

WATER TREATMENT RESIDUALS AMENDED SOILS RELEASE Mn, Na, S, AND C

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Drinking water treatment facilities remove impurities from raw water sources using various chemicals. The by-product produced from the purification process is called water treatment residuals (WTR). If WTR contain residual chemicals from the purification process, soluble elements may be released potentially causing chemical imbalances in soil and groundwater systems. The study objectives were to: (i) examine Mn, Na, S, and total organic carbon (TOC) released from soil and deionized water leachate from a Norfolk soil (fine-loamy, kaolinitic, thermic Typic Kandiudult) incubated for 60 days with 0 (untreated) and 60 g kg⁻¹ of three different WTR; and (ii) assess effects of oxidation-reduction potential on Mn stability and solubility. The WTR were obtained from a North and South Carolina drinking water treatment facility that treated raw water using alum [Al₂(SO₄)₃], caustic soda (NaOH), and potassium permanganate (KMnO₄). During incubation, treatments were maintained between 5% and 10% moisture, and oxidation-reduction potential was measured using a Pt electrode. After 60 days, treatments were leached with 1.2-pore volumes of deionized water. Soils were then analyzed for Mn, Na, and S, and leachates were analyzed for TOC and similar elements using inductively coupled plasma spectroscopy. At this time, WTR-treated soils were slightly acidic, moderately reduced, and enriched in extractable Mn, Na, and S concentrations. Water leachates from WTR-treated soil were also enriched with Mn, Na, S, and TOC. Divalent Mn was the dominant oxidation state, making Mn more susceptible to leaching. One WTR enriched with Mn caused Norfolk soil Mn concentrations to exceed crop sensitive stress threshold levels. It is recommended that a prescreening procedure should be used to determine if WTR applied to soil will release elements that may cause plant growth problems. (Soil Science 2007;172:992-1000)

Key words: Soil, water soluble elements, water treatment residuals.

DRINKING water treatment facilities purify raw water using various chemicals including alum [Al₂(SO₄)₃], caustic soda (NaOH), and potassium permanganate (KMnO₄). Alum is used to flocculate sediments in the raw water,

whereas NaOH and KMnO₄ provide taste and odor control. These purification chemicals, along with organic material from the raw water, will ultimately contribute to the chemical composition of WTR. When WTR are used to remediate P-impacted soils, consideration should be given to potential chemical releases.

Examination of contaminant leachability and total elemental composition of WTR has shown contrasting results. Jain et al. (2005) leached seven WTR isolated from Florida water treatment plants using a synthetic precipitation leaching procedure and reported very low leachate concentrations of As, Ba, Cd, Cr, Pb,

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Hg, Mo, and Ni. Some Fe-, and Al- WTR tested by Elliott and Dempsey (1991) revealed that their mean total Cr, Ni, Pb, and Zn concentrations were within a common range found in soils. These researchers concluded that WTR applications to soils should not alter their total metal concentrations.

On the other hand, research has also shown that the trace elemental composition of WTR can be much higher than corresponding levels in soils. Peters and Basta (1996) reported that an Al-WTR contained 11 g kg^{-1} of total Mn, whereas the typical range in mineral soils is only 0 to 5 g kg^{-1} . Titshall and Hughes (2005) measured diethylenetriaminepentaacetic acid (DTPA) extractable metals from six South African WTR and reported low Co, Cu, Fe, Mn, Pb, and Zn concentrations. Two of the six WTR, however, had substantial amounts of DTPA-extractable Mn (420 and 725 mg kg^{-1}). These results show that some WTR applied to soils will have minimal influence on extractable metal concentrations; whereas other WTR may cause trace metal nutrient imbalances.

