Characterisation of some South African water treatment residues and implications for land application

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Abstract

Land application of water treatment residue (WTR) the by-product from the production of potable water, is becoming the preferred method of disposal, as there are environmental concerns and increasingly high costs associated with other disposal options. However, before WTR can be applied to land, consideration needs to be given to their chemical and physical characteristics to determine potential impacts. Six WTR samples were obtained from five South African water treatment facilities (Faure Water Treatment Plant (two samples), Rand Water, Umgeni Water, Amatola Water and Midvaal Water Company). The Rand Water WTR was a CaO, $FeCl_3$, long-chain organic polymer (LCP) residue with activated silica and CO_2 being added. The Umgeni and Amatola Water WTRs were lime and LCP residues. The Midvaal Water WTR was an $Al_2(SO_4)_3.nH_2O$, $FeCl_3$, lime and LCP residue and the Faure WTRs were $Fe_2(SO_4)_3$, activated charcoal, lime and LCP residues. These WTR samples were analysed for some physical (particle size distribution, particle density and plant available water) and chemical attributes (pH, electrical conductivity, cation exchange capacity, calcium carbonate equivalence, exchangeable acidity, extractable bases and metal cations, total and plant available nutrients, total elemental analysis and metal fractionation) and mineralogical properties, and their potential for application to land considered. The WTRs tended to be neutral to alkaline in pH, with low electrical conductivity. Generally, amounts of N, P and K were low, but some of the WTRs showed potential to supply other plant nutrients (Ca, Mg, S, Zn, Cu and Fe). Their physical characteristics were variable, showing a wide range in particle size distribution as well as plant available water. Heavy metal concentrations tended to be low, but Mn was elevated in some WTRs, especially in the Faure WTRs, which may lead to plant growth problems. Land application of these WTRs appears to be a feasible disposal option, but currently they are regulated by the 'minimum requirements for disposal of hazardous waste'. Delisting would firstly be required for land application and if then permitted by legislation, the application rates would need to be based on existing soil conditions, the characteristics of a particular WTR, and the proposed land use.

Keywords: Water treatment residue, land application, potable water, minimum requirements, disposal

Introduction

Water treatment residue (WTR) is the by-product from the production of potable water. It consists mainly of the precipitated hydroxides of the treatment chemicals that are added to coagulate and flocculate dissolved and suspended material in the raw water source and also during the residue dewatering process (Elliott et al., 1990b). Types and dosages of treatment chemicals vary depending on the quality of the raw water and their cost and availability. The chemicals typically include $Al_2(SO_4)_3.nH_2O$, $FeCl_3$, $Fe_2(SO_4)_3$, long-chain organic polymers (LCP), activated charcoal, activated silica and lime.

In the past, WTRs were discharged into watercourses (AWWARF, 1969), and more recently have been disposed of in landfills, due to the environmental concerns over direct river discharge (Basta, 2000). In many parts of the world, including South Africa, WTR has conventionally been disposed of by landfilling (Department of Water Affairs and Forestry, 1998). Basta (2000), in a review paper, has indicated that currently landfill is the most commonly used disposal option, but due to increased costs, land application is becoming the preferred disposal method. In South Africa, the reason for the previous popularity of landfills was that, with environmental concerns being

of low priority, landfill constituted a convenient method of waste disposal. Since 1994, however, South Africa has seen the closure of numerous landfill sites for both social and environmental reasons (Department of Water Affairs and Forestry, 2003). International agreements since 1994 have also put increasing pressure on the South African government to improve environmental policy (Department of Water Affairs and Forestry, 2003). As South Africans become more environmentally aware of the potential hazards of landfills, and legislation is made stricter, alternatives for waste disposal are being sought. Land disposal presents an appealing alternative to conventional disposal as it suggests that wastes can be assimilated, without inducing negative effects on soil quality. Indeed, there have also been reports suggesting that land disposal of WTR may improve soil quality (Roy and Couillard, 1998).

Land disposal of waste, a methodology also known as land application or treatment, has been described by Overcash and Pal (1979) as 'the intimate mixing or dispersion of wastes into the upper zone of the soil-plant system, with the objective of microbial stabilisation, adsorption, immobilisation, selective dispersion or crop recovery, leading to an environmentally acceptable assimilation of the "waste"'. Therefore, land disposal constitutes an open system offering potential for waste treatment, as opposed to simply waste disposal such as is associated with landfill. Elliott et al. (1990a) and USEPA (1996) consider some processes and management practices for land disposal to be a viable option, while Basta (2000) reviews a number of the studies that have considered the effects on soil properties and plant growth of land application of WTR. Most studies report

on some of the basic physical and chemical characteristics of WTRs used in any particular study, with some describing specific characteristics of the WTR used (Schmitt and Hall, 1974; Elliott et al., 1990b; Elliott and Taylor, 2000; Hyde and Morris, 2000; Dayton and Basta, 2001).

