AN EVALUATION OF ARSENIC UPTAKE BY MARINE SEDIMENTS

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I certify that I have read this thesis and that, in my opinion, is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

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ABSTRACT

After World War I and through the end of World War II, the United States military dumped unused chemical warfare munitions (CWM) into coastal waters off Oahu. A number of studies are currently researching how the condition of CWM and effect environmental quality in the marine environment. Lewisite, an arsenic-rich compound, is found in CWM and hydrolyses in water, allowing arsenic to seep into the marine environment. To supplement current ongoing studies, controlled laboratory batch reactor experiments evaluated the potential mobility of arsenic (As) derived from sea-disposed lewisite in the marine environment. Sediment cores obtained from the CWM sites were evaluated for their ability to absorb and retain arsenic. Sediment-water suspension experiments, with different As concentrations (5 μM, 10 μM, and 20 μM) and species added (As(III) and As(V)), have been run from one minute to 7 days and experiment sediment samples were analyzed by ICPMS to determine As content.

Arsenic uptake onto sediments continued over time but the relative or absolute uptake at the end of the experiment does not necessarily increase with increasing As spike concentrations. The uptake of As(V) was also greater over time (as compared to experiments with an equivalent concentration of As(III). It was concluded that over the 7 day experiment duration, none of the experiments reached equilibrium, therefore suggesting that As adsorption on the sediments at the CWM sites is much less than anticipated, and the amount of As going into the surrounding water is greater than expected. The calculations of As that is added to sediment and seawater, based on the experimental data, concludes that the impact on the environment is minimal.

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LIST OF ABBREVIATIONS

$AlCl_3$ – aluminum chloride

Ar - argon

As – arsenic

As(V) – arsenate (AsO_4^{3-})

As(III) – arsenite (AsO_3^{3-})

$AsCl_3$ – arsenic trichloride

AsH_3 – arsine

ATP - adenosine triphosphate

C_2H_2 – acetylene

$C_2H_2AsCl_3$ – Lewisite

C – Celsius

CEM – channeltron electron multiplier

CWM – chemical warfare munitions

CWA – chemical warfare agents

DI - deionized

DOD – Department of Defense

DMM – discarded military munitions

FeOx – iron oxides (of various oxidation state)

g – gram

H_2O – water

HCl – hydrochloric acid

HDPE - high-density polyethylene

HF – hydrofluoric acid

HNO_3 – nitric acid

HUMMA – Hawaii Undersea Military Munitions Assessment Project

HURL – Hawaii Undersea Research Laboratory

ICP – inductively coupled plasma

kg - kilogram

km – kilometers

L - liter

m – meter

MHz - megahertz

μg – microgram

μm – micrometer

μM - micromolar

mg - milligram

mm – millimeter

MPRSA – Marine Protection, Research and Sanctuaries Act

NOAA – National Oceanic and Atmospheric Administration

MS – mass spectrometry

OES – optical emission spectrometry

P – phosphorus

pH – power of hydrogen

PO_4^{3-} - phosphate

ppb – parts per billion

ppm – parts per million

PVC – polyvinyl chloride

S – sulphur

SRM – standard reference materials

T (U.S.) – short ton (2000 pounds)

U.S. – United States

U.S.C. – United States Code

v/v – volume to volume

WWI – World War One

WWII – World War

CHAPTER 1: INTRODUCTION

History of Munitions Disposal at Sea

According to 10 U.S.C. 101(e)(4)(A) through (C), military munitions are defined as:

> "ammunition products and components produced for or used by the armed forces for national defense and security, including ammunition products of components under the control of the Department of Defense, the Coast Guard, the Department of Energy, and the National Guard. The term includes confined gaseous liquid, and solid propellants; explosives, pyrotechnics, chemical and riot control agents, smokes, and incendiaries, including bulk explosives, and chemical warfare agents; chemical munitions, rockets, guided ballistic missiles, bombs, warheads, mortar rounds, artillery ammunition, small arms ammunition, grenades, mines, torpedoes, depth charges, cluster munitions and dispensers, demolition charges; and devices and components thereof."

As stated, this defines only U.S. munitions. Additionally, discarded military munitions (DMM) are "all such munitions that have been removed from storage in a military magazine or storage area for the purpose of disposal" (10 U.S.C. 210(e)(2)) (uscode.house.gov).

Despite these terms as defined by the United States, this practice was not particular to U.S. forces, but was widespread and considered an acceptable means of disposing of unwanted munitions by many other nations as well. Ocean disposal of military munitions was common all over the world after World War I, and continued well past World War II. Worldwide, there are 127 known DMM sites, which have been located based on disposal records or human exposure (Figure 1) (Ong et al., 2009).

Figure 1: World map of DMM sites (cns.miss.edu)

Of the 127 known sites, 74 are catalogued as associated with the U.S. Army (Bearden, 2007). The former Soviet Union has military archives describing the disposal of at least 160,000 tons of chemical weapons materials (CWM) into the Baltic Sea, with much more unaccounted for (Jegelevicious, 2011). After World War II, the U.S. discarded the Japanese chemical munitions stockpile in at least 15 locations off the coast of Japan (Brankowitz, 1987). In Germany, leftover chemical munitions totaling 302,857T were discarded into the North Atlantic, the North Sea, and the Baltic Sea (Laurin, 1991, Missaiaen, 2002). It is assumed that there are many more DMM, but poorly documented written accounts of locations, quantities or depths of disposal, and because of the extent of DMM occurrences near coasts, discovery of the DMM is often unintentional and has led to human exposures.

Since 1946, DMM have injured nearly 500 people around the world. Injuries are often associated with fishing activities, where CWM are caught in nets or accidentally dredged up during trawling operations. Danish fishermen have reported the most accidents: 450 since 1976. Most of these occurrences have taken place in the Baltic Sea, where fishing vessels are required to report and recover all discovered DMM (Laurin, 1997). In the United States, fishermen in New York were severely burned when a clamming vessel inadvertently brought mustard gas canisters onto the deck of their boat in 2010 (CDC.gov, 2013). In Hawaii, three U.S. Army Corp of Engineers dredged up a CWM canister, injuring three men in 1976. Additionally, a fisherman received chemical burns after inadvertently pulling up a mustard gas mortar in the 1970's (HUMMA, 2010).

Unused conventional and chemical warfare munitions were dumped into coastal waters off Oahu, Hawaii beginning after World War I (Figure 2). In Hawaii, most munitions were either surplus or obsolete but, because of the tropical climate, corroding, leaking, and damaged military munitions were also discarded into the ocean. The DMM included small arms rounds, large caliber projectiles, but also included highly noxious chemical agents or CWM, such as mustard gas and lewisite (Ong, et al*.,* 2009).

Munitions were often discarded at sea because, at the time, this method was considered the safest alternative in poisonous munitions disposal.

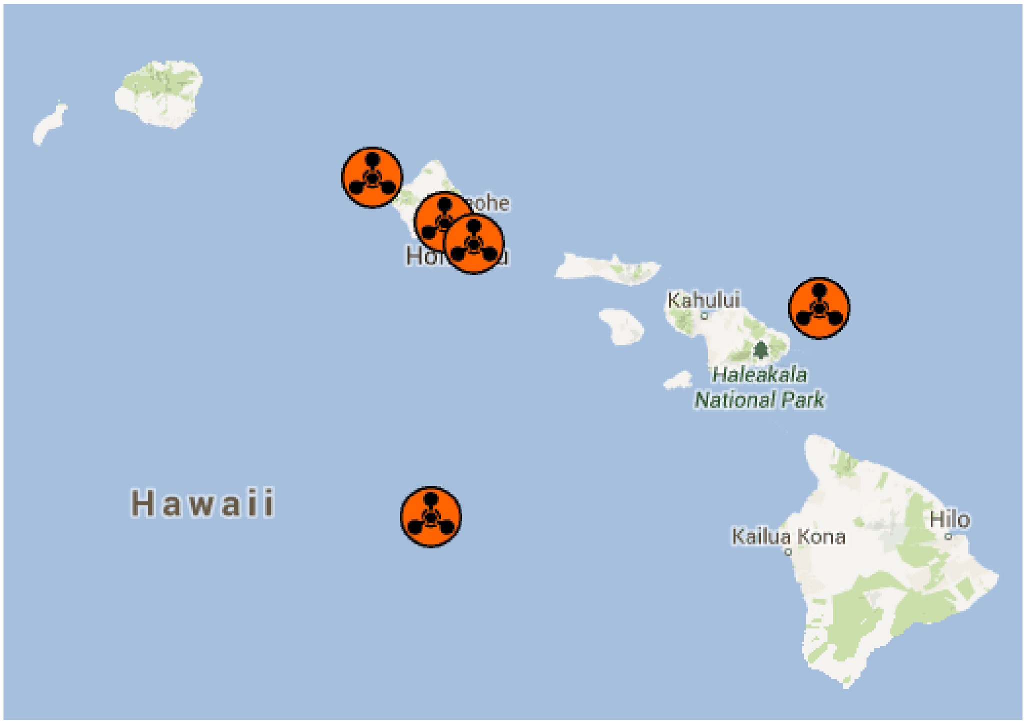


Figure 2: Known DMM around Hawaii (cns.miis.edu)

In 1972, however, human health, environmental, and economic impact concerns led to congressional prohibition of the sea-disposal of "material that would reasonably degrade or endanger human health or the marine environment." The ensuing legislation was part of the Marine Protection, Research and Sanctuaries Act (MPRSA) (EPA, 2013).

While the majority of CWM were documented as being disposed of at depths greater than 300 feet (~90 m) and distances further than 10 miles (16 km) offshore, many have been found in shallower water and closer to shore than military records specify. The names of reefs along the west side of Oahu, such as, 'Ammo Reef' and 'Ordnance Reef' illustrate this fact. Discarded military munitions have often washed up along beaches on the West side of Oahu after swell events (Bettinger, 2007). Military records indicate that large quantities of CWM were dumped in 1945, in the deep ocean off the Waianae coast. Exact locations and depths were not recorded, however, discarded weapon records include, 204T of chloride bombs, 1,531T of mustard (bombs, shells, containers), and 253T of lewisite (U.S. Army Research, 2001).

For this study, controlled laboratory experiments will evaluate the potential mobility of arsenic (As) derived from sea-disposed lewisite in the marine environment. Sediment cores obtained from the HUMMA DMM sites will be evaluated for their ability to adsorb and retain arsenic. It is expected that the As adsorption would be be very rapid inititally and then reach an equilibrium over an extended but relatively short time. The data collected from these experiments will assist in better understanding the environmental impacts from CWM sites.

