

# Drinking Water Treatment Residuals: A Review of Recent Uses

J. A. Ippolito,\* K. A. Barbarick, and H. A. Elliott

Coagulants such as alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ],  $\text{FeCl}_3$ , or  $\text{Fe}_2(\text{SO}_4)_3$  are commonly used to remove particulate and dissolved constituents from water supplies in the production of drinking water. The resulting waste product, called water-treatment residuals (WTR), contains precipitated Al and Fe oxyhydroxides, resulting in a strong affinity for anionic species. Recent research has focused on using WTR as cost-effective materials to reduce soluble phosphorus (P) in soils, runoff, and land-applied organic wastes (manures and biosolids). Studies show P adsorption by WTR to be fast and nearly irreversible, suggesting long-term stable immobilization of WTR-bound P. Because excessive WTR application can induce P deficiency in crops, effective application rates and methods remain an area of intense research. Removal of other potential environmental contaminants [ $\text{ClO}_4^-$ , Se(+IV and +VI), As(+III and +V), and Hg] by WTR has been documented, suggesting potential use of WTR in environmental remediation. Although the creation of Al plant toxicity and enhanced Al leaching are concerns expressed by researchers, these effects are minimal at circumneutral soil pH conditions. Radioactivity, trace element levels, and enhanced Mn leaching have also been cited as potential problems in WTR usage as a soil supplement. However, these issues can be managed so as not to limit the beneficial use of WTR in controlling off-site P losses to sensitive water bodies or reducing soil-extractable P concentrations.

WATER TREATMENT PROCESSES that are used to produce safe drinking water generate a wide variety of residual products depending on the untreated water source, chemicals used for purification, and types of unit operations used. In the conventional coagulation-filtration treatment process, suspended solids and natural organic matter are removed from the raw water supply by the addition of aluminum and iron salts as coagulants, resulting in the production of water treatment residuals (WTR) (National Drinking Water Clearinghouse, 1998). In addition to the chemical coagulant used, WTR also carry the mineral and elemental signature of the source water. Based on the final WTR properties, the material may be used as a soil amendment or soil substitute; however, the material typically has a strong affinity for anionic species. Thus, when used as a soil amendment, soil conditions, plant growth and nutrient uptake (with regard to at least Al or Fe), and anionic species should be closely monitored.

Since the first comprehensive study of WTR land application (Elliott et al., 1990), research has significantly advanced our understanding of the nature, environmental behavior, and potential usefulness of WTR. Therefore, the objectives of this review are to (i) present current WTR characteristics with regard to elemental concentrations and macro- and microscopic properties; (ii) describe the P sorption phenomenon at bench- to field-scale; (iii) identify the potential of WTR to remove other anionic contaminants from water sources; (iv) show how WTR affect microfauna, insects, and animals; (v) review the negative and beneficial environmental effects of WTR soil usage in terms of metals; and (vi) identify how radioactivity may accumulate in WTR.

## Water Treatment Residual Characterization

Major components of WTR are soil separates, organic materials, and Al and Fe hydrous metal (hydr)oxides, depending on the metal salt used for coagulation. Alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ] is the most commonly used coagulant in the United States and Canada (Elliott et al., 1990); the iron salts  $\text{FeCl}_3$  and  $\text{Fe}_2(\text{SO}_4)_3$  are also used. Average Al- and Fe-based WTR component concentrations, based on scientific results from 2005 through 2008, as compared with compiled American Society of Civil Engineers et al. (1996) values, are presented in Table 1. In general, WTR macro-element

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\*Corresponding author (jim.ippolito@ars.usda.gov).

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5585 Guilford Rd., Madison, WI 53711 USA

J.A. Ippolito, USDA-ARS NWISRL, Kimberly, ID, 83341; K.A. Barbarick, Dep. of Soil and Crop Sciences, Colorado State Univ., Fort Collins, CO, 80523-1170; H.A. Elliott, Agricultural and Biological Engineering Dep., Pennsylvania State Univ., University Park, PA, 16802. Assigned to Associate Editor Kenneth Sajwan.

**Abbreviations:** COD, chemical oxygen demand; DTPA, diethylene triamine pentaacetic acid; SEM, scanning electron microscopy; TENORM, Technology-Enhanced Naturally Occurring Radioactive Materials; TOC, total organic carbon; US NPDES, United States National Pollutant Discharge Elimination System program; WTR, water treatment residuals.

**Table 1. Physicochemical properties of aluminum- and iron-based water treatment residuals, 2005–2008, as compared with ASCE et al. (1996).**

Parameter	Al-WTR†	Fe-WTR‡	1996 WTRS
pH	6.5 ± 0.3¶	7.0 ± 1.3	7.0 to 8.8
EC, dS m <sup>-1</sup>	1.6 ± 0.9	0.2 ± 0.0	0.6 ± 0.5
	%		
Sand	69 ± 8	85 ± 2	nd
Silt	17 ± 5	14 ± 2	nd
Clay	14 ± 3	1.0 ± 0.3	nd
	mg kg <sup>-1</sup>		
Total N	4,065 ± 740	10,000	4950 ± 2560
NH <sub>4</sub> -N	22 ± 14	nd#	160 ± 160
NO <sub>3</sub> -N	298 ± 207	nd	3 ± 3
Soluble reactive P	23 ± 6	nd	nd
Olsen P	28 ± 4	nd	nd
Oxalate-extractable P	2,320 ± 451	610	nd
Oxalate-extractable Al	65,820 ± 9,030	927 ± 498	nd
Oxalate-extractable Fe	13,930 ± 7,695	109,300 ± 29,780	nd
Total P	2,157 ± 361	710	2,260 ± 2,480
Total Al	118,700 ± 24,260	61,390 ± 35,920	60,100 ± 52,100
Total Fe	37,000 ± 19,740	220,900 ± 32,200	52,750 ± 63,640
Total Ca	10,360 ± 4,299	nd	20,820 ± 33,110
Total Mg)	2,407 ± 572	nd	nd
Total Na	355 ± 142	nd	nd
Total K	3,547 ± 582	nd	2,250 ± 3,170
Total S	6,763 ± 2,955	nd	nd
Total Mn	2,998 ± 1,122	1,088 ± 178	385 ± 398
Total Zn	98 ± 31	36 ± 4	1,050 ± 3,040
Total Cu	624 ± 581	46 ± 12	270 ± 326
Total Ni	28 ± 10	64 ± 14	38 ± 54
Total Pb	22 ± 12	47 ± 1	80 ± 100
Total Cr	20 ± 7	38 ± 4	50 ± 56
Total Cd	0.12 ± 0.02	nd	5.15 ± 11.7
Total Hg	0.46	nd	1.5 ± 2.5
Total Mo	0.9 ± 0.5	nd	9.1 ± 12.9

† WTR, water treatment residual. Average and SEM Al-WTR values were calculated from Agyin-Birikorang et al. (2007, 2008), Babatunde et al. (2008), Bayley et al. (2008a), Codling et al. (2007), Hsieh et al. (2005), Ippolito and Barbarick (2006), Mahdy et al. (2007), Makris et al. (2006a), Mortula et al. (2007), Novak et al. (2007); Oladeji et al. (2007, 2008), Ramirez Zamora et al. (2008), Razali et al. (2007), Sarkar et al. (2007a, b), Sotero-Santos et al. (2005), Wagner et al. (2008), Yang et al. (2006), and Zhao et al. (2007).

‡ Average Fe-WTR values were calculated from Agyin-Birikorang and O'Connor (2007), Leader et al. (2008), Sarkar et al. (2007a, b), and Sotero-Santos et al. (2005).

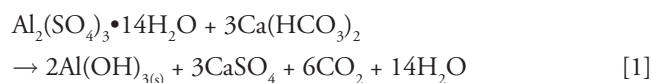
§ Values from ASCE et al. (1996) based on 12 WTR (10 Al-WTR and 2 Fe-WTR).

¶ Numbers are means ± SEM.

