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Arsenic Speciation in Soils and CCA-Treated Wood Leachate.

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INTRODUCTION

Use of Chromated Copper Arsenate (CCA) as a wood preservative began in the 1970's. Since concern for arsenic has increased, it has become necessary to accurately quantify the amount of arsenic which is present and available to cause potential harm. Since the toxicity of arsenic can vary greatly among its different elemental species, it is important to preserve them during analysis in order to properly assess potential health hazards. Soils and sediments provide a unique challenge for the extraction and preservation of such arsenic species. Re-adsorption or possible species interconversion may occur during the extraction process, which can lead to false interpretation since sediment/soil standard reference materials for arsenic speciation are not currently available for verification. This study focuses on method development for the preservation and stabilization of arsenic species during chemical extraction to develop a method to be applied to soils and sediments exposed to CCA-Treated Wood Leachate. A number of chemical extractants have been used to test their potential for extraction and stabilization of arsenic species during the extraction process. The results of using NaDDC as chelating agent in an effort to prevent soil re-adsorption and reduce specific arsenic availability for conversion is presented.

Experimental Procedures

0.5 grams of soil is placed in 60 ml Amber Nalgene Bottles. The appropriate amount of Arsenite and Arsenate are spiked into the soil directly. Two Solutions are used for this experiment. One is 10mM Phosphate solution containing a 1:1 ratio of K_2HPO_4 and KH_2PO_4 . The other contains the same Phosphate mixture with the addition of 0.5% diethyldithiocarbamate trihydrate (NaDDC). 20ml of extraction solution is then placed in the appropriate bottles taking care to rinse the sides. The bottles are then placed on an orbital shaker set to 300 rpm and allowed to shake for a 12 hour time period. 10ml of the solution is then removed from each bottle and placed in individual plastic tubes. The tubes are then centrifuged at 5000 rpm for a period of 5 minutes. Samples are then filtered through a $0.45\mu m$ PVDF syringe filter. The samples containing only phosphate are ready for analysis. The samples containing phosphate and NaDDC are slightly acidified with $50\mu L$ of 6M HCl to break the complex formed with Arsenite (As^{III}). The pH is then adjusted with $10\mu L$ of 6M NaOH. These samples are then ready for analysis. All samples are then analyzed by HPLC-HG-AFS.

INSTRUMENTATION

- Thermo Separations product SpectraSystem P4000 pump and AS3000 autosampler.
- PSA PS Analytical Millennium System Hydride Generation Atomic Fluorescence Detector.
- Column: Hamilton PRP-X100 Anion Exchange Column
- VWR Scientific Products Orbital Shaker

Soil Composition Used

- PACS2

(Marine Reference Sediment)

High Concentrations of:

- Iron
- Manganese
- Aluminum

- Uncoated Sand

-Quartz

- Deck Soil

- High Carbonate Soil

- Naturally Coated Sand + Peat

- Clay Fraction:

-Hydroxy-interlayered vermiculite

-Kaolinite

-Gibbsite

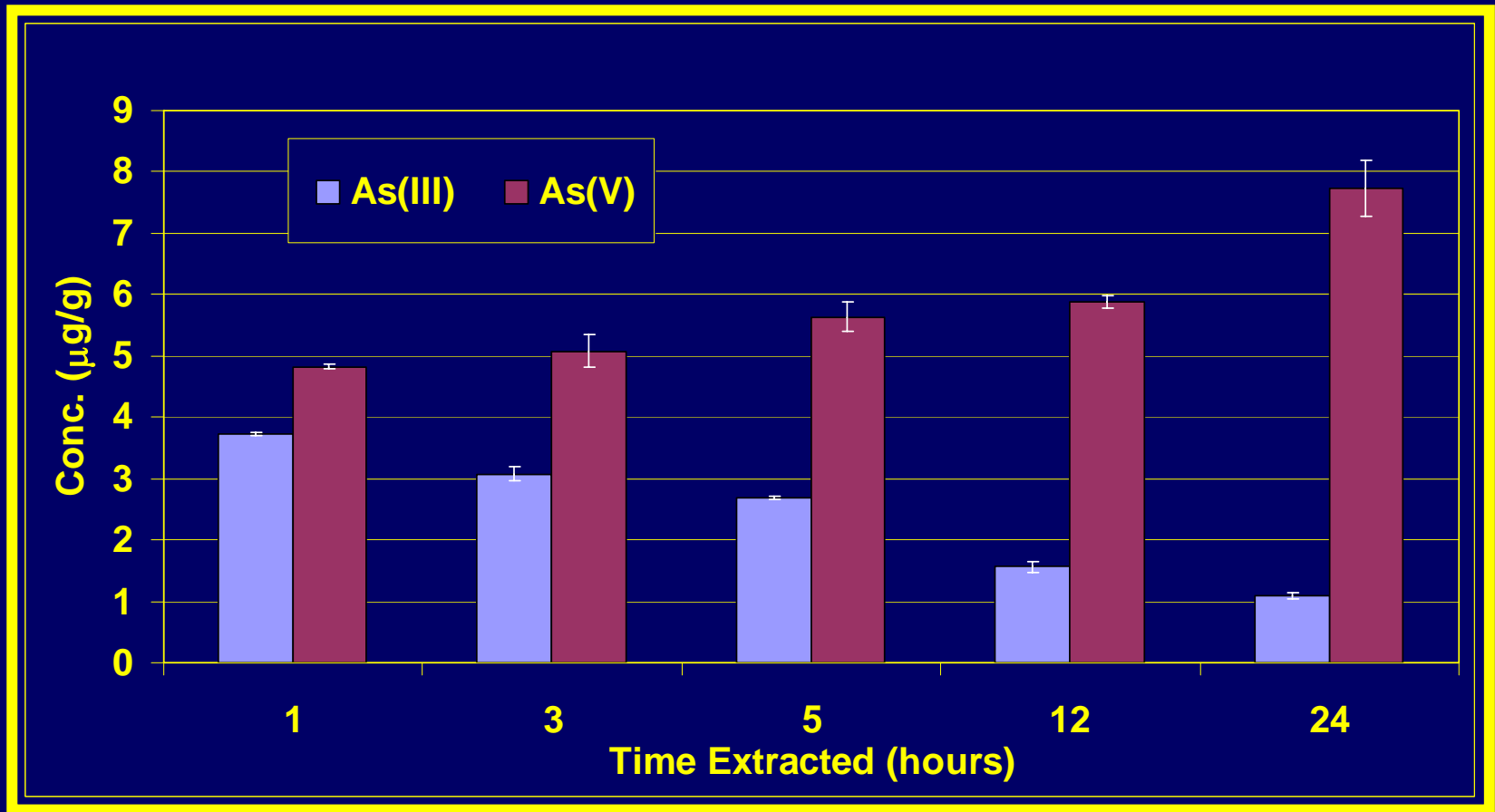
-Goethite

-Quartz

- Silt Fraction:

-Quartz

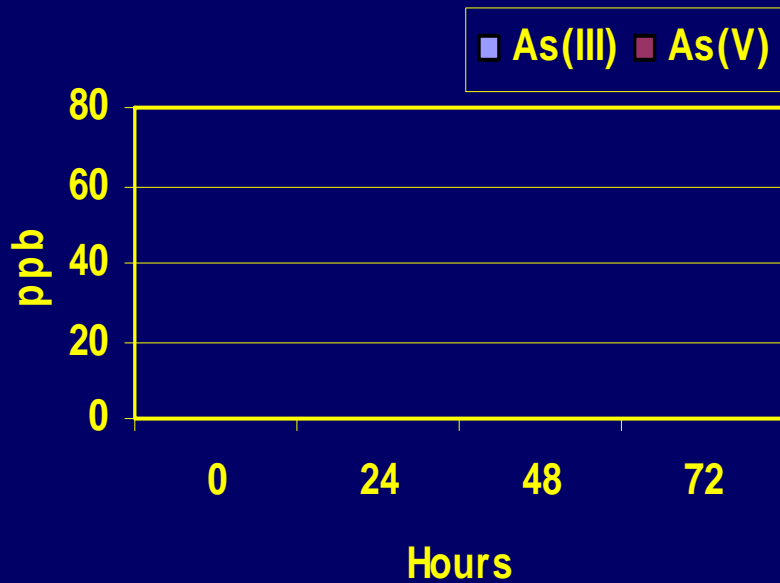
Arsenic Concentration vs Time



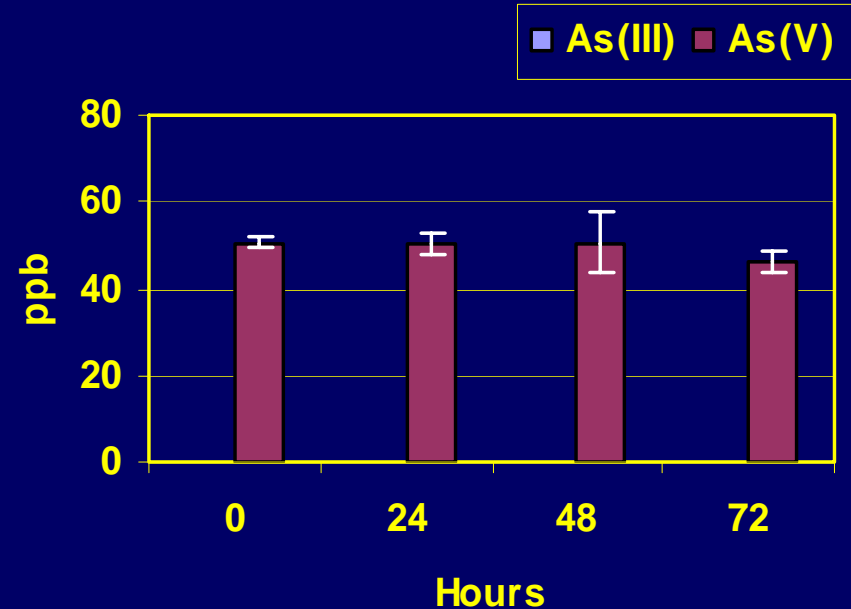
Above shows an extraction time period of up to 24 hours with 10mM phosphate solution. It was found that the amount of arsenic of each species changes with extraction times. The As(III) concentration decreases as the extraction time increases. This may be due to interconversion between species or soil re-adsorption.

Stability test for NaDDC over a 72 hour time period.

NaDDC 50 ppb As(III) Spiked

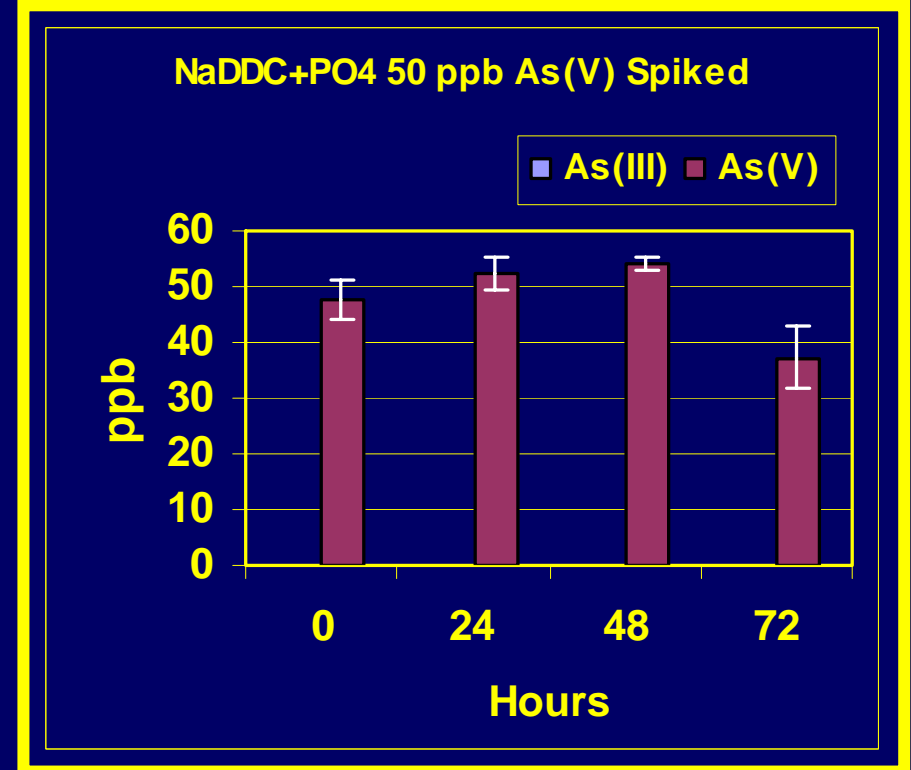
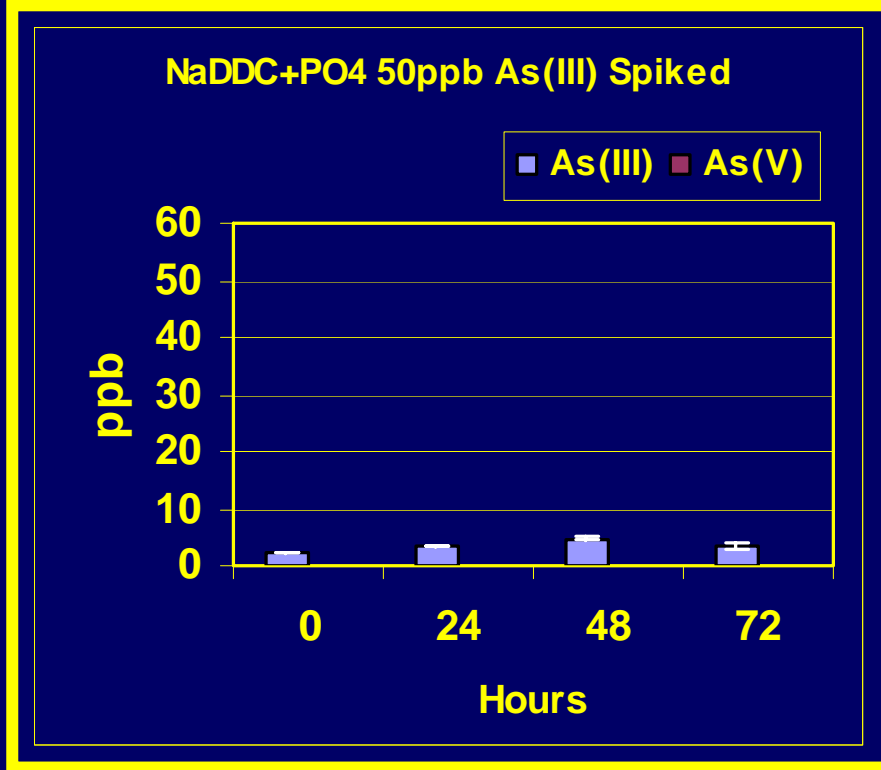


NaDDC 50 ppb As(V) Spiked



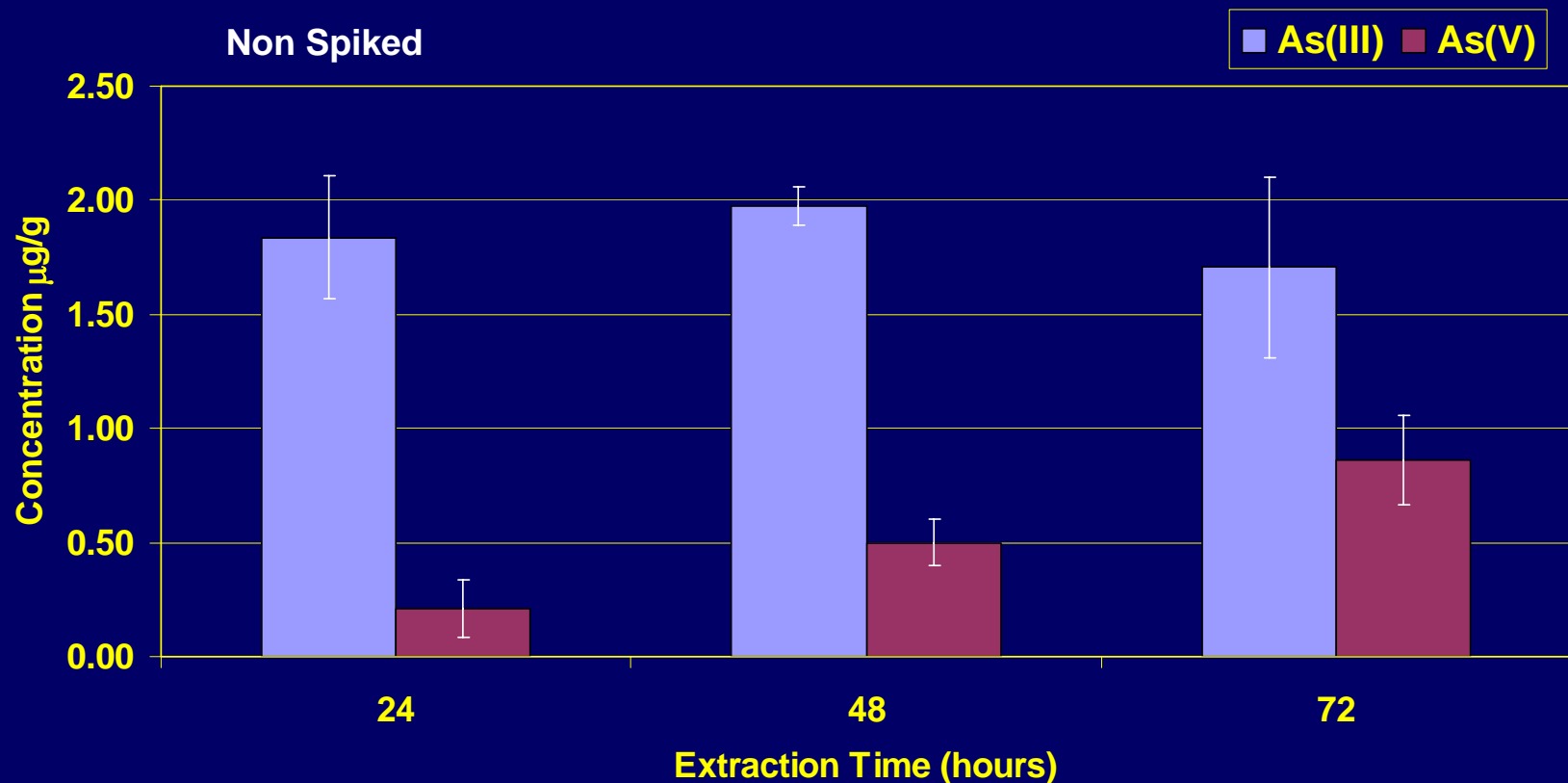
An appropriate amount of arsenic was spiked and shaken with no soil present to test the stability of NaDDC in solution. Only unbound Arsenic will be detected. No arsenic was detected in As(III) spiked samples indicating that all As(III) was complexed and no conversion to As(V) occurred. No evidence of conversion from As(V) to As(III) was seen in the As(V) spiked solution due to good As(V) recovery.

Stability test for NaDDC + Phosphate over a 72 hour time period.



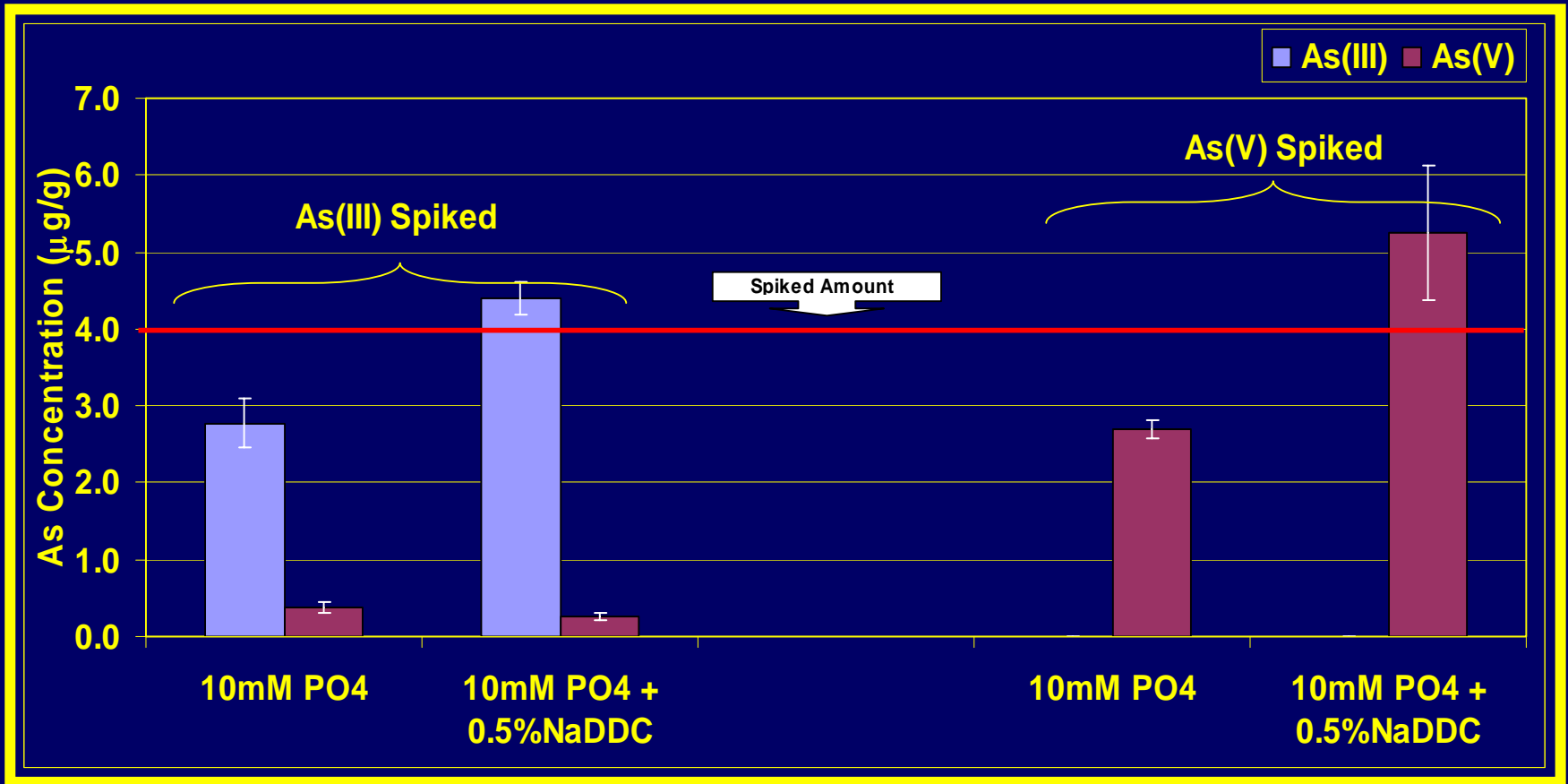
An appropriate amount of arsenic was spiked and shaken with no soil present to test the stability of 0.5% NaDDC in 10mM phosphate solution. Only unbound Arsenic will be detected. Some As(III) was detected in the As(III) spiked solution. This may be due to some phosphate interaction with As(III) making it unavailable to be bound to NaDDC. Good recoveries were achieved for As(V) spiked solution until a period of 72 hours. Conversion might have occurred possibly due to NaDDC instability with phosphate after a 72 hour time period.

PACS2 Extraction with 10mM PO₄ + 0.5% NaDDC



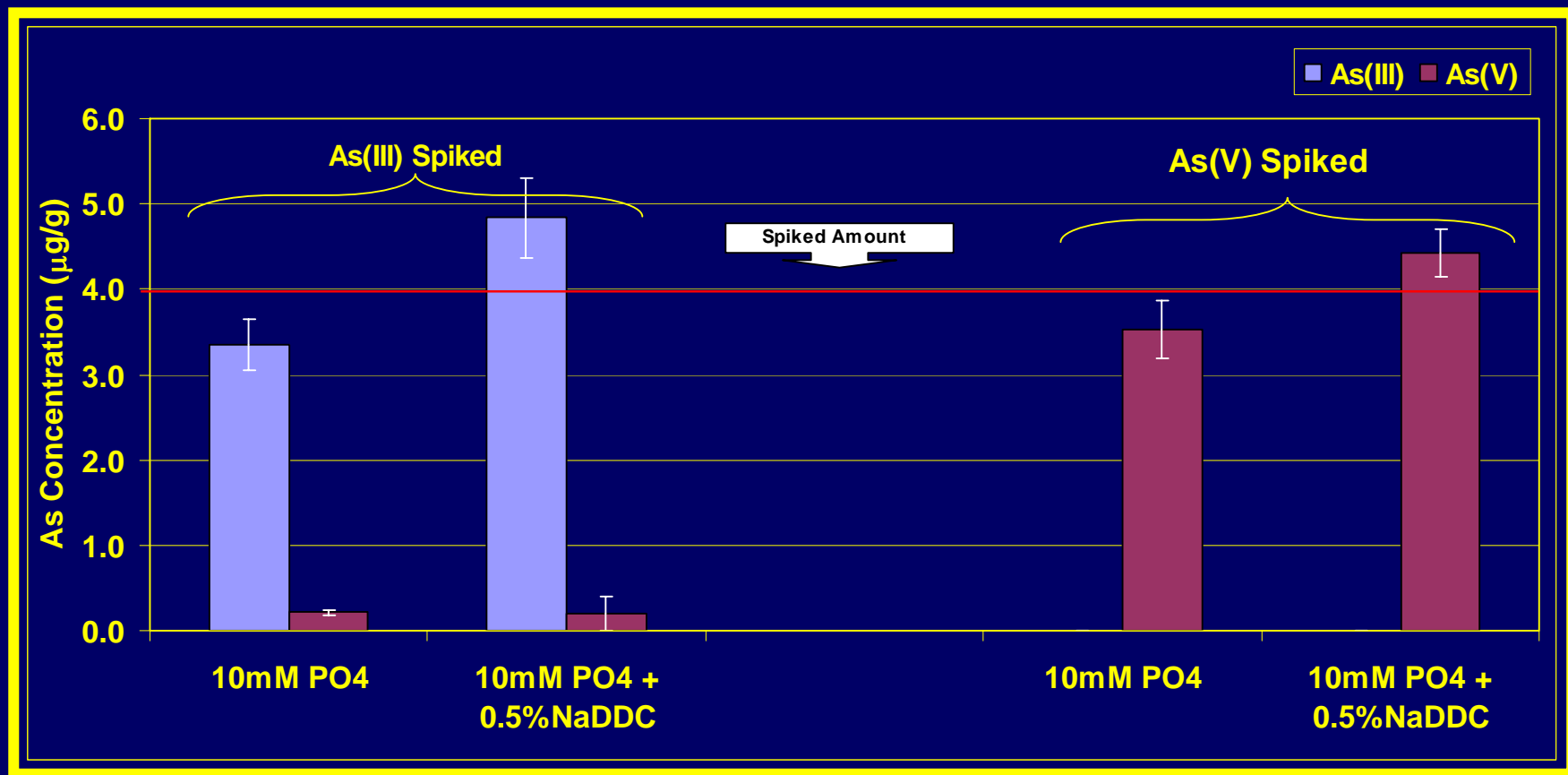
Above shows PACS2 Marine Reference Sediment extracted with 10mM + 0.5% NaDDC from 24 to 72 hour time period. The concentration extracted remains constant throughout the extended time period with some variability at 72 hours. This may be due to stability issues with NaDDC at such a prolonged extraction time.

Uncoated Sand 12 Hour Extraction



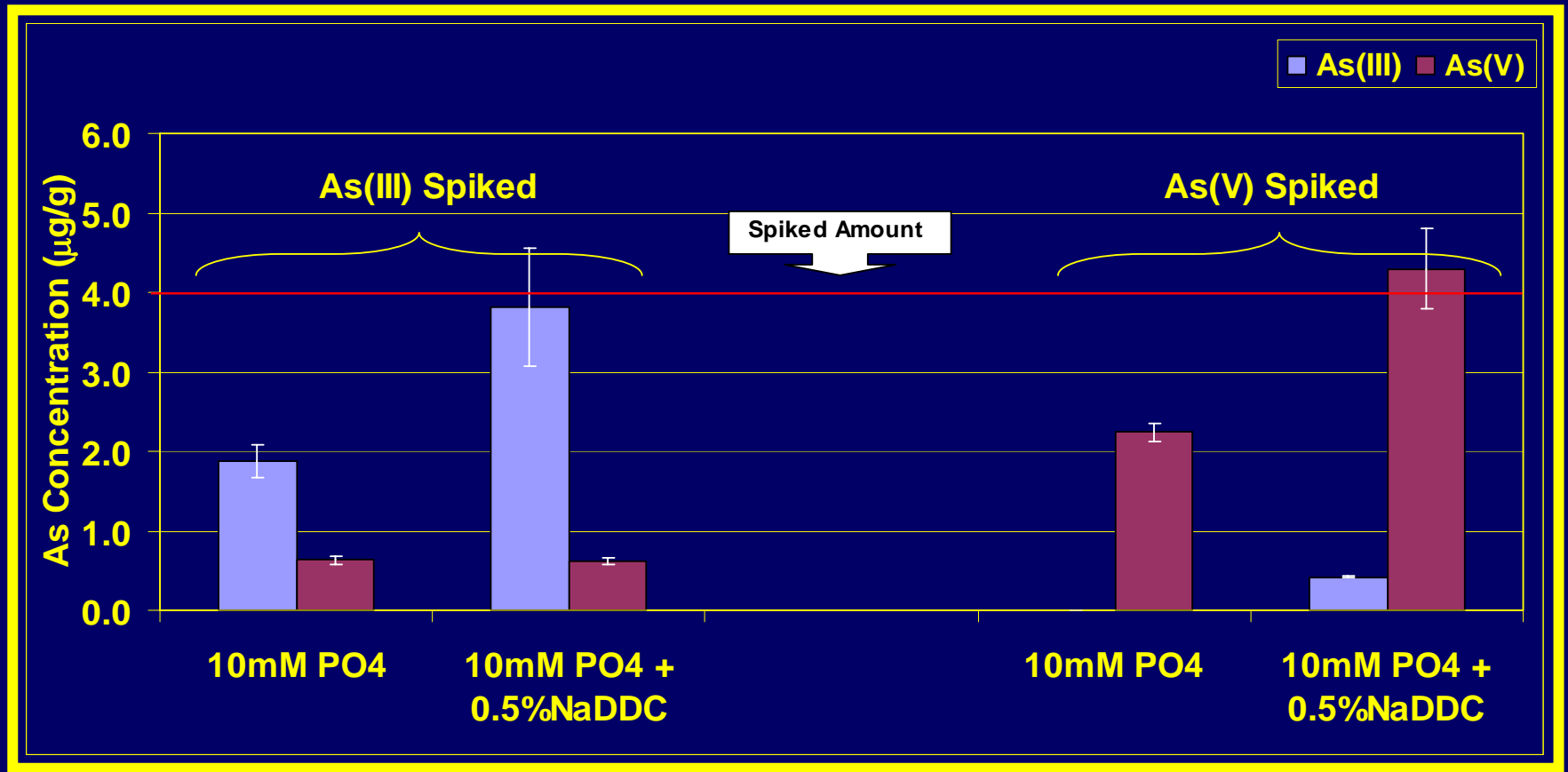
Good recoveries for both As(III) spiked and As(V) spiked uncoated sand was achieved indicating NaDDC helps preserve As(III) species and minimizes re-adsorption.