HI-05

The CWM disposal site off the Southern coast of Oahu, designated by the U.S. Department of Defense as HI-05, is a known deep-water location of DMM (HUMMA, 2010). Records indicate that three disposals events were associated with this area between 1944 and 1945. Known DMM include 16,000 M47A2 100-lb bombs filled with mustard gas plus an additional 29T of mustard gas, 4,220T of an unspecified material (CNS.miis.edu). The HUMMA research project, conducted by the University of Hawaii (HUMMA, 2010) has been monitoring and studying this site since 2007 to better understand the location and the fate of sea-disposed munitions, in general.

HI-06

DMM were discovered close to shore in 1992 by a City and County of Honolulu, Wastewater Management Oceanographic team during benthic studies of the area This new site, designated HI-06 by the U.S. military was discovered in near-shore waters of Waianae, on the western side of Oahu, in 18 to 36 meters of water (Cox et al., 2007). Since then, DMM and CWM, in particular, have been a subject of controversy among community and environmental activists who believe the munitions pose an immediate threat to human health. Eventually, public concern led the NOAA Marine Sanctuaries Program, the U.S. DOD and the University of Hawaii at Manoa into an agreement to study and evaluate potential explosive and human health hazards of military munitions around Oahu (Cox et al., 2007).

CHAPTER 2. BACKGROUND

Chemical Warfare Agents (Mustard, Lewisite, etc.)

Chemical weapons were first used on a wide scale in Europe during World War One (WWI). Because of the widespread use of CWM, WWI was considered "The Chemists' War" (Fitzgerald, 2008). At least 40 different chemical weapon agent (CWA) compounds were produced and deployed, and about one third of all shells fired contained toxic compounds (Missiaen, 2002). During and after WWI, the Germans introduced war gases of chlorine, phosgene, and mustard, while the allies had prepared the arsenical compounds Lewisite and Adamsite (Fitzgerald, 2008).

PhD student J.A.Nieuwland first synthesized Lewisite in 1904. Nieuwland was sent to the hospital while studying the interaction of the hydrocarbon acetylene (C_2H_2) with As trichloride ($AsCl_3$) and a catalyst aluminum chloride ($AlCl_3$). Unknowingly, Nieuwland had produced $C_2H_2AsCl_3$. A U.S. Chemist and soldier, W. L. Lewis, eventually synthesized and named that compound Lewisite (Figure 3), while working for the Chemical Warfare Service (Vilensky, 2005) (lewisite production Appendix C).

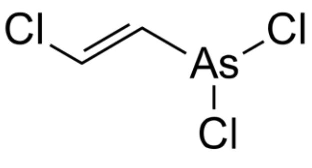


Figure 3: Lewisite structure

From the First World War onwards, organoarsenicals, including Lewisite were developed, stockpiled and also used as harassing, vomiting or vesicant agents in chemical warfare (Leermakers, et al., 2006). The majority of Lewisite produced prior to World War Two (WWII) was disposed of, along with thousands of tons of other CWM, at sea.

Arsenic

Arsenic (As) is a commonly occurring element. It is found in terrestrial and aquatic environments, both freshwater and marine, with geology being the most important factor controlling its natural distribution and abundance. As is the 47th most abundant of the 88 naturally occurring elements (Plant et al. 2005). It is ubiquitous in the lithosphere, however at relatively low concentrations ranging from 0.5 to 2.5 ppm (Kabata-Pendias, 2000). It is the 48th most abundant element in the Earth's continental crust, with an average concentration of 1.7 ppm (Wedepohl, 1995). Natural concentrations of As, however, are highly variable. Weathering of As-containing rocks is considered to be the dominant natural source of As to the environment (Tamaki & Frankenberger, 1992). Volcanic eruptions and hydrothermal activity are two other important natural sources of As (Matschullat, 2000). As forms a broad range of organic and inorganic compounds, and strongly complexes to solid metal oxides, especially those of iron (Fe), when present as an oxyanion (Fuller et al. 1993). The most important As-containing minerals are metal sulfides, including arsenopyrite, orpiment, and realgar. Mining of sulfide ores provides important metal resources in many areas but mining activities can concentrate As, and often subsequently release it to the environment in large quantities (Matschullat 1996; Matschullat, 2000).

In the U.S. and worldwide, industrial activities have left vestigial As in surface and near-surface soils. Smelting, S and P mineral processing, cement production, fossil fuel combustion, geothermal power plants, waste incineration, fertilizer application, and the widespread use of As based pesticides during the 20th century have all contributed to increased As abundances. Concentrations of residual anthropogenic As ranges from 10s to 1,000s ppm (Matchullat, 2000; Kabata-Pendias, 2001). Soil As accumulations from agricultural pesticide applications have been reported at sites across the U.S. (Belluck, et al., 2003; Yang & Donahoe, 2007; Robinson, et al., 2007), including Hawaii (Cutler, 2006, De Carlo et al., in press).

Due to the range of natural and anthropogenic controls over localized enrichment of As, there is great variability in the abundance and availability of As in aquatic systems (Mcintyre and Linton, 2012). Worldwide, however, As concentrations in the open ocean tend to be less variable than that of freshwater environments. This is due to the proximity of freshwater to geochemical environment and anthropogenic influences (Mcintyre and Linton, 2012). In the marine open-water environment, As concentrations typically range from 0.5 to 2.0 $\mu g\ L^{-1}$ (Francesconi and Kuehnelt, 2002). Biological processes, pH, and redox potential all play an important role to determine As speciation and consequently influence its toxicity to marine life (Sharma et al., 2009).

The main properties of As are as follows; As is an element with the atomic number 33. It is in group 15 of the periodic table and is described as a metalloid that is readily oxidized. As exists in four oxidation states; +5 (AsO_4^{3-}), and +3

(AsO_3^{3-}), are the most common, but also found are, 0 (As), and -3 (AsH_3) (Sharma, et al.*,* 2009). AsO_4^{3-} shows many similarities in chemical behavior with the isostructural PO_4^{3-} (Goldschmidt, 1958). In the soil and sedimentary environments, inorganic and organic As may be present as salts of available cations, in the form of precipitates, or as adsorbates on hydrous oxides, clays and other surface active materials (Stoeppler, 1992; Francesconi & Kuehnelt, 2002; Plant, et al., 2005). The relative omnipresence and inherent toxicity of As are cause for concern, and the contamination of groundwater and coastal ecosystems has gathered much recent attention.

The toxicity of As to biotic receptors is of great concern owing to a potential for bioaccumulation and biomagnification in ecosystems. As is classified as both an essential trace element to some animals, including humans, and also a proven carcinogen and mutagen (Mcintyre & Linton, 2012; Sharma & Sohn, 2009). Some toxic effects of As occur due to its substitution for P in the cellular ATP cycle, which effectively reduces the energy normally produced during that process (Wurl et al.*,* 2013). Additionally, As may inhibit metabolic reactions by binding with the sulfhydryl groups of enzymes (Edenborn, et al., 1986). Bacteria and some phytoplankton have evolved methods to alter the toxic effects on their by reducing AsO_4^{3-} to AsO_3^{3-} or methylation, to make excretion of toxins easier, therefore changing the concentration of more toxic As forms in the water column (Andreae & Klumpp 1979; Sanders & Riedel 1993; Hellweger, et al., 2003). Microbes may play an important part in the chemical transformation of As species, and can increase mobility of the more toxic AsO_3^{3-} in the environment (Bhattacharya et al, 2007).

Arsenic in Saltwater

The distribution and abundance of As in seawater are less variable than in freshwater. Concentrations generally range from 0.5 to 2.0 µg L^{-1} and the distribution of this element in the open ocean is like those of essential nutrients (Geng, et al., 2009). In estuaries, concentrations of As rarely exceed 4.0 µg L^{-1}, but increased salinity and pH can influence Fe flocculation and As co-precipitation, leading to variation in As concentrations (Smedley & Kinniburgh, 2011). Conversely, in the clean waters of the coastal and open ocean, average As concentrations are around 1.7 µg L^{-1}, with a range of 1-3 µg L^{-1} (Neff, 1997).

The common species of inorganic As in the marine environment are AsO_4^{-3} (arsenate (As(V)) which is the more stable oxidation state and AsO_3^{-3} (arsenite (As(III)) a more reduced form (Ferguson & Gavis, 1972). The principal form of As in well-oxygenated seawater is AsO_4^{-3} because of its enhanced thermodynamic stability (Mcintyre, 2012). In contrast, AsO_3^{-3} is thermodynamically unstable in oxygenated environments and is therefore usually not present in significant quantity in oxidizing environments (Mandal & Suzuki, 2002). Redox potential (Eh) and pH (Figure 4) exert important control on the speciation of As. AsO_3^{-3} is dominant at pH less than 6.9; conversely at higher pH AsO_4^{-3} becomes dominant. (Yan, et al., 2000).

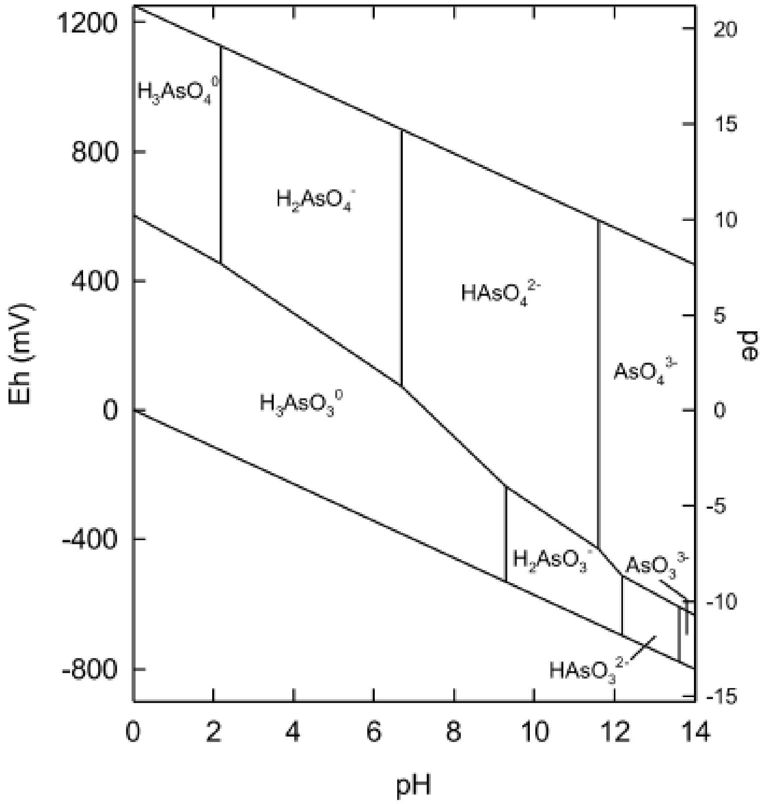


Figure 4: Arsenic speciation vs. pH and Eh (Smedley & Kinniburgh, 2011)

Additionally, three organoarsenic compounds are found in seawater and produced through biological transformations in organisms such as sea grasses (Fourqurean & Cai, 2001).

