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FEATURE

Recycling of Water Treatment Plant Sludge via Land Application: Assessment of Risk

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ABSTRACT: Water treatment sludges (WTS) offer potential benefits when applied to soil and recycling of the waste stream via land application has been proposed as a management option. Recycling of WTS to the land helps conserve landfill disposal capacity and natural resources, but potential environmental and human health risks must be properly evaluated. In this study, alum, ferric and lime WTS samples were collected from 34 water treatment facilities in Florida, US. The concentrations of several inorganic and organic pollutants were analyzed. The results were compared to risk-based soil contaminant thresholds to assess possible human health risk. Leached concentrations were compared to water quality thresholds to examine the potential for groundwater contamination. Although As concentrations did exceed contaminant thresholds in some lime WTS samples, as a whole the land application of lime WTS was found to pose minimal risk. Several elements in the ferric and alum WTS samples exceeded the soil and groundwater thresholds. These include the Fe and Al from the chemical coagulants themselves, as well as trace elements such as As and V. Coagulant analysis suggested that a major source of the As and V in the alum and ferric WTS could be the treatment chemical itself. Other factors are recommended for consideration when evaluating the risk posed by ferric and alum WTS land application, including the rates of application (and thus the final concentration of the amended soil) and the elemental content of existing soil amendments that the WTS might replace or supplement.

INTRODUCTION

WATER treatment plant sludges are a byproduct of conventional drinking water treatment processes. The treatment of surface water using alum ($Al_2(SO_4)_3 \cdot 14.3H_2O$) and ferric salts ($FeCl_3$ or $FeSO_4$) provides the removal of turbidity, pathogens, natural organic matter and color which impact the aesthetics of the treated water and could potentially cause adverse health effects. Lime softening of groundwater removes hardness that would otherwise cause scaling of pipes and fixtures. Coagulation with metal salts and lime softening produce chemical precipitates which are separated from the treated water in a sedimentation tank. Sludge removed from the sedimentation tank, which in some cases is dewatered, requires management as a solid waste. Waite and Dharmappa (1993) predicted that on a global scale, water treatment facilities produce 10,000 metric tons of sludge per day. Ippolito et al. (1999) estimated that 350,000 metric tons of dry sludges is produced from municipal drinking water treatment plants in the US every year.

Management practices for water treatment sludges (WTS) generally include storage and dewatering on site followed by disposal in landfills or by recycling. Transportation and disposal costs as well as pollution concerns involving landfills have spurred interest in increasing the amount of WTS recycled. Reported recycling methods include land application as a soil amendment, road base, landfill cover, turf farming, nutrient control, coagulant recovery, land reclamation, cement and brick manufacture, and top soil production

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(Bowen at al., 1988; Che et al., 1988; SenGupta and Shi, 1992; Copeland et al., 1994; Cornwell and Lee, 1994; Lucas et al., 1994; Geertsema et al., 1994; Peters and Basta, 1996; Gallimore et al., 1999; Basta et al., 2000; Codling et al., 2000; Cornwell et al., 2000; Dayton and Basta, 2001; Huang et al., 2001; Nowak et al., 2003; Zhuang et al., 2003; Hyde and Morris, 2004; Prakash et al., 2004; Wu et al., 2004). When recycled as an amendment to soil, the benefits provided must be weighed against the possible risks posed by chemicals in the WTS. Heavy metals are removed from the raw water during chemical coagulation and lime softening (Sorg et al., 1977). Coagulation has also been shown to be effective in removing significant amounts of organic compounds (Hall and Packham, 1965; Edzwald, 1979; and Randtke, 1988). The potential, therefore, exists for elevated concentrations of pollutants in WTS to limit land application under current regulatory requirements or guidelines. In recent years, regulations and guidelines have been developed to control the land application of waste materials. In the US, regulations have been promulgated for the land application of wastewater treatment plant biosolids (US EPA, 1995). A similar regulatory program has not been developed for WTS. Many states in the US, however, do have guidelines for recycling of solid wastes to the land (Koorse, 1993; FDEP, 1998; WDNR, 1998; FDEP, 2001).

Limited data for elemental composition of WTS are available (Schmitt and Hall, 1975; Elliott et al., 1990; and Cornwell et al., 1992; Peters and Basta, 1996; Geertsema et al., 1994). Schmitt and Hall (1975) evaluated the composition of 73 elements in alum sludge from a facility in Tennessee, US. Elliott et al. (1990) reported the composition and distribution of several heavy metals (Cd, Cu, Cr, Ni, Pb, and Zn) in alum (3 samples) and ferric (5 samples) sludges from water treatment facilities in Pennsylvania, US. Cornwell et al. (1992) reported the total metal content and leachability of metals from two alum sludge samples and one ferric sludge sample when subjected to rainfall. Cornwell et al. (1992) also reported leachability of these samples using the toxicity characteristic leaching procedure (TCLP) and extraction procedure toxicity test. Geertsema et al. (1994) reported concentrations of some metals (Cd, Pb, Cr, Cu, Mn, Zn, Fe, Al) in an alum sludge sample from a facility in Virginia. Peters and Basta (1996) reported total and toxicity characteristic leaching procedure extractable content of Cd, Cu, Mo, Ni, Pb and Zn in two alum sludge samples from two water treatment facilities. Meng et al. (2001) investigated the redox transformations of As and Fe in a ferric WTS during aging and evaluated the impact of those transformations on the leachability of As using the TCLP.

