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Effect of dissolved organic matter derived from waste amendments on the mobility of inorganic arsenic (III) in the Egyptian alluvial soil

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Abstract

Dissolved organic matter (DOM) is one of the decisive factors affecting pollutants mobility in soils receiving waste amendments. The aim of this study was to investigate the effects of DOM1 derived from agricultural solid waste (ASW) and DOM2 derived from municipal solid waste (MSW) on the mobility of inorganic arsenic (As) in two alluvial soils from the Nile River Delta. In column experiments, addition of DOM solutions significantly increased As concentration in the effluents. There was no significant difference between the two soils, the obtained results from soil2 columns revealed that DOM2 has stronger capability than DOM1 to facilitate As mobility. The pH of the studied soils is alkaline (8.1) which promoted the dissociation as well as deprotonation of DOM and as a consequence, humic substances in DOM become negatively charged organic anions, leading to their substantial competition with As for the adsorption sites on both soil surfaces. The results emphasized that in alkaline soils there is a risk of groundwater pollution in the long run by arsenic either naturally found in soil or originated at high soil pH when dissolved organic carbon (DOC) released from various organic amendments ASW and/or MSW and leached through soil profile.

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Keywords: DOM; Waste amendments; Arsenic; Mobilization; Alkaline soils.

1. Introduction

The intensification of agricultural production has become a global concern, as results the ecological and chemical impacts on soil and water are increased and nations around the globe have been establishing conservation measures [1, 2]. In soils the mobility of a highly toxic element such as arsenic (As) is relatively low compared with most mobile elements such as cadmium (Cd) and zinc (Zn). According to a lot of studies and literatures, arsenic in paddy soils presents mostly in four arsenic species: arsenite: As(III), arsenate: As(V) dimethylarsenate and monomethylarsenate [3-5]. Arsenic mobility in soils is largely governed by adsorption/desorption on mineral surfaces, especially Fe (hydro) oxides [6]. There are several factors affecting arsenic mobility: pH [7], dissolved organic carbon [8], competing anions such as phosphate, carbonate, sulfate and to a minor extent chloride and nitrate [9, 10], aging processes [11], and microbially mediated redox transformations [12, 13]. Precipitation, co-precipitation and



dissolution of As with other phases, e.g. with iron (hydro) oxides and calcite, can also play an important role in the mobility process [14, 15]. Little studies have been done on the effect of dissolved organic matter (DOM) on As mobility and transport in soil. In the soil-water system arsenic distributes between the two phases, liquid soil solution, and solid soil substrate. In the liquid solution, arsenic species may exist in free form and/or in association with DOM or colloids derived from soil [16]. In paddy soils, under flooded conditions the soil has high capability to release not only DOM, but also DOM associated with several accumulated pollutants and heavy metals including As [17-21]. In previous studies a substantial increase of As mobility was found in wetland soils in the presence of large dissolved organic carbon (DOC) concentrations [22]. Some studies indicated that As oxyanions may associate with humic substances directly through covalent binding mechanisms [23, 24] or by metal cation bridges [25] contributing to a higher mobility of As. Despite such findings, the mobility of As affected by DOM derived from compost, in the presence of soil colloidal and solid phases, Fe and Al has not yet been studied sufficiently. We expect that the interactions between As and DOM from different sources would play an important role in As mobility in the Egyptian soil based on the fact that the soils under investigation, in the Nile River Delta, used in rice cultivation for more than 80 years ago and still in use. In addition, these soils were amended with a lot of organic matter derived from different sources such as agricultural solid waste (ASW) compost and municipal solid waste (MSW) compost to improve nutrient uptake and availability. The large amount of colloidal materials derived from frequent watering in the presence of organic materials (ASW and/or MSW) could move rapidly through the soil components. The As movement accompanying these colloids could have environmental negative impacts. Out of this expectation, the main objective of this study was to investigate a possible mobilization of As in an alluvial soil as affected by DOM from different sources such as ASW, MSW.

