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Evaluation of Contamination of Soil by Trace Metals from Dairy Wastewater in Limpopo Province, South Africa

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ABSTRACT

The contamination of soil by metals from dairy wastewater (DWW) has been evaluated in Limpopo Province. The pH, electrical conductivity (EC) and total dissolved solids (TDS) of DWW were measured in the field using a portable Crison MM 40 multi meter, while the pH of soil was measured using a pH meter. The concentrations of Al, Ca, Cu, Fe, K, Mg, Mn, Pb, Na, Zn and Al, Cu, Fe, K and Mn were measured in triplicate using Perkin Elmer 520 Atomic Absorption Spectrometry (AAS) for DWW and soil respectively. The results of DWW were compared with the South African standards for wastewater (WW) discharge of the Department of Water Affairs (DWA). The results of DWW and soil were compared to evaluate the probable effects of the disposal of dairy wastewater onto soil. pH ranges of 6.36 - 8.18 and 7.08 - 8.52 were observed for DWW and soil respectively and were within the set guideline of DWA. EC and TDS of DWW ranged from 193-593 mS/m and 1293.10-3973.10 mg/L respectively and were higher than the recommended guideline. The study revealed a high concentration of Al (0.13-0.44 mg/L), Fe (0.16-1.14 mg/L) Cu (0.05-0.10 mg/L), Na (66.50-520.90 mg/L), K (5.10-122.40 mg/L), and Mn (0.04-0.47 mg/L) in DWW and Al (4770-142182 mg/kg), Fe (1052-3910mg/kg), K (2544-4596mg/kg), Cu (520-5000mg/kg) and Mn (219-4332 mg/kg) in soil respectively. DWW in Limpopo Province is of poor quality and should not be discharged into the environment without proper treatment.

Keywords: Contamination, discharge, dairy wastewater, soil, trace metals, treatment

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INTRODUCTION

Dairy farming is one of the main industries in Limpopo Province of South Africa. Dairy activities began in the Province in 1979. It is one of the leading food industries in the province, growing with the latest technology. At present, one of the dairy companies in Limpopo province is recognized as the biggest goat's milk factory in South Africa and produces 700 litres to 3500 litres of goat's milk per day; of this, 70% is used for the production of fresh goat's milk and 30% for the production of goat's cheese and other products [1]. In addition, it produces variety of dairy products from dairy cows predominately sold in various supermarkets in Limpopo Province.

Dairy industry consumes approximately 4.5 million m^3 water per annum in over 150 dairies in South Africa. 75% to 95% of the water intake volume is discharged as effluent (Water Research Commission[2]. Dairies are responsible for discharging large quantities of effluent arising from either the process itself and/or cleaning processes [2]. DWW is currently disposed of mainly through land application and irrigation of pastures with little or no pre-treatment. This could have adverse impact on the animals that feed on the pastures and possible contamination to groundwater.

Water is largely used in dairy processes together with some chemicals which often add to the generation of large volume of wastewater. DWW has become a controversial subject in recent years, which increasingly presents a considerable threat to the environment [3]. This is largely due to poor containment of wastes, discharge of untreated dairy washings and surface run off of slurries following application to land; causing the most pollution by dairy farming than any other agricultural sources combined [4]. Larger dairy factories dispose their effluent into municipal sewers, though cases of disposal into sea and by means of land irrigation do occur. In contrast, smaller dairy factories dispose their effluent basically through land application and irrigation. Such practices pose potential threats to surface and groundwater contamination [2].

Trace elements in dairy effluent can reach concentrations that have adverse impacts on the dairy production system and also on the environment. Trace elements like copper, zinc and other heavy metals such as cadmium, arsenic, chromium, mercury and some organic contaminants can occur in dairy effluent. When contaminant levels in soil become excessive, there is potential for negative impacts on the productivity of the soil and the environment, and the risk of plant and animal uptake to levels that can pose a threat to the health of livestock and humans [5-6]. This study was undertaken to investigate the possible contamination of soils by trace metals from DWW.

Study area

Limpopo province (Figure1) is the fifth largest province of South Africa situated in the Northern region. The area is characterised by Savannahs, or open grasslands on the western part of the province, while the north is a subtropical zone containing plains scattered with baobab trees. The average temperatures range from 17° to 27° C in the summer and from 4° to 20° C in the winter. Average annual rainfall totals about 300 mm with most of it falling in the summer months.