In the context of South African legislation, the responsibility for regulating the final disposal of waste to a landfill site is assigned to the Department of Water Affairs and Forestry (DWAF), in terms of Section 20 of the Environment Conservation Act, 1989 (Act 73 of 1989) (ECA). In terms of Section 20, no person may dispose of waste unless under the authority of a permit issued in terms of the ECA (DWAF, 2003).

In terms of the National Water Act (NWA, Act 36 of 1998), WTR is classified as a waste as follows, '"waste" includes any solid material or material that is suspended, dissolved or transported in water (including sediment) and which is spilled or deposited on land or into a water resource in such volume, composition or manner as to cause, or to be reasonably likely to cause, the water resource to be polluted'. Further, in terms of this Act 'water use' includes 'disposing of waste in a manner which may detrimentally impact on a water resource'.

This implies that for regulation of the substance, a water licence would be needed. This licence would be guided by the Minimum Requirement Series for Waste Disposal that informs users in terms of waste disposal standards, waste classification and monitoring (DWAF, 1998). However, the NWA is not only concerned with sacrificial disposal of waste but allows for a 'general authorisation' that does not require a licence, but is subject to the relevant regulations under Section 26 and conditions imposed under Section 29. These Sections require *inter alia* that waste standards be prescribed, and that adequate monitoring and analysis be undertaken based on 'permissible levels for some or all of its (the waste) chemical and physical components'.

However, a major problem is that WTR is currently classified as a 'waste' in terms of the definition given above, i.e. that it may 'cause or be reasonably likely to cause' pollution of a water resource. It is thus considered together with wastewater treatment sludge (sewage sludge or biosolids) and thus land disposal would require, at the very least, a general authorisation to be granted. Although the research presented uses the term WTR, in order to stress that it has a different nature to biosolids, South African regulations must also draw this distinction to allow for more effective handling and disposal of WTR.

Contaminated land has been defined as 'land where substances are present in concentrations higher than those in which they would normally expect to occur and where they pose a serious threat to public health and the environment' (Simms, 1988). The work reported here and elsewhere (Moodley et al., 2004; Hughes et al., 2005) shows that the classification of WTR as a waste material that is 'reasonably likely' to pollute water resources should be reconsidered and that its disposal under a 'general authorisation' section allowed by the NWA be permitted. This would largely remove the present restrictions on its use and disposal. However, if WTRs are to be applied to land, be it to agricultural, derelict (mined areas) or recreational (parks) land, consideration needs to be given to the nature of the WTR to determine any potential negative impacts the material may have. As the source of raw water (and treatment process) varies between water treatment works, properties of WTRs from different areas differ drastically. While there is an increasing amount of literature describing the range of WTRs produced in developed countries, in particular the USA, little published literature pertaining to South African WTRs could be found, with most

considering engineering aspects (Geldenhuys, 1992; Hodgkinson and Rencken, 1992; Polasek, 1997a;b). This paper describes some of the chemical and physical properties of WTRs from the major water treatment plants in South Africa as a starting point for future developments regarding WTR land disposal primarily from an agricultural perspective. In addition, it should be noted that this study forms part of a larger investigation examining the effects of applying WTR on soil chemical, physical and microbiological properties. These investigations have examined the effect of applying different WTRs to different soils from both agricultural and industrial perspectives (Moodley et al., 2004; Hughes et al., 2005).

Materials and methods

Six air-dried WTR samples were obtained from large water treatment works in South Africa. Three of the WTR samples were from the largest bulk water suppliers, i.e. Rand Water, Cape Metropolitan Council – Faure Water Treatment Plant (Faure 1 and 2), and Umgeni Water – Midmar Water Treatment Works. The other WTRs were from Amatola Water (East London) and Midvaal Water Company (Stilfontein). The Rand Water WTR was a lime-softening residue with high amounts of CaO, as well as $FeCl_3$, LCP, activated silica and CO_2 being added. The Midmar and Amatola Water WTRs were lime and LCP residues. The Midvaal Water WTR was an $Al_2(SO_4)_3.nH_2O$, $FeCl_3$, lime and LCP residue and the Faure WTRs were $Fe_2(SO_4)_3$, activated charcoal, lime and LCP residues. The second Faure WTR (Faure 2), obtained from the Faure Water Treatment Plant, represented a drastic change in the raw water quality, when algal blooms caused odour problems. While the treatment chemicals remained the same as for the Faure 1, there was a change in the dosages.

Chemical and physical analyses

The air-dry WTR samples were milled and passed through a 2 mm sieve. pH was measured in distilled water and 1 M KCl using a Radiometer PHM210 pH meter with a standard glass electrode. A WTR: solution ratio of 1:2.5 was used, and left to stand for 45 min with occasional stirring using a glass rod. Electrical conductivity (EC) was measured at 25ºC using a Radiometer CDM83 electrical conductivity meter in a 1:5 WTR: water solution (United States Salinity Laboratory Staff, 1954). Extractable cations were measured by saturating with Sr^{2+} and cation exchange capacity (CEC) by subsequent replacement with NH_4^+ (Hughes and Girdlestone, 1994).