2. Materials and methods

2.1 Soil sampling sites

Two soil samples of A-horizons (0-20 cm) from different sites in the Nile River Delta were collected, both samples is an alluvial (Typic Torrerts). The first soil sample (soil 1) represents the agricultural land of El-Monofeya governorate at $30^{\circ}28'15.56''$ N and $30^{\circ}56'58.19''$ E. The second sample (soil 2) was collected from Kafr El-Shaikh governorate at $31^{\circ}18'30.91''$ N and $30^{\circ}48'13.40''$ E. Both of soils are typical for the extensive flood plains in the delta. The potential evaporation rate is 1500 mmyr–1 and far in excess of precipitation (~120 mmyr–1). These two sites have been selected as representing sites for the most extensive rice cultivation in Egypt in addition to some major crops such as sweet corn, cotton, and clover. Surface irrigation is the common system in this area and the water table in the open drains is generally maintained at 2.5 m below the soils surface. Typically the soils contain 35% clay, are crypto alkaline calcareous and non saline to moderately saline [26].

2.2 Soil properties and sample preparation

The collected soil samples were air-dried and allowed to pass through 2mm sieve. Sieving and sedimentation (pipette method) was used for the determination of sand, silt and clay contents. Soil 1 had 27% sand, 33% silt and 40% clay, while values of 26% sand, 32% silt and 42% clay were found in soil 2. The CaCO₃ content quantified by gaseous CO₂ release from the soil upon acidification with 10% HCl was 62 mg g⁻¹ and 54 mg g⁻¹ for soil 1 and soil 2 respectively. Soil pH measured with a pH meter equipped with a glass electrode in 1:2.5 soil-water suspensions was 8.1 for both soils. The cation exchange capacity (CEC) measured by performing the Ag-thiourea method [27] using acetate buffer at soil pH was found to be 356 mmol_c kg⁻¹ soil 1 and 274 mmolc kg⁻¹ soil 2. Electrical conductivity (EC) for soil 1 and soil 2 measured in 1:10 (solid: liquid) aqueous extracts was 783 µS/cm and 892 µS/cm respectively. Soluble cations and anions were extracted with deionized water (1:10) and quantified by atomic absorption spectroscopy (Perkin Elmer, PE 3300) and anion chromatography (DIONEX, ICS-90). In both soil samples Na^+ was extracted in higher amount than the sum of Ca^{2+} and Mg^{2+} divalent cations (Table 1). In the two soils Cl⁻ concentration was the largest among other anions. Compared to SO_4^{2-} concentration in both soil samples, Cl⁻ concentration was larger by about 3 times of magnitude. Due to the high pH value in both soils, active carbonates are present as HCO₃⁻ and distinct amounts of functional groups of DOM are deprotonated. According to X-ray diffraction analysis, large amounts of smectite and minor contents of kaolinite and quartz are present in the clay fraction of both soils.

	Na^+	K^+	Mg ²⁺	Ca ²⁺	Cl	NO ₃ -	PO_4^{3-}	SO_4^{2-}	Σ cations	Σ anions
$mol_c kg^{-1}$										
Soil 1	1.6	0.15	0.22	0.46	0.76	0.05	0.003	0.26	2.43	1.07
Soil 2	1.72	0.18	0.26	0.51	0.78	0.08	0.004	0.28	2.66	1.14

Table 1. Soluble cations and anions in 1:10 aqueous extract of the studied soils

2.3 Arsenic extraction from soils

Water soluble As and As bound to aluminium, iron, calcium in both soils i.e., Al–As, Fe–As, and Ca–As were sequentially extracted with 1 M NH4Cl, 0.5 M NH4F (pH 8.2), 0.1 M NaOH, and 0.25 M H_2SO_4 solutions [28]. The total As content was determined according to [29], the soil was digested with H_2O_2 and then As extracted with 9.6 M HCl and measured using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Liberty 200; Varian). Soluble Fe and Al in the studied soils and DOMs determined using Dithionite-citrate-bicarbonate (DCB) method and measured using ICP-AES are presented in Table (2).