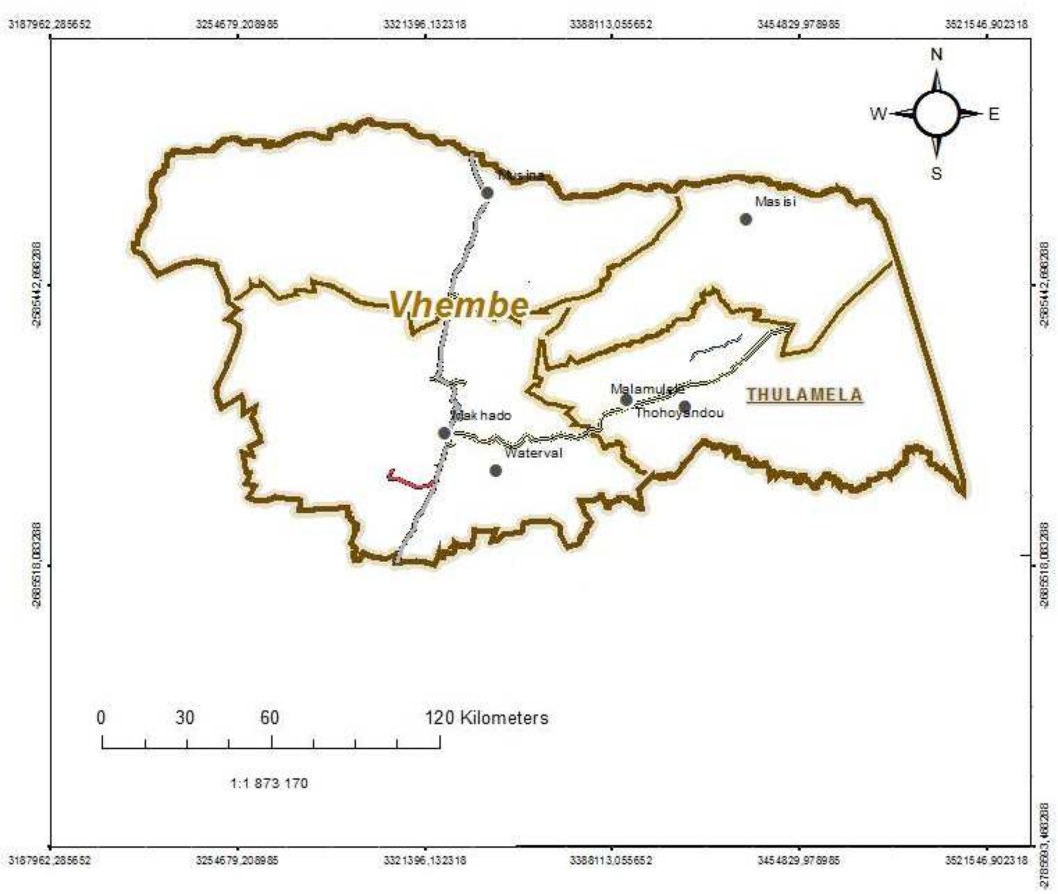

Figure 1: Map of Study Area

MATERIALS AND METHODS

Sampling

DWW samples were randomly collected from six different sites following the bottle submersion method. The sampling bottles were washed thoroughly and dried prior to sampling. They were rinsed several times with the DWW to be collected before collecting 1000 mL from each of the sites. The samples were preserved with 3 mL of 55% concentrated nitric acid and were subsequently transported to the university in a cooler box with ice cubes and later refrigerated below 4^oC. The pH, EC and TDS were measured in the field using a Crison MM 40 multi meter. The instrument was calibrated according to the manufacturer's guidelines before measurement.

Soil samples were randomly collected at the top soil profile (0-15 cm), with a clean spade from seven sampling points around the dairy farm. The collected samples were left to dry at room temperature for approximately a week. Large soil clods were crushed to facilitate the drying process and later sieved with a 2 mm sieve.

pH of soil samples was determined using a 1:2 soil water ratio. 10 g of 2 mm sieved air-dried samples were weighed into a conical flask and 20 cm^3 of distilled de-ionized water was added. The mixture was stirred for about 30 minutes. Then the sample suspensions were allowed to stand for 30 minutes undisturbed. The electrode of the pH meter was then inserted into the settled suspension and the pH of soil measured. Before use, the pH meter was calibrated with standard buffers of pH solutions 4, 7, and 9.

