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Aging effects on reactivity of an aluminum-based drinking-water treatment residual as a soil amendment

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ABSTRACT

Several studies have shown that drinking-water treatment residuals (WTR) could be used to control mobility of excess phosphorus (P) and other oxyanions in poorly sorbing soils. Presently, only “aged” WTRs (those left, or manipulated, to dewater) are land applied. However, if demand for WTRs increase in the near future, freshly-generated WTRs could be considered for land application. To our knowledge, few studies have examined the reactivity and equilibration time of freshly-generated alum-based WTR (Al-WTR). A laboratory thermal incubation study was, therefore, conducted to determine various extractable Al forms in Al-WTR as a function of WTR “age”, and the time required for freshly generated Al-WTR to stabilize. Freshly-generated Al-WTR samples were collected directly from the discharge pumps of a drinking-water treatment plant, and thermally incubated at 52 °C, either with or without moisture control, for ≤ 24 wk. Additional dewatered Al-WTR samples of various ages (2wk- to 2y old) were also included in the study. Various methods of extracting Al [total-, oxalate (200 and 5mM), and Mehlich 1 extractants] were utilized to assess Al extractability over time. Freshly-generated Al-WTR samples were potentially more reactive (as reflected in greater 5mM oxalate extractable Al concentration) than dewatered Al-WTR samples stockpiled for ≥ 6 mo. Aluminum reactivity of the freshly-generated Al-WTR decreased with time. At least 6wk of thermal incubation (corresponding to ≥ 6 mo of field drying) was required to stabilize the most reactive Al form (5mM oxalate extractable Al concentration) of the Al-WTR. Although no adverse Al-WTR effects have been reported on plants and grazing animals (apparently because of low availability of free Al^{3+} in Al-WTR), land application of freshly-generated Al-WTRs (at least, those with similar physicochemical characteristics as the one utilized for the study) should be avoided.

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1. Introduction

The use of drinking-water treatment residuals (WTR) to control the mobility of excess phosphorus (P) (Elliott et al., 1990; O'Connor et al., 2002; Makris et al., 2004; Novak and Watts, 2004; Agyin-Birikorang et al., 2007) and other oxyanions (Makris et al., 2006b; Sarkar et al., 2007) in poorly sorbing soils has received increased attention in recent times. The process of producing potable water from surface water supplies typically involves coagulation and flocculation of suspended

solids. The precipitated material is separated by filtration or gravity and the solid material is known as WTR. More than 2million metric tons of WTR are generated daily from drinking-water treatment plants in USA (Prakash and Sengupta, 2003). Drinking-water treatment residuals 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 toxicity characteristic leaching procedure (TCLP) test; and d) by land application (Chwirka et al., 2001).

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Land application is an attractive and less expensive alternative means of WTRs disposal and may have the added benefit of immobilizing excess P and other oxyanions in poorly sorbing soils. The high amorphous aluminum (Al) or iron (Fe) contents of the WTRs (depending on the coagulant used) can increase a soil's P sorption capacity (Elliott et al., 1990; O'Connor et al., 2002; Hyde and Morris, 2004; Novak and Watts, 2004; Dayton and Basta, 2005; Rhoton and Bigham, 2005; Agyin-Birikorang et al., 2007). Haustein et al. (2000) used alum-based WTR (Al-WTR) (rates up to 18 Mg ha⁻¹) to reduce soluble P concentrations in runoff from fields having excessively high soil test P. Gallimore et al. (1999) observed ≥60% reduction of soluble P in surface runoff when Al-WTR was applied to poultry litter-amended soils. Peters and Basta (1996) significantly reduced (~50% of the initial values) soil test-extractable P concentrations of an acidic and a calcareous soils incubated with high loading rates of two Al-WTRs (~60 and 200 Mg ha⁻¹). Ippolito et al. (2003) showed that P is adsorbed by WTR initially as an outer-sphere complex or found in the diffuse ion swarm near individual WTR particles and, with time, P becomes more strongly adsorbed as an inner-sphere complex onto WTR (Ippolito et al., 2003). Using spectroscopic measurements, Makris et al. (2004) reported that adsorption of P by WTRs was strongly hysteretic. The authors observed that P diffuses into the bottleneck-shaped micropores of the WTR and resists desorption, which favors long-term stability of sorbed P by WTRs (Makris et al., 2004). Agyin-Birikorang and O'Connor (2007) used isotopic dilution technique; coupled with stepwise acidification procedure to show that within the commonly encountered pH range of agricultural soils (4–7), WTR immobilized P is stable and essentially non-labile.

Similarities in the chemical nature of phosphate and As(V) molecules (tetrahedral geometry; atomic radii; bonding radii; ionization potential; and electro-negativities) (Badruzzaman et al., 2004), suggest that WTRs should exhibit high affinity for As(V). Makris et al. (2006b) demonstrated that WTRs are excellent low-cost sorbents for As(V) and As(III). Both Al-WTR and Fe-based WTR (Fe-WTR) exhibited high As(III) and As(V) affinities with minimal desorption of WTR immobilized As (Makris et al., 2006b). Sarkar et al. (2007) showed that WTRs have large arsenic sorption capacities (≥7500 mg As kg⁻¹), and that sorption of As by an Al-WTR was almost instantaneous (>90% of initial As load of up to 7500 mg As kg⁻¹ was sorbed by the Al-WTR within 0.5 h). The Al-WTR was effective in immobilizing soluble As(V) in two FL soils (with contrasting physicochemical properties) that exhibited little indigenous As sorption capacities (Sarkar et al., 2007). In a different study, Makris et al. (2006a) observed that Al-WTR is an effective sorbent for perchlorate in contaminated water, and perchlorate containing ammunition wastes.