Although concentrations of the element As vary widely in terrestrial systems because of geologic and, more recently, anthropogenic fluxes, marine concentrations display considerably less variability. In seawater, the residence time of As has been estimated to be 60,000 to 100,000 years (Henke, 2009; Matschullat, 1996). Estuaries and rivers, when unpolluted, traditionally have not delivered significant amounts of particulate or dissolved As in the ocean

(Smedley, et al., 2011). As discussed earlier, industries, such as mining and agriculture, however, have caused increased transport of As into marine ecosystems. Riverine run-off of As from pollution sources can contribute a large proportion of As in localized areas (Hinkle et al., 1998). In areas where activities such as mining occur, concentrations of As can reach 16 μg L^{-1} in estuarine waters (Smedley, et al., 2011).

Additional inputs of As to the ocean can be attributed to atmospheric deposition. Deposition of As from industrialized sources, and mineral aerosols from deserts and seasonal events can be a major source of this element into the ocean (Cutter, et al*.,* 2001). In areas of relatively low industrialized outputs, such as Tacoma Washington, As deposition ranges from 0.5 to 2.5 μg m^{-2} (Sanders et al., 1998). In contrast, on the central Atlantic Coast, where industrial coal combustion is common, As deposition ranges from 38 to 266 μg m^{-2} per yr (Scudlark, et al., 1988?).

Anthropogenic sources typically impact concentrations of As in marine environments to a greater extent than natural sources. Various studies, however, have found that rivers in areas with geothermal activity are often enriched in As (Smedley, 2011). It is important to note that riverine and estuarine inputs of As to the ocean may not ultimately affect its seawater concentration because of the propensity for As to coprecipitate with or adsorb onto iron oxides, which remove As from suspension in the water column (Andreae, 1983). Estuarine flocculation, which occurs at freshwater and saltwater interface (Sholkovitz, et al., 1978), also reduces the flux of dissolved As from polluted freshwater sources to the ocean (Cullen & Reimer, 1989).

Arsenic in Marine Sediment

Marine sediments are the largest global geochemical reservoir of As (Maher & Butler, 1988). In contrast to the residence time of As in seawater, ocean sediments can hold the element for one million years (Mackenzie et al., 1979). Natural depositories include estuarine deposition, coastal sediment delivered by river runoff, and deep-ocean sediments, where As incorporates with detritus and settles to the bottom (Edenborn et al., 1986). Concentrations of As in deep ocean sediment are affected very little by human activities, however along the coast, sediment concentrations may vary depending on anthropogenic influences. Sediments unaffected by anthropogenic or natural hydrothermal activity, however, display concentrations of As from 0.1 and 3.5 $\mu g\ g^{-1}$ and are similar in near-shore and deep-ocean locations (Maher & Butler, 1988). Deep-ocean content typically increases near mid-ocean ridges, where hydrothermal activity is common.

In the marine environment, As is strongly associated with iron oxide phases and is typically present in anionic form. Adsorption of As onto iron oxides (FeOx) is highly sensitive to pH and the presence and abundance of additional anions in the environment, such as those of P and S (Henke, 2009). The typical environmental speciation of As as an oxyanion allows it to readily adsorb onto

FeOx particles in the water column and within sediments on the seafloor (Maher & Butler, 1998).

As adheres to sediments through adsorption reactions, however changes in sediment characteristics (i.e., elemental composition and mineralogy) can cause changes in the amount of As adsorbed as well as the solid phases onto which it partitions. Sedimentary material that undergoes early diagenesis can also release As into porewaters if dissolution of the host carrier phases takes place. In such cases, the As may still remain in close proximity to sediments and potentially be taken up again by other phases as sedimentary conditions change subsequently. Furthermore, diffusion of As from the porewater into the overlying water column may also take place. Some of the main parameters that can affect the mobility of As in/on the seafloor include redox potential, mineral phase composition, and animal or plant pertubation of the sediment (e.g., bioturbation), in addition to physical mixing processes (Maher & Butler, 1998). Desorption and dissolution of As from sediments is most likely to be enhanced by reducing conditions and the dissolution of any As-bearing phases (Kocar*,* et al., 2008). As sediment compacts, any dissolved As can diffuse up through the sediment column, eventually becoming involved in surficial mixing or escape to the overlying water column. If sufficient quantities of inbenthic organisms exist in the sediments, the flux of As from deeper porewater may be greater than in unbioturbated sediments, thereby allowing for greater dissolved concentrations of As in the benthic boundary layer (Edenborn, et al., 1986).

CHAPTER 3: METHODS

HUMMA Sediment Characterization

Laboratory experiments utilized homogenized sediment samples collected during HUMMA. The study area is thought to host CWM and the fine-grained hemipelagic sediments at this location are generally similar to those found in other deep ocean CWM disposal locations. The HUMMA munition site, labeled HI-05 by the Department of Defense, is located 5 miles south of Pearl Harbor off the coast of Oahu (Figure 5). The primary HUMMA study area has been categorized by the U.H. Environmental Center (1996a) as a “flat silty plain with no significant topographic features”. The southwestern part of the study area has some morphological diversity, such as, irregularly shaped mounds and Pleistocene reefs covered with thin sediment layers (HUMMA, 2010).

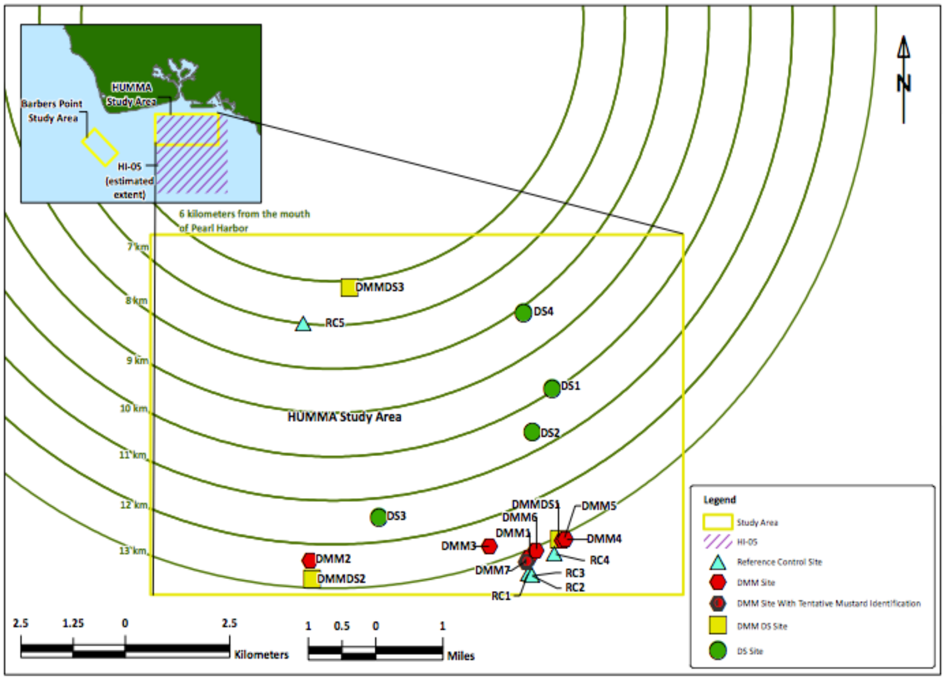


Figure 5: Map of HUMMA site off Oahu

HUMMA sediment samples taken in clear polyvinyl chloride (PVC) sediment scoops labeled with unique identifier numbers were collected by HURL submersibles in March of 2009 (image). Sediment was collected within 1-2 meters of randomly chosen munitions. The recovered samples were then analyzed on ship for chemical agent and, cleared (in the absence of CWA) for subsequent laboratory processing and analysis of explosives and metals. The minor and major element composition of sediments was determined on acid digested material by inductively coupled plasma (ICP) spectrometry optical emission spectrometry (OES) and mass spectrometry (MS) as described below.

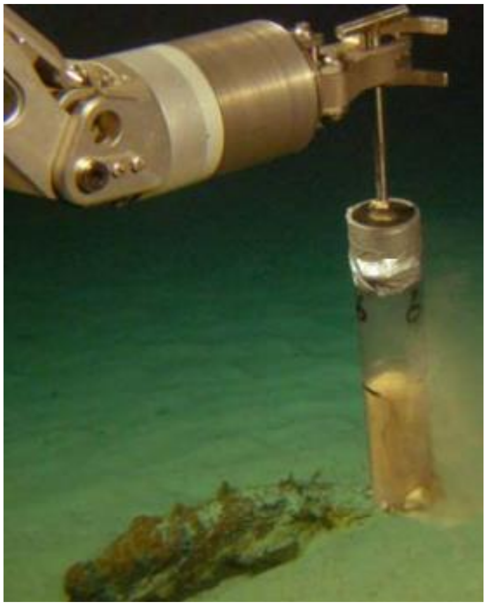


Figure 6: PVC sediment scoop designed by HURL for HUMMA sediment collection

Selected samples from the HUMMA project were composited to yield a sufficient quantity of material to use in subsequent experiments. Five splits of the well-mixed composite were subsequently analyzed to determine it’s As content.

The original samples used to generate the experimental composite were HUM001 through HUM007, which individually contained from 5.75 to 6.76 mg/kg of As.

Batch Reactor Experiments

A series of controlled experiments was conducted to evaluate the capacity of the hemi-pelagic sediment to sequester and retain As. All experiments in this study were conducted with batch reactors (Figure 7). Fifteen individual free drift (i.e., there is no adjustment made to the system during the experiment) batch reactor experiments were completed during this study. Experiments were numbered 1-15; these include a blank, and seven paired (duplicate) As spike concentration experiments.