Previous P-sorption investigations using Norfolk soils amended with WTR (Novak and Watts, 2004; 2005) revealed that background equilibration solutions often contained Mn, Na, and S. Release of these elements may be a soil fertility concern, especially if their concentrations create plant nutrient imbalances. Soil Na and S accumulation can cause modifications in electrical conductivity (EC) and pH values (Thompson and Troeh, 1978). However, Na and S accumulation is a short-term problem in humid regions because they will eventually leach. Of more concern is Mn accumulation because Mn is a plant micronutrient with a small range between deficient, sufficient, and phytotoxic soil concentrations. The critical Mehlich 1 extractable Mn concentration for soybean (*Glycine max* L. Merr.) production in southeastern USA Coastal Plain soils ranges between 1 and 10 mg kg^{-1} (Cox, 1968; Mascagni and Cox, 1984). Because Mn is not required in large amounts, it is conceivable that Mn-enriched WTR applications to acidic soils with reduced ORP could elevate soil Mn concentrations to phytotoxic levels (Adriano, 2001; Jones, 2003).

We hypothesized that WTR will release elements after soil application through solubilization reactions and/or by reduced ORP. Literature exists pertaining to releases of elements from WTR that are considered toxic (Title 40; Code of Federal Regulations, Part

503; USEPA, 1994). In contrast, there is little information on soluble Mn, Na, and S releases from soil-applied WTR. The processes governing dissolution of Na (Bohn et al., 1979) and S redox transformations (Connell and Patrick, 1969) are straightforward; however, Mn chemistry is dynamic. Manganese occurs in multivalent oxidation states; but primarily as the divalent ion in water and soil solution and the less soluble trivalent and quadrivalent states when bound to hydroxides (Adriano, 2001). Because Mn chemical structure, solubility, and valency are dependent on system's pH, ORP, and presence of counter ions, it is important to determine these properties to model Mn thermodynamic stability and speciation. Prior knowledge of soil chemical conditions can be used as a decision support tool to identify P-impacted soils that should not be treated with Mn-enriched WTR. The study objectives were to (i) examine the organic and inorganic chemical characteristics of soil and leachate from a Norfolk soil that had been incubated for 60 days after addition of 0 (untreated) and 60 g kg^{-1} of three different WTR; and (ii) assess the effects of soil ORP on Mn stability and solubility.

MATERIALS AND METHODS

Soil and WTR Collection and Characterization

A Norfolk soil was collected from an agricultural field near the U.S. Department of Agriculture-Agricultural Research Service-Coastal Plains Research Center, Florence, South Carolina. The field has a cropping history consisting of corn (*Zea mays* L.), soybean, and wheat (*Triticum aestivum* L.). Both the Ap (0–20 cm deep) and E horizon (20–45 cm deep) were collected, air-dried, and 2-mm sieved to remove coarse debris. The WTR incubations were conducted using a soil blend consisting of 90% E mixed with 10% Ap horizon (wt wt⁻¹). This mixture was chosen to coincide with another investigation designed to evaluate if dissolved organic carbon desorbed from WTR would promote aggregation (Busscher et al., 2007). The Ap horizon should supply a microbial presence to the E horizon whose oxidation of polymeric carbon compounds into simpler type carbon structures may increase aggregation.

Three WTR, sources of raw water, and treatment protocols and procedures were obtained from water treatment facilities in

North and South Carolina. Water treatment residual 1 was obtained from a South Carolina facility that used $\text{Al}_2(\text{SO}_4)_3$ to flocculate sediments in raw water from the Catawba River. Water treatment residual 2 was collected from a North Carolina drinking water treatment facility that used raw water from the Neuse River and used $\text{Al}_2(\text{SO}_4)_3$, NaOH, and KMnO_4 in the purification process (Novak and Watts, 2004). Water treatment residual 3 was obtained from a South Carolina water treatment plant that used $\text{Al}_2(\text{SO}_4)_3$ and NaOH to treat raw water from Lake Murray. The WTR were air-dried and ground to pass through a 2-mm sieve.