2.4 Dissolved organic matter extraction

Two commercial composts ASW and MSW were collected from Nahdet Misr Company for Environmental serves (formally it was named Veolia) in Alexandria city. DOM was extracted from composts and soil samples in (1:5 w/v aqueous solution) using deionized water (Table 2). After shaking for 24 h the suspensions were allowed to stand for 24 h and finally filtered through a 0.45 µm cellulose nitrate membrane filter (Millipore Inc., Bedford, MA). DOM solutions were stored for the experimental work at 4 °C. Dissolved organic carbon (DOC) concentrations in the 1:5 aqueous extracts of ASW, MSW and soils were quantified using a TOC analyzer (elementar, liquiTOC trace). The total concentrations of different amino acids (Table 2) found in DOM solutions determined using Beckman-Coulter Porton LF3000G protein sequencer.

 Table 2. Selected parameters of ASW, MSW and soils

Parameter	ASW	MSW	Soil 1	Soil 2
TOC (%)	31.4	25.3	2.24	2.24
DOC mg l ⁻¹	236	185	58	60
(measured in DOM solutions)				
N (%)	2.13	3.17	0.17	0.17
P_2O_5 (%)	1.60	1.06	0.12	0.12
K ₂ O (%)	1.12	0.73	0.03	0.03
Total amino acids mg kg ⁻¹	144.16	254.12	0.41	0.44
(measured in DOM solutions)				
Soluble Fe g kg ⁻¹ dry weight	0.82	0.56	3.51	3.42
Soluble Al g kg ⁻¹ dry weight	0.47	0.62	2.17	2.51

TOC is total organic carbon

The pH of ASW and MSW measured in (1:5) aqueous extract was 7.86 and 7.75 respectively. EC measured in the same extract was 857 μ S/cm for ASW and 800 μ S/cm for MSW.

2.5 Leaching studies

A number of 6 Soil columns were used; the first two columns refer to soils as control without DOM amendments and defined as soil1c, soil2c these columns were treated only with arsenic solutions. The other four columns are representing soils that were amended with water extracted DOM mixed with arsenic, DOM1 from ASW and DOM2 from MSW. The treated soil columns were defined as soil1-DOM1, soil2-DOM1, soil2-DOM2 and soil2-DOM2. DOC concentration in each DOM was measured and presented in Table 2. Before starting columns packing and leaching all natural samples were autoclaved at 121 °C in wet heat for 30 min; this procedure for reducing the microbial influences [30]. Then, the experiments were conducted by packing 45 g dried and autoclaved soil (passed through a 2-mm sieve) into polypropylene tubes having an internal diameter of 2.5 cm and a height of 10 cm. In order to remove air pockets, the soil columns were firstly percolated with deionized H₂O. For homogenization, all soil columns were saturated with 0.01 M NaNO₃. After saturation, the soils were leached with 0.01 M NaNO₃ until the input and output solutions had equal electrolyte concentrations,

which were 10 pore volumes for each soil. Thereafter the percolating solutions (influents) with analytical grade (SIGMA ALDRICH) were prepared and the following steps were carried out: (1) Sodium arsenite (NaAsO₂) solution containing 20 mg l⁻¹ As to be percolated in the columns of soil1c and soil2c in order to study the adsorption capacity of As for both soils in the absence of DOM solutions. (2) Two solutions of DOM1 and DOM2 with NaAsO2 diluted with deionized H2O to have solutions in final conditions of 20 mg l⁻¹ As and 50 mg l⁻¹ DOC. These solutions were prepared to be percolated in the columns of soil1-DOM1, soil2-DOM1, soil1-DOM2 and soil2-DOM2 to investigate the effect of DOM on the mobility of arsenic. Bromide ion (Br-), applied in the influents at a concentration of 0.6 mM, was used as a nonsorbing tracer to determine the hydraulic characteristics of the columns. The concentration of Brwas determined by a Br- selective electrode (Accumet, Fisher Scientific). The interpretation of such percolating experiments may be bothered by the occurrence of slow desorption or dissolution reactions, which could influence the metal release patterns [31]. Therefore in this study a peristaltic pump (IPC-ISMATIC, Germany) was used to give the desired flow rate of 3 ml/h for a total run time of 504 h. The column leachates (effluents) were collected every 24 h and the concentrations of As, Fe and Al in the leachates were determined using ICP-AES and DOC concentration was determined in the leachates using the above mentioned TOC analyzer. The relative concentrations of As were calculated as the ratio of As concentration in the effluents to its concentrations in influents (C/Co). Pore volumes (Vo) of the used soils calculated from the difference between weights of water saturated and oven-dried columns relating to water density (0.99777 g/cm³) at room temperature (22 °C) were 32 cm3 for soil 1 and 30 cm3 for soil 2. The bulk densities calculated depending on column volumes were found to be 1.33 g cm-3 for soil 1 and 1.27 g/cm³ for soil 2. The breakthrough curves were plotted using (C/Co) versus (Vo).