The main concerns with the land application of Al-WTR are the potential for induced plant P deficiencies, Al toxicity (Basta et al., 2000), and arsenic (As) toxicity (Townsend et al., submitted for publication). Townsend et al. (submitted for publication) reported that all Al-WTR produced in Florida, USA, contain total As concentrations (8.5–16.9 mg kg⁻¹) that greatly exceed the industrial limit of soil cleanup target level (SCTL) for arsenic (3.7 mg kg⁻¹). However, recent studies have shown that As contained in Al-WTR is essentially non-labile, and that Al-WTR could indeed be used as a sorbent for As in

soils (Makris et al., 2006a; Sarkar et al., 2007). Studies have shown that application of Al-WTR at rates up to 20 Mg WTR ha⁻¹ slightly 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; Oladeji et al., 2006). Oladeji et al. (2006) reported that dry matter yield and tissue P concentrations of ryegrass and bahiagrass were not negatively affected when Al-WTR (22.4 Mg ha⁻¹) and different P sources (224 kg P ha⁻¹) were co-applied to the grasses grown on a Florida sandy soil. Gallimore et al. (1999) found that land application of Al-WTR (44.8 Mg ha⁻¹) did not increase dissolved solids or total soluble Al in surface runoff. Haustein et al. (2000) reported no significant increase of dissolved Al in surface runoff from Al-WTR (18Mg ha⁻¹) amended soils.

Although pH control of soluble Al concentrations dominates Al ecological risks to plants and at least some wildlife (McBride, 1994; Lindsay and Walthall, 1996; USEPA, 2003), additional concern relates to solid (WTR) Al form and “age”. Freshly generated Al-WTRs are largely amorphous solids of widely varying size, and specific surface, which can affect Al solubility and mobility in ecosystems. “Aged” Al-WTRs (those left, or manipulated, to dewater) reportedly have lower Al solubility, less tendency to form mobile colloidal forms, and lower P-sorption potential. Unpublished data suggest a greater reactivity and potential ecological risk for the freshly generated WTRs than “aged” WTRs. Some regulators in Australia suggest limiting land application of Al-WTRs to the “aged” materials to minimize potential ecological Al risk. However, little is known about the reactivity of freshly generated Al-WTR, and the time required for freshly-generated Al-WTRs to stabilize is unknown, making the definition of “aged WTR” rather vague. The objectives of this study were therefore to determine (i) the extractable forms of Al in an Al-WTR as a function of WTR “age”, and (ii) the time required for freshly deposited Al-WTR to stabilize.

2. Materials and methods

2.1. Collection of Al-WTR

Alum-based WTR of various ages (‘freshly-generated’, 2-, 4-, 6-, 8-wk, 6mo, 1y, and 2y old samples) were collected from the Manatee Co. water treatment plant in Bradenton, FL. The freshly-generated Al-WTR was collected directly from the discharge pumps of the water treatment plants, and contained ~2% solids. Freshly-generated residuals are usually discharged bi-weekly into shallow lagoons outside the treatment plant to dewater. The Al-WTR in each lagoon is tilled at 2-d intervals to expedite drying. The WTRs are lagooned for 8wk, and then stockpiled outside the lagoon for an additional 6mo. The stockpiled WTRs that are not collected for land application after the 6-mo period are land-filled. The Al-WTRs of various ages (2-, 4-, 6-, 8-wk old) were obtained from the lagoons by compositing ~50 cores (7.5cm diameter) from the top 10cm depth of each corresponding lagoon. Additional “old” samples (~6 mo, 1y, and 2y old) were collected from piles of dewatered WTRs and

included in the study, together with the newly generated (≤ 8 wk old) Al-WTR samples.

2.2. Characterization of and analyses of Al-WTR

Subsamples of the Al-WTR were air-dried, ball-milled, and analyzed for total Al, Fe, and P by ICP-AES (Perkin-Elmer Plasma 3200, Perkin-Elmer, Wellesley, MA) following acid-peroxide digestion according to the EPA Method 3050A (USEPA, 1986). Oxalate (200mM and 5mM) extractable P, Fe, and Al concentrations were also determined by ICP-AES after extraction at a 1:60 solid:solution ratio, following the procedures of Schoumans (2000). Phosphorus saturation index ($PSI = [P_{ox}] / [Al_{ox} + Fe_{ox}]$) was calculated from the molar concentrations of oxalate (200mM) extractable P (P_{ox}), Al (Al_{ox}), and Fe (Fe_{ox}) in the WTR (Elliott et al., 2002). The PSI is a measure of P retention/release potential from a particular amendment. Total C and N concentrations of the Al-WTR were determined by combustion the material at 1010°C using a Carlo Erba analyzer (NA-1500 CNS, Carlo Erba, Milan, Italy). Percent solids were determined by drying materials at 105°C (Gardner, 1986). Mehlich 1 extractable Al was determined on the Al-WTR samples as described in Mehlich (1978). The pH measurements of the Al-WTRs were performed on the materials (1:2 solid:solution ratio), whereas electrical conductivity (EC) measurement was done on a saturated paste of the Al-WTR.