Because $\text{Al}_2(\text{SO}_4)_3$, NaOH, and KMnO_4 were used during the purification process, this investigation focused on Mn, Na, and S as trace elements of concern. Digestion and inductively coupled plasma (ICP) measurement for soil and WTR elemental composition were performed on triplicate samples using a modified EPA method 3050b (USEPA, 1986). The method was modified to add more hydrogen peroxide (H_2O_2) and heat because of the WTR's high TOC content (see Table 1). This method was chosen to provide an estimate of environmentally available elements as well as the H_2O_2 extractant ability to release organically chelated trace elements. As a check for toxic metals (Title 40; Code of Federal Regulation, Part 503, USEPA, 1994), the three WTR were further analyzed for total As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn (USEPA, 1994). Digestion using EPA method 3052 and ICP analysis revealed that the three WTR contained below detectable concentrations of Cd and Hg ($<0.05 \text{ mg kg}^{-1}$), low As, Ni, and Pb concentrations ($<16 \text{ mg kg}^{-1}$), and medium concentrations of Cr, Cu, and Zn ($27\text{--}210 \text{ mg kg}^{-1}$). The total concentrations of these eight metals in the WTR were below the maximum allowable concentration for land application of biosolids (USEPA, 1994).

The Norfolk ApE soil mix and the WTR were characterized for pH (1:1, solid-solution weight ratio), and TOC content using a LECO CN 2000 analyzer (LECO Corp., St. Joseph, MI). The soil was analyzed for particle size analyses using the micropipette method of Miller and Miller (1987). The Norfolk ApE mix consisted of 66% sand, 30% silt, and 4% clay.

Incubations of Soil With WTR and Hydrogen Electrode Readings Measurements

Prior laboratory research showed that satisfactory P binding results by WTR were obtained using a 60 g kg^{-1} WTR: soil mixture ratio, 10% soil moisture content, soil C:N ratio of 20:1, and 87 days' incubation period (Novak and Watts, 2005). These conditions were repeated for this experiment except that the incubation period was shortened to 60 days. Incubations were conducted using 10-cm-diameter pots filled with Norfolk soil treated with 0 and 60 g kg^{-1} of WTR. Treatments were a mix of 27 g + 450-g of air-dried, 2-mm sieved WTR and Norfolk soil. Untreated Norfolk soil without WTR (noted as 0 g kg^{-1}) served as a control. Pots were packed to a soil bulk density of 1.2 g cm^{-3} , and the bottom of each pot had a 20-mesh screen to minimize soil loss out a drain hole.

In situ ORP measurements of each pot during the incubation were determined using platinum (Pt) and reference electrode pair as described by Nordstrom and Wilde (2005). The Pt electrode was inserted approximately 4 cm deep (representing midpoint of soil depth) near the center of each pot. The reference electrode-salt bridge was inserted in the soil approximately 3 cm from the Pt electrode to a depth of about 1.5 cm. The Pt tips of the electrodes were constructed using 1.2-cm length segments of 20-gauge (0.81-mm-diameter) Pt wire. Reference electrodes were single junction Ag/AgCl

TABLE 1
Chemical properties of the Norfolk soil and WTR (SD are in parentheses)

Sample	pH	Elemental composition [†]			
		TOC g kg^{-1}	Mn	Na mg kg^{-1}	S
Norfolk soil	5.6	1.9	10 (3)	9 (2)	31 (6)
WTR 1	3.8	68	551 (44)	218 (41)	2046 (128)
WTR 2	5.8	120	8717 (386)	208 (32)	12205 (676)
WTR 3	5.0	190	717 (70)	639 (23)	6039 (12)

[†]Determined using EPA method 3050b ($\text{HNO}_3 + \text{H}_2\text{O}_2$ at $25 \text{ }^\circ\text{C}$ – $100 \text{ }^\circ\text{C}$).

with epoxy body and filled with a gel electrode (Jenco Instruments, San Diego, CA). Before insertion, the Pt tips were cleaned using Milli-Q water, and the ORP of the electrode system was tested against Zobells solution. The obtained millivolt (mV) readings were corrected for differences in the standard potential of the reference electrode and the potential of the Pt electrode.