The objective of research presented here was to characterize the chemical content of WTS generated by water treatment facilities in Florida, US, and to use the results to assess limitations to recycling WTS via land application. The risk assessment was performed following current guidelines for Florida, which are similar to protocols in place for other US states and other countries. Ferric, alum and lime sludges were all tested. Both total (mg/kg) and leachable (mg/L) analyses for inorganic elements and organic compounds were performed. While the results represent WTS collected from one geographic region, the data and the examination of possible risk should prove valuable for assessing WTS in other regions. Methodologies for assessing risk from the recycling of waste materials via land application continue to evolve, and several limitations with existing approaches, especially as related to WTS, are identified and discussed in the paper.

MATERIALS AND METHODS

Sample collection and analysis was conducted in two phases. In phase I, 58 WTS samples were collected from 8 water treatment facilities (24 ferric sludge samples from 2 water treatment facilities, 11 alum sludge samples from one facility, and 23 lime sludge samples from 5 facilities). Each sample was analyzed for the total concentration (mg/kg) of As, Cd, Cr, Cu, Pb, and Zn. In phase II, composite WTS samples were collected from 28 water treatment trains (20 lime, 5 alum and 3 ferric) at 26 facilities. The smaller number of alum and ferric sludge samples were collected (relative to the lime softening samples) because of the prevalence of lime softening water treatment facilities in Florida. The phase II samples were collected over five sampling trips in four months. Additional chemicals were analyzed for the samples collected during phase II, including a larger suite of metals and metalloids (Al, As, Ba, Be, Cd, Cr, Cu, Fe, Pb, Hg, Mn, Mo, Ni, Se, V and Zn) and a number of organic chemical groups (volatile organics, semi-volatile organics, and pesticides). The synthetic precipitation leaching procedure (SPLP) test was performed on the phase II samples. The SPLP simulates the leaching of pollutants from contaminated soils or land-disposed wastes when subjected to slightly acidic rainfall (US EPA, 1996a). The SPLP

SW-846 Method 1312 EPA, 1994d
TCLP (Method 1311) use HAc pH ~5

leachates from all 28 phase II samples were analyzed for metals, total dissolved solids, and several inorganic anions. SPLP leachates from nine of the phase II samples (5 lime sludges, 2 alum sludges, and 2 ferric sludges) were analyzed for organic pollutants. A description of the phase II facility locations and the detailed lists of the organic compounds analyzed can be found in Townsend et al. (2002).

Sample Collection

WTS samples were collected from a variety of locations at the treatment facilities, including drying beds, stockpiles, mechanical dewatering system discharges and sludge storage tanks. In general, the samples were collected from the source that most represented the material that would be hauled off-site for reuse or disposal. In most cases, the samples were dewatered, but several of the lime sludge samples were still very wet as this material was being recycled in an industrial process where the wet form was desired (power plant flue gas scrubbing). The wet samples were discharged from the appropriate storage tank into the sampling containers. Dewatered samples were collected using stainless steel scoops. In phase I, piles or beds of stored WTS were divided into sections and individual samples were collected from each of the different sections. In phase II, one composite sample was collected from each of the 28 sources; samples were collected from representative locations throughout the source and mixed in a stainless steel bowl. The samples used for the majority of the analytical techniques were placed in 2-liter glass jars with Teflon-lined lids. Samples for volatile organic compound (VOC) analysis (approximately 5 g) were collected directly into 40-ml VOC vials containing 10 ml of deionized water and equipped with Teflon-lined septa.

Once collected, the samples were stored in a cooler with ice and maintained at a temperature below 4°C while being transported to a cold-storage room (below 4°C). Trip blanks, field blanks, equipment blanks, and duplicate samples were carried or collected during each sampling trip. Approximately 5% of the samples were analyzed in duplicate and spiked in duplicate to assess the precision and accuracy of the analytical procedures. In addition to the chemical parameters described below, the solids content (% total weight) and pH of the WTS were measured as well. For the solid content measurement, approximately 20 g of each phase I and II sample were weighed and then dried at 105°C until a constant sample weight was achieved. The pH of the phase II samples was determined by measuring the pH of a suspension of 20 g of WTS in 20 ml of reagent water (Method 9045C, US EPA, 1996a).

