Chapter 28

Beneficial utilization of drinking-water treatment residuals as contaminant-mitigating agents

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Abstract

Waste recycling and re-utilization are two energy-efficient processes that have gained popularity due to environment-friendly and cost-reductive advantages. This chapter deals with an example of such processes: the beneficial utilization of the waste by-product generated from the drinking-water treatment process as cost-effective sorbents for contaminants, such as arsenic (As) and phosphorus (P). Drinking-water treatment residuals (WTRs) are primarily amorphous masses of iron (Fe), aluminum (Al) hydroxides or $CaCO_3$ that also contain sediment and humic substances removed from the raw water, as well as coagulating agents added to raw water, such as activated carbon and polymers. WTRs are produced in large quantities at the drinking-water treatment plants and are typically disposed of in landfills. This chapter begins with WTR-relevant definitions and types of WTRs produced, and explains how WTRs are produced. Regulations and alternatives for WTR disposal are discussed. General physical and chemical properties of different types of WTRs are presented. Most of the WTR-pertinent literature focuses on P immobilization by WTRs in poorly P-sorbing soils, and the long-term stability of sorbed P. The data suggest that land application of WTR can be a best management practice to reduce the environmental effects of P. We also discuss the potential for using WTRs as sorbents for arsenic (As). Potential limitations associated with WTR use are discussed, and future research needs addressed.

Advances in science and technology have provided steadily increasing energy and material efficiencies in the production of goods and services (Batterham, 2003). Waste recycling and re-utilization are two energy-efficient processes that have gained popularity due to environment-friendly

and cost-reductive advantages. An example of such processes is the beneficial utilization of the waste by-product generated from the drinking-water treatment process as cost-effective sorbents for prospective contaminants. Drinking-water treatment residuals (WTRs) are primarily amorphous masses of iron (Fe), aluminum (Al) hydroxides or $CaCO_3$ that also contain sediment and humic substances removed from the raw water, as well as coagulating agents added to raw water, such as activated carbon and polymers (Elliott and Dempsey, 1991; Dayton and Basta, 2001). More than 2 million Mg of WTRs are generated from drinking-water treatment facilities in the U.S. every day (Prakash and Sengupta, 2003). Several authors (Elliott et al., 2002a, b; Dayton et al., 2003; Lind, 2003; Makris, 2004; Novak and Watts, 2004) have suggested that WTRs can serve as low-cost soil amendments to reduce environmental impacts of various oxyanions, notably phosphorus (P). Our purpose is to review the properties of WTRs and to demonstrate how WTRs can serve as contaminant-remediation agents.

28.1. What are WTRs?

New drinking-water treatment technologies (membrane separation, ion exchange, precipitative softening, granular activated carbon, and disinfection/UV) have emerged, but the majority of drinking-water treatment plants are still based upon coagulation/filtration principles. Addition of Fe, Al, or Ca salts in conjunction with polyelectrolytes, such as polymers and/or granulated activated carbon to raw water removes colloids, color, sediment and common contaminants from surface and groundwater supplies intended for potable water use. In the basic pH environment of a typical drinking-water treatment facility, Fe or Al salts added in the raw water hydrolyze to form Fe or Al hydroxides. These remove phosphorus (P), arsenic (As), and other contaminants from solution through adsorption and/or co-precipitation reactions similar to the removal reactions in soils (Livesey and Huang, 1981). Iron and/or Al salts combined with small quantities of polyelectrolytes (e.g., polymers) or activated carbon are typically used by the waste- and drinking-water treatment industry to remove different inorganic and organic contaminants (Maurer and Boller, 1999). For example, coagulation using ferric chloride can reduce As concentrations by as much as 90% with minimal cost (McNeil and Edwards, 1995; Scott et al., 1995). Elliott and Dempsey (1991) reported that 56% of 32 facilities used alum as the coagulant, 28% used ferric chloride, 9% used polyaluminum chloride, and 6% used only polymer. A more recent survey in 100 FL drinking-water treatment plants showed

that 49, 20, and 6 plants used lime, ferric chloride, and alum, respectively (Townsend et al., 2001). Depending on the metal salt used, the resulting WTRs are referred to as Al-WTRs (use of Al salt) or Fe-WTRs (Fe salt) or Ca-WTRs ($CaCO_3$).

28.1.1. Disposal of WTRs

Drinking-WTRs can be disposed: (a) directly to a receiving stream; (b) to sanitary sewers; (c) to a landfill, assuming that the residual contains no free-draining water and does not have toxic characteristics as defined by the TCLP test; and (d) by land application (Chwirka et al., 2001). A 1991 survey of 612 utilities serving populations of $>50,000$ showed that landfill disposal was the predominant disposal method followed by land application > sanitary sewer disposal > direct stream discharge > lagooning (Kawczyinski and Achtermann, 1991). In the state of Florida, the most acceptable long-term disposal method of WTRs is landfilling (Townsend et al., 2001). The disposal cost of non-hazardous WTRs is low; estimated at $<\$50\,Mg^{-1}$ (Meng et al., 2001).

Environmental concerns over the direct disposal of WTRs to streams or landfilling have shifted the attention to more environmentally benign disposal methods, such as land-application. Disposal of WTRs is currently regulated at the state and not at the federal level, thus, different regulations exist for WTR disposal at different US states. Drinking-WTRs are specifically exempt from the 40 CFR Part 503 land disposal regulations for biosolids (USEPA, 1996). Thus, WTRs can be land-applied without having to meet metal (including As) limitations of the Part 503 regulation. However, land applications of mixtures of drinking-water and waste-water residuals (biosolids) are subject to the Part 503 rule. Combining biosolids with WTRs typically increases Fe/Al concentrations in the mixed biosolids, and subsequent land-application of the mixtures can significantly increase P sorption in amended soils (Elliott et al., 2002a).

28.1.2. Contaminants in WTRs

Contaminant leachability from land-applied WTRs is of major concern for regulatory agencies. Total mean arsenic (As) concentrations for 5 Al-WTRs ($11.3\,mg\,kg^{-1}$) and 3 Fe-WTRs ($7.0\,mg\,kg^{-1}$) were above the industrial direct exposure limit for As in FL ($3.7\,mg\,kg^{-1}$), but leachable As concentrations using the SPLP test were well below FL groundwater guidance concentration (FGGC) ($0.05\,mg\,l^{-1}$), posing little threat for groundwater contamination with As (Jain et al., 2005). Total mean As

concentrations for 20 Ca-WTRs were well below the residential direct exposure limit for As in FL ($0.8\,mg\,kg^{-1}$) (Jain et al., 2005). Total volatile and semi-volatile organic compounds, as well as nitrogen-, or phosphorus-, or chlorine-based pesticide concentrations, are usually well below detection limit (Jain et al., 2005). Mean total Al concentrations in 5 Al-WTRs were above the residential soil clean-up target level (SCTL) of $72,000\,mg\,kg^{-1}$, but not for Fe- or Ca-based WTRs (Jain et al., 2005). In 3 out of 5 Al-WTRs tested, SPLP-based leachable Al concentrations were above the FGGC value of $0.2\,mg\,l^{-1}$ (Jain et al., 2005). Mean SPLP-based leachable Ba, Cd, Cr, Cu, Pb, Hg, Ni, and even Mo concentrations in Fe-, Al-, and Ca-based WTRs collected in FL were below their respective FGGC values (Jain et al., 2005). Special attention has been given to Mo because relatively small forage-Mo concentrations can induce Cu deficiency (molybdenosis) in grazing animals, if the forage Cu concentration is also low ($<10\,mg\,kg^{-1}$) (Elliott and Taylor, 2000). State regulations in Pennsylvania mandate a ceiling limit of $18\,mg\,kg^{-1}$ Mo in WTRs for land application (Elliott and Taylor, 2000). Other Fe-, and Al-WTRs tested by Elliott and Dempsey (1991) showed that mean total Cr, Ni, Pb, and Zn concentrations were within the common range for soils, implying that total metal soil concentrations will remain largely unaffected by WTR application at typical loading rates. In addition, air-dried Fe- and Al-based WTRs usually contain small numbers of coliforms (<20 coliforms g^{-1}) arising from air-drying, long-term storage, and chlorine addition during the drinking-water purification process (Elliott and Dempsey, 1991).