The leads from the Pt and reference electrode were connected to a voltmeter, and three ORP readings per week were taken before adjusting the soil moisture to 10% (wt wt⁻¹). The ORP readings were transformed to standard hydrogen electrode readings (Eh) using Eq. 1:

$$Eh = E_{\text{measured}} + 199 \text{ mV} \quad (1)$$

where Eh is the corrected value of the ORP in mV with respect to the standard hydrogen electrode, and E_{measured} is the electromotive force of the system measured at laboratory temperature and with respect to the Ag/AgCl electrode. The Ag/AgCl reference electrode had a difference of +199 mV with respect to the standard hydrogen electrode, with this value included in Eq. 1. The laboratory room temperatures did not vary substantially (20 °C–22 °C), and thus corrections for temperature were not performed because the error involved from this source was much smaller than other errors in the measuring system (Patrick et al., 1996). The Eh readings were normalized to pH 7 (Eh₇) to interpret ORP data between soil leachates because leachate pH values were far below neutrality, and ranged from 4.3 to 6.1 standard units. This was accomplished using a modified method of Tabatabai and Walker (1970) where 59 mV was subtracted from the standard hydrogen electrode potential per unit of pH change. Soil Eh₇ values were grouped (Szogi et al., 2004) into four classes: oxidized (+300 mV), moderately reduced (+100 to +300 mV), reduced (-100 to +100 mV), or highly reduced (<-100 mV).

Four replicates per treatment were incubated for 60 days at room temperature and between 50% and 70% relative humidity. Pots were leached with 1.2-pore volumes (285 mL) of deionized water after 60 days of incubation to ensure that soil void spaces were flushed. Pots were allowed to drain for several hours into plastic cups. After free drainage had ceased,

leachate volumes were measured, and a portion was then passed through a 0.45- μm nylon filter. Leachates were refrigerated until analyses for Mn, Na, and S using ICP. Unfiltered leachate TOC concentrations were measured using a Shimadzu TOC-VCSN (Shimadzu Corp., Kyoto, Japan) analyzer; EC and pH of the unfiltered leachate (undiluted) and treated soil (at a 1:2 wt vol⁻¹ ratio) were determined using standard techniques (Novak and Watts, 2005). After 60 days of incubation, all soils were extracted for plant available Mn, Na, and S using Mehlich 1 reagent (HNO₃ + HCl) by the Clemson University Soil Testing Laboratory and for elemental Mn, Na, and S using EPA method 3050b (USEPA, 1986). The elements were quantified using ICP spectroscopy having a method detection limit (MDL) of less than 8 mg kg⁻¹.

The 60-day soil Eh₇ values and leachate pH values were used to construct a pH versus Eh₇ stability diagram for Mn according to Brookings (1988) assuming the molar concentration of TOC and S were 10⁻⁶ and 10⁻³ at standard temperature and pressure (25 °C and 0.1 MPa). Prediction of the percent distribution among the three Mn oxidation states (i.e., Mn⁺², Mn⁺³, and Mn⁺⁴) was accomplished using the chemical speciation model MINTEQA2 version 1.5 software. (Allison Geosciences, 2003). MINTEQA2 was ran using the mean Eh₇ value per treatment and mean leachate Mn, S, C concentrations and pH measured on the 60th day of incubation. In addition, the pH and Eh were fixed using the mean values per treatment on 60 days. The ionic strength was not fixed, and no solid phases were allowed to precipitate. For these calculations, S activity was described as SO₄⁻² because this would be the prominent oxidation state under the system conditions (Bohn et al., 1979). Sulfate will electrostatically bind to Mn (as MnSO₄), thereby influencing Mn form and solubility. The influence of OH⁻ on Mn solubility was considered negligible because of leachate acidic pH values.