2.3. Analyses of supernatant liquid of the Al-WTR

Subsamples (5g, oven-dry weight equivalent) of the ‘freshly-generated’, 2-, and 4-wk old Al-WTRs were obtained from the respective samples and centrifuged at a relative centrifugal force of ~ 8000 g for 20 min (based on preliminary study) to obtain supernatant liquid. One-half of the supernatant liquid was immediately filtered (0.45 μ m) for analysis. Electrical conductivity and pH values were determined on each of the filtered and unfiltered samples. Total “dissolved” Al concentration was measured in the filtered supernatant samples after digesting 10mL of the samples with 0.5mL 11N H_2SO_4 and 0.15g of potassium persulfate in an autoclave for 1h (Pote and Daniel, 2000a,b). Total Al in the unfiltered supernatant samples was determined by digesting 5mL of the samples with 1mL of 11N H_2SO_4 and 0.3g of potassium persulfate on a digestion block and then diluting with 10mL of water (Pote and Daniel, 2000b). All digested samples were analyzed for Al with ICP-AES (Perkin-Elmer Plasma 3200, Perkin-Elmer, Wellesley, MA). Colloidal Al was calculated by subtracting total dissolved Al values from the total Al values.

2.4. Artificial aging of Al-WTR samples

Artificial aging of the Al-WTR samples was achieved through thermal incubation. Subsamples of all the Al-WTR samples (of different ages) were placed in a growth chamber and maintained at 52°C. Studies have shown that thermal incubation of metal oxides at elevated temperatures (>45 °C) encourages structural changes that predict long-term weathering reactions in the field (Spadini et al., 1994; Ford et al., 1997; Martínez et al., 1999; Makris et al., 2004). Two batches of samples were maintained in the growth chamber. No attempt was made to

control soil moisture during incubation of one batch, whereas moisture was controlled for the second batch during incubation to maintain the initial moisture content of the Al-WTR samples. We hypothesized that elevated temperatures would provide the necessary thermal energy for structural rearrangements with time. Subsamples of the two batches of incubated samples were collected biweekly and analyzed for the various extractable forms of Al as described above.

2.5. Quality control

All sample collection/handling/chemical analysis was conducted according to a standard QA/QC protocol (Kennedy et al., 1994). For each set of sample analysis, a standard curve was constructed ($r^2 > 0.9999$). Method reagent blanks were included in the extraction process. Additional 5% of the samples were randomly selected and spiked with a certified Al reference material, and included in the extraction process to assess the reliability of the extraction procedure. Further, another set of additional 5% of the samples were randomly selected, and the extracts spiked with a known Al concentration to ascertain the accuracy of the ICP-AES measurements. Recoveries from the spiked samples ranged between 97 and 103% of the expected values. Analyses that did not satisfy the above QA/QC protocol were rerun.

2.6. Statistical analysis

Data of the extractable Al concentrations of the Al-WTR (before the samples were thermally incubated) were analyzed with the general linear model (PROC GLM) of the SAS software (SAS Institute, 2002). Means of the various treatments were separated using Tukey’s studentized range (HSD) test (Tukey, 1949) at significance (α) level of 0.05. Time series analysis was conducted using the PROC TSCSREG procedure of the SAS software (SAS Institute, 2002). Correlation analysis, with the PROC CORR procedure of the SAS software (SAS Institute, 2002), was used to evaluate relationships between the two incubation methods (with and without moisture control), and artificial (thermal) aging method and the “natural-aging” of the Al-WTR.

3. Results and discussion

3.1. Chemical characteristics of Al-WTR

Selected chemical characteristics of the Al-WTR used for the study are presented in Table 1. The pH of the Al-WTR, irrespective of the age, was acidic with pH values ranging from ~ 5.1 [for the newly-generated (≤ 8 wk old) samples] to 5.9 [for the “older” (1y, and 2y old) samples]. The pH of the samples used was slightly below the range of pH values reported previously for Al-WTR samples collected from Bradenton water treatment plant (~ 6.3 – 6.8 , Makris, 2004; Agyin-Birikorang, 2006), and a host of Al-WTR samples collected elsewhere (6.0–8.4; Makris and O’Connor, 2007). The newly-generated Al-WTR samples contained no activated carbon but had increased alum content relative to the “older” samples. Most of the Al-WTRs characterized

Table 1 – Selected chemical properties of the various Al-WTR samples of different approximate ages used for the study

Selected properties	Fresh	2 wk old	4 wk old	6 wk old	8 wk old	6 mo old	1 y old	2 y old
pH	5.12±0.22	5.20±0.14	5.11±0.32	5.03±0.20	5.12±0.13	5.25±0.20	5.92±0.24	5.94±0.45
EC ^a (dS m ⁻¹)	1.66±0.04	1.68±0.12	1.65±0.09	1.66±0.05	1.66±0.05	1.64±0.10	1.66±0.04	1.66±0.04
total c	10.6±1.70	10.4±1.79	10.8±1.94	11.2±1.45	10.5±1.98	10.2±1.42	13.9±2.13	13.4±1.36
total N	0.60±0.08	0.59±0.08	0.64±0.06	0.62±0.09	0.56±0.07	0.54±0.06	0.74±0.04	0.76±0.07
% Solids	2.21±0.40	9.59±1.82	27.4±2.20	42.3±1.83	55.2±4.61	61.2±3.90	63.6±6.21	82.4±7.28
Total P	3.13±0.48	2.98±0.62	3.04±0.42	2.95±0.36	3.21±0.92	3.08±0.45	3.13±0.14	3.32±0.42
Total Al	153±20.1	154±18.3	154±17.2	152±15.7	156±16.8	150±20.1	135±3.32	137±1.59
Total Fe	4.87±0.59	5.12±0.85	4.99±0.56	5.02±0.86	4.96±0.58	4.82±0.56	4.43±0.44	5.15±0.67
Oxalate ^b P	2.77±0.44	2.66±0.61	2.78±0.37	2.75±0.44	2.69±0.35	2.91±0.32	2.83±0.12	2.76±0.19
Oxalate ^b Al	148±13.9	136±14.6	138±15.2	137±13.4	136±12.8	124±15.3	112±4.22	118±9.84
Oxalate ^b Fe	4.01±0.82	3.88±0.57	3.79±0.48	3.88±0.52	4.15±0.37	3.96±0.41	3.84±0.16	4.02±0.35
Mehlich 1 P	1.92±0.51	1.87±0.31	2.01±0.31	1.89±0.32	1.73±0.22	1.92±0.14	1.84±0.20	1.86±0.24
Mehlich 1 Al	119±10.2	121±11.9	116±12.4	118±12.7	117±14.0	118±9.35	75.8±6.98	78.3±7.05
Mehlich 1 Fe	2.62±0.62	2.51±0.34	2.66±0.51	2.54±0.38	2.82±0.33	2.71±0.29	2.48±0.31	2.56±0.32
PSI ^c	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

