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4 **Insights into the Mechanisms of Mercury Sorption onto Aluminum Based**
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6 **Drinking Water Treatment Residuals**
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Capsule: This paper reports on mechanistic sorption studies of mercury designed to add value to a readily available and abundant drinking water treatment residuals (WTR).

Abstract

Several studies have demonstrated the ability of drinking water treatment residuals (WTRs) to efficiently sorb metal cations from aqueous solutions. Reported results have stimulated interest on the potential use of WTRs as sorbent for metal removal from contaminated aqueous effluents as well as in metal immobilization in contaminated soils. However, knowledge on mechanisms of metal sorption by WTRs remains very limited and data on the long-term stability of formed metal-WTR complexes as a function of changing key environmental parameters are lacking. In this study, chemical selective sequential extraction (SSE), scanning electron microscopy combined with X-ray energy dispersive spectrometer (SEM-EDS), and X-ray photoelectron spectroscopy (XPS) were used to gain insight into the different mechanisms of mercury (Hg) binding to Aluminum based WTR (Al-WTRs). Results from sorption studies show that a significant portion of Hg becomes incorporated in the operationally defined residual fraction of Al-WTRs, and therefore, not prone to dissolution and mobility. The results of solid phase analyses suggested that Hg immobilization by Al-WTR occurs largely through its binding to oxygen donor atoms of mineral ligands driven by a combination of electrostatic forces and covalent bonding.

Keywords: WTR, Mercury, Sorption mechanisms, Solid phase analysis

Introduction

Past and current releases of mercury (Hg) from anthropogenic activities continue to raise concerns due to the well documented adverse effects of this metal on both human health and ecosystem functions. Lately, soil remediation technologies based on *in situ* immobilization of metals have regained heightened attention because of ease of application and relatively low costs. Accordingly, several sorbents are being tested for their abilities to immobilize metals within the contaminated soils. Overall, these studies have defined ideal sorbents for metal cation immobilization as fine particles, with large specific surface areas (SSA) and containing sulfur (S), nitrogen (N) and oxygen (O) as electron donors[1, 2]. The ultimate goal of this study is to elucidate the potential role of drinking water treatment residuals (WTRs) as sorbent for the immobilization of metal cations in contaminated soils. However, the focus of this paper is limited to the understanding of the mechanisms of Hg sorption by aluminum based WTRs, to help predict the stability of formed metal-WTR complexes if formed within treated soils. In fact, WTRs have been used as sorbent for the immobilization of several pollutants including both negatively and positively charged ions [3-7]. WTRs are produced in abundance worldwide during drinking water treatment processes, and in the United States alone, >2 million metric tons of WTRs are produced daily[8]. However, large quantities of these produced WTRs are simply discarded in landfills, stored in onsite lagoons, or discharged into waterways[9]. We believe that one way to add value to this abundant and readily available waste material is to take advantage of its physicochemical reactivity and high sorption capacity for a wide variety of inorganic pollutants.

Research on the potential use of WTRs as cost-effective sorbent focused initially on the immobilization of oxyanions such as PO_4^{3-} , AsO_4^{3-} , SeO_4^{2-} [4, 7, 10]. However, recent studies point to the ability of WTRs to also immobilize metal cations [5, 6]. Our own preliminary investigations showed that aluminum based WTRs (*referred to herein as Al-WTRs*) can efficiently sorb Hg from aqueous solutions [6], which can be seen as an indication of the ability to potentially immobilize Hg from soil water. Prior to considering Al-WTRs as amendment for remediation of Hg contaminated soils, current knowledge gaps on the mechanisms of Hg sorption onto Al-WTR needs to be addressed to help predict the stability of formed Hg-Al-WTR complexes under changing soil's key parameters such as pH, dissolved organic carbon, and redox potential.

In this study, laboratory experiments were conducted to gain insight into the mechanisms of Hg binding to Al-WTRs using a combination of chemical fractionation and spectroscopic methods.

Materials and Methods

Collection and characterization of used Al-WTR sample. The Al-WTR used in this study was collected from the Manatee County Drinking Water Treatment Plant in Bradenton, Florida, USA. The pH, cation exchange capacity (CEC), organic carbon (OC) content, and elemental composition of this Al-WTR have been published elsewhere [4]. The specific surface area (SSA) was determined on both air-dried non-spiked (control) and Hg-spiked Al-WTRs using the Brunauer-Emmett-Teller N_2 adsorption method at 77 K (BET- N_2) and the CO_2 adsorption method at 273 K (Quantachrome Autosorb-1 apparatus, Quantachrome Corp). BET- N_2 and CO_2 were both used in the determination of SSA to allow for the assessment of

adsorption potential limited to surface sites and that of both surface and internal micropore sites, respectively.