28.1.3. Macroscopic properties of WTRs

Drinking-water treatment plant facilities use different water sources and different chemicals. Thus, the WTRs produced can have widely different elemental compositions and sorption capacities. Drinking-WTRs are commonly characterized by broad particle size distributions. Very coarse fragments ($>2\,mm$) exist in small numbers, and the greatest number of WTR particles is usually found in the micrometer ($1–5\,\mu m$) size range. The broad size distribution is evidenced by the predominance of large amounts (% number distribution) of small particles ($0.1–10\,\mu m$) (Makris, 2004). Depending on the residuals' organic carbon (C) content, Al- or Fe-WTR particles are dark, or light in color. Calcium-WTRs are typically white, reflecting the high $CaCO_3$ content. Drinking-WTR particles normally resist dissolution in aqueous solutions, unless exposed to strongly acidic ($pH<3$) and/or chemically reducing conditions (applicable only for Fe-WTRs).

Table 28.1. Selected properties of WTRs

Properties	Al-based	Fe-based	Ca-based	Reference
pH	5.0–8.2	4–9.2	8.4–11.0	1, 2, 3
KCl-P (mg kg^{-1})	2.2–5.6	6.2–6.3	0.8	1, 4
Total C (g kg^{-1})	8.5–225	94–206	114	1, 2, 3, 4
Total N (g kg^{-1})	3.0–10.0	5.0–11.0	0.3	1, 4
Total Al (g kg^{-1})	15–300	2.2–10.0	0.5	1, 2, 3
Total Fe (g kg^{-1})	5.0–66	109–251	0.4	1, 2, 3, 4
Total Ca (g kg^{-1})	3.0–50	16.4	310–520	2, 4
Total P (g kg^{-1})	0.2–4.4	0.3–3.2	0.04–0.2	1, 2, 3, 4
Oxalate Al (g kg^{-1})	1.3–91	0.2–9.8	0.03	1, 2, 4
Oxalate Fe (g kg^{-1})	2.3–5.8	108–195	0.35	1, 2, 4
Oxalate P (g kg^{-1})	0.05–3.0	0.15–2.6	0.05	1, 2, 4

1: Makris, 2004; 2: Dayton et al., 2003; 3: Elliott and Dempsey, 1991; 4: Elliott et al., 2002a.

The pH of Al-WTRs is commonly circumneutral (5.0–7.0), although some exhibit alkaline pH values as great as 8.2 (Table 28.1). Typically, Fe-based WTRs are alkaline (pH values 7.2–9.2) although the pH values for two Fe-WTRs investigated by Makris (2004) were 4 and 5.6. Calcium-WTRs are highly alkaline with pH values in the order of 8.2 to 11 (Elliott and Dempsey, 1991).

Phosphorus solubility (KCl-extractable P) in WTRs is typically low and represents only a small fraction ($<$0.2–0.7%) of total P for all three WTR classes. The KCl-extractable P is considered the most available (labile) pool of P (Elliott et al., 2002b). The very low KCl-extractable P levels in WTRs implies that WTRs can serve as additional sinks for P immobilization in poorly P-sorbing soils.

Total C values for the Al- and Fe-WTRs vary widely depending on the raw water source (surface- or ground-water). Often, however, total C values are high, reaching levels on the order of 200 g kg^{-1} regardless of the WTR class. Total C determinations could overestimate organic C content because the combustion method normally used measures both organic and inorganic C. However, organic C determination with the Walkley–Black method gave similar results to total C analysis data for 7 WTRs, suggesting minimal inorganic C (Makris et al., 2005a). Iron- and Al-WTRs are also characterized by fair amounts (up to 10 g kg^{-1}) of total N that could serve as N sources for plants when WTRs are land applied. Calcium-WTRs typically contain negligible amounts of N, as N is volatized at high pH (Table 28.1).

Total Al concentrations range from 15 to 300 g Al kg^{-1} in Al-WTRs (Table 28.1). Small amounts of Al can also occur in Fe- and Ca-WTRs. Total Fe concentrations range from 109 to 251 g Fe kg^{-1} in Fe-WTRs;

small amounts of Fe are often found in Al-WTRs, but minimal amounts in Ca-WTRs. Total Ca concentrations are commonly high in Ca-WTRs ($310–520 \, g \, kg^{-1}$), and minimal in Fe- or Al-WTRs. The variability in total Al, Fe, and Ca concentrations in the WTRs can partially be explained by the fact that different drinking-water treatment facilities add different amounts of Al/Fe/Ca salts in the treatment of raw waters, and by differences in the chemical composition of inorganic colloids suspended in the raw water.

Total P concentrations of Fe- and Al-WTRs typically range from 0.2 to $4.4 \, g \, P \, kg^{-1}$, and about 10-fold less in Ca-WTRs. Phosphorus in WTRs originates from the raw water treated in drinking-water treatment plants, and ultimately becomes part of WTR structure. As the KCl-extractable P data show, most of the P in WTRs is insoluble in aqueous suspensions. Other data (Makris et al., 2004b) showed that the P is occluded in the WTR structure and is minimally released over time.

X-ray diffraction analysis of Fe- and Al-WTRs (data not shown) suggests that amorphous Al or Fe hydroxides dominate the Al- and the Fe-WTRs, respectively, with no apparent crystalline components (Makris, 2004). Oxalate-extractable P, Fe, and Al are usually associated with the amorphous phase of the particles. Oxalate-extractable Al values are highly variable, but typically represent 30–90% of total Al of Al-WTRs (Dayton et al., 2003; Makris, 2004; Dayton and Basta, 2005), which supports the amorphous model of Al-WTRs. Typically, Fe-WTRs have lower (45–64%) oxalate-extractable Fe values as a fraction of total Fe (Makris et al., 2005a). Phosphorus retention is strongly related to amorphous Fe and Al concentrations. Gallimore et al. (1999) and Dayton et al. (2003) concluded that the amorphous, as determined with the oxalate extraction, rather than the total Al content of WTRs determines their effectiveness in reducing runoff-P. Thus, the lower oxalate-extractable metal percentage in Fe-WTRs than Al-WTRs suggests less P sorption effectiveness.

28.1.4. Microscopic properties of WTRs

Limited information exists on microscopic properties of WTRs, such as specific surface area (SSA) and porosity (Ippolito et al., 2003; Makris et al., 2004b). Scanning-electron microscope secondary images revealed the irregular shapes and variable sizes of Fe- and Al-WTR particles (Makris et al., 2004b). Particle surfaces range from rough to fairly smooth. Elemental spectra, obtained with scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS), verified the presence of P, Al, and Fe, as well as Si, Ca, and Na. No clustering of P (zones of

obvious P precipitation) was evident, proving that P originally in the WTRs existed as an integral part of the particles (Makris et al., 2004b).