# Not determined.

(e.g., N, P, Al, and Fe) concentrations were comparable to those presented by ASCE et al. (1996), whereas trace metal (e.g., Zn, Pb, Cr, Cd, and Mo) concentrations appear lower in 2005–2008 WTR than in 1996. Trace metal reductions were likely a result of the United States National Pollutant Discharge Elimination System program (USNPDES).

Water treatment residuals tend to be amorphous in nature. For example, as shown in Eq. [1], when alum is added to water it reacts with bicarbonate to form amorphous Al(OH)<sub>3</sub>(s):



Similar reactions occur with Fe salts used during water treatment. Ippolito (2001) studied Al-WTR using X-ray diffraction

(XRD) analysis but did not observe the presence of crystalline Al mineral phases (Fig. 1). Ippolito et al. (2009b) also used XRD analysis, verifying quartz, feldspar, calcite, illite/smectite, and kaolinite, but no crystalline Al(OH)<sub>3</sub> phase in Al-WTR, suggesting that an amorphous Al form was present. Amorphous oxide phases are assumed to be extracted with acidified ammonium oxalate (Bertsch and Bloom, 1996). Thus, the quantity of oxalate-extractable Al and Fe concentrations in Al- and Fe-WTR, respectively (Table 1), as compared with total Al and Fe, also reflect the amorphous nature of WTR.

Water treatment residuals also have been shown, via scanning electron microscopy (SEM), to be of various shapes and sizes (Makris et al., 2004) and are highly porous (Fig. 2) (Ippolito et al., 2003; Babatunde et al., 2008). Using SEM, Yang et al. (2006) compared dewatered Al-WTR to pure

aluminum hydroxide and noted that the Al-WTR was virtually amorphous, having no distinct shape or form, in contrast to pure aluminum hydroxide, which exhibited a regular crystalline structure. Ippolito et al. (2003) and Makris et al. (2004) used SEM with energy dispersive spectroscopy to identify elements present in WTR. Ippolito et al. (2003) noted the presence of Ca and Al in Al-WTR, whereas Makris et al. (2004) verified the presence of Al, Fe, P, Si, Ca, and Na in Al- and Fe-WTR. These reports imply that WTR are composed of a heterogeneous mixture of inorganic elements.

Due to their porosity and amorphous nature and the presence of Al and Fe (hydr)oxides, WTR have the propensity to adsorb tremendous quantities of anions. Anion sorption on to WTR should be a function of the WTR particle size, charge, and surface area. Yang et al. (2006) sieved an Al-based WTR into <0.063-, 0.063- to 0.125-, 0.125- to 0.25-, 0.25- to 0.425-, 0.425- to 1.00-, and 1.00- to 2.36-mm-size fractions, noting that smaller particles (<0.25 mm) sorbed greater quantities of phosphate. The authors suggested that this was related to the amount of surface area present across the size fractions studied, with smaller size fractions containing greater surface area allowing for easier access of phosphate to micropores. Makris et al. (2004) determined Fe- and Al-WTR macro- and microporosity using mercury intrusion porosimetry. Macroporosity-specific surface area values were 2.5 and 33  $\text{m}^2 \text{g}^{-1}$ , respectively, for both WTR, whereas microporosity was an order of magnitude greater (27.5 and 104.9  $\text{m}^2 \text{g}^{-1}$ , respectively); the total micropore volumes for Fe- and Al-WTR were 0.012 and 0.042  $\text{cm}^3 \text{g}^{-1}$ , respectively. The authors noted that the WTR-specific surface area was reduced by treating WTR with P, suggesting that micropore sorption of P blocked micropore openings, leading to the decrease in specific surface area. The findings of Yang et al. (2006) and Makris et al. (2005) support the contention that WTR micropores sorb the majority of anions.

Results are in agreement that WTR are highly porous in nature, containing a greater area of microporosity per gram as compared with macroporosity. In addition, characterization findings suggest that the dominant metals found in WTR, Al and Fe, are present as amorphous phases and their concentrations are similar to reported earlier. In contrast, it appears that heavy metal concentrations have been reduced in WTR over the past 15 yr, likely due to the USNPDES.

## Phosphorus Sorption Properties of Water Treatment Residuals

In terms of WTR anion sorption, most bench-scale sorption research has focused on the ability of WTR to bind P under a variety of conditions (e.g., WTR particle size, equilibration time, solution pH, and P concentration). Ippolito et al. (2003)

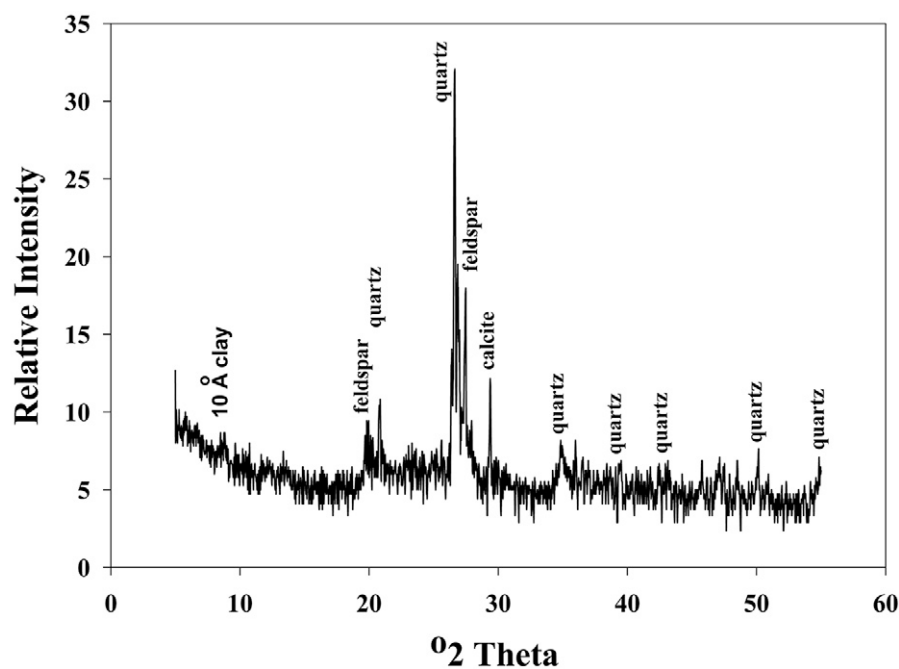


Fig. 1. X-ray diffraction analysis of an aluminum-based water treatment residual (Ippolito, 2001).

used a particle size range of 0.1 to 0.3 mm (no pH control), showing that Al-WTR retained 12,500  $\text{mg P kg}^{-1}$  after a 1-d shaking period. Makris et al. (2004) studied P sorption over time (no pH control) to an Al- or Fe-WTR (<2 mm size fraction), noting P sorption to be 7700 and 2000  $\text{mg kg}^{-1}$  over 1 d, respectively. However, the Al-WTR adsorbed ~10,000  $\text{mg kg}^{-1}$  P after 10 d, whereas the Fe-WTR adsorbed 9100  $\text{mg kg}^{-1}$  P after 80 d of shaking. Dayton and Basta (2005a) used 18 Al-WTR (<0.15 mm) and a 6-d shaking period and observed