Total Metal Analysis

Each WTS sample collected was thoroughly mixed in the laboratory with a stainless steel scoop. A 2-g portion of each sample (not dried) was digested following Method 3050B (US EPA, 1996a) prior to metals analysis. Arsenic, Mo, and Pb were analyzed using a graphite furnace atomic absorption spectrometer (GFAA, Perkin-Elmer 5100) equipped with Zeeman correction, following Methods 7060A, 7481 and 7421, respectively (US EPA, 1996a). All other elements, except Hg, were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, Model 36 Thermo Elemental, Inc.), following Method 6010B (US EPA, 1996a). Total Hg concentrations were measured using the cold-vapor atomic absorption technique (Method 7471, US EPA, 1996a). The concentrations of Cd, Cu, and Zn in the phase I samples were analyzed using Flame Atomic Absorption techniques following Methods 7130, 7210, 7520 and 7950, respectively (US EPA, 1996a). The concentrations of the wet samples (mg/kg) were converted to dry weight concentrations using the measured solids contents.

Organic Compound Analysis

Volatile organic compounds (VOCs) were analyzed following Method 8260B (US EPA, 1996a) on a purge-and-trap concentrator (Tekmar 3100) attached to a gas chromatograph/mass spectrometer (GC/MS, Finnigan GCQ). A total of 74 volatile organic compounds were targeted in this study. VOC samples collected from the water treatment facilities were purged with an inert gas (helium) to transfer the volatile components from the aqueous phase to the vapor phase, where they were swept through an adsorbent trap. After purging (10 minutes), the sorbent trap was heated and back-flushed with the inert gas to desorb the trapped sample components. The desorbed analytes were separated on a DB-VRX capillary column (75 m × 0.45 mm i.d., 2.55 μm film thickness, J&W Scientific, Folsom, CA), and detected with an ion trap mass spectrometer interfaced to the gas chromatograph.

Semi-volatile organic compounds (SVOCs) and pesticides were extracted from the WTS samples using

Method 3550A (US EPA, 1996a), using ultrasonic extraction (Sonicator™ Model W-375, Heat Systems-Ultrasonics, Inc.) in 1:1 acetone/hexane (by volume) solvent. A 2-g sludge sample was weighed into a 400-ml Erlenmeyer flask and 25 ml of the extraction solvent was added. The samples were extracted for 3 minutes. The extract was filtered through sodium sulfate to remove water, fresh extraction solvent (25 ml) was added to the Erlenmeyer flask and the extraction process was repeated two more times. After filtration, a solvent evaporation apparatus (Turbovap® II, Zimark, Inc.) was used to reduce the solvent volume to 1.0 ml using a gentle stream of dry nitrogen gas. The extracted samples were analyzed for semi-volatile organic compounds using Method 8270C (US EPA, 1996a) on a Finnigan Trace 2000 gas chromatograph/mass spectrometer (GC/MS). Separation was performed by a DB-5MS capillary column (30 m 0.25 mm i.d., 0.5 m film thickness, J&W Scientific, Folsom, CA). The analysis for pesticides was performed using Methods 8081A and 8141A (US EPA, 1996a). A total of 116 semi-VOCs and 89 pesticides compounds were analyzed. A list of all the organic compounds can be found in Townsend et al. (2002).

Analysis of Leachable Elements and Compounds

The SPLP (Method 1312, US EPA, 1996a) was performed on all of the phase II samples. The SPLP leaching solution (pH of 4.20 ± 0.05) was prepared by the addition of a 60:40 (% by weight) mixture of diluted sulfuric and nitric acids to reagent water to reach a solution pH of 4.2 ± 0.05. Two liters of the SPLP solution were then added to 100 g of WTS sample in a 2.2-L Teflon coated glass container. The container was placed on a rotary extractor and rotated for 18 ± 2 hours at 30 rpm. At completion, the mixture was filtered using a pressurized filtration apparatus with a 0.7-μm glass fiber filter. An aliquot of each sample was digested following Method 3010A (US EPA, 1996a) for subsequent prior to analysis of Al, Ag, Ba, Be, Cu, Fe, Mn, Ni, Na, and Zn using the ICP-AES. Arsenic (Method 7060A), Cd (Method 7131A), Pb (Method 7421), Mo (Method 7481), and Se (Method 7740) were analyzed using the graphite furnace atomic absorption spectrometer. Mercury concentrations in the SPLP extracts were measured using the cold-vapor atomic absorption technique, following Method 7471 (US EPA, 1996a).

Inorganic ions (fluoride, chloride, and sulfate) and total dissolved solids (TDS) were measured in the SPLP leachate from all of the samples. TDS was measured using Standard Method 2540C (Standard Methods, 1995), while ion chromatography (Dionex DX 500) was used to determine the concentration of the anions in the extracts (Method 9056; US EPA, 1996a).

Nine of the SPLP leachates were extracted (Method 3510B; US EPA, 1996a) with methylene chloride using a separatory funnel for measurement of leachable SVOCs and pesticides. Extracts were analyzed using the instruments described previously. For VOC leaching analysis, a separate SPLP were conducted on the samples using a zero head extraction (ZHE) vessel (Analytical Testing Corporation) Approximately 25 g of WTS were placed in the ZHE, followed by the addition of 500 ml of SPLP solution. In an effort to minimize the loss of VOCs that might be present, sample loading was performed in a refrigerated room maintained at a temperature below 4°C. The ZHE units were placed on a rotary extractor and rotated at 30 rpm for 18 ± 2 hours. The filtered leachate was then collected with a glass syringe (Hamilton Gastight™ Syringe) and analyzed for VOCs following Method 8260B (US EPA, 1996a) using the instrument described for the total VOC analysis.

