Nano-Scale Drinking Water Treatment Residuals Affect Arsenic Fractionation and Speciation in Biosolids-Amended Agricultural Soil

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Received: 28 June 2020; Accepted: 24 July 2020; Published: 14 August 2020

Abstract: An incubation experiment was conducted to determine the effects of nanoscale drinking water treatment residuals (nWTRs) on arsenic (As) fractionation and speciation in agricultural soil amended with biosolids. The soils were treated with biosolids of 3% (w/w), along with nWTR application rates of 0, 0.25, 0.50, or 1.00% (w/w). The results revealed that the As adsorption rate increased with increasing the As treatment level from 50 to 800 mg/L. The maximum efficiency of As adsorption was 95%–98% in the soil treated with nWTRs of 1%, while the least As adsorption was 53%–91% in the soil treated with nWTRs of 0.25%. The overall As bioavailability in the biosolids-amended soil followed a descending order of nWTRs treatment: (0%) > 0.25% nWTRs, >0.50% nWTRs, and >1% nWTRs. The addition of nWTRs significantly changed As speciation in biosolids-amended soil. The X-ray absorption near-edge structure spectroscopy (XANES) and MINEQL+4.6 analyses showed that most of As was in a oxidized form of As\(^{5+}\) that likely incorporated in As pentoxide, and thus, with low mobility, bioavailability, and toxicity. This study demonstrated that nWTRs were effective in adsorbing and immobilizing As in biosolids-amended agricultural soils by forming stable As-nWTR surface complexes.

Keywords: Arsenic; bioavailability; biosolids; WTRs; nanoparticles

1. Introduction

Arsenic (As) is a common contaminant in soils and waters. The large environmental input of As has mainly been related to anthropogenic activities including those originated from agricultural land application of fertilizers, pesticides, and/or biosolids (treated sewage-sludge originating from municipal wastewater treatment plants). Thus, As pollution has been recognized as an important matter of concern for worldwide public health [1]. Thus, As remediation technologies have been developed to reduce As contents or limit As bioavailability in the environment [1–4]. Arsenic remediation can be expensive [5] and have application limitations [6,7]. In recent years some “green” remediation techniques have been proposed, and different As-adsorbents including nanomaterials have been evaluated to reduce As bioavailability in soil and water [8–10].
Arsenic presents in different valence states in the environment, including arsenide (As\(^{3-}\)), elemental As (As\(^0\)), arsenite (As\(^{3+}\)), and arsenate (As\(^{5+}\)). The As speciation in soil is highly depending on soil pH and redox potential (Eh). For example, arsenite becomes stable at pH 4–9 \([11,12]\), H\(_2\)AsO\(_4^-\) is dominant at pH 2–7, and HAsO\(_4^{2-}\) is prevailing in alkaline soils \([11,13]\). Arsenite and arsenate are the most dominant species in soils under aerobic conditions, and both are toxic to humans \([13,14]\). Therefore, As toxicity depends not only on the quantity (or the concentration) but also on its speciation. As (III) is generally more toxic to organisms than As (V). As (III) can be biologically transformed to As (V) and thus reduce As toxicity in the environment \([13]\). Arsenic speciation or chemical transformation influences As reactivity, mobility, and bioavailability. Therefore, it is important to determine the chemical behavior of As in agricultural soils or in other contaminated environments such as As ions, complexes, and chelates in soil solution, as well as its amorphous and crystalline forms present in soil \([15]\). In addition, soil microbes play important roles in As methylation, de-methylation, and oxidation/reduction, which bio-transform As into different compounds and their distribution among different environmental components \([16]\). For instance, As sorbs preferably to metal oxides, carbonates, and other clay minerals \([13]\). The As sorption capacity is also dependent on the As physical, chemical, and biological properties and adsorptive ions \([17,18]\).

Nanoscale particles with a diameter of < 100 nm \([19–21]\) have a large surface area, highly porous surface, and large numbers of active adsorbing sites, compared to bulk sized adsorbent materials that made them more significant for As stabilization than micro-sized adsorbents with the same composition and/or under similar soil conditions. Elkhatib et al. \([22]\) recently reported that mechanically-produced nanoscale drinking water treatment residuals (nWTRs) can be used as nanoparticles to sorb and reduce metal bioavailability in soils. Residues of drinking water treatment (WTRs) are a byproduct from drinking water treatment facilities and have been applied to agricultural soil in many countries because its high contents of organic matter and plant nutrients \([23]\). WTRs have been recently considered as green adsorbing materials for controlling phosphorus (P) and heavy metals in agricultural soils. It has been demonstrated that nWTRs greatly influence the soil active adsorbing surface area and significantly increase the soil sorption capacity \([24,25]\).