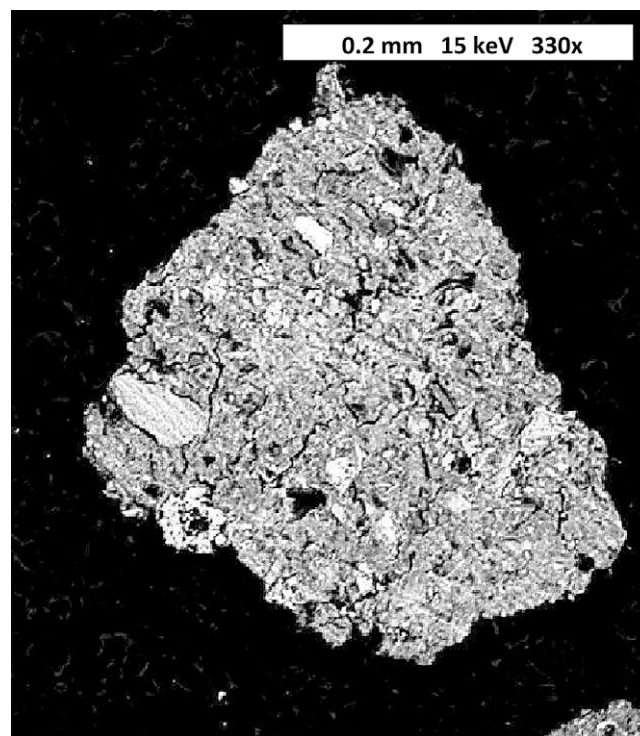


Fig. 2. Backscattered scanning electron microscope image of an aluminum-based water treatment residual (Ippolito et al., 2003).



a P sorption ranging from 10,400 to 37,000 mg kg<sup>-1</sup>. Yang et al. (2006) used an Al-WTR particle size of 0.063 mm and determined P sorption as a function of pH (4.3, 6.0, 7.0, 8.5, and 9.0). The Al-WTR P sorption capacity was maximized near 3500 mg kg<sup>-1</sup> at a pH of 4.3 and 6.0 and decreased with increasing pH (700 mg kg<sup>-1</sup> at pH 9). Babatunde et al. (2008) used a 48-h shaking period and found that Al-WTR (1.18 mm mean particle size) adsorbed 4520 mg P kg<sup>-1</sup> at a pH of 4.0, whereas P sorption decreased with increasing pH up to 9.0 (1740 mg P kg<sup>-1</sup>). Razali et al. (2007) also performed P batch adsorption research using Al-WTR of <2.36 mm in size. They observed a sorption capacity of 10,200 mg kg<sup>-1</sup> for PO<sub>4</sub> at a solution pH of 4.0. Fu et al. (2008) optimized Al-WTR P removal from solution, observing 99.6% removal efficiency for orthophosphate, or 2990 mg kg<sup>-1</sup>, by holding the pH at 4.2 and using a WTR particle size of 0.125 mm.

Initial P sorption to the external WTR surfaces has been shown to be fast. Wagner et al. (2008) shook 1.0 g Al-WTR with 25 mL of 10 mg P L<sup>-1</sup> for up to 24 h. The authors observed a 50% reduction in total dissolved P within 2 min, 90% removal in 15 min, and nearly 100% removal after 24 h. Leader et al. (2008) equilibrated 2.0 g Fe-WTR with 20 mL of 100 mg P L<sup>-1</sup> for up to 24 h. A rapid binding occurred because nearly a 100% reduction in total dissolved P was observed within 30 min. Makris et al. (2005) found similar results and suggested that the fast stage of P sorption encompassed highly accessible surfaces, such as particle exteriors and macropores. Although these findings suggest that initial P binding kinetics occur quickly, Makris et al. (2005) suggested that P sorption with time was kinetically biphasic (i.e., a quick sorption phase followed by longer-term sorption), with the slower sorption kinetic phase being associated with P diffusion into micropores.

Phosphorus diffusion into and eventual sorption onto WTR micropore surfaces leads to long-term P fixation. Leader et al. (2008) showed that an Fe-WTR loaded with 950 mg P kg<sup>-1</sup> desorbed <10 mg kg<sup>-1</sup> after shaking for 24 h in 20 mL of 0.01 mol L<sup>-1</sup> KCl, suggesting that the sorbed P is almost irreversibly fixed to WTR. In an attempt to encourage metal oxide structural changes and lower free energy of the system, Agyin-Birikorang and O'Connor (2007) artificially aged four WTR (three Al-WTR and one Fe-WTR) soil (25 g WTR kg<sup>-1</sup> soil; Alaquod) mixtures using thermal or wet and dry incubations. The authors spiked mixes with 100 mg P kg<sup>-1</sup>, held mixture pH values from 3 to 7, and incubated at 70°C for 4.5 yr. The authors measured labile P concentrations, finding that WTR-immobilized P remained fixed and was not readily released over the time period studied. Ippolito et al. (2003) used an Al-WTR loaded with 12,500 mg P kg<sup>-1</sup> and tried to desorb P over a 211-d period by shaking in a 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution. Results showed that as shaking time increased, P was further chemisorbed to Al-WTR. Using SEM–energy dispersive spectroscopy, Ippolito et al. (2003) showed that P uniformly sorbed throughout Al-WTR particles; Makris et al. (2005) showed similar results. Thus, WTR P retention may be explained by several mechanisms, including intraparticle P diffusion into micropores, becoming stable and immobilized over long periods (Makris et al., 2004). Additionally, strong P retention has been explained by reaction with hydrous oxide surfaces, which replaces singly coordinated OH<sup>-</sup> groups and

then undergoes a rearrangement into a more stable binuclear bridge-type bond between cations (Bohn et al., 1985).

Various sorption studies suggest that WTR can retain from 1740 to 37,000 mg P kg<sup>-1</sup> and that sorbed P is not readily desorbed. The literature reports that the P sorption maximum is quite variable between WTR. Discrepancies in P sorption are related to several experimental variables, such as the WTR size fraction used, shaking time, and solution pH. Suggestions for laboratory standardization follow.

## Phosphorus Sorption and Water Treatment Residual Size Fraction Used

Smaller particle sizes (e.g., <0.15 mm) contain greater surface area for reaction, and thus greater P sorption is typically observed as compared with larger particle sizes (e.g., <2.36 mm). From a land application use standpoint, WTR particles will likely not be separated based on size, indicating that P sorption on undisturbed samples would be a practical approach.

## Phosphorus Sorption and Shaking Time

Shorter shaking times (e.g., minutes to several hours) provide sufficient time for fast P sorption to occur onto the external surfaces and macropores of WTR, whereas longer shaking periods (24 h to several days) provide for WTR diffusion into micropores, increasing the WTR P sorption maximum values. For instance, Dayton and Basta (2005a) suggested a 6-d shaking period, whereas Makris et al. (2004) used a 10-d shaking period. Both shaking periods are convenient for laboratory studies; therefore, to ensure maximum P sorption, it is suggested that a 10-d shaking period be used.

## Phosphorus Sorption and Solution pH

Acidic solution conditions (e.g., pH 4) show greater P sorption onto WTR as compared with basic solution conditions (e.g., pH 9). From a practical use standpoint, solution pH should closely match that under which WTR will be used.

## Laboratory, Greenhouse, and Field-Scale Phosphorus Sorption Experiments

The single greatest disadvantage, but also a potential advantage as described later, of WTR land application is its ability to sorb plant-available P (Ippolito et al., 2003). Previous studies have associated plant P concentration decreases, P deficiency symptoms, and decreased plant yields with WTR soil application (Rengasamy et al., 1980; Bugbee and Frink, 1985; Elliott and Singer, 1988; Heil and Barbarick, 1989; Ippolito et al., 1999); recent studies have corroborated these findings. Codling et al. (2002) added an equivalent of 0, 22, 56, and 112 Mg Al-WTR ha<sup>-1</sup> to Evesboro, Matapeake, and Woodstown soil series (Quartzipsamments, Hapludults, and Hapludults, respectively). All three series contained Mehlich-3–extractable P concentrations above 800 mg kg<sup>-1</sup>. They were incubated with WTR for 7 wk, and then three consecutive cycles of wheat (*Triticum aestivum* L.) were grown. Plant and Mehlich-3 P concentrations decreased in the three soils with increasing Al-WTR rates during the three cropping cycles. After the second and third cropping cycle associated with the 56 and

112 Mg ha<sup>-1</sup> Al-WTR application rates, plant tissue P concentrations were low or deficient. Mahdy et al. (2007) added Al-WTR to calcareous (Calciorthids), sandy (Torripsammets), and clay (Torrifluents) soils at rates of up to and equivalent to 90 Mg ha<sup>-1</sup> and then grew corn (*Zea mays* L.). In all three soils, application of Al-WTR at rates up to 67 Mg ha<sup>-1</sup> increased plant P concentrations and yield. Further increases in Al-WTR application rate decreased plant P concentrations in the calcareous and clay soil. In contrast, Al-WTR application at greater rates continued to cause an increase in P concentrations in the sandy soil.