Statistical Analysis

The mean and the upper confidence limit (UCL) of the mean were calculated for purposes of presenting the central tendency of the data and comparing the data to risk-based threshold concentrations, respectively. When calculating the mean and standard deviation of a data set, in cases where less than 15% of the samples were below the detection limit, a value of one-half of the detection limit was substituted for non-detected measurements. In cases where 15 to 50% of the measurements were below detection, an adjusted mean and standard deviation were calculated using Aitchison's method (US EPA, 2000). Means and standard deviations for data sets where more than 50% of the data were below detection were not calculated. The mean and standard deviations were calculated assuming a normal distribution. While environmental data sets are often log-normally distributed, Gibbons and Coleman (2001) suggest that data sets containing seven or fewer samples are insufficient to confidently determine the distribution of the data. While some of the data sets did contain eight or more samples, arithmetic means and standard deviations were reported for consistency purposes.

The 95% UCL of the mean of the alum, ferric and lime WTS data sets were calculated for comparison to the risk-based soil contaminant thresholds. For elements that were detected in 50% or more of the samples, the means and standard deviations discussed above were used in the 95% UCL calculation. If an element was detected in less than 50% of the samples, a nonparametric 95% UCL of median was calculated. For a few elements in the alum and ferric data sets, 95% percent confidence level for the calculation of nonparametric UCL of median could not be achieved (a result of the smaller number of samples). In these cases, the nonparametric UCL of the median corresponding to maximum achievable confidence level (93.8% for alum and 75% for ferric) was determined (Gibbons and Coleman, 2001).

RESULTS

Total Concentration of Metals and Metalloids

Table 1 presents the mean concentrations (mg/kg dry weight) of the elements analyzed in the phase I WTS samples. Cd was not detected in any sample, and results are thus not presented. Of the six elements analyzed, Cu concentrations were the greatest, with average values of 316 and 443 mg/kg for the two ferric sites. The Cu concentrations were also greatest for the lime WTS samples. The Cu and Cr concentrations were highest in the alum sample. In general, the metal concentrations tended to be higher in the ferric and alum samples as compared to the lime samples. The concentration of each element was below detection in at least one of the lime samples. Since wet samples were digested (the results converted to mg/kg-dry using measured moisture contents), the detection limits vary as a function of initial sample moisture content.

Table 2 summarizes the results for phase II. Several elements were consistently below instrument detection limits and are not reported in Table 2. Be, Cd, Hg, Mo, Se and Ag were not detected in any of the samples above the respective detection limits of 0.13, 0.28, 0.05, 50, 10 and 1.5 mg/kg (based on a 2 g dry sample). Not surprisingly, Al was found at high concentrations in the alum WTS (accounting for approximately 14 % of the dry weight of the samples) and Fe was present at large concentrations in the ferric WTS (contributing approximately 37% of the dry weight). In a similar fashion as the phase I samples, most elements were encountered at greater concentrations in the ferric and alum samples relative to the lime samples.

Zn, Ni, Cu, Cr, and Pb concentrations in the ferric WTS samples were much lower than those reported by Elliott et al. (1990). While Al, Ba, Hg, Mn, Ni, Pb, and Zn concentrations in the ferric WTS samples were lower than those reported by Cornwell et al. (1992), the As, Cr and Cu concentrations were encountered in the same range. Zn and Ni concentrations in the alum WTS samples were lower than those reported by others (Schmitt and Hall, 1975; Elliott et al., 1990; Cornwell et al., 1992; Geertsema et al., 1994; Peters and Basta, 1996). Differences in WTS metal content among different treatment facilities and geographic locations are likely a result of differences in raw water quality and the treatment chemicals used.

Table 2 also includes soil cleanup target levels (SCTL) for each of the elements examined. The SCTL are risk-based contaminant thresholds used by the Florida Department of Environmental Protection (FDEP) to assess the human-health risk posed by direct exposure to soils at contaminated sites (FAC, 1999), and are frequently used as part of the process for determining whether waste-derived materials can be land applied (FDEP, 1998, 2001). Other US states and many countries have developed similar thresholds for human-health risk assessments and beneficial use deter-

Table 1. Average WTS metal concentrations in phase I (mg/kg dry weight basis).