Preparation of calibration standards
The calibration standards for total metal determination were prepared from 1000 mg/L stock solutions using the dilution formula. The calibration standard concentrations for Al, Mn, Cu, Zn, Fe and Pb, were 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L and 10 mg/L; while that of Na, Ca, Mg, K were of 5 mg/L, 10 mg/L, 20 mg/L, 50 mg/L, 100 mg/L and 250 mg/L.

Digestion of DWW
3 mL of 55% of concentrated nitric acid was added to 50 mL wastewater sample in a 250 mL conical flask with a 10 mL pipette. The mixture was heated on a hot stove (Labcon model MPC 30) in a fume cupboard until clear fumes was formed from the solution which was then allowed to cool. The mixture was filtered using Whatman No.1 filter paper into a 100 mL conical flask and made up to mark with distilled water[7].

Digestion of soil samples
The method developed by the United States Environmental Protection Agency (USEPA) for heavy metals in soils, sediments and sludge was employed in the preparation of the samples for analysis: 5.0 g of the sample was weighed into a 250 cm^3 conical flask. 10 cm^3 of 1:1 HNO_3 was added, and the slurry was mixed and covered with a watch glass and heated on a water bath for 2 hours. The digest was allowed to cool and 5 cm^3 of conc. HNO_3 was added with continued heating for additional 1 hour on the water bath. The last step was repeated until the oxidation of the sample by nitric acid was completed. The sample was allowed to cool again and 2 cm^3 of de-ionized H_2O along with 3 cm^3 of 30% H_2O_2 were added with the beaker covered; the sample was heated on water bath to start the peroxide reaction. A continuous addition of 30% H_2O_2 in 1 m^3 increments was done, followed by gentle heating until reaction with peroxide became minimal (or effervescence subsided). 5 cm^3 of conc. HCl along with 10 cm^3 of de-ionized H_2O was added and refluxed for an additional 30 minutes. The sample was allowed to cool and filtered through a Whatman filter paper into a 50 cm^3 volumetric flask. The conical flask and filter paper were rinsed with small volumes of 1:100 HCl, and the filtrate made up to 100 mL volume with distilled water. The prepared sample was analysed for the various metals concentrations in triplicate using a Perkin Elmer 520 flame atomic adsorption spectrophotometer[8].

RESULTS AND DISCUSSION

Physicochemical characterization of DWW
The pH values of DWW and Soil ranged from 6.36 to 8.18 and 7.08 - 8.51, respectively. These pH values fell within the recommended guidelines of the South African Department of Water Affairs for wastewater discharge [9]. The pH in DWW varied from slightly acidic to alkaline in most of the sites investigated. The acidic nature of the DWW may be due to the breakdown of milk lactose into lactic acid and could also be due to acidic chemicals such as phosphoric, nitric and hydrochloric acids used for cleaning purposes. While the use of detergents and basic sanitizers could be responsible for the observed alkaline pH values. pH of soil is regarded as its primary property that controls every chemical and biological processes occurring in it [10]. Some sites showed pH values higher than the Canadian Soil Quality Standard of 6-8 [11]. Metal ions behave differently at different pH. Crops usually show a very poor response to yield in a pH range <4.5 [12]. pH is one of soil characteristics that affect the adsorption and bioavailability of heavy metals [13].

Electrical conductivity is an indicator of the amount of dissolved salts in water and usually used to estimate the amount of total dissolved solids rather than measuring each dissolved constituent separately [14-15]. EC concentration greater than 150 mS/m indicates the presence of high concentration of calcium, sodium, magnesium, total hardness, chloride and sulphate which may have negative impacts on aquatic organisms if disposed into surface water. The EC and TDS varied from 193-593 mS/m and 1293.1-39731 mg/L respectively (Table 1). Average EC (321.67 mS/m) was higher than the DWA standard of <250 mS/m [9]. This could be due to increase in concentrations of sodium and potassium ions in soaps and detergents used for the cleaning of factory equipment.