3. Results and discussion

3.1 Soil and DOM properties

Chemical analysis of the A-horizon samples (Table 1) collected from both soils represented the alkaline nature of the studied soils. Total organic carbon in both soils 2.24% was not high compared with ASW 31.4% and MSW 25.3% (Table 2). The total amino acid concentrations measured in the four DOM solutions revealed that DOM from MSW contained the highest amount followed by DOM from ASW, while the amount of amino acids in DOM from both soils was very low (Table 2). Total inorganic As concentrations in soil 1 and soil 2 were 10.25 mg kg⁻¹ and 11.87 mg kg⁻¹ respectively. These concentrations are small compared with the soil guideline value for arsenic contamination which is 32 mg kg⁻¹ [32]. For ASW and MSW the inorganic As was not detected in their digested and water extracted parts. Water soluble As was not detected in both soils, but pronounced amounts of Al-As, Fe-As and Ca-As were found in both soils (Table 3) these amounts are relatively high compared with the total As concentrations.

Table 3. Concentration of inorganic As (mg kg⁻¹) in A-horizons of both soils as total, water extractable and bound with Al, Fe and Ca

	Total inorganic As	Water soluble As	Al-As	Fe-As	Ca-As
	$mg kg^{-1}$				
A-horizon (soil1)	10.25	ND	4.02	3.17	1.97
A-horizon (soil2)	11.87	ND	5.23	3.21	2.08

ND: not detected ($< 0.002 \text{ mg kg}^{-1}$)

Each measurement is mean of three replicates and the standard deviation for each data is within 2% of each mean.

3.2 Aromaticity of DOM from different sources

The Fourier Transform infrared (FTIR) spectra were recorded in the range 4000-400 cm⁻¹ on pellets obtained by pressing a mixture of 1 mg of freeze dried DOM and 300 mg of dried KBr. A TENSOR 27, BRUKER FTIR spectrophotometer. The FTIR spectra of the examined DOM samples appeared similar with a slight difference in DOM of MSW (Figure 1), featuring a number of common absorption bands with small differences in their relative intensity. In Comparison with FTIR spectra [33] we have almost the same absorption bands: (a) 3450 cm⁻¹ (O–H stretching of inter and intra-molecular hydrogen bounds and N–H stretching); (b) 1636 cm⁻¹ (aromatic C=C skeletal vibrations, asymmetric stretching of C=O of quinones and ketones, symmetric stretching of COO–, C=O stretching of amide I band); (c) 1386 cm⁻¹ (asymmetric stretching of aliphatic groups); (d) 1135 cm⁻¹ (C–O stretching of

secondary alcohol, aromatic C–H bending). These results indicate the occurrence of similar molecules of the four DOM samples. The less marked peaks of the four DOM samples at 1386 cm⁻¹ compared with other peaks [33] may indicate a lower aliphaticity of DOM samples under this investigation.



Figure 1. FTIR spectra of DOM samples in the range from 4000-400 cm⁻¹. Comparison of DOM separated from the A-horizon and those from agricultural solid waste (ASW) compost and municipal solid waste (MSW) compost