The objectives of this study were (1) to evaluate the ability of nWTRs for As sorption in agricultural soils, (2) to determine potential effects of nWTRs on As-fractionation and speciation in the soil amended with biosolids, and (3) to characterize treatment effects on As speciation changes using both nondestructive X-ray absorption near-edge structure spectroscopy (XANES) and a chemical equilibrium calculation Mineral-Equilibrium Model (MINEQL+ model).

2. Materials and Methods

2.1. Soil, Biosolids and nWTRs

Calcareous sandy loam soil (Typic haplocalcids) was collected from agricultural land in Borg Al-Arab, Alexandria Governorate, Egypt (30°50′56″ N; 29°36′42″ E). The surface soils (0–0.3 m depth) were collected, air-dried, ground, and then sieved (<2 mm) Municipal biosolids (treated sludge) were obtained from the General Organization Sanitary (GOS) of Alexandria City (Station 9). They were air-dried, ground, and then sieved (<2 mm) before use \([26]\). Drinking water treatment residuals (WTRs) were collected from Al-Siouf drinking water purification plant in Alexandria. WTRs were also air-dried, ground, and sieved (<2 mm) prior to use according to Makris and Harris \([26]\). Then, WTRs were mechanically milled into nanoscale particles using the method according to Elkhatib et al. \([22]\). The general physio-chemical properties of studied soil, biosolids, and nWTRs were determined according to the standard methods \([27]\) and further compiled in Table 1.
Table 1. General physical and chemical properties of experimental soil, nanoscale drinking water treatment residuals (nWTRs), and biosolids.

|                      | Soil  | nWTRs | Biosolids |
|----------------------|-------|-------|-----------|
| pH                   | 8.32 ± 0.06 | 7.66 ± 0.09 | 6.38 ± 0.05 |
| Electrical conductivity (EC) (dS/m) | 2.13 ± 0.04 | 1.12 ± 0.03 | 8.33 ± 0.17 |
| Organic Matter (g/kg) | 2.60 ± 0.18 | 48.00 ± 2.33 | 410.00 ± 3.77 |
| Cation Exchange Capacity (CEC) (cmol(+) /kg) | 21.00 ± 1.07 | 77.77 ± 2.58 |
| Sand (g/kg)          | 738.00 ± 3.70 | N/A † | N/A |
| Silt (g/kg)          | 106.40 ± 1.90 | N/A | N/A |
| Clay (g/kg)          | 155.60 ± 3.20 | N/A | N/A |
| Soil Texture         | Sandy loam | N/A | N/A |
| CaCO₃ (g/kg)         | 326.20 ± 3.69 | N/A | N/A |
| KCl-Al (mg/kg)       | 0.12 ± 0.03 | 18.12 ± 1.07 | 3.82 ± 0.14 |
| Olsen-P (mg/kg)      | 15.30 ± 0.50 | 20.00 ± 2.11 | 44.40 ± 1.74 |
| Total As (mg/kg)     | 1.23 ± 0.11 | 1.55 ± 0.13 | 6.22 ± 0.58 |
| Exchangeable As (mg/kg) | 0.07 ± 0.01 | 0.06 ± 0.01 | 0.16 ± 0.06 |
| Soluble As (mg/kg)   | 0.04 ± 0.01 | 0.03 ± 0.01 | 0.09 ± 0.02 |

†: not applicable.

2.2. Soil Stabilization

The biosolids- and nWTR-treated soils were incubated at 25 ± 2 °C under the laboratory conditions for 60 days for stabilization. The biosolids application rate was 3% (w/w) in the experimental soils, and the soil nWTR treatments were 0, 0.25, 0.5, and 1.0% (w/w). The control soil was amended with 3% of biosolids but without nWTR treatment (i.e., 0%). The treated soil was homogenized and distributed into different jars. The soil water content in each jar was kept at 80% of the soil water holding capacity. Soil water loss was compensated daily during the experimental time period. At the end of the incubation time period, soil samples were collected from jars and stored at 4 °C for chemical analysis. A completely randomized experimental design was selected, and each treatment had three replicates.