Values for all measurements (except pH, EC, % Solids and PSI values) are expressed in g kg⁻¹. Numbers are mean values (oven dry basis) of three replicates ± one standard deviation.

^a Electrical conductivity.

^b Oxalate (200 mM) extractant was used in determination.

^c Phosphorus saturation index = $[P_{ox}]/[(Al_{ox} + Fe_{ox})]$, where P_{ox} , Al_{ox} , and Fe_{ox} are oxalate (200 mM) extractable P, Al and Fe respectively.

previously (Makris and O'Connor, 2007) contained activated carbon. The greater alum content in the newly-generated Al-WTR samples may explain the lower pH values observed for those samples, compared to previously characterized samples. The average EC value of the Al-WTR (1.64 dS m⁻¹) was well below the critical value (4.0 dS m⁻¹) for salt-sensitive crops (Brady and Weil, 2002). Total P and Fe values, irrespective of the initial Al-WTR age, were typical of WTRs (0.3 to 4.0, and 0.9 to 6.4 g kg⁻¹ respectively, Dayton et al., 2003). Total Al values ranged from 135 g Al kg⁻¹ (“1y” and “2y” old samples) to 156 g Al kg⁻¹ (newly-generated samples). Consistent with the greater alum load added to purify fresh water at the Bradenton water treatment plant in recent times, the total Al concentration of the newly generated samples were greater than the values reported previously for Bradenton Al-WTR (~90–130 g Al kg⁻¹; Makris, 2004; Agyin-Birikorang, 2006), but were within normal ranges reported by others (15–177 g Al kg⁻¹; Dayton et al., 2003). Oxalate (200 mM) extractable Al, Fe, and P values were ~80–90% of the total Al and P concentrations, suggesting an amorphous nature of the Al-WTR, irrespective of the initial WTR age. Gallimore et al. (1999), Dayton et al. (2003), and Dayton and Basta (2005) concluded that the amorphous (200 mM oxalate extractable Al), rather than the total Al content determines Al-WTR effectiveness in reducing runoff P. The low PSI value (~0.02) suggests that the Al-WTR has high P sorption capacity. The PSI is a measure of the degree to which P is potentially bound with Fe and Al. Thus, PSI values < 1 suggest excess Fe and Al for binding of P (little available P), whereas values > 1 suggest available P beyond that associated with Fe and Al precipitates (Elliott et al., 2002).

3.2. Extractable aluminum forms in Al-WTR samples

We utilized four Al extraction procedures [total-, oxalate (200 and 5 mM), and Mehlich 1 extractants] to assess extractable Al forms in the various Al-WTR samples of different ages (freshly-generated- to 2y old Al-WTR samples). No significant

differences in total Al concentrations were observed among the various Al-WTR samples, irrespective of the initial approximate age. Although the newly-generated Al-WTR samples (≤8 wk old) had slightly greater absolute total Al concentrations (Table 1), the differences were not statistically significant. The slightly increased total Al concentrations in the newly-generated Al-WTR samples possibly resulted from increased alum [Al₂(SO₄)₃·14H₂O] loads, part of which substituted for activated carbon, during the drinking-water treatment process. The oxalate (200 mM) extractable Al concentrations closely mirrored the trend of the total Al concentrations, showing no significant differences among the Al-WTR samples, irrespective of the initial approximate ages (Table 1). The data suggest that the 200 mM oxalate extractant was sufficiently rigorous to extract all the Al (both reactive and unreactive forms) contained in the Al-WTR samples.

Mehlich 1 extractant was also used to assess Al extractability in the Al-WTR samples. Mehlich 1 is commonly used in Florida to measure soil test P and other metals in soils. Similarly to the trends of the total and oxalate (200 mM)-extractable Al concentrations of the Al-WTR samples, no significant differences were observed in the Mehlich 1 extractable Al concentrations among the various Al-WTR samples, irrespective of the initial approximate age (Table 1).