Isothermal (70°C, 10 h), thermogravimetric plots of weight losses for an Fe-WTR revealed an initially fast release of water, followed by a kinetically driven stage where hysteretic water was slowly released from the interior of the WTR particles (Makris and Harris, 2006). The data suggest that sufficient amounts of water exist in the internal surfaces of air-dried WTRs (Makris and Harris, 2006). Hyde and Morris (2000) incubated raw, dry and frozen Al- and Fe-WTR particles (up to $120 \, Mg \, ha^{-1}$) with two soils having above-optimum soil test extractable P concentrations at 25°C for 21 days. Soil test P levels were reduced by 64%, 28%, and 23%, respectively, suggesting a potential WTR drying effect on P extractability. Drinking-WTRs usually contain significant amounts of carbon ($17–149 \, g \, kg^{-1}$; Dayton and Basta, 2005). The large amount of organic C in WTRs can cause WTRs to deviate from ideal metal hydroxide physicochemical behavior. Hydrophobic and hydrogen bonding forces (rather than electrostatic) between organic molecules and mineral surfaces may influence solute retention by WTRs. Such interactions can also affect the physicochemical nature of WTRs and differentiate them from ideal metal hydroxides. For example, cationic polyelectrolytes added during the raw water treatment process accounted for a significant portion of sorbed P by Fe-WTRs (Butkus et al., 1998). Steric effects and hydrophobicities imposed by organic compounds present in WTRs may influence P (and other oxyanions) sorption kinetics and diffusivities. Clearly, WTRs are complex and simple electrostatic attraction for anions is insufficient to fully explain solute retention on WTRs.

Traditional specific surface area (SSA) measurements utilizing N_2 gas (BET-N_2) revealed large differences in SSAs among different Fe- and Al-WTRs (Fig. 28.1) (Makris et al., 2005a). Phosphorus loaded to WTRs reduced N_2-based SSAs, except for the Lowell and Holland materials. However, BET-N_2 SSAs did not correlate significantly with the P sorption capacities of the materials (maximum initial P load $10 \, g \, P \, kg^{-1}$). Makris et al. (2005a) hypothesized that N_2 molecules may not have reached all sorption sites due to diffusional restrictions. De Jonge and Mittelmeijer-Hazeleger (1996) showed that SSAs of three soil organic matter samples were underestimated by BET-N_2 measurements. The significant C contents (34 to $210 \, g \, kg^{-1}$) of WTRs studied by Makris et al. (2005a) were hypothesized to affect BET-N_2 SSA measurements.

Makris et al. (2005a) also found that micropore volume distributions determined by the Saito-Foley (SF) method (Saito and Foley, 1991) increased with increasing N_2-based SSAs for all WTRs. Micropore volumes decreased when P was added, except for the two materials (Lowell and
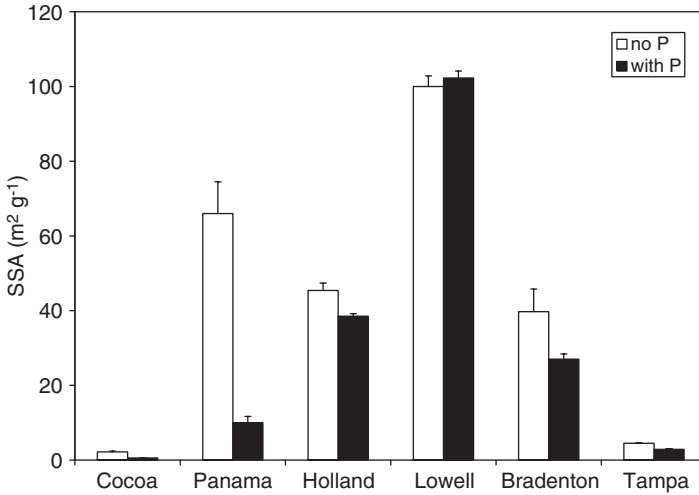
Figure 28.1. BET-N_2 SSA measurements for untreated and P treated WTRs (10 g P kg^{-1} initial load) after 40 days. Error bars denote one standard deviation of two replicated runs (Makris et al., 2005a).

Holland) with the smallest C contents. Figure 28.2 represents micropore distributions for two materials: one from the group that showed micropore volume reduction when P was added (Bradenton), and one from the group that did not (Lowell). The contrasting behaviors may be related to differences in microporosity (Table 28.2). The Lowell and Holland Al-WTRs had the smallest proportion of micropore volume (18 and 9%, respectively), whereas the Bradenton Al-WTR had the greatest (46%).

Materials with relatively large micropore volumes experienced significant pore volume reductions following P addition. Materials with relatively small meso- and micro-pore volumes were unaffected by P addition. The data were interpreted as being consistent with restricted micropore access imposed by sorbed phosphate molecules.

The CO_2- and N_2-based SSA data suggest that organic compounds trapped in WTR-micropores regulate the diffusion of gas molecules in and out of micropores. A strong linear negative correlation ($r^2 = 0.86$) was observed between total C and the N_2/CO_2 SSA ratios (Fig. 28.3). Materials with low total C contents (Holland and Lowell, WTRs) showed little difference in the amounts of N_2 and CO_2 sorbed (N_2/CO_2 SSA ratio close to 1). However, as total C content of WTRs increased, so did the difference in SSAs measured by CO_2 and N_2 (CO_2N_2). Apparently, organic C restricted diffusion and sorption of N_2 to a much greater extent than for CO_2. Similar use of the N_2/CO_2 SSA ratio normalized to the
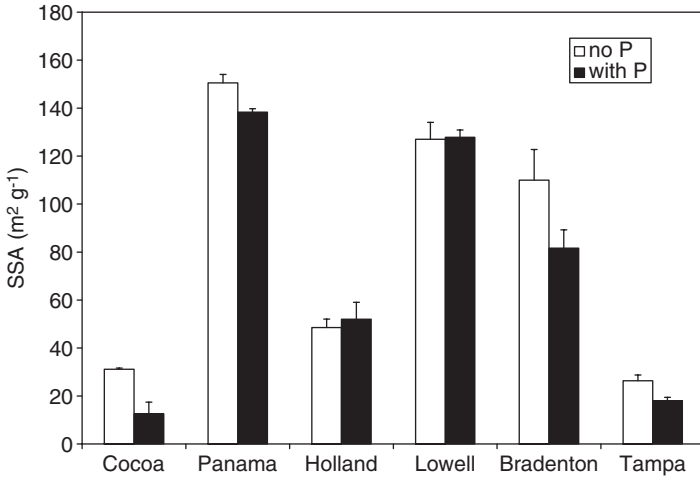
Figure 28.2. Micropore CO_2 SSA measurements for untreated and P treated WTRs (10 g P kg^{-1} initial load) after 40 days (Makris et al., 2005a). Error bars denote one standard deviation of two replicated runs.

Table 28.2. Micro-pore volumes of untreated (no P added) WTRs obtained from BET-N_2 isotherms with the Saito–Foley method and total pore volumes obtained at 0.99 P/P_0 (Makris et al., 2005a).

WTRs	Micro-pore volume ($cm^3 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)	Micro-pore volume % of total
Al-WTR, Melbourne	8×10^{-2}	2.0×10^{-1}	40
Al-WTR, Lowell	4.3×10^{-2}	2.4×10^{-1}	18
Al-WTR, Bradenton	4.2×10^{-2}	9.2×10^{-2}	46
Al-WTR, Holland	1.05×10^{-2}	1.2×10^{-1}	9
Fe-WTR, Tampa	1.45×10^{-3}	4.3×10^{-3}	34
Fe-WTR, Panama	1.4×10^{-3}	1.2×10^{-2}	12
Fe-WTR, Cocoa	1.2×10^{-3}	7.5×10^{-3}	16

C content was employed by Ravikovitch et al. (2005), studying native grassy and forest Chicago soils. The researchers proposed using N_2/CO_2 SSA ratios to characterize and predict various soils' behavior in sequestration processes involving humic substances (Ravikovitch et al., 2005).