	Mean Concentration (mg/kg, dry weight basis) (AM ± SD)[1]							
Element	**Site 1 (Ferric)**	**Site 2 (Ferric)**	**Site 3 (Alum)**	**Site 4 (Lime)**	**Site 5 (Lime)**	**Site 6 (Lime)**	**Site 7 (Lime)**	**Site 8 (Lime)**
Number of sample analyzed	12	12	12	8	2	2	3	8
As	15.1 ± 1.48	11.3 ± 3.46	9.24 ± 12.1	1.98 ± 0.28	<0.84	0.81	<1.48	1.19 ± 0.02
Cr	30.7 ± 4.71	13.4 ± 1.75	58.5 ± 26.9	3.66 ± 1.18	1.52	1.17	1.90 ± 0.28	<0.5
Cu	316 ± 139	443 ± 205	61.5 ± 23.1	8.46 ± 1.04	11.2	8.95	<14.6	8.79 ± 0.53
Pb	22.4 ± 5.68	3.00 ± 0.78	2.71 ± 0.64	1.58 ± 0.90	1.91	1.03	1.52 ± 0.69	<1.0
Zn	41.2 ± 14.8	14.1 ± 1.73	19.8 ± 7.71	15.9 ± 8.1	<4.13	<4.07	<7.31	4.46 ± 2.78

[1] AM=Arithmetic mean, SD=standard deviation

Table 2. *WTS metal concentrations in phase II (mg/kg dry weight basis).*

Cleanup Target

g/kg

g/kg

Metal	Detection Limit^1 (mg/kg)	Florida SCTL (mg/kg)	Lime: Number of Samples^2	Lime: AM ± SD^3	Lime: Range	Lime: 95% UCL^4	Alum: Number of Samples^2	Alum: AM ± SD^3	Alum: Range	Alum: 95% UCL^4	Ferric: Number of Samples^2	Ferric: AM ± SD^3	Ferric: Range	Ferric: 95% UCL^4
Al^5	0.004	72	20(20)	1.8 ± 3.1	0.4–15	3.0	5(5)	140 ± 26	110–180	170(5)	3(3)	4.4 ± 1.5	2.8–5.9	7.0
As	0.25	0.8	20(19)	1.2 ± 1.3	0.18–4.9	1.6(9)	5(5)	11.3 ± 3.5	8.5–17	14.7(5)	3(3)	7.0 ± 4.4	1.9–9.7	14.5(3)
Ba	0.50	110	20(20)	59 ± 46	18–210	76(3)	5(5)	85 ± 130	16–320	210(1)	3(3)	36 ± 21	16–58	71
Cr	0.85	210	20(15)	3.2 ± 3.3^6	<0.9–13	4.5	5(5)	120 ± 45	55–180	160	3(3)	34 ± 17	17–52	64
Cu	0.70	110	20(20)	6.4 ± 8.3	1.4–39	9.6	5(5)	32 ± 21	15–64	52	3(3)	150 ± 220	24–410	530(1)
Fe^5	0.002	23	20(20)	3.0 ± 3.6	0.3–13	4.4	5(5)	11 ± 51	5.6–17	16	3(3)	370 ± 180	160–480	660(3)
Mn	0.55	1600	20(20)	47 ± 37	11–130	62	5(5)	83 ± 46	28–140	130	3(3)	230 ± 320	42–600	760
Ni	0.75	110	20(12)	1.7 ± 2.4^6	<0.82–9.5	2.6	5(5)	8.3 ± 3.5	5–13	12	3(3)	26 ± 26	7.7–56	70
Pb	0.25	400	20(7)		<0.32–1.8	0.4^7	5(5)	5.7 ± 3.9	2.7–11.7	9.4	3(3)	3.1 ± 1.7	1.4–4.8	6
V	0.50	15	20(6)		<0.3–29	0.9^7(1)	5(5)	67 ± 13	50–85	80(5)	3(3)	290 ± 140	140–400	530(3)
Zn	1.25	23000	20(20)	7.9 ± 4.8	3.9–24	9.7	5(5)	19 ± 4.9	14–27	24	3(3)	19 ± 13	8.3–34	40

[1] Detection limits provided are based on digestion of 2.0 g of dry sample. Since 2.0 g of wet samples were digested and samples had different moisture contents, actual detections limits vary among samples.

[2] Numbers in parentheses are the number of samples with a concentration above the detection limit.

[3] AM=Arithmetic Mean, SD= Standard Deviation.

[4] Numbers in parentheses are the number of samples with a concentration above the Florida soil cleanup target level.

[5] Concentrations and detection limit in g/kg.

[6] Aitchison's adjusted mean and standard deviation.

[7] Nonparametric upper confidence limit of median.

Table 3. *SPLP leaching results (mg/L) for phase II WTS samples.*

Metal	Detection Limit (mg/l)	GWCTL (mg/L)	Lime: Number of Samples^1	Lime: Range^2	Lime: Number of samples above GWCTL	Alum: Number of Samples^1	Alum: Range^2	Alum: Number of samples above GWCTL	Ferric: Number of Samples^1	Ferric: Range^2	Ferric: Number of samples above GWCTL
Al	0.07	0.2	20(3)	<0.07–0.17	–	5(3)	<0.07–4.1	3	3(3)	0.12–0.67	2
Ba	0.01	2.0	20(6)	<0.01–1.4	–	5(4)	<0.01–0.02	–	3(2)	<0.01–0.08	–
Cr	0.017	0.1	20(6)	<0.017–0.09	–	5(3)	<0.017–0.024	–	3(0)	<0.017	–
Cu	0.014	1.0	20(4)	<0.014–0.11	–	5(1)	<0.014–0.02	–	3(1)	<0.014–0.12	–
Fe	0.045	0.3	20(8)	<0.045–0.28	–	5(3)	<0.045–0.25	–	3(3)	4.4–115	3
Mn	0.011	0.05	20(0)	<0.011	–	5(3)	<0.011–0.12	1	3(3)	0.04–0.42	2
Mo	0.0025	0.035	20(2)	<0.0025–0.007	–	5(0)	<0.0025	–	3(0)	<0.0025	–
Ni	0.015	0.1	20(5)	<0.015–0.04	–	5(1)	<0.015–0.018	–	3(0)	<0.015	–
Pb	0.005	0.015	20(1)	<0.005–0.03	1	5(1)	<0.005–0.04	1	3(0)	<0.005	–
V	0.01		20(0)	<0.01	–	5(0)	<0.01	–	3(2)	<0.01–0.1	
Zn	0.025	5.0	20(11)	<0.025–0.7	–	5(2)	<0.025–0.06	–	3(3)	0.3–0.5	

