# DYNAMICS OF ARSENIC IN CONSTRUCTED WETLAND TREATING WATER FROM FLOODING SHAFT OF AN ABANDONED URANIUM MINE

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## ABSTRACT

Partitioning of arsenic in sediments from a constructed wetland for treating water from flooding shafts of an abandoned uranium mine in south-eastern Saxony in Germany were analysed for partitions of arsenic using chemical sequential extractions and X-ray diffraction. The aim was to identify the As removal processes from the water and how to engineer them for remediation efficiency and capacity. The fresh sediments and water were sampled from three of the surface-flow-bed treatment ponds (B 2A, B 3A and B 4A) of the four-celled (in-series) constructed wetland system. The As partition were analysed using chemical sequential extraction and characterised with SEM-EDX microscopy and X-ray diffraction analyses. The As removal process and their influencing factors were identified using laboratory bench-scale experiments. The water had a pH between 3.5 and 6.5. The organic fractions of the sediments increased from 12 % B 2A to 65% in B 4A. The total As contents were 84.3, 41.0, and 16.3 g kg-1 in the sediment samples of B 2A, B 3A, and B 4A, respectively. Most of As were residual (58%) in B 2A. In B 3A and B 4A the major fraction were the organic bound As (ca. 70%). SEM-EDX results also indicate that residual arsenic fractions were mainly in the form iron arsenic (Fe-As) and less calcium arsenic (Ca-As). Although there were substantial contents of As and Fe in the sediments, the amounts were not sufficient for accurate crystallography and mineralogical identification with X-ray diffraction. Supplementary bench-scale laboratory experiments revealed that As behaviour is governed by redox chemistry of Fe(III) and Mn(IV) oxides, where increase in sediment redox potential equally increased the affinity between either Fe(III) or Mn(IV) oxides and As, while decrease in sediment redox potential resulted in high affinity between particulate organic matter and As. Therefore, keeping redox potential high by increasing oxic status in B 3A and B 4A, while reducing the redox potential in B 2A would increase the removal capacity of arsenic of the constructed wetland.

## 1. INTRODUCTION

Generally, the closure of underground uranium mines and the withdrawal of dewatering pumps resulted in the flooding of mine workings extending over a large area. The mine drainage was historically very acidic and high in metals. After almost two decades of flooding of shafts in closed uranium mines, the concentration of radionuclide and metalloid pollutants from the shaft discharges have drastically decreased and even changed their chemical composition (Kießig et al. 2004). In some instances, the concentration of the discharge have reduced by more than 50%, and uranium is no longer the main concern but metals and metalloids like arsenic, iron, zinc and cadmium (Enderle and Friedrich 1995). However, the discharges from the shaft, though low in concentration of radionuclides and metals, remain a threat and pollution concern because it will continue discharging contaminants for many decades to come.

The pattern of discharge has warranted the search for passive remediation technologies as alternatives to currently used classical and active water treatment plants based on chemical and civil engineering techniques. The reasons for the need of alternatives include the unjustifiable economic cost involved in the establishment and running of classical water treatment for the low concentrated discharges for a long period**.** Hence, adoption of constructed wetland has been one of the passive remediation technologies advocated for removal of radionuclide and metalloid from the mine water. Originally, constructed wetlands have most commonly been used in wastewater treatment for controlling organic matter; nutrients, such as nitrogen and phosphorus; and suspended sediments. Mechanisms of metal and metalloid removal in wetland ecosystem include processes of ion exchange, adsorption, absorption, and precipitation with geochemical and microbial oxidation and reduction. Ion exchange occurs as metals in the water contact with organic substances in the wetland. Oxidation and reduction reactions catalyzed by bacteria that occur in the aerobic and anaerobic zones, respectively, play a major role in precipitating metals as hydroxides and sulphides. Precipitated and adsorbed metals settle in quiescent ponds or are filtered out as water percolates through the medium or the plants. However, the applicability and effectiveness of the wetlands remediation technology may be limited due to (1) slow removal rates, (2) probabilities of re-discharge of immobilised contaminant from wetland compartments when the physicochemical conditions of the waters changes thereby creating a secondary source of pollution, (3) uncertainty of their the long-term effectiveness, and (4) they are sometimes not responsive enough to sudden changes in discharges.