28.2. Beneficial use of WTRs: The case of phosphorus

Intensified agricultural activities have increased P inputs and concentrations in soils. Water bodies can then be contaminated with P via surface
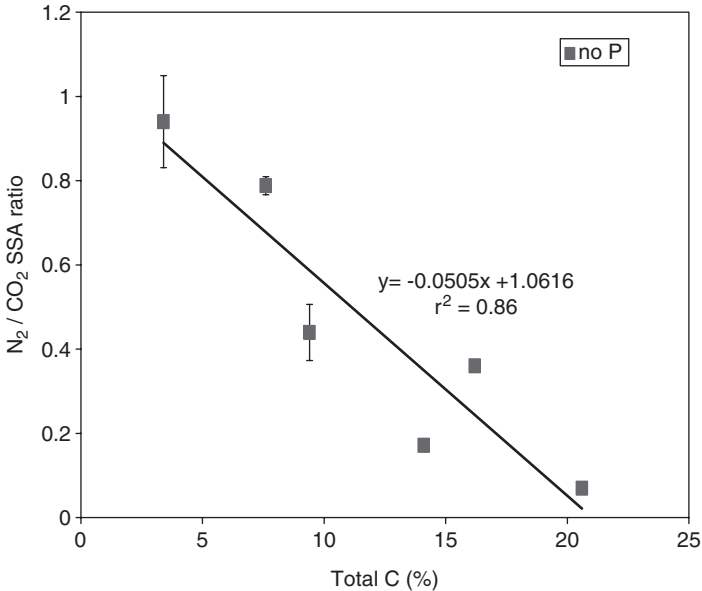
$y= -0.0505x +1.0616$
$r^2 = 0.86$

Figure 28.3.   Correlation between the ratios of SSA determined with BET-N_2 and CO_2 gas and total C of the untreated (no P added) WTRs examined by Makris et al. (2005a). Error bars denote one standard deviation of two replicates.

runoff, or leaching of soluble and particulate P. Increased P loading of streams, lakes, and rivers can encourage algal blooms and subsequent decreases in water quality. In addition to direct environmental concerns, water quality degradation can increase costs associated with drinking-water treatment.

Poor P-sorbing soils are abundant in southeastern states of U.S.A. These sandy (coarse-textured) soils are characterized by low P-sorbing capacities, and are often accompanied by high water tables. The combination of characteristics makes such soils vulnerable to P losses and negative water quality impacts (He et al., 1999; Novak et al., 2000). Land application of WTRs can be a cost-effective treatment for effectively sorbing excess levels of labile P in soils. The high amorphous Al or Fe content of the WTRs can increase a soil's P sorption capacity (Elliott et al., 1990; Novak and Watts, 2004; Dayton and Basta, 2005; Rhoton and Bigham, 2005).

Phosphorus sorption maxima differ among WTRs with contrasting physicochemical properties. Phosphorus sorption experiments (25 C) with one Al-WTR showed a maximum P sorption capacity of 12,500 mg kg^{-1} (Ippolito et al., 2003). Butkus et al. (1998) were able to load a Fe-WTR

with $\sim$20% P by wt. (200,000 mg kg^{-1}). Makris (2004) reacted Al- and Fe-WTR particles with inorganic P solutions at P loads up to 10,000 mg P kg^{-1}. Almost all of the added P was sorbed by most WTRs, although some WTRs sorbed little P. Work by O'Connor et al. (2001) showed that a Ca-WTR was much less effective in sorbing P than a Fe- and an Al-WTR.

Long-term (80 days) P sorption kinetics of WTRs are usually biphasic (Makris et al., 2005a), although Novak and Watts (2005) suggest that first-order kinetics adequately describe the reactions. Both models suggest that P sorption reactions with $<$2-mm WTR particles may not reach equilibrium in short contact times (up to 1 or 2 days). Phosphorus sorption kinetic data for Al- and Fe-based WTRs (Table 28.3) were best fit to a second-order reaction rate model (Azizian, 2004) except for the Cocoa Beach Fe-WTR, which fit neither a first- or second-order model due to limited P sorption (Makris et al., 2005a). Phosphorus sorption by the other WTRs was initially fast, and was followed by a slow P sorption stage (Makris et al., 2005a). The fast stage of P sorption presumably characterized P retention on highly accessible surfaces like particle exteriors and macropores (Van Riemsdjik and Lyklema, 1980). The slower stage has been characterized as P association, via diffusion, in micropores (Axe and Trivedi, 2002; Makris et al., 2004b).

The magnitude of the slow P sorption stage varies among different WTRs (Table 28.3) (Makris et al., 2005a). The second-order reaction rate coefficients increased with the P sorption capacities of the WTRs. The WTR samples with the greatest final P sorption generally showed significant time-dependency up to 40 or 80 days, whereas WTR samples with low P sorption did not. Apparently, WTRs with relatively low P sorption capacities had minimal rate-limited P surface access (to certain

Table 28.3. Reaction rate constants in Al- and Fe-based WTRs suspensions after a 1000 mg P l^{-1} initial pulse input (Makris et al., 2005a)

Source	Form	First-order rate fit (r^2)	Second-order rate fit (r^2)	Second-order reaction rate k $(1 s^{-1} mg^{-1})$[a]
Holland, MI	Al-based	0.87	0.98	2×10^{-7}
Lowell, AR	Al-based	0.86	0.95	3.4×10^{-5}
Bradenton, FL	Al-based	0.84	0.94	1.3×10^{-4}
Melbourne, FL	Al-based	0.89	0.96	2.4×10^{-4}
Tampa, FL	Fe-based	0.80	0.97	1.07×10^{-7}
Panama City City, FL	Fe-based	0.71	0.77	5.8×10^{-9}
Cocoa Beach City, FL	Fe-based	0.12	0.12	1.24×10^{-9}

[a]Where the slope of a linear fit to a *n*-order reaction equals $(n{-}1)k_n C_o^{n-1}$.
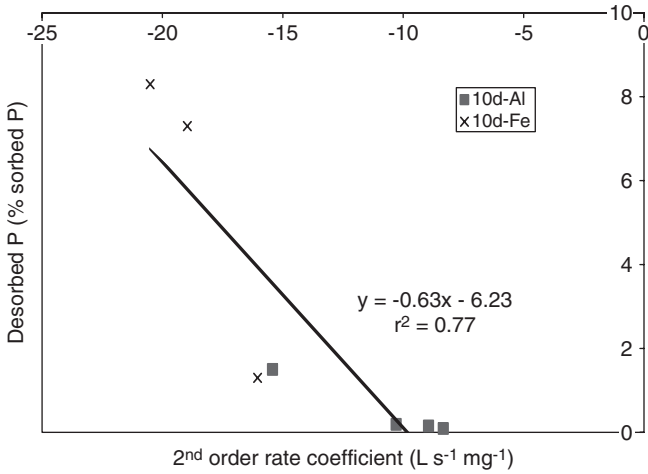
Figure 28.4. Semi (X-axis) log-transformed plot of the second-order rate coefficient changes with the amount of P desorbed after 80 days of reaction for three Fe-WTRs (10 day-Fe) and four Al-WTRs (10 day-Al) (Makris et al., 2005a). The logarithmic transformation was utilized to accommodate large differences in the reaction rate coefficients for the seven WTRs.

micropores) compared with samples with high P sorption capacity. The same trend in rate limitation applies to desorption; the greater the second-order rate coefficient, the smaller the proportion of P desorbed (Fig. 28.4). Despite the large differences (4–5 orders of magnitude) in rate coefficients of Al- and Fe-based WTRs, a log-linear model explained differences in P desorption reasonably well. Limited P desorption suggests great stability of P immobilized by highly-retentive WTRs. Second-order rate coefficients for Fe-based WTRs were generally smaller than those of Al-based WTRs, consistent with less P sorption for the second biphasic (longer-term) sorption stage of the Fe-based WTRs (Makris et al., 2005a). Phosphorus sorption kinetic rates were greater for smaller WTR aggregate sizes ($< 500 \, \mu m$), than for larger aggregate sizes (500–4000 μm) (Novak and Watts, 2005a), consistent with the effect of increased specific surface area on the smaller size aggregates' P sorption maxima.