Only the oxalate (5 mM) extractable Al concentrations showed significant differences among the various Al-WTR samples, and reflected an aging effect on Al extractability. Some researchers have utilized oxalate (5 mM) extractant to quantify the most reactive Al forms in Al-WTR samples (Makris, 2004; Agyin-Birikorang, 2006). The freshly-generated-, and 2-wk old Al-WTR samples had the greatest oxalate (5 mM) extractable Al concentrations (~82 g Al kg⁻¹ and ~78 g Al kg⁻¹, respectively) (Fig. 1). The oxalate (5 mM) extractable Al concentrations decreased with age of the Al-WTR (Fig. 1), suggesting that the freshly-generated Al-WTR was the most reactive form, and that the reactivity decreased with Al-WTR

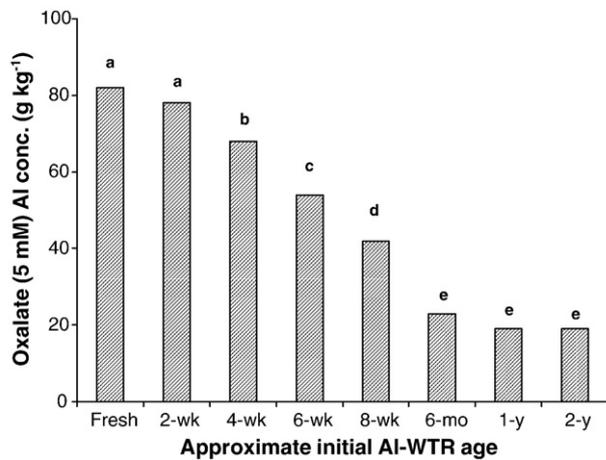


Fig. 1 – Oxalate (5 mM) extractable Al concentrations of the Al-WTR samples as a function of the initial approximate age (before the samples were thermally incubated). Treatments having the same letter are not different by the Tukey multiple comparison at significance level (α) of 0.05.

age. The oxalate (5mM) extractable Al concentrations of the “older” (≥ 6 mo old) samples were statistically similar, although the ‘6mo old’ samples had greater absolute values than the “1y” and “2y” old samples. The data suggest an exponential reduction in the reactivity of Al-WTR with age, showing minimal decreases in oxalate (5mM) extractable Al concentration as the Al-WTR is field dried beyond 6mo (Fig. 1).

3.3. Changes in extractable aluminum forms with aging time

3.3.1. Moisture-controlled thermally incubated samples

No significant changes with time occurred in total, oxalate (200mM)-, and Mehlich 1-extractable Al concentrations of the thermally incubated Al-WTR samples, irrespective of the initial approximate age (data not presented). However, significant time effects of the thermal incubation were observed with the milder (5mM) oxalate extractant. For the freshly-generated Al-WTR samples, significant reductions in 5mM oxalate extractable Al occurred 2wk after thermal incubation, and the reduction in Al concentration continued to be significant until 16wk of thermal incubation (Fig. 2a). Time series analysis confirmed that an equilibrium 5mM oxalate extractable Al concentration was achieved after 16wk of thermal incubation. Thus, at least 16wk of thermal incubation was required to stabilize freshly-generated Al-WTRs. Similar time-effect trends were observed in the 5mM oxalate extractable Al concentrations of the ‘2-wk old’- (data not presented) to “8wk old” thermally incubated Al-WTR samples (Fig. 2b).

The “older” (≥ 6 mo) Al-WTR samples also showed significant decreases in 5mM oxalate extractable Al from the Al-WTR with thermal incubation time (≥ 6 wk of thermal incubation). Oxalate (5mM) extractable Al concentrations of the ~6 mo old samples stabilized after 10wk of thermal incubation (Fig. 2c). As expected, 5mM oxalate extractable Al concentration of the “1y”- and “2y”-old Al-WTR samples stabilized in the shortest thermal incubation time (~6 wk) (Fig. 2d).