Nitrogen was determined on <0.5 mm samples by combustion using a LECO nitrogen analyser. Nitrate and ammonia were extracted with 2 M KCl (Maynard and Kalra, 1993) and solution concentrations determined colorimetrically using a TRAACS 2000 continuous-flow auto analyser. Plant-available phosphorus was extracted with AMBIC (ammonium bicarbonate) solution and determined colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990) on a Varian Cary 1E UV-Visible spectrophotometer (UV-Vis). Exchangeable acidity and exchangeable Al were extracted according to Sims (1996), with Al being measured by atomic absorption spectrophotometry (AAS, Varian SpectraAA-200). Calcium carbonate equivalence (CCE) was measured according to Jackson (1958). Organic carbon (OC) was digested by potassium dichromate oxidation and determined titrimetrically (Walkley, 1947). Total C and S were analysed by combustion using a LECO CNS 2000 auto analyser.

TABLE 1							
Some chemical properties of six South African water treatment residues							
Property		Rand	Midmar	Midvaal	Amatola	Faure 1	Faure 2
pH	KCl	8.66	7.78	7.66	6.94	6.19	7.23
	H_2O	9.16	8.00	8.36	7.66	6.56	7.84
Electrical conductivity (mS/m)		35.10	71.50	31.27	25.33	16.40	40.50
Total C (g/kg)		82.20	48.80	25.60	23.80	118.90	nd[a]
Organic carbon (%)		1.23	2.77	1.60	1.96	3.34	10.27
Exchangeable acidity ($cmol_c$/kg)		0.00	0.20	0.10	0.10	0.10	nd
Exchangeable aluminium ($cmol_c$/kg)		0.07	0.06	0.06	0.07	0.05	nd
Calcium carbonate equivalence (%)		109.06	5.92	4.48	4.09	6.94	nd
[a] not determined.							

TABLE 2							
Some physical properties of six South African water treatment residues							
Property		Rand	Midmar	Midvaal	Amatola	Faure 1	Faure 2
Particle size distribution (%)	Sand (0.053-2 mm)	1.2	91.6	37.5	67.5	91.0	14.4
	Coarse silt (0.02-0.053 mm)	1.6	2.4	2.0	1.1	1.3	5.7
	Fine silt (0.002-0.02 mm)	34.3	2.5	31.4	2.1	4.3	61.2
	Clay (<0.002mm)	62.9	3.5	29.1	29.3	3.4	18.7
Particle density (g/cm³)		2.43	2.23	2.09	2.02	2.02	nd[a]
Plant available water (g/kg)		18.17	53.81	40.46	8.66	29.64	197.72
[a] not determined.							

Particle size distribution was determined by the pipette method (Gee and Bauder, 1986) and particle density by the method of Blake and Hartge (1986). Gravimetric water content was determined at -33 and -1 500 kPa using pressure plate apparatus. Plant available water (PAW) was considered to be the difference in water content between -33 and -1500 kPa (Dayton and Basta, 2001).

X-ray diffraction (XRD) analysis of randomly oriented powders was carried out on a Philips PW1050 diffractometer using monochromated Co Kα radiation from 3° to 75° 2θ with a scanning step of 0.02° at 1° per minute. The diffraction data were captured by a Sietronics 122D automated micro-processor. The samples were then qualitatively analysed to determine major mineralogical components.

Total elemental concentrations were measured by X-ray fluorescence spectrometry and plant available Cd, Cu, Co, Cr, Mn, Fe, Ni, Pb and Zn were determined by extraction with DTPA (Liang and Karamanos, 1993). A five-step fractionation procedure was used to determine exchangeable (1 M $MgCl_2$), dilute acid extractable (1 M NaOAc at pH 5), Fe/Mn bound (0.175 M $(NH_4)_2C_2O_4$ and 0.1 M $H_2C_2O_4$), organically bound (0.1 M $Na_4P_2O_7$) and residual fractions (acid digest, HF, HNO_3 and $HClO_4$) of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (Elliott et al., 1990b). Elemental solution concentrations were determined by AAS.

Results

Chemical characteristics

The pH of the WTR samples ranged from 6.19 to 8.66 in KCl and from 6.56 to 9.16 in water (Table 1). In most instances, the WTR samples were neutral to alkaline, with only the Faure 1 WTR having a slightly acidic pH. Electrical conductivity ranged from 16.4 to 71.5 mS/m. The Faure 1 WTR sample had the highest measured total C concentration. The Faure 2 sample probably had a higher concentration, but the C concentration exceeded the measuring parameters of the instrument used and so its

total C could not be determined. The other WTRs had considerably lower amounts than the Faure 1 sample, though the Rand Water WTR had a moderately high total C content. Organic carbon content ranged from 1.23 to 10.27%. Exchangeable acidity ranged from 0.0 to 0.2 $cmol_c$/kg and exchangeable Al from 0.05 to 0.07 $cmol_c$/kg. Calcium carbonate equivalence generally showed low liming potential for the WTRs (all <7%), with the exception of Rand WTR that had a CCE of 109% due to the high dosing with CaO.