As yet unidentified factors apparently limit the ability to adequately predict the highly-variable P sorption capacities of both Fe-, and Al-based WTRs. Traditionally, measurements of oxalate extractable P, Fe and Al in organic wastes, soils, WTRs and their mixtures have been used to explain trends in runoff-P (Gallimore et al., 1999; Dayton et al., 2003), and P leaching losses in soils amended with organic P sources and/or WTRs (Elliott et al., 2002a; Dayton and Basta, 2005). Oxalate extracts

non-crystalline forms of Fe and Al and, thus, is expected to release P bound to Fe and/or Al amorphous hydroxides.

Elliott et al. (2002b) explained differences in P-fixing capacities of an Al- and a Fe-WTR by variations in the reactive Fe- and Al-hydroxide contents, as measured by oxalate extraction. Their results indicated that an Al-WTR was more effective in sorbing P than a Fe-WTR. Dayton et al. (2003) found that variations in oxalate-extractable Al concentrations of 20 Al-WTRs explained differences in runoff-P reductions by WTRs ($r^2 = 0.69$, quadratic model). However, Dayton et al. (2003) used short (15 h) equilibration times and modest initial P loads (up to $2500\,mg\,kg^{-1}$). A recent attempt to improve P sorption maxima predictions for the same Al-WTRs utilized a different solid:solution ratio (1:100), smaller size aggregates ($<150\,\mu m$), and longer equilibration times (6 days), and resulted in a significant ($r^2 = 0.91$) linear relationship between oxalate-extractable Al and P_{max} for Al-WTRs (Dayton and Basta, 2005). Similar work was not conducted for either Fe-, or Ca-based WTRs). Surprisingly, the linear model reported by Dayton and Basta (2005) suggests significant P retention ($11.3\,g\,kg^{-1}$) at zero oxalate extractable Al. Thus, the empirical regression model predicts that a material with negligible oxalate-extractable Al concentrations would sorb more than 1% soluble P (1.1%). In a long-term (up to 80 days) P sorption study utilizing P loads of $10,000\,mg\,kg^{-1}$ and 7 Fe-, and Al-based WTRs (<2-mm), no significant correlation existed between oxalate-extractable Fe + Al concentrations with P sorption maxima for the 7 WTRs (Makris et al., 2005a). Oxalate-extractable [Fe + Al] accounted for 50–65% of total [Fe + Al] for the Fe-WTRs and 80–90% of total [Fe + Al] for Al-WTRs (Makris et al., 2005a).

A model to accurately predict P sorption capacities for both Fe- and Al-based WTRs of a relatively practical particle size ($<2\,mm$) was developed by Makris et al. (2005a). The model envisioned that organic compounds inherently present in WTRs, impose steric and diffusion restrictions to P diffusion toward the interior of WTR particles. Different CO_2 and N_2 SSA values of WTRs used suggested a significant role of organic compounds trapped in WTR-micropores in regulating the diffusion of gas molecules in and out of micropores. Prediction of the long-term P sorption capacities of WTRs is complex, and seems to require information collected from both N_2- and CO_2-based SSAs. The CO_2-based SSA values better explained P sorption than N_2-based SSA values, but predictions were not perfect. The model utilizes N_2/CO_2 SSA ratios to predict the long-term capacities of the WTRs (Makris et al., 2005a). Organics retard P diffusion toward internal sites, but apparently do not serve as sorption sites for P.

Normalizing P sorption capacities after 40 days to C content of WTRs may provide a means of predicting the long-term P sorption capacities. Makris et al. (2005a) found a significant ($p < 0.001$) positive linear relationship between the normalized amount of P sorbed after 1 or 40 days with the N_2/CO_2 SSA ratios of the WTRs (Fig. 28.5). Using measurements of three independent variables, total C, and N_2- and CO_2-based SSAs, Makris et al. (2005a) were able to explain 87% of the variability in the long-term measured P sorption capacities of the WTRs after 40 days. The number (6) of WTRs used in the model was limited, but covered a span of WTRs varying significantly in total C, Fe and Al contents. Accordingly, SSAs of the WTRs varied an order of magnitude. A potential limitation of this model would be the availability of instrumentation required to measure the specific surface areas of the materials.

The model may allow *a priori* predictions of WTR P-sorption capacities and avoidance of having to conduct tedious long-term batch equilibration studies. Model results are encouraging, but further validation using Fe- and Al-based WTRs from different facilities are needed. Clearly, not all WTRs possess the same P retention capacities, and potential users must be aware of these differences before blindly
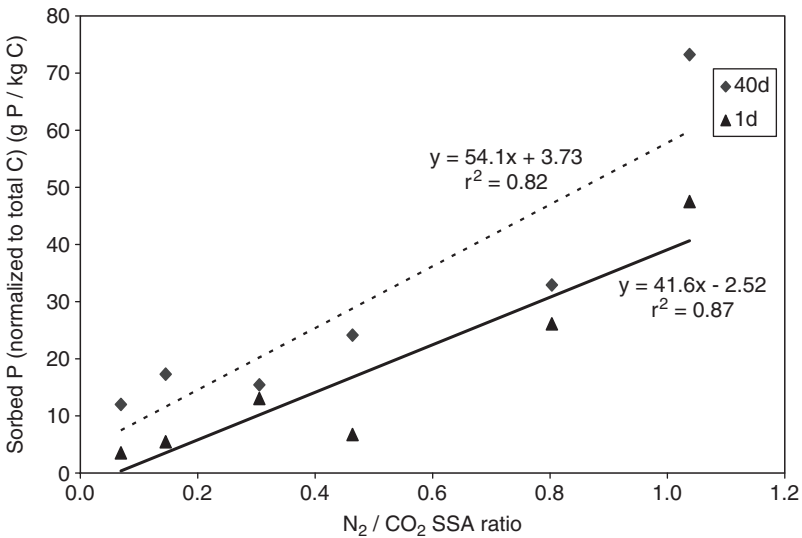

Figure 28.5. Correlation between the SSA ratio of BET-N_2 and CO_2 gas with long-term (40 days) pseudo P sorption capacities of WTRs. Initial P load (2500 mg P kg^{-1}) (Makris et al., 2005a).

depending on any WTR as a best management practice to minimize off-site P losses.

28.2.1. Reduction in runoff-P

Land-application of WTRs can significantly reduce runoff-P from agricultural fields. Haustein et al. (2000) documented decreasing soluble P concentrations in runoff from fields excessively high in soil test P following amendment with an Al-WTR (rates up to $18 \, \mathrm{Mg \, ha^{-1}}$). Gallimore et al. (1999) applied an Al-WTR to poultry litter-amended soils, and reduced soluble P in surface runoff. Peters and Basta (1996) significantly reduced ($\sim 50\%$ of the initial values) soil test-extractable P concentrations of an acidic and calcareous soil incubated with high loading rates of two Al-WTRs ($\cong 60$ and $200 \, \mathrm{Mg \, ha^{-1}}$).

Drinking-WTRs can also reduce runoff-P when used in buffer strips near water bodies (Basta et al., 2003; Dayton et al., 2003). Concentrating the WTRs in strips of land, rather than applying the residuals to an entire watershed, reduces the amount of WTR needed while protecting surface waters from P pollution. Buffer strips are a best management practice to reduce surface water pollution, and the effectiveness of the strips can be greatly improved by amendment with WTRs.