Total metal concentration in DWW

The concentration of zinc and copper within the sites varied from 0.07-0.15 mg/L and 0.05-0.1 mg/L, respectively (Table 1). The average concentration of Zn was at the threshold value of DWA of 0.1 mg/L [9]. The concentration of Cu for each site exceeded the DWA guideline value of 0.01 mg/L. Zn and Cu are usually introduced into DWW as an added ingredient to livestock feeds, so as to prevent diseases and aid digestion. However, animals can only absorb 5-15% of the metals they ingest while the majority is excreted in manure [16]. Steinfeld [16] reported that the remaining 85% of the metals are released and absorbed into the soil. Zinc and Cu contaminated soil can pose problem to plants since they can absorb some of the metals as they build up in the soil. This could also lead to poor plant growth and eventually poison grazing animals which ingest the soil while grazing [17].

Pb concentration varied between 0.01 - 0.04 mg/L; with an average concentration of 0.02±0.01 mg/L, which exceeded DWA guideline of 0.01 mg/L [9]. Lead is a non-essential and toxic metal when present in trace levels in environmental media [18] which easily accumulates in different parts of plant. Exposure to Pb can be cumulative over time and could have both acute and chronic toxic effects on the animals that feed on the irrigated plant which provides a possible route to humans.

Aluminium concentration varied from 0.13 - 0.44 mg/L with an average concentration of 0.29 mg/L. Currently there is no DWA guideline value for Al in wastewater discharge but in the future, the maximum effluent value should not exceed 0.03 mg/L [9]; the concentration of Al found from this study is higher than the future guideline.

Table 1: Mean concentrations of some physicochemical parameters of DWW

	W1	W2	W3	W4	W5	W6	Average	DWA [9] guideline
pH	7.86	8.18	6.65	7.02	6.36	6.86	7.16	6.00-9.50
TDS(mg/L)	3088.70	3973.10	1407.00	1447.20	1293.10	1721.90	2155.17	1200
EC (mS/m)	461.00	593.00	210.00	216.00	193.00	257.00	321.67	<250
Fe (mg/L)	0.16±0.00	0.44 ±0.00	1.14 ±0.02	0.59 ±0.01	0.72 ±0.02	0.90±0.03	0.66±0.01	0.30
Mg(mg/L)	149.80±1.12	158.00±3.58	10.73±0.14	19.80±0.75	11.18±0.20	84.48± 0.97	72.33±1.13	100.00
Pb(mg/L)	0.03±0.02	0.01 ±0.01	0.02±0.01	0.04 ±0.01	0.02 ±0.02	bdl	0.02±0.01	0.01
Zn(mg/L)	0.15±0.01	0.07±0.02	0.07±0.00	0.08±0.01	0.11±0.02	bdl	0.10±0.01	0.10
K(mg/L)	6.70 ±0.03	5.10 ±0.02	16.50±0.05	19.60±0.05	17.2 ±0.01	122.40±0.23	31.25±0.07	-
Na(mg/L)	444.50±0.63	520.90±1.16	186.30±0.38	150.50±0.59	180.10±0.18	66.50±0.17	258.13±0.52	200.00
Ca(mg/L)	60.21±1.75	22.52 ±0.33	9.64±0.24	40.93±0.17	8.05 ±0.12	107.40±2.32	41.46±0.82	100.00
Mn(mg/L)	0.20 ±0.00	0.04 ±0.00	0.09 ±0.20	0.70±0.01	0.05 ±0.00	0.47 ±0.01	0.26±0.04	0.10
Al(mg/L)	0.24±0.00	0.34±0.00	0.22±0.00	0.44±0.10	0.13±0.00	0.34±0.10	0.29±0.10	0.03
Cu(mg/L)	0.10±1.12	0.08±0.00	0.05±0.00	0.10 ±0.00	0.09±0.00	0.05±0.00	0.08±0.19	0.01

bdl: below detection limit, -: not available, W1-W6: Sample

Al is a non-essential element and its activity is pH dependent. It is not bioavailable for uptake at neutral and alkaline pH but becomes bioavailable at low pH. Therefore Al toxicity is unlikely to occur to plants when irrigated with this water owing to the slight acidic and alkaline nature of the DWW and Soil.