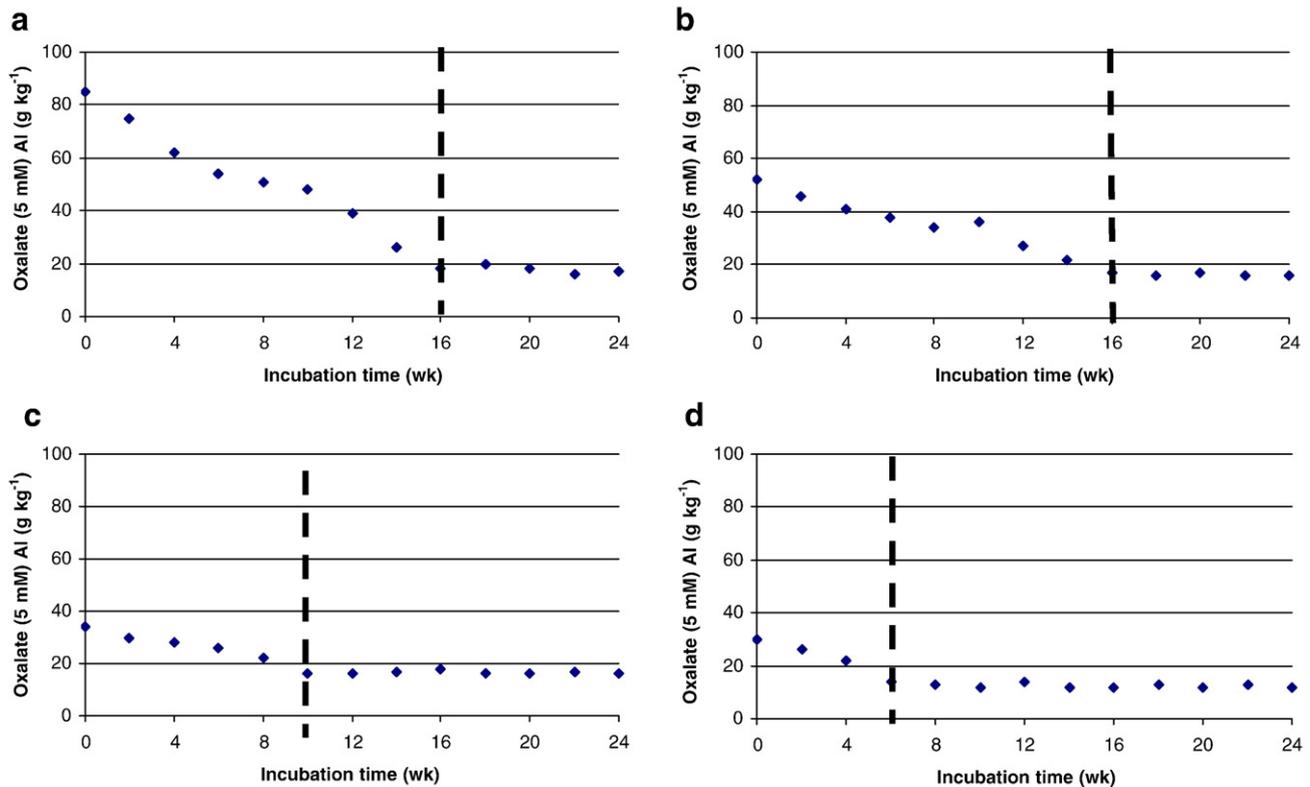


Fig. 2 – Changes in oxalate (5 mM) extractable Al concentrations of the (a) ‘freshly-generated’-, (b) ‘8-wk old’-, (c) ‘6-mo old’-, (d) 2-y old Al-WTR samples as function of time (moisture controlled thermal incubation). Vertical (dash) line indicates the apparent time required for the 5 mM oxalate extractable Al concentration to stabilize.

Data from the thermal incubation study suggest that the Al reactivity of Al-WTRs decreases with time. Makris (2004) showed significant structural changes in a similar Al-WTR after 6mo of thermal incubation at 70°C, which reduced the specific surface of the material. Specific surface positively correlates with reactivity of soil minerals (Taubaso et al., 2004) and soil particles (Brady and Weil, 2002; Yukselen and Kaya, 2006). Thus, reduction in 5mM oxalate extractable Al as a function of thermal incubation time can be attributed to (possible) structural changes of the Al-WTR particles, resulting in decreased specific surface, and reduced reactivity.

3.3.2. Incubated Al-WTR samples without moisture-control
Similarly to the moisture-controlled thermally incubated Al-WTR samples, no significant time effects were observed on the total, oxalate (200 mM), and Mehlich 1-extractable Al concentrations of samples incubated without moisture control (data not presented). Only the oxalate (5mM) extractable Al concentrations significantly decreased as a function of thermal incubation time. A significant reduction in oxalate (5mM) extractable Al concentrations of the freshly-generated Al-WTR samples occurred after 2wk of thermal incubation, and extractable Al concentrations continued to decline with time (Fig. 3a). Time series analysis suggests that an equilibrium oxalate (5mM) extractable Al concentration was reached after ~6 wk of thermal incubation (without moisture control) of the freshly-generated Al-WTR samples (Fig. 3a). The moisture content of the newly generated Al-WTR samples (≤ 8 wk old samples) greatly decreased after 2 wk of thermal incubation

(data not presented). The drier conditions possibly slowed chemical reactions in the Al-WTR, and resulted in similar changes in oxalate (5mM) extractable Al concentrations as observed in the “6mo old” samples (Fig. 3c). Consistent with the observations of the moisture-controlled thermal incubation method, oxalate (5mM) extractable Al concentrations of the “1y” and “2y” old Al-WTR samples incubated without moisture control decreased with time, but only up to 2wk of thermal incubation (Fig. 3d).

3.4. Artificial versus field aging of Al-WTR samples

Trends in oxalate (5mM) extractable Al concentrations obtained from the freshly-generated Al-WTR samples aged through moisture-controlled thermal incubation closely mirrored those measured in the thermally incubated freshly-generated Al-WTR samples without moisture control. The moisture controlled, thermally incubated Al-WTR samples appeared to stabilize at 16wk (Fig. 2a), whereas the freshly-generated samples incubated without moisture control apparently reached equilibrium about 6wk after initiation of incubation (Fig. 3a). When the data generated from time zero until the apparent ‘stabilized’ times of the two incubation methods (i.e., 16wk for thermal incubation with moisture control, and 6wk for incubation without moisture control) were statistically analyzed, a strong ($r \sim 0.96$) and highly significant ($p < 0.001$) correlation was observed between the two incubation methods (Fig. 4). The data suggest that the thermal incubation without moisture control did not result in