[1] Numbers in parentheses are the number of samples with a concentration above the detection limit.

[2] mg/L.

minations (WDNR, 1998; DEFRA and EA, 2002; MHSPE, 2000). The EPA 503 biosolids rule also contains risk-based threshold concentrations for a variety of inorganic elements (US EPA, 1995). The numbers of samples exceeding STCL derived for residential exposure settings are described below; a comparison to other thresholds will be discussed later in the paper.

The following elements were observed to exceed a residential SCTL in at least one sample from phases I or II: As, Al, Ba, Cu, Fe and V. The mean Cu concentrations from the two ferric sites in phase I and from one of the ferric sites in phase II exceeded the SCTL (110 mg/kg). All of the phase II ferric and alum samples exceeded the SCTL for Fe (23,000 mg/kg) and for Al (72,000 mg/kg), respectively. All of the alum and ferric samples, and approximately one-half of the lime sludge samples, exceeded the residential SCTL for As (0.8 mg/kg). Three of the 20 phase II lime samples and one of the five alum samples exceeded the SCTL for Ba (110 mg/kg). The concentration of V exceeded the SCTL in one phase II lime sample and all of the phase II alum and ferric samples. When the 95% UCL for the different elements measured in the phase II lime WTS samples were compared to the residential SCTLs, only As exceeded the threshold. For the phase II alum WTS samples, the 95% UCL for Al, As, Ba and V exceeded the SCTLs, while for the phase II ferric WTS samples, the 95% UCL for As, Cu, Fe and V exceeded the SCTLs.

Total Concentration of Organic Pollutants

No SVOC (acid and base/neutral extractable), nitrogen-phosphorus pesticides or organochlorine pesticides were detected in any of the WTS samples above the detection limits of 5 mg/kg, 0.25 mg/kg and 0.025 mg/kg, respectively. No VOC (except acetone and methylene chloride) was detected (<5.0 µg/kg) in any of the WTS samples. Acetone and methylene chloride were detected on multiple occasions above the detection limit of 5.0 µg/kg, but these compounds were also detected in the laboratory and trip blanks. These compounds are routinely used as solvents for laboratory extraction and glassware cleaning.

Leachable Contaminants

Table 3 presents the SPLP leaching results for the phase II samples. As, Be, Cd, Hg, Se, and Ag were not detected in any of the samples above their respective detection limits (2.5, 2.5, 0.5, 0.25, 2.5 and 100 µg/L) and thus are not presented or discussed further. Most of the elements detected in the lime WTS SPLP leachates were detected in less than one-half of the samples. Only Zn was detected in more than 50% of the lime SPLP leachates (11 of 20 samples). Ba was detected in 4 of the 5 alum SPLP leachates, while Al, Cr, Fe and Mn were detected in 3 of the alum leachates. Al, Fe, Mn, and Zn were detected in all three of ferric WTS SPLP leachates.

The SPLP metal concentrations were compared to the Florida's risk-based groundwater cleanup target levels (GWCTLs). The FDEP uses the GWCTLs in a similar fashion as the SCTLs. When an SPLP leachate concentration exceeds a GWCTL, the tested material is viewed to pose a potential for groundwater contamination. The GWCTLs are for the most part the same as the US drinking water standards. The only element in which a GWCTL based on a primary drinking water standard was exceeded was Pb (exceeding the 0.015 mg/L) in one lime WTS sample and one alum WTS sample. Three GWCTLs based on secondary drinking water standards were exceeded. Al exceeded 0.2 mg/L in 3 of the 5 alum samples and 2 of the 3 ferric samples. Fe exceeded 0.3 mg/L in all 3 ferric samples. Mn exceeded 0.05 mg/L in 1 alum sample and 2 ferric samples.

No SVOC, nitrogen-phosphorus pesticides or organochlorine pesticides were detected in any of the SPLP leachates above the detection limits of 10, 0.5 and 0.05 µg/L, respectively. The only VOCs detected (>5 µg/L) were acetone and methylene chloride, which again were also found in the blanks were thus not attributed to the WTS samples themselves.