Statistics

The mean chemical composition of treatments was compared after 60 days of incubation using a one-way analysis of variance to determine if WTR modified the soil or leachate chemical composition. All means and statistical comparisons were determined using SigmaStat

software version 3.01 (SSPS, 2005) at a $P < 0.05$ level of significance.

RESULTS AND DISCUSSION

Chemical Properties of Norfolk Soil and WTR

The Norfolk soil had chemical properties characteristic of highly weathered, well-drained Coastal Plain topsoils (Daniels et al., 1999). It had an acidic pH value with low TOC, Mn, Na, and S contents (see Table 1). Well-drained Coastal Plain soils have low TOC (Novak et al., 2007) and low trace element contents (Franklin et al., 2003). The regions' high soil temperatures and precipitation increase mineral weathering and their removal from the soil profile.

All three WTR had acidic pH values but had greater TOC contents as compared with Norfolk soil. The WTR acidic pH values were not unexpected because their raw water sources had pH values less than 6.5 as per water treatment facility records. In addition, the use of $\text{Al}_2(\text{SO}_4)_3$ caused the WTR to have higher exchangeable acidity values than the Norfolk soil (data not presented). When WTR are obtained from raw river sources, it is common for them to be TOC-enriched. Alum precipitates organic debris (i.e., algae, stream water humic material, etc.) suspended in the water column that later binds with WTR. The three WTR had TOC contents similar to values reported by Dayton et al. (2003) and Makris et al. (2004).

Total elemental composition of WTR can vary because of differences in suspended sediment mineralogy, raw water background elements, and choice of purification chemicals. For instance, the total Na composition of WTR obtained from Maryland and Colorado was 121 and 450 mg kg^{-1} , respectively (Codling and Isensee, 2005; Ippolito and Barbarick, 2006). The total S content in six WTR from South Africa ranged from 720 to 2500 mg kg^{-1} (Titshall and Hughes, 2005); Oklahoma and Maryland WTR contained 11,000 and 2100 mg kg^{-1} of total Mn, respectively (Peters and Basta, 1996; Codling and Isensee, 2005). In addition, two of the six South African WTR contained 420 and 725 mg kg^{-1} of DTPA-extractable Mn (Titshall and Hughes, 2005). There were no reports available documenting the DTPA or Mehlich (1 or 3 reagent) extractable Na or S contents of WTR.

The three WTR in this study contained varying concentrations of total Mn, Na, and S

(see Table 1). This finding was explainable after examining each facility's water treatment protocols and chemical composition of raw water sources. Both water treatment facilities that produced WTR 1 and 3 use $\text{Al}_2(\text{SO}_4)_3$ and NaOH. Consequently, the remnants of these purification chemicals influenced the WTR elemental composition. The high Mn concentration in WTR 2 was caused by a combination of KMnO_4 treatment along with the raw water containing Mn. The annual mean Mn concentration in 2004 was 0.43 mg L^{-1} . The WTR in this study contain 2 to 3 order of magnitude higher concentrations of Mn, Na, and S than the Norfolk ApE soil mixture.

Chemical Characteristics of Norfolk Soil Incubated With WTR

Incorporating 6% WTR into the Norfolk soil significantly altered the pH and Eh_7 of these systems compared with the untreated Norfolk soil (see Table 2, soil \pm 0% WTR). Norfolk soil treated with WTR 1 experienced a significant reduction in pH and Eh_7 potential. In contrast, pH and Eh_7 both increased after treatment with WTR 2 and 3. Norfolk soils have an inherently low pH buffer capacity because of their low soil TOC contents. The soil EC values were significantly different; however, all values were less than 1 dS m^{-1} . This finding implies that these WTR added at 6% did not cause a salinity concern. If WTR had increased soil EC to greater than 3 dS m^{-1} , then crop growth may be affected (Sparks, 1995).