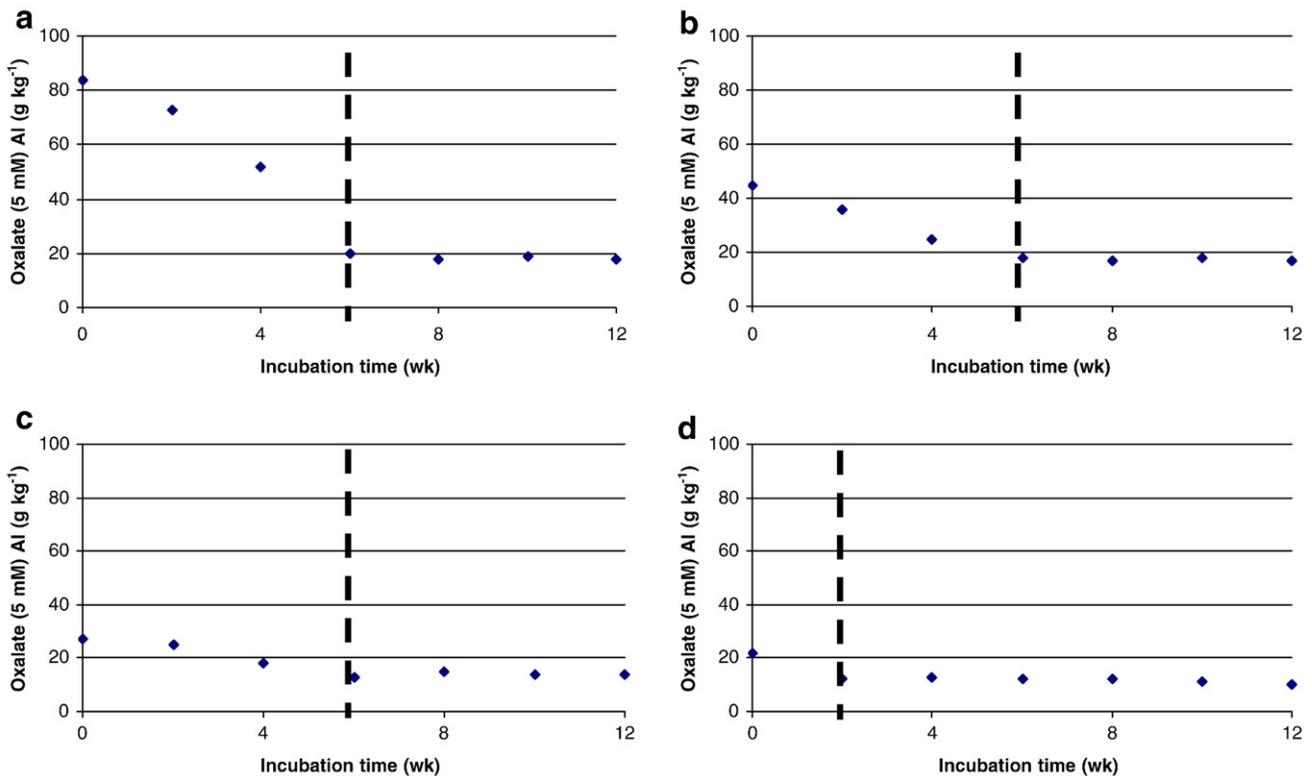


Fig. 3—Changes in oxalate (5 mM) extractable Al concentrations of the (a) ‘freshly-generated’-, (b) ‘8-wk old’-, (c) ‘6-mo old’-, (d) 2-y old Al-WTR samples as function of time (thermal incubation without moisture control). Vertical (dash) line indicates the apparent time required for the 5 mM oxalate extractable Al concentration to stabilize.

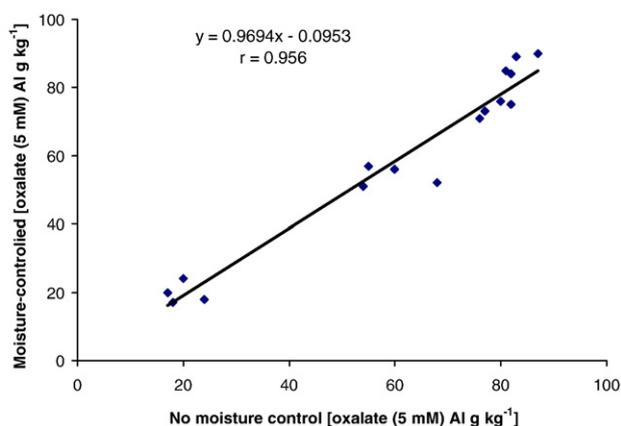


Fig. 4 – Relationship between oxalate (5 mM) extractable Al concentrations of the Al-WTR samples thermally incubated either with or without moisture control. Measurements were taken from time zero to apparent equilibrium.

the production of ‘artifacts’, and that given time, the slower moisture controlled thermal incubation is ultimately equally as effective as thermal incubation without moisture control.

To determine how the apparent equilibration time of the artificial (thermal) aging translates to natural (field) aging of the Al-WTR, we statistically analyzed the oxalate (5mM) extractable Al concentration values of the thermally incubated freshly-generated Al-WTR samples (without moisture control), from time zero to the apparent equilibration time, together with the initial oxalate (5mM) extractable Al concentrations of the Al-WTR samples of various ages. A strong ($r \sim 0.76$) and highly significant ($p < 0.001$) correlation was observed between the ‘stabilized’ artificially aged freshly-generated Al-WTR and the ‘6mo old’ field aged Al-WTR samples (Fig. 5). Time series analysis suggested that oxalate (5mM) extractable Al concentrations of the ‘stabilized’ artificially aged freshly-generated Al-WTR samples were $\sim 20 \text{ g Al kg}^{-1}$ (Figs. 2a and 3a), whereas the initial oxalate (5mM) extractable Al concentrations of the ‘6mo old’ field dried samples were $\sim 23 \text{ g Al kg}^{-1}$ (Fig. 1). Data analysis