Preparation of Hg-spiked AI-WTR samples. Hg spiked AI-WTR samples were prepared by using a flooding technique followed by wet and dry cycles. Briefly, a known amount of AI-WTR was brought into contact with a solution of HgCl_2 in a 1:4 ratio (mass/volume). For these Hg sorption experiments, two sets of AI-WTR samples prepared at different times were spiked using the flooding approach.

For the first set of Hg-spiked AI-WTR samples, an acidic aqueous solution of HgCl_2 containing 1% concentrated HNO_3 was added to the solid phase AI-WTR to produce a total Hg concentration >20000 mg/kg. This high concentration was selected initially to facilitate detection with solid phase analytical methods. The Hg spiking experiments were conducted in triplicates and Hg-AI-WTR mixtures left to equilibrate for an initial period of 7 days in closed containers placed in a fume hood. At the end of the seven days, the lids of the containers were removed and the samples were allowed to dry at room temperature in the fume hood. Following this initial step, a series of flooding (wet) and drying (dry) cycles were conducted, except that this time, deionized water containing no Hg was added to pre-dried AI-WTR samples. This process was designed to facilitate the incorporation of Hg into the pores of AI-WTRs, and was performed for a period of 4 months. Aliquots from this first set of samples were used for measurements of changes in micropore volumes before and after Hg spiking, the chemical determination of Hg distribution among the different geochemical fractions of AI-WTR, and solid phase analyses. The remaining Hg spiked samples were left to age at room temperature and in the fume hood for 4 years.

The second set of Hg-spiked AI-WTR samples were prepared 4 years later. In this case, Hg as HgCl_2 was added to the AI-WTRs as described earlier, but to produce a lesser final total-Hg concentration of about 3000 mg/kg. This concentration reduction was driven by concerns raised with regard to the handling of samples with Hg levels >2 g/kg during solid phase

analyses. The Hg incorporation process was similar to the one described above and the results presented for this second set of samples are based on 4-month old samples.

In summary, the Hg-spiking experiments resulted into 3 different types of AI-WTR samples. First, a 4-month old Hg-spiked AI-WTR with a total Hg (THg) concentration >20000 mg/kg. Second, a 4-year old Hg-spiked AI-WTR with total Hg concentration >20000 mg/kg. Finally, and third, a 4-month old Hg-spiked AI-WTR with a THg concentration >3000 mg/kg.

Determination of Hg concentrations in AI-WTR samples. After the completion of the above wet-dry cycles, aliquots of the dry and well homogenized Hg-spiked AI-WTR samples as well as samples of the non-spiked AI-WTR were used to determine THg concentrations following samples hot acid digestion. Briefly, 5 ml of aqua regia (mixture of concentrated HNO₃ and HCl) and 5 ml of hydrofluoric acid (HF) were added to ~0.5 g of dried AI-WTR sample. Hot digestion was performed overnight at 110°C in capped Teflon® vessels; upon cooling, digested samples were diluted to 50 ml with a saturated solution of boric acid to dissolve any formed fluorides. Next, produced digestates were analyzed for THg concentrations using the SnCl₂-reduction technique and detection by cold vapor atomic fluorescence spectrometry (CV-AFS) as described in US-EPA Method 1631[11]. Liquid extracts with excessively high THg concentrations were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) as described in our earlier publications [6, 12, 13]. QA/QC criteria were met by running digestion reagent blanks in parallel and analysis of Hg standard solutions. Details on analytical methods used have been published earlier [6, 12, 13].

Chemical fractionation of Hg bound to AI-WTR by selective sequential extraction (SSE) procedures. Two different SSE procedures were used in this study. Initial speciation studies on the 4-month old Hg spiked AI-WTR (THg>20000 mg/kg) were completed using the method published by Tessier et al[14]. Four years later, the same samples and the newly prepared (4-month old) AI-WTR samples spiked with Hg to a final concentration of about 3000 mg/kg were fractionated using the method proposed by Bloom et al[15]. This change in Hg

speciation method was intentional, as to take advantage of the capacity of the SSE procedure proposed by Bloom et al. to separate Hg into biogeochemical fractions that can be related to Hg methylation potentials in soil/sediment[15]. Therefore, this latter approach allows insight into the potential bioavailability of sorbed Hg instead of simple Hg association with specific geochemical fractions[14].