Adoption of constructed wetland to treat mine water is being piloted at former WISMUT Uranium Mining Site at Pöhla in the west of the Erzgebirge in Free Staten of Saxony, Germany. The pilot constructed wetland was commissioned in 1998 and it will operate until 2012. After closure of mining, the mine shafts were flooded in September 1995.

The shaft flood-water was associated with uranium, radium, arsenic, and manganese and iron contamination. However, manganese and uranium concentrations have gradually decreased to a level below the regulatory limits for discharge, while the arsenic and radium concentrations have significantly increased and exceed the directive limits by 2-3 orders of magnitude (Kießig et al. 2004). On one hand this has justified the establishment of the constructed wetland. On the other hand, arsenic has become the major pollutant that the constructed wetland is targeting, because arsenic contamination is linked to cancer in humans and to reduced biodiversity. Thus, one of the most important environmental issues facing the post uranium mining is the long-term stability of arsenic in mine water. In view of this, evaluation of arsenic removal from the water and quality of the fixation of As in the wetland compartment is an important procedure at the pilot constructed wetland of Pöhla. Therefore, the partition of arsenic in sediments of the wetland would give important information for evaluation as well as knowledge of processes that need to be engineered to accelerate As removal rates and to induce processes that result in long-term immobilisation like biomineralisation.

Hence, the objectives of this study were to quantify the distribution of As phases in the sediment of treatment ponds of the constructed wetland, evaluate the present-day geochemical controls on dissolved As, and investigate potential processes that can be engineered for rapid remediation and permanent immobilisation of As. These objectives were met by analyzing sediment samples collected from the ponds, measuring physicochemical condition of the ponds, conducting sequential extractions on sediment samples, and conducting laboratory experiments under controlled and simulated conditions. Further the sediment from constructed wetlands was investigated to determine the mineralogy and long-term stability of secondary arsenic precipitates formed from iron-rich.

## 2. MATERIAL AND METHODS

### Sediment Sampling

The sediment were sampled from a pilot constructed wetland of the project partners WISUTEC GmbH (a subsidiary of WISMUT GmbH) at Pöhla in western Ore Mountain (Erzgebrige) in Free State of Saxon, Germany. The constructed wetland is a pilot facility for passive treatment of shaft flood waters of an abandoned uranium mine. It consists of two parallel sets ("Becken" A and B) of four serial reaction cells (aka ponds B 1, B 2, B 3, and B 4) and a pre-aeration cascade. The current study was conducted in "Becken" A series only where sediment traps were placed at the inlets and outlets of pond 2 to 4, which hereafter are coded B 2A-1 to B 4A-1 for inlets and B 2a-2 to B 4-2 for outlets. About six month old sediments were collected in the sediment traps and used in the current experiments. Physical-chemical properties of the sediments during the sampling are provided in Table 1. Detailed information on the constructed wetland's construction and operation, chemical content of the shaft flood water, and the history of uranium mining at Pöhla have been outlined by Kiessig et al. (2004).

Table 1. The physical-chemical properties of the sediment pore water

| Parameter | Units | Becken 2A | | | Becken 3A | | Becken 4A | |
|---|---|---|---|---|---|---|---|---|
| | | **Inlet** | **Middle** | **Outlet** | **Inlet** | **B3A-2** | **Inlet** | **Outlet** |
| pH | | 7.0 | 7.1 | 7.1 | 7.4 | 7.5 | 7.7 | 7.6 |
| Redox | mV | 377.0 | 379.0 | 379.0 | 349.0 | 356.0 | 346.0 | 349.0 |
| Conductivity | mS/cm | 0.5 | 0.5 | 0.5 | 0.4 | 0. 5 | 0.4 | 0.4 |
| Dissolved Oxygen | mg/l | 0.8 | 0.4 | 2.8 | 2.0 | 2.3 | 2.2 | 3.6 |
| Temperature | °C | 26.3 | 24.6 | 24.4 | 26.8 | 26.4 | 26.4 | 25.1 |

### Sediment Fractionation Experiments

In the laboratory, the sediment samples were centrifuged to remove water, before determination of fresh (wet) mass. Then they were dried in an oven at 50° C until a constant weight was reached. The dried samples were ground, and sieved to < 2 mm before determination of organic matter, carbonate content and sequential extraction experiments.

