceptable to zero. The reason for this is the same as explained in section 8.1.1 (higher leaching fraction leads to more salt loading).

These results suggest that the relative yield of maize irrigated with acidic mine water on clay soil will be less than 70% most of the time when minimal leaching is applied. As previously mentioned, maize is a salt-sensitive crop and an improvement in soil salinity does not necessarily translate to an improvement in relative yield, therefore,

[1] Acceptable = 80 – 90 %, Tolerable = 70 – 80 %, Unacceptable = <70 %

it could be that relative yield is improving but it is still within the unacceptable fitness for use category.

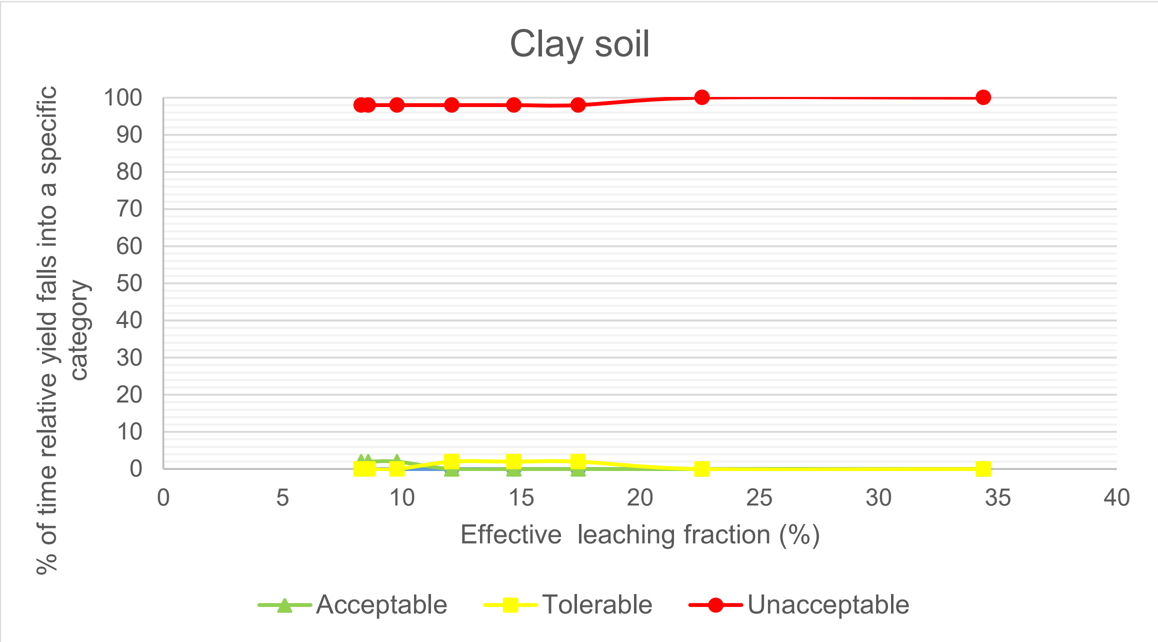

Figure 8.4: Percentage of time relative yield of maize irrigated with acidic mine water was within a specific fitness-for-use category, as influenced by clay soil root zone salinity for a range of effective leaching fractions.[1]

8.1.3 Accumulation of aluminium, iron and manganese in soil

The clay and sandy loam soil displayed similar patterns of aluminium (Al), iron (Fe) and manganese (Mn) accumulation (Figure 8.5 and 8.6). Soils irrigated with acidic mine water reached the Fe and Mn accumulation thresholds in less than a year. Al, on the other hand, reached the accumulation threshold only after a few decades, at the lowest leaching fraction. Increasing the leaching fraction decreased the number of years it would take for Al to accumulate to the threshold level. Trace elements do not 'leach', and as such, increasing water application increases the rate of trace element accumulation.

[1] Acceptable = 80 – 90 %, Tolerable = 70 – 80 %, Unacceptable= <70 %

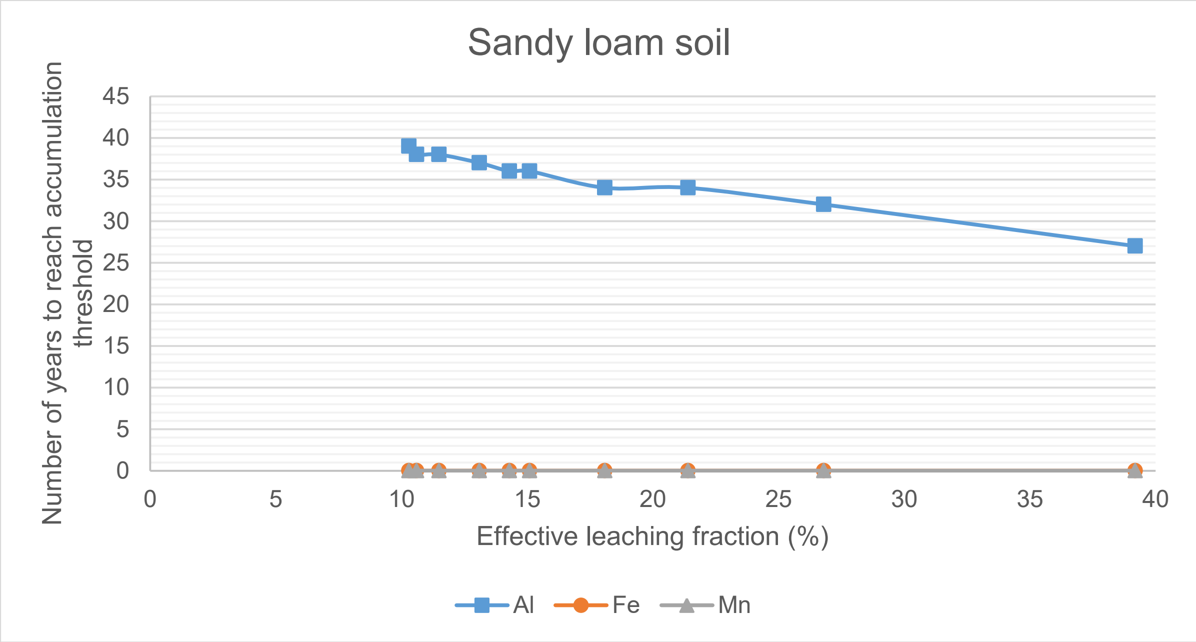

Figure 8.5: Al, Fe and Mn accumulation in a sandy loam soil as influenced by long term maize irrigation with acidic mine water for a range of effective leaching fractions.

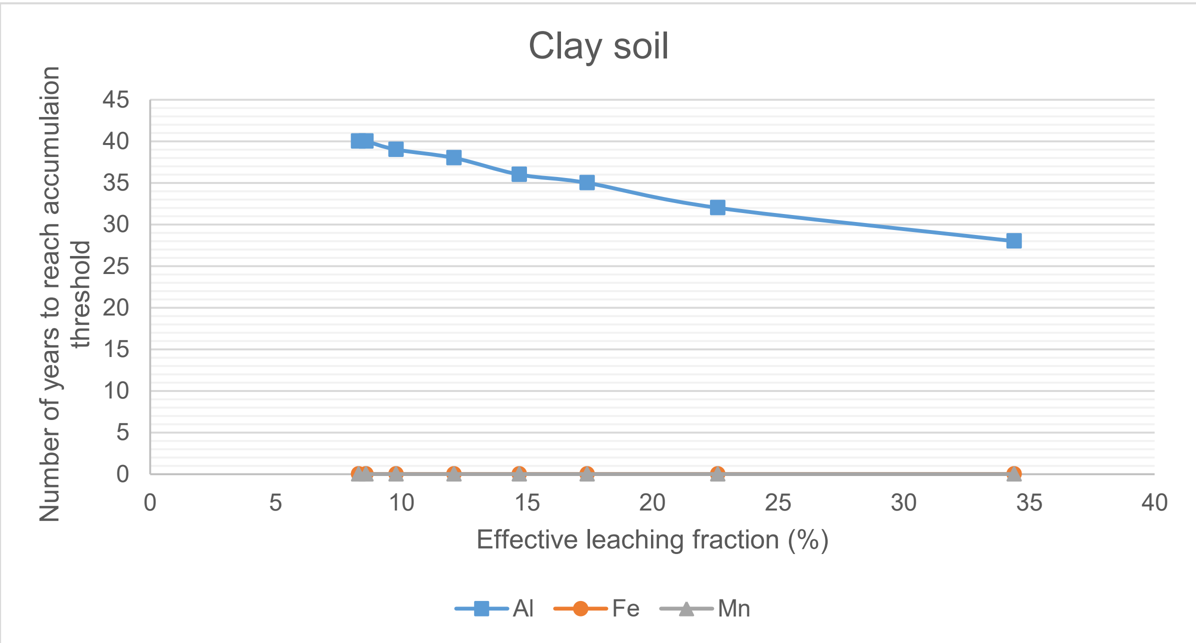

Figure 8.6: Al, Fe and Mn accumulation in a clay soil as influenced by long term maize irrigation with acidic mine water for a range of effective leaching fractions.

8.1.4 Surface infiltrability (SI)

Surface infiltrability was ideal most times and acceptable the rest of the time in both the clay and sandy loam soil at all leaching fractions (Figure 8.7 and 8.8). Increasing the leaching fraction did not have much of an effect on surface infiltrability. These results suggest that long term irrigation with such acidic mine water is unlikely to have adverse effects on soil permeability.

The effects of irrigation water on soil permeability is mainly determined by sodium (Na) levels in the water, which influence the exchangeable sodium percentage (ESP) of soils, as well as the salinity of the water. High levels of Na in irrigation water increases the ESP of soils and decreases infiltrability, however, according to Du Plessis and Shainberg (1985) high salinity can mitigate these effects as it prevents clay dispersion by releasing soluble electrolytes. The acidic mine water used in this study had high salinity and low Na, hence, it is predicted that it will typically have little or no effect on soil permeability.

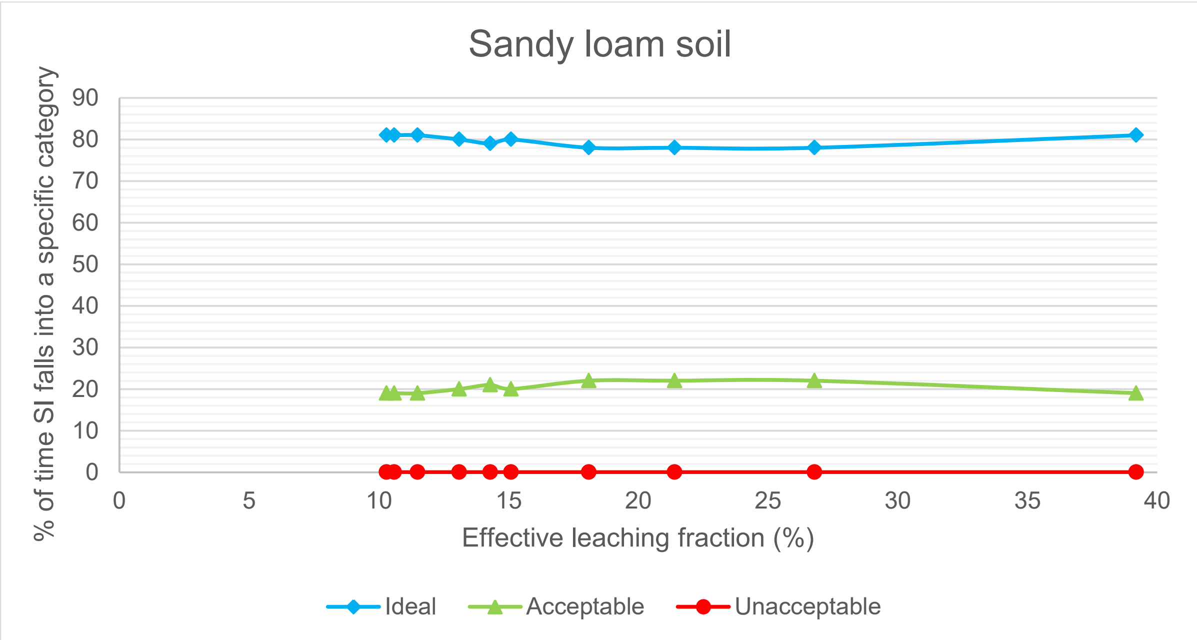

Figure 8.7: Percentage of time surface infiltrability of the sandy loam soil was within a specific fitness-for-use category following maize irrigation with acidic mine water for a range of effective leaching fractions.[1]

[1] Ideal = No reduction in permeability, Acceptable = Slight reduction in permeability, Unacceptable Severe reduction in permeability