For the SSE procedure adapted from Tessier et al[14], the first Hg fraction (F1), was obtained by equilibrating the Hg-spiked Al-WTR samples with Nanopure[®] water for a specific time, followed by centrifugation (using a Beckman J2-HS, Tritech Field Eng. Inc.) at 10, 000 rpm for 30 min. The supernatant was then removed with a pipette. The residue was rinsed with Nanopure[®] water and the mixture centrifuged again at 10,000 rpm for 30 min. This rinsing step was repeated and the supernatants carefully withdrawn and added to the first supernatant. If this F1 fraction is commonly defined as the water extractable metals, in this specific study, the water extract solubilized primarily excess Hg that was not either electrostatically nor chemio-sorbed onto Al-WTR. Next, the combined supernatants were filtered (0.45 µm) and analyzed as described earlier for THg concentrations by either ICP-AES or CV-AFS depending on the concentrations of Hg in harvested supernatants. The solid Al-WTR residue was then used in the next extraction step. Besides differences in the chemicals used in each extraction step, the overall procedure remained the same as described above for all steps. The second fraction (F2) was extracted by using a 1M solution of MgCl₂ at pH 7 and corresponds to the easily exchangeable Hg fraction. In the third fraction (F3), Hg bound to carbonate minerals was targeted and was dissolved using a 1M sodium acetate (NaOAc) solution (pH adjusted to 5.0 with acetic acid). The fourth fraction (F4) was obtained by reduction of the oxides of Mn and Fe and subsequent dissolution of previously sorbed Hg using a 0.04M solution of NH₂OH.HCl in a 25% acetic acid (v/v) acetic acid. In this case, the extraction was conducted in a water bath for 6 hours at 96±3°C, with occasional agitation by hand. Upon cooling, the mixture was centrifuged,

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4 rinsed, and the supernatant filtered as described in F1. Fraction 5 (F5) corresponds to Hg bound
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6 to organic matter and was extracted with a 30% H₂O₂ solution, pH was adjusted to 2 using
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8 0.02M HNO₃. The mixture was heated to 85 ± 2°C in a water bath for 3 hours with intermittent
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10 agitation by hand. An additional 3 mL of 30% H₂O₂ (pH 2) were added and the mixture heated
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12 for an additional 3 hours. Upon cooling, and to prevent the adsorption of extracted Hg onto
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14 oxidized Al-WTRs components, 5 mL of a 3.2M ammonium acetate (NH₄OAc) prepared in a
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16 20% (v/v) HNO₃ solution were added. The sample was then diluted to 20 mL and agitated
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18 continuously for 30 min on an orbital shaker at 200 rpm. These steps were then followed by
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20 centrifugation and filtration as described in F1. The residual fraction (F6) was quantified by
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22 subtracting the sum of Hg obtained in fractions F1 to F5 from the amount of Hg obtained in the
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24 total Hg analysis. All extractions were carried out in triplicates. The concentrations of dissolved
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26 Al, Fe and Si were also determined in the supernatant of each extracted Hg fraction.
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32 The second set of Al-WTR samples containing a much lower THg concentration was
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34 fractionated using the SSE method adapted from Bloom et al[15]. Briefly, about 0.5 g of Hg-
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36 spiked and dried Al-WTR samples were equilibrated with Nanopure® water and as in the SSE
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38 method described above, Hg fraction 1 (F1) corresponds to water-soluble Hg. However, unlike
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40 in the Tessier et al. SSE procedure[14], from this point on, this method uses different chemicals
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42 or chemical mixtures to solubilize different geochemical Hg-fractions. Fraction 2 (F2) was
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44 dissolved by use of 10 mL of CH₃COOH/HCl (pH=2) and corresponds to Hg present in the
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46 sample primarily as HgO and HgSO₄ species. Fraction 3 (F3) targets Hg bound to humic acids
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48 and is extracted with 10 mL of a 1M KOH solution. Fraction 4 (F4) was extracted by a 12M
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50 HNO₃ solution and corresponds to Hg in amorphous minerals, organo-sulfur, Hg amalgams and
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52 Hg associated with crystalline Fe-Mn oxides. Finally, Fraction 5 (F5) targeting residual/refractory
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54 Hg species, mainly Hg sulfide minerals was determined by difference between THg
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56 concentrations and the sum of Hg concentrations extracted by the above 4 fractions (F1 through
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4 F4). Therefore, the residual Al-WTRs after F4-extraction were not acid digested, but rinsed
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6 thoroughly with DI water, air-dried, and then analyzed by X-ray photoelectron spectroscopy
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8 (XPS) to determine the potential sites of Hg binding in the refractory fraction (F5).
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11 ***Solid phase analysis of Al-WTR.*** Al-WTR samples were first pulverized using a ball
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13 mill grinder. The morphology and elemental composition were determined using a scanning
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15 electron microscopy equipped with an X-ray energy dispersive spectrometer (SEM-EDS; JSM-
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17 6330F field emission scanning electron microscope). Near-surface analysis of the Al-WTR
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19 samples including the residual fractions saved from SSE procedures was performed by X-ray
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21 photoelectron spectroscopy (XPS) using a Perkin Elmer 5100 XPS System with AugerScan
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23 software. For the latter, the sample would be loaded into the sample chamber on double-sided
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25 copper tape (3M) and pumped down to a vacuum of 10^{-8} Torr. Samples were then radiated
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27 using photons of Mg K α with energy of 1253.6 eV. The survey scans were recorded using a
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29 fixed pass energy of 89.45 eV and narrow scan spectra of the Hg_{4f}, Al_{2p}, O_{1s}, Cl_{2p3} and C_{1s} levels
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31 were recorded using a fixed pass energy of 35.75 eV and a range of 10-30 swaps. The
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33 recorded lines were fitted using a curve-fitting program with Gaussian-Lorentzian peak shape.
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35 Once the peaks were fitted, each spectrum was calibrated to the binding energy of C1s
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37 photoelectrons at 284.6 eV (calibration varied between samples from 2-2.75 eV). The binding
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39 energy (BE eV) of each fitted and calibrated peak was compared to the NIST XPS database 20,
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41 version 3.5 (<http://srdata.nist.gov/xps/>) for full characterization and speciation of surface-bound
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51 RESULTS AND DISCUSSION

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53 ***Physicochemical characterization of Al-WTR samples.*** As stated earlier, data on
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55 physicochemical characterization and elemental composition of Al-WTR samples have been
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57 published earlier[6]. Briefly, relevant parameters can be summarized as follows. Measured pH
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59 and electrical conductivity were 5.6 and 0.36 dS/m, respectively. The cation exchange capacity
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(45.8 cmol/kg) was higher than values reported for most soils[16], and the macro-elemental composition was similar to those reported in previous Al-WTR studies[17, 18]. The concentrations of trace elements such as As (8.01 mg/kg), Cr (81.1 mg/kg), Hg (0.02 mg/kg), Pb (1.99 mg/kg), and Zn (14.37 mg/kg) were 1 to 3 orders of magnitude lower than regulatory limits for soils. The organic carbon content determined as loss on ignition was 12.7%.

After the completion of the spiking of the Al-WTR samples with Hg solutions and drying process, the determined THg concentrations averaged 24050 mg/kg and 3212 mg/kg for the first and second sets of samples, respectively. These concentrations do not correspond to the maximum adsorption capacity of the studied Al-WTR. The latter (79000 mg/kg) was determined separately and reported elsewhere[6]. Instead, these values correspond simply to Hg loads per mass of sorbent.

Determination of SSA-N₂ and SSA-CO₂ of Al-WTRs before and after Hg sorption.

The SSA-N₂ characterization (BET method) of Al-WTRs before Hg sorption revealed a rather high surface area averaging 48 m²/g. However, the measured SSA-CO₂ (DRK method) was much higher (120 m²/g), suggesting that Al-WTRs have a large internal surface area that is not accounted for by the BET-N₂. Using the first set of Hg spiked Al-WTR samples with a THg concentration of 24050 mg/kg, SSA measurements revealed a significantly lower SSA-N₂ and SSA-CO₂ as compared to those determined in control samples (**Figure 1**).

A further interpretation of CO₂ sorption data was done by use of the grand canonical Monte Carlo simulation model, a technique that allows for the determination of the micropore volume distribution. This model presents the pore structure as a collection of idealized slit-shaped pores with smooth graphitic walls[19]. The most decrease in micropore volume was observed in the 3.98-5.01 Å pore width interval (**Figure 2**), a range within which the diameter of the hydrated divalent Hg cation (4.74 Å) fits well[20]. Overall, these porosity results support the hypothesis that the mechanisms of Hg sorption by Al-WTRs include intra-particle diffusion. The latter could be an important aspect from the remediation viewpoint as it might favor the long-

term stability of Hg trapped within pores. In fact, it has been suggested that molecules diffusing deeper into the micro-pores may never escape from the force field of the walls of such pores[21].

Distribution of Hg among the different and operationally defined geochemical fractions of AI-WTRs. The Hg fractionation results for the first set of AI-WTR samples (4-month old, THg=24050 mg/kg) are presented in Table 1. In addition to Hg data, concentrations of Al, Fe, and Si solubilized during each extraction step are also given. These fractionation results show that up to 82% of sorbed Hg is found in the refractory/residual fraction (F6), an increase from ~5% of 0.02mg Hg/kg present initially in the AI-WTR prior to spiking with HgCl₂. This could be significant since metal fractions corresponding to the residual fraction can be leached only under extreme extraction conditions not commonly found in natural systems. Therefore, such metals are usually not bio-available. Next, Hg bound to organic matter represented up to 9% (Fraction F5), and unlike the residual fraction, this Hg fraction could become bioavailable as organic matter (OM) in soils behaves as electron donors during microbial respiration and become oxidized over time, releasing the previously OM-bound Hg. The other Hg fractions, including Hg bound to (hydr)oxides of Mn and Fe represented <10% of THg concentration. The determination of Al, Fe, and Si in the same supernatants showed that similar to Hg Si was predominantly in the residual fraction (98.6%). In contrast, Al and Fe were prevalent in the fraction dissolved by NH₂OH.HCl, which corresponds to metals bound to (hydr)oxide minerals. The residual fraction contained only 8.4% of the total Fe concentration, but >30% of the total-Al concentration. This is likely an indication of the presence of crystalline minerals containing these elements, but with different degrees of abundance. Overall, this chemical fractionation shows that a significant amount of Hg becomes locked into the residual fraction, and probably bound to the oxygen atoms of silica minerals (>98% of Si in the residual fraction) in addition to Hg that might be present as sulfides and/or bound to other refractory Al and Fe oxide minerals.

Using the SSE-procedure adapted from Bloom et al.[11], the 4-year old (THg=24050 mg/kg) and the second set 4-month old (THg=3212 mg/kg) Hg-spiked AI-WTR samples were fractionated. The results showed that the 4-year-old Hg-spiked AI-WTR had 65.47% of initial THg concentration locked in the residual fraction (F5). In contrast both the 4-month old Hg-spiked AI-WTR (THg=3212 mg/kg) and the non-spiked AI-WTR (control) had only 15.95% and 5.03% of THg, respectively in the residual fraction. This increase from 5.03% in the non-spiked AI-WTR to up to 65.47% with increasing concentrations of Hg used in the loading process seems initially to indicate that Hg incorporation into the residual fraction is concentration-dependent (**Table 2**). However, the control and the 4-month old AI-WTR samples had Hg dominantly associated with the F4 (e.g. Hg bound to amorphous minerals, organo-sulfur compounds, and crystalline oxide minerals). It is possible that the aging process past the 4-month period increases the degree of crystallinity of initially amorphous minerals, making Hg associated to such fractions to become refractory over time once the wet-dry cycles were terminated. These results suggest that over time, Hg loaded to AI-WTR could become part of the operationally defined residual fraction. Accordingly, AI-WTR contact time with the contaminant could be a significant factor[7].

Finally, it can be noted that the strength of the different chemicals used in the 2 SSE methods might influence the levels of Hg solubilized by each fraction. For instance, the use of rather mild chemicals in the approach by Tessier et al. tends to leave behind Hg that is then accounted for in the residual fraction (82.3%), while the method proposed by Bloom et al. solubilizes large amounts of Hg in steps using KOH and 12M HNO₃ prior to reaching the residual fraction (65.47%).

With regard to the use of AI-WTRs in remediation of Hg-contaminated soils, an important observation is the low proportion of water-soluble Hg fraction (F1), followed by the easily exchangeable fraction (F2) (Table 2). In fact, Hg dissolved by these fractions is anticipated to be the most mobile, and thus, potentially of environmental concern. Finally, the KOH solubilized

fraction (F3), which has shown a good correlation with the Hg fraction methylated in soil/sediment ranged from ~20% in Hg-spiked AI-WTR samples to 30% in control samples (Table 2)[15]. This could be of concern if this much Hg remains accessible to soil/sediment Hg-methylating bacteria.

Scanning electron microscopy combined with X-ray energy dispersive spectrometer. SEM images showed that AI-WTR samples are highly heterogeneous mixtures of particles with variable particle sizes (Figure 3A). A closer view shows particles with irregular surfaces and edges (Figure 3B), which could potentially provide these sorbents with highly reactive surface sites for sorption of Hg or other metals. The elemental analysis revealed spectra dominated by Al, O, Si, P, S, Cl, Ca, and Fe (Figures 3C and 3D) as previously reported by others[4,13]. The EDS analysis using a 4-yr old Hg-spiked AI-WTR samples showed a spectrum similar to those reported earlier[6], with a Hg peak in addition to that of the above listed elements (Figure 3D). Based on the presence of oxygen (O) and sulfur (S) in these spectra, and which could act as potential electron donor atoms, a classification which divides metals into type A, type B, and borderline or transition groups[22] can be used to help formulate a hypothesis with regard to the potential chemical binding sites of Hg onto AI-WTR. Briefly, the divalent Hg ion is a “type B” metal ion (equivalent to the soft metal ion in the Pearson system), characterized by high polarizability. For such metal ions, covalent bonding would play an important role in complex formation, and therefore, an electrostatic model alone cannot explain sorption and stability relations involving them[22]. Additionally, a major factor affecting the binding of type B metal ions and the stability of complexes they form is their ability to accept electrons from atom ligands. The trend of electronegativity of ligand donor atoms, and stability of complexes they form with type B metal ions is: $S > I > Br > Cl > N > O > F$. While type B metal ions have the strongest affinity for sulfur donor atoms than type A metal ions (e.g. Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}), they do also form stronger and more stable complexes with N and O donor atoms than do type A metal ions. Therefore, based on the SSE analysis, it appears that in Hg spiked AI-WTR,

chemical bonds could be formed primarily between the added ionic Hg and the prevalent oxygen (O) and sulfur (S) donor atoms present in organic ligands or minerals (Figures 3C and 3D).

X-ray photoelectron Spectroscopy. XPS analyses were conducted on non-spiked Al-WTR's, Hg-spiked Al-WTR, and the residual fractions of Hg-spiked Al-WTRs (4-month old and 4-year old) subjected to the chemical SSE method adapted from Bloom et al[15]. XPS wide-scan surveys revealed that the surface of Al-WTR particles prior to chemical fractionation and Hg spiking were mainly composed of C, O, and Al. Nitrogen (N) was barely detectable (**Figure 4A**). A similar composition was observed on Hg-spiked samples (**Figure 4B**). However, on the residual Al-WTR fractions obtained after SSE, in addition to C and O, Si became detectable, suggesting that Si in Al-WTRs is present in layers >10 nm deep under the surface and not easily detectable with this technique (**Figure 4C**). In contrast to the EDS spectra (**Figure 3B**), these XPS spectra do not show sulfur (S). The absence of a Sulfur (S) signal could be due to a limitation of the XPS technique. While X-rays in XPS can penetrate up to 1 μm into the sample, the useful e-signals are only obtained from the first 1-30 monolayers (i.e., 0.3-10 nm). Therefore, S may be simply found in layers beyond the reach of this technique. The absence of an Al peak in the residual fractions of Hg-spiked Al-WTR can be explained by either (i) the removal of Al-oxide fraction during the SSE, (ii) location of amorphous Al-oxides in deeper layers, or (iii) shadowing from other elements that are bound to Al and covering the surface of Al-oxides, such as Hg. In general, apparent differences in the recorded elemental composition of WTR's surfaces could be a consequence of (i) limited deeper layer screening, (ii) changes in the composition of the WTR's surfaces after the chemical selective sequential extraction, and (iii) the chemical interactions between elements present in the sample.

Narrow scan spectra from the residual fractions of the 4-month and 4-year Al-WTR samples showed Hg peaks, confirming its sorption. Characterization of the Hg_{4f} peaks for the residual fraction of 4-month old Hg-spiked Al-WTRs showed two major species (**Figure 5A**),

Hg(H₂NC(O)NHC(O)NH₂)₂Cl₂ at 101.31 eV (57.2%) and HgO at 105.04 eV (42.8%). The Hg_{4f} peak of the 4-year old Hg-spiked Al-WTR (**Figure 5B**) was deconvoluted into two major peaks at 100.80 eV (60.2%) and 105.12 eV (39.8%), both corresponding to Hg-O bonds such in HgO species. The presence of Hg-O bond types in both samples and a higher abundance of HgO species in the residual fraction of the 4-year old Hg-spiked Al-WTRs confirmed that Hg added initially as HgCl₂ gets incorporated into the residual fraction, and over time, Hg forms chemical bonds with oxygen containing ligands. High-resolution scans of O_{1s} were rather wide, giving some indication of a possible multiplicity of adsorption sites. Deconvolution of O_{1s} peak for the residual fraction of 4-month old Hg-spiked Al-WTRs only showed peaks for SiO₂, and no-matching peaks for HgO (**Figure 5D**). A non-matching peak in the 4-month old sample could be the result of binding energy (BE) shift from the anticipated 529.91 eV as reported for HgO in the National Institute of Standards and Technology (NIST) database[23], giving rise to a new BE value that is not characteristic of HgO. Such BE shifts can be explained by (i) changes in the oxidation state of the sample, and (ii) collisions from electrons in the inner layers of the samples. The O_{1s} peak for the residual fraction of 4-year old Hg-spiked Al-WTR was deconvoluted in two components at 532.5 eV, and 530.86 eV, corresponding to O atoms in SiO₂ and HgO species, respectively (**Figure 5C**).

Because the residual fraction of Hg-spiked Al-WTRs has a higher concentration of Si and Hg than Al (**Table 1**), and XPS analysis revealed Hg-O bonds in the residual fraction of chemically fractionated WTR, one could assume the Hg is forming oxides or chemically binding to SiO_x species.

EXAFS studies by Kim et al[1] on modes of Hg (II) sorption to synthetic and well-characterized γ -alumina (γ -Al₂O₃) indicated that both outer-sphere and inner-sphere monodentate surface complexation could be involved in Hg- γ -alumina sorption. Likewise, results of solid phase analysis suggest that the initial incorporation of Hg to Al-WTR occurs through a combination of outer-sphere and inner-sphere complexation driven by electrostatic

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4 attraction on negatively charged particles[1], but also covalent bonding on Al-WTR mineral
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6 fractions containing O donor atoms.
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10 **CONCLUSION**

13 Understanding the binding mechanisms of Hg onto Al-WTRs is important as it can help
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15 predict the long-term fate of Hg, if Al-WTRs were to be used for in-situ immobilization of Hg in
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17 contaminated soils. The use of chemical and physical analytical techniques showed that a
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19 significant fraction of Hg added to Al-WTRs becomes locked in the operationally defined
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21 residual fraction, and therefore, should not be mobile nor bioavailable under natural
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23 environmental conditions. However, the large Hg fraction associated with the organic fraction of
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25 Al-WTR after the spiking and aging processes is of concern as it could become prone to
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27 methylation by bacteria. It appears that Hg binding and/or incorporation to the residual fraction
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29 of Al-WTR occurs primarily through binding to the oxygen donor atoms of oxide minerals likely
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31 dominated by Al and Si oxides, in addition to electrostatic attraction at the surface of the mineral
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33 lattice. However, specific Hg compounds formed after sorption onto Al-WTR could not be fully
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35 elucidated by use of SSE and XPS analyses. Solid phase analytical techniques such as
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37 extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure
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39 (XANES) may be more appropriate in pinpointing the different bonds between Hg and electron
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41 donor atoms[24, 25] present in the Al-WTR.
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Table 1. Mercury (Hg), aluminum (Al), iron (Fe), and silicon (Si) concentrations and distribution (%) in the operationally defined geochemical fractions of Hg-spiked Al-WTRs, aged for 4 years, and determined using the fractionation method adapted from Tessier et al [14]; fractions **F1-F5** were chemically extracted, while **F6** (residual/refractory fraction) was determined by subtracting the sum of Hg from the above fractions from THg concentration of 24050 mg/kg.

Element	Fractions (F)	Extracting Solution	Concentration mg/kg ^a	% of total
Hg	F1: Water soluble	H ₂ O	146±6	0.60
	F2: Exchangeable	MgCl ₂ , pH7	766±32	3.18
	F3: Carbonate	CH ₃ COONa/CH ₃ COOH, pH5	230±23.1	0.95
	F4: Fe/Mn oxides	NH ₂ OH.HCl/CH ₃ COOH	889.5±150	3.69
	F5: Organic	H ₂ O ₂ /HNO ₃ , pH 2	2162.8±306	8.99
	F6: Residual	-	19855±172	82.3
	Total	-	24050±842	-
Al	F1: Water soluble	H ₂ O	<DL ^b	-
	F2: Exchangeable	MgCl ₂ , pH7	<DL	-
	F3: Carbonate	CH ₃ COONa/CH ₃ COOH, pH5	7056±463	4.14
	F4: Fe/Mn oxides	NH ₂ OH.HCl/CH ₃ COOH	85833±15269	50.37
	F5: Organic	H ₂ O ₂ /HNO ₃ , pH 2	25875±3856	15.18
	F6: Residual	-	51618±17835	30.29
	Total	-	170383±1820	-
Fe	F1: Water soluble	H ₂ O	<DL	-
	F2: Exchangeable	MgCl ₂ , pH7	<DL	-
	F3: Carbonate	CH ₃ COONa/CH ₃ COOH, pH5	100 ± 14	2.67
	F4: Fe/Mn oxides	NH ₂ OH.HCl/CH ₃ COOH	3204± 139	85.06
	F5: Organic	H ₂ O ₂ /HNO ₃ , pH 2	143±10	3.82
	F6: Residual	-	317±239	8.4
	Total	-	3764	-
Si	F1: Water soluble	H ₂ O	<DL	-
	F2: Exchangeable	MgCl ₂ , pH7	<DL	-
	F3: Carbonate	CH ₃ COONa/CH ₃ COOH, pH5	78±8	0.11
	F4: Fe/Mn oxides	NH ₂ OH.HCl/CH ₃ COOH	811±82	1.19
	F5: Organic	H ₂ O ₂ /HNO ₃ , pH 2	44±6	0.06
	Residual	-	66815±1206	98.6
	Total	-	67750±1125	-

^aMean ± one standard deviation; ^bDL = detection limit

Table 2. Distribution (%) of chemical fractions of Hg in non-spiked (THg = 0.02mg/kg) and two different Hg-spiked AI-WTR and aged samples (the 4-month old sample (THg = 3212 mg/kg) and 4-year old sample (THg = 24050 mg/kg)) by the selective sequential extraction method adapted from Bloom et al [15]. Fractions F1-F4 were chemically extracted and F5 (refractory/residual Hg fraction) was determined by subtracting the sum of Hg from the above fractions from THg concentration.

AI-WTR samples	Fractions (F)	Extracting Solution	% THg
Non-spiked AI-WTR (control)	F1: Water soluble	H ₂ O	2.88
	F2: HgO, HgSO ₄	CH ₃ COOH/HCl	1.18
	F3: Humic acids	KOH	30.30
	F4: Crystalline oxides	12M HNO ₃	60.61
	F5: Residual/HgS		5.03
4-month old Hg-spiked AI-WTR	F1: Water soluble	H ₂ O	0.67
	F2: HgO, HgSO ₄	CH ₃ COOH/HCl	3.88
	F3: Humic acids	KOH	22.43
	F4: Crystalline oxides	12M HNO ₃	57.08
	F5: Residual/HgS		15.95
4-year old Hg-spiked AI-WTR	F1: Water soluble	H ₂ O	0.32
	F2: HgO, HgSO ₄	CH ₃ COOH/HCl	0.12
	F3: Humic acids	KOH	20.13
	F4: Crystalline oxides	12M HNO ₃	17.63
	F5: Residual/HgS		65.47

FIGURE CAPTION

Figure 1: Mean specific surface area (SSA) determined by N₂-BET and CO₂-BET using plain Al-WTRs with no mercury (Hg) addition (black bars, THg = 0.02 mg/kg) and 4-year old Hg-spiked Al-WTRs (open bars, THg = 24050 mg/kg). Error bars represent 1SD of 3 replicates. Different letters indicate a significant difference ($\alpha < 0.05$) between SSA measured on Hg spiked and non-spiked Al-WTR samples.

Figure 2: Micropore volume based on pore size distribution of Al-WTRs with no mercury (Hg) addition (black bars, THg = 0.02 mg/kg) and Hg-spiked Al-WTRs (grey bars), with a total-Hg concentration of 24050 mg/kg of Al-WTRs. Triplicate samples ($n=3$) were analyzed.

Figure 3: SEM micrographs and EDS spectra of control (A and C) and aged (4-year old) Hg-spiked Al-WTRs (B and D). The EDS spectra show peaks of relevant elements (e.g. O, S, Al), with Hg peak appearing only on the spiked sample spectrum (see arrow, panel D).

Figure 4: XPS wide scan survey spectrum of (A) non-spiked Al-WTR (THg = 0.02 mg/kg), (B) Hg-spiked Al-WTR, and (C) residual fraction of Hg-spiked Al-WTR obtained after a sequential extraction as described in the text.

Figure 5: X-ray photoelectron spectroscopy spectra of Hg4f in the residual fraction of a 4-month aged Hg-spiked Al-WTR (THg = 3212 mg/kg) and a 4-year aged Hg-spiked Al-WTR (THg = 24050 mg/kg) shown in panel (A) and (B), respectively. In addition, XPS spectra of O1s in the same residual fractions are shown in panel (C) and (D), respectively. These analyses were conducted on air dried left over materials from selective sequential extraction as described in the material and method section.

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5