High concentrations of magnesium were determined in site 1 (149.8 mg/L) and site 2 (158 mg/L), respectively. These values were higher than the DWA standard value of 100 mg/L. The concentrations of Mg in other sampling sites complied with the DWA standard[9]. The highest level of calcium was found to be 107.40 mg/L and the least 8.05 mg/L in site 6 and site 5, respectively. Calcium in plants is present in ionic form though it is not readily absorbed due to competition from other ions such as K^+ and Mg^{2+}. Deficiency of Ca results in root-rot infection[19]. Calcium is required for cell elongation and cell division. It also helps delay leaf senescence and slows down or prevents leaf and fruit fall (abscission)[19].

The highest concentration of Fe was observed insite 3 (1.14 mg/L), which was higher than DWA guideline of 0.3 mg/L (Table 1). This high concentration could be as a result of its leaching from sewer pipes. Also, the presence of iron may be responsible for the brownish-red colour of the water when allowed to stay for a long time [20]. Soluble iron and iron-loving bacteria can cause blockages in pipes, drippers and sprinklers which can damage equipment such as pressure gauges. In the farm, DWW from site 2 is sprayed to suppress dust along the road. This contributes to discolouration of leaves and reduces the efficiency of transpiration and photosynthesis.

Low concentration of Fe (0.2 mg/L) can stimulate aerobic slime deposits[21]. These slimes are sticky and can attach themselves to irrigation pipes, causing blockages [21]. Heavy iron deposits can make pasture unpalatable to stock. If eaten, they cause dairy cattle to scour and contribute to drop in milk production [22]. Iron deposits on vegetables, fruit and ornamental plants make them difficult to sell because of their stained appearance.

Average manganese concentration of 0.26 mg/L was determined and was higher than DWA (0.1 mg/L) and the Malaysian standards for the discharge of sewage and industrial effluents (0.2 mg/L)[23]. The highest concentration of Mn (0.7 mg/L)was determined at site 4. This value is higher than the Malaysian standard by a difference of 0.5 mg/L and exceeded it by 250%. Manganese is known to form coatings on pipes at a concentration above 0.2 mg/L, which may slough off as a black precipitate [24].

The concentrations of potassium varied from 5.10 mg/L at site 2 to 122.40 mg/L at site 6, respectively. High K values determined in the DWW could be due to high influx of potassium into water used in milk industry for various works. Slurry is majorly composed of liquid manure, which is discharged into site 6. Potassium forms part of the nutrient content (N-P-K) in manure, which could be a major contributor to the high value K determined at site 6. Another source could be due to the microbial accumulation of anaerobic nutrient rich bacteria within site 6 because DWW was left for a long period of time without treatment. Also high K levels indicate poor waste management practices in the farm.

Na concentration was found to be the highest of all the metals investigated (Table 1). The highest concentrations were found to be 444.5 mg/L and 520.90 mg/L at sites 1 and 2, respectively. The average concentration of (258.13 mg/L) was above the DWA standard of 200mg/L. The high concentration found could be due to sodium hydroxide which is often used as a chemical for the removal of fats and proteins from milk lines and other surfaces. Another contributing factor could be that the farm uses sanitizers containing high levels of sodium hypochlorite, which is used as a strong oxidant or bleach for sanitising equipment [26].

The computed data indicates that DWW has a relatively high content of sodium compared to potassium; hence its use for irrigation will result in the soil becoming strongly sodic. High concentration of sodium in soil causes soil dispersion, clay platelet and aggregate swelling[27]. This occurs when the forces that bind clay particles together are disrupted when very many large sodium ions come between them. Furthermore, when this separation occurs, the clay particles expand, causing swelling and soil dispersion. Sodium induced dispersion causes reduced infiltration, reduced hydraulic conductivity, and surface crusting [27].

Hence, high sodium content reduces porosity and increases the risk of poor movement of water through soil. This can lead to chemicals in the effluent reaching the broader environment [27]. This could have been responsible for the high values of EC and TDS observed. Since the DWW is used to irrigate land, it is adequate to calculate the risk associated with its application. Dairy effluent sodicity levels can be assessed by calculating sodium adsorption ratio (SAR), which is a measure of the amount of sodium present in the effluent relative to calcium and magnesium [28]. The moderate risk of applying wastewater to land should be less than 3 mg/L[29]. The average SAR was calculated by using the formula in equation 1 and gives an equivalent of 3.97 mg/L, which was higher than the recommended guidelines for the safe use of waste water in irrigation. The use of this water for irrigation as seen within the farm could pose serious harm to soil flora and fauna.