28.2.2. Reduced phosphorus leaching

Land-application of WTRs can also significantly reduce P leaching, but is most beneficial when full contact of soil soluble P with the WTR particles is ensured (Silveira et al., 2006). Surface applications of WTRs reduced runoff-P losses, but P leaching losses continued due to inadequate soil/WTR mixing. Long-term P retention by WTRs is diffusion-controlled (Makris et al., 2004b), so P must be close to WTR particles to be retained. Researchers (Codling et al., 2000) that incorporated either Fe- or Al-based WTRs into poultry litter-amended soils significantly reduced P-leaching. Similarly, surface-applied Al-WTR had little effect on P availability to wheat (*Triticum aestivum* L.) in a greenhouse study, but incorporation into the entire soil significantly decreased P availability (Cox et al., 1997). In a greenhouse column setup, Elliott et al. (2002b) showed that either Fe- or Al-WTRs were able to reduce P leaching in a low P-sorbing FL sand amended with dewatered biosolids and triple superphosphate (TSP) fertilizer. In a greenhouse setting, WTRs reduced P losses to 3.5% (Ca-WTR), 2.5% (Fe-WTR) and $<1\%$ (Al-WTR) of

applied TSP-P. For the biosolids treatments, all WTRs retarded P vertical movement such that leachate P was not statistically different from the controls.

28.2.3. Stability of sorbed P by WTRs

There is abundant evidence (e.g., Gallimore et al., 1999; Ippolito et al., 1999; Haustein et al., 2000; Dayton et al., 2003; Novak and Watts, 2004, 2005b) that WTRs are effective P sorbents that reduce the environmental lability of P. However, almost all studies have been short-term (<80 days). Insufficient data are available on the long-term stability of P retained by WTRs, or soils amended with WTRs, or metal salts, and the long-term stability of immobilized P is a major concern of state and federal regulators.

To fully understand interactions between P and soil constituents, the effects of time needs to be considered (Scheidegger and Sparks, 1996). Phosphorus sorption kinetics by metal hydroxides and soils are well characterized and generally show a fast sorption phase, followed by a slower reaction rate where sorption may never reach true equilibrium (Bolan et al., 1985). The fast reaction is ascribed to low-energy external surface sites, where ligand exchange is believed to be the main mechanism of adsorption (Bolan et al., 1985). The slow reaction between P and metals with metal hydroxides proceeds for days, months, and even years, and has been attributed to continuing surface precipitation reactions (Van Riemsdijk and Lyklema, 1980; Nooney et al., 1998) or intraparticle diffusion into micropores (Axe and Trivedi, 2002; Makris et al., 2004a). Makris et al. (2004a) identified the latter mechanism as prominent in the retention of P by WTRs, and suggested that P immobilized by WTRs should be essentially irreversibly bound. A 6.5 year field study of WTR effectiveness in reducing water extractable P in two soils with excessively high soil test P levels seems to confirm the contention (Jacobs and Teppen, 2000). Soil samples taken each year for up to 6.5 years after an initial WTR application showed sustained reduction (up to 63% initial values) of water soluble P levels in the WTR-amended plots; the standard soil test for P (Bray I) was unable to detect changes in P lability (preliminary results). Incubation experiments (84 days) conducted by mixing three soils high in Mehlich III-extractable P concentrations with an Al-WTR applied at rates of 1–6% (wt.) showed that WTR incorporation in soils high in soluble P caused larger relative reductions in water-extractable P than Mehlich III-extractable P concentrations (Novak and Watts, 2005b).

Potential WTR particle dissolution, particularly under acidic conditions, is a concern with respect to WTR field applications in humid

regions. Particle dissolution in acid soils or aqueous suspensions could release significant quantities of potentially toxic Al and previously immobilized P to the environment. Makris (2004) conducted long-term (80 days) equilibrations of Al-WTRs in unbuffered 0.01 M KCl solutions. Soluble Al concentrations of untreated (no P added) Al-WTRs were below the instrument's (ICP-AES) detection limit (0.03 mg All^{-1}). Most P-treated (10,000 mg kg^{-1} initial P load) Al-WTR suspensions released small ($<$10 mg kg^{-1}) quantities of soluble Al, but one released 46 mg Al kg^{-1}. Overall, the amount of KCl-extractable Al concentrations released from Al-WTRs within 80 days was minimal ($<$0.1% of oxalate-extractable Al) (Makris, 2004).

Metal (Fe and Al) concentrations were also measured by Makris (2004) during P desorption experiments to a 5 mM oxalate solution. Oxalate (5 mM)-extractable Fe after 160 days (80 days for P sorption and subsequent 80 days for P desorption) was minimal for a highly acidic (pH 3.9) Fe-WTR. Oxalate (200 mM) extractions are commonly performed at pH 3 (McKeague et al., 1971), which dissolves significant amounts of noncrystalline Fe and Al components in WTRs. However, such a large oxalate concentration (200 mM) is rarely encountered in natural systems, so Makris (2004) used 5 mM oxalate to more closely mimic practical conditions (Bhatti et al., 1998). One Fe-WTR released a small amount of oxalate (5 mM)-extractable Fe to solution ($\sim$1.0% of the 200 mM-oxalate extractable levels) in the absence of added P. No soluble Fe was detected in supernatants of P-treated WTRs within 1 day. Iron desorbed from WTR surfaces after 20 or 40 days (in the absence of added P) apparently reacted with the added P, resulting in minimum soluble Fe concentrations ($<$0.02 mg Fel^{-1}) even at the highest initial P load (10,000 mg kg^{-1}).

Phosphorus desorption from Al-WTRs actually decreased with increasing desorption time, suggesting continuous P sorption (Makris, 2004; Dayton and Basta, 2005). Phosphorus desorption with a 5 mM oxalate solution from different WTRs was minimal (0.2% of sorbed P) (Makris et al., 2005a). Similarly, P desorption with a 0.1 M KCl solution from 5 Al-WTRs after a 6-day equilibration was $<$10% of the final P sorption maxima (Dayton and Basta, 2005). This phenomenon was also observed in a long-term (211 days) P desorption experiment with another Al-WTR (Ippolito et al., 2003). Maximum percentages of oxalate (5 mM)-desorbable P (% of that previously sorbed) were generally $<$0.2% for all but one of seven WTRs; one WTR desorbed 1.5% (Makris, 2004). The percentages were observed for desorption experiments conducted either for 10 or 20 days. As desorption time increased to 40 or 80 days, no soluble P concentrations greater than 0.3 mg Pl^{-1} were measured for any Al-WTR, suggesting continuous P sorption. Residual
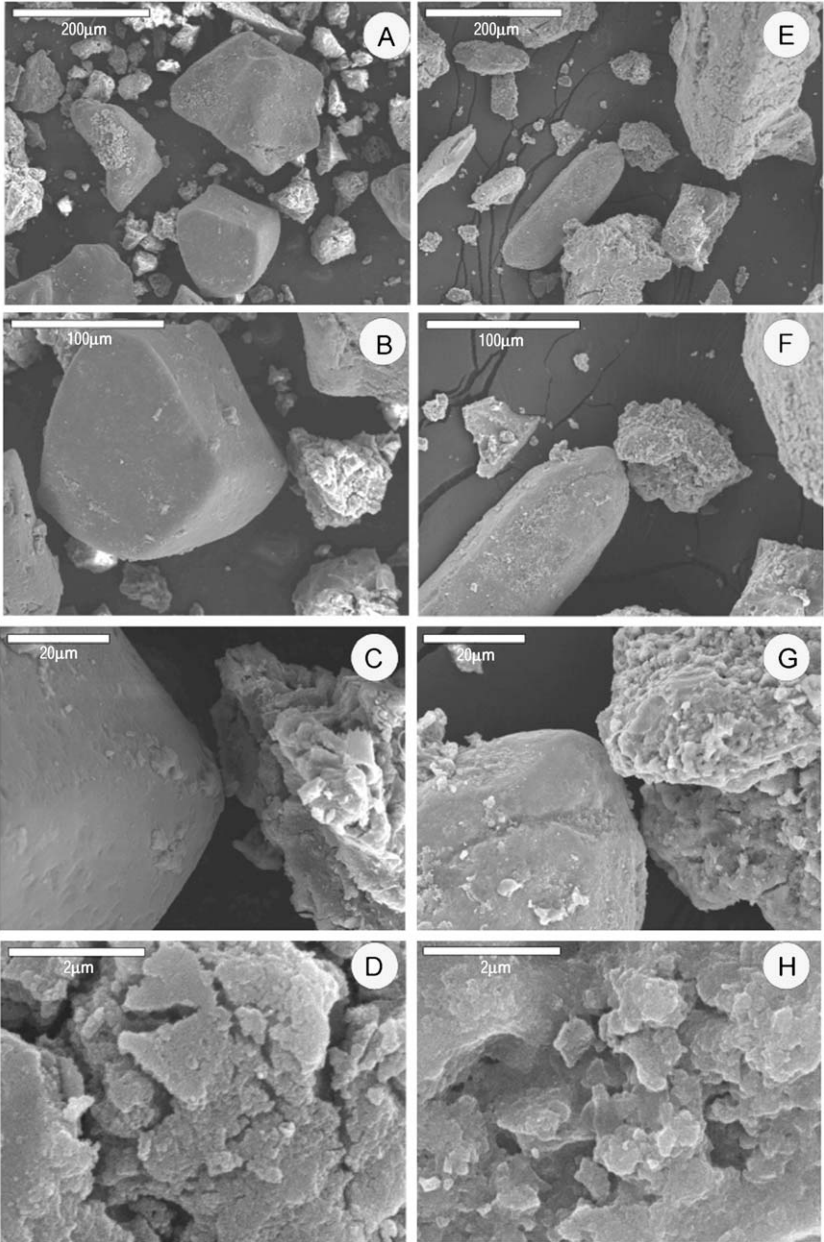
P sorbed during desorption came from the entrained solution after sorption. Apparently, P sorbed by WTRs is chemisorbed on WTR surfaces, and resists desorption to a 5 mM oxalate solution.

Spectroscopic and solid-state characterization of P-loaded WTR particles has been employed to better understand the long-term stability of sorbed P (Ippolito et al., 2003; Makris et al., 2004b). Makris et al. (2004b) reacted Fe- and Al-WTR particles with P for 80 days and then subjected the particles to SEM-EDS (Figs. 28.6 and 28.7) and to electron microprobe analyses. No discrete surficial metal-P phases were detected with SEM-EDS spectroscopy, which led to the hypothesis that P diffuses into particles to reach meso- and micro-pore domains rather than precipitating on external surfaces of the WTRs. Thin cross-sections were prepared that allowed monitoring of the profile depth P distribution in the WTR particles over time. SEM-EDS dot maps of cross-sections from both WTRs qualitatively supported an intraparticle sorption mechanism.

Phosphorus was evenly distributed within the particles, except for some near edge P zonation in Fe-WTR particles after P treatment (Fig. 28.7).

Electron microprobe analysis using wavelength-dispersive spectroscopy (EPMA-WDS) on thin-sections of P-treated WTR particles supported intraparticle P diffusion more quantitatively than SEM-EDS. Cross-sectional P distribution analysis of the P-treated WTRs showed significant ($p < 0.001$) increases in the relative P concentrations in the interior of the particles (approximately 60 μm inside) with time (from 1 to 80 days) (Makris et al., 2004b). Phosphorus concentrations of 80 day-treated particles were significantly greater than 1 day-treated particles, both at the edge and interior (Makris et al., 2004b). Average P concentrations for P-treated particles were slightly greater near the edge, but edge-versus-interior differences were not statistically different at the 95% confidence level.

Ippolito et al. (2003) used EPMA-WDS dot maps to assess P distribution in a P-treated Al-WTR equilibrated for 211 days. Dot maps showed no evidence for P surface precipitation, but a uniform amorphous

Figure 28.6. Scanning electron secondary images of the Al- and Fe-based WTRs. (A) secondary image of representative Al-WTR particles; scale bar = 200 μm. (B) Magnified secondary image of a portion of image (A); scale bar = 100 μm. (C) Secondary image of representative Al-WTR surfaces; rough and smooth surfaces; scale bar = 20 μm. (D) Magnified secondary image of the rough surface of the Al-WTR particle from image (C); scale bar = 2 μm. (E) Secondary image of representative Fe-WTR particles; scale bar = 200 μm. (F) Magnified secondary image of a portion of image (E); scale bar = 100 μm. (G) Secondary image of representative Fe-WTR surfaces; rough and smooth surfaces; scale bar = 20 μm. (H) Magnified secondary image of the rough surface of the Fe-WTR particle from image (G); scale bar = 2 μm. Images D and H show surface porosity, but magnification is not large enough to show microporosity (Makris et al., 2004b).
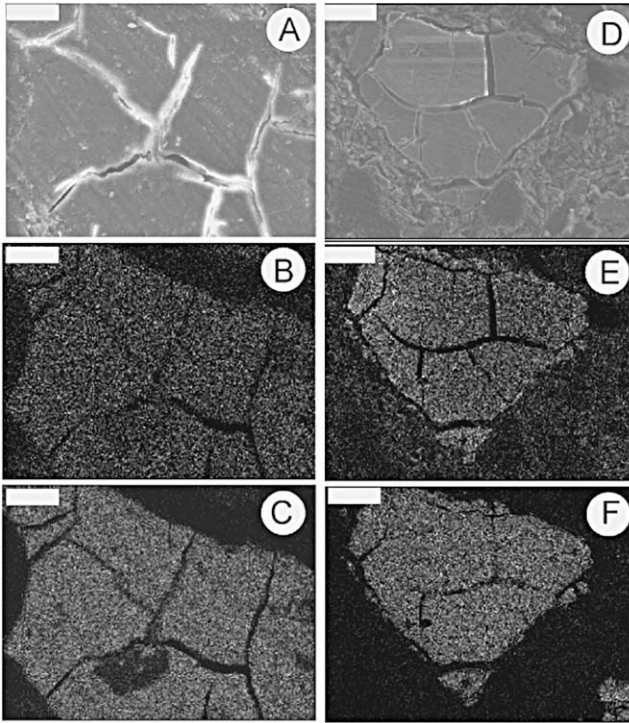
Figure 28.7. Scanning electron secondary images (A, D) and the corresponding P and metal dot maps (B, C, E, and F) of thin cross-sections after 80 days P treatment for both WTRs. (A) Secondary image of a representative Al-WTR cross-section; scale bar = 20 μm. (B) P dot map of the secondary image in (A). (C) Al dot map of the secondary image in (A). (D) Secondary image of a representative Fe-WTR cross-section; scale bar = 20 μm. (E) P dot map of the secondary image in (D). (F) Al dot map of the secondary image in (D). P dot maps of cross-sections for both WTRs show uniform P distribution, with no evidence for surface precipitation. Rarely, and only for the P-treated Fe-WTR, there were indications of zonal P enrichment near the particle edge (Makris et al., 2004b).

Al-P association throughout the particles (Ippolito et al., 2003). EPMA-WDS data support the notion that P moves in a three-dimensional fashion toward the interior of the WTR particles rather than accumulating significantly at the particle surface as by precipitation.

The collective data of Makris et al. (2004b) and Ippolito et al. (2003) have favorable implications for long-term P immobilization. Apparently, once P reaches the WTR microsites, very strong adsorption, and highly hysteretic desorption is likely. Thus, once immobilized by the WTR particles, the P is likely irreversibly bound, barring destruction of the WTR particles.

28.3. Potential limitations of WTR use

28.3.1. Agronomic impacts on phosphorus availability

Studies dealing with land-applied WTRs have identified both negative and positive effects of WTR application to crop yields. Ippolito et al. (1999) conducted a greenhouse study to investigate the efficacy of co-application of Al-WTR and biosolids to two native short grass species (blue gramma-*Bouteloua gracilis*, and western wheatgrass- *Pascopyrum smithii*). Results suggested a linear positive relationship between increasing WTR rate and yield, but a negative relationship between increasing WTR rate and shoot P and Al concentrations. No P deficiency or Al toxicity symptoms were observed, but the trends suggested that very large WTR applications could cause agronomic problems. Other studies have shown that application of WTR10 g WTR kg^{-1} ($\sim$20 Mg WTR ha^{-1}) reduced tissue P concentrations, but did not induce other nutrient deficiencies or toxicities (Elliott and Singer, 1988; Heil and Barbarick, 1989; Cox et al., 1997).

The primary concern with the land application of WTRs is the potential for induced plant P deficiencies (Basta et al., 2000). Plant (*maize*) P uptake reductions and germination problems were observed when Al-WTR was applied (up to 40 Mg ha^{-1}) (Rengasamy et al., 1980). Fescue grass yields were decreased in WTR-amended soil columns (up to 80 Mg ha^{-1}), apparently in response to decreasing plant-available P (Lucas et al., 1994).

Others have reported insignificant effects of WTR applications on crop P nutrition. Reductions in exchangeable P concentrations were not accompanied by plant growth limitations in soils amended with biosolids and Al-WTR during a 7-year field experiment (Naylor and Carr, 1997). Harris-Pierce et al. (1993) reported minimal negative effects of WTR (5.6–22.4 Mg ha^{-1}) and biosolids (11.2 Mg ha^{-1}) co-application on native rangeland vegetation. Brown and Sartain (2000) showed that a 2.5% by wt. (56 Mg ha^{-1}) Fe-WTR application rate significantly reduced P leaching from applied fertilizer P, with minimal negative impact on Bermuda grass P uptake.

In addition to agronomic limitations involving P (over-applied WTRs induced plant P deficiencies), there are concerns about potential Al phytotoxicities or elevated soluble Al concentrations in runoff from amended land. Few data exist on the potential for Al-WTR to cause Al phytotoxicity or water quality degradation. Alum applications to agricultural fields had no effect on plant Al concentrations or crop yields (Moore and Miller, 1994; Moore et al., 2000). Land application of

Al-WTR at rates of 11.2 and 44.8 Mg ha^{-1} did not increase dissolved solids or Al in surface runoff (Gallimore et al., 1999). Haustein et al. (2000) reported no significant increase of dissolved Al in surface runoff of soils amended with an Al-WTR (2.2–18 Mg ha^{-1}).

28.3.2. Limited WTR supply

The availability/accessibility of sufficient quantities of WTRs can be a major limitation for projects that require continuous or large WTR applications. Field application rates of WTRs are usually large (25–56 Mg ha^{-1}), and can out-strip local WTR supplies when hundreds of hectares require treatment. Partial or complete substitution of Al-WTRs for alum may be a cost-effective practice to reduce soluble P in animal waste (Makris et al., 2005b). Complete substitution of Al-WTRs for alum could be practiced in cases of year-around, abundant WTR availability.

28.3.3. Arsenic sorption by WTRs

Another contemporary environmental problem that could be amenable to remediation with WTRs is contamination of soils, waters and wastes with arsenic (As). Arsenic is toxic to man and other living organisms. Arsenic can be found in the waste stream from a variety of industrial processes (petroleum refining, glass melting and smelting of ores). For example, fly ash, a coal combustion residue, can contain As concentrations reaching 180 mg kg^{-1} (Qafoku et al., 1999). Arsenic can be also released to the environment through pesticide and fertilizer use (Loebenstein, 1992; Woolson, 1992). Arsenate ($H_2AsO_4^-$ and $HAsO_4^{-2}$) is the predominant As form in well-oxidized soil/water systems, whereas arsenite ($H_3AsO_3^0$ and $H_2AsO_3^-$) occurs mostly in low redox potential environments.

Use of the chromated copper arsenate (CCA)-pressurized lumber is a common practice to preserve wood supplies throughout the U.S. and safe disposal of the As-containing waste lumber can be problematic. Deposition in unlined construction and debris landfills can generate leachate enriched in As, which can endanger local ground waters. Soils associated with playgrounds, abandoned dipping vats, under porches constructed with CCA wood can become As point sources and potentially endanger children playing nearby.

Several As removal techniques exist for As-contaminated soils and waters, but most are cost-prohibitive. Small communities are likely to face expensive and technically imposing challenges to meet the 2006-mandated maximum contaminant level of 10 µg As l^{-1}. Drinking-WTRs are inexpensive sorbents expected to readily sorb As (similar chemistry to

P) and may help address current and future As issues. However, little is known about the extent of As immobilization by WTRs in general and about the retention of various As species [As(V) or As(III)] in particular.

Arsenic(V) (and P) removal in the water treatment industry is based on the well-known sorption of oxyanions by Fe and Al hydroxides (Livesey and Huang, 1981). Sorption of As, like P, on metal hydroxides is initially rapid, but then decreases with increasing equilibration time (O'Reilly et al., 2001). Pierce and Moore (1982) found that for up to $1\,\mathrm{mg\,l^{-1}}$ initial arsenate concentrations, the adsorption isotherm of As(V) on ferrihydrite could be described by the Langmuir model. At greater As loads (up to $50\,\mathrm{mg\,l^{-1}}$ initial arsenate concentration), data were better described by a two-stage linear model, suggesting a two-site type of As adsorption. Maximum arsenate adsorption occurred at pH 4 and decreased as pH increased. We hypothesize that WTRs can be similarly effective and represent a cost-effective amendment for immobilizing As(V) in As-contaminated sites.

Recent studies showed the strong affinity for soluble As(V) or As(III) by Fe-based or Al-based WTRs (Vandanapu et al., 2005; Makris et al., 2006). After only 2 days reaction, an Al-WTR sorbed nearly all ($>90\%$) of the added As(V) at all initial As loads (up to $20{,}000\,\mathrm{mg\,kg^{-1}}$); an Fe-WTR was less effective (sorbed 50–85%) (Vandanapu et al., 2005). Arsenite sorption experiments with an Fe-, and Al-based WTRs showed that both sorbents exhibited As(III) sorption maxima in the order of $\sim15{,}000\,\mathrm{mg\,kg^{-1}}$, within a 2-day equilibration period (Makris et al., 2006). Arsenic desorption with a $1\,\mathrm{mg\,P\,l^{-1}}$ solution was minimal, and decreased with increasing As load (Makris et al., 2006). The data are encouraging in the sense that WTRs apparently behave toward As as they do toward P, with huge As sorption capacities, and minimal As desorption. The desorption study with background P also suggest that WTRs could be effective As sorbents even in systems containing appreciable soluble P. Additional work is necessary to confirm the preliminary results, characterize both As(V) and As(III) sorption by WTRs, and to devise the most practical means to use WTRs to address As contamination concerns.

28.4. Future research needs

1. Field validation of WTR beneficial effects and the lack of negative influences on crop yields is needed to convince farmers of the practicality of using WTRs.
2. Techniques to better characterize WTRs a priori are needed (e.g., wet chemical, and spectroscopic techniques) to identify which WTRs are expected to be effective P and As sorbents and the rates necessary.

3. Studies that promote use of WTRs, independent of as a soil amend-
   ment (i.e., using barrels of WTR through which drainage water or
   potential drinking water is passed to remove contaminants). Field ap-
   plication rates of WTRs are usually large (25–56 Mg ha^{-1}), and can
   out-strip local WTR supplies when hundreds of hectares require treat-
   ment. Treating the drainage water from the fields (rather than the soil)
   may be a more efficient means of utilizing WTRs to remove P or As
   before the pollutants reach water supplies. Use of WTRs in barrels to
   decontaminate As-polluted water from wells may represent a "low-
   tech" solution to expensive water treatment plants for small commu-
   nities faced with meeting more stringent As drinking water.

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