Table 4 presents the pH, TDS concentrations, and inorganic ion concentrations of the SPLP leachates for the phase II samples. The solids content and pH data are summarized as well. All the lime WTS SPLP extracts were elevated in pH, while the pH of the alum and ferric WTS SPLP leachates were neutral or slightly acidic. The TDS concentration ranged from below detection limit (50 mg/L) to 2,500 mg/L. Sulfate and chloride ions were consistently detected in small amounts in SPLP leachate from each WTS type. The sulfuric acid used in the preparation of the SPLP extraction fluid was one of the sources of sulfate (approximately 4 mg/L). The alkaline pH measurements of the SPLP leachates for the lime WTS samples were outside the GWCTL range (6.5 to 8.5). TDS exceeded the GWCTL of 500 mg/L in one lime WTS sample.

Table 4. Summary of solids content, pH, anion concentrations and TDS for phase II SPLP leachates.

			Lime		Alum		Ferric	
	GWCTL	Detection Limit (mg/L)	Number of Samples[1]	Range[2]	Number of Samples[1]	Range[2]	Number of Samples[1]	Range[2]
Solids Content (%)		–	20	19–87	5	9.1–74	3	30–64
Sample pH		–	20	8.6–12.3	5	5.58–7.3	3	5.4–6.4
SPLP pH	6.5–8.5	–	20	8.8–12.6(20)	5	5.5–7.3(3)	3	5.2–6.9(2)
Fluoride	2	1.0	20(2)	1.5–1.8	5(3)	1.5–1.6	3	<1.0
Chloride	250	1.0	20(20)	3.2–95	5(5)	5.1–21	3(3)	3.4–4.1
Sulfate	250	1.0	20(20)	3.8–55	5(5)	31–120	3(3)	21–125
TDS	500	50	20(12)	53–2500(1)	5(2)	110–160	3(3)	75–370

[1] Numbers in parentheses are the number of samples with a concentration above the detection limit.

[2] Units are mg/L unless otherwise specified. Number is the parenthesis is the number of samples with concentration above the GWCTL.

Analysis of Treatment Chemicals

One sample of each treatment chemical type was collected and analyzed to determine if they might represent a source of the As and V observed at relatively high concentrations in some of the WTS samples. The concentrations of As in the alum and ferric coagulants were 13.4 and 15.1 mg/kg, respectively, while the lime sample contained 1.46 mg/kg of As. The concentrations of V in the alum and ferric coagulants were 12 and 180 mg/kg, respectively, while the lime sample tested contained 7.6 mg/kg. While this exercise was conducted on only one sample of each chemical, the results suggest that one source of these elements may have been the treatment chemicals.

IMPLICATIONS FOR RECYCLING VIA LAND APPLICATION

As described earlier, risk to human health from exposure to land applied WTS was evaluated by comparing the measured concentrations to risk-based soil contaminant thresholds and As was the one element occurring in all three WTS categories that posed possible limitations. The 95% UCLs of As in the phase II lime, alum and ferric samples were 1.6, 14.7, and 14.5 mg/kg, respectively. It is common practice by regulatory agencies to utilize the 95% UCL as a conservative estimate of the mean. While the limited number of alum and ferric WTS samples results in an estimate much greater than mean, every one of the samples tested did exceed the As SCTL. Based on the data collected, existing policies would limit the land application of alum and ferric sludges because of As. The As concentrations in the lime sludges were much closer to the SCTL; many of the samples fell below 0.8 mg/kg. While Table 2 presents the 95% UCL based on the assumption of a normal distribution of the data, the larger number of lime WTS samples provided sufficient data to conclude that As was better represented by a lognormal distribution. The 95% UCL for As in the lime WTS samples assuming a lognormal distribution was 1.0 mg/kg, just above the residential SCTL.

Other than As, the lime WTS characterized in this study met the criteria for land application in a residential setting. Organic pollutants were not found to be a direct exposure risk for any of the WTS types. Several other inorganic elements were found to possibly limit land application of the alum and ferric sludges. The 95% UCL for Al and Fe in the alum and ferric sludges (respectively) exceeded the residential SCTLs. The 95% UCL for V also exceeded the residential SCTL for both the alum and ferric sludges. While the 95% UCLs for Cu and Ba suggested a possible limitation for ferric and alum WTS, respectively, only one sample in each data set exceeded for these parameters. Additional samples would need to be collected and analyzed to assess whether these elements truly pose a concern. Based on the analysis above, the land application of alum and ferric WTS might be limited under current policies in Florida, and possibly in other states with similar policies. The lime WTS appears to have much less limitations, though the concentrations of As may pose some problems based on current risk levels. A more complete and realistic risk assessment, however, requires a discussion of additional issues.