Total metal content in Soil

The total average metal content of the soil samples followed the sequence Al>K>Cu>Fe>Mn (Figure 2). All the metals investigated are considered essential for plant growth except Al. These elements are usually introduced in soluble forms by intensive use of agrochemicals.

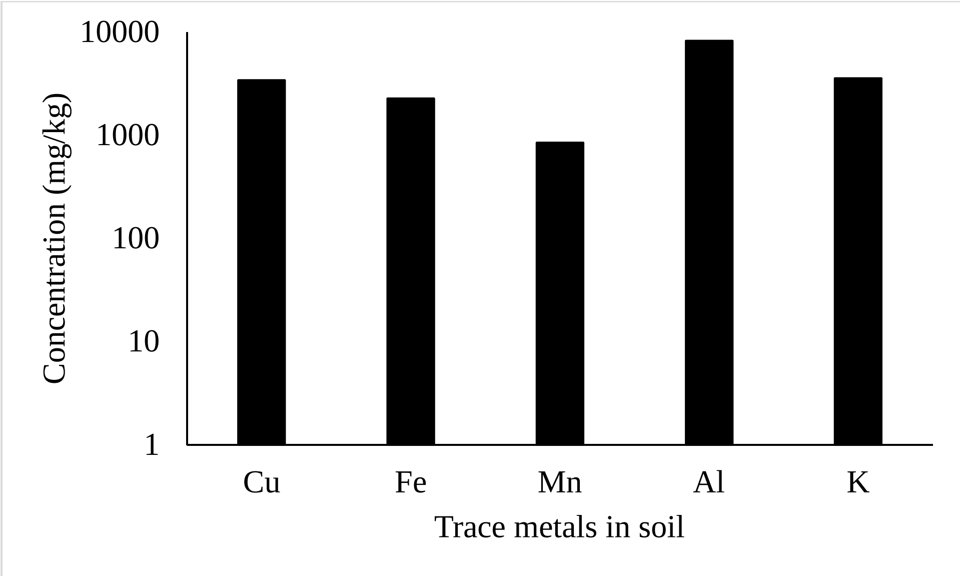

Figure 2: Trace metals concentrations in Soil

Hence they can be absorbed by crops or transferred from soil to other agro ecosystems components such as surface and groundwater [30]. Trace metal guidelines in agricultural soils vary between countries due to background concentration and the nature of crops that are cultivated.

Generally, Fe and Mn are not usually considered as contaminants to plants. They are crucial in plant nutrition as they are essential crop micronutrients. Therefore, insoluble forms of Fe and Mn in calcareous soils can cause deficiencies such as ferric chlorosis [31]. The mean concentration of Fe (2272 mg/kg) was lower than those obtained from similar studies. Millian et al. [32] reported an average concentration of 20787 mg/kg while Campos [33] and Mico et al. [34] reported 34000 mg/kg and 15274 mg/kg respectively (Figure 3). Similarly, the mean concentration of manganese from this study (850 mg/kg) was higher than those reported by Millian et al. [32]; 382 mg/kg, Campos, [33]; 533 mg/kg, Marian et al. [34]; 263 mg/kg and Mico et al. [34]; 320 mg/kg (Figure 4).