3.3 Effect of DOM on As mobility in soil columns

The mobility of As and tracer Br in the soil columns under different experimental conditions was evaluated using the ratio of As or Br⁻ concentrations in the effluent vs. those in the influent. A ratio around 1 indicates that the adsorption of As or Br on the column reached equilibrium [34]. The soil columns were leached with NaAsO₂ solution containing 20 mg l⁻¹ As(III) in presence and absence of 50 mg l⁻¹ DOC from different sources in order to investigate the effect of DOM on As mobility and retention by both soils. The results for soil1 as presented in Figure 2 revealed that the amount of As in effluents in the absence of DOM1 (from ASW) was very low and almost the same until 9 pore volumes. From the beginning of 10 pore volumes the As effluent concentration started to increase gradually reaching the maximum at 25 pore volumes. In the effluents of DOM1 treated column As concentrations were larger than in the untreated column (control), the concentration of As in the effluent started to increase at 7 pore volume and reached the maximum at 28 pore volumes, in this experiment As was monitored until 32 pore volumes. The difference between the DOM1 treated column and the control in As concentrations was more pronounced after 7 pore volumes until the end of the leaching period i.e., 32 pore volumes. The concentrations of As in the control effluents indicated the occurrence of As adsorption by soil1 and this can be attributed to the presence of Al, Fe and Ca oxides in this soil as previously investigated [35] that alumina (Al₂O₃) can adsorb fulvic acid leading to the formation of predominantly negative charged surfaces that reduced the adsorption of As onto alumina, the later mechanism is favorable by Fe and Ca. Figure 3 summarized the mechanisms of As adsorption that may be occurred on clay surfaces [36]. On the other hand presence of DOM1 enhanced As mobility in soil1 where the interference of humic acid increased As mobility during the adsorption of As onto metal oxide surfaces [37]. The same trend was observed in DOM2 (from MSW) treated column except in this case As concentration in effluents started to increase earlier than in the case of DOM1 treated columns i.e., at 5 pore volumes indicating that soil1 has high As adsorption capability. In other words As mobility in soil1 was facilitated by DOM2 more than by DOM1 and this can be attributed to the amino acid contents of each DOM, where DOM2 contains amino acids more than DOM1 by about 1.75 times of magnitude (Table 2). The maximum As concentration in the effluents from DOM2 treated column was monitored at 22 pore volumes. After 22 pore volumes As concentration started to decrease until the end of the experiment.

Arsenic mobility in the columns of soil2 was monitor up to 30 pore volumes (Figure 4). There was no significant difference between the two soils, the obtained results from columns of soil2 proved that DOM2 has stronger capability than DOM1 to enhance As mobility in the soil column. In addition, the results clarified that Soil1 retained As in higher amounts than soil2. The fractions of As leached from soil columns were calculated against the As added in the influents. It was observed again that the presence of DOM derived from ASW and MSW in the influents enhanced As mobility and leaching as shown in Figure 5. The total amount of As added for each columns during the entire experimental period was 20

mg as As(III). For the columns leached with As(III) only as a control, about 13% of the total amount of As added was leached from soil1 while about 14% was leached from soil2 until the end of the experiment. For the columns leached with DOM solutions mixed with As(III), about only 20% of the total inorganic As was leaching from soil1 using DOM1+As while 23% was leached from soil2 using the same leaching solution. The most pronounced amount of As leached was observed by using the influent DOM2+As in both soil columns. About 30% of the total inorganic As added was leached from soil1 while 38% of the As added was released from soil2 indicating the high ability of DOM2 from MAW to enhance DOM mobility. The role of DOM in enhancing As mobility can be attributed to the competitive adsorption between As and DOM, in previous work [38] the smaller DOM concentration found in the effluents compared to that in the influents supported the process of DOM adsorption on packed soil. When DOM adsorbed on soil surface it occupied the adsorption sites and compete with both free and associated As and as a consequence only less amount of As will be adsorbed and the more of As will be leached out of the soil column.



Figure 2. Arsenic as relatively released with time from soil1 columns. Soil1c (control) leached with NaAsO₂ containing 20 mg l⁻¹ As(III). Soil1-DOM1 leached with DOM1 from ASW containing 50 mg l⁻¹ DOC and 20 mg l⁻¹ As(III). Soil1-DOM2 leached with DOM2 from MSW containing 50 mg l⁻¹ DOC and 20 mg l⁻¹ As(III). Each data point was the average of the results from the duplicated columns



Figure 3. Possible interactions which may take place in the soil ecosystem between As(III)/As(V), clay minerals and humic acids (HA) [36]

3.4 Effect of soil pH on As mobility

It is well known that both pH and the redox potential are important in assessing the fate of arsenic in soil. At high redox levels, As(V) predominates and arsenic mobility is low. But under alkaline conditions as the pH increases or the redox decreases As (III) predominates [39]. Our study was carried out under the initial soil pH without any change as a decisive environmental factor for As mobility in soil profile. The pH of the studied soils is alkaline (8.1) which promoted the dissociation as well as deprotonation of DOM and as a consequence, humic substances in DOM become negatively charged organic anions, leading to their substantial competition with As for the adsorption sites on both soil surfaces [40]. Therefore, in alkaline soils of the Nile River Delta there is a risk of groundwater pollution by As either naturally found in soil or originated at high soil pH when DOC released from various organic amendments ASW and/or MSW during cultivation and leached through soil profile.