Additional studies have also shown how WTR soil application can reduce plant-available P concentrations. In a greenhouse experiment using an Immokalee fine sand (Alaquods), Oladeji et al. (2007) evaluated Al-WTR (equivalent rates of 0, 22, and 56 Mg ha<sup>-1</sup>) and four P sources (two biosolids, poultry manure, and triple superphosphate) on bahiagrass (*Paspalum notatum* Fluggae) plant yields and tissue P concentrations. Phosphorus application rates were based on P-based or N-based nutrient management guidelines. For all P-source treatments at P- or N-based rates, the Al-WTR application increased the soil P storage capacity, and plant yields and tissue P concentrations tended to be greatest in the absence of Al-WTR and least with the greatest WTR rate.

The disadvantage of reducing plant-available P is actually an advantage in situations where soil P concentrations are grossly in excess of the amount required for plant growth. Application of WTR to soil with excessive P concentrations was found to reduce extractable soil P concentrations and to decrease the amount of P available for off-site transport (Novak and Watts, 2004). The addition of WTR on manure- or biosolids-amended soils could be a solution for reducing water body P pollution by increasing the soils ability to retain P (Penn and Sims, 2002; Novak and Watts, 2004). If found to occur at the field-scale, applications of WTR with elevated P sorption maximum values could be a part of a best management practice for biosolids or manure field applications.

In a laboratory study, Ippolito and Barbarick (2006) used a Platner loam (Paleustolls) soil with a history of biosolids application (eight biosolids applications at agronomic N rates [6.7 Mg ha<sup>-1</sup> yr<sup>-1</sup>]) for dryland winter wheat [*Triticum aestivum* (L.)]. In the soil, extraction with Olsen, Bray-1, and Mehlich-3 for extractable P concentrations revealed that they contained 57, 95, and 53 mg kg<sup>-1</sup>, respectively. Increasing amounts of Al-WTR (up to an equivalent of 22.4 Mg ha<sup>-1</sup>) were added to the loam soil, and then it was shaken for 1 wk. Extractable P from all three P tests decreased with increasing WTR rate; however, Bray-1 and Mehlich-3 methods demonstrated that WTR addition could lower P concentrations initially considered high or medium to low according to the Colorado P Risk Index. In a simulated rainfall experiment on a Dickson silt loam (Fragiudults), Gallimore et al. (1999) broadcast-applied poultry litter (6.72 Mg ha<sup>-1</sup>) to a bermudagrass (*Cynodon dactylon* L. Pers.) pasture and then broadcast-applied Al-WTR at 11.2 and 44.8 Mg ha<sup>-1</sup> or buffer strip applied Al-WTR at 44 Mg ha<sup>-1</sup>. After rainfall simulation, the mean dissolved runoff P concentrations decreased from 15.0 to 8.6 (43% reduction) or to 8.12 (46% reduction) mg kg<sup>-1</sup> for the broadcast- and buffer strip-applied 44.8 Mg ha<sup>-1</sup> application rates, respectively; dis-

solved P was not significantly reduced with the lower broadcast Al-WTR application.

Bayley et al. (2008a) studied the long-term effects (12–13 yr) of biosolids (10 Mg ha<sup>-1</sup>) and Al-WTR (5, 10, 21 Mg ha<sup>-1</sup>) coapplications to semiarid soils (Altvan sandy loam, Argiustolls). After the field experiment, a conceptual model of P flow was developed to evaluate corresponding changes in inorganic and organic soil P fractions. They reported that, 13 yr after application, the Al-WTR remained as the major inorganic P sink. In a field study on Immokalee sand (Alaquods), Agyin-Birikorang et al. (2007) also evaluated the long-term P immobilization by an Al-WTR. Two sites with a history of heavy poultry manure application received 114 Mg Al-WTR ha<sup>-1</sup>. After 7.5 yr, the Al-WTR still reduced total labile P in runoff and leachate by >60% as compared with control plots. It was suggested that WTR-immobilized P was stable and will remain fixed indefinitely as long as the Al-WTR solid integrity is maintained (Agyin-Birikorang et al., 2007).

Wagner et al. (2008) investigated the use of Al-WTR on grassed buffer strips for managing biosolids runoff P. Biosolids were surface-applied to an Andover channery loam (Fragiults) based on a target P rate of 100 kg P ha<sup>-1</sup> to the upper 75% of sloped areas. Meanwhile, WTR were surface applied at 20 Mg ha<sup>-1</sup> to a grassed buffer strip encompassing the lower 25% of sloped areas (average slope, 9.5%). The authors performed rainfall simulations at a rate of 62.4 mm h<sup>-1</sup>, which exceeded the 100-yr storm event for the area. Water treatment residuals usage in grassed buffer strips did not statistically lower total or dissolved P as compared with grassed buffer strips alone. These findings were attributed to insufficient contact time between Al-WTR and runoff P due to low WTR application rates (20 Mg ha<sup>-1</sup>) and nonuniform application (Wagner et al., 2008). The authors suggested increased buffer length and slope reduction to achieve greater P runoff removal. Additionally, it was suggested that adjustments in contact time should reduce P movement into water bodies. These reports are in contrast to the findings of Dayton and Basta (2005b), who showed a 67 to 86% reduction in runoff P from a silt loam soil (Fragiudults). These reductions were due to P sorption onto the WTR amorphous Al oxide phase, with the use of 20 Mg ha<sup>-1</sup> Al-WTR in grassed buffer strips. To achieve these results, the authors used 5% slope with a 70 mm h<sup>-1</sup> rainfall intensity. Although Dayton and Basta (2005b) used a slightly greater rainfall intensity as compared with Wagner et al. (2008), the reduction in slope appeared to support Wagner's conclusion that slope reduction would increase P runoff removal.

Large-scale P removal from water bodies via WTR usage has also been researched. Mortula and Gagnon (2007) investigated the use of Al-WTR for P adsorption from secondary municipal wastewater effluent. The authors noted a 94 to 99% orthophosphate removal using 4 to 16 g Al-WTR L<sup>-1</sup> and some Al leaching (<0.5 mg L<sup>-1</sup>), but the Al leaching was not high enough to be of concern for aquatic species in receiving waters. In addition, Al-WTR were able to sorb organic matter from process waters, as shown by a decrease in biochemical oxygen demand.

Zhao et al. (2008) explored the possibility of using Al-WTR as the sole media for a reed bed farmyard wastewater treatment system. In unvegetated vertical flow systems, the authors showed a removal rate of 25, 50, and 99.5% for chemical

oxygen demand (COD), suspended solids, and P, respectively. Unvegetated horizontal flow systems also removed significant quantities of biochemical oxygen demand, COD, suspended solids, and P (78, 82, 93, and 92%, respectively). No serious operational problems, such as clogging or Al release, were observed, and the authors suggested further large-scale research be performed.

Yang et al. (2007) used Al-WTR as a potential co-conditioner and dewatering agent in anaerobically digested biosolids. A 2:1 biosolids/Al-WTR ratio was the optimal mix ratio on a volume basis, resulting in 99% P reduction in reject waste water. The authors also showed that Al-WTR enhanced the dewaterability of biosolids because the Al-WTR played a role in charge neutralization and lowered the specific resistance to filtration and capillary suction time. Polymer dosage, for biosolids dewatering purposes, could also be reduced from 120 to 15 mg L<sup>-1</sup> with Al-WTR usage and should be reflected as a substantial cost savings to municipalities.