Naturally Coated Sand + Peat 12 Hour Extraction



Good Recoveries were again observed with the use of NaDDC with naturally coated sand containing peat spiked with As(III) or As(V).

Deck Soil 12 Hour Extraction

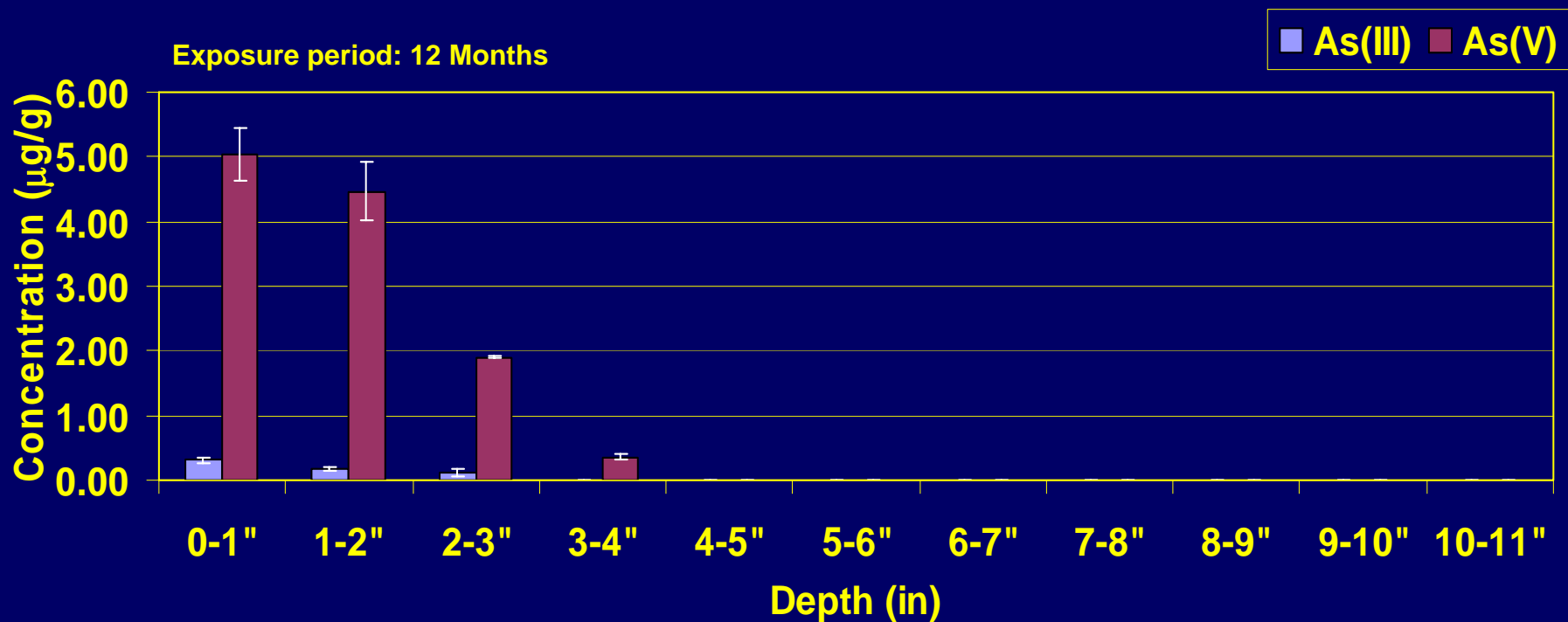


Good recoveries for both As(III) spiked and As(V) spiked high carbonate containing soil was achieved indicating that NaDDC helps preserve As(III) species and minimizes re-adsorption.

CCA-Treated Wood Deck Experiment



CCA Treated Wood Deck Soil Depth Study



Above is a depth profile of the arsenic speciation found from the surface of the soil to a depth of 11 inches of soil underneath a CCA-Treated Wood Deck. The majority of the arsenic found in the soil which leached from CCA-Treated wood is arsenate. No arsenic species was found deeper than 4 inches.

Conclusions

It is important to understand that there are numerous processes which may play a part to alter the chemical species during chemical extraction. It was found that the amount of arsenic of each species changes with extraction times. Efforts were made to stabilize As(III) concentration by adding NaDDC to the extraction mixture. The premise for using NaDDC is to complex with As(III) making it unavailable for these processes to occur. NaDDC has shown an improvement in the preservation of As(III) species during the an extraction time period for PACS2 Marine Reference Sediment, naturally coated sand + peat, uncoated sand, and the deck soil.

Acknowledgments

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