2.3. Arsenic Sorption and Sorption Efficiency

The arsenic sorption capacity of each treated soil was determined, compared to the control soil, using the conventional batch equilibration technique. In brief, a unit mass of the treated soil sample (0.2 g) was mixed with 20 mL As solution of known concentration (0, 5, 50, 100, 200, 300, 400, 500, 600, 700, and 800 mg/L as NaAsO₂) in a flask, and the flask was placed on a shaker at 120 rpm at 25 °C for 24 h (i.e., the equilibrium time from kinetics experiment). Then, the treated soil samples with the As (III) solution was centrifuged at 5000 × g for 15 min prior to sampling. The difference in As (III) sorption between un-amended and nWTRs-amended soils were quantified. At the end of this experiment, final As concentrations in the solutions were measured by Inductively-coupled Plasma/Mass Spectroscopy (ICP/MS). The amount of As adsorbed to the soil was calculated using the following equation:

\[ q_e = \frac{V (C_0 - C_e)}{m} \] (1)

where \( q_e \) is the amount of As sorbed by a unit mass of soil at equilibrium (mg/kg), \( V \) is the solution volume (mL), \( m \) is the mass of soil sorbent (g), and \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations of As, respectively.

To describe the As sorption in treated soils, the isotherm classification concept was applied to distinguish four main types of isotherms corresponding to different solute adsorbent interactions, named as L, H, C, and S curves. Soil isotherms were characterized by a decreasing slope as equilibrium concentration increased. The As sorption efficiency of sorbent for arsenic was calculated using the following equation:

\[ E (%) = \frac{[(C_i - C_e)/C_i] \times 100}{2} \] (2)
where \( E \) is the sorption efficiency, while \( C_i \) and \( C_e \) are the initial and equilibrium As concentrations, respectively.

2.4. Arsenic Fractionation

Fractionation analysis of As in the soil treated with biosolids was carried out before and after the nWTR-treatments by using the sequential extraction technique [28]. The sequential extraction method was used to divide soil As into five fractions: Exchangeable As, carbonate-bound As, Fe-Mn oxide absorbed As, organic matter-bound As, and As residual. Concentrations of As in extraction solutions were measured using ICP/MS.

2.5. Soil Solution Collection

Soil pore water samples were extracted by centrifuging soil samples for 20 min at relative centrifugal force (RCF) of \( 4.8 \times 10^5 \) m/s\(^2\), according to the method described previously by Elkhatib et al. [29]. Soil pore water samples were analyzed for concentrations of As and other major ions, along with pH and temperature.

2.6. Arsenic Speciation in Soils

2.6.1. Speciation Modeling Using MINEQL+

In the pore water samples, soil reaction, electrical conductivity, major ions, toxic metals, and soluble As concentrations were determined. Using the measured As and other element concentrations, pH, temperature, \( \log K \), \( \text{pCO}_2 \), \( \text{pO}_2 \), \( \text{pE} \), and calculated ionic strength, As speciation in soil pore water was calculated Modeled using the MINEQL+ (version 4.6) according to Schecher and McAvoy [30].

2.6.2. X-ray Absorption Near-Edge Structure (XANES) Analysis

XANES analysis was carried out at the Advanced Photon Source (APS) of Argonne National Laboratory in the U.S. XANES spectra of selected As standards and treated soil samples were collected at Beamline 13-ID-E. The incident beam and energy reading of As K edge was set to 12 keV. All spectra were collected at room temperature and normal atmospheric pressure. Arsenic standards included arsenic oxide (As\(_2\)O\(_3\)), diarsenic pentoxide (As\(_2\)O\(_5\)), arsenic sulfide (AsS\(_2\)), sodium arsenate (HAsNa\(_2\)O\(_4\)), and cacodylic acid [(CH\(_3\))\(_2\)AsO\(_2\)H]. When needed, the chemicals were ground into fine powders and transferred on the sample holder. The prepared sample slides were mounted on a sample holder and attached to the detector for analysis. Two scans were collected for As standards, and three scans were collected for each soil sample. SixPack software [31] was used to average replicate spectra from each sample and fit the averaged spectra to those of As standards.

2.7. Statistical Analysis

The least significant difference (LSD) was used for comparison between the biosolids and the nWTR treatments. The level of significance (\( \alpha \)) was 0.05. The statistical analysis was done using COSTAT Software [32].