With respect to As, it is noted that Florida's residential As SCTL has been the subject of much controversy, as the concentration approaches background concentrations in the state. Baseline concentrations of As in Florida soils are reported to range from 0.02 mg/kg to 7.0 mg/kg, with a geometric mean of 0.4 mg/kg (Chen et al., 1999). The Florida SCTL for As is based on a 10^{-6} cancer risk through a direct exposure pathway including ingestion, inhalation and dermal contact. The US EPA's soil screening guidance used as part of the superfund program employs a similar risk assessment methodology and lists a soil screening level of 0.4 mg/kg (US EPA, 1996b). Risk-based soil threshold concentrations in other states range from 0.1 mg/kg to 250 mg/kg (AEHS, 1998), the wide range a result of different assumptions, algorithms, and exposure scenarios used to derive these standards. If the EPA 503 biosolids pollutant concentration for As (41 mg/kg) was applied to the WTS samples tested here, As would not be limiting for any of the three WTS types. The 503 biosolids pollutant concentration for As is higher than most state risk-based thresholds because it was calculated assuming a non-cancer risk endpoint. Recent research on the bioavailability of As (Roberts et al., 2002) will likely result in Florida's As SCTL to increase to concentrations above the 95% UCL calculated for the lime WTS, but still below the alum and ferric WTS As concentrations (MFG, 2003).

The setting in which the materials are land applied should be considered when assessing risk. In the assessment described above, measured concentrations were compared to risk-based contaminant thresholds developed for residential settings. Most of the proposed recycling options for land applied WTS would be in agricultural or similar environments. Thus, thresholds developed for other exposure scenarios might be more appropriate. However, one could argue that settings where WTS is land applied in the present may at some point in the future be developed as residential housing. The manner in which the WTS is applied should also be evaluated. When the SCTLs, which were developed for soils, are used to assess risk from a land applied waste, the waste materials are essentially assumed to be present in a manner where they replace the soil. In the case of an amendment such as WTS, the waste is mixed with soil and the concentration of chemicals that an individual is exposed to is not only a function of the WTS composition, but also of the background soil concentration and the rate of application.

The quality of the materials that the WTS replaces in a recycling operation merits evaluation. For example, when the EPA evaluated the land application of cement kiln dust (CKD) as an agricultural soil amendment, concentrations of As in the CKD were found limiting based on a risk assessment. EPA cited, however, that the concentration of As in agricultural lime ranged up to 13 mg/kg, and thus set the limit at this concentration (FR, 1999). Many iron-based fertilizers have been found to contain As in the concentration range found for the ferric WTS reported here (MDA, 2000, 2002). In all likelihood, an iron-based fertilizer product would exceed risk-based contaminant thresholds for Fe. Consideration of the material that is being replaced is certainly something that would be worth investigating as part of a risk assessment.

The primary concerns raised when risk of groundwater contamination was assessed pertained to secondary contaminants such as Fe, Al and Mn. Secondary drinking water standards address chemicals that may cause problems in odor, taste and color. These elements are often very abundant in soils and would be expected to leach from natural materials used as a soil amendment. In a similar fashion as described above, the manner is which a WTS was applied should impact leaching. WTS tilled into a soil would not be expected to pose the same leaching risk as WTS disposed in a uniform layer.

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SUMMARY AND CONCLUSIONS

Recycling of water treatment plant sludges through land application provides an opportunity to conserve natural resources and landfill disposal capacity. It may also prove more economically attractive for treatment facility operators. The benefits of recycling must be weighed against possible environmental risk posed by the chemicals contained within the waste. Unlike domestic sewage sludge, the land application of WTS is not regulated at the federal level in the US. Most US states have regulations or policies in place for recycling of waste materials to the land, as do many countries. These regulations or policies in most cases involve testing the waste materials for the presence and concentration of potentially harmful pollutants, and comparing these concentrations to risk-based contaminant thresholds.

Samples of WTS were collected from multiple facilities in Florida, US and characterized. When compared to risk-based contaminant thresholds, lime WTS was found only to be limited by As. The 95% UCL of As from 20 facilities producing lime WTS was 1.0 mg/kg, which was just above the Florida risk-based threshold for direct exposure in residential settings of 0.8 mg/kg. In consideration of the manner in which lime WTS would typically be tilled into soil as an amendment, and in light of future changes in the As risk threshold, the land application of lime WTS will in all likelihood not be limited by current policy. The ferric and alum samples do raise concerns when compared to the existing risk thresholds, most notably for Al, As, Fe and V. Al and Fe are, of course, primarily a result of the treatment chemicals themselves. In addition, coagulant analysis suggested that a major source of the As and V in the alum and ferric WTS could be the raw coagulants. Given the potential benefits resulting from the recycling of these waste materials, other factors were discussed that should be considered as part of a thorough risk analysis. These include the rates of application (and thus the final concentration of the amended soil) and the elemental content of existing soil amendments that the WTS might replace or supplement.

While the results presented in this paper reflect one geographic region of the US, they do provide insight to the types of contaminants likely to be encountered in WTS, and of the possible concerns that may arise when evaluating risk from land application. Nonetheless, WTS characteristics may differ for other water sources and treatment chemicals. For example, in many areas of the Western US, naturally-occurring As concentrations in water are greater than found in Florida, and more stringent treatment requirements will likely result in water treatment facility residuals of higher concentration than reported in this paper. The risk assessment methodology presented here is typical of that used in other locations. Site-specific risk thresholds should, however, always be consulted when available.

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