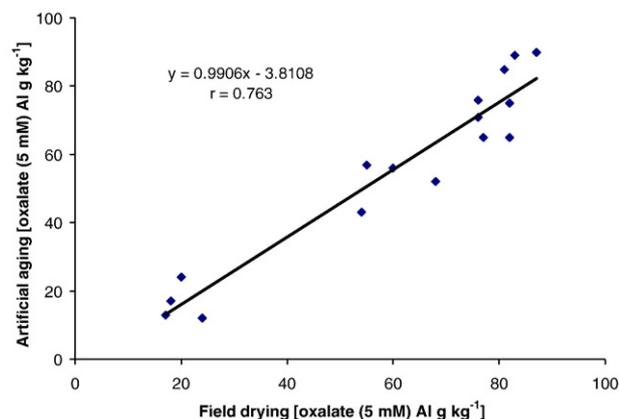


Fig. 5 – Relationship between oxalate (5 mM) extractable Al concentrations of the thermally incubated (without moisture control) freshly-generated Al-WTR samples (measurements were taken until time to apparent equilibrium) and samples field dried for up to 6 mo.

using t-test (PROC TTEST) procedure of the SAS software (SAS Institute, 2002) suggests that the ‘stabilized’ artificially aged freshly-generated Al-WTR and the ‘6mo old’ Al-WTR samples were similar. Thus, at least 6mo of field drying was reasonable for Al-WTR to stabilize.

3.5. Aluminum concentrations of supernatant liquid of Al-WTRs

Supernatant liquid was obtained from the freshly-generated-, 2 wk old-, and 4wk old Al-WTR samples. The total Al concentrations of the Al-WTR samples (measured before thermal incubation) increased with initial approximate age of the Al-WTR samples, from $\sim 2.0 \text{ mg L}^{-1}$ to $\sim 2.6 \text{ mg L}^{-1}$ (Table 2). Similarly, total dissolved Al concentrations of the supernatant liquid increased (from $\sim 1.8 \text{ mg L}^{-1}$ and $\sim 2.4 \text{ mg L}^{-1}$) with the initial approximate age of the Al-WTR (Table 2). The total Al concentrations were within values ($2.03\text{--}2.96 \text{ mg L}^{-1}$) reported for effluent collected from some water treatment plants where aluminum-based coagulants are used (Srinivasan et al., 1999; Maleki et al., 2005), but exceeded the EPA drinking water standard of $50 \mu\text{g Al L}^{-1}$ (Dezuane, 1997). Percent solids of the freshly generated- to 4 wk old Al-WTR samples increased from $\sim 2\%$ to $\sim 27\%$ (Table 1), suggesting that as the samples aged, “native” moisture contents decreased and Al became more concentrated in the supernatant liquid. During the moisture-controlled thermal incubation, distilled deionized (DDI) water was added to the Al-WTR samples throughout the incubation period to maintain the initial moisture content of the samples. Consequently, similar total- and total dissolved Al concentrations were observed in the supernatant liquid samples collected throughout the incubation period (data not presented). The data suggest that much of the Al concentration of the Al-WTR occurred in the sediments rather than the supernatant liquid. No supernatant samples were obtained from the Al-WTR samples thermally incubated without moisture control (>2 wk of thermal incubation) because the Al-WTR samples dried up after 2wk of thermal incubation. The pH of the supernatant liquid of Al-WTR samples was ~ 5.1 . At this pH value, Al speciation is likely dominated by hydrolysis species of Al (Lindsay, 1979; Sloan et al., 1995; Lindsay and Walthall, 1996; Vance et al., 1996), and other organic-complexed Al forms

Table 2 – Aluminum forms and concentrations in the supernatant liquid of the Al-WTR samples measured at time zero

WTR Age ^a	Total Al	Total dissolved Al	Colloidal Al
Fresh	2.03 ± 0.35	1.84 ± 0.23	0.19 ± 0.04
2 wk old	2.24 ± 0.82	2.16 ± 0.69	0.08 ± 0.03
4 wk old	2.62 ± 0.74	2.41 ± 0.20	0.21 ± 0.06
6 wk old	nd ^b	nd ^b	nd ^b
8 wk old	nd ^b	nd ^b	nd ^b
6 mo old	nd ^b	nd ^b	nd ^b
1 y old	nd ^b	nd ^b	nd ^b
2 y old	nd ^b	nd ^b	nd ^b

Numbers are mean values of 3 samples \pm one standard deviation. All concentrations are expressed in mg L^{-1} .

^a Initial approximate age of Al-WTR samples.

^b Not Determined (No supernatant).

(Dong et al., 1995; Lindsay and Walthall, 1996; Vance et al., 1996; Fest et al., 2007), rather than free Al^{3+} . Thus there is little fear that the supernatant liquid of the freshly-generated Al-WTR will cause serious ecological risks.

4. Summary and conclusions

A laboratory incubation study was conducted to determine the concentrations of extractable forms of Al in Al-WTR as a function of WTR “age”, and the time required for freshly generated Al-WTR to stabilize. The Al-WTR samples were thermally incubated at 52 °C either with or without moisture control for ≤ 24 wk. Freshly-generated Al-WTR samples were potentially more reactive (greater 5mM oxalate extractable Al concentration) than dewatered Al-WTR samples stockpiled for ≥ 6 mo. Aluminum reactivity of the freshly-generated Al-WTR decreased with time. At least 6wk of thermal incubation, without moisture control, (corresponding to ≥ 6 mo of field drying) was required to stabilize the reactive Al (5mM oxalate extractable-Al) concentration of the Al-WTR. Although no adverse Al-WTR effects have been reported on plants and grazing animals (apparently because of low availability of free Al^{3+} in Al-WTR) land application of freshly-generated Al-WTRs (at least, those with similar physicochemical characteristics as the one utilized for the study) should be avoided.

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