The Mehlich 1 extractable and elemental Mn, Na, and S concentrations in the untreated Norfolk soil were low (<8–17 mg kg^{-1} , see Table 3). Mehlich 1 extractable and elemental Na concentrations were below the MDL in all treatments probably caused by water leaching. On the other hand, after incubating with 6%

TABLE 2

Mean chemical characteristics of Norfolk soil after 60 days incubation with WTR

Norfolk soil with	Chemical characteristics		
	pH [†]	Eh_7 mV	EC dS m^{-1}
0% WTR	5.41 ^a	379 ^a	0.31 ^a
6% WTR 1	4.58 ^b	199 ^b	0.80 ^b
6% WTR 2	5.82 ^c	287 ^c	0.68 ^c
6% WTR 3	5.78 ^c	279 ^c	0.53 ^{bc}

[†]Means within a column followed by a different letter are significantly different at $P < 0.05$.

TABLE 3

Mean Mehlich 1 extractable and elemental composition of Norfolk soil after 60 days incubation with WTR

Norfolk soil with	Mehlich 1 extractable [†]			Elemental composition [†]		
	Mn [§]	Na	S	Mn	Na	S
	mg kg ⁻¹					
0% WTR	*** [¶]	***	***	***	***	17 ^a
6% WTR 1	29 ^a	9	62 ^a	27 ^a	***	144 ^b
6% WTR 2	239 ^b	***	88 ^b	285 ^b	***	416 ^c
6% WTR 3	21 ^c	***	19 ^c	52 ^c	***	200 ^d

[†]Mehlich 1 reagent (HNO₃ + HCl).[‡]EPA method 3050b (HNO₃ + H₂O₂ at 25 °C–100 °C).[§]Means within a column followed by a different letter are significantly different at a *P* < 0.05.[¶]***Mean values are less than the MDL of 8 mg kg⁻¹.

WTR, the soil Mehlich 1 and elemental S and Mn concentrations were significantly modified. The S concentration increase should be a soil fertility benefit because S is a plant macronutrient required in relatively high concentrations (17–45 kg ha⁻¹; Jones, 2003). The S concentrations in Norfolk soil mixed with these WTR were not expected to cause plant phytotoxic conditions (Kabata-Pendias, 2001).

The soil Mehlich 1 and elemental Mn concentration after incorporating the 6% WTR increased to between 21 and 285 mg kg⁻¹ (see Table 3). The increase in Mehlich 1 extractable Mn is a serious soil fertility concern. Because soil Mn is a plant micronutrient, Mn concentration in the measured range could cause phytotoxic conditions, especially under low soil pH (<4.8) and low Eh conditions (Adriano, 2001; Kabata-Pendias, 2001). For sandy Coastal Plain soils, between 1 and 10 mg kg⁻¹ of Mehlich 1 extractable Mn is sufficient for soybean production (Mascagni and Cox, 1984). Application of these three WTR to acidic soils in the Coastal Plain region increased plant available (Mehlich 1) soil Mn concentrations higher than the recommended concentration sufficient for soybean production. Soybeans will

probably experience Mn stress under these soil chemical conditions.

Movement of Elements Through Norfolk Soil

As shown in Table 4, water leachate chemistry was significantly influenced by the addition of 6% WTR. Leachate collected from Norfolk soil treated with WTR 1 was highly acidic (pH 4.46), although treatment with WTR 1 and 2 caused a significant increase in TOC concentration (75 mg L⁻¹). In contrast, there were no significant effects of the WTR on the leachates EC values.