Water treatment residuals have been used to reduce wastewater and water P concentrations, and, depending on the dosage, between 94 and 99.5% P removal efficiency has been realized. Water treatment residuals also have the proven ability to sorb plant-available soil P, which could be construed as a negative in situations where P is limiting or as a positive when P is in excess. Increasing WTR application rates generally cause decreases in plant-available soil P and plant P concentrations. Water treatment residuals can also be used in buffer strips down slope from soils containing elevated P concentrations. Based on our results, it is suggested that a 20 Mg ha<sup>-1</sup> WTR buffer strip application rate could be used to reduce runoff P by 67 to 86% on slopes no greater than 5%. More research is needed in this area to identify the soil types and initial P conditions, slopes, rainfall intensities, and WTR types and application methods that are most effective in reducing offsite P transport.

## Water Treatment Residual Usage for Removing Other Anionic Contaminants and Mercury from Water Sources

In addition to removing P from soils and waters, WTR have the proven ability to sorb and remove other anions from the environment. Thus, WTR could help improve human and environmental health conditions.

### Perchlorate Sorption by Water Treatment Residuals

In humans, perchlorate (ClO<sub>4</sub><sup>-</sup>) interacts and reduces iodine uptake into the thyroid gland, with changes in thyroid hormone secretion potentially resulting in hypothyroidism (USEPA, 2008). Changes are typically reversible in adults, but fetuses, infants, and young children require proper thyroid hormones for normal growth and development (USEPA, 2008). Irreversible changes, particularly in the brain, are associated with hormone insufficiencies during human development (Chan and Kilby, 2000; Glinoe, 2007). These issues led Makris et al. (2006a) to study of ClO<sub>4</sub><sup>-</sup> adsorption on Al-WTR via batch equilibration. The Al-WTR were reacted with inorganic ClO<sub>4</sub><sup>-</sup> at concentrations up to 200 mg L<sup>-1</sup>, and solutions were shaken for up to 96 h. The authors found that the greatest

amount of ClO<sub>4</sub><sup>-</sup> (65%) was removed with the lowest initial ClO<sub>4</sub><sup>-</sup> concentration and that removal efficiency increased to 76% after 24 h. The authors also found no significant difference in the amount of ClO<sub>4</sub><sup>-</sup> removed between 1 and 2 h, but removal significantly increased after 24 h at all ClO<sub>4</sub><sup>-</sup> concentrations. This suggested that the initial ClO<sub>4</sub><sup>-</sup> sorption occurred on surfaces and that diffusion into micropores was a rate limiting step. Makris et al. (2006a) further showed the inability of perchlorate to desorb from Al-WTR, which suggested stable immobilization and that Al-WTR may be a promising sorbent for perchlorate removal in contaminated systems.

### Selenium Sorption by Water Treatment Residuals

Aluminum-WTR also show promise at sorbing soluble selenium (Se) forms in water sources. Environmental Se risks include bioaccumulation, reproduction failure, deformities, and die-off of migratory waterfowl, fish, insects, and plants (USGS, 2005; USGS, 2008; U.S. Fish and Wildlife Service, 1999). This prompted Ippolito et al. (2009b) to study selenate [Se(VI)] and selenite [Se(IV)] adsorption by Al-WTR across a pH range typically found in waters and soils. The Al-WTR were reacted with Na<sub>2</sub>SeO<sub>4</sub> [Se(VI)] or Na<sub>2</sub>SeO<sub>3</sub> [Se(IV)], and mixtures were shaken for 24 h while exposed to laboratory atmospheric conditions or a stream of N<sub>2</sub> gas, respectively. The Se(VI) samples were allowed to dry under atmospheric conditions, whereas the Se(IV) samples were dried in an anaerobic glove bag. Aluminum-WTR adsorbed between 1400 and 2100 mg Se(VI) kg<sup>-1</sup> and between 1400 and 1950 mg Se(IV) kg<sup>-1</sup>. Using X-ray absorption spectroscopy, the authors showed that Se(VI) and Se(IV) sorption occurred as outer-sphere versus inner-sphere complexes, respectively. Peak (2006) suggested that Se(VI) adsorption onto a hydrous aluminum oxide, regardless of pH, was as an outer-sphere complex. Peak (2006) also found similar Se-O and Se-Al shell values for Se(IV) adsorbed onto hydrous aluminum oxide at pH 8 and suggested inner-sphere complexation as the adsorption mechanism at this pH. The Ippolito et al. (2009b) study found that Se(IV) sorption to Al-WTR under anoxic conditions reduced Se(IV) to Se(0) possibly due to redox interactions with organic matter, Fe(II) or Mn(II, III) bearing mineral/oxide phases, or with biofilms present in the Al-based WTR. The authors further showed that the oxidation of Se(0) or Se(IV) was irreversible once sorbed to Al-WTR, suggesting stability. Thus, Al-WTR could play a favorable role in sequestering excess Se in affected water sources.

### Arsenic Sorption by Water Treatment Residuals

Water treatment residuals have shown promise in sorbing arsenic (As). Arsenic can enter ecosystems from natural geologic deposits or from agriculture or industrial practices (USEPA, 2006). Long-term ingestion of As causes symptoms including thickening and discoloration of the skin, stomach pain, nausea, vomiting, diarrhea, partial paralysis, and blindness (USEPA, 2006). Arsenic has been linked to bladder, lung, skin, kidney, nasal passage, liver, and prostate cancer (USEPA, 2006). Thus, removing As from drinking water sources is important for protecting human health. Makris et al. (2006b) initiated research in WTR-As adsorption and removal from solution. The researchers studied As(III) and As(V) sorption on Fe- and Al-based WTR using batch equilibration. Results showed that



Al-WTR sorbed a greater quantity of As(V) than Fe-WTR (~14,000 versus 10,000 mg kg<sup>-1</sup>, respectively), whereas the opposite was true for the As(III) species (~8000 versus 15,000 mg kg<sup>-1</sup>, respectively). The greater external and internal specific surface area of the Al-WTR could explain the difference in As(V) adsorption (Makris et al., 2004). Reductive dissolution of the Fe phase in Fe-WTR increased the amount of sorption sites by creating new surfaces; thus, greater As(III) sorption occurred with the Fe-WTR (Makris et al., 2006b). Increasing solid/solution ratios also resulted in a significant increase in As(V) sorption by Fe-WTR, although Al-WTR sorbed a greater percentage of As(V) as compared with Fe-WTR across solid/solution ratios. The amount of As(III) sorbed by Al-WTR was always less than the amount sorbed by Fe-WTR at any specific solid/solution ratio. The authors further showed that As(V) or As(III) desorption from Al- or Fe-WTR was low, which suggested, as with the Makris et al. (2006a) and Ippolito et al. (2009b) studies, that sorption could essentially be considered as stable immobilization.

Sarkar et al. (2007a) studied As immobilization in two poor (i.e., sandy) As-adsorbing Florida soils (Alaquods, Paleudults) amended with Al- or Fe-WTR. The WTR were mixed with soil at a rate of up to 10% by weight and reacted for 2 d with As(V) loads up to 8000 mg kg<sup>-1</sup>. After the adsorption period, mixtures were reacted with P for 2 d to determine the potential for As desorption. The authors showed that Al-WTR-amended soils sorbed 98% of the introduced As within 0.5 h regardless of the initial As load. Arsenic sorption by Fe-WTR was linear but proceeded slower after 0.5 h; 100% of the As was sorbed by Fe-WTR after 48 h. Greater WTR application rates resulted in greater As sorption, whereas As desorption was not dependent on WTR rate. Rather, As desorption was linearly related to the amount of previously sorbed As onto WTR (Sarkar et al., 2007a).