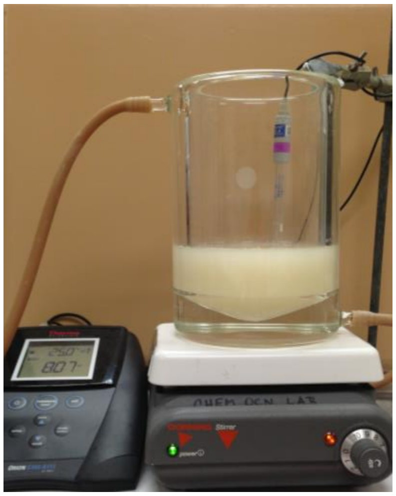


Figure 7: Batch reactor and pH monitor

Experiments consisted of temperature-controlled batch equilibrations of one liter of seawater spiked with specific concentrations of inorganic As either in the form of the metastable (reduced) arsenite (As(III)) or the thermodynamically stable arsenate (As(V)), and known amounts (~1g) of suspended sediment. Duplicate runs of individual experiments were conducted with each of the following concentrations: 3μM, 5μM, 10μM, and 20μM dissolved As(III) and 5μM of As(V). Fifteen experiments were completed and these included duplicates and a few replicates that addressed prior experimental procedure difficulties.

In order to prepare solutions with the individual As(III) spike concentrations described above, a stock concentrated solution of ~1 mM $NaAsO_2$ was initially prepared volumetrically. Exactly 135.0 mg $NaAsO_2$ (77.86 mg As) were placed in a one liter volumetric flask and diluted to the mark with DI H_2O to yield an exact concentration of 1.04 mM As(III). The stock solution was stored sealed and utilized subsequently to prepare working micromolar solutions of $NaAsO_{2.}$ Working solutions were prepared in seawater.

A constantly stirred jacketed batch reactor was set up to keep sediment (~1g) in suspension and the temperature was maintained constant (25.0^{o} C) within 0.1^{o}C during experiment runs with recirculation of jacket water through a Thermo Fisher Scientific thermostat and refrigerated bath/circulator. The sediment-seawater suspension was then sampled at predetermined intervals: 1 min, 3 min, 5 min, 10 min, 20 min, 40 min, 60 min, 120 min, 12 hours, 24 hours, 3 days and 7 days. The pH of the suspension was also monitored throughout the experiment as one means of evaluating ion exchange reactions on substrate surfaces.

At designated times throughout individual batch reactor runs, fifty milliliters of seawater were sampled with a syringe using the depth-integrated technique. The samples were then filtered through pre-weighed 0.22 μm membrane and the filtrate collected in acid cleaned, 25 mL HDPE bottles and stored for later analysis. After experiments 1 & 2, 10 mL DI H_20 were passed through the membranes to rinse them of remaining seawater. Any remaining seawater would contribute Cl^- to the digested sediment solutions and interfere with As analysis by ICPMS (see below). Sediment loaded filter membranes were placed in a drying oven maintained at 60° C for at least 24 hours. Dried membranes were weighed on an analytical balance to the nearest 0.1 mg and the weight of suspended sediment recovered then recorded.

Dry membranes were subject to acid digestion in preparation for ICPMS analysis. For all experiments, dried membranes were transferred to Teflon® Savillex screw cap beakers for sediment dissolution. The digestion protocol of experiments 1-9 involved pipetting a small amount of DI H_2O onto the dry membrane to prevent violent reaction of dry particles with acid; this was followed by addition of 0.4mL of concentrated trace-element grade 15M HNO_3 and the sample then heated in the oven to dissolve particles. For experiments 10-15, a slightly different digestion protocol was used to assure complete dissolution of refractory minerals that remained when using only 15M HNO_3. The modified procedure is similar to the method described by Wen et al. (1997). The digestion mixture consisted of 0.4mL of HNO_3, 0.4mL of HCl, and 0.1mL of HF. The digestion vessels were then placed in an oven at 60°C until the sediment and membrane were completely dissolved, generally within 48 hours. Digested materials were transferred quantitatively into pre-weighed 25 mL HDPE bottles and diluted to approximately 25mL with de-ionized H_2O. Samples were then weighed to the nearest 0.01g. Digested sample solutions were diluted an additional 10-fold with 2% (v/v) trace element clean HNO_3 immediately before injection into the ICPMS.

Arsenic Analysis by ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICPMS) was utilized to carry out analysis of arsenic in solutions derived from adsorption experiments. ICPMS is a sensitive and precise analytical method capable of detecting metals, metalloids, and certain non-metals in liquid samples. The ICP provides a high temperature plasma discharge that produces positively charged ions, which are then transmitted through a mass spectrometer (MS) and detected with a channeltron electron multiplier (CEM).

A simplified description of the principles of operation of the ICPMS is as follows. An oscillating RF field (~50 MHz) is used to generate and sustain aninductively coupled argon (Ar) plasma that generates a temperature of 6000-7000K. This plasma serves as an ionization source for the sample and is located at the inlet to the mass spectrometer. Sample solutions are pumped through a nebulizer into a spray chamber where an aerosol is transported to and passed through the super-heated Ar plasma, which ionizes most elements in solution. The ions are introduced into the mass spectrometer (MS) through a small orifice into an expansion chamber where they are supersonically accelerated into the high vacuum section of the mass spectrometer. The mass spectrometer then separates ions by their mass/charge ratio. A CEM collects the ions separated by the mass spectrometer, which generate a cascade of electrons thereby generating a current that is proportional to ion concentration. Computer electronics then produce a record of current versus mass/charge ratio that is subsequently used to quantify the concentration of isotopes of elements of interest. The ICPMS is standardized by aspiration of a series of known calibration standards to generate a (linear) response curve that is applied to unknown sample ion counts. For this study, a VG PQ2S quadrupole mass spectrometer was utilized.

In order to ensure the precision and accuracy of ICPMS data, it is important to continuously evaluate the quality of the instrument performance during spectrometric analysis. Instrument calibration is verified throughout the run, blanks are analyzed periodically, and internal standard solutions allow monitoring of instrument stability. Sample duplicates and solutions of standard reference materials (SRM), digested by the same procedure as samples, were included in all analyses, thereby allowing assessment of analytical variability.

A range of working standards for calibration of the ICPMS was prepared daily. The standards, ranging from 1 to 40 μg/L, were prepared by volumetric dilution of a stock 100 μg/L certified multielement solution with 2% (v/v) trace element clean HNO_3.

Calculations

Data from the experiments were entered into Microsoft Excel spreadsheets in order to organize and compare sediment uptake between experiments. The concentration of As, as measured by ICPMS, was transformed to a mass As adsorbed (µg). The concentration of As in solution was multiplied by the dilution factor and the solution weight in grams, and divided by the dry weight of the solid sediment sample (mg) measured prior to digestion, then multiplied by the sediment mass (g). An example calculation, taken from experiment 5 (Appendix A) is as follows:

$$\frac{\left(24.96\ \frac{\mu mg\ As}{kg\ sed}\right)\left(\frac{1\ kg}{1000\ g}\right)(2)(9.58\ g\ sol.wt.)}{(31.6\ mg\ dry\ wt.sed)\left(\frac{1\ g}{1000\ mg}\right)}(1.0807\ g\ sed) = 16.36\ \mu g\ As$$

The absolute amount of As adsorbed to the sediment was calculated by subtracting the concentration of As in the original material and then dividing by weight of sediment added to the reactor:

$$16.36\ \mu g\ As - \left(5.75\ \frac{\mu mg\ As}{g\ sed}\right)(1.0807\ g\ sed) = 10.14\ \mu g\ abs\ As$$

Finally, the percent uptake of arsenic in the reactor experiments was calculated by dividing the amount adsorbed by the concentration of As added to the solution (µM) and multiplied by the atomic weight of As and then multiplied by 100, as follows:

$$\frac{10.14\ \mu g\ abs\ As}{(3\ \mu M\ sol)\left(\frac{1\ mol}{10^6\ \mu M}\right)\left(75\ \frac{g}{mol}\right)\left(\frac{10^6\ \mu g}{1\ g}\right)}(100) = 4.5072\ \%\ uptake\ As$$

CHAPTER 4. RESULTS

Table 1 shows concentrations of As in sediment samples collected during the HUMMA study in 2010, which were used to generate composite test sediment in reactor experiments. Also included in this table is the concentration of As found in the composite sediment prepared from the individual HUMMA samples. As discussed previously, the original HUMMA sediment samples labeled HUM001 through HUM007 contain from 5.74 to 6.79 mg/kg As. The average of the composite prepared in this study (6.29 mg/kg or ppm) is consistent with what would be expected based on individual HUMMA sample concentrations of arsenic.

Sample ID #	Arsenic (mg/kg)	date	Sample location
HUM 001	6.02	3-Mar-09	RC1
HUM 002	6.76	3-Mar-09	RC1
HUM 003	6.79	3-Mar-09	RC1
HUM 004	5.75	3-Mar-09	RC1
HUM 005	6.04	3-Mar-09	RC1
HUM 006	6.25	3-Mar-09	RC1
HUM 007	5.74	3-Mar-09	RC1

Table 1: HUMMA As concentrations for sediment batches HUM 001-007

Arsenic Recovery

A comparison of relative uptake of As by sediments for all experiments is presented in Appendix A and shown in figure 8. In general, uptake increases over time but the relative or absolute uptake at the end of the experiment does not necessarily increase with increasing As spike concentrations. The uptake of As(V) is also greater over time as compared to experiments with an equivalent concentration of As(III).