### Determination of Organic Matter and Carbonate Content

A representative portion of the dry sediment sample weight ($M$) was measured on an analytical balance. Sample portions were put into a furnace and burned at 550° C for 2 hours to remove organic matter. After cooling in a desiccator, the samples were reweighed ($M_b$) before heating at 925° C for 4 hours to remove carbonate. The samples were reweighed ($M_c$), and organic matter ($OM$) and carbonate ($CO_3$)percentages were determined as follows:

$$OM(\%) = \left[100 - \left(\tfrac{M - M_b}{M}\right)\right] * 100 \qquad \textbf{(1)}$$

$$CO_3(\%) = \left[\left(100 - \left(\tfrac{M - M_c}{M}\right)\right) * 100\right] - OM(\%) \qquad \textbf{(2)}$$

### Chemical Sequential Extraction

To determine the arsenic partition in the sediments, 1 g of sediment was separated from each sample and subjected to chemical sequential extraction following the eight steps outlined in Table 2. After conducting each step, the samples were washed and centrifuged.

Table 2. Sequential extraction for determination arsenic partitions in the sediments

| Step | | Extraction reagent and procedure |
|---|---|---|
| 1 | Weakly adsorbed | 40 ml distilled Water added to ca. 1 g of dry sediment, shaken for 10 minutes, the centrifugation maximal 5 min at 4000 rpm |
| 2 | Ionic-bound | 40 ml of 1 M $MgCl_2$ added to residues of Step 1, buffered at pH 7, continuously shaken for 2 h, and then centrifugation at 10000 RPM for 15 Minutes |
| 3 | Organic-bound | 40 ml of 0,7 M NaOCl added to residues of Step 2, buffered at pH 8,5, boiled for 30 min, after cooling, the samples were centrifuged at 10000 RPM for 15 Min. |
| 4 | Carbonate-bound | 40 ml of 1 M NaOAc added to residues of Step 3, buffered at pH 5, continuous shaking for 5 h, the centrifugation at 10000 RPM for 15 Minutes |
| 5 | Mn-Oxide and amorphous Fe-Oxihydroxide-bound | $NH_2OH$•HCl of 0,25 M HCl added to residues of Step 4, shaken for 30 min at 50 °C. Centrifuge after cooling down |
| 6 | Crystalline Fe-Oxihydroxide-bound | Boil the residues of Step 5 in 40 mL of equal volumes of 0.2 M $(NH_4)_2C_2O_4$, $H_2C_2O_4$ 0.2 M, and 0.1 M Ascorbic acid for 30 min, the centrifugation after cooling |
| 7 | Apatite-bound | 40 ml of 1 M $NCl_3$ added to residues of Step 6, shake for 16 h at room temperature |
| 8 | Residual | Microwave digestion with 40 mL of 30% $H_2O_2$ – 65% $HNO_3$ in ratio 3:1 |

### Laboratory Experiments – Determination of Factors Influencing Arsenic Partitioning in Sediment

The factors that influence sorption of arsenic in sediments under oxic and anoxic conditions were investigated using a laboratory column experiment. The experiment was conducted in a facility illustrated in Figure 1. The column had a 10 cm diameter and length of 60 cm. It was packed with 2 kg artificial sediments composed of a mixture of 50% of a 10-year-old uncontaminated sediment from a pond and 50% of sand with grain size lower than 2 mm. Then, 5 L of water with 1 mg As $L^{-1}$ was circulated at a defined flow rate. Oxic conditions were facilitated by continuous bubbling into the column with air, while anoxic conditions were created by bubbling $N_2$ gas for 15 minutes every two days. The amount of dissolved oxygen was regularly measured. Approximately 20% of the water was renewed once a week. After 35 days, the sediment was collected from the column and sequential extraction with respect to arsenic fractions adsorbed to iron, organic matter and carbonate was performed.

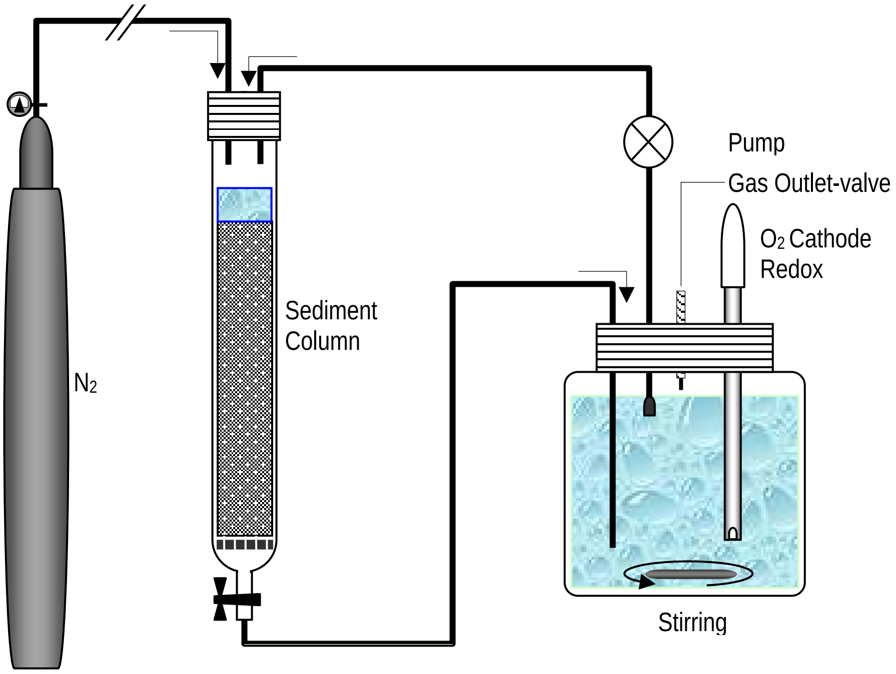

Figure 1. Schematic illustration of the equipments and experimental set-up to investigate the influence of redox condition on adsorption und distribution of arsenic in the sediments

### As, Metals and Statistical Analyses

All sediment samples underwent total digestions in aqua regia and the concentration of arsenic and heavy metals was analyzed by ICP-MS (inductively coupled plasma-mass spectrometry, Perkin Elmer). The mean of the values were calculated and the data was analysed for variation with ANOVA using computer statistical package SPSS version 14.0. Graphs were developed using Xact Version 8.0.

## 3. RESULTS AND DISCUSSION

### Organic and Carbonate Distribution in the Pond Sediments

The distribution of organic and carbonate fractions in the sediment of the constructed wetland ponds are presented in Figure 2. The results indicate that sediment samples collected in December 2008 had the highest distribution of organic matter in pond B 3A and B 4A. The results are quite obvious because of growth of Characea and biofilm. The carbonate is mainly from the release of $CO_3^{2+}$ during respiration of both plants and microorganism. The pH (see Table 1) and high content of $Ca_2^+$ ions leads to the formation of carbonation of $CO_2$ in the sediments. The findings confirm that there is low biological activity in B 2A and increased bioactivity in B 3A and B 4A.

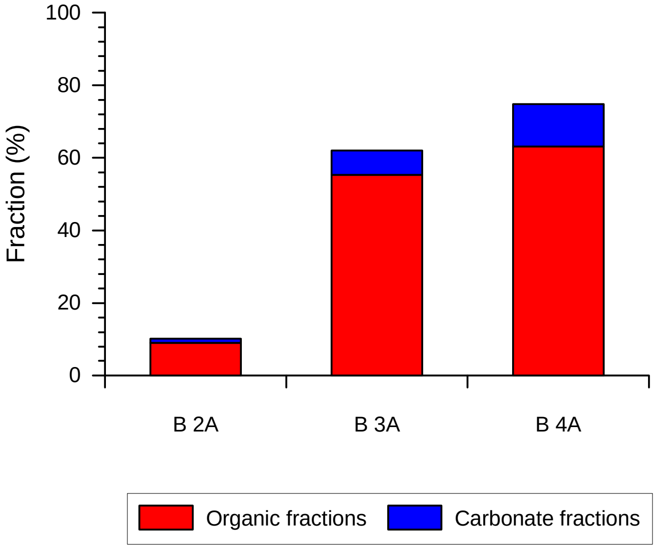

Figure 2. Distribution of organic matter and carbonate fractions in the sediment samples from treatment ponds of the constructed wetland Pöhla in December 2008

## Gradient Distribution and Arsenic Speciation in the Sediments

Total arsenic, uranium and iron concentrations in sediment samples of the treatment ponds ranged from 1400 to 8000 mg kg$^{-1}$, from 10 to 30 mg kg$^{-1}$ and 6000 to 50000 mg kg$^{-1}$, respectively. Figure 3 shows that the Fe content in the sediment dropped significantly from B 2A to B 3A by almost 60%. The drop in concentration from B 3A to B 4A is about 40%. For As, the drop from B 2A to B 3A was 45% and B 3A to B 4A was by 50%. The correlation test between Fe and As content in the sediments was significant with $r^2$=0.98. This indicates that removal of arsenic as well as uranium from the shaft-flood water in treatment pond B 2A was through co-precipitation between Fe and As as well as U. The processes involved are oxidation of Fe due to mixing with air as the water cascades down to the treatment pond. Conditions in the shaft were almost completely anoxic. On the basis of stability field diagrams generated from pH, Eh, and other physicochemical properties of the sediment, arsenic and iron in the tailings were stable as $As^{5+}$ and $Fe^{3+}$. Under the physicochemical conditions, the ferrihydrite does not undergo any measurable conversion to more crystalline goethite or hematite (Moldovan et al. 2003). Thus, it would be important to facilitate secondary mineralisation of arsenic in the Fe-rich treatment pond especially in B 2A.

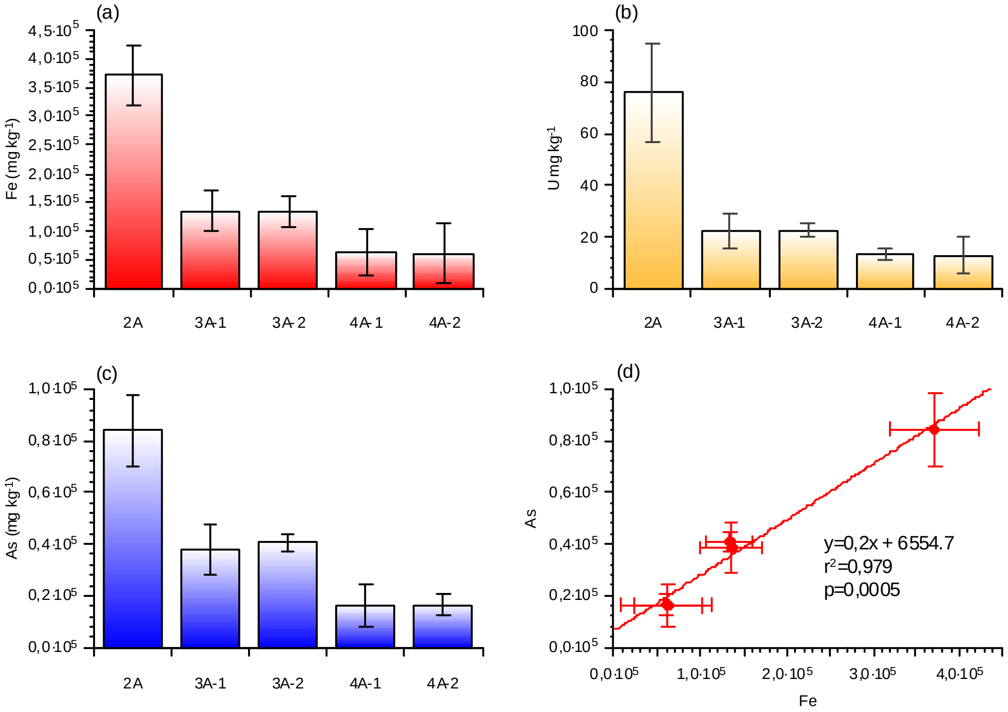

Figure 3. The gradient distribution of arsenic in relation to Fe and uranium in the treatment ponds of constructed wetland

From sequential extraction experiments to determine the speciation of arsenic, the result shows that As V slightly dominated As III in all pond sediments in the ratio of approximately 5:3 (Data not shown). The results are similar to those found in a natural wetland pond at a former uranium mining site (Mkandawire *et al.* 2008).

## Arsenic Partitions in the Pond Sediments

Sequential extraction analyses of sediment samples showed that the most abundant fraction of arsenic in the wetland sediment changed from domination of residual fraction associated As in B 2A to organic fraction associated As in the vegetated treatment ponds B 3A and B 4A. The residual fraction are mineral bound material. The current results indicate that most of the arsenic in the shaft flood-water are bound to fine colloidal mineral particles which settle in B 2A, probably due to coagulation resulting from exposure to oxidising conditions. The high arsenic associated with organic fraction is obviously a result of biosorption and uptake by algae and the biofilms. The second dominant form is the arsenic associated with Fe-Mn-oxides fraction (Figure 4). These results indicate that the arsenic immobilisation was also very much associated with the chemistry of Fe and Mn. The flooding water had pH of about 7 in the underground, while it contained a considerable amount of dissolved Fe in form of Fe(II). Thus, the only condition that leads to stability of dissolved Fe was low oxidation condition due to anaerobic condition in the underground. Once the Fe comes up to the surface, the water oxygen content increased considerably due to mixing with air. Consequently Fe(II) oxidises to Fe(III) and precipitate as hydroxide species. This led to arsenic co-precipitation with Fe and Mn. This may lead to nucleation of mineralisation processes. In view of this, the sediments were examined for signs of arsenic mineralisation using scanning electronic microscopy coupled with X-ray analysis procedure (SEM-EDX) and X-ray diffractometry. Whilst some crystalline fractions were observed with the SEM, where EDX indicated the presence of arsenic in the crystalline form, X-ray diffractometry studies did not find any crystal structure apart from quartz (Data not shown). The failure to identify crystals may have been due to the age of the sediments – they were still too new (i.e. young) to be analysed with the x-ray diffractometry procedure. On the other hand, the high Ca:As ratio in shaft flood-water would likely lead to precipitation of $Ca_4(OH)_2(AsO_4)_2.4H_2O$ type Ca arsenate minerals (Donahue and Hendry 2003).

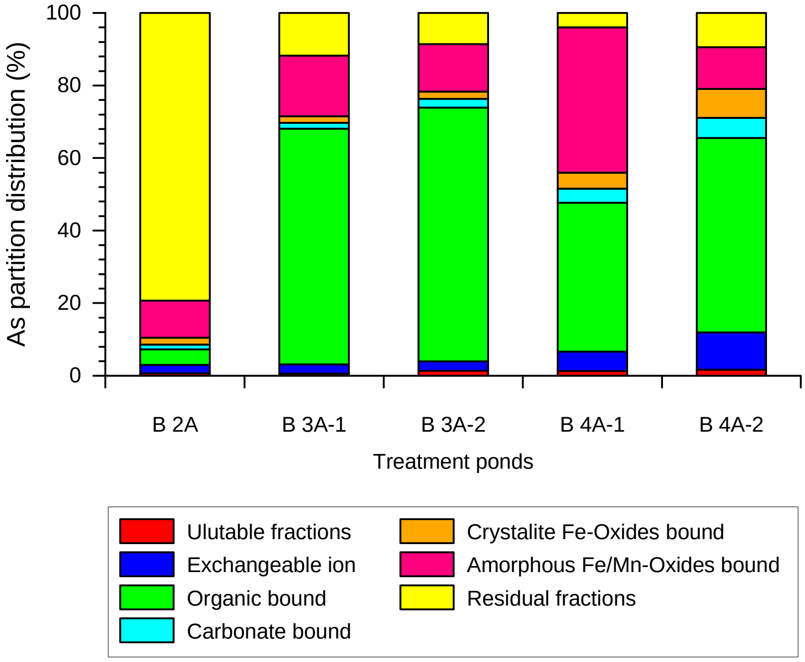

Figure 4. The fractionation of arsenic in different sediment partition determined

(The samples were collected in July 2008. The digits 1 and 2 at the of the pond code name stand for sampling points at the inlet and outlet, respectively. B 2A samples were a mixture of inlet, middle and outlet sampling points. The values used are a mean of four repeated measurements)

## Influence of Redox Status on Arsenic Distribution

The sorption of arsenic and radium in sediments under aerobic and anaerobic conditions was investigated using laboratory column experiments in order to determine their influence in determining arsenic partitioning in the sediments. Figure 5 presents the results of arsenic enrichment in sediment after 35 days. They reveal that most of the arsenic was loosely adsorbed on the sediment material, and that almost half of the adsorbed arsenic was easily washed out and remobilised with distilled water. There was almost equal enrichment of arsenic in Fe-oxide and organic fractions in the column bubbled with air. The arsenic adsorbed to organic material in the air-bubbled column was half the amount of arsenic in the organic fraction in the column bubbled with nitrogen. In the latter column, the Fe-oxide fraction accounted for less than 3% of the total arsenic that would not be re-mobilised with distilled water washing.