Physical characteristics

The particle size distribution of the WTR samples was variable (Table 2). Samples that were easily dispersed tended to have high amounts of fine silt and clay (Faure 2, Rand and Midvaal), while the other, less easily dispersed, WTRs had higher amounts of sand (Faure 1, Amatola and Midmar). There was also a marked change in the particle size distribution of the Faure WTRs, due to the change in raw water quality and treatment processes. To demonstrate the effect of air-drying on the particle size characteristics of WTR a fresh (wet) sample of the Midmar WTR was analysed and found to consist of 6% sand, 4% coarse silt, 6% fine silt and 84% clay. The particle densities of the dry WTRs ranged from 2.02 to 2.43 g/cm³. Plant- available water ranged considerably from 8.66 to 197.72 g/kg, but was generally low.

Nutrient concentrations

Nutrient concentrations were variable (Table 3), depending on the source of the residue.

Total S determined by combustion was generally quite low, with only the Faure 1 WTR showing an elevated concentration. Nitrate-N ranged from 9.7 to 94.2 mg/kg and NH_4-N from 26.3 to 358.4 mg/kg. Total N concentrations ranged from 200 to 5 200 mg/kg. This indicates that a considerable proportion of the N is bound in less soluble (or less available) forms in the WTRs,

TABLE 3						
Nutrient concentrations of six South African water treatment residues						
Property		**Rand**	**Midmar**	**Midvaal**	**Amatola**	**Faure 1**	**Faure 2**

Property		Rand	Midmar	Midvaal	Amatola	Faure 1	Faure 2
Total S (mg/kg)		10	210	130	320	1 200	nd[a]
Total N (mg/kg)		200	1 000	2 800	2 600	5 200	4 800
$NO_3 – N$ (mg/kg)		94.23	16.80	12.76	31.80	9.65	11.53
$NH_4 – N$ (mg/kg)		26.33	170.15	358.38	62.40	108.48	32.10
AMBIC P (mg/kg)		4.70	4.46	31.51	0.74	6.33	21.50
Extract-able cations $(cmol_c/kg)$	Ca	4.54	31.01	38.28	28.49	25.29	37.31
	Mg	15.75	9.13	14.33	8.76	13.42	22.12
	Na	1.37	0.52	0.56	0.88	0.66	0.81
	K	0.38	0.51	0.78	0.39	0.30	0.14
Cation exchange capacity $(cmol_c/kg)$		15.85	26.59	41.81	25.38	33.47	35.79
[a] not determined.							

TABLE 4												
X-ray fluorescence analysis of six South African water treatment residues												
Sample	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	**Total**	**LOI**[a]
(%)												
Midmar	54.57	22.60	11.95	1.53	1.92	4.20	0.15	1.47	0.86	0.24	99.49	23.91
Midvaal	53.07	22.36	14.24	0.41	1.83	4.45	0.33	1.89	0.74	0.47	99.79	27.70
Amatola	52.59	29.06	10.31	0.07	1.82	1.55	0.43	2.98	0.86	0.12	99.79	25.63
Rand	24.36	9.89	4.85	0.66	5.25	53.19	0.61	0.82	0.31	0.09	100.03	36.93
Faure 1	29.93	8.70	53.80	0.96	0.72	3.15	bd[b]	0.93	0.78	0.39	99.36	43.07
Faure 2	37.96	17.78	32.13	2.31	1.54	3.35	0.49	1.86	0.62	0.37	98.40	55.28

Sample	Cd	Co	Cr	Cu	Ni	Pb	Zn	S	Sr	As	V	U
(mg/kg)												
Midmar	4.00	39.0	161.0	44.0	53.0	37.0	84.0	720	71.0	17.0	154.0	bd
Midvaal	nd[c]	32.0	246.6	53.2	117.7	26.0	142.1	2402	66.2	5.0	187.8	0.2
Amatola	nd	19.0	134.3	23.0	39.7	36.0	84.5	911	91.4	11.0	175.8	3.8
Rand	nd	3.5	77.3	5.4	22.9	5.8	33.1	700	273.4	1.7	61.1	2.1
Faure 1	nd	nd	43.0	bd	21.0	nd	182.0	2500	nd	nd	93.0	nd
Faure 2	nd	nd	70.0	11.0	27.0	nd	124.0	2500	nd	nd	134.0	nd

Sample	Nb	Ce	Nd	Zr	Y	Sc	Th	Ba	La	Rb	Ga	
(mg/kg)												
Midmar	11.0	96.0	25.0	126.0	27.0	33.0	10.0	1007.0	19.0	94.0	20.0	
Midvaal	7.8	51.0	24.0	101.6	23.1	30.7	7.9	438.7	5.4	109.2	19.0	
Amatola	10.6	71.0	38.0	105.1	29.4	30.1	16.1	705.7	30.6	171.5	23.0	
Rand	2.7	5.1	bd	32.2	38.1	13.5	5.0	398.4	bd	38.1	8.9	
Faure 1	nd	nd	nd	nd	nd	nd	nd	nd	38.0	nd	nd	
Faure 2	nd	nd	nd	nd	nd	nd	nd	nd	26.0	nd	nd	
[a] loss on ignition. [b] below detection. [c] not determined.												

except in the Rand WTR, where NO_3-N and NH_4-N accounted for about 60% of the total nitrogen, even though the total concentration was low. The AMBIC extractable P was generally very low, except for the Midvaal and Faure 2 WTRs. The CEC of the WTRs ranged from 15.9 to 41.8 $cmol_c/kg$ and, with the exception of the Rand WTR, all were above 25 $cmol_c/kg$. Extractable Ca concentrations were surprisingly low in the Rand WTR, while the other WTRs showed considerably higher Ca concentrations, the highest being recorded for the Midvaal WTR. Magnesium concentrations were lower than the Ca concentrations, except for the Rand WTR. The Rand WTR had a Ca: Mg ratio of about 1:3, whilst the remaining WTRs were 2:1 or 3:1. Potassium and Na concentrations were low for all WTRs.

Other analyses

X-ray diffraction revealed small amounts of quartz in all samples. Except for the Faure and Amatola WTRs, all samples contained calcite with most, as expected, in the Rand WTR. Clay minerals were present in all samples. Illite and kaolin were observed in all samples except Rand (where no clays could be determined due to the large amount of calcite) and Faure 1 (where there was no clear presence of illite). The Midvaal WTR appeared to also contain smectite and the Midmar WTR a 1.4nm mineral. Apart from quartz and calcite, the other non-clay minerals found were gibbsite (Midmar), and feldspar (Amatola). Amorphous material occurred especially in the Faure WTRs where it appeared to

				TABLE 5		
			PA extractable metals (mg/kg) of six South African water treatment residues			
Element	Rand	Midmar	Amatola	Midvaal	Faure 1	Faure 2
Cd	0.66	0.42	0.45	0.50	bd[a]	0.30
Co	0.42	0.63	0.70	1.06	1.82	2.59
Cr	1.16	1.18	1.45	1.86	bd	bd
Cu	1.76	5.78	1.39	7.16	0.41	0.29
Fe	48.70	87.70	63.30	246	65.00	42.70
Mn	38.80	88.90	13.23	22.10	725	420
Ni	0.56	1.34	0.61	3.39	bd	bd
Pb	0.20	1.07	2.67	1.43	0.79	1.64
Zn	1.48	3.01	2.04	8.64	10.27	10.89
[a] below detection						

be the dominant phase, and in the Midvaal and Amatola WTRs.

The major elements (XRF, Table 4) of the Midvaal and Amatola WTRs were similar to those of the Midmar WTR, although trace elements tended to be more variable. The Rand and Faure WTRs showed markedly different characteristics from the aforementioned WTRs and each other. A notable point is the very high Ca and Mg content of the Rand WTR when compared to the other WTRs, this possibly contributing to the high CCE. The Faure WTRs had a very high Fe content, in particular the Faure 1 WTR. Both the Rand Water and Faure 1 WTRs had low Al and Si contents, with the Faure 2 WTR having slightly higher concentrations.

Generally, DTPA extractable metal concentrations were low (Table 5), although Fe and Mn concentrations were elevated in most of the WTRs. The Midvaal WTR had the highest concentration of Fe. The Faure WTRs had exceptionally high Mn values. This was attributed to contaminants in the $Fe_2(SO_4)_3$ and brown lime used to treat the raw water (Flower, 2003). The Midvaal and Faure WTRs also had elevated concentrations of Zn, possibly also from the Fe-salts used to treat the raw water. Nickel concentrations in the Midvaal WTR were slightly elevated, again probably due to contamination from the Fe-salt used for water purification. Copper concentrations were elevated in the Midvaal and Midmar samples.

In the five-step fractionation for selected metals (Table 6), little was removed as exchangeable, with the Fe concentration of the Midvaal and Faure being notable, probably due to the use of Fe-salts in their treatment processes. Only small amounts of Mn were exchangeable, with the Rand Water WTR being below detection.

As expected, dilute acid extraction removed a greater concentration of metals, with Fe and Mn tending to show the greatest increase in concentration. Also notable was the increase in Zn concentration of the Faure WTR and the Pb concentration of the Rand Water WTR. The chromate extractable (Fe/Mn oxide bound) fractions tended to show high Fe and Mn concentrations, with Zn increasing in concentration for the Faure WTR. For all the WTRs Fe concentrations were highest in the chromate extractable fractions (apart from residual concentrations) accounting for between 7 and 27% of the total Fe content. Manganese accounted for a high proportion of the Fe/Mn oxide bound fraction (2 to 68% of the total Mn concentration). The organically bound fraction again showed moderate levels of Mn and Fe. Concentrations of Cr were also notable in the Midmar, Amatola, Midvaal and Faure Water WTRs. The residual frac-tion showed sharp increases in all metal concentrations for all WTRs.

Discussion

The pHs of the WTRs are similar to the typical pH range of 5.10 to 8.00 reported by Basta (2000). The very high pH of the Rand WTR, and to a lesser extent the Midmar WTR give these WTRs moderately high acid neutralising potential. The exceptionally high CCE of the Rand WTR suggests that this WTR has a very reactive acid neutralising component, probably in the form of Ca and Mg carbonates. This is supported by the high concentrations of Ca and Mg shown in the XRF data. The CCE of WTRs examined by Elliott et al. (1990a) ranged from 10 to 20%, although they did not include a lime WTR. The ECs suggest low to moderate water solubility of salts in the WTRs, indicating that these should not present a problem for land disposal. Dayton and Basta (2001) similarly report ECs ranging from 22.0 to 110.0 mS/m for 17 Oklahoma WTRs. The high total C reported for the Faure 1 WTR was expected, as the residue is a product of the removal of dissolved organics and the use of activated charcoal and lime during the treatment process. The other residues probably reflected the amount of lime and organic polymer added during water treatment, and the amount of organic material removed from the raw water. Basta (2000) reports values from 0.8 to 6.5%, and Dayton and Basta (2001) values from 1.7 to 14.9%. Elliott et al. (1990a) report a mean total OC content of 3% for WTRs from seven Pennsylvania water treatment facilities. The low exchangeable acidity and aluminium values reflect very low acid producing potential, a result of their lime component and neutral to alkaline pHs. The alkaline nature, high CCE and low exchangeable acidity and aluminium of most of the WTRs suggest the potential for land application on a variety of soils or wastes. An exception may be where extreme acidity may render the neutralising capacity of the WTR ineffective potentially releasing metals into that particular environment, but this is also dependant on the amounts present in a particular WTR.

It might be expected that the residues would exhibit high clay and silt fractions. However, the residues are formed by the coagulation of fine particles into larger stable aggregates, and may exhibit a coarse texture once dried, this depending on the strength of the bonds between the particles (Skene et al., 1995; Ahmed et al., 1997). This is further supported by the difference found in particle size distribution between the wet and dry Midmar WTRs. Plant available water showed a considerable

TABLE 6
Five step fractionation of metals (mg/kg) from water treatment residues from five of South Africa's water treatment facilities. Results from Elliott et al. (1990b) are given for comparative purposes.

Rand	MgCl₂	Weak Acid	Fe/Mn bound	Organic bound	Residual	Midmar	MgCl₂	Weak Acid	Fe/Mn bound	Organic bound	Residual
Cd	bd[a]	2.9	0.4	8.20	24.0	Cd	bd	bd	bd	bd	30.0
Co	bd	5.2	bd	bd	47.0	Co	bd	0.3	bd	bd	80.0
Cr	bd	bd	bd	2.60	339.0	Cr	bd	bd	bd	21.4	254.0
Cu	0.1	7.8	9.0	8.80	32.0	Cu	bd	4.5	15.2	0.6	58.0
Fe	bd	62.6	4 908.8	2 004.4	24 743.0	Fe	bd	244.5	14 373.5	4 962.4	5 6450.0
Mn	bd	941.8	1 541.4	141.8	1 057.0	Mn	23.3	1 026.7	6 869.6	1 668.4	528.0
Ni	3.6	13.3	bd	bd	38.0	Ni	1.17	bd	bd	bd	62.0
Pb	bd	84.8	4.0	bd	340.0	Pb	bd	26.4	bd	bd	460.0
Zn	bd	8.9	0.9	bd	87.6	Zn	bd	3.6	bd	bd	129.2

Amatola	MgCl₂	Weak Acid	Fe/Mn bound	Organic bound	Residual	Midvaal	MgCl₂	Weak Acid	Fe/Mn bound	Organic bound	Residual
Cd	0.3	bd	0.2	bd	41.0	Cd	0.2	0.3	bd	bd	57.0
Co	bd	1.3	bd	bd	121.0	Co	bd	1.9	bd	bd	114.0
Cr	bd	bd	bd	26.4	417.0	Cr	bd	bd	20.0	47.4	352.0
Cu	bd	0.3	8.4	bd	41.0	Cu	bd	3.3	21.8	3.6	67.0
Fe	bd	47.5	4 522.2	2 386.8	58 373.0	Fe	245.9	1 062.2	23 998.2	5 889.6	58 378.0
Mn	4.5	36.3	96.0	bd	248.0	Mn	7.1	426.7	854.2	222.8	275.0
Ni	4.5	1.7	bd	bd	63.0	Ni	bd	16.2	37.6	4.6	84.0
Pb	bd	18.4	bd	bd	620.0	Pb	bd	12.0	bd	bd	740.0
Zn	bd	1.3	bd	bd	150.5	Zn	bd	14.2	27.5	6.3	186.5

Faure 1	MgCl₂	Weak Acid	Fe/Mn bound	Organic bound	Residual	Elliott et al. (1990b)[b]	MgCl₂	Weak Acid	Fe/Mn bound	Organic bound	Residual
Cd	0.1	0.3	1.6	bd	58.0	Cd	5.8	19.0	bd	38.0	38.0
Co	bd	1.8	10.0	5.40	138.0	Co	nd[c]	nd	nd	nd	nd
Cr	bd	bd	16.0	47.4	225.0	Cr	1.0	2.4	38	10.0	49.0
Cu	bd	0.2	7.4	2.6	57.0	Cu	1.0	5.8	32	6.3	55.0
Fe	737.0	1 111.4	91241.8	2 111.6	289850.0	Fe	nd	nd	nd	nd	nd
Mn	5.0	897.1	1 847.0	991.4	3 235.0	Mn	nd	nd	nd	nd	nd
Ni	3.7	6.6	20.6	bd	73.0	Ni	0.6	12.0	31.8	4.5	51.0
Pb	bd	11.2	bd	bd	830.0	Pb	4.2	2.6	8.4	13.0	72.0
Zn	bd	63.3	134.2	44.3	362.8	Zn	0.5	17.0	34	6.0	42.0

[a] below detection.   [b] mean values reported by Elliott et al. (1990b) using the same procedure on 7 WTRs.
[c] not determined.

range, this being similar to Dayton and Basta (2001) who report a range from 26 to 416 g/kg. A number of studies have reported on improved soil physical properties as a result of WTR additions (Rengasamy et al., 1980; Skene et al., 1995; Ahmed et al., 1997; Moodley, 2001). While not intensively investigated here, some of the WTRs had high water-holding capacity. This may improve water retention of some soils, while improving infiltra-tion of heavy textured soils, if the WTRs are applied to land. However, Moodley (2001) indicated that if the WTR applied to a soil were to degrade to its constituent fractions (clay and silt in most instances) then clogging of soil pores may lead to reduced infiltration and water retention in affected soils. Furthermore, this may increase the reactive sites for release of potentially toxic elements from the WTR.

TABLE 7
Summary table of the acceptable environmental risk (mg/ℓ) and disposal allowed (g/ha·m) for selected metals as outlined by the 'Minimum requirements for waste disposal'[a].

Element	Acceptable environmental risk (mg/ℓ)	Disposal allowed (g/ha·m)
Cd	0.031	47
Co	6.9	10 454
Cr	4.7	7121
Cu	0.1	151
Fe	9	13 636
Mn	0.3	454
Ni	1.14	1727
Pb	0.1	151
Zn	0.7	1061
[a] Department of Water Affairs and Forestry		

However, in an investigation using the field trials reported on by Moodley (2001), data suggest that, after five years, the physical properties of a Hutton Soil (Soil Classification Working Group, 1991) treated with WTR at application rates as high as 1 280 Mg/ha are returning, after initially having shown increased water retention, to similar conditions as the control treatments (Moodley et al. 2004; Personal observation, 2003).

Although some of the WTRs studied had low nutrient concentrations, in particular N, K and P, they may be useful to improve conditions for plant growth in degraded or nutrient-poor soils. The alkaline nature of most of the WTRs (in particular the Rand Water WTR) would enable them to increase the pH of acid soils. Fertiliser additions may help overcome some of the nutrient deficiencies, possibly with the exception of P. A number of studies have reported on the high P sorbing capacity of WTRs and the potential of these WTRs to reduce P uptake by plants grown in either pure WTR or mixtures of soil or potting media and WTR (Elliott and Singer, 1988; Heil and Barbarick, 1989; Skene et al., 1995; Ahmed et al., 1997; Basta et al., 2000; Codling et al., 2002). However, field experiments have shown that plant uptake of P is apparently not adversely affected by additions of WTR (Grabarek and Krug, 1987; Geertsema et al., 1994; Buyeye, 2003).

While total N was moderately high for most 'WTRs, the available fraction tended to be low. Dayton and Basta (2001) report a much higher range in total N from 1300 to 18 400 mg/kg, but the concentrations of NO_3-N (22 to 140 mg/kg) and NH_4-N (3.5 to 123.0 mg/kg) were similarly low. The high availability of Mg in the Rand Water WTR suggests that a Ca:Mg imbalance could occur in soils treated with the Rand Water WTR. Although the Rand Water WTR had very high concentrations of total Ca (Table 4), it is clear that this Ca is in an unavailable form. Generally, however, extractable Ca and Mg appear to be at adequate plant available concentrations, but K may be too low for satisfactory plant growth.

The source of quartz in the WTRs may be from sand particles that are removed from the raw water, although the most likely source is the introduction of sand grains to the WTR during backwashing of sand filters used during water treatment. The obvious source of calcite is the lime used in the water treatment process, and although Rand Water uses CaO, calcite is formed as a result of the use of CO_2 during water treatment. All the WTRs showed the presence of various clay minerals, and some had considerable amounts of X-ray amorphous material. Rengasamy

et al. (1980) also found that, apart from small amounts of quartz in their alum residue, the XRD pattern consisted largely of disordered materials, probably amorphous hydrous oxides of Al, Fe and Mn, as well as organic fractions.

As indicated by Schmitt and Hall (1974), who examined a sediment basin residue from the Oak-Ridge Water Treatment Plant (Tennessee, USA) for 72 elements, Si, Ca, Mg, K, Fe and Ti were generally the most abundant elements in the WTRs. The concentrations of these were to some extent dependant on the treatment chemicals used. In the case of the Rand Water WTR, use of high amounts of CaO in the treatment process is reflected in high Ca concentrations in the residue produced. A similar situation exists for the Faure WTRs, where use of an Fe-salt in the treatment process has resulted in a high Fe concentration in the residues. The DTPA extractable metal concentrations suggest that generally these would not be problematic for plant uptake, and in some instances may supply some trace nutrients (e.g. Zn). Of some concern was the high Mn concentration of the Faure WTRs, which may lead to symptoms of toxicity in plants or perhaps cause antagonistic effects in the uptake of other elements (Ca, Mg, Fe). The use of total element or metal content is a poor indicator of the toxicity of a waste as it does not reflect the mobile or available fraction (Tiller, 1989). At most it gives an indication of the worst potential toxicity of an element assuming complete release of that element.

The five-step fractionation perhaps gives a better indication of how mobile or available these metals may be. This showed that generally most metals are not readily exchangeable, except for Fe in the Midvaal and Faure 1 WTRs. Extraction with a weak acid, however, showed increases in the concentration of most metals from all samples. This indicates that these elements may become mobile under acid conditions. Gibson and Farmer (1986, cited by Elliott et al., 1990b) indicate that the sum of the exchangeable and dilute acid extractable fractions represents the maximum availability of the metals to plants. On this basis, Elliott et al. (1990b) found Cd to be the likely cause of concern in the WTRs they studied, accounting for some 25% of the total Cd concentration. In the WTRs examined here, the Cd fractions accounted for very small proportions (0 to 8%) of the total Cd concentration. For these WTRs, high levels of Mn would appear to represent a major concern, especially for the Rand, Midmar, Amatola and Faure 1 WTRs. In Rand Water WTR, Pb and Ni may also represent toxicity problems, although this was not reflected in the DTPA extraction. This suggests that under even slightly acid conditions moderate concentrations of these elements may be released. The Faure 1 WTR also showed a high Zn concentration when extracted with dilute acid.

It is likely that under the recommendations of the minimum requirements (DWAF, 1998) most of these WTRs would not be delisted as hazardous material. Table 7 summarises the criteria set by the minimum requirements (DWAF, 1998) for some of the metals measured in this study. The 'acceptable environmental risk' values refer to the LC_{50} x 0.1 and are compared to the 'estimated environmental concentration'(EEC). The EEC represents 'the concentration of a substance in the aquatic environment when introduced under worst case scenario conditions, i.e., directly into a body of water. It is used to indicate possible risk, by comparison with the minimum concentration estimated to adversely affect aquatic organisms or to produce unacceptable concentrations in biota, water or sediment' (DWAF, 1998). 'Disposal allowed' refers to the acceptable amount of hazardous waste that can be safely disposed of per hectare per month. The minimum requirements, however, seem excessively stringent for purposes of land disposal, as they do not consider existing soil

background conditions and the ability of soil to buffer additions of heavy metals.

When one considers limits set by other environmental organisations, specifically for soil, then the levels reported here for these WTRs are generally not excessive, especially if one considers the effects of dilution when land disposing such waste. For example the limits set by Environment Canada for agricultural soils indicate that for Cd, Co, Cu, Cr, Ni, Pb and Zn the limits are 1.4, 40, 63, 64, 50, 70 and 200 mg/kg, respectively (CCME, 1998). One can assume the $MgCl_2$ and weak acid extractable fractions (Table 6) estimate the likely amount of contamination from the WTRs, as the remaining fractions are unlikely to be available. Using these data it can be seen that the only elements of probable concern are Cd and Pb in the Rand Water WTR. The release of the remaining fractions of metals would depend largely on the rate of WTR breakdown, and the environmental conditions (e.g. reducing or acidic environments). The metals in the residual fraction are considered unavailable, as they are bound in mineral lattices, are not readily released, and as for the XRF data, represent the worst case for toxicity.

Conclusions

Generally it appears that the WTRs examined have potential for land application. Concerns relate to the release of metals under certain conditions, in particular Mn, Cd and Pb in some instances. As it is probable that the source of the Mn is the treatment chemicals, the use of a 'cleaner' coagulant would reduce the amount of Mn in the WTRs. If the Rand Water WTR were to be applied to land then careful consideration would need to be given to the acidity of the soil. This is to ensure that the pH remains in a range that will not cause excessive release of some heavy metals, in particular those bound in carbonate compounds. Furthermore, for land application of WTRs (as with any other waste) consideration needs to be given to existing background soil characteristics, as well as the intended purpose of the land to be treated with a WTR (Elliott et al., 1990a). These factors will influence the rate and frequency of application to any given area.

In addition, although the WTRs examined here include the main WTRs produced in South Africa, it would be beneficial to examine a far greater number of residues from different water treatment processes and from other locations to improve understanding on the range of WTRs produced and their potential for land application under a variety of conditions. Temporal variability in WTR production that may affect both volumes and quality of the waste should also be considered.

Acknowledgements

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