3. Results and Discussion

3.1. Sorption Isotherms and Sorption Efficiency of Arsenic

The nanoscale drinking water treatment residuals significantly affected the sorption isotherm of As in calcareous sandy loam soil that was treated with different levels of biosolids (Figure 1). Differences in As sorption capacity were observed between different nWTR-application rates of 0.25, 0.50, and 1.00% (w/w). The initial As concentration significantly affected the As adsorption to the soil treated with both biosolids and nWTRs. When the initial As concentration increased from 5 to 800 mg/L at room temperature, the amount of As sorbed per unit mass of the treated soil also increased. The soil
As concentration increase would allow more As molecules to move from soil solution to the surfaces of adsorbents in soil. Thus, the As sorption in soil is highly dependent on the initial As concentration. At a lower initial As concentration, the As mass in solution is relatively small to the amount of available sorption sites, so it was highly sorbed with available sorption sites [33]. Importantly, if without any nWTR treatments, the soils with or without biosolids treatments had shown moderate affinity for As sorption. With the nWTR treatments, As sorption isotherms changed from S-type to H-type isotherms (Figure 1). In this study, the H-type isotherm became dominant especially at a high nWTR application rate of 1%. Therefore, the quantity of As sorbed by the soil followed a descending order of: 1% nWTR-treated soil, > 0.5% nWTR-treated soil, > 0.25% nWTR-treated soil, and > control soil (or no nWTR treatment) (Figure 1). The nWTR treatments have contributed many more sorption sites such as aluminum, iron, and calcium hydroxides in the soils, in addition to high organic matter contents and high cation exchange capacity of biosolids-amended soils (Table 1).

Figure 1. The amount of sorbed arsenic (As) in the calcareous soil amended with biosolids (3%, w/w) and with different levels of nWTRs of 0%, 0.25%, 0.5%, and 1% (w/w) at different equilibrium concentrations of As. Data shown are means and standard deviation (n = 3). The error bars were too small to be visible in the figure.

The amount of sorbed As in the biosolids-amended (3%) soil was 8000, 66,100, 68,200, and 76,700 mg As/kg or 8, 66.1, 68.2, and 76.7 mg As/g soil when the soil was treated with nWTRs of 0%, 0.25%, 0.5%, and 1% (w/w), respectively (Figure 1). High specific surface areas of nWTRs (125 m²/g) mainly containing Al-, Ca, and/or Fe (hydr) oxides significantly enhanced the anion sorption due to nanoscale nWTR particles and the amorphous nature of metal hydroxides [24]. Arsenic sorption on metal hydroxide surfaces replaces singly coordinated OH⁻ groups, and then undergoes a re-arrangement into a more stable binuclear bridge-type bond between cations [34]. The results from our study (desorption rate was about 1%–5% at all treatments for 800 mg As(III)/L-treated soil) generally agree with those of Mahmoud et al. [35] and Elkhatib et al. [24], showing that nWTR-adsorbed As are stable or immobilized over a long time period [26,36].
Increasing the treatment level of nWTRs from 0.25% to 1% also likely increased the efficiency of As retention in the soil (Figure 2). For examples, at 0.25% nWTRs application rate the removal efficiency significantly ($p < 0.05$) increased from 67.5% at As concentration 50 mg/L to 82.6% at 800 mg As/L-treated soil (Figure 2). In similar, at 0.50% nWTRs application rate the removal efficiency of As significantly ($p < 0.05$) increased from 58.8% at As concentration 50 mg/L to 85.3% at 800 mg As/L. In addition, at 1% nWTRs application rate the removal efficiency significantly ($p < 0.05$) increased from 95.6% at As concentration 50 mg/L to 95.6% at 800 mg As/L (Figure 2).

Figure 2. Arsenic sorption efficiency in the calcareous soil amended with biosolids (3%, w/w) and treated with different levels of nWTRs of 0%, 0.25%, 0.5%, and 1% (w/w). Data shown are means and standard deviation ($n = 3$). The error bars were too small to be visible in the figure.

3.2. Investigation of As Removal Mechanism

To investigate the role of nWTRs in As retention in biosolids-treated soil, a Fourier Transmission Infrared Spectroscopy (FTIR) analysis was performed (Table 2).

The FTIR spectrum of nWTRs/biosolids-treated soil before and after As saturation are presented in Table 2. Table 2 showed the shifting and disappeared of some functional groups revealed that changes in sorbent properties occurred after As sorption. These shifts are a strong evidence for chemical complexation between As and functional groups of nWTRs and biosolids. Before As saturation (Table 2), most changes between 1700 and 500 cm$^{-1}$ refers to complexation of As ions with COOH and O-H groups present in phenolic and carboxylic compounds present in biosolids and nWTRs [24,37]. In conclusion, the FTIR spectra of the biosolids-amended soil that was treated with different levels of nWTRs during a 60-day incubation period showed initial HOH stretching and bending, as well as a bending vibration of hydroxyl groups on metal oxides, and then some peaks completely disappeared or shifted, suggesting that those OH groups on the WTR particle surface reacted with As.
Table 2. The FTIR spectral characteristics of 1% nWTRs/biosolids-treated soil before and after As sorption (with initial As concentration of 800 mg/L).

| Wavenumber Range, cm⁻¹ | Before As-Saturation | After As-Saturation | Difference | Functional Groups                      |
|------------------------|----------------------|---------------------|------------|----------------------------------------|
| 3411–3200              | 3411                 | 3412                | 1          | C-H methyl and methylene group         |
| 3000–2921              | 2921                 | 2921                | 0          | Bounded hydroxyl group (OH)            |
| 1737–1625              | 1622                 | 1621                | −1         | C-H stretching                         |
| 1508–1330              | 1508                 | 1508                | 0          | Symmetric binding of CH₃               |
| 1508–1330              | 1462                 | 1462                | 0          | Carboxylic group                       |
| 1330–1375              | 1320                 | 1320                | 0          | C-O stretching of COOH                 |
| 1290–1000              | 1246                 | 1245                | −1         | O-H alcohol and aliphatic ether        |
| 1290–1000              | 1053                 | 1055                | 2          | C-O stretching of COOH                 |
| 800–600                | 780                  | Absent              | −           | stretching vibration of NH₂             |
| 800–600                | 608                  | 609                 | 1          | stretching vibration of NH₂             |

3.3. Effect of nWTRs on As Fractionation in Biosolids-Amended Soil

Figure 3 shows fractionation changes of As in biosolids-amended soil treated with different levels of nWTRs. The As fractionation result in the control soil was significantly different from those in the soils treated with biosolids and nWTRs. In the control soil, exchangeable As was 4.1%, carbonate-bound As was 22.8%, Fe-Mn oxides-bound As was 8.9%, organic matter-bound As was 8.1%, and residual As was 56.1%. In the biosolids-amended soil, exchangeable As was 8.1%, carbonate-bound As was 22.1%, Fe-Mn oxides-bound As was 12.5%, organic matter-bound As was 30.9%, and residual As was 26.5%. However, when the biosolids-amended soil was treated with nWTRs, As fractionation has been significantly affected (Figure 3). The nWTR treatment of 0.25% significantly increased the residual fraction of As (RS) up to 73.7%, while other As fractions decreased in comparison with the soils with or without biosolids treatments. Further, increasing the nWTR application rate from 0.5% to 1% drastically increased the stable and immobilized residual fraction (RS-As) of As from 82.5% to 87.7%, respectively (Figure 3), due its accumulation in silicates [28].

![Figure 3](image-url) Percentage of arsenic (As) fractions in the calcareous soil amended with biosolids (3%, w/w) and treated with different levels of nWTRs of 0%, 0.25%, 0.50%, and 1% (w/w). OM: organic matter; RS: residual fraction.

The relatively high percentage of carbonate-bound As in the soils was mainly due to high calcium carbonate content (326 g/kg) in the studied soil (Table 1). The overall mobility and potential
bioavailability of As in the studied soil amended with 3% biosolids and treated with different levels of nWTRs followed a descending order of: control soil without nWTR treatment, > 0.25% nWTR treated soil, > 0.5% nWTR-treated soil, and > 1% nWTR-treated soil (Figure 3). These results were generally in accordance with previous research findings [37–39], showing the effect of nWTR treatments on the bioavailability of some heavy metals. It was concluded that nWTRs can significantly reduce the bioavailability of As, Cr, and Hg in contaminated calcareous soil.

3.4. Effect of nWTRs on As Speciation in Biosolids-Amended Soil

Table 3 shows the dominant chemical forms of As in the solution of soils with different treatments via the MINEQL+ modeling calculations that determine the soluble chemical As forms. The As speciation analysis showed that arsenous acid (H$_3$AsO$_3$) was the predominant chemical form (94.1%) in the control soil, followed by cacodylic acid [(CH$_3$)$_2$AsO$_2$H] of 1.3%, hydrogen arsenite (HAsO$_2$) of 1.2%, arsenic trioxide (As$_3$O$_5$) of 1.1%, H$_4$AsO$_5$ of 1.1%, and di-hydrogen arsenite (H$_2$AsO$_3$) of 1.1%. In the biosolids-amended soil the dominant chemical forms of As was arsenic acid (80%), followed by cacodylic acid of 9.7%, hydrogen arsenic of 2.2%, H$_4$AsO$_5$ of 2.2%, claudetite (As$_2$O$_3$) of 1.4%, arsenolite (As$_2$O$_5$) of 1.4%, di-hydrogen arsenite of 1.3%, arsenic trioxide of 1.2%, and di-arsenic pentoxide (As$_2$O$_5$) of 0.6%.

Table 3. Arsenic speciation (%) in soil solution of the calcareous soil that was amended with biosolids and nanoscale WTRs, using the MINEQL+ modeling calculation.

| As Compounds                  | Control Soil | Biosolids (3%) | nWTRs (%) |
|-------------------------------|--------------|----------------|-----------|
|                               |              | Control Soil   | 0.25      | 0.5      | 1        |
| AsO$_3^{3-}$                  | 1.13         | 1.33           | 1.19      | 2.28     | 1.05     |
| HAsO$_2^{2-}$                 | 1.22         | 2.23           | 1.27      | 2.27     | 0.57     |
| H$_3$AsO$_3$                  | 94.11        | 80.02          | 36.04     | 19.59    | 13.98    |
| H$_2$AsO$_5^{2-}$             | 1.09         | 1.33           | 1.45      | 1.14     | 1.06     |
| H$_4$AsO$_5$                  | 1.12         | 2.2            | 1.21      | 1.57     | 1.0      |
| As(OH)$_5$ (amorphous)        |              |                |           |          |          |
| Cacodylic Acid                | 1.33         | 9.66           | 10.58     | 12.22    | 17.55    |
| Arsenolite (As$_2$O$_5$)      | 1.37         | 0.75           | 1.68      | 1.37     |          |
| Claudetite (As$_2$O$_3$)      | 1.42         | 0.85           | 1.1       | 1.3      |
| di-arsenic pentoxide (As$_2$O$_5$) | 0.55       | 1.66           | 2.11      | 2.67     |

The application of nWTRs to the biosolids-amended soil significantly affected As speciation results, depending on the application rate of nWTRs (Table 3). The 0.25% nWTR treatment resulted in approximately 45% amorphous arsenic hydroxide or As (OH)$_5$ and 36% arsenous acid (As(III)) (Table 3), and also increased the proportions of cacodylic acid and di-arsenic pentoxide. However, with a higher level of nWTR treatment (0.5%), amorphous arsenic hydroxide increased to 56% but arsenous acid decreased to 19.6%. Cacodylic acid and di-arsenic pentoxide also increased with increasing the level of nWTR treatment. The WTR application of 1% in the biosolids-amended soil increased the percentage of amorphous arsenic hydroxide, but arsenous acid percentage decreased (Table 3). Overall, the nWTR treatment was efficient in immobilizing As in the biosolids-amended soil. These research findings also support those reported previously by Elkhatib et al. [24] and Moharem et al. [40], showing reduced solubility of Cr and Hg in biosolids that were treated with Al$_2$(SO$_4$)$_3$ or FeCl$_3$ compounds that are commonly used in drinking water treatment. Different As species have different physiochemical properties that determine their relative tendency to precipitate, adsorb, or dissolve in soil solution. Thus, evaluating nWTR effects on As speciation in agricultural soil is essential for developing the best environmental management practices with As-contaminated soil and water. Choi et al. [41] reported that over 80% of As(V) and Zn(II) were steadily removed at solution pH 6 by the hybrid ion-exchange fabric/ceramic membrane system. Reduced flow rate and removal capacity were recovered through a backwashing process during continuous treatment with the hybrid ion-exchange fabric/ceramic membrane system. Hwang et al. [42], in their study about how arsenic leaches from different soil
and sediment types and responds to hydrologic conditions to identify areas susceptible to arsenic contamination, revealed that most arsenic-loaded sediments accumulated in the vicinity of a reservoir inlet, and arsenic in reservoir beds has a higher leaching potential than that from agricultural land and stream beds. Arsenic deposited at the bottom of reservoirs had higher mobility than that in the other soils and sediments, and arsenic leaching was closely associated with the acidity of water.

Arsenic speciation analyses in the soils were also directly measured using XANES, a non-destructive analytical method (Table 4 and Figure 4) that determine the total chemical forms of As in soil sample. The XANES of control soil sample show that the dominant As chemical form was sodium arsenate of 74.8%, followed by arsenic pentoxide of 25.2%. Moreover, The XANES of original nWTRs show that the dominant As chemical form was sodium arsenate of 28.8%, followed by cacodylic acid of 14.5%, and arsenic pentoxide (36.7%). On the contrary, in the biosolids-amended soil, arsenic pentoxide was 61.5%, sodium arsenate was 22.4%, cacodylic acid was 14.9%, and arsenic sulfide was 1.2% (Table 4). Similarly, the application of 1% nWTRs to the biosolids-amended soil changed the percentage of As species such as arsenic pentoxide was 68.0%, sodium arsenate was 10.0%, and cacodylic acid was 22.0% (Table 4). Wang et al. [43] indicated that the XANES is efficient in determining arsenic oxidation states of the sediments with low arsenic contents and multiple arsenic species.

Table 4. Speciation fraction (%) of arsenic (As) in the soils that were treated with biosolids (3%) and nanoscale WTRs (1%) using X-ray absorption near-edge structure spectroscopy (XANES) analysis.

| As Compounds                  | Control Soil | Original nWTRs | Biosolids-Treated Soil | Biosolids- and nWTR-Treated Soil |
|-------------------------------|--------------|----------------|-----------------------|----------------------------------|
| Sodium arsenate (HAsNa₂O₄)   | 74.77        | 28.80          | 22.42                 | 10.00                            |
| Cacodylic acid                |              | 14.50          | 14.88                 | 22.00                            |
| Arsenic pentoxide (As₂O₅)    | 25.23        | 56.70          | 61.48                 | 68.00                            |
| Arsenic sulfide (As₂S₅)       |              |                |                       | 1.22                             |

Figure 4. Spectra of arsenic (As) chemical components in the soil that was treated with biosolids (3%) and nanoscale drinking water treatment residuals (1% nWTRs), along with the As standards and the fit line. A: Control soil; B: Original nWTRs; C: Biosolids-treated soil; D: Biosolids- and nWTRs-treated soil.
4. Conclusions

The initial As concentration significantly affected the As adsorption to biosolids and nWTRs-soil mix. Increasing the application rate of nWTRs increased the efficiency of As retention in soil. The overall mobility and potential bioavailability of As in the studied soil treated with biosolids and/or nWTRs follows the following order: biosolids amended soil, > nWTRs-biosolids amended soil. Moreover, application of nWTRs affected the soil As speciation depending on the application rates of biosolids and nWTRs. It has been found that the dominant chemical form of As was in an oxidized form, nominally As$^{5+}$. It was likely to be incorporated in arsenic pentoxide, and this phase generally retained As in a state of low mobility, toxicity, and bioavailability. The high capability of nWTRs to immobilize As in biosolids-treated soil and the stability of As-nWTRs surface complexes suggest the strong affinity of nWTRs as economic and effective sorbents for removal of As from contaminated sites. In conclusion, nano-scale particles of drinking water treatment have proven to be effective in As removal from biosolids-treated soil.

Author Contributions: A.M.M.: Conceptualization, methodology, validation, formal analysis, investigation, data curation, writing—original draft preparation, writing—review and editing. E.E.: Conceptualization, validation, investigation, resources, project administration and funding acquisition. T.Z.: MENIQL+ speciation funding. N.O.F.: Methodology, data curation, writing—original draft preparation. Z.-Q.L.: Methodology, validation, resources, writing—review and editing, supervision, project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: Egyptian Science and technology development funds (STDF No.4977).

Acknowledgments: The authors acknowledged the financial support from Egyptian Science and Technology Development Funds (STDF No. 4977 to Elkhatib), and also the Beamtime Award from the Advanced Photon Source (to Lin). The authors also highly appreciated the assistance provided by research staff at Beamline 13-ID-E at the Advanced Photon Source, a User Facility operated by Argonne National Laboratory for the US Department of Energy Office of Science under Contract No. DE-AC02-06CH11357.

Conflicts of Interest: The authors declare no conflict of interest.

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