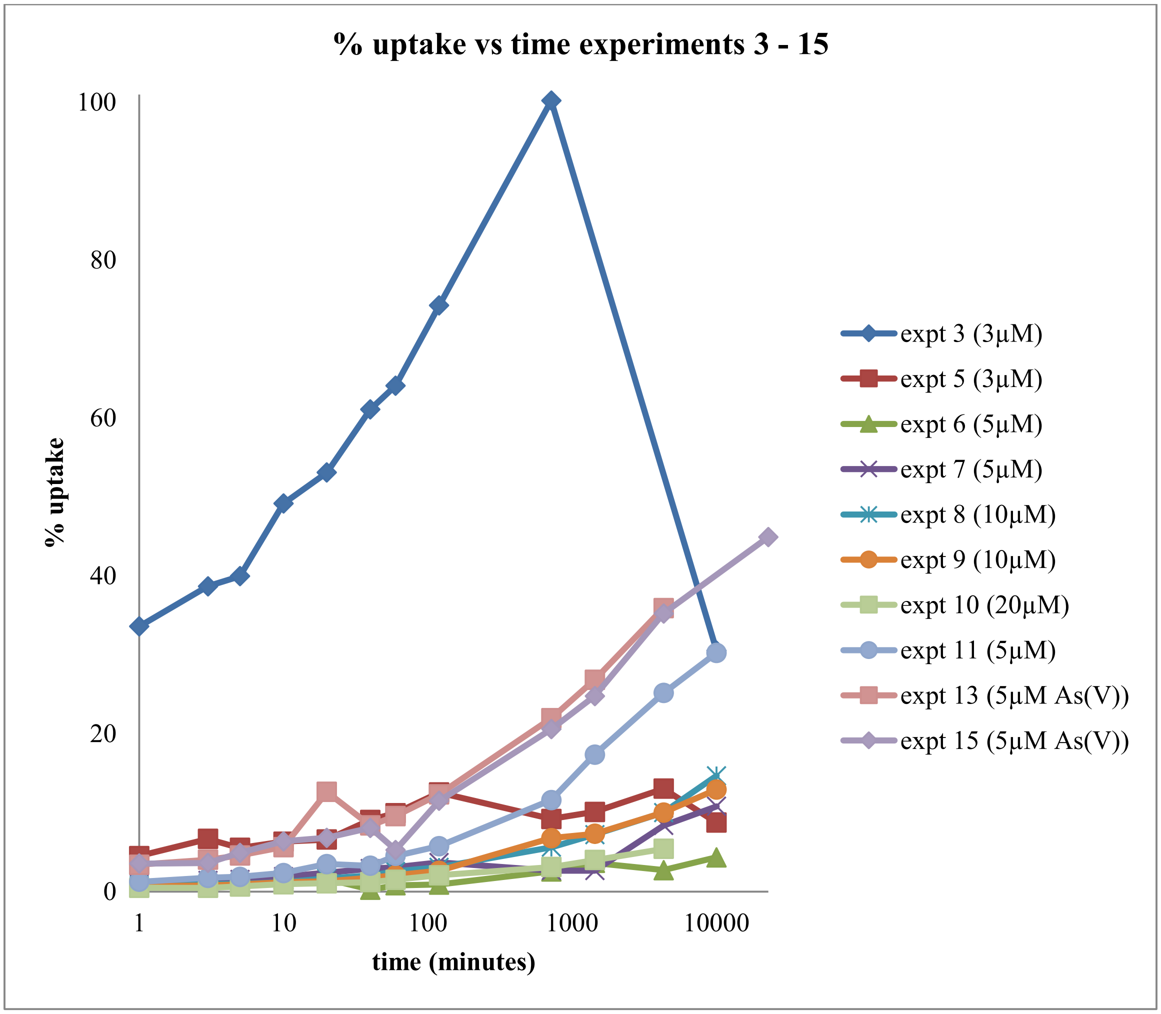


Figure 8: Percent uptake plotted vs time for experiments 3 through 15 (expt 4 not plotted)

Experiments 1 and 2 were discarded due to initial experimental problems with filtration and recovery of suspended materials. Experiment 4, a blank (i.e., no As was added to the seawater) adsorption experiment (data not shown in the above figure), showed a nearly constant amount of arsenic in each sample.

Data for duplicate experiments 3 and 5, in which the seawater was spiked with 3µM with As(III), appeared to show extremely different amounts of As uptake, by 30% or more, in the two experiments (Figure 9). Experiment 3 displayed an upward trend of As adsorption from 37% after one minute to 100% at 720 minutes, while Experiment 5 displayed only a 3% increase of adsorption between the sample collected after one minute and that collected after 720 minutes (12 hours). There was no sample collected after one day or three days during Experiment 3, and the relative uptake appeared to drop drastically by the 7 day sample. This rather anomalous behavior and lack of reproducibility between what was supposed to be two replicate experiments is discussed

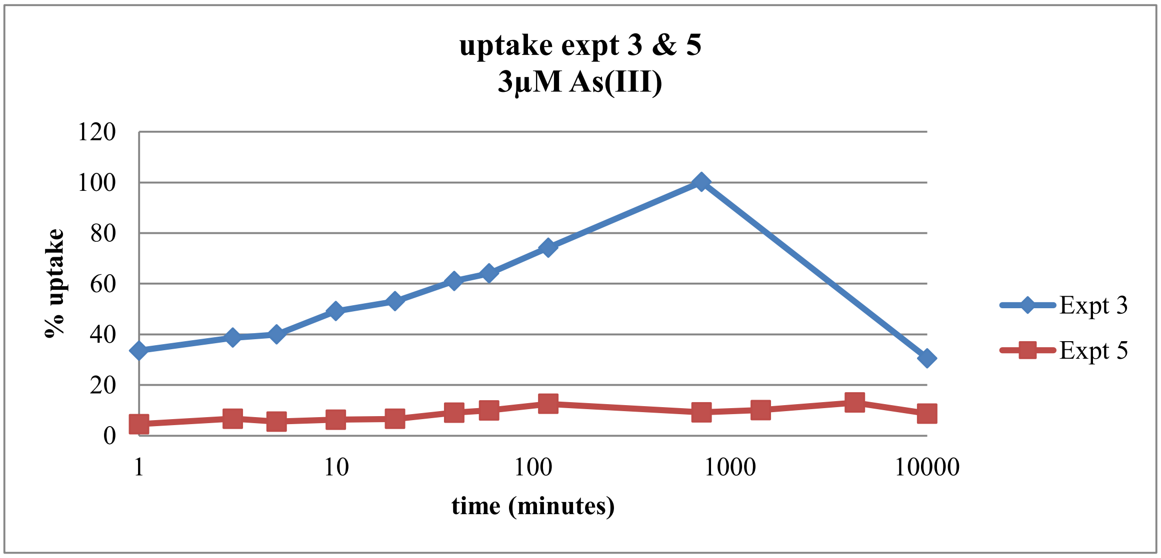


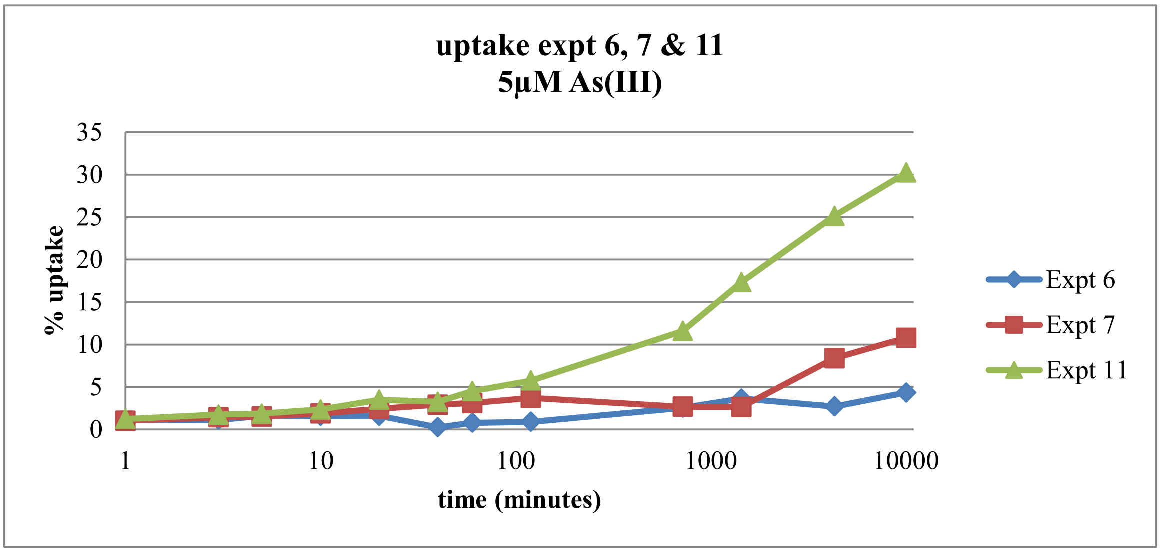
Figure 9: Comparative plot for duplicate experiments 3 & 5

The experiments in which the seawater was spiked with 5µM As are Experiments 6, 7, and 11 (Figure 10). The maximum As uptake at after 7 days, however, was only 4.34% for Experiment 6, while Experiment 7 displayed a maximum As uptake of 10.8%, while the maximum uptake for Experiment 11 was 30.25%. Again, discrepancies

Figure 10: Comparative plots for experiments 6, 7 & 11

between these replicate runs will be discussed later. The uptake curve for Experiment 11, however, was smooth and gradually increased through the final 7-day sample

Results for Experiments 8 and 9 (figure 11) were consistent, unlike what was observed for previous experiments. These experiments, in which the seawater was spiked with 10µM As, displayed very similar uptake curves. The largest difference in uptake was at the 7 day experiment. The maximum uptake was observed at the final time increment and was 14.68% in Experiment 8-7d and 12.94% in Experiment 9-7d.


uptake expt 6, 7 & 11
5µM As(III)

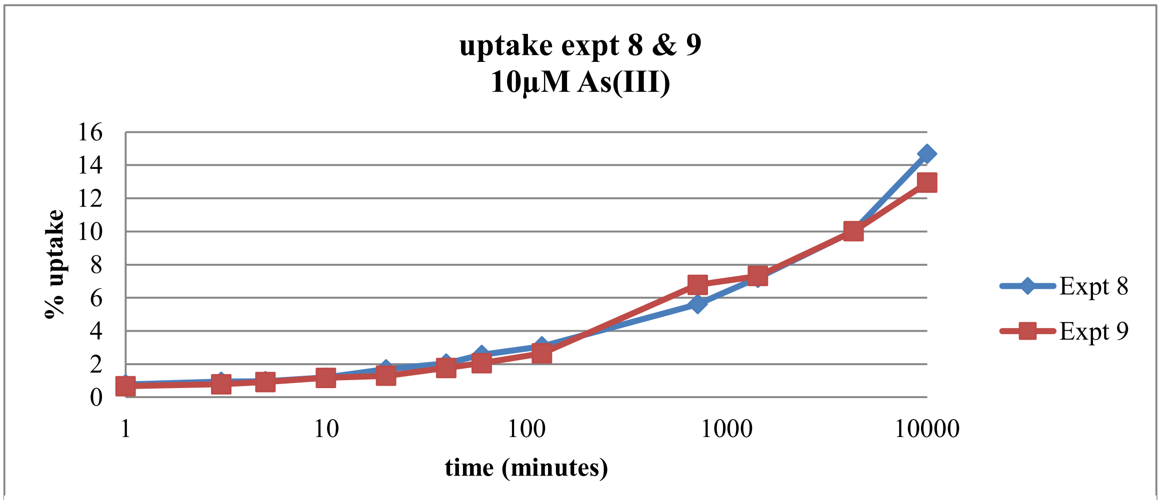

uptake expt 8 & 9
10µM As(III)

Figure 11: Percent uptake plotted vs time for comparison of experiments 8 and 9

Figure 12 displays the uptake plot for Experiment 10, in which the seawater was spiked with 20µM of As(III). The uptake for Experiment 10 follows a relatively smooth curved trend upward, with a maximum uptake of 5.4% after three days.