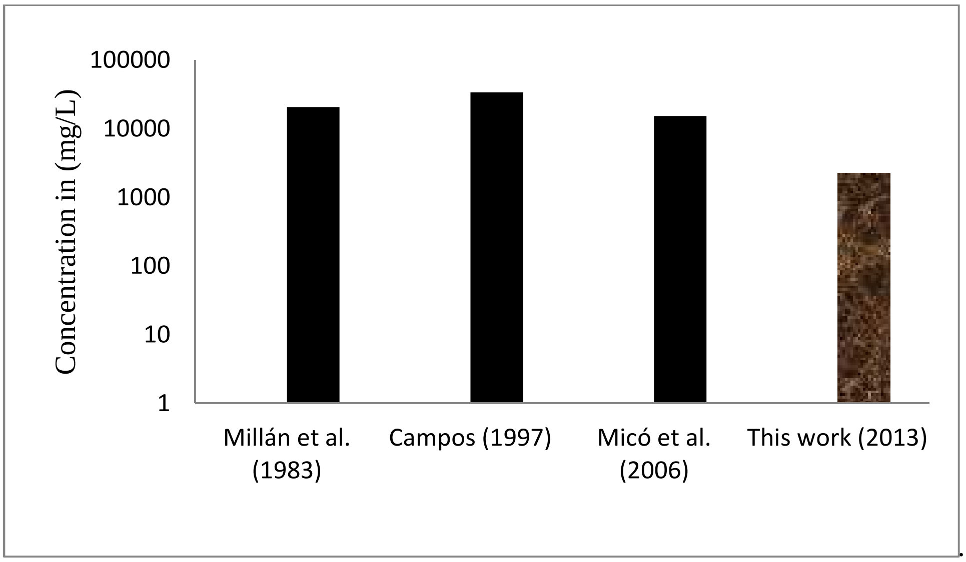

Figure 3: Comparative average Fe concentration in agricultural soils

Total iron and manganese are not good indicators of their availability to plants. Iron is mainly present in precipitated forms, such as oxides and hydroxides, in soils. Thus the high availability of these elements in soil would depend on the soil characteristics, such as the type of soil within the area, the pH and type of crop that is cultivated. In soils, the background manganese concentration ranges from 20 to 300 mg/kg [31] but its availability increases as pH decreases. Mn toxicity is common in acid soils of pH below 5.5. Manganese deficiency result in damaged structure of the chloroplasts of plants and decrease in net photosynthesis and chlorophyll amounts [36].

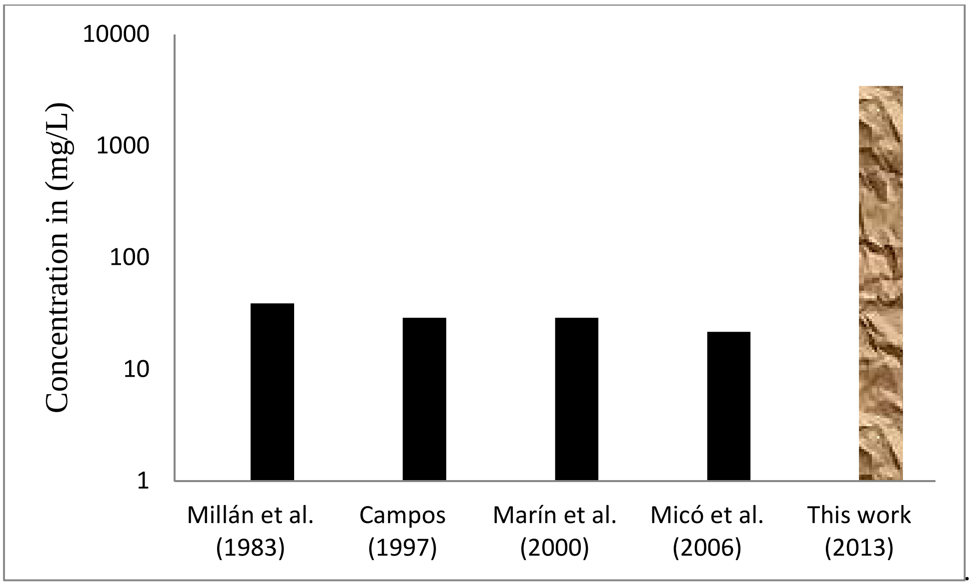

Figure 4: Comparative average Mn concentration in agricultural soils

A high aluminium concentration of 8222 mg/kg was found in this study. Wastewater effluent has been implicated as a major anthropogenic route of the accumulation of Al in terrestrial environment[37]. Aluminium toxicity is not a matter of concern as it is not likely to significantly bio-accumulate along the food chain. However, when present in relatively high concentration in acidic soils, it is usually considered as the most important growth limiting factor for plants [38].

The concentration of copper (3434 mg/kg) was higher than those reported by Millan et al. [32]; 39 mg/kg, Campos [33] and Marín et al. [35]; 29 mg/kg and Mico et al.[34]; 21.6 mg/kg, respectively (Figure 5). The normal copper content of agricultural soils varies between 5 to 50 mg/kg and the maximum permissible limit is 100 mg/kg [39]. The average concentration of copper from this study exceeded the reference value for agricultural soils in some European countries. It also exceeded the Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health of 60 mg/kg [40].