Sarkar et al. (2007b) performed a companion study to determine the effect of Al- and Fe-WTR on As(V) bioaccessibility and phytoavailability in a low As-sorbing soil (Immokalee sand, Alaquod) contaminated with arsenical pesticides and fertilized with triple superphosphate. This is an important area of science because P fertilizer added to As-containing soils has been shown to cause competition for exchanges sites, resulting in As release into solution; this condition causes As concentrations to increase in groundwater (Codling and Dao, 2007). A poor As-sorbing soil was amended with Al- or Fe-WTR at rates between 0 and 5% by weight and then spiked with sodium arsenate and triple superphosphate at 90 and 115 mg kg<sup>-1</sup> of As or P, respectively. The authors used an *in vitro* gastrointestinal test to estimate bioaccessibility (mimicking the human stomach and intestinal phases) and found that that increasing WTR application rates decreased bioaccessibility, whereas Fe-WTR were more effective than Al-WTR in resisting As release. Arsenic phytoavailability was found to decrease in the presence of both WTR at rates >1.25% WTR. However, greater WTR rates were required to decrease soil bioaccessibility (>2.5%). It was recommended that a minimal rate of 2.5% of these studied Fe- or Al-WTR could be a viable and effective *in situ* remediation method for low As-sorbing soils even in the presence of P fertilizer (Sarkar et al., 2007b).

Similar to the results of Codling and Dao (2007), Makris et al. (2007) showed that an Fe-WTR could adsorb 13,500 mg As(III) or As(V) kg<sup>-1</sup> and did not readily release As in the presence of P due to the abundance of adsorption sites or strong As immobilization by Fe-WTR. Camacho et al. (2009) observed similar results with As(V) adsorption onto Fe-WTR treated with lime. To explain the stability findings, Makris et al. (2007) then used extended X-ray absorption fine structure to determine As(III) or As(V) stability by Fe-WTR. The extended X-ray absorption fine structure spectroscopy suggested that As(III) or As(V) formed inner sphere mononuclear, bidentate complexes. These are strong associations between Fe-WTR adsorption sites and As, supporting minimum release findings and supporting the previous findings of Makris et al. (2006a, 2006b) and Ippolito et al. (2009b) with regards to WTR sorption phenomenon.

Arsenic in an organic form has been added to livestock feed since 1907 to promote growth or suppress bacterial and parasitic diseases (Woolson, 1975). In particular, roxarsone (3-nitro-4-hydroxyphenylarsonic acid) is one of the most widely used organoarsenical feed additives to promote growth, control parasites, and improve feed efficiency in intensive animal production, such as poultry (Yao et al., 2009). Organoarsenical compounds not assimilated by chickens are excreted and are known to be converted to inorganic As (Ikehata et al., 2006). Brown et al. (2005) noted that roxarsone degradation could increase soil As mobility in poultry litter-amended soils. O'Connor et al. (2005) showed that roxarsone, and consequently As, in residential homes near poultry litter-applied fields was transported via air and represented a significant human health risk. The authors recommended that arsenical feed additives be abandoned and replaced with other sources. Thus, means of reducing As availability in roxarsone-containing poultry litter should be of paramount importance. Makris et al. (2008) examined the use of Al-WTR in reducing As availability via roxarsone degradation from poultry litter by amending it with 2.5, 5, 10, and 15% Al-WTR by weight; these percentages are typical for controlling poultry litter P availability (Moore et al., 1999). In incubation studies, the authors found that dissolved As concentrations for all Al-WTR rates, except the 2.5% rate, were significantly lower than the control (unamended poultry litter). Based on their findings, Makris et al. (2008) suggested that mixing or composting poultry litter with Al-WTR could minimize poultry litter-amended soil As mobility and movement into water bodies.

## Mercury Sorption by Water Treatment Residuals

Aluminum-WTR also have the ability to sorb Hg from solution. Mercury is a highly toxic element, with risk determined by the likelihood of exposure, the form of Hg, and geological and ecological factors that influence how Hg moves and changes form in the environment (USGS, 2000). Methylmercury (CH<sub>3</sub>Hg) is the most toxic form, affecting the immune system, altering genetic and enzymatic systems, and damaging the nervous system (USGS, 2000). Issues with Hg in aqueous solutions prompted Hovsepian and Bonzongo (2009) to research the ability of Al-WTR to sorb and immobilize Hg. In a series of batch experiments, the authors showed a maximum sorption capacity of 79 mg Hg g<sup>-1</sup> Al-WTR. Mercury desorption was

low at 1.5% of that previously sorbed. Sorption and desorption characteristics were similar to the perchlorate and Se findings of Makris et al. (2006a) and Ippolito et al. (2009b), respectively, suggesting that Al-WTR could also play a role in sorbing excess Hg in affected waters.

Similar to previous WTR-P research, the above findings showed that sorption of  $\text{ClO}_4^-$ , Se(0, IV, VI), As (III, V), and Hg was due to diffusion into and sorption onto micropore surfaces, rendering these contaminants essentially immobile. Micropore diffusion is likely to be the rate-limiting step, and thus WTR contact time with the contaminant is of primary concern. Although most work has used a 24- to 48-h contact time period, to be successfully used in remediation situations, the following conditions need to be considered: (i) WTR type and particle size, (ii) contaminant stream flow rates, (iii) climatic conditions (e.g., winter vs. summer), and (iv) contact time. Nonetheless, the work by Camacho et al. (2009), Hovsepyan and Bonzongo (2009), Ippolito et al. (2009b), Makris et al. (2006a, 2006b, 2007, 2008), and Sarkar et al. (2007a, 2007b) emphasize the utility of WTR to improve environmental quality.

## Water Treatment Residual Effects on Microfauna, Insects, and Animals

### Water Treatment Residual Effects on Microfauna

Land application of WTR can affect plant and soil chemistry, so it follows that WTR should also affect soil microfauna. Bayley et al. (2008b) examined the long-term effects of a single co-application and short-term effects of a repeated co-application of biosolids ( $10 \text{ Mg ha}^{-1}$ ) and Al-WTR (5, 10, and  $20 \text{ Mg ha}^{-1}$ ) on P-cleaving enzymes in semiarid rangeland soil (Altvan sandy loam, Argiustolls). After WTR application, the authors observed a decrease in soil phosphodiesterase and pyrophosphatase and an increase in acid phosphatase and phytase activity. The decrease in phosphodiesterase enzymatic activity suggested less P mineralization from biomass sources (i.e., nucleic acids and phospholipids), whereas increases in acid phosphatase and phytase activity indicated that ester-P and inositol-P may be important plant-available P sources in soils amended with Al-WTR. More importantly, Bayley et al. (2008b) suggested that Al-WTR application may have triggered a perceived P deficiency response, causing microorganisms or plants to secrete acid phosphatase and phytase. Ippolito et al. (2009a) studied plant community structure at the Bayley et al. (2008a) research site, noting that plant community composition and percent cover were unaffected by Al-WTR. However, a decrease in plant P content occurred, but no observable P deficiency symptoms were present. Ippolito et al. (2009a) also used total ester-linked fatty acid methyl ester analysis and found that biosolids and Al-WTR co-applications did not affect the soil microbial community structure.

### Water Treatment Residual Effects on Insects and Animals

Few studies have researched WTR toxicity on insects or animals. Sotero-Santos et al. (2005) studied Fe- and Al-WTR survival and reproduction toxicity effects on water flea (*Daphnia*

*similis*) performed in 25, 50, or 75% (wt/vol) WTR-diluted systems. In general, Fe- and Al-WTR did not cause acute toxicity, but long-term Fe-WTR exposure caused some mortality and decrease in reproduction potential. The Al-WTR caused reductions in reproduction. The authors could not make a direct connection between WTR parameters (e.g., turbidity, solids content, N, P, Al, Fe, and COD) and the degree of toxicity. Van Alstyne et al. (2007) researched Al-WTR ingestion in lambs (*Ovis aries*), pointing out WTR land application concern with regard to possible grazing animal intake because grazing herbivore soil ingestion can be as great as 24% of total diet (Medvitz, 1998). Water treatment residual intake was of further concern especially with regard to the antagonistic relationship of Al to P within the animal. Dietary treatments included a control of 10% sand, 9.3% sand + 0.7%  $\text{AlCl}_3$ , 2.5% Al-WTR + 7.5% sand, 5% Al-WTR + 5% sand, 10% Al-WTR + 0% sand, and 10% Al-WTR + 0% sand + double the mineral-vitamin premix quantities. Over the 14-wk study duration, body weights increased for all treatments, and average daily gains and feed intake also increased with time. Increases were attributed to heightened appetite, which occurs in growing animals (Van Alstyne et al., 2007), along with the low bioavailability of Al in WTR (O'Connor et al., 2002). Lambs receiving dietary Al-WTR were heavier than animals consuming  $\text{AlCl}_3$ , and those lambs receiving the control or any Al-WTR had a greater apparent P absorption than those receiving  $\text{AlCl}_3$ . Thus, relatively low bioavailable Al sources should not depress P absorption because the Al would not readily react with P in the gastrointestinal tract (Van Alstyne et al., 2007). These results suggest that the co-consumption of land-applied Al-WTR in a forage system does not pose a risk to grazing animals.

The limited amount of research regarding the effects of WTR on microfauna, insects, and animals are optimistic. Land application of WTR may trigger a perceived P deficiency response in microorganisms, but microbial community structure is not affected. Long-term exposure to Fe-based WTR may cause increased water flea mortality, but a correlation between mortality and WTR characteristics could not be made. It has also been shown that no risk is associated with Al-WTR consumption by grazing herbivores. Although these findings are enlightening, more research is needed to ensure that terrestrial and aquatic ecosystem health is maintained across sites receiving WTR applications.

## Water Treatment Residuals and Metals

When added during water treatment, Al or Fe salts precipitate as amorphous (hydr)oxides, and thus Al or Fe concentrations in WTR are greater than most other constituents. In terms of Al-based WTR, elevated Al concentrations have been a general land application concern due to potential plant Al toxicities and Al movement into surface waters, which may damage aquatic environments (Codling et al., 2007). However, it is at low soil pH values ( $\text{pH} < 5.2$ ) (Foy 1996, 1997) where Al becomes more soluble and can be toxic to plants (Sparks, 2003). The pH of Al-based WTR is on average 6.7 (Table 1); thus, Al toxicity from WTR should not be an issue. Regardless, Al from Al-WTR has been studied under a number of scenarios.



In a continuous flow column test, Babatunde et al. (2008) demonstrated that Al-based WTR (pH not determined) could be used to remove P from water with Al content remaining below 0.1 mg L<sup>-1</sup>. Mahdy et al. (2008) applied Al-WTR (pH 7.4) to a clay (Torrifluvent), sand (Torripsamment), and calcareous (Calciorthid) soil (pH 7.7–8.1) at rates up to 40 g kg<sup>-1</sup> and did not observe an increase in soil-extractable Al content (Al removed via 1 mol L<sup>-1</sup> KCl). Codling et al. (2007) amended a Woodstown fine sandy loam (Hapludults; pH 5.8) and an Evesboro sand (Quartzipsamments; pH 6.2) with two poultry litters (pH 8.3–8.5) and up to 11.2 Mg Al-based WTR ha<sup>-1</sup> (pH 7.2) and noted no change in extractable soil Al content (Al extracted by 0.02 mol L<sup>-1</sup> CaCl<sub>2</sub>) 1 or 2 yr after application. Codling (2008) studied an Evesboro sand (Quartzipsamments; pH 5.2) and a Matapeake silt loam (Hapludults; pH 4.4) amended at a 1:1 ratio (molar by-product of Al to molar soil P) with two different Al-based WTR (Al-WTR pH 7.7 and 7.5) and then acidified the soils to a pH of 4.0 to 5.0. After 18 wk of acidification, the author noted an increase in Mehlich-3-extractable Al concentration only with the Evesboro sand (up to 911 mg kg<sup>-1</sup>) as compared with a control (521 mg kg<sup>-1</sup>). Gallimore et al. (1999) land-applied two WTR (pH 7.0 and 7.6) up to 45 Mg ha<sup>-1</sup> to Dickson silt loam (Fragiudults) and a Pirum fine-sandy loam (Hapludults) (both strongly acid) (USDA-NRCS, 2008) and did not observe increases in dissolved or total soluble Al in runoff. In a field study, Agyin-Birikorang et al. (2009) surface-applied biosolids (pH ~8.0) or poultry litter (pH 6.8) at N-application rates required for bahiagrass (*Paspalum notatum*) and then surface-applied Al-WTR (pH 5.6) at 22.4 Mg ha<sup>-1</sup> to an Immokalee fine sand (Alaquoqs) with pH values of 5.5, 5.9, and 5.1 in the A, E, and Bh horizons, respectively. The authors showed that groundwater total dissolved Al concentrations were unaffected by Al-WTR application, suggesting that Al-WTR could be safely used in a land-application program. Oladeji et al. (2009) applied up to 25 g kg<sup>-1</sup> of Al-WTR in a greenhouse and a field experiment to Bahiagrass or ryegrass (*Lolium perenne* L.) grown in an Immokalee fine sand (Alaquoqs). No increase in plant Al content was observed in either experiment. These diverse reports corroborate that Al toxicity or leaching from the solubilization of WTR should not be an issue under most conditions. Because most WTR are typically stockpiled on site, it could be assumed that the WTR used in these studies were aged; however, changes in chemical properties due to aging of the WTR used were not considered.

Some studies have shown that age influences WTR' reaction with elements. Agyin-Birikorang and O'Connor (2009) showed that Al reactivity of freshly generated Al-WTR decreased with time and suggested that >6 mo of field drying was required to reduce and stabilize the most reactive Al form in WTR. Some regulators in Australia suggest limiting land application of Al-WTR to the "aged" materials to minimize ecological Al risk (Agyin-Birikorang and O'Connor, 2009). However, Agyin-Birikorang and O'Connor (2009) obtained supernatant liquid from freshly generated 2- and 4-wk-old Al-WTR samples. The supernatant pH was ~5.1; thus, Al speciation would likely be dominated by hydrolysis and organically complexed Al forms rather than free Al<sup>3+</sup>. The authors

concluded that supernatant liquid from freshly generated Al-WTR should not pose an ecological risk.

Land application of WTR has also been shown to affect other soil metals and constituents. Residual metals from the drinking water chemical purification process can be associated with Al-WTR and if solubilized could potentially stress plants. For instance, Novak et al. (2007) examined Mn, Na, S, and total organic carbon (TOC) in leachate from a Norfolk loamy sand (Kandiudults, pH 5.6) amended with three different Al-WTR (pH 3.8, 5.0, and 5.8), each applied at an equivalent rate of 134 Mg ha<sup>-1</sup>. The WTR were obtained from treatment facilities using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, NaOH, and KMnO<sub>4</sub> for water purification. All Al-WTR increased leachate Na, S, TOC, and Mn content. The authors contended that Na and S concentrations were sufficiently soluble that they would be reduced to background after significant rainfall. The TOC losses were due to Al-WTR containing one to two orders of magnitude greater TOC as compared with background soil. One of the Al-WTR reduced soil pH, whereas the remaining two raised soil pH. The change in pH and the oxidation-reduction potential of the soil/Al-WTR mixture favored Mn solubilization and increased Mehlich-1-extractable Mn concentrations in soils amended with Al-WTR enriched with Mn (control extractable Mn was below detection; WTR Mn+soil concentrations ranged between 21 and 239 mg kg<sup>-1</sup>). These conditions could potentially cause plant stress to Mn-sensitive crops such as soybeans (*Glycine max* L. Merr.) because, according to Mascagni and Cox (1985), between 1 and 10 mg kg<sup>-1</sup> Mehlich-1-extractable Mn is sufficient for soybean production. Thus, Novak et al. (2007) recommended a WTR prescreening procedure to determine if WTR land application would release elements that may cause plant growth problems.