This indicates that oxidising conditions favour the adsorption of arsenic on iron sediment particles, in accordance with the affinity of arsenic to the iron fraction of the sediment. On the other hand, reducing conditions favoured the affinity of arsenic adsorption on the organic fraction of the sediment. Bringing these findings to the constructed wetlands, it would be import to create more oxidising conditions in the treatment pond B 2A in order to facilitate the co-precipitation of arsenic with iron, while it may be necessary to create anoxic condition in the sediment of ponds B 3A and B 4A which would result in reducing conditions that would eventually facilitate adsorption of arsenic on the organic fraction of the sediments.

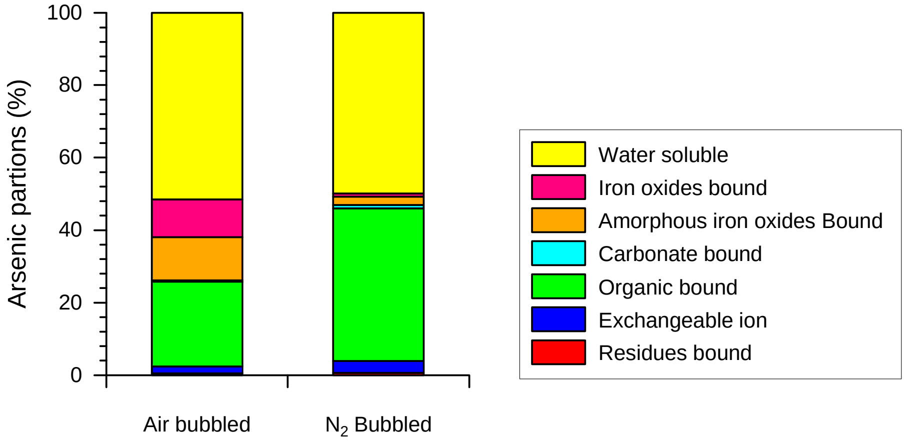

Figure 5. Sorption of arsenic into different sediment fractions after 35 days in oxygen rich and poor conditions in a column experiment. The column was bubbled with air and had a maximum of 8.0 mg $L^{-1}$ dissolved oxygen, while the dissolved oxygen in the nitrogen bubbled column was almost immeasurable.

## 4. CONCLUSION

The results of the current research reveals that there are two main mechanisms of arsenic removal from the shaft flood water and fixation into the sediment in the constructed wetland. The mechanisms are co-precipitation with Fe-oxides caused by the oxidation of Fe II to Fe III as well Mn-oxides, and adsorption on organic matter. Thus, the As behaviour is governed by redox chemistry of Fe(III) and Mn(IV) oxides under oxidising conditions, where increases in sediment redox potential equally increased the affinity of both Fe(III) and Mn(IV) oxides for As, while decreases in sediment redox potential resulted in high affinity between particulate organic matter and As. Therefore, keeping redox potential high by increasing oxic status in B 3A and B 4A, while reducing the redox potential in B 2A would increase the removal capacity of arsenic in the constructed wetland facility. SEM-EDX results also indicate that residual arsenic fractions were mainly in the form iron arsenic (Fe-As) together with calcium arsenic (Ca-As). Although there were substantial contents of As and Fe in the sediments, the amounts were not sufficient for accurate crystallography and mineralogical identification with X-ray diffraction. Further, the high organic fraction probably limited the characterisation of these "young" sediments with X-ray diffraction techniques. Nevertheless, the main arsenic removal processes from the water pathway seem to be binding to organic matter , and co-precipitation with Fe, Ca and Mn oxides.

## 5. ACKNOWLEDGEMENT

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