The baseline value for copper in South African soil ranges from 2.96-117 mg/kg [10]. This shows that irrigation with DWW could be the possible source of copper contamination. When copper accumulate in the soil over a long period, it could reduce food quality and quantity. Hence a high load of copper in the soil reduces the functioning of soil biota resulting in reduced microbial activity [41].

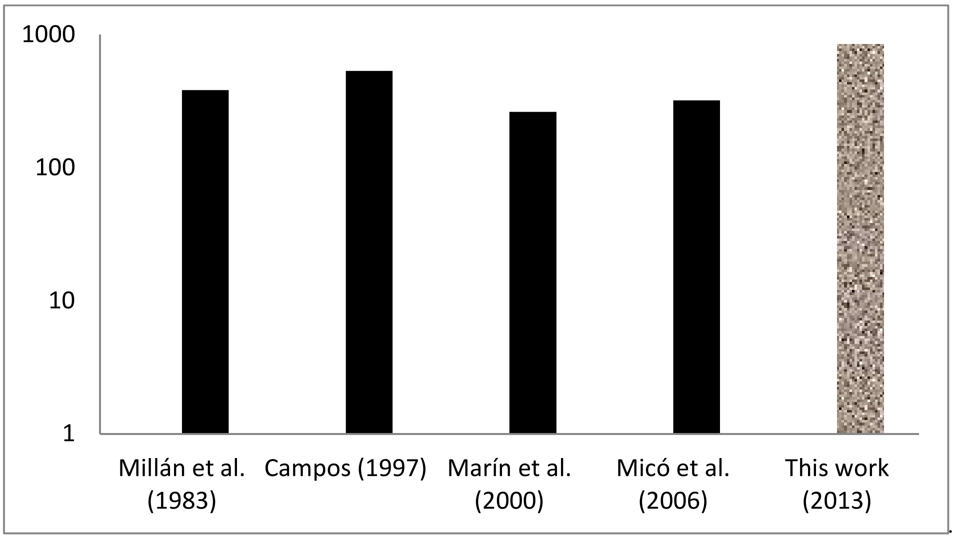

Figure 5: Comparative average Cu concentration in agricultural soils

Potassium is a macro element that is found on agricultural soils, it is not usually reported in most studies as it is not considered to be a metal of environmental concern. High accumulation of potassium exceeding the metabolic requirements is possible in plants and it is easily taken up and absorbed in plants although the uptake is usually affected by the absorption of nitrate ions [19]. When potassium uptake in forages exceeds acceptable concentrations, there can be a significant impact on cattle's health. This can occur as a result of high application of potassium rich manure or potassium fertilizers high above plant requirements [42]. With increased potassium concentration, calcium and magnesium uptake in cow's digestive tract is affected. This imbalance often leads to many health complications in dairy cows including mild fever, calving problems and displaced abomasum[42].

High soil potassium levels can inhibit magnesium uptake by pasture, potentially resulting in hypomagnesaemia in grazing stock. Like sodium, potassium has a high affinity for clay minerals and being a monovalent ion it has the potential to cause clay swelling and dispersion. This can lead to reduced infiltration due to loss of soil structural stability [43-44] and hence lead to reduced land productivity. Excess K concentration may interfere with crop uptake of other nutrients and also decreases soil hydraulic conductivity and permeability, and increase soil erodibility [45]. Pratt [46] reported that potassium concentrations are high in livestock manures and may become dominant soluble cation in manured soils.

From this study, K concentration ranged from 2544-4595 mg/kg and the highest was found at site 6 while the lowest at site 2. High potassium in soil is often an indicator of improper handling of the quantity of manure generated [42]. According to Carrow et al. [47], the desired value for potassium in soil should be less than 110 mg/kg. Consequently, from this study the concentration is higher than this maximum acceptable concentration.

CONCLUSION

The concentration of trace metals was higher in soil than in wastewater. This is consistent as the wastewater is used to irrigate crops on the farm and could have accumulated over a period of time. The presence of a very high concentration of Cu is worrisome as it is easily absorbed by plants and enters the food chain when animals eat these metal rich plants. Most of the parameters investigated were present in higher than acceptable concentration. The DWW is of poor quality and not suitable for irrigation. It must be treated properly before use or discharge into the natural environment.

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