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Figure 4. Arsenic as relatively released with time from soil2 columns. Soil2c (control) leached with NaAsO₂ containing 20 mg l⁻¹ As(III). Soil2-DOM1 leached with DOM1 from ASW containing 50 mg l⁻¹ DOC and 20 mg l⁻¹ As(III). Soil2-DOM2 leached with DOM2 from MSW containing 50 mg l⁻¹ DOC and 20 mg l⁻¹ As(III). Each data point was the average of the results from the duplicated columns



Figure 5. Released amounts of As from the two soils under different experimental conditions. The released amounts are percentage of the total percolated amounts during the whole period of the experiments

3.5 Fe, Al and DOM release from soil columns

In previous study [38] the effect of different electrolytes on the release of DOM from the Egyptian alluvial soil was studied. In the recent study the cumulative release of DOM. Fe and Al from soil1c was investigated as affected by different influents (Figure 6) and the same trend was observed in the soil2c. The cumulative release of Fe and Al using the influent solution containing As(III) only was negligible and this can be attributed to soil alkalinity leading to precipitation of Fe and Al in the soil solution in addition to the strongly adsorbed amount of Fe and Al on the soil clay surfaces. While the release of Fe and Al using the other influents, DOM1 and DOM2 containing As(III) was high compared with As(III) only. The cumulative amounts of Fe and Al released from soillusing influent solutions of DOM1 containing As (III) were 35.28 and 26.17 mg kg⁻¹ respectively and using DOM2 containing As they were 29.26 and 17.84 mg kg⁻¹ respectively. The cumulative release of DOM from the studied soil was highly significant using different influent solutions. DOM release by using influent solution containing only As(III) was very low at the beginning of this experiment. The release rate was steady until reaching 240 h of percolation then from the 264th h the release of DOM from soil started to increase gradually. The desorption of DOM is attributed not only to the increase in electrostatic repulsion between organic compounds, but also to the decrease of electrostatic and specific attraction between the organic molecules and the Fe-oxide surface. On the other hand the reaction of As(III) with DOM, as an active anion, is described by an interaction with amino acids protein found in DOM. This interaction induced structural changes at ligand binding sites. Consequently, the effects of this complexation will include structural stabilization and will promote interaction between soluble cations found in DOM and the protein leading to cation-protein interaction [41], at the end of this interaction and completion of possible reactions the release of DOM is occurred.



Figure 6. Cumulative release of Fe, Al and DOC in mg kg⁻¹ soil as affected by different influents. This experiment was carried out for soil1 during 480 h, the whole period of the experiments

4. Conclusion

In conclusion, the results demonstrated that DOM has the potential to chemically mobilize arsenic in the soil. The percolation experiments showed that the addition of DOM from different sources ASW, MSW in the influents increased As concentration in the leaching solutions of the two alluvial soils concluding that DOM from different sources facilitated As mobility in soil. On the other hand, the naturally occurring dissolved substances in soil, especially DOM, can enhance As transport in soil by direct complexation and competition for the adsorption sites on soil surfaces. The DOM added can enhance the dissolution of Fe and Al oxides facilitating the desorption of As from the soil surface. Therefore, deprotonated as well as negatively charged organic substances have the potential to compete for the adsorption sites with As on soils, and increasing As mobility in soil and the associated environments. The alkaline nature of the studied soils promoted the dissociation and as a consequence competition with As for the adsorption sites on the two soils is occurred. As a final conclusion the result emphasized that in alkaline soils of the Nile River Delta there is a risk of groundwater pollution in the long run by arsenic either naturally found in soil or originated at high soil pH when DOC released from various organic amendments ASW and/or MSW during cultivation and leached through soil profile.

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