Likewise, another study was concerned about environmental metal effects from Al-WTR-amended soil. Ippolito et al. (2009a) researched the long-term effects of a single co-application and short-term effects of a repeated co-application of biosolids (10 Mg ha<sup>-1</sup>) and Al-WTR (5, 10, 21 Mg ha<sup>-1</sup>) on rangeland soils (Altvan, Argiustolls) and plants. The authors noted no change in soil pH, EC<sub>e</sub>, NO<sub>3</sub>-N, NH<sub>4</sub>-N, total C, or total N by WTR application. However, ammonium-bicarbonate diethylene triamine pentaacetic acid (DTPA)-extractable soil Mo decreased with increasing Al-WTR rate, likely due to WTR adsorption. Ippolito et al. (2009a) also showed that Mo content in the two dominant on-site plant species (western wheatgrass [*Pascopyrum smithii* (Rydb.) A. Love] and squirrel-tail [*Elymus elymoides* (Raf.) Swezey]) decreased with repeated WTR application as compared with a single WTR application. Similar greenhouse research by Ippolito et al. (2002) showed a decrease in western wheatgrass Mo tissue content with increasing WTR application to an Altvan (Argiustolls) soil. In both cases, however, Mo deficiencies were not observed. Due to their amorphous nature, WTR act much like noncrystalline Fe and Al soil mineral species and have the ability to sorb anions such as Mo. Soils that contain appreciable quantities of Fe or Al, especially in noncrystalline forms, also tend to have low Mo availability due to adsorption (Tisdale et al., 1985).

Mahdy et al. (2008) studied the effects of Al-WTR application (up to an equivalent of 90 Mg ha<sup>-1</sup>) to three soils (a clay, Torrifluvents; a sand, Torripsamments; and a Calciorthid) on

corn and soil DTPA-extractable heavy metal concentrations. In general, greater Al-WTR applications tended to decrease corn shoot, root, and soil DTPA-extractable Cd, Pb, Cu, and Ni concentrations. The authors concluded that the reduction in DTPA-extractable heavy metals, and thus the reduction in plant concentrations, was due to floc-adsorption and coprecipitation processes that are typically used to remove heavy metals from waters and soil.

Water treatment residuals have also been used as a heavy metal adsorbent. Brown et al. (2007) used Al- and Fe-WTR at the Tar Creek National Priorities List Superfund Site to determine if these amendments could restore vegetative cover and reduce in situ metal availability. Water treatment residuals were applied at 50 Mg ha<sup>-1</sup> in combination with diammonium phosphate, composted biosolids, or lime-stabilized biosolids to soils (unclassified) or tailings containing between 623 and 4003 total Pb, 5308 to 6830 total Zn, and 25.5 to 28.7 total Cd. Composted biosolids + Al-WTR resulted in low bioaccessible Pb and a healthy plant cover with low Zn content.

## Water Treatment Residuals and Radioactivity

Radioactive suspended particles may occur in drinking water if source waters are in contact with radioactive-containing geologic materials. In these cases, source water radionuclides are dilute, but when flocculated during drinking water purification they can concentrate. The term “Technology-Enhanced Naturally Occurring Radioactive Materials,” or TENORM, pertains to anthropogenic materials such as WTR that accumulate radioactivity through industrial processing. The majority of radionuclides in TENORM are found in the U<sup>238</sup>, Th<sup>232</sup>, and K<sup>40</sup> decay chains (TENORM, 2007). The removal of radionuclides from drinking water via treatment technologies and applicable rules and regulations pertaining to TENORM is beyond the scope of this manuscript. However, detailed information can be found in a recent USEPA (2005) document.

O'Brien and Cooper (1998) stated that the dominant radioactivity exposure pathways in most situations are external gamma radiation, inhalation of radon gas and its decay products, inhalation of radioactive dust, and ingestion of contaminated food or water. The authors implied that WTR use as fertilizers may be a means of radioactivity exposure due to the radioactive concentrating effect during coagulation/flocculation. Jimenez and De La Montana Rufo (2002) supported O'Brien and Cooper's (1998) contention, showing that under certain water treatment purification conditions radioactivity can be decreased in the drinking water supply. The addition of salts to water during the purification process favors the elimination of <sup>226</sup>Ra because Ra is known to be eliminated from

solution via coprecipitation with sulfates or sorbed onto oxides (Jimenez and De La Montana Rufo, 2002). The authors also found that adjusting water pH to between 7.1 and 7.8, increasing the presence of salts in water, or decreasing the Fe content (by precipitation of Fe(OH)<sub>3</sub>) of water could eliminate up to 90% of dissolved uranium isotopes.

The previous findings of O'Brien and Cooper (1998) and Jimenez and De La Montana Rufo (2002) imply that radioactivity accumulated in WTR because of radioactivity in the water source. Kleinschmidt and Akber (2008), however, studied the direct accumulation of elevated radioactivity concentrations in Al-WTR generated by the city of Brisbane in Queensland, Australia. Brisbane generates over 5000 Mg Al-WTR yr<sup>-1</sup> from raw water sources and potable-treated water, which meets Australian drinking water guidelines for radionuclides. The WTR generated from surface water treatment, however, contained elevated concentrations of <sup>238</sup>U, <sup>226</sup>Ra, and <sup>210</sup>Pb as compared with reference soils. The authors concluded, via dose modeling, that the disposal or use of this particular Al-WTR could contribute to radiation dose via external gamma radiation exposure. Extended occupancy times and ingestion of food cultivated in TENORM-enhanced soils were considered the most significant exposure pathways. These findings suggest that one must consider the potential for WTR radionuclide accumulation before any beneficial use program because this will limit or eliminate WTR usage.

## Conclusions

The generation of WTR will likely increase with increasing population and more stringent drinking water standards; therefore, finding beneficial WTR reuse options will become paramount as environmental and economic pressures limit disposal options (i.e., landfilling, lagooning, and discharging to sewers). The studies outlined in this manuscript emphasize the utility of WTR in various environmental settings. Pros and cons of WTR usage (Table 2), based on the above findings, should be considered before starting a WTR beneficial use program.

Water treatment residual chemistries showed a reduction in heavy metal concentrations as compared with WTR from the early to mid 1990s. These changes are positive, further ensuring safe WTR use in beneficial reuse programs. One must, however, consider the generation of WTR and its implications for plant metal toxicity, especially with regard to potassium permanganate usage and the potential for Mn toxicity to sensitive crop species, such as soybean. One should also consider geologic materials in contact with source waters and the potential for accumulated radioactivity in WTR. After ensuring that WTR pose little to no metal or radioactive risk, land applica-

**Table 2. Positive and negative attributes of water treatment residuals.**

Positive WTR† attributes	Negative WTR attributes
a. Increases soil P sorption capacity in P-enriched soils.	a. Can adsorb P in P-poor soils, leading to plant P deficiencies.
b. Sorbs P in high P-containing materials such as poultry litter, other manures, biosolids, waters.	b. May contain excess Mn or Na, which may be detrimental to sensitive plant species.
c. Sorbs As(III/V) Se(IV/VI), ClO <sub>4</sub> <sup>-</sup> , Hg, heavy metals.	c. May contain radionuclides depending on geologic materials in contact with source water.
d. May be used as a best management practice in nutrient sensitive ecosystems.	d. May be expensive to landfill depending on hauling costs, tipping fees, etc.

† WTR, water treatment residual.

tors should focus concern on identifying WTR with elevated adsorptive properties for sequestering environmental contaminants (e.g., P, As, Se,  $\text{ClO}_4^-$ , and Hg) and advancing these concepts to develop field-scale methodologies for maximized contaminant removal and containment.

The utility of WTR has been proven positive in a wide variety of environmental applications, from small-scale laboratory to field-scale settings. Water treatment residuals are considered an industrial waste product in some states, and as such apprehension exists in terms of using this material for environmental enhancement. Educating water works operators, municipalities, governmental officials, and the general public as to the benefits, along with the relative lack of negative effects, will be the greatest hurdle to overcome before widespread WTR environmental usage.

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