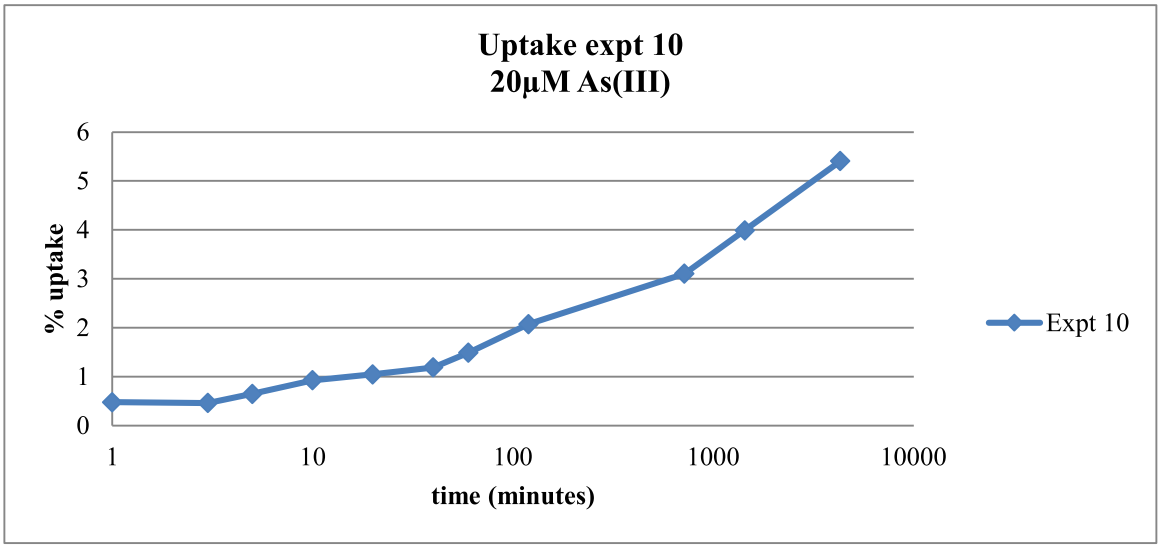


Figure 12: Percent uptake plotted vs time for experiment 10

A comparison of As(III) and As(V) uptake experiments is shown in Figures 13a and 13b, which plot relative uptake on logarithmic and linear time scales, respectively. Experiment 11 was conducted with a 5µM As(III) spike , whereas Experiments 13 and 15 were carried out with an As(V) spike of 5µM. The uptake curves for As(V) exhibit a consistently higher rate of recovery throughout the duration of the experiment compared to the As(III) experiment. There was one outlier in each of the As(V) experiment; at the fifth and seventh time intervals of Experiments 13 and 15, respectively. Additionally, the final sample point in Experiment 15 was collected after16 days, whereas the final sample point for Experiment 11 was collected after seven days.

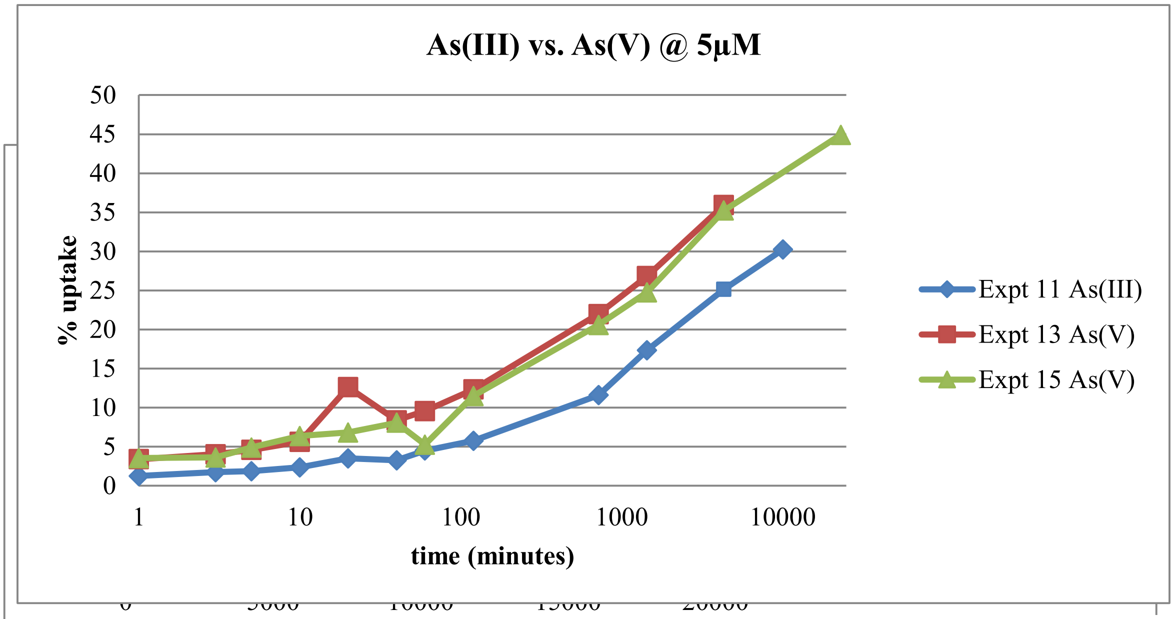


Figure 13a: above - Comparative plot of As(III) and As(V) experiments (log time)

Figure 13b: below - Comparative plot of As(III) and As(V) experiments (linear time)

CHAPTER 4. DISCUSSION

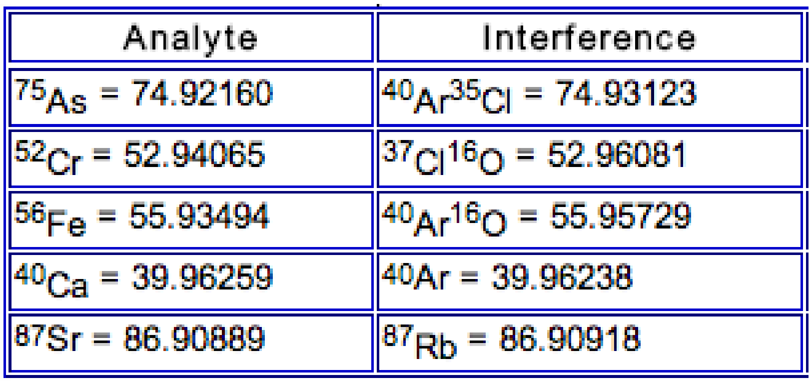
The study of DMM sites and the marine sediments surrounding CWM has been ongoing in waters around Oahu for nearly a decade. Understanding the potential impacts of these synthetic chemical warfare agents on the marine environment is clearly important. One reason is because the local population of Hawaii is strongly linked to the ocean not only as subsistence or recreational fishermen who consume local seafood, but also culturally. How marine sediments are impacted by CWM/CWA and how these impacts might transfer up the food chain are particularly important topics to the local community.

The characteristics of marine sediment vary widely. The chemical composition, mineralogy, and particle size all differ depending on a number of factors that are largely determined by the origin of the sediment. Primarily, particles that compromise marine sediments originate from skeletons of marine organisms (biogenic), or they are carried from land to the ocean (terrigenous). Additionally, some marine sediments form through other processes, such as, hydrothermal activity and authigenic mineral formation (Libes, 1992). Coastal and deep ocean sediments may vary in the prevalence of sediment type, depending on their distance from shore. Furthermore, the abundance and composition of sediment has been altered in many areas of human activities (van Geen & Luoma, 1999). Consequently, the variability of physical properties and the chemical composition of sediments can influence how chemical pollutants partition between the surrounding seawater and sediment at a particular location. As a result of this, broad scale predictions may be inaccurate for some specific situations.

Hawaiian coastal sediments are comprised of particles from two primary sources, and the formation and general makeup of these particles depends principally on a few processes. In Hawaii, marine sediments consist of fluvial/erosional or of biogenic deposits and the composition of sediments is generally controlled by the weathering of volcanic basalts and marine biological processes (Calhoun and Fletcher, 1999). Sediments at the HUMMA sampling sites are composed of carbonate sand/silt, reef platform carbonates, and dredge spoil (largely terrigenous) material originally removed from Oahu harbors and dumped at the EPA approval dump site south of Pearl Harbor (HUMMA).

Because the properties of sediments used in this study were different from pure model phases used in laboratory adsorption studies due to their complex mineralogy and chemical composition, it became necessary to modify experimental procedures from the initially envisioned approach in order to generate reproducible results. During the ICPMS analysis of samples derived from Experiments 1-3, it was deduced that spectral interferences might be causing inconsistent results and that an isobaric interference from Cl was occurring on ^{75}As . Because uptake experiments were carried out in seawater and solution aliquots collected at various time intervals were filtered through glass fiber filter (GFF) membranes held in capsule filters, some seawater remained on the filters and on the particles after filtration. The residual seawater contributed to both a slight increase in apparent particle mass from NaCl left behind that was subsequently digested and injected into the ICPMS. The presence of Cl in solution also leads to the formation of ^{40}Ar^{35}Cl molecular ions, which cause a positive interference on ^{75}As (figure 14) (Wolf, 2005). Because As is a monoisotopic element no alternative mass could be monitored on the

ICPMS to avoid this interference. In order to remove the isobaric interference, subsequent experiments (after Experiment 3) included two changes. The GFF were first replaced by Millipore (cellulose acetate) membrane filters, and second, all filters were rinsed with a small volume of DI to eliminate any residual NaCl.



Analyte	Interference
$^{75}As = 74.92160$	$^{40}Ar^{35}Cl = 74.93123$
$^{52}Cr = 52.94065$	$^{37}Cl^{16}O = 52.96081$
$^{56}Fe = 55.93494$	$^{40}Ar^{16}O = 55.95729$
$^{40}Ca = 39.96259$	$^{40}Ar = 39.96238$
$^{87}Sr = 86.90889$	$^{87}Rb = 86.90918$

Figure 14: Examples of molecular interference during ICPMS analysis of solutions.

Despite efforts to reduce the isobaric interference through the two previous measures, there were still considerable inconsistencies within the As uptake results. These disparities were then attributed to a combination of a variable efficiency of collection of particles from solution during sampling and a subsequent incomplete digestion of the particles. Beginning with Experiment 8, a new digestion and dilution method was implemented to remedy the incomplete recovery of As from the solid phase. Prior to implementation of the new digestion method, it was assumed that all As was **adsorbed** on the surface of particles and that it would only require a weak acid treatment to remove quantitatively the As from the solid phase. However, some of the As in the sediment particles was likely bound within mineral particles and not readily released with a weak acid treatment; so a more complete digestion was required in order to determine how much total (original + adsorbed) As was recovered from the sediment. After this new step, as described in the methods, was put in place, all remaining experiments showed consistent, reproducible outcomes. Figures 15a & 15b display the difference in results prior to, and after the resolutions.

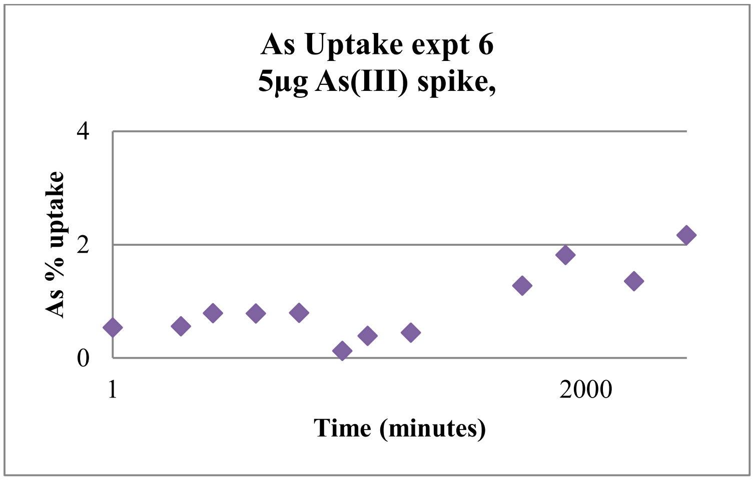
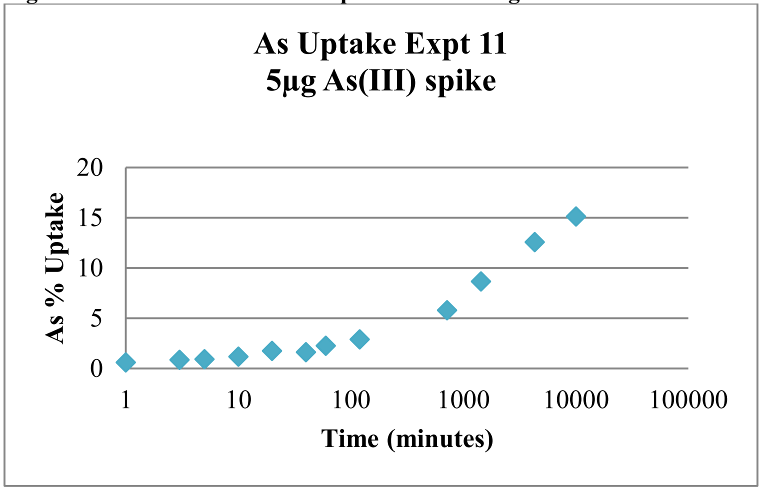


Figure 15a: above - Percent As uptake prior to change in methods

Figure 15b: below - Percent As uptake after change in methods



Despite the consistent and reproducible outcomes of later experiments, the uptake curves do not entirely support the hypothesis that As adsorption would be be very rapid inititally and then reach an equilibrium over an extended but relatively short time. Other studies have shown that, under certain conditions, As adsorption onto particles follows very rapid kinetics, displaying uptake patterns consistent with those of the stated hypothesis (e.g., O'Reilly, *et al*., 2001). The rate of adsorption in the first series of experiments from the current study, however, may have been lower as a result of the (reduced) oxidation state of As.

During all experiment time frames, pH slowly increased (figure 16a & 16b). The shift to a more alkaline environment is often associated with oxidizing conditions. Although this may have occurred through protonation of arsenite when initially placed in seawater, this should have occurred in the seawater spike solution before it was added to the sediment-seawater suspension. Another more likely alternative, is that upon mixing of the spike solution and the sediment suspension, exchange reactions begin to take place at the particle surface and release OH^- to solution. It is well-known that the adsorption of ligands on metal oxides can be compared to complex formation reactions that release OH^- to solution (e.g., Stumm 1992), Another alternative is that a slow oxidation of As(III) under the slightly basic conditions of these experiments consumes H^+, thereby increasing pH (Sharma & Sohn, 2009; Zhao et al., 2011). Which of these processes predominates in controlling pH cannot be ascertained unequivocally, the slightly lower pH increase observed during the As(V) uptake experiment is consistent with an additional increase in pH associated with the oxidation of As(III) to As (V).

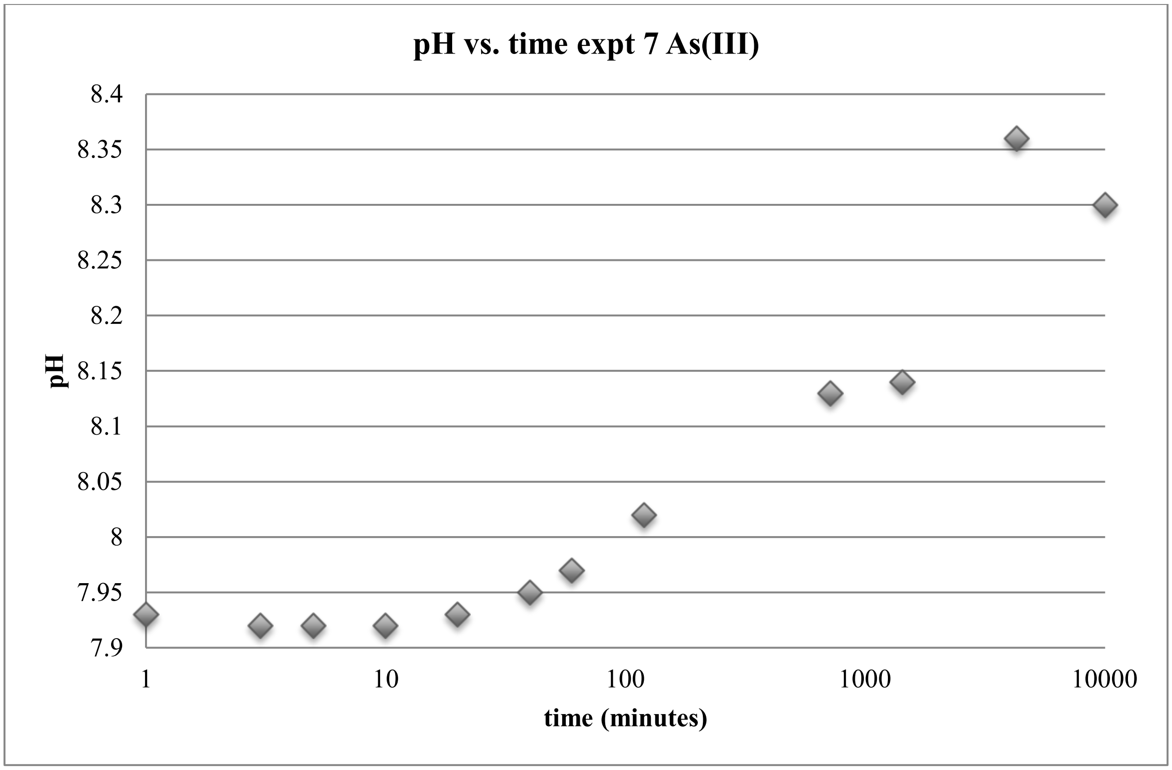


Figure 16a: pH versus time during As(III) experiment

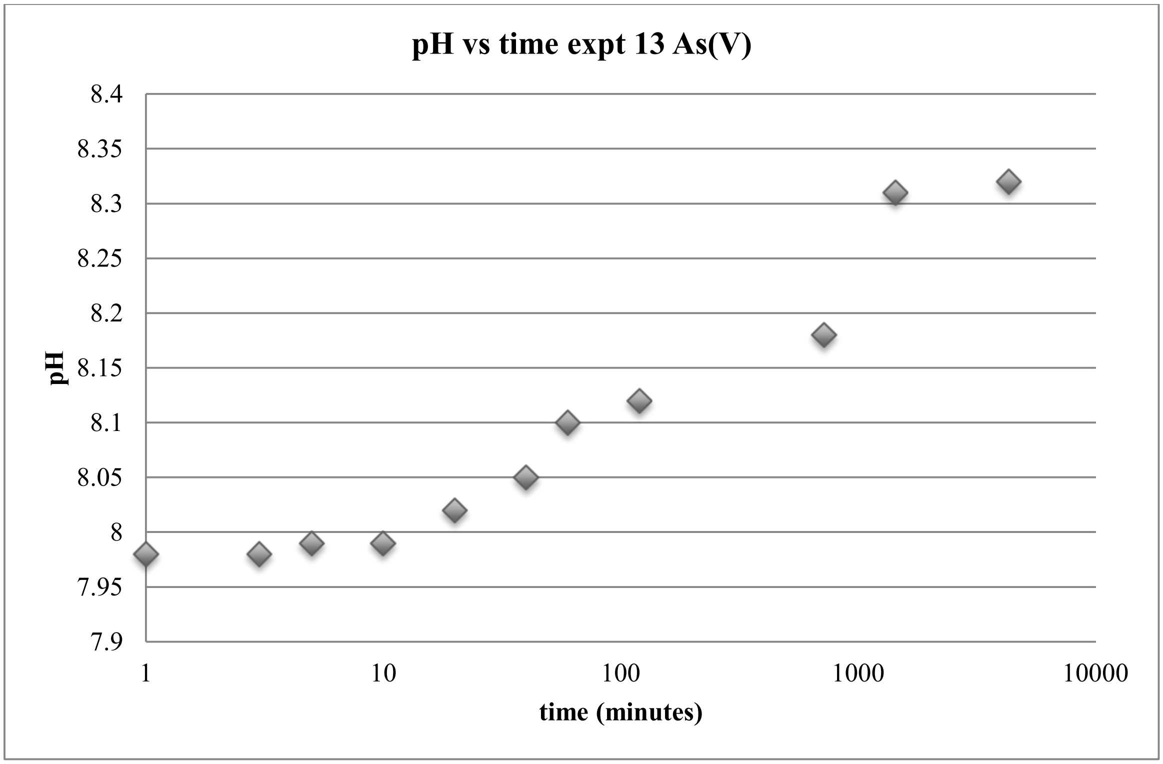


Figure 16b: pH versus time during As(V) experiment

In order to help elucidate why the uptake curves from the As(III) experiments all showed relatively low adsorption and a slower uptakethan hypothesized, similar experiments were run using As(V). The oxidized form of As is known to be more particle reactive than As(III) (Glendon-Baclig, 2007). Thus it was necessary to determine what extent of adsorption would be observed with As(V) under the same conditions as used for the As(III) experiments. A comparative plot (figure 17) showing the uptake by HUMMA sediment of equimolar spikes of (5 μM) As(III) and As(V) displays sub-parallel curves for the two As species but with a greater extent of adsorption of As(V) relative to As(III) The greater extent of uptake of As(V) the suggests that sediment used in this study has a greater sorption capacity than would be predicted only from uptake experiments with As(III) and confirmed the preferential uptake by particles of As(V) over As(III) observed in prior work. Additionally, the apparent continued uptake over longer time intervals also implies that more reaction time was needed in order to reach equilibrium and/or fully saturate the sediment surface with As.

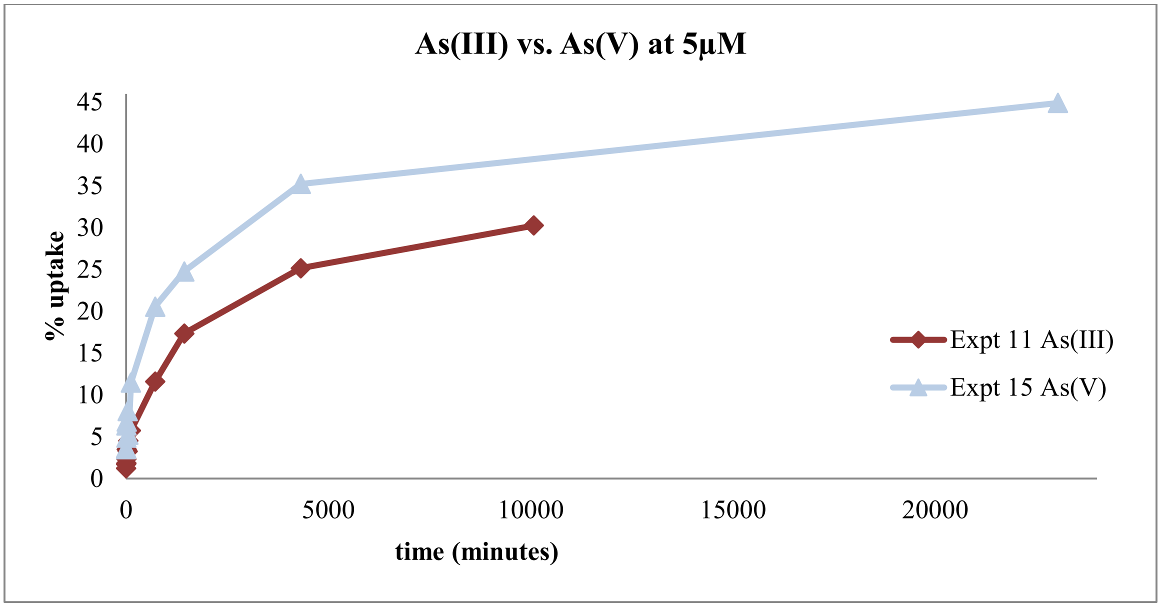


Figure 17: Comparison plot of As(III) and As(V) experiments at 5µM (linear)

The lesser and especially slower uptake of As(III) onto the sediment relative to As(V) likely reflects the inherent differences in the propensity of As in these two different oxidation states to bind to particle surfaces but may also be indicative of other processes taking place in solution. It is possible that the continued uptake of As(III) over extended times may be due to a slow but continued oxidation to As(V), leading to a lesser extent of adsorption than would be predicted from extrapolation of the plots of As uptake versus the inverse square root of time.

If As(III) slowly oxidizes in the batch reactors during the course of the experiments, its transformation to As(V) should lead to a greater propensity for uptake by particles, although this process is expected to be relatively slow (Smedley & Kinniburgh, 2011). Furthermore, because the rate of uptake of As(III) is slower than that of As(V), oxidation in seawater of dissolved As derived from Lewisite would be beneficial from two perspectives. First, if oxidation occurred quickly, As(III) would transform quickly to the less toxic As(V) species, reducing the amount of the more toxic form that might be taken up by biota (other than in-benthic sediment feeders). Additionally, uptake of As by sediment should then be enhanced both in extent and possibly in rate, further decreasing its concentration in solution and availability. Counter to this argument, however, is the fact that in-benthic species would then be exposed to a greater concentration of As during their ingestion of sediment. If incorporation of As into their tissues was sufficient, bioaccumulation of As could occur, potentially leading to greater transfer and biomagnification through the food chain. Recent work, however, suggests that holothurians, for example, have a relatively high gut pH compared to humans, thereby minimizing dissolution of particles and solubilization of adsorbed (toxic) species (Mayer, et al., 1997). Polychaetes, however, are thought to be greater accumulators of As and predation on these organisms by higher trophic levels could lead to greater biomagnification of As through the food chain..

During the current experiments, the pH of the seawater/sediment suspension was monitored and , although it increased slightly over time, remained near pH 8 (see figure 16a and 16b). In such a mildly basic solution oxidation of As(III) to As(V) should not be favored thermodynamically, although prior work has shown that even in basic solution some oxidation of As(III) to As(V) does take place (e.g., Zhao et al., 2011).

Uptake of As as a Function of Seawater Spike Concentration

The amount of As(III) taken up by solid phases from seawater by suspended sediments in these experiments displays an increase as a function of time for all spike concentrations. However, the total (absolute) amount of As taken up by the solid phase does not always follow the same trend (see Figures 18-22). In fact it appears that, at higher spike concentrations, there is a lesser fraction of the spike taken up by the solid phase, suggesting that saturation of the solid surface may be taking place.

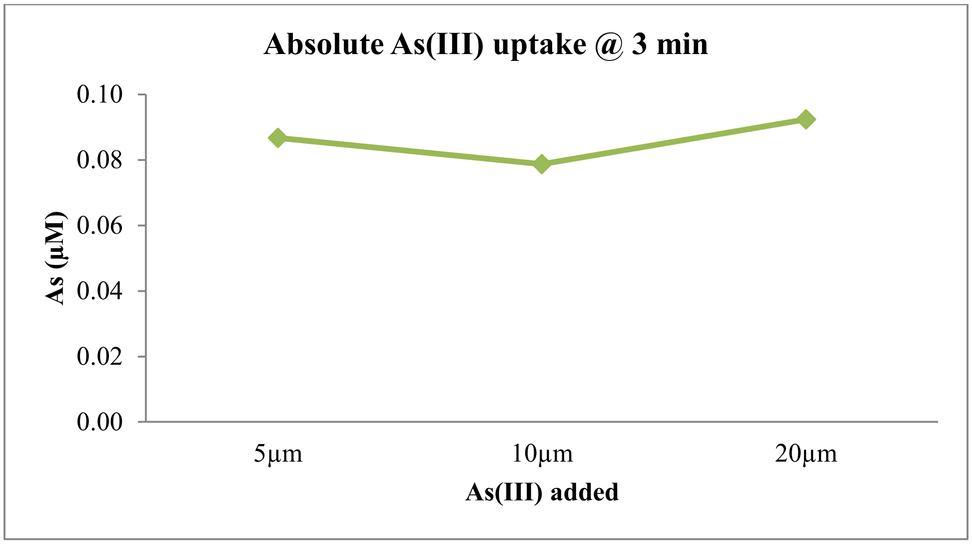


Figure 18: Absolute As uptake (in µM) at 3 minutes for 5, 10, and 20 µM spikes

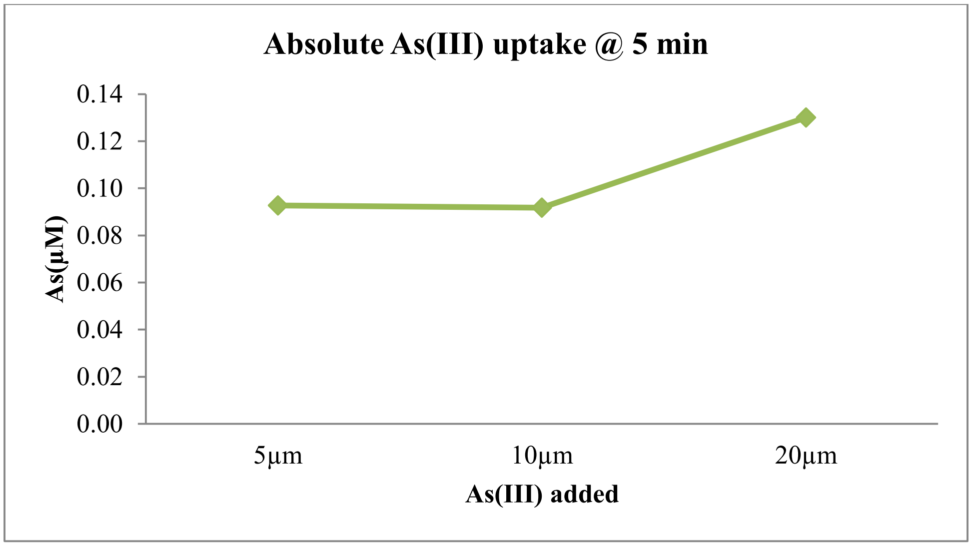


Figure 19: Absolute As uptