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Evaluation of the risk of heavy metals in sewage sludge intended for agricultural application in Swaziland

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ABSTRACT

Sewage sludge generated from municipal wastewater treatment plants is widely acknowledged as an important source of nutrient and soil conditioner for agricultural use. Determination of levels of heavy metals in sewage sludge is necessary prior to application of the sludge to agriculture because of the inherent risk of heavy metal toxicity to soil, plants and humans. At present large amounts of sewage sludge are being generated and stockpiled in several waste water treatment plant premises in Swaziland and agricultural application is being considered as a future viable option of disposal. Sewage sludge generated from seven wastewater treatment plants in Swaziland were analyzed for a range of total metals using ICP-OES. Most of the samples analyzed show compliance with respect to the regulatory limits set by the USEPA, South Africa and EU guidelines for levels of heavy metals in sewage sludge intended for agricultural application. Sewage sludge generated from the Matsapha wastewater treatment plant in general show high levels of heavy metals due to the presence of several industries in the area. No visible trend in heavy metals increase was observed among sewage sludge samples generated at different time periods.

Keywords: Sewage sludge, heavy metals, toxic pollutants, sludge reuse, metal toxicity. Nutrient recycling, bio-solids.

1. Introduction

Sewage sludge is a waste product generated at the end of municipal and industrial wastewater treatment processes and is being produced in increasingly large volumes worldwide due to growing population and increasing urbanization. Disposal of sewage sludge presents a problem that touches a set of complex issues including health, environment, aesthetics and economics. The options available for sludge disposal are rather limited because of expressed objections to pollutants contained in sludge (Lau, et al., 2001). The European Union Directive (91/271/EEC) for instance forbids disposal of sludge to the sea (EU, 1991). Land application is simple and inexpensive but land is becoming scarce. Moreover, regulations and increasing environmental concern restrict the option for land disposal of sewage sludge (Wong et al., 1999). Incineration is expensive although the heat can be recovered as a source energy.

Although sewage sludge is traditionally considered as waste, the recycling and reuse of valuable nutrients contained in the sludge are nowadays being considered as important

resources for sustainable development (Lundin, 1999). In fact, the practice of applying sewage sludge to agricultural lands dates back to centuries (Foller et al., 1981). Treated sewage sludge can be recycled in various ways including its use as fertilizer with significant nutrient supplements improving plant growth. Sewage sludge is also used as a soil conditioner for improving the physical and chemical properties of soils in farmland, forests and home gardens (Dolgenet al.,2007; Wong and Su 1997; Debosz et al. ,2002; Wang et al., 2003).

The estimated percentages of sewage sludge applied to agricultural lands have been quoted as 29% in the USA, 40% in the UK, 60% in France, 30% reuse potential in Russia and 230,000 ton/year in Japan (Johnson and Corcelle, 1989; Smith, 1996; Deneuvy and Chassande, 1998; Ministry of Construction Japan,1998;Pakhnenkoa, 2009;Pakhnenkoa, 2007). In developing countries, the experience of using sewage sludge application for agricultural purposes is often confined to municipal farms and few peri-urban farms. However, the escalating cost of commercial fertilizer is providing increased motivation for farmers to consider sewage sludge as cheaper substitute (Nyamangara, 2001). In Swaziland, currently a clear strategy for a proper disposal of sewage sludge is not available. Sewage sludges generated from wastewater treatment plants in Swaziland are dewatered and stored temporarily in the premises of wastewater treatment plants until they are eventually disposed somewhere in the future. There is a perceived risk to human health and the environment that prevented sewage sludge from being applied to agricultural lands. Other means of sewage sludge disposal such as land filling and incineration have been discounted on the grounds of cost and environmental safety.

Fear of toxic metals and pathogens are risks that are often cited against the use of sewage sludge for nutrient supplementation of soils (Azevedo and Stout 1974; Chaney, 1983; Robert and Winkler, 1991, Wong et al., 1995). However, in addition to heavy metals and pathogens, other harmful and toxic pollutants such as pharmaceuticals, detergents, various salts, pesticides, toxic organics, flame retardants and hormone disruptors can also be present in sewage sludge (Antonious et al., 2003; Aparicioet al. ,2007; Singh and Agrawal, 2008; Sánchez-Brunete et al., 2008). Sewage sludge can also inject in soils excessive amount of nutrients, pesticides and can increase soil salinity (Barry et al., 1995). Besides, raw sewage sludge has objectionable odour and is not aesthetically accepted by farmers and as a result has to undergo extensive treatment before it is considered for agricultural application.

Heavy metals are mainly found in sewage sludge because due to their hydrophobic nature, they are associated with the solid portion of the wastewater (Page et al., 1981). Usually, domestic wastes have lower heavy metal contents than industrial wastes. As a result, toxic metals such as lead, cadmium, mercury, nickel and chromium may be present in municipal wastewaters due to heavy urbanization and the entry of untreated industrial wastewater into the municipal wastewater system (McGrath et al., 2000 ; Pires and Mattiazzo, 2003 ; Singh et al., 2004). On the basis of relative toxicity to plants and animals, two groups of heavy metals can be identified. The first group comprising cadmium, mercury and lead are highly toxic to humans and animals but are less toxic to plants. The second group comprising zinc, nickel and copper are, when present in excess concentration, more damaging to plants than to humans and animals (Gowrek and Ratenska, 2009).

Selenium and molybdenum can cause toxicities in animals and humans. However, they are present in low concentrations and hence do not often limit the rate of sludge application to soil. Cadmium is reported to have caused adverse health effects in humans who ingested plants grown on soils contaminated with high levels of Cadmium (Chaney, 1980). Lead can

also enter the food chain by grazing animals that feed on grass grown on sludge-soil mixture contaminated with lead (Chaney, 1980).

Increased contents of heavy metals can produce adverse effects on soil biological properties while being toxic to plants. Most commonly, the background levels of heavy metals in soils are often lower than the heavy metals present in sludge (Sloan et al., 1998). There is evidence that application of sewage sludge that contains heavy metals in excess concentrations not only affects the property of soils (Sauerbeck, 1987) and soil microbial population in general (Kelly, et al., 1999), but also soil borne symbiotic microorganisms such as rhizobacteria (Wetzel and Werner, et al., 1997 Del Val, et al., 1999) and arbuscular mycorrhizal fungi (Del Val, et al., 1999, Jacuote, et al., 2000). Such symbiotic microorganisms contribute to nutrient acquisition by plants which are important for reducing fertilizer inputs in sustainable plant production systems. Above the admissible level, toxic metals significantly reduce soil fertility. Metals also inhibit enzyme activity in the soil and alter soil acidity (Gawdzik and Gawdizik, 2012). The mechanisms of harmful reactions of metals are diversified. Metals inactivate enzyme systems thus leading to physiological changes which in the most extreme cases can cause tissue and cell necrosis.

The long-term use of sludge can cause heavy metal accumulation in soils (López-Mosquera et al, 2000). Even after a short term application of sewage sludge, the levels of heavy metals in soils can increase considerably. For example, Oliveira and Mattiazzo (2001) observed increases in Cu, Cr, Ni and Zn concentrations in soils amended for two years with sewage sludge. There are two opposing theories that explain the long term impact of application of sewage sludge to agricultural lands, namely the time bomb theory and the plateau theory. The plateau theory argues that the long term application of sludge leads to stabilization of metals in soils as a result of the organic matter and minerals present in the sludge. This, according to the theory, leads to a maximum limiting rate of uptake by plants (the plateau). The time bomb theory on the other hand hypothesizes that metals could be released from the immobile matrix over the long term as a result of mineralization of the organic matter (Silvera, et al., 2003). According to McBride (1995), the plateau theory is aided by the fact that a fraction of the organic matter resists decomposition providing protection against metal uptake by plants.

There are seemingly conflicting evidences supporting or refuting both theories which only serve to add to the uncertainty regarding the long term impact of heavy metals in sludge. For example, according to Chang et al. (1997) data obtained from a 10-year land application of sewage sludge showed that the cadmium concentration in soils and in plant tissues increased with increasing sewage sludge application, and that no plateau was reached even at a mass loading that reached 1080 tons/hectare. This contradicts the plateau theory. However, although there was no plateau, ten years after the termination of sewage sludge application, the metal concentration in plant tissue did not rise, refuting in turn the time bomb theory of increasing uptake of metals due to mineralization of organic matter. These observations suggest that neither the plateau theory nor the time bomb theory has an overriding acceptance.

Heavy metal effects on plants

The heavy metals Cd, Cu, Mo, Ni and Zn are classified as a potential hazards in land application of municipal sludges as they can accumulate in plants causing reduced plant yields or health problems to humans and animals that consume the plants (CAST, 1976). According to DeVries and Tiller(1978), significant concentrations of Cd, Cu, Mn, Ni, Pb and

Zn were found on the edible parts of lettuce tops and onion bulbs that were grown on soils amended with sewage sludge. Cereal and legumes accumulate less cadmium in shoots than do leafy vegetables. Tomato plants accumulate more cadmium than barley or bean plants (Bradford et al., 1975).

Sensitivity of plants to metal toxicity can be associated with the tendency to accumulate the metal in shoots. Bingham et al (1975) observed that Spinach, soybeans, lettuce were injured by soil Cd levels of 4 to 13 μg/g of soil. These plants accumulate cadmium in shoots whereas low shoot accumulators like tomato and cabbage could tolerate soil cadmium levels of 170 μg/g without injury. In wheat, concentrations of trace metal elements in plant parts follow a pattern with the concentration in roots > leaves > stems > grain. Thus, the potential hazard from metals is apparently reduced if only the seed is harvested and used as a food source. But according to Wang et al. (2003), 22 to 24% of the total metal contents in the rice biomass grown in paddy soils which were contaminated with cadmium, chromium and zinc were concentrated in the grains indicating a potential risk associated with the consumption of rice grown on contaminated soils.

The translocation factor (TF) is a common index that is used for estimating the movement of heavy metals from roots to shoots there by evaluating the relative risks associated with consumption of the shoot parts of plants. Lakhdar et al. (2012) found decreasing values of translocation factors for heavy metals with increasing application of sewage sludge indicating stronger accumulation of heavy metals in roots than in shoots. On the contrary, Kumar, et al. (2013) found out that increasing the rate of application of sludge caused a progressive increase in the accumulation of metals (Fe, Zn, Cd, Cu, Cr and Pb) in the roots, shoots, leaves and fruits of the plant P. Vulgaris. The accumulation was in the order: Fe > Zn > Cd > Cu > Cr >Pb. Zinc was found highest in the leaves and the lowest in the fruits. The translocation of zinc was in the order (leaves > shoot > root > fruits). For cadmium the order was: shoot > root > leaves > fruits. For copper and lead the order was: shoot > leaves > root > fruits. Chromium was found maximum in the root and the translocation order was root > shoot > leaves > fruits of P. Vulgaris.

Sludge application rate is an important parameter that determines the extent of accumulation of heavy metals in soils and their absorption by plants. Increased concentrations of lead, cadmium, nickel and chromium have been observed in plant seeds as a result of increased application of sludge (Amin and Sheriff, 2001). The level of plant uptake, bio-accumulation and tolerance of plants to heavy metals varies among different crops at different rates of application of sewage sludge (Yilmaz, et al., 2012).Some plants can continue storing toxic heavy metal elements, and with increased rate of application of sludge, this leads to bioaccumulation of heavy metals and increased level of toxicity along the food chain (Justeet al., 1995).

Heavy metals toxicity is also known to affect plant photosynthesis processes (Ouzounidou and Ilias, 2005; Wang et al., 2009). The presence of excess concentration of metals in plants can directly inhibit photosynthetic electron transport as well as photosynthetic metabolism (Burzyhski and Zurek, 2007). Toxic elements can also enter the photosynthetic apparatus by decreasing the photosynthetic pigment damaging chloroplast structure and inducing changes in the lipid and protein composition of the thylakoid membrane leading to lipid peroxidation related to the generation of toxic oxygen species (Wang, et al., 2009).

2. Mobility of heavy metals

Another risk of contamination in the environment is observed through leaching of heavy metals from soils to ground water. The risk increases with time as metals are persistent in soils over a longer time and many metals do not undergo bio-chemical degradation thereby increasing the risk of bio-availability of metals and their leaching to ground water table (Gadepalle et al., 2008). According to the study of Antoniadis and Alloway (2003), in soils that received heavy loads of sewage sludge, heavy metals showed a movement down to a depth of 0.8 m within the soil indicating that there is a risk of leaching of metals. However, even though such experiments that were carried out on the field indicated limited mobility of metals (compared to the movement of water within the soil) and their confinement only up to the depth of application of sewage sludge, the mass balance calculation shows that metals are lost from the soil by other mechanisms than plant uptake (Williams et al., 1987; McGrath and Lane, 1989). Dowdy et al. (1991) mentioned the possibility that metals may be leached through cracks and macro pores present within the soil, a process they termed non-matrix flow or generally known as preferential flow.

The regulatory limits of heavy metals in sewage sludges from a number of countries are summarized in Table 1. These limits will be used to compare the heavy metal contents in sewage sludge obtained from the laboratory analysis and to judge the suitability of sewage sludge for agricultural applications in Swaziland.

3. Materials and Methods

3.1 Sludge sampling

Sludge samples were collected from seven wastewater treatment plants in Swaziland for the analysis of total metals and determination of physico-chemical characteristics of the sludge. The wastewater treatment processes that take place in each of the treatment plants are given in Table 2. Samples were collected using plastic bags that were pretreated with diluted nitric acid and rinsed with distilled, deionized water. Some of the sludge samples collected such as the ones from Matsapaha and Ezulwini wastewater treatment works represent different the sludges were stored for several years. Therefore, separate samples of sludge from the fresh as well as old part of the sludge pile have been collected in order to investigate the variation in metals contents as well as variation of sludge characteristics over time. Sludge samples, after collection, were dried at room temperature and there after stored in a refrigerator at 4 ^{0}C until they were analyzed.

Table 1: Regulatory limits of heavy metals in sewage sludge intended for agricultural application (McGrath et al., 2000; Nilsson and Dahlström, 2005)

Heavy Metal	Units	EU Directive 86/278/EEC		Chinese Regulation GB 18918-2002		USA Regulation 40 CFR Part 503, 503.13		South African Guideline (Pollutant Class a)	
		Limit value (mg/kg)	Limit value (kg/ha.year)	Acidic soil pH<6.5	Neutral and Basic soil pH >6.5	Pollutant concentration Limits (mg/kg)	Annual pollutant loading rate (kg/ha. year)	Pollutant limit mg/Kg (Class a)	Pollutant limit mg/Kg (Class b)
Arsenic	mg/kg			75	75	41	2	40	75

Heavy Metal	Units	EU Directive 86/278/EEC		Chinese Regulation GB 18918-2002		USA Regulation 40 CFR Part 503, 503.13		South African Guideline (Pollutant Class a)	
		Limit value (mg/kg)	Limit value (kg/ha .year)	Acidic soil pH<6.5	Neutral and Basic soil pH >6.5	Pollutant concentration Limits (mg/kg)	Annual pollutant loading rate (kg/ha. year)	Pollutant limit mg/Kg (Class a)	Pollutant limit mg/Kg (Class b)
Boron	mg/kg			150	150			23	72
Cadmium	mg/kg	20 - 40	0.15	5	20	39	1.9	40	85
Chromium	mg/kg	Not set	Not set	600	1000			1200	3000
Copper	mg/kg	1000 - 1750	12	250	500	1500	75	1500	4300
Mercury	mg/kg	16 - 25	0.1	5	15	17	0.85	15	55
Molybdenum	mg/kg							4	12
Nickel	mg/kg	300 - 400	3	100	200	420	21	420	420
Lead	mg/kg	750-1200	15	300	1000	300	15	300	840
Selenium	mg/kg					100	5.0	5	15
Zinc	mg/kg	2500 - 4000	30	500	1000	2800	140	2800	7500

Table 2: wastewater treatment processes that take place at the seven wastewater treatment plants in Swaziland included in the research.

	Treatment Plant Location	Wastewater treatment processes	Location of sludge sampling
1	Hlathukulu	Settlement tank, waste stabilization pond, constructed wetland.	From sludge pile taken from waste pond
2	Matsapha	Waste stabilization pond	From stored sludge pile taken from waste pond
3	Nhlambeni	Settlement, Trickling filter and anaerobicdigester.	Sludge sample taken after anaerobic digestion. Dried sludge and fresh sludge from sludge drying bed.
4	Nhlangano	Waste stabilization pond	Anaerobic pond
5	Piggspeak	Waste stabilization pond	Anaerobic pond
6	Siteki	Settlement, trickling filter and anaerobicdigester.	Sludge sample after secondary settlement tank
7	Ezulwini	Settlement, trickling filter and anaerobicdigester.	Sludge sample taken after anaerobic digestion. Dried sludge and fresh sludge from sludge drying bed.

3.2 Sample Pretreatment

The dried sludge samples were first passed through a 2 mm sieve eliminating roots, stones, plastics, grass and other impurities. The samples were then powdered to fine sizes using mortar and pestle and thoroughly mixed to achieve homogeneity. The powdered sludge samples were then sieved mechanically to obtain fractions that are less than 63µm. The sludge samples after these steps were stored in plastic containers at 4 ^{0}C until they were analyzed.

4. Determination of sludge Physico-chemical characteristics

A minimum of three replicates from each of the prepared sample following the procedure described in the sample pretreatment above were taken for the determination of physico-chemical characteristics of the sludge samples. The parameters determined include: pH, electrical conductivity, moisture content, percentage of dry solids, volatile and fixed solids, organic matter, organic carbon, available nitrogen, available phosphorous and cation exchange capacity.

4.1 Total metal determination

The total metal determination was done using two methods for comparison and quality assurance purposes. The methods used were atomic absorption spectrometer (Varian–AAS) and Inductively coupled plasma atomic emission spectrometry (ICP-OES). The metals analysed include: Al, As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Sn, Ti, V, Zn, Zr. Sample digestion was carried out according to METHOD3050B of the USEPA: Acid Digestion of Sediments, Sludge and Soils (USEPA, 2012).

4.2 Sample digestion

For the digestion of sludge samples, 1 g. of prepared sludge was weighed using analytical balance of ± 0.001 precision and transferred to heating mantles with reflux (vapor recovery device). Initially 10 ml of 1:1 HNO_3 was added and the samples were heated to 95 ^{0}C and refluxed for 10 to 15 minutes without boiling. After cooling, 5 ml of concentrated HNO_3 was then added to the samples and the samples were refluxed for 30 minutes and the procedure of adding 5 mL of concentrated HNO_3 was repeated until no brown fumes were generated indicating completion of reaction with HNO_3. The samples were then heated further for 2 hours at 95^{0}c. After completion of the above steps and the samples have cooled, 2 mL of water and 3 mL of 30% H_2O_2 were added and the samples were slowly warmed to start the peroxide reaction. The H_2O_2 addition was continued in 1 mL aliquots to a maximum of 10 mL and the samples were heated for two hours at 95^{0}c with a reflux. After completion of the peroxide digestion, the samples were cooled and 10 mL of concentrated HCl was added and the samples were slowly heated to 95^{0}C and the heating continued for 15 minutes with a reflux. The digested samples, after cooling, were filtered through a 0.45µ filter and the filtered digested samples were transferred to 100 mL volumetric flasks and filled to the 100 mL mark with distilled, deionized water. After this, the samples were split into two 50 mL volumes for analysis by the AAS and ICP-OES.

All quality control measures have been observed throughout the sample preparation and analysis steps. Distilled-deionized water has been used for dilution and rinsing. All containers and glassware have been thoroughly washed and rinsed with 2% HNO_3 prior to use in the analysis. For each of the metals analyzed, stock solutions of analytical grade chemicals were used for preparation of primary and secondary standards. For determination of parameters describing sludge characteristics, analytical regent grade chemicals have been used and the standard operating procedures as prescribed for the respective methods were followed. For the determination of method detection limits of metals, a number of blank samples containing distilled- deionized water were processed through the same steps as those of the samples and metal determinations were similarly made. Spike recovery analysis of each metal was made to determine the recovery due to matrix effects.

5. Results and discussion

The results of analysis of the physico-chemical characteristics of the sludge are summarized in Table 3. Summaries of the results of the ICP-OES analysis of heavy metals in the sludge samples collected from the seven wastewater treatment plants are given in Table 4 and Table 5. The data include the average, and ranges of variation for each of the heavy metals determined. The overall range of variation, as explained by the coefficient of variation is mostly in the 20-30% range for most of the heavy metals and can be seen in the plots provided in Figure 1. Sludge samples collected from the Matsapha and Ezulwini waste water treatment plants include old as well as fresh sludge. However, the range of variation of metal concentrations from these treatment plants is not much different from the other wastewater treatment plants which indicate a limited trend in concentration changes with time. Matsapha wastewater treatment plant which receives effluents from several industries showed relatively higher concentrations of heavy metals compared with the other wastewater treatment plants. This is perhaps expected since Matsapha town is known to be an industrial area. Some of the heavy metals such as cadmium and selenium are omitted because the concentrations determined were below the limits of detection for the respective heavy metals. In general, most of the heavy metals are present in moderate concentrations and below the regulatory limits provided by the USEPA, South Africa and the European Union. A discussion of the variation with the individual heavy metals is provided below.

The concentrations of copper (average, minimum and maximum) are shown in Figure 2 for the seven wastewater treatment plants. These concentrations of copper are generally low and well below the USEPA, South African and EU guidelines. This indicates that the sludge samples carry lower risk with respect to copper toxicity. The Chinese guidelines are exceeded but the limiting concentrations given by Chinese regulations are generally low. Copper is among the trace elements that are essential to life although at high concentrations copper is toxic. Copper may be derived from cleaning products, cosmetics and shampoos, fuels, inks, medicines and ointments, food products, oils and lubricants, paints and pigments, polish and wood preservatives, electronics, plating, paper, textile, rubber, fungicides, printing, plastic, and brass and other alloy industries and it can also be emitted from various small commercial activities and warehouses, as well as buildings with commercial heating systems.

Table 3: Physico-chemical characteristics of sludge samples collected from waste treatment plants in Swaziland

Parameter	Unit	Value	Hlathu-kulu	Matsa-pha	Nhlam-beni	Nhlan-gano	Piggs Peak	Siteki	Ezulwini
Cation Exchange Capacity	(meq/100 gm)	Median average	88	123	253	138	159	153	105
		Range	71 - 151	65 - 205	144 - 259	106 - 173	103 - 615	138 - 244	81 - 112
Electrical Conductivity	(µS/Cm)	Median average	1775	2840	3130	2220	939	2780	983
		Range	1014 - 2090	1062 - 7220	2530 - 3720	1181 - 2460	611 - 1087	2640 - 2920	648 - 1646
pH	(pH Units)	Median average	5.93	6.025	6.96	6.81	6.43	7.08	6.72
		Range	5.35 - 6.27	5.77 - 6.21	6.58 - 7.02	6.21 - 7.84	6.00 - 6.75	7.04 - 7.45	6.50 - 6.90
Organic carbon	(%)	Median average	10	15	23	27	30	19	29
		Range	5 - 25	12 - 22	21 - 25	25 - 29	6 - 31	18 - 22	28 - 30
Organic matter	(%)	Median average	20	30	46	53	60	38	57
		Range	11 - 51	24 - 43	43 - 49	49 - 57	12 - 61	37 - 43	55 - 59
Volatile solids	(%)	Median average	14	33	52	47	83	35	51
		Range	9 - 45	28 - 42	45 - 84	47 - 48	9 - 85	35 - 48	43 - 55
Nitrogen	(%)	Median average	1.7	1.6	3.7	1.8	2.3	2.3	3.9
		Range	0.8 - 1.9	1.3 - 2.6	3.3 - 4.5	1.6 - 2.4	0.5 - 3.2	2.2 - 2.9	3.1 - 4.1
C/N ratio		Median average	5.9	9.4	6.2	15.0	13.0	8.3	7.4
		Range	2-31	4-16	4-7	10-18	2-62	6-10	7-10
Phosphorous	(%)	Median average	1.2	2.1	2.2	1.5	1.0	1.4	2.4
		Range	1.1 - 1.3	2.1 - 2.2	2.1 - 2.3	1.4 - 1.5	0.7 - 1.5	1.4 - 1.6	2.4 - 2.5

Table 4: Result of heavy metals analysis sewage sludge samples collected from Ezulwini, Hlathukulu, Matsapha and Nhlambeniwaste water treatment plants.

Location	**1. Ezulwini**		**2. Hlathukulu**		**3. Matsapha**		**4. Nhlambeni**	
Parameter	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)
As	141-169	154	45-134	85	115-169	141	100-106	102
Co	103-118	107	57-163	102	80-107	93	88-99	96

Location	1. Ezulwini		2. Hlathukulu		3. Matsapha		4. Nhlambeni	
Parameter	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)
Cr	468-542	512	317-543	427	642-1396	940	493-579	550
Cu	417-536	481	103-696	295	405-606	510	491-518	506
Fe	22993-29465	27836	16581-36188	25970	18647-31597	25322	22796-25393	24486
Mn	306-378	345	83-168	134	145-478	272	283-369	333
Mo	4 - 7	5	1-6	4	10-25	17	4-7	6
Ni	48-65	45	27-66	285	128-327	233	57-115	82
Pb	64-76	69	12-65	32	65-96	82	80-96	89
Sn	141-207	183	210-324	274	294-601	435	323-382	362
Ti	151-308	216	159-305	236	300-621	485	142-302	213
V	31-37	33	1-62	27	33-52	42	30-32	31
Zn	1331-1610	1450	553-1046	743	478-2311	1301	1238-1400	1324

Table 5: Result of heavy metals analysis of sewage sludge samples collected from for Nhlangano, PigsPeak and Sitekiwastewater treatment plants.

Location	5. Nhlangano		6. Pigspeak		7. Siteki	
Parameter	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)	Range (mg/Kg)	Mean (mg/Kg)
As	107-118	114	5-139	59	137-151	145
Co	104-110	108	19-100	52	0-120	93
Cr	462-507	476	409-648	486	403-453	429
Cu	227-251	238	8-146	68	215-328	252
Fe	27381-28613	28044	8559-25579	15373	28461-30050	29448
Mn	274-298	287	160-278	231	525-565	542
Mo	5-7	6	0-4	2	4-524	109
Ni	31-75	40	21-131	55	25-65	52
Pb	28-32	29	0-35	8	21-92	36
Sn	280-310	302	277-303	290	159-248	196
Ti	194-361	281	48-474	215	366-546	464
V	49-51	50	2-49	21	61-68	65
Zn	1549-1659	1593	69-882	247	1082-1216	1163

The primary sources of copper in industrial wastewaters are metal process pickling baths and plating baths. Elevated chloride contents decrease adsorption of copper on soil, due to chloride complexation which results in greater solubility and mobility (Bourg, 1988; Gambrell et al., 1991). Copper toxicity is also related to low abundances of zinc, iron, molybdenum, and sulfate (Chaney, 1988).

The chromium and nickel concentrations are given in Figure 3 and Figure 4 respectively. The concentrations are mostly below the Chinese and South African guidelines except the maximum concentration of chromium for the Matsapha sludge samples. The se results also indicate that the sludge samples carry low risk with respect to chromium and nickel toxicity.

Nickel and chromium are toxic to humans and both can reach the food chain via plant uptake from contaminated soil (Hazlett et al., 1983). Wastewater containing nickel originate from cosmetics, paints and pigments, production of alloys, electroplating, catalysts and nickel-cadmium batteries, corrosion of equipment from launderettes, jewelry shops, metal processing industries, motor vehicle and air craft industries, printing and chemical industries. The sources of chromium are alloys, preservatives, dying, and tanning activities, paint and plating baths, tannery industries that use chrome tanning, metal industries, cleaning products, oil and lubricants, photographing and pesticide products. Chromium III is widely used as a tanning agent in leather processing. The use of Chromium VI is nowadays restricted and there are few commercial sources.

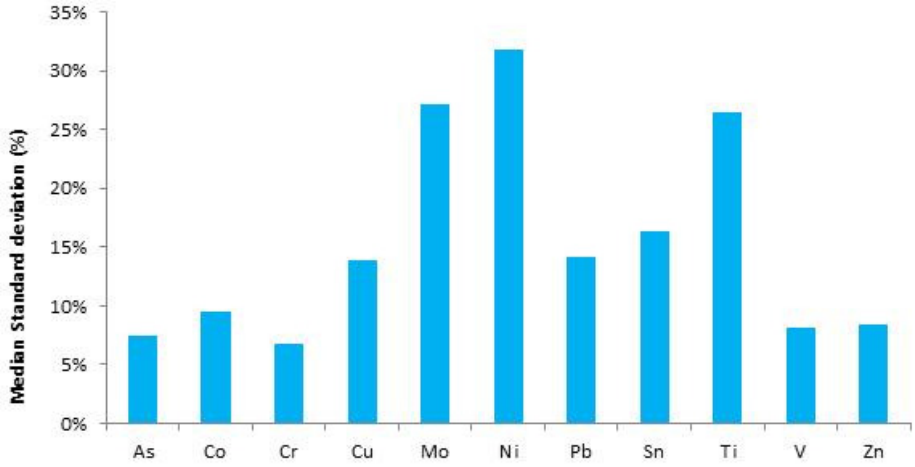

Figure 1: Median standard deviations of heavy metal variations over the seven wastewater treatment plants

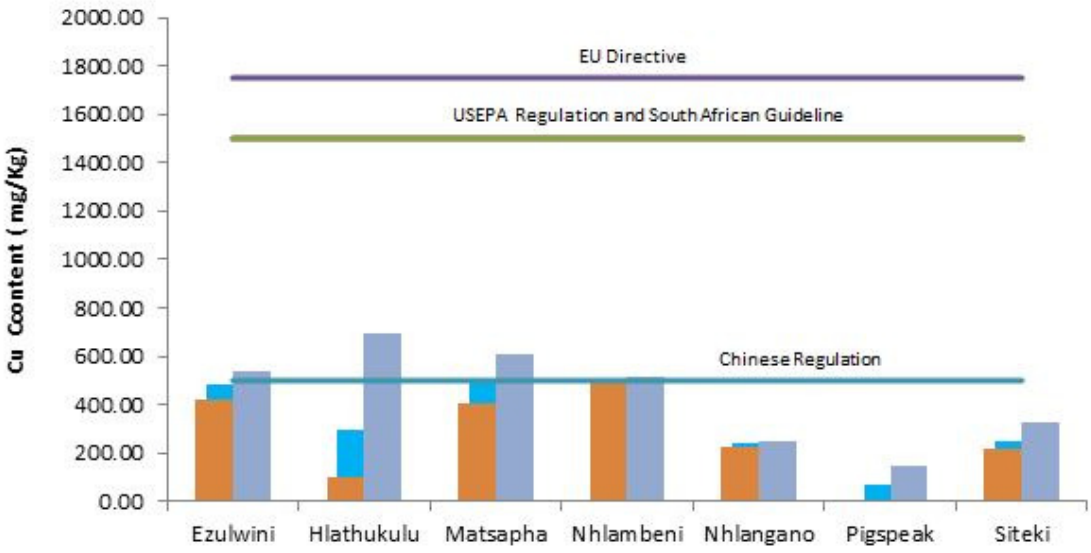

Figure 2: Copper contents of sludge from wastewater treatment plants in Swaziland

The lead concentrations as shown in Figure 5 are low and well below all the regulatory guidelines considered (shown with horizontal line in Figure 5). Lead is known for its immobility and limited translocation in plants. The data indicate once again the low risk of the sludge samples collected from the seven wastewater treatment plants with respect to lead toxicity on the basis of total lead metal concentrations. Lead is defined by the United States Environmental Protection Agency (USEPA) as potentially toxic to most forms of life (USEPA, 1986).

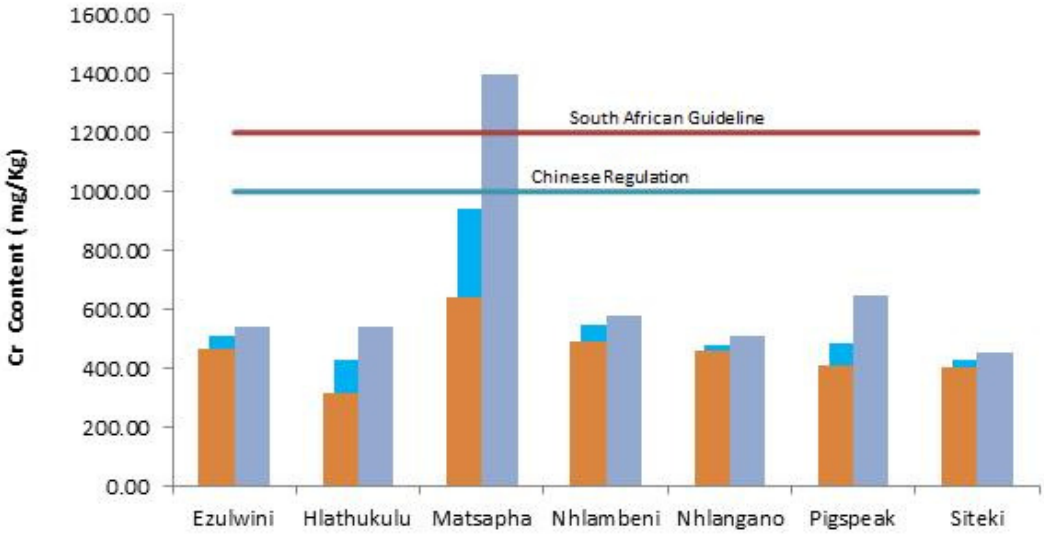

Figure 3: Chromium contents of sludge from wastewater treatment plants in Swaziland

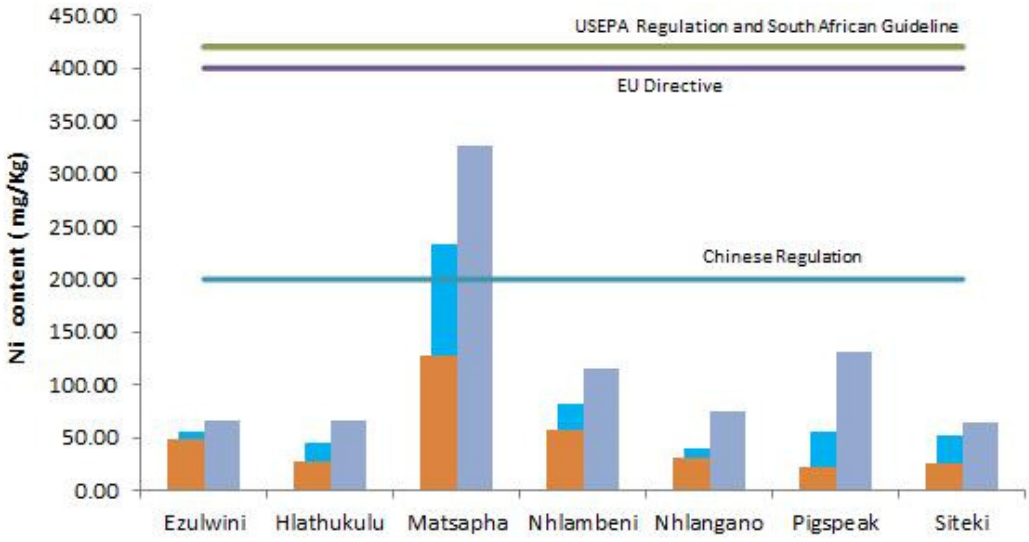

Figure 4: Nickel contents of sludge from wastewater treatment plants in Swaziland

A major source of lead in sewage sludge could be from lead-containing dust fall-out, which reaches the drainage system with rain. Concentration of lead from such source would vary widely depending on traffic density, industrial emissions and climatic factors (Chow, 1978). Sources include batteries, pigments, solder, roofing, cable covering, lead jointed waste pipes and PVC pipes (as an impurity), ammunition, chimney cases, fishing weights. Lead is toxic to humans, its chronic effects being neurological disorders, especially in the fetus and in children. This can lead to behavioral changes and impaired performance in IQ tests (Lansdown, 1986; Needleman, 1987). Lead is very effectively immobilized by precipitated iron oxide minerals under well-oxidized conditions (Gambrell et al., 1991).

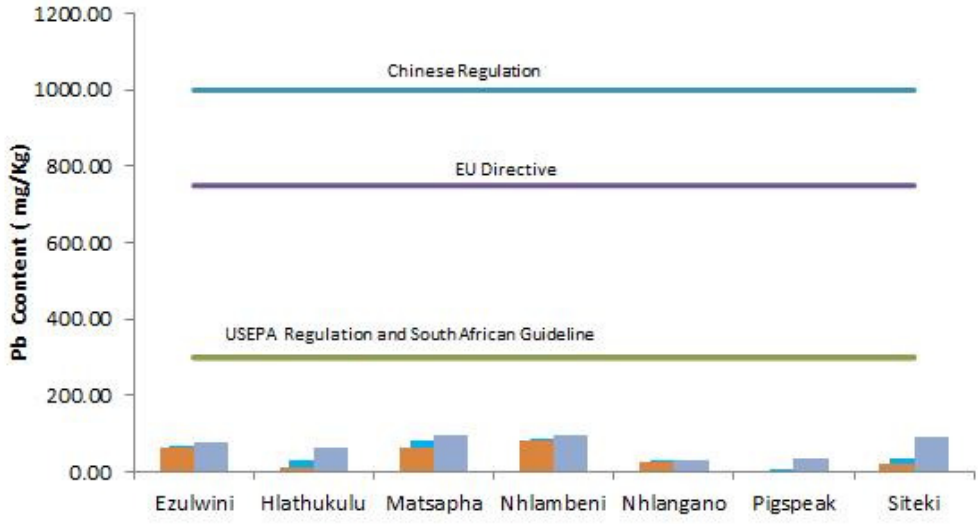

Figure 5: Lead contents of sludge from wastewater treatment plants in Swaziland

The zinc concentrations (average, maximum and minimum) for the seven wastewater treatment plants are provided in Figure 6. The concentrations are below the limits provided by South Africa, USEPA and EU guidelines indicating again the relatively low risk the of the sludge samples with respect to zinc toxicity based on the regulatory limits specified in terms of the total zinc metal concentrations. Zinc is an essential trace element for humans, animals and plants. However, high concentrations of zinc are potentially toxic to plants, humans and animals (Ohnessorge and Wilhelm, 1991). Though Zn has relatively low toxicity to humans and animals, studies have shown some allergies associated with zinc at high amounts and zinc poisoning could occur along the food chain, which may interfere with copper metabolism (Ohnessorge and Wilhelm, 1991).Zinc can be derived from both natural, domestic and industrial sources. Domestic sources include cosmetics and shampoos, lubricants, medicines and ointments, paints, oil and lubricants, polish and washing powders, galvanization processes, brass and bronze alloy production, tires, batteries, plastics, rubber, fungicides, paper, textiles, taxidermy (zinc chloride), embalming fluid (zinc chloride), building materials and special cements (zinc oxide, zinc fluorosilicate), dentistry (zinc oxide), and also in cosmetics and pharmaceuticals. Industrial sources of zinc could be wastewater streams from steel works, fiber manufacture, wood-pulp production, etc. Zinc is also present in wastewaters from the plating and metal processing industries. Cities with metal industries and high traffic can contribute to high levels of zinc in sewage sludge (Morrison, et al., 2004).

5.1 Conclusion

The total metal concentrations present in sewage sludge samples taken from the seven waste water treatment plants in Swaziland showed a range of variations in accordance with the characteristics of the wastewater generated from the respective cities and the level of industrial establishments present in the cities.

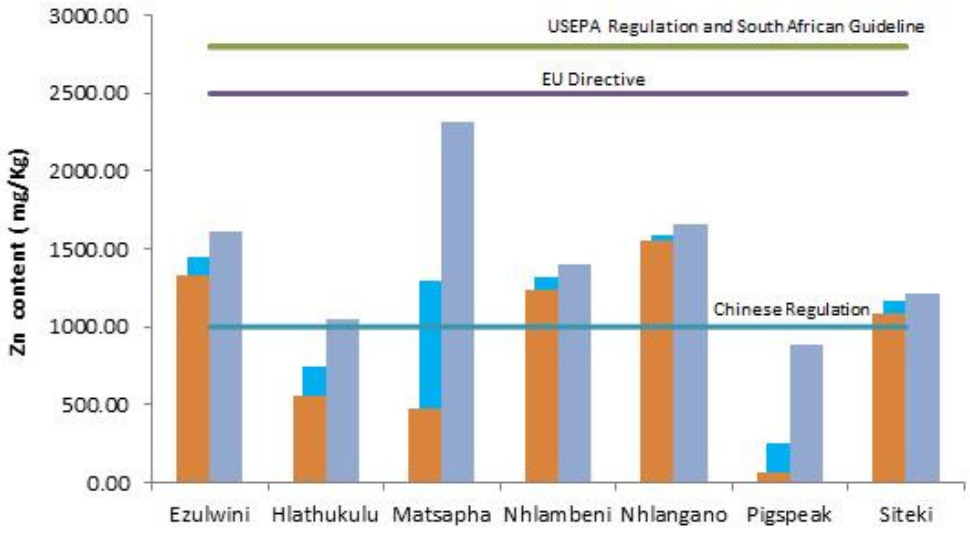

Figure 6: Zinc contents of sludge from wastewater treatment plants in Swaziland

The Matsapha wastewater treatment plant sludge samples showed generally higher heavy metal concentrations compared with the sludge samples taken from the other wastewater treatment plants. This is apparent as Matsapha is an industrial area and several of the effluents generated from the industries have minimal treatments such as equalization basins before being discharged to the municipal sewer system.

In terms of the regulatory limits of total metal concentrations mentioned in the USEPA, South Africa guidelines and EU directives, the sludge samples largely show compliance for agricultural application with respect to the majority of heavy metals. The experimental results by and large indicated that most of the heavy metals are present in moderate concentrations well below the regulatory limits specified based on total metal concentrations and the sludge generated from the wastewater treatment plants may be considered further for agricultural application.

It has been mentioned by several researchers that limits based on total metals concentrations may be too restrictive as metals have different levels of mobility in soil and some of the heavy metals are present largely in the immobile fraction. Therefore, the regulatory limits based on total metals will have to be interpreted in terms of the relative mobility of the different heavy metals.

Further research is required with plant trials of the sewage sludge applied in different soil environments and plants and with different degree of treatment of soils with sewage sludge in order to ascertain the actual degree of toxicity of the heavy metals and their translocation within the plant structures. However, as it appeared from the result of the experiment in this research, there is a good potential for the sludge from the wastewater treatment plants to be used for agricultural application. This positive information can be good news to the treatment plants which currently store large piles of sludge in their wastewater treatment plants premises in Swaziland with the possible future option of using the sludge for agricultural applications. Considering the nutrient and soil conditioning values of the sludge and reusing them for agriculture is an economical and environmentally sound option and deserves given greater attention.

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