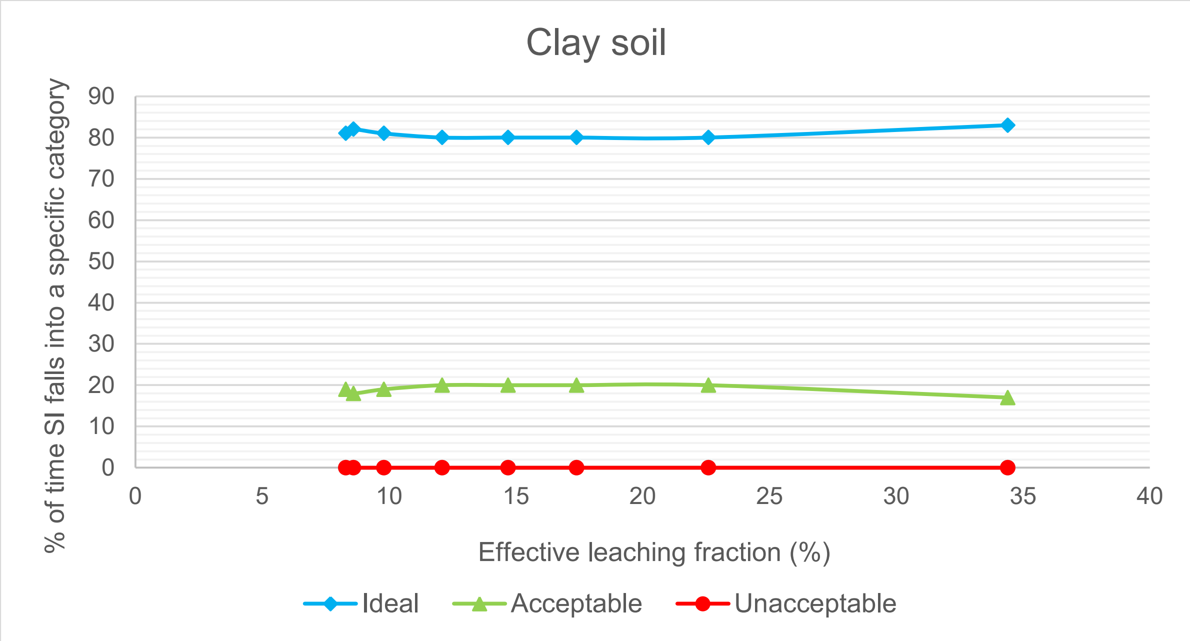

Figure 8.8: Percentage of time surface infiltrability of the clay soil was within a specific fitness-for-use category following maize irrigation with acidic mine water for a range of effective leaching fractions.[1]

8.2 Long-term simulation of barley irrigation with acidic saline mine water

8.2.1 Root zone salinity

Sandy loam soil

Barley irrigation with acidic mine water on a sandy loam soil was predicted to result in root zone salinity that is unacceptable 95% of the time, at the lowest leaching fraction (Figure 8.9). Root zone salinity under barley was also unacceptable more frequently than for maize, because barley received less rainfall and more irrigation water, as barley is grown in the winter season. As a result, there is less dilution of salinity by rainfall, and accumulation of salts occurs at a higher degree due to relatively higher volumes of irrigation water applied. Similar to what was observed for the sandy loam soil planted with maize, as leaching fraction increased, root zone

[1] Ideal = No reduction in permeability, Acceptable = Slight reduction in permeability, Unacceptable = Severe reduction in permeability

salinity became unacceptable 100% of the time up to a point, past which root zone salinity became less unacceptable and more tolerable. Furthermore, barley is a tolerant crop and grows better than maize in saline conditions. Therefore, barley transpires more than maize, resulting in higher concentrations of salts in the rootzone.

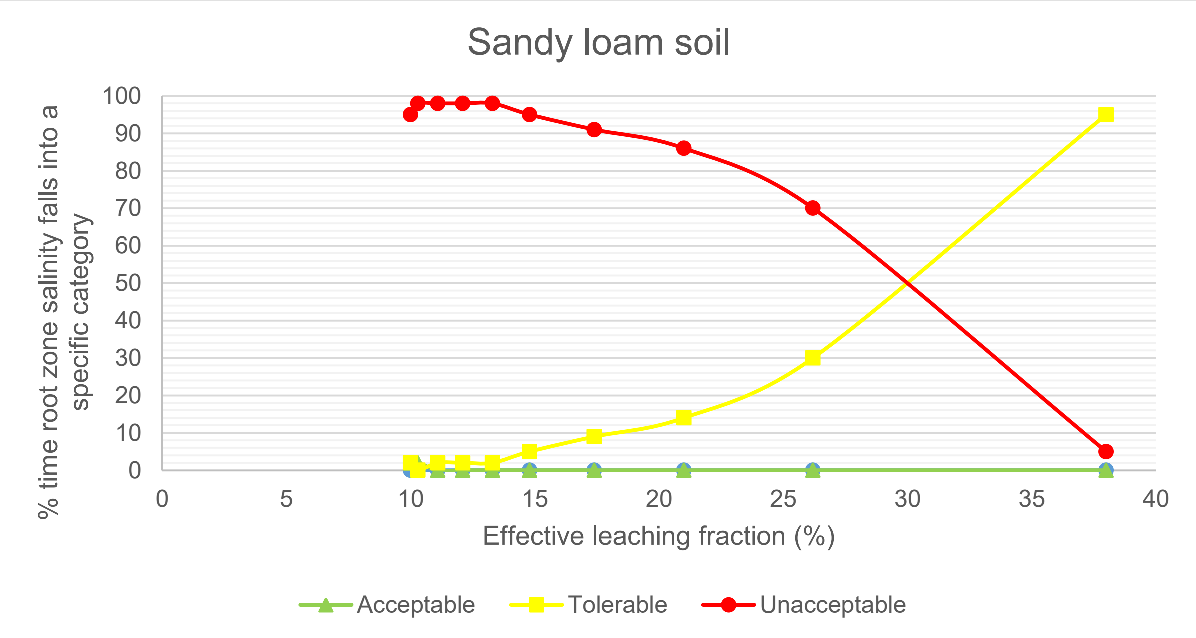

Figure 8.9: Percentage of time root zone salinity of the clay soil was within a specific fitness-for-use category following irrigation of barley with acidic mine water for a range of effective leaching fractions.[1]

Clay soil

Root zone salinity of clay soil irrigated with acidic mine water was unacceptable 98% of the time, and tolerable 2% of the time, at the lowest leaching fraction (Figure 8.10). Similar to what was observed for the clay soil planted with maize, root zone salinity of the soil planted with barley decreased as leaching fraction increased to a point, past which, increasing the leaching fraction results in the root zone salinity being less unacceptable and more tolerable. Furthermore, clay soil salinity was in the tolerable category less frequently than sandy loam soil salinity. This is due to

[1] Acceptable = 200 - 400 mS/m, Tolerable = 400 – 800 mS/m, Unacceptable >800 mS/m)

sandy loam soil being easier to leach than clay soil as is indicated by the higher effective leaching fraction in the sandy loam soil, despite similar leaching requirements being applied to both soils.

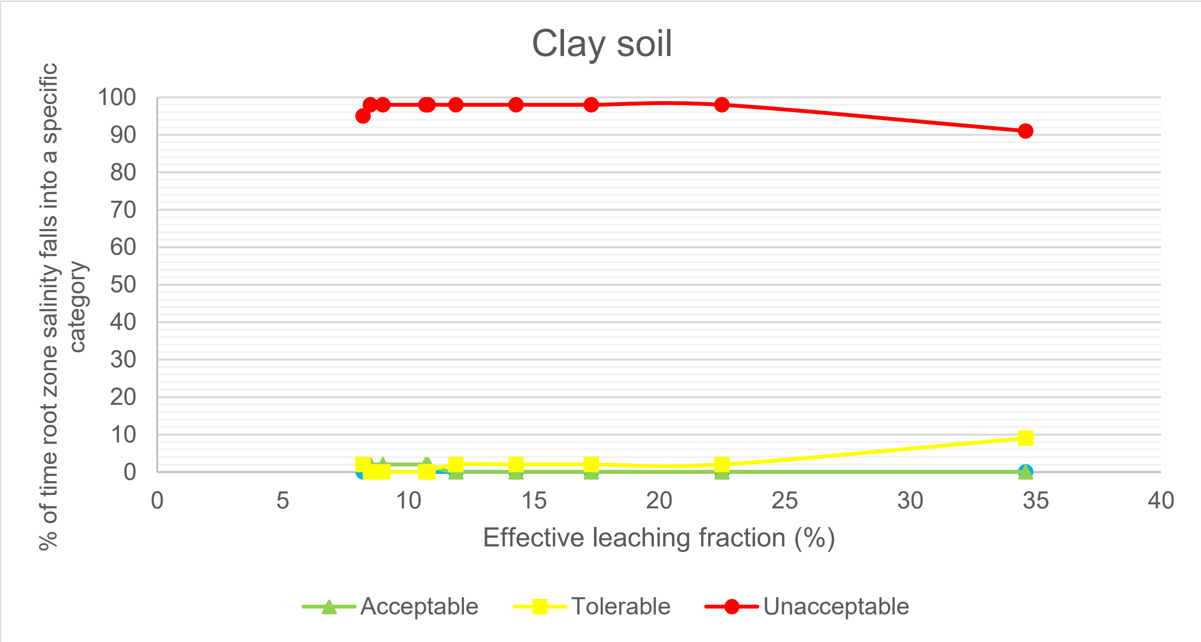

Figure 8.10: Percentage of time root zone salinity of the clay soil was within a specific fitness-for-use category following barley irrigation with acidic mine water for a range of effective leaching fractions.[1]

8.2.2 Relative yield as influenced by soil salinity

Sandy loam soil

Relative yield of barley grown on a sandy loam soil was predicted to be ideal 32% of the time, acceptable 48% of the time, tolerable 18% of the time and unacceptable 2% of the time (Figure 8.11). Increasing the leaching fraction decreased the percentage of time yield will be acceptable and ideal and increased the percentage of time yield would be tolerable and unacceptable, up to a certain leaching fraction. Increasing the leaching fraction, even more, increased the percentage of time yield will be ideal and decreased the percentage of time yield would fall into the other

[1] Acceptable = 200 - 400 mS/m, Tolerable = 400 – 800 mS/m, Unacceptable >800 mS/m)

fitness-for-use categories. These results indicate that salt-tolerant crops, grown on soils that are easier to leach are likely to have satisfactory yields when irrigated with acidic saline mine water, at least from a salinity perspective.

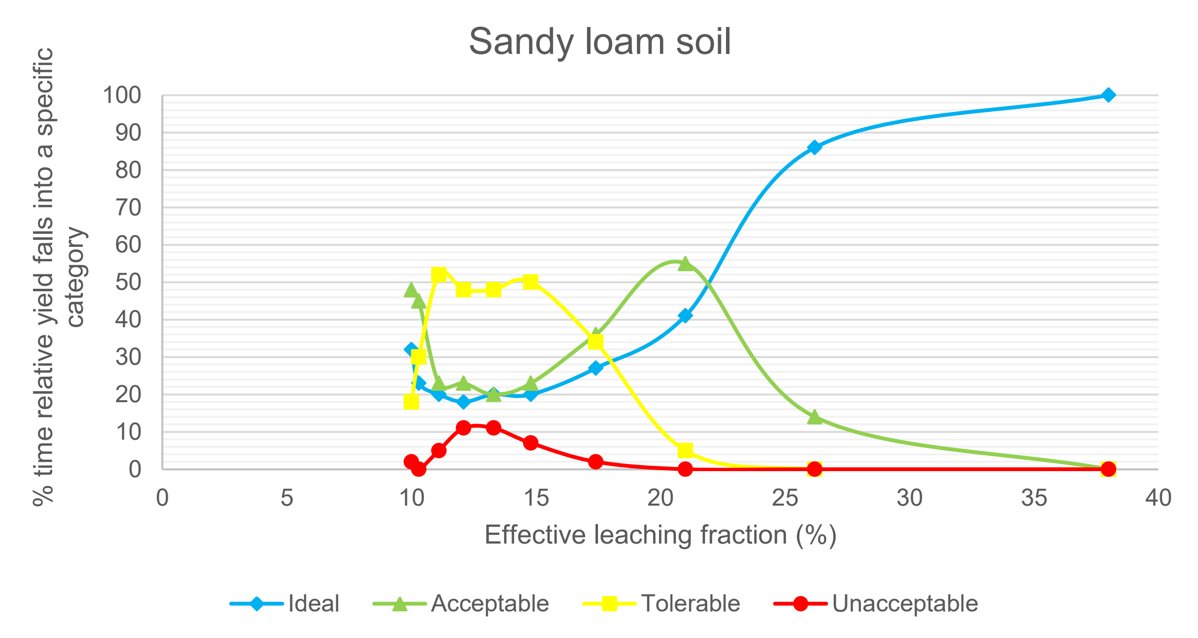

Figure 8.11: Percentage of time relative yield of barley irrigated with acidic mine water was within specific fitness-for-use categories, as influenced by sandy loam soil root zone salinity for a range of effective leaching fractions.[1]

Clay soil

The relative yield of barley grown on a clay soil was predicted to be ideal 100% of the time at the lowest leaching fraction (Figure 8.12). Counterintuitively, as leaching fraction increased, yield became less ideal up to a point, past which yield became ideal 100% of the time again. Barley, being a salt tolerant crop, can grow successfully in saline soils.

[1] Ideal =90-100%, Acceptable =80 – 90 %, Tolerable = 70 – 80 %, Unacceptable = <70 %

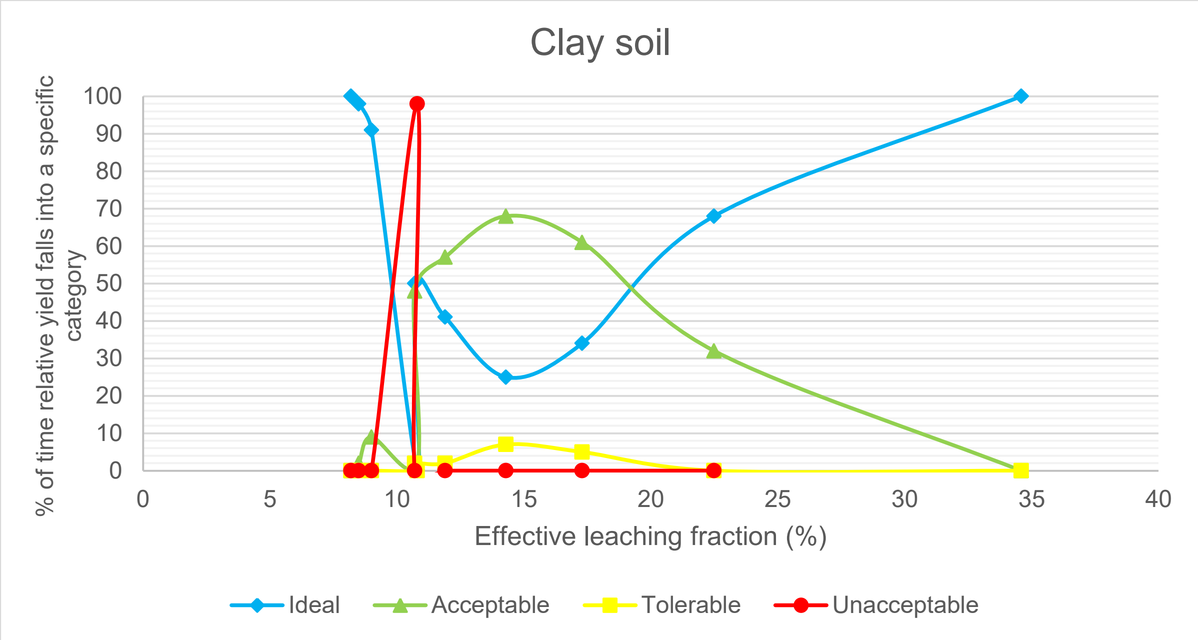

Figure 8.12: Percentage of time relative yield of barley irrigated with acidic mine water was within a specific fitness-for-use category, as influenced by clay soil root zone salinity for a range of effective leaching fractions.[1]

8.2.3 Accumulation of Al, Fe and Mn in soil

The clay and sandy loam soil displayed similar patterns of Al, Fe and Mn accumulation (Figure 8.13). Fe and Mn were predicted to accumulate above the threshold in less than a year regardless of the leaching fraction applied. Al, on the other hand, accumulated at a slower rate and accumulation was affected by the application of a leaching fraction. Increasing leaching fraction resulted in a decrease in the number of years it would take for Al to accumulate to the threshold level as the considered trace metals do not leach and increasing water application increases the rate at which the trace elements accumulate. Al accumulation on clay soils typically reached the threshold a year later than sandy loam soil.

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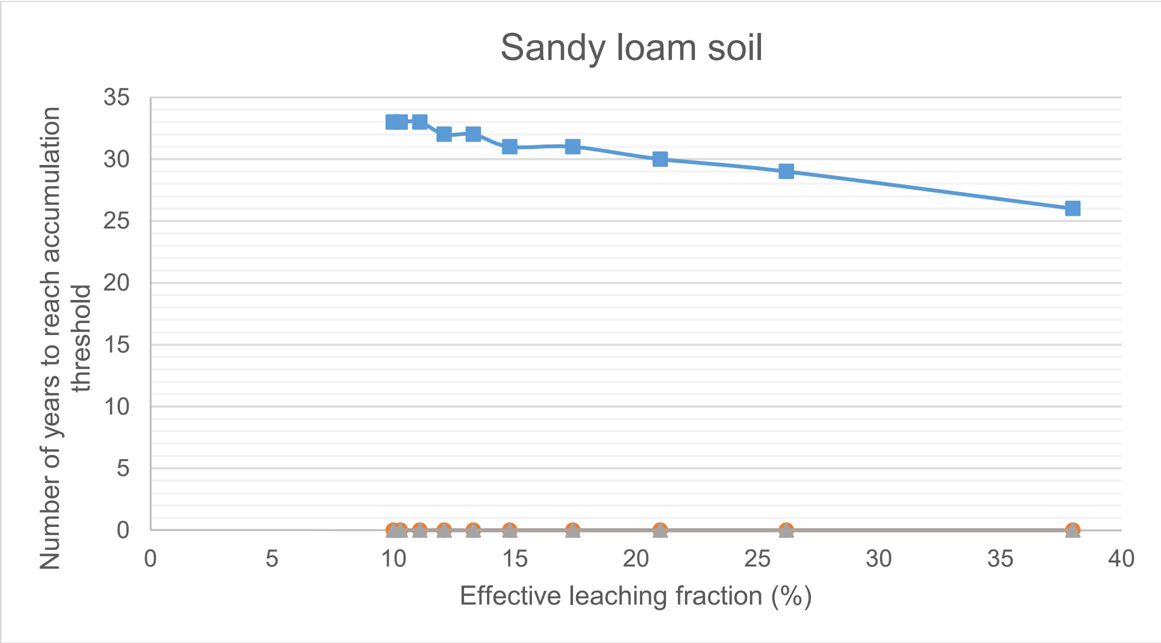
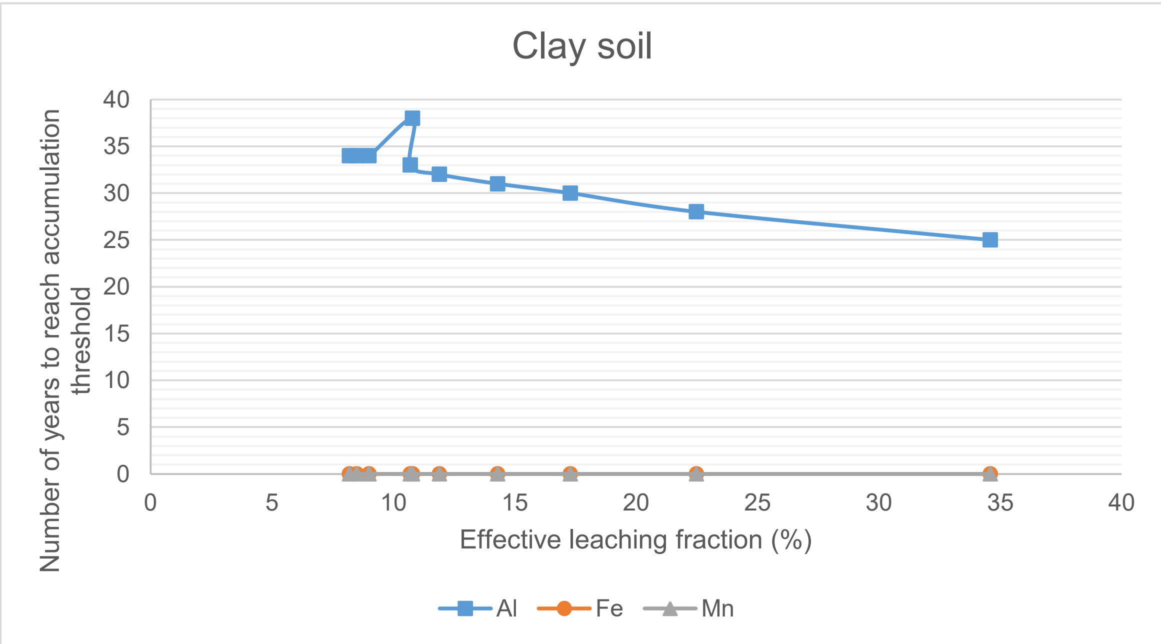
[1] Ideal =90-100%, Acceptable =80 – 90 %, Tolerable = 70 – 80 %, Unacceptable <70 %



a)

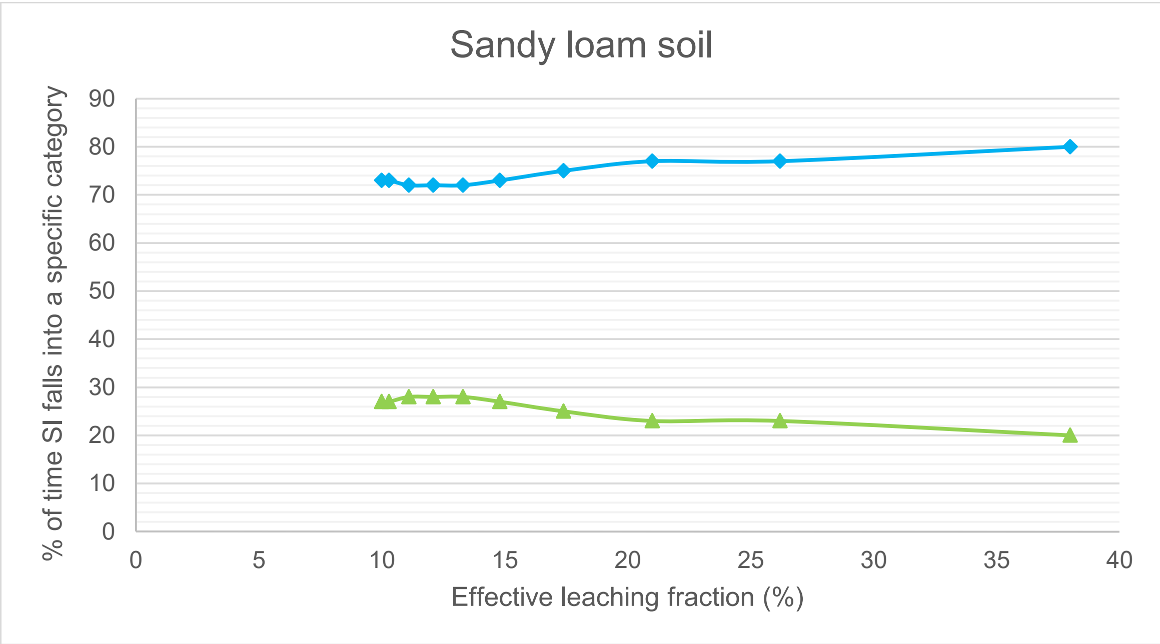


b)

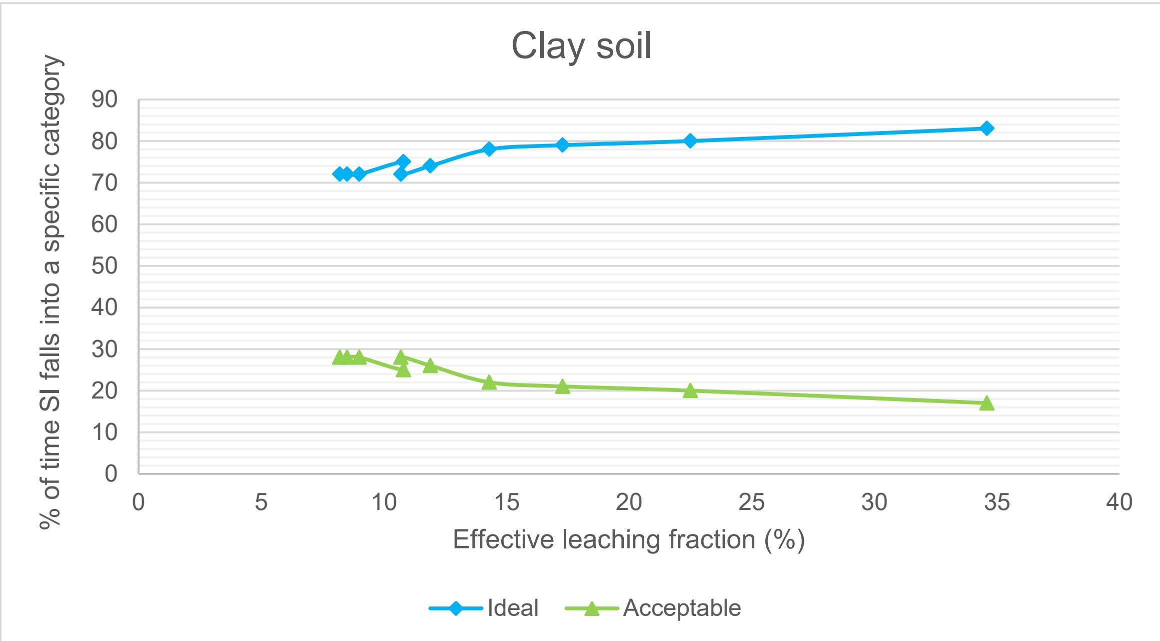
Figure 8.13: Al, Fe and Mn accumulation in a) clay soil and b) sandy loam soil as influenced by long term barley irrigation with acidic mine water for a range of effective leaching fractions.

8.2.4 Surface infiltrability

Surface infiltrability was ideal most times and acceptable the rest of the time in both clay and sandy loam soil (Figure 8.14). Increasing the leaching fraction resulted in an increase in the percentage of time surface infiltrability was ideal and a decrease in the percentage of time surface infiltrability was acceptable. This suggests that long-term irrigation of barley with acidic mine water of similar quality to the water used in this study is unlikely to have adverse effects on surface infiltrability. This is due to high salinity and relatively low Na levels in the acidic mine water used in this study.



a)



b)

Figure 8.14: Percentage of time surface infiltrability of a) a sandy loam soil and b) a clay soil was within a specific fitness-for-use category following barley irrigation with acidic mine water for a range of effective leaching fractions.[1]

[1] Ideal = No reduction in permeability, Acceptable = Slight reduction in permeability.

8.3 Long term simulation of maize irrigation with neutralized saline mine water

8.3.1 Root zone salinity

Irrigation with neutralized mine water resulted in either acceptable or ideal root zone salinity in both clay and sandy loam soils, regardless of applied leaching fraction (Figure 8.15 and 8.16). The percentage of time root zone salinity was ideal was typically higher in sandy loam soil than in clay soil. This is due to the differences in water movement between the two soils. Clay soil has a lower hydraulic conductivity than sandy loam soil and is, therefore harder to leach than sandy loam soil. As a result, root zone salinity resulting from irrigation with neutralized mine water will likely be higher in clay soils than in a sandy loam soil.

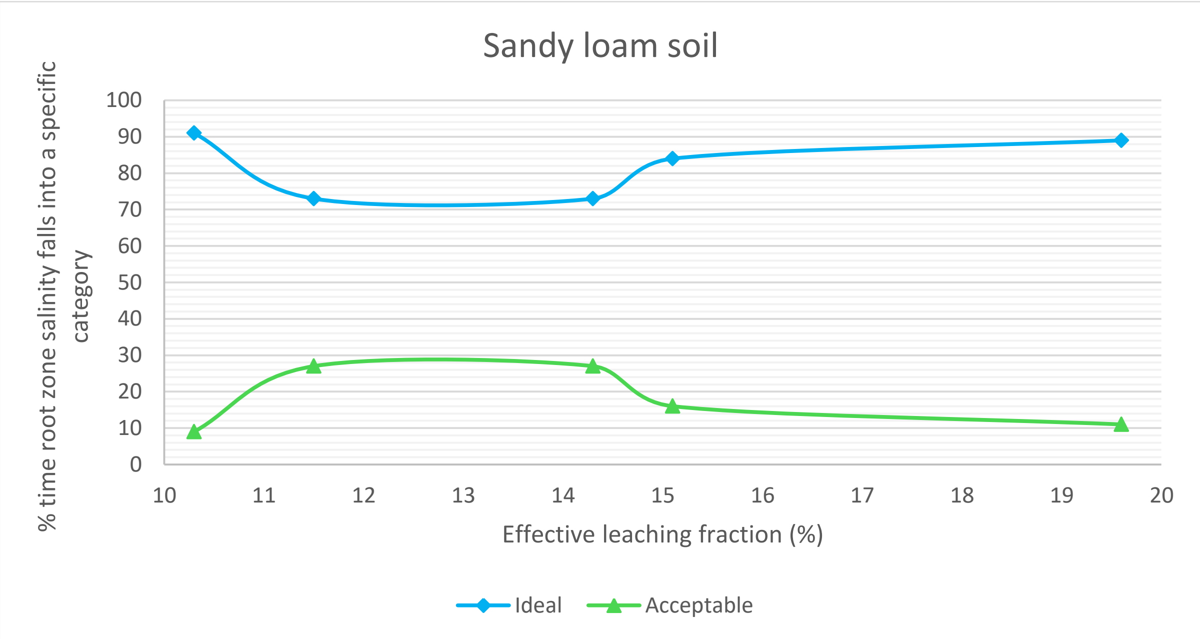


Figure 8.15: Percentage of time root zone salinity of the sandy loam soil was within a specific fitness-for-use category following maize irrigation with neutralized mine water for a range of effective leaching fractions.[1]

[1] Ideal = 0 - 200 mS/m, Acceptable = 200 – 300 mS/m.

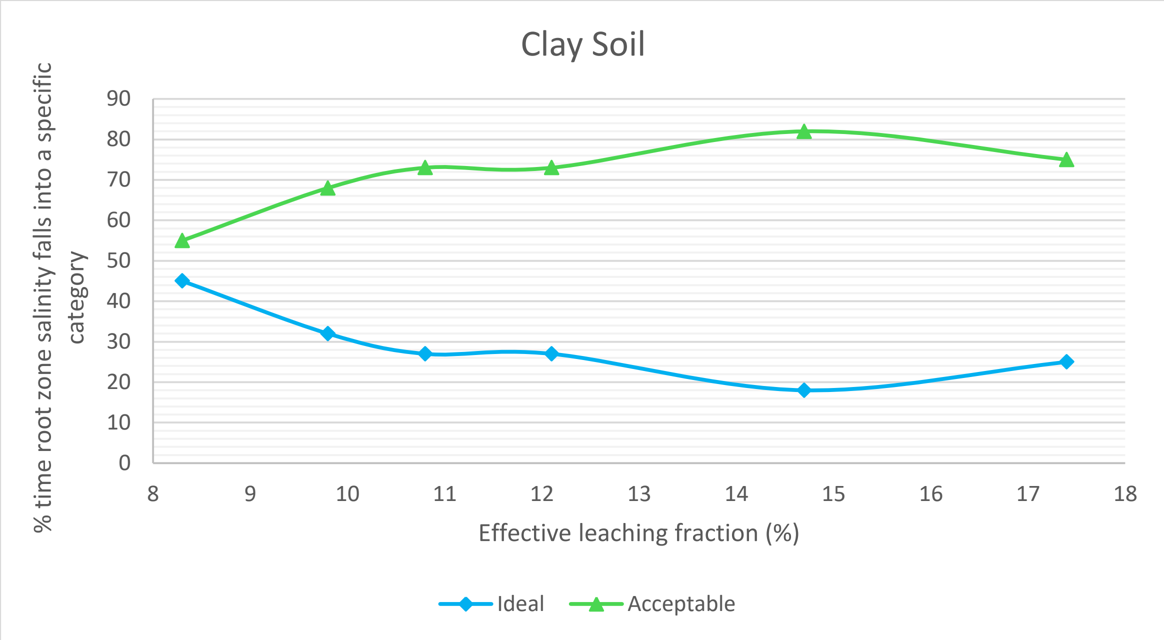


Figure 8.16: Percentage of time root zone salinity the clay soil was within a specific fitness-for-use category following maize irrigation with neutralized mine water for a range of effective leaching fractions.1

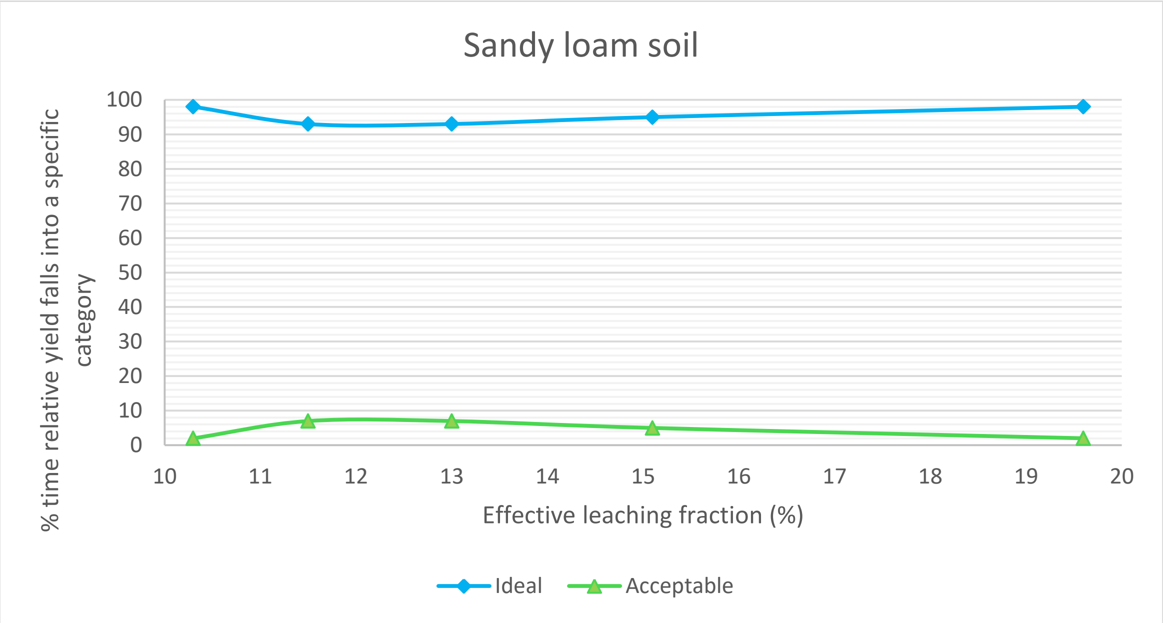
8.3.2 Relative yield as influenced by soil salinity

On the sandy loam soil, maize relative yield was ideal 100 % of the time at the lowest leaching fraction assessed, 10.3% (b)). As leaching fraction increased from 10.3% to 11.5%, the percentage of time relative yield was ideal decreased, and the percentage of time relative yield was acceptable increased by 5%. As the leaching fraction increased further, the percentage of time relative yield of maize was ideal increased, and the percentage of time relative yield was acceptable decreased. The relative yield of maize irrigated with neutralized mine water was ideal 100% of the time when grown on a clay soil (Figure 8.18). This can be attributed to increased gypsum precipitation for the neutralized mine water. Applying a leaching fraction had no effect on the relative yield of maize grown on clay soil.

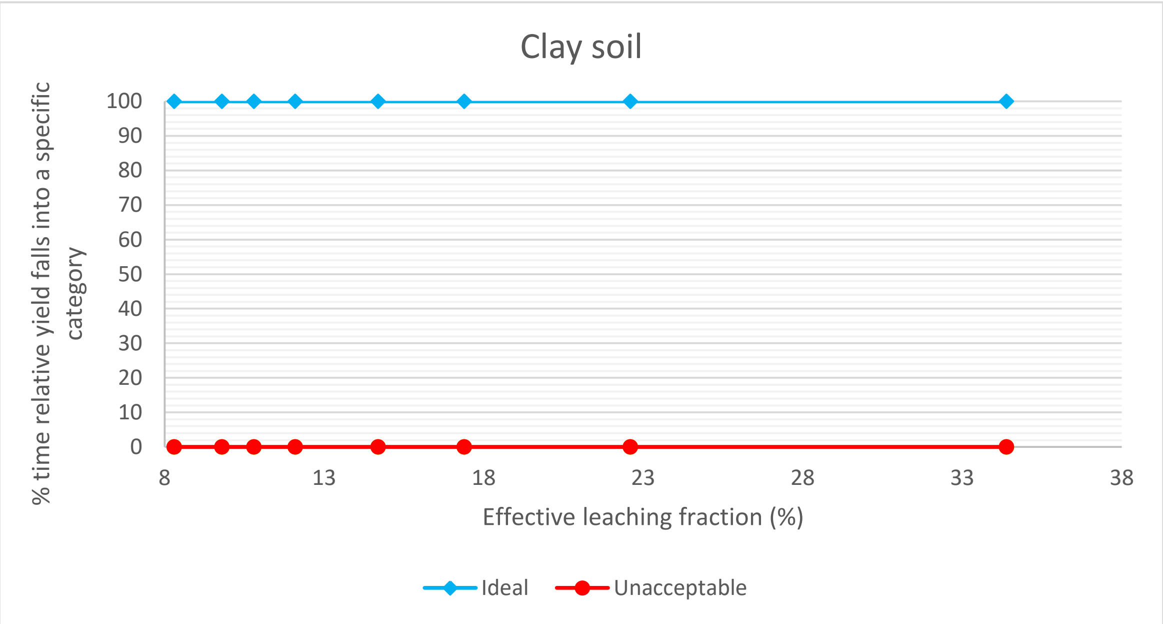
These results suggest that root zone salinity resulting from long term irrigation with neutralized mine waters is unlikely to be limiting to the relative yield of maize, on both fine and heavy textured soils. However, applying a leaching fraction to fine textured soil might result in a decrease in the relative yield of maize irrigated with

[1] Ideal = 0 - 200 mS/m, Acceptable = 200 – 300 mS/m.

neutralized mine water, as this practice adds more salt to the profile. This means that in the model, the effect of root zone salinity on relative yield is mostly influenced by the balance between salt loading and leaching.



a)



b)

Figure 8.17: Percentage of time relative yield of maize irrigated with neutralized mine water was within a specific fitness-for-use category, as influenced by a) a sandy loam soil and b) a root zone salinity for a range of effective leaching fractions.[1].

[1] Ideal =90-100%, Acceptable = 80 – 90 %.

8.3.3 Al, Fe and Mn accumulation

Irrigation with neutralized mine water resulted in Al and Fe accumulation that was within the ideal fitness-for-use category (Figure 8.19). Al did not accumulate above the threshold concentration as there was no Al in the irrigation water. Fe took more than 200 years to accumulate above the threshold concentration, as it was present at very low concentrations in the irrigation water. Mn, on the other hand, accumulated above the threshold concentration in less than a year as it was present at relatively higher concentrations in the irrigation water. Increasing the leaching fraction led to a decrease in the number of years it would take for Fe to accumulate above the threshold concentration. This is due to an increase in the loading of Fe as more irrigation is applied. Applying leaching had no notable effect on the number of years it would take for Mn to accumulate above the threshold concentration because Mn does not leach.

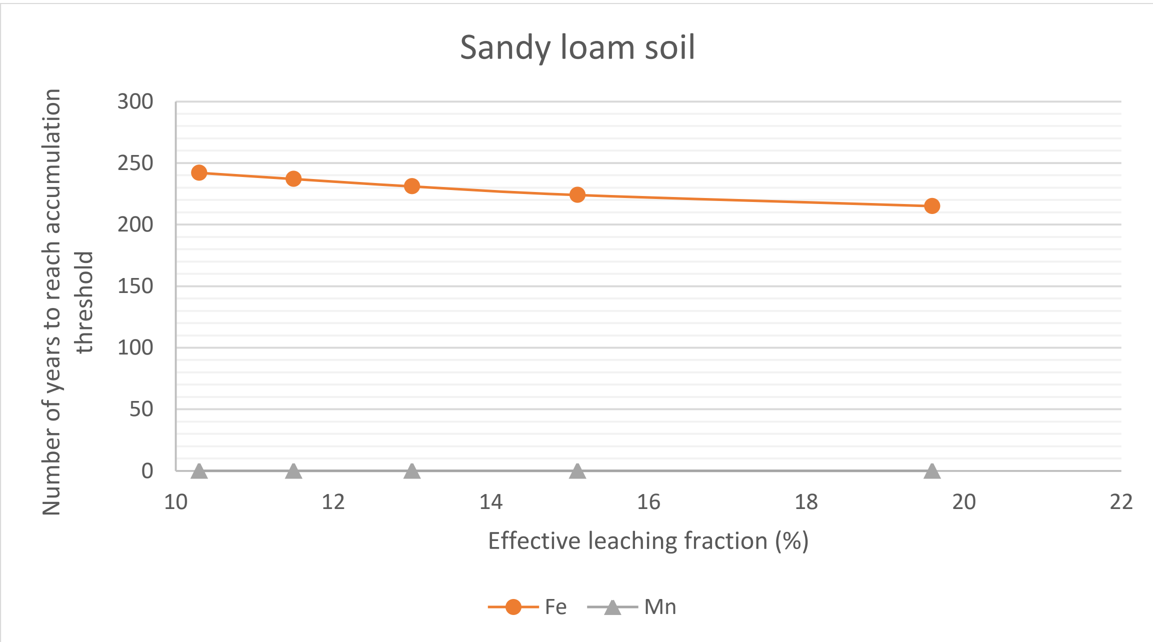


Figure 8.18: Al, Fe and Mn accumulation in a) a sandy loam soil and b) a clay soil as influenced by long term maize irrigation with neutralized mine water for a range of effective leaching fractions.

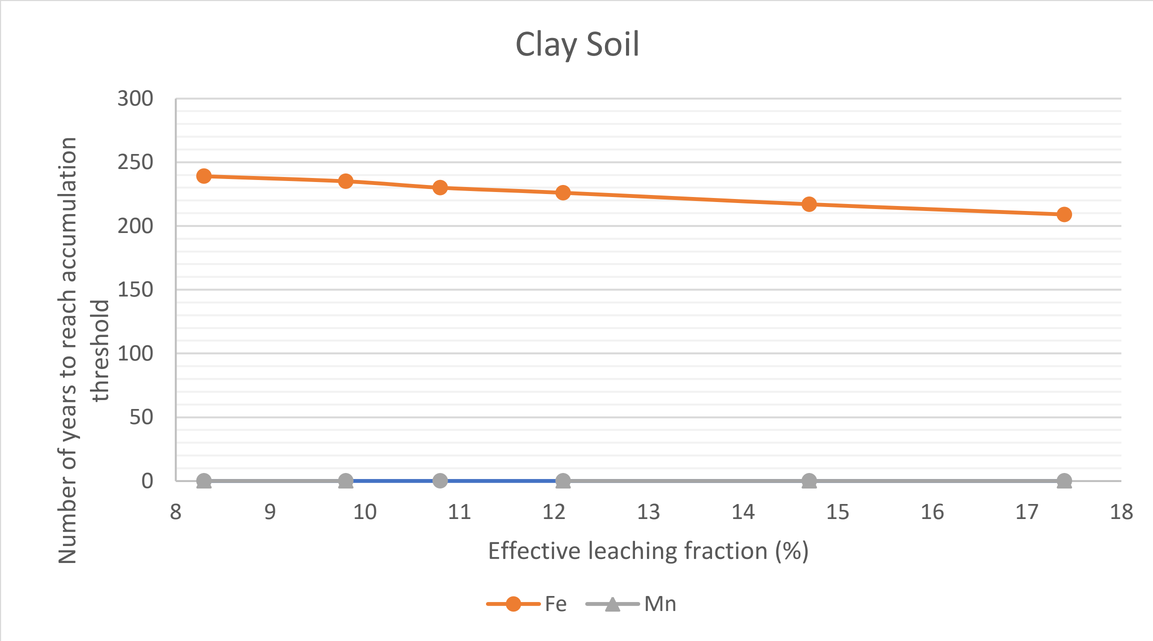
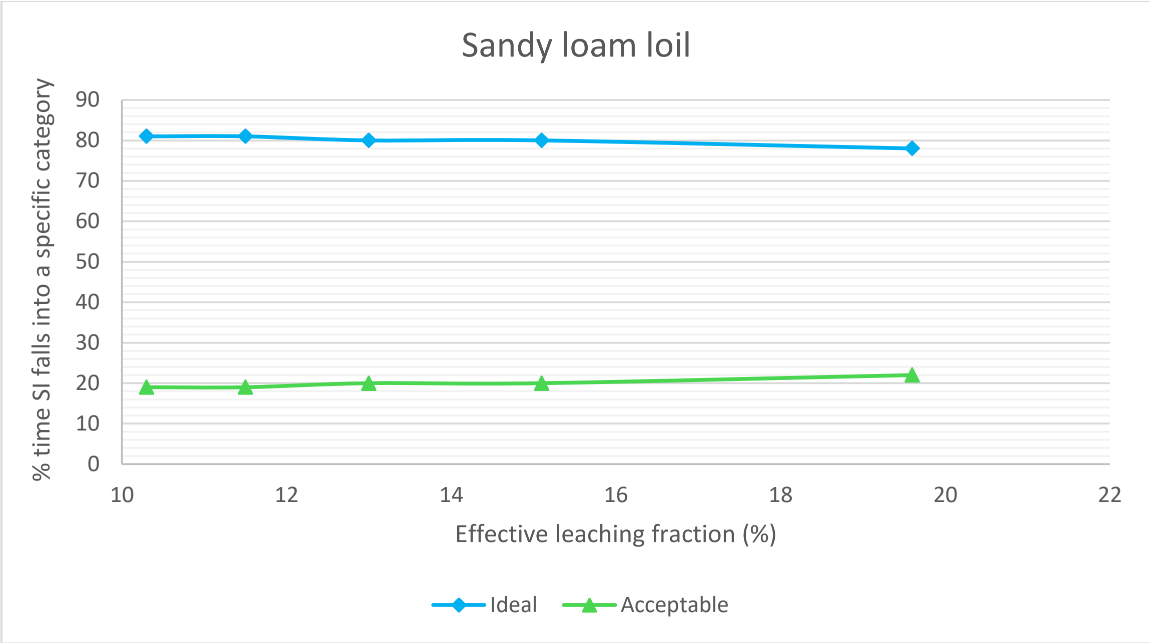


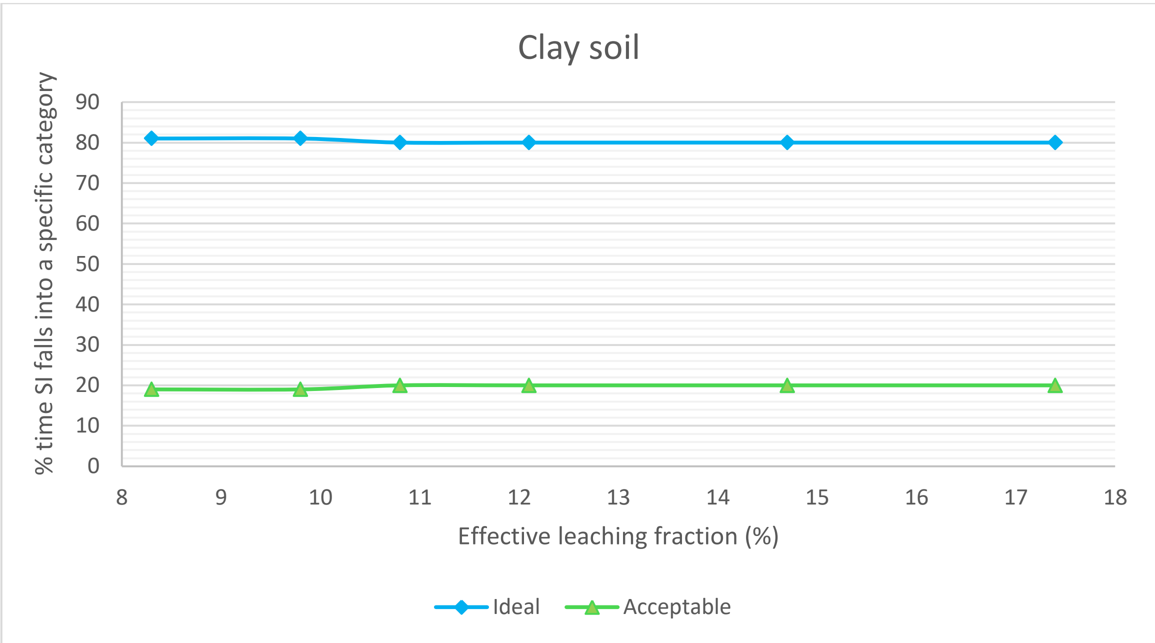
Figure 8.19: Al, Fe and Mn accumulation in a) a sandy loam soil and b) a clay soil as influenced by long term maize irrigation with neutralized mine water for a range of effective leaching fractions.

8.3.4 Surface infiltrability

Irrigation with neutralized mine water resulted in surface infiltrability that was ideal 80% of the time and acceptable 20% of the time in both clay and sandy loam soil (Figure 8.20). Applying a leaching fraction had no effect on soil infiltrability in clay soil, however, it slightly decreased surface infiltrability in sandy loam soil. This suggests that long-term irrigation with neutralized mine water will typically have little or no effect on surface infiltrability.



a)



b)

Figure 8.20: Percentage of time surface infiltrability of a) a sandy loam soil and b) a clay soil was within a specific fitness-for-use category following maize irrigation with neutralized mine water for a range of effective leaching fractions.[1]

[1] Ideal = No reduction in permeability, Acceptable = Slight reduction in permeability.

8.4 Long term simulation of barley irrigation with neutralized saline mine water

8.4.1 Root zone salinity

Root zone salinity of a sandy loam soil irrigated with neutralized mine water was acceptable 91% of the time at the lowest leaching fraction, 8.2% (Figure 8.21). As leaching fraction increased from 8.2% to 10.2%, root zone salinity became acceptable 100% of the time. Increasing the leaching fraction even further decreased the percentage of time root zone salinity was acceptable and increased the percentage of time root zone salinity was ideal. This indicates that that root zone salinity improved as leaching increased, similar to what has been observed in previous sections.

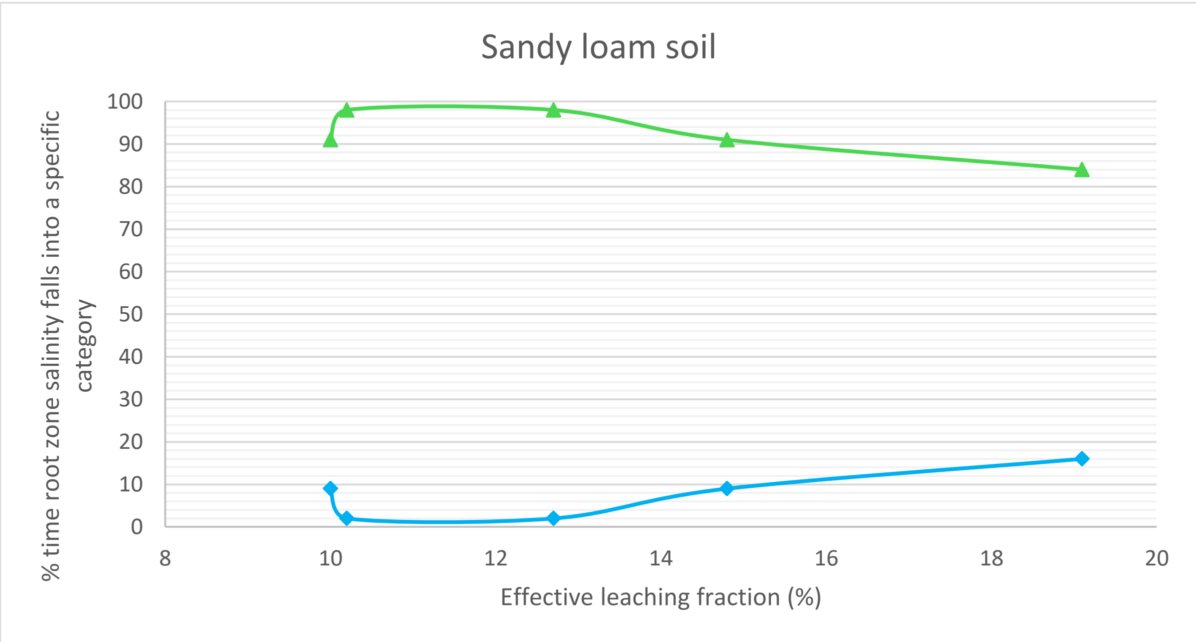


Figure 8.21: Percentage of time root zone salinity of sandy loam soil was within a specific fitness-for-use category following barley irrigation with neutralized mine water for a range of effective leaching fractions.[1].

[1] Ideal = 0 - 200 mS/m, Acceptable = 200 – 300 mS/m.

Root zone salinity of clay soil irrigated with neutralized mine water was acceptable 95% of the time and ideal 5% at the lowest leaching fraction (Figure 8.22). As leaching fraction increased, the percentage of time root zone salinity would be acceptable increased to 100%. This indicates that root zone salinity increased as the leaching fraction increased.

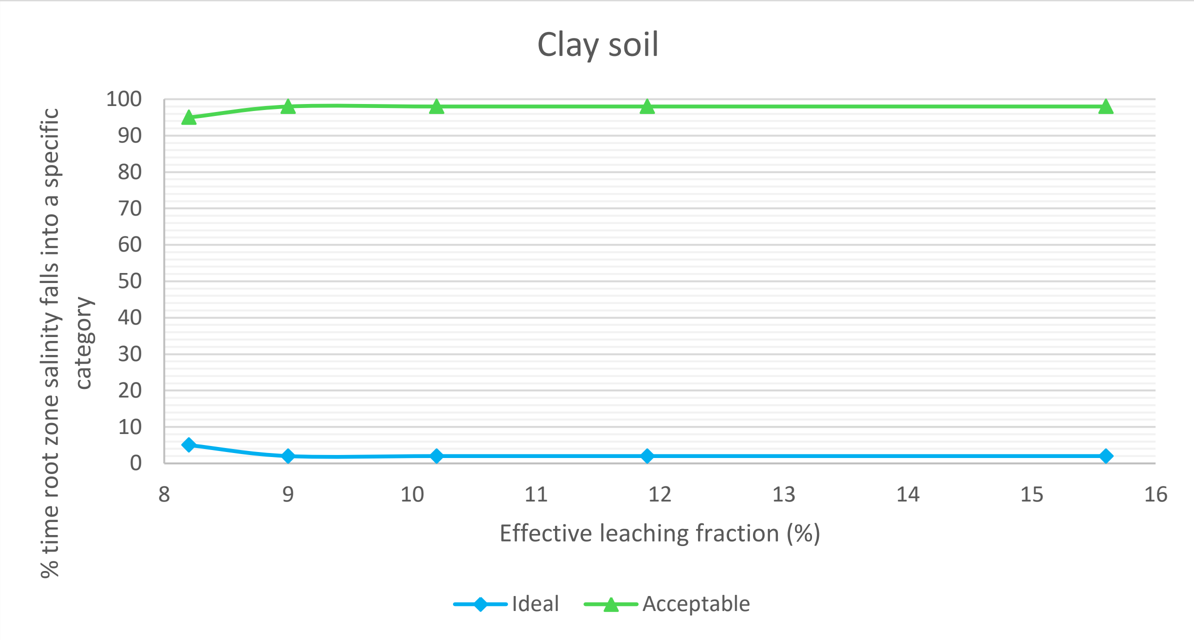
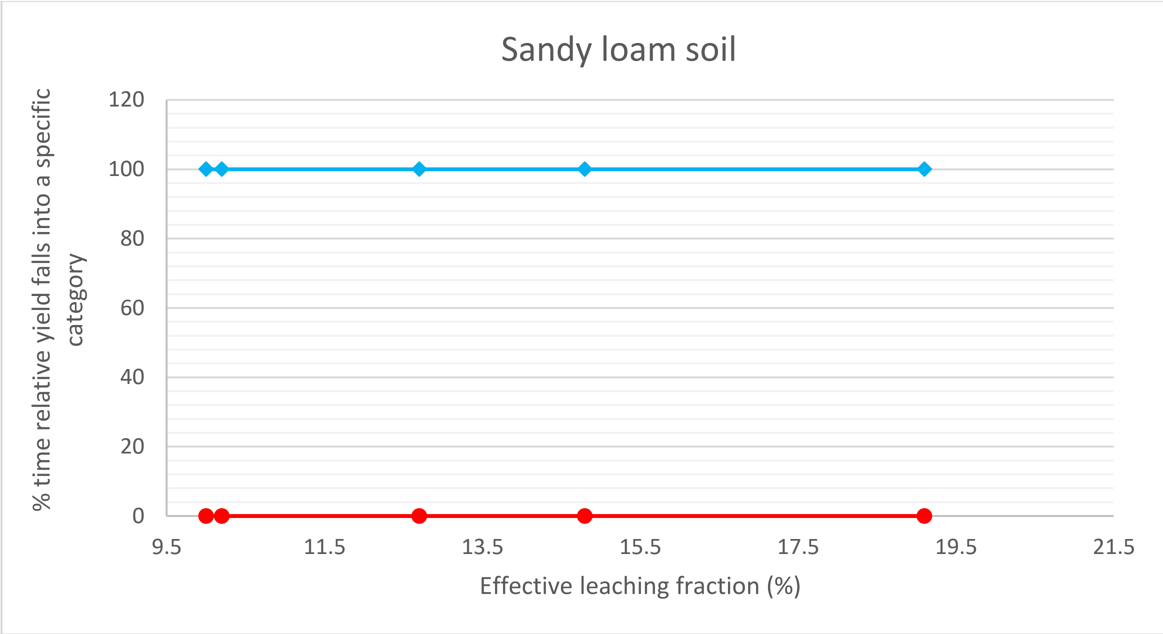


Figure 8.22: Percentage of time root zone salinity of a clay soil was within a specific fitness-for-use category following barley irrigation with neutralized mine water for a range of effective leaching fractions.[1]

8.4.2 Relative yield

The relative yield of barley irrigated with neutralized mine water was ideal 100% of the time on both sandy loam and clay soils (Figure 8.23). Applying a leaching fraction had no effect on the relative yield. This suggests that root zone salinity resulting from long-term irrigation with neutralized mine water is unlikely to be limiting to the relative yield of barley.

[1] Ideal = 0 - 200 mS/m, Acceptable = 200 – 300 mS/m.



a)

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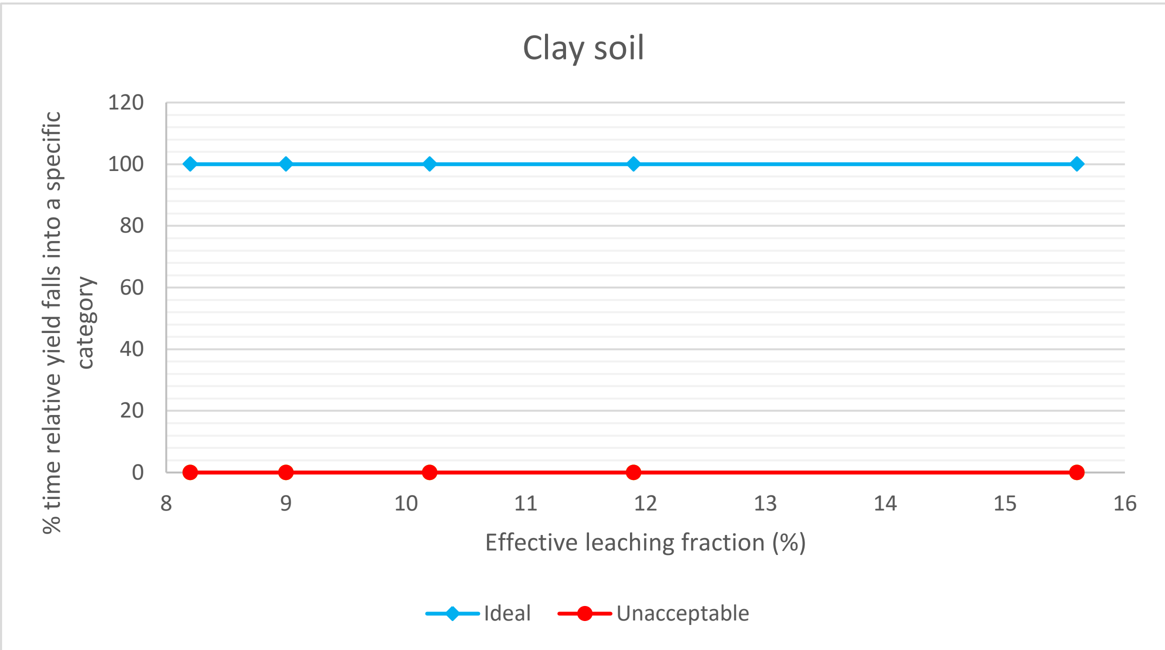


Figure 8.23: Percentage of time relative yield of barley irrigated with neutralized mine water was within a specific fitness-for-use category, as influenced by a) sandy loam soil and b) clay soil root zone salinity for a range of effective leaching fractions.[1]..

[1] Ideal =90-100%, Unacceptable <70 %.

8.4.3 Al, Fe, Mn accumulation

Al, Fe and Mn accumulation were similar in clay and sandy loam soils (Figure 8.24). The number of years irrigation with neutralized mine water would result in Al accumulation above the threshold concentration was infinite. The number of years irrigation with neutralized mine water would result in Fe accumulation above the threshold concentration was over 200 years. As leaching was increased, the number of years irrigating with neutralized mine water would result in Fe accumulating above the threshold toxicity decreased. This suggests that applying leaching increases Fe accumulation. Mn accumulated above the threshold concentration in less than a year, suggesting that Mn accumulation is likely to be a concern, even when irrigating with neutralized mine water.

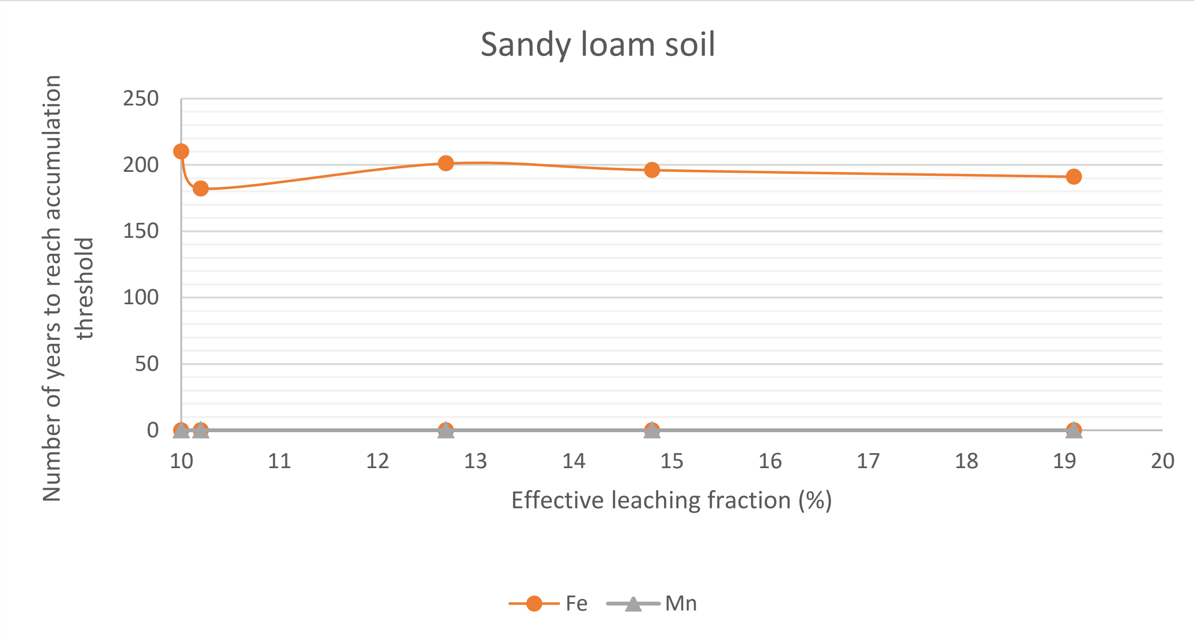


Figure 8.24: Fe and Mn accumulation in a sandy loam soil as influenced by barley irrigation with neutralized mine water for a range of effective leaching fractions.

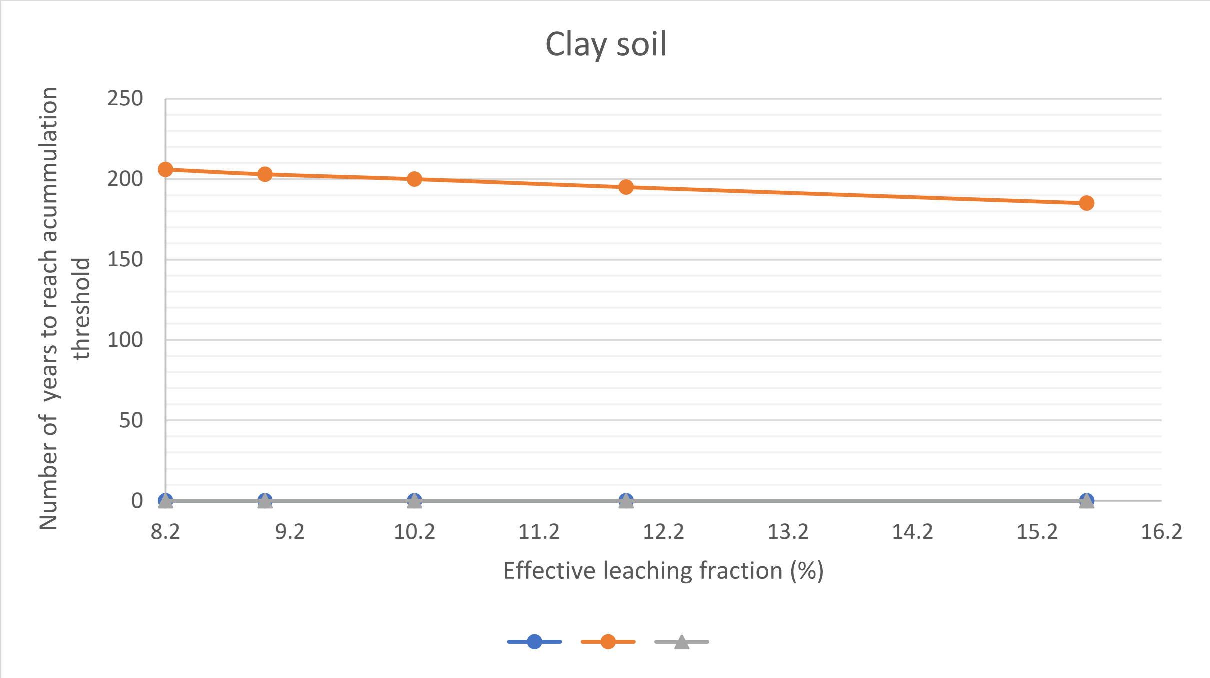
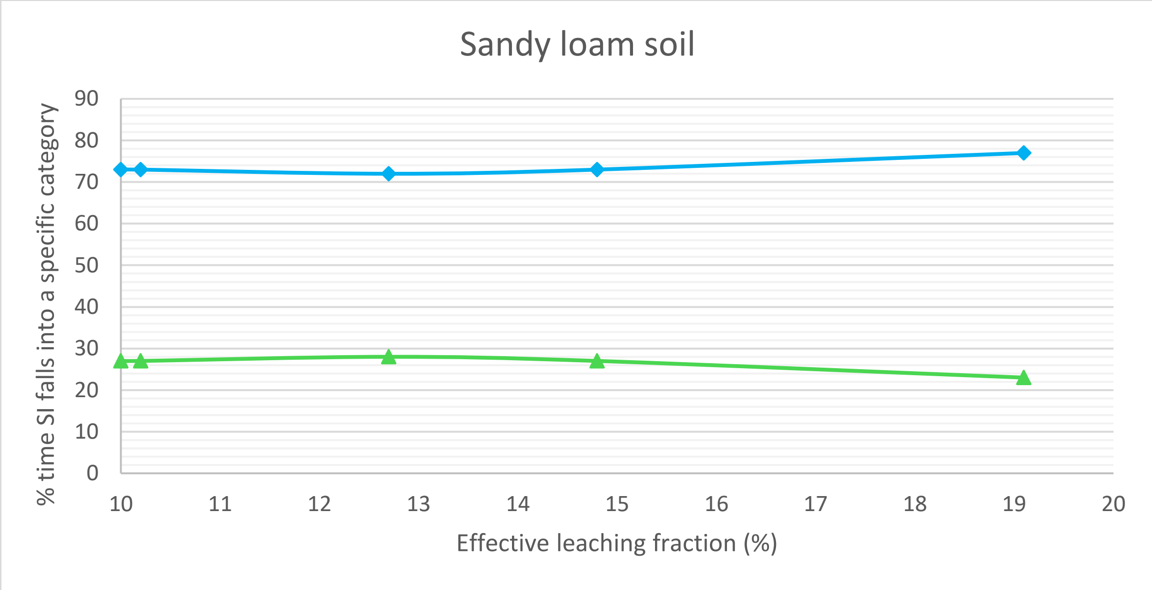


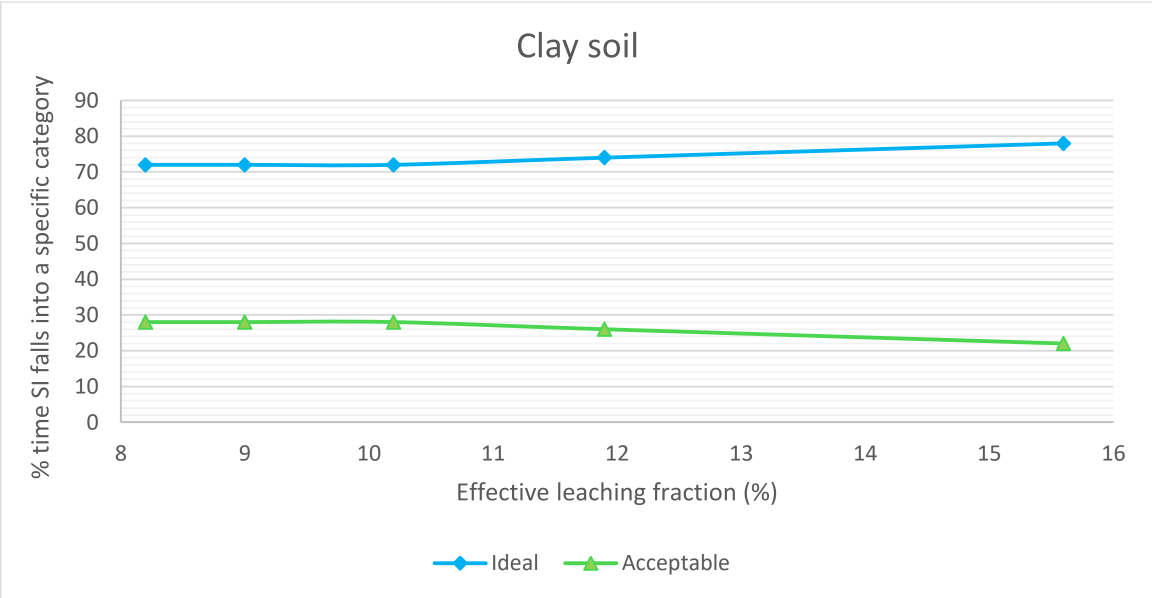
Figure 8.25: Fe and Mn accumulation in a clay soil as influenced by barley irrigation with neutralized mine water for a range of effective leaching fractions.

8.4.4 Surface infiltrability

Irrigating with neutralized mine water resulted in ideal soil infiltrability 72% of the time and was acceptable 28% of the time in clay soil at the lowest leaching fraction (Figure 8.26). The percentage of time surface infiltrability would be ideal increased as leaching fraction increased. The effects of neutralized mine water constituents on surface infiltrability following barley irrigation on sandy loam soil were similar to what was predicted for clay soil. These results suggest that barley irrigation with neutralized mine water will typically have little or no effect on surface infiltrability.



a)



b)

Figure 8.26: Percentage of time surface infiltrability of a) a sandy loam soil and b) a clay soil was within a specific fitness-for-use category following barley irrigation with neutralized mine water for a range of effective leaching fractions.[1]

8.5 Long term simulation of mine water effects on irrigation equipment

The results of the fitness-for-use assessment of mine water in relation to their effect on irrigation equipment are presented in Figure 8.27 and Figure 8.28. The

[1] Ideal = No reduction in permeability, Acceptable = Slight reduction in permeability.

assessment shows that acidic mine water is likely to cause corrosion and clogging of drippers, owing to the low pH and high concentrations of Fe and Mn. The neutralized mine water is unlikely to cause corrosion and scaling, but it may cause clogging of drippers. The SAWQI-DSS uses the Langelier Saturation Index (LI) to predict the scaling or corrosion potential of water, however, Du Plessis et al. (2017b) have indicated that this index might not be appropriate for sulphate-rich waters.

Corrosion or Scaling of Irrigation Equipment				
Fitness-for-use	Fitness for Use Category determined by the corrosion or scaling potential indicated by the Langelier Index			
	Corrosion (Langelier Index)		Scaling (Langelier Index)	
Ideal	0 to -0.5		0 to +0.5	Not Scaling
Acceptable	-0.5 to -1.0		+0.5 to +1.0	
Tolerable	-1.0 to -2.0		+1.0 to +2.0	
Unacceptable	<-2.0	-6.08	>+2.0	

Clogging of Drippers										
Fitness-for-use	Fitness for Use Category determined by the potential of an irrigation water constituent to cause clogging of drippers									
	Suspended Solids (mg/L)		pH		Manganese (Mn) (mg/L)		Total Iron (Fe) (mg/L)		*E.coli* (10^6 per 100 mL)	
Ideal	<50	No data	<7.0	3.0	<0.1		<0.2		<1	No data
Acceptable	50 - 75		7.0 - 7.5		0.1 - 0.5		0.2 - 0.5		1 - 2	
Tolerable	75 - 100		7.5 - 8.0		0.5 - 1.5		0.5 - 1.5		2 - 5	
Unacceptable	>100		>8.0		>1.5	158.0	>1.5	734.0	>5	

Figure 8.27: Fitness-for-use assessment output for acid mine water with regard to irrigation equipment

Corrosion or Scaling of Irrigation Equipment				
Fitness-for-use	Fitness for Use Category determined by the corrosion or scaling potential indicated by the Langelier Index			
	Corrosion (Langelier Index)		Scaling (Langelier Index)	
Ideal	-0.5 to 0	-0.07	0 to +0.5	Not Scaling
Acceptable	-0.5 to -1.0		+0.5 to +1.0	
Tolerable	-1.0 to -2.0		+1.0 to +2.0	
Unacceptable	<-2.0		>+2.0	

Clogging of Drippers										
Fitness-for-use	Fitness for Use Category determined by the potential of a constituent to cause clogging of drippers									
	Suspended Solids (mg/L)		pH		Manganese (Mn) (mg/L)		Total Iron (Fe) (mg/L)		*E.coli* (10^6 per 100 mL)	
Ideal	<50	No data	<7.0	6.5	<0.1		<0.2		<1	No data
Acceptable	50 - 75		7.0 - 7.5		0.1 - 0.5		0.2 - 0.5		1 - 2	
Tolerable	75 - 100		7.5 - 8.0		0.5 - 1.5		0.5 - 1.5		2 - 5	
Unacceptable	>100		>8.0		>1.5	15.0	>1.5	3.0	>5	

Figure 8.28: Fitness-for-use assessment output for neutralized saline mine water with regard to water constituent effects on irrigation equipment

8.6 Summary

The SAWQI-DSS fitness-for-use assessments were useful in providing an indication of long term mine water constituent effects on soil and crop quality. The results suggest that long term irrigation with acidic mine water will typically have a negative effect on soil quality and crop yield, particularly of salt-sensitive crops. Long-term irrigation with the acidic water was predicted to result in excessive rootzone salinity. Application of a leaching fraction mitigated salinization of the soils, however, this mitigation did not translate to a notable improvement in the yield of the salt-sensitive crop. Furthermore, the application of a leaching fraction increased the rate at which trace elements accumulated in soils.

Long-term irrigation with the acidic mine water was predicted to have a less detrimental effect on the yield of the salt-tolerant crop. However, climatic conditions also have an influence on irrigation water effects. Since the salt-tolerant crop was grown in the winter season, and there was no rainfall, water application increased which increased the loading of salinity and trace elements. The model predicted that Mn and Fe would accumulate to toxic levels in less than a year if the acidic mine water is used for irrigation. This suggests that irrigation with acidic mine water would be unsuitable for long term irrigation, however, the application of lime could mitigate the accumulation of Al, Fe and Mn.

The model predicted that long term irrigation with neutralized mine water is likely to have little or no negative effects on soil and crop quality. The results also indicated that factors such as soil type, crop choice and leaching are likely to influence mine water effects on soil and crop quality. However, the model did not adequately describe the effects of acidity on soil and crop quality. Furthermore, the model predicted that the acidic mine water may cause corrosion of irrigation equipment and both the acidic and neutralized mine waters might result in clogging of irrigation equipment. However, the model used to predict water constituent effects on irrigation equipment might not be suitable for sulphate-rich waters.

Conclusion

Irrigation with acidic mine water acidified and salinized the soils used in the pot experiment. Irrigation with neutralized mine water also salinized soils but to a lower degree than irrigation with acidic mine water. It was noted that the red sandy loam soil was typically more saline than the vertic soil when irrigated with the mine waters, suggesting that the vertic soil had a higher salinity buffering capacity than red sandy loam soil. However, this was in a closed system with no leaching applied, which is not sustainable.

Soils irrigated with acidic mine water accumulated high levels of phyto-available Fe, which may be a concern in soils that are prone to waterlogging. There was no accumulation of Al, Fe and Mn in soils irrigated with neutralized mine water. The vertic soil typically contained higher levels of Al, Fe and Mn than red sandy loam soil, at the end of the trial. However, an account of the distribution of these metals in plants and soils suggests that they were in a form that was not readily accessible by crops. Addition of liming material to the red sandy loam soil appears to have mitigated the accumulation of Al, Fe and Mn, and decreased their availability to plants to a degree, as was indicated by the relatively low percentages taken up by crops in comparison to what was theoretically available, particularly in the case of Al.

An assessment of the effects of irrigation with mine waters on crop quality indicated that irrigation with mine water, particularly acidic mine water, will likely only cause foliar injury in sensitive crops. However, foliar injury could not be attributed solely to scorching caused by spraying with the mine water, as the crops were irrigated and sprayed with the water. Most of the considered crops did not show signs of foliar injury, however, they did show symptoms of stress in the form of phytotoxicity symptoms, symptoms of nutrient deficiencies, stunted growth and wilting when irrigated with acidic mine waters. The latter two symptoms were only observed in crops grown on the red sandy loam soil.

Irrigation with mine waters on the vertic soil had no significant effects on crop growth. Even the salt and acid sensitive crops, peas and lucern produced dry matter content that was comparable to that of the control crops, when irrigated with mine waters. Irrigation with acidic mine water on vertic soil only had an adverse effect on the yield of crops that were grown on soils that had previously been irrigated with mine waters. This has some implications for long term use of acidic mine water for irrigation. It suggests that irrigation with acidic mine water for longer than a season may result in yield reductions. However, it should be noted that the vertic soil used in this study was not limed, which allowed for the investigation of the soil's innate ability to mitigate the effects of the mine water constituents.

Crop tolerance to mine water constituents was more evident in crops grown on the red sandy loam soil. The acid and salt sensitive crops grew poorly on this soil when irrigated with acidic mine water. However, poor growth on the red sandy loam soil may likely be attributed to the soil reaction with the lime, which is suspected to have not equilibrated as rapidly as anticipated.

Crops irrigated with acidic mine water typically accumulated higher levels of Al, Fe and Mn than those irrigated with neutralized mine water or municipal water. This indicates that irrigation with the neutralized mine water produced crops of better quality than irrigation with acidic mine water. Crops grown on red sandy loam soil typically had higher levels of Al, Fe and Mn than those grown on vertic soil. This suggests that the vertic soil was able to sequester these metals and render them less accessible to crops.

The neutralized mine water had no adverse effect on crop growth and yield, however, irrigation with this water may result in the accumulation of phytotoxic levels of manganese in irrigated soils. Furthermore, accumulation of zootoxic levels of manganese may be of concern in crops irrigated with neutralized mine water as it poses health risks to the considered livestock, particularly if they consume the foliage. However, manganese is unlikely to accumulate to zootoxic levels in grain, at least in the short-term, therefore grain of crops irrigated with neutralized mine water is unlikely to pose health risks to the considered domestic livestock. This indicates that irrigation with neutralized mine water should be acceptable for the production of grain to be used as fodder.

The accumulation of Al, Fe and Mn in crops typically followed the order peas> maize>sorghum >barley>stooling rye. Peas and maize typically accumulated higher levels of Al, Fe and Mn than the other crops, which has implications for their safety for human and livestock consumption. Analyses indicated that irrigation with acidic mine water in these crops is likely to pose health risks associated with Al and Mn phytotoxicity in humans and livestock. However, it was the foliage that posed the highest risk to livestock, particularly the foliage of crops grown on the red sandy loam soil.

The pot trials demonstrated the influence of soil properties in mitigating the effects of the irrigation water constituents. The results suggest that heavy textured soils with high CEC and, therefore, high theoretical acid buffering capacity and metal retention capacity, are likely to be more efficient in mitigating the effects of mine water constituents on crops, than fine-textured soils with low CEC and lower theoretical acid buffering capacity and metal retention capacity, at least in the short term. However, fine-textured soils should not be discarded as potential growth media for crops irrigated with mine waters. Fine textured soils are typically easier to leach than heavier soils, which is prefered when considering long term irrigation because salinity is expected to build up rapidly as was demonstrated in the pot trials. If adequate lime is applied to the soils to counteract the loading of acidity through irrigation with acidic mine waters, the growth of crops on fine-textured soils will likely be more successful. The trials also demonstrated the influence of crop tolerance/susceptibility on crop response to mine water constituents, particularly in soils that have a low theoretical acid buffering capacity, salt buffering capacity and metal retention capacity.

Due to financial constraints, the scope of tests that could be performed were limited, as a result, there was a lack of sufficient data to explain the main factors that influenced the solubility of Al, Fe and Mn. In addition, the data collected was not sufficient to elucidate whether the differences in growth and yield between crops grown on vertic soil and those grown on red sandy loam soil are attributed to nutrient effects or metal toxicities. Further investigations are required to gain clarity on this matter.

Results obtained from the SAWQI-DSS fitness-for-use assessments were mostly in agreement with those obtained from the actual glasshouse trials. The SAWQI-DSS predicted that long term irrigation with mine waters will result in salinization and in relative yield reductions, which will be more severe in salt-sensitive crops. The model also predicted that Al, Fe and Mn will accumulate in soils, with unacceptable Fe and

Mn accumulation in less than a year. The SAWQI-DSS has great potential for modelling long-term irrigation with mine waters, however, in its current state, it has limitations particularly with regards to modelling the effects of acidity.

Irrigation with acidic saline mine water has major cost saving implications, as it means that there would be no need to build mine water treatment plants. Irrigation with neutralized mine water is also a promising alternative for mine water management, as it would eliminate the need to construct desalinization facilities and the running costs associated with the process. This study has demonstrated that crops can be produced successfully through irrigation with mine waters, especially neutralized mine water, which showed positive results regardless of the soil type used. Further studies are, however, required to determine the effects of irrigation with such waters in field conditions for different soil types. In the case of acidic saline mine water, the influence of lime application, irrigation management (i.e. type of irrigation system, irrigation timing, etc.) and leaching on soil and crop responses are required. In the case of the neutralized mine water, the effects of leaching and irrigation management on soil and crops.

With the growing use of metal-contaminated water for irrigation, there is a need for robust methods of assessing the risks associated with consuming metal contaminated crops. This is especially important for farmers who often require quick answers when making decisions about irrigation management and in the case of mine water irrigation, implementing the necessary agronomic practices to ensure that potentially toxic elements do not accumulate to zootoxic levels. Currently, there is a knowledge gap with regards to the effects of certain trace elements on human health, furthermore, South Africa does not have food safety regulations with regards to trace element content of foods. Further studies are required to establish relevant health risk assessments with regard to the trace element content of foods, in the South African context.

The SAWQI-DSS has displayed great potential for use in evaluating long-term effects of irrigating with water that would typically be considered undesirable. The option to introduce site specificity gives users the flexibility to assess the effect that alternative options, for managing the water they have available, will have when used for irrigation. The SAWQI-DSS does, however, have limitations in assessing the fitness-for-use of acidic mine waters as it does not give a comprehensive account of the effects of irrigation water acidity on soil quality, and crop yield and quality. For instance, the fitness-for-use assessments do not indicate the degree of soil acidification or foliar injury associated with the direct effects of irrigation water acidity. Furthermore, the assessments do not indicate how relative yield would be affected by trace element toxicity as it does for Na, Cl, and B. Further studies are therefore required to account for foliar injury resulting from irrigation water acidity, similar to what has been done for foliar injury resulting from irrigation water salinity. There is also a need to incorporate the effects of trace element toxicity on relative yield, similar to what has been done for Na, Cl and B. In cases whereby, toxicity thresholds and yield reductions associated trace element toxicity have not been established, experiment trials should be conducted to fill those knowledge gaps. In addition, the incorporation of health risk assessments associated with trace element accumulation in grain is required.

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Appendix

A. Mine water synthesis

The following process was followed to synthesize the mire water:

1. <u>Calculation of required amounts of salts</u>

Once the dominant salt in the target water quality is identified and required salts selected, calculations were performed to determine the amount of salt that is required to obtain the desired concentrations of specific elements. These calculations were performed using the equation below:

$$\frac{\text{mg salt}}{\text{L of water}} = \text{Element concentration mg/L} \times \frac{\text{molar mass of salt (g/mol)}}{\text{molar mass of element (g/mol)}}$$

$$\times \frac{\text{mols of salt}}{\text{mols element}} \quad (0.1)$$

The ion concentrations used for the calculations were taken from the Western Basin feed water quality used by Maree et al. (2013) in their AMD neutralization treatment study. The feed water reportedly contained 6 mg/L Al, 602 mg/L Ca, 37 mg/L Cl, 625 mg/L Fe^{2+}, 228 mg/L Mg, 147 mg/L Mn and 50 mg/L Na. The following salts were selected; $FeSO_4.7H_2O$, $MnSO_4.7H_2O$, $MgSO_4.7H_2O$, Na_2SO_4, $Al_2(SO_4)_3.18H_2O$, and $CaCl_2$. A summary of the calculation input and output is presented in the table below:

Element/ Ion	Element/ion concentration (mg/L)	molar mass of salt (g/mol)	molar mass of element (g/mol)	Salt: element mol ratio	Required amount of salt (mg/L)
Al	6	666.44	26.982	0.5	74.09829
Cl	37	110.98	35.453	0.5	57.91132
Mg	228	246.47	24.305	1	2312.082
Mn	147	223.07	54.94	1	596.8564
Na	50	142.04	22.989	0.5	154.4652
Fe	625	278.02	55.845	1	3111.514

Note: The values presented in the tables above were ‘target’ values, they vary slightly from the measured concentrations, due to slight inaccuracies in measuring masses and volumes.

Preparation of a saturated gypsum solution

An excess of gypsum was added to deionized water to make a saturated gypsum solution. The gypsum was mixed with deionized water for an hour and allowed to equilibrate overnight, allowing any undissolved particles to settle at the bottom of the container. The next day the supernatant was decanted into another container, in which the other salts would be added, taking care not to disturb the settled gypsum particles. Ideally, the water used for synthesising the mine water should be boiled to remove dissolved oxygen.

2. Addition of other salts to the gypsum solution

The other salts were added to the gypsum solution one at a time by weighing the required amount into the solution. It is important to ensure that all the salts have dissolved. Iron was added in last as it is prone to oxidation if exposed to oxygen, care needs to be taken to ensure that the solution does not get aerated. One of the ways, this can be done, is by storing the solution in an airtight container.

3. Adjusting pH

If the pH of the solution was higher than expected, H_2SO_4 was added to the solution. If the pH was lower than expected the pH was increased by adding a $Ca(OH)_2$ solution.

B. Food safety assessment

The human health risk of dietary Al intake was assessed by comparing the PTWI and the estimated dietary Al intake. The units of the PTWI were converted to mg by multiplying the defined PTWI for Al (2 mg/kg body weight) by the average weight of South African children aged 1 - 2 (11 kg) taken from Shisana et al. (2014). Weekly dietary Al intake (mg) was then estimated as the product of the Al content in the crop (mg/kg DM) and the amount of crop consumed weekly (kg fresh mass). To convert dry mass content to fresh mass (FM) content, dry mass content was multiplied by a conversion factor as suggested by Seiler (2003).

A summary of crop consumption, adapted from statistics provided by the Department of Agriculture, Forestry and Fisheries (DAFF, 2017), as well as dry mass to wet mass conversion factors are provided in the table below:

	Annual	Weekly (kg)	Daily	Conversion factor
Maize	77	1.5	0.2	0.75
Sorghum	1.8	0.03	0.005	0.73
Barley	5.6	0.1	0.015	0.71
Vegetables	44	0.8	0.12	0.75

Daily crop consumption was calculated by dividing annual consumption by 365 and weekly consumption was calculated by dividing annual consumption by 52. Peas were categorised as vegetables. The human health risk of dietary Fe intake was assessed by comparing the provisional maximum tolerable daily intake, specified as 0.8 mg/kg bm/day by the FAO-WHO (2011), with the estimated dietary Fe intake, calculated similarly to Al. The human health risk of dietary Mn intake was assessed by calculating HQ, according to Equation 2.1. An example of the calculations is provided below.

- Example of Al PTWI conversion from mg/kg bm to mg/week:

  PTWI (mg/week) = 1 mg/kg bm X 11.4 kg bm
  = 11.4 mg/week

- The conversion factor for dry mass to wet mass content was calculated as follows:

  Conversion factor = 1- (%moisture/100)

- Example of estimated weekly Al intake (mg/week) through barley consumption, for barley irrigated with synthetic acidic saline mine water:

  Weekly Al intake = Metal content in grain x amount of grain consumed in a week
  = 24.8 mg/kg dm barley x 0.71 x 0.1 kg FM barley
  = 1.8 mg

- Example of HQ calculation for Mn in barley irrigated with synthetic acidic saline mine water:

$$HQ = \frac{W_{plant} \times M_{plant}}{R_fD \times B} \quad (0.2)$$

$$= \frac{0.015 \text{ kg} \times 59 \text{ mg/kg} \times 0.71}{0.14 \text{ mg/kg bm/day} \times 11 \text{ kg bm}}$$

$$= 0.41$$

C. Dissolution potential and salt loading

The dissolution potential (DP) of salts in soils was calculated as follows:

$$DP\ (mg/kg) = \frac{\text{solubility of salt (mg/L) x volume of solvent (L)}}{\text{mass of soil (kg)}}$$

Input values are presented in the table below:

	Vertic soil			**Red sandy loam soil**		
	Na_2SO_4. $10H_2O$	**$MgSO_4$. $7H_2O$**	**$CaSO_4$. $2H_2O$**	**Na_2SO_4. $10H_2O$**	**$MgSO_4$. $7H_2O$**	**$CaSO_4$. $2H_2O$**
Solubility (mg/L)	281000[1]	360000[2]	2400[3]	28100	357000	2050
Volume of the solvent (L)	0.025	0.025	0.025	0.015	0.015	0.015
Mass of soil (kg)	0.045	0.045	0.045	0.055	0.055	0.055

Salt loading was calculated as follows:

$$\text{Salt loaded (mg/kg soil)} = \frac{\text{salt added to water (mg/L) x volume of water(L)}}{\text{mass of soil (kg)}}$$

[1] Haynes, W. (2016). CRC handbook of chemistry and physics: A ready-reference book of chemical and physical data. Boca Raton. *Fla: CRC*.
[2]Ashford, R. D. (1994). "Ashford's dictionary of industrial chemicals: properties, production, uses," Wavelength.
[3] *: http://www.ilo.org/dyn/icsc/showcard.display?p_version=2&p_card_id=1215*

Input values are presented in the table below:

		Vertic soil		Red sandy loam	
		$Na_2SO_4 . 10H_2O$	**$MgSO_4 . 7H_2O$**	**$Na_2SO_4 . 10H_2O$**	**$MgSO_4 . 7H_2O$**
	Salt added (mg/L)	201	2241	201	2241
Acidic mine water	**Volume of water (L)**	20	20	10	10
	Mass of soil (kg)	10	10	10	10
	Salt added (mg/L)	192	1988	192	1988
Neutralized mine water	**Volume of water (L)**	20	20	14	14
	Mass of soil (kg)	10	10	10	10

D. Distribution of metals in soils and plants

The distribution of metals in soils is an estimated account of the metal content in soils and in plants. The content of metals in soils was determined experimentally while the uptake of metals by plants was estimated as follows:

$$\text{Foliar uptake (mg/kg)} = \frac{\text{Total metal content in crop}\left(\frac{\text{mg}}{\text{kg}}\right) \text{x Total dry mass of crop (kg)}}{\text{mass of soil (kg)}}$$

The total metal content in the crops was estimated based on metal distribution ratios found in literature (Alam et al., 2002; Drazic et al., 2006; Ouellette and Dessureaux, 1958). The root: top ratios for Al, Fe and Mn used in the calculations were 4:1, 5:1 and 1.2: respectively. The total dry mass was also estimated based on dry matter partitioning ratios found in literature (Temple-Smith and Koen, 1982). The root: top ratio used was 1:0.4.

A summary of the metal distribution in vertic soil is presented in the table below:

		Initial metal content	Applied metal	Total available metal	Crop metal uptake	Final metal content	Total removed
				mg/kg soil			
Al	**Acidic**	72	12	84	11	44	40
	Neutralized	72	0	72	6	18	54
	Municipal	72	0	72	7	21	51
Fe	**Acidic**	67	1769	1835	14	477	1358
	Neutralized	67	3	70	9	24	46
	Municipal	67	2	69	10	22	46
Mn	**Acidic**	180	305	485	52	69	415
	Neutralized	180	24	204	5	113	91
	Municipal	180	0	181	2	81	99

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A summary of the metal distribution in red sandy loam soil is presented in the table below:

		Initial metal content	Applied metal	Total available metal	Crop metal uptake	Final metal content	Total removed
				mg/kg soil			
Al	**Acidic**	129	6	135	34	10	101
	Neutralized	129	0	129	22	12	107
	Municipal	129	0	129	20	7	109
Fe	**Acidic**	21	907	928	163	11	765
	Neutralized	21	2	24	8	10	16
	Municipal	21	1	23	6	8	17
Mn	**Acidic**	49	156	205	29	57	176
	Neutralized	49	18	66	14	25	53
	Municipal	49	0	49	6	14	43

E. Lime requirement for soils irrigated with acidic mine water

The amount of lime that is required to counteract applied acidity was calculated as follows:

$Ca(OH)2 + 2H^{+} \leftrightarrow Ca + 2H_2O$

$$\text{Lime requirement} = \frac{\text{mmol } H^{+}}{L} \times \frac{1 \text{ mmol } Ca(OH)_2}{2 \text{ mmol } H+} \times \frac{\text{mg } Ca(OH)_2}{\text{mmol } Ca(OH)_2}$$

$$= \frac{162 \text{ mmol } H^{+}}{L} \times \frac{1 \text{ mmol } Ca(OH)_2}{2 \text{ mmol } H+} \times \frac{39.99 \text{ mg } Ca(OH)_2}{\text{mmol } Ca(OH)_2}$$

=3239.919 mg/L water