Leachate Mn, Na, and S concentrations significantly increased with the addition of the three WTR relative to the untreated soil. Leachate Na and S concentrations were at least one order of magnitude greater than the untreated soil but were not excessive enough to cause a soil nutrient imbalance (Adriano, 2001; Jones, 2003). Adriano (2001) reported that soluble Mn concentrations in soil solution were between 0.054 µg and 54 mg L⁻¹. The leachate Mn concentrations in the Norfolk soil treated with 0% and with 6% WTR 1 and 3 were within this range reported by Adriano (2001). Of concern, 234 mg Mn L⁻¹ in leachate

TABLE 4

Chemical characteristics of leachates collected from Norfolk soil after 60 days of incubation with WTR

Treatment	pH	EC dS m ⁻¹	Concentration in leachates [†]			
			TOC	Mn	Na	S
			mg L ⁻¹			
0% WTR	5.40 ^a	2.32 ^a	26 ^a	0.4 ^a	3 ^a	4 ^a
6% WTR 1	4.46 ^b	3.17 ^a	66 ^b	14 ^b	15 ^b	51 ^b
6% WTR 2	5.92 ^c	3.76 ^a	75 ^b	234 ^c	17 ^c	123 ^c
6% WTR 3	5.90 ^c	3.40 ^a	19 ^c	7 ^d	16 ^b	19 ^d

[†]Means within a column followed by a different letter are significantly different at *P* < 0.05.

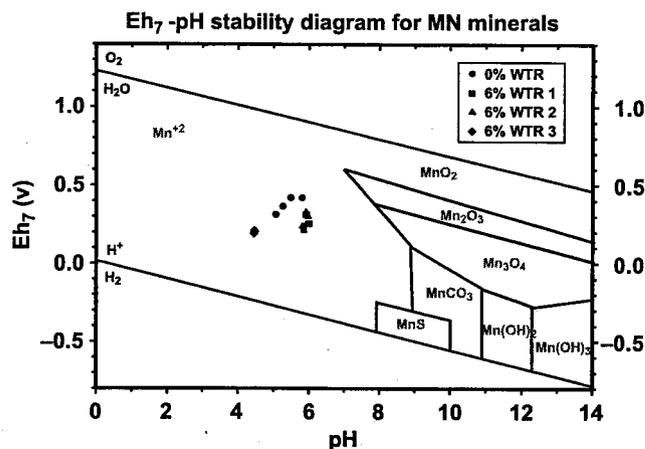


Fig. 1. Eh₇-pH stability diagram for Mn minerals in systems containing Norfolk soil mixed with and without WTR (points plotted were values for each pot after 60 days).

from soil treated with WTR 2 was a gross soil fertility matter. Although no crop bioassay tests were conducted in this study, the literature suggests that there is a strong likelihood of crop stress or toxicity by exposure to this much soluble Mn (Bohn et al., 1979; Marschner, 1998).

Eh₇ Versus pH Stability Diagram for Mn Minerals and Mn Oxidation States

Because Mn solubility and stability are influenced by pH and ORP, each treatment's soil Eh₇ and leachate pH values were used to develop a Mn mineral stability diagram (see Fig. 1). Although Mn will occur in many mineral phases (Lindsay, 1979), only a few were included to construct the stability field including pyrolusite (MnO₂), manganite (Mn₂O₃), hausmannite (Mn₃O₄), rhodochrosite (MnCO₃), a Mn-sulfur phase (MnS), and two variants of pyrochroite [Mn(OH)_x]. The mean soil Eh₇ values for all treatments ranged between 199 and 379 mV, whereas the mean leachate pH values ranged between 4.46 and 5.92. Plotting these two variables for each treatment showed that the data points clustered in the Mn⁺² stability field. Formation of Mn⁺² was favored because of the oxidized/moderately reduced ORP environment along with the low pH. This was corroborated by MINTEQA2 results showing that Mn⁺² was the predominant (>90%) oxidation state (see Table 5). The predicted Mn molar concentration was negligible (10⁻²⁰–10⁻³⁵) of Mn occurring in the Mn⁺³ and Mn⁺⁴ oxidation states. This is in agreement with Adriano (2001)

who reported that very low levels of Mn⁺⁴ will occur in soil solution because of low solubility of Mn-oxide minerals, whereas the concentrations of Mn⁺³ are low because of rapid reduction to Mn⁺². MINTEQA2 also predicted the predominance of SO₄⁻² under these conditions, the predominant S species in aerobic soils (Bohn et al., 1979). Formation of MnSO₄ caused by the presence of S from the WTR slightly reduced the predominance of Mn⁺². Both the Eh₇-pH and MINTEQA2 results showed that Mn-enriched WTR application to acidic sandy soils with moderately reduced conditions should be avoided because Mn-bearing WTR were not thermodynamically stable. Although total Mn in solution was measured, MINTEQA2 simulation indicated that Mn was released into solution predominantly as the soluble Mn⁺² species, thus rendering it susceptible to leaching.

TABLE 5

Component distribution among Mn and SO₄⁻² species in leachates collected from Norfolk soil treated with WTR[†]

Treatment	Mn ⁺² as (%)		SO ₄ ⁻² as (%)	
	Mn ⁺²	MnSO ₄	SO ₄ ⁻²	MnSO ₄
0% WTR	99.5	0.5	94	6
6% WTR 1	94	6	97	3
6% WTR 2	93	7	76	24
6% WTR 3	94	6	97	3

[†]Determined using mean soil Eh₇, mean leachate pH, Mn, and S measured on 60 days of incubation as inputs for MINTEQA2 chemical speciation model.

CONCLUSIONS

The WTR used in this study contained chemical residues of Mn, Na, and S left over from the drinking water purification process or as background in the raw water source. It was hypothesized that trace elements in the WTR would be released into soil and alter its chemical characteristics. To test this hypothesis, a laboratory incubation experiment was conducted using untreated Norfolk mixed ApE horizon soil and soil containing 6% WTR. Incubation of soil with WTR followed by leaching with deionized H₂O showed significant characteristic modifications of both soil and water leachates. One WTR significantly reduced soil pH, whereas another WTR significantly raised soil and leachate Mn concentrations. Measuring soil pH and ORP confirmed that conditions were thermodynamically favorable for Mn⁺² species. Modeling using MINTEQA2 also confirmed that Mn⁺² was the predominant oxidation state under system conditions. This was important because Mn-enriched WTR applied to a sandy Coastal Plain soil possessing a low pH and alternating ORP conditions will favor Mn solubilization and potentially increasing Mn leaching. The 6% WTR 2 application rate contributed sufficient Mn to the Norfolk soil that under low soil pH and ORP conditions probably would cause plant stress to Mn-sensitive crops.

Reports have shown that some WTR have a chemical composition that will not release soluble elements or alter the total metal composition of soils. Results from this study, in contrast, show that WTR can introduce chemical residues into the soil ecosystem. These chemical residues can alter the chemical composition of soil and water leachates, but this alteration can be inconsequential for some elements. For example, Na and S concentrations were increased after WTR incorporation; however, they were sufficiently soluble so that concentrations would probably be reduced to background after significant rainfall. The change in soil EC after WTR incorporation was significant; however, measured EC values were below those considered as saline-impacted soils.

Background soil characteristics (Titshall and Hughes, 2005) as well as chemical properties of WTR (Elliott et al., 2002) should be carefully considered before WTR are field applied. Our results confirm these recommendations in that WTR should be prescreened before field appli-

cation. This is especially apparent when WTR are suspected of containing chemical residues of consequence. A simple prescreening procedure can be a water leachability test after incubating WTR in a test soil or by simply extracting the WTR using Mehlich 1 reagent. The benefit of this prescreening procedure is that potentially phytotoxic chemical residues will be identified before field application. Accomplishing a prescreening test can be an expensive and time-consuming venture; it may be simpler to select a WTR that is not enriched with trace elements. It may also be prudent to request the chemical characteristics of the raw water source from the treatment facility to ensure that background trace element concentrations are as low as possible or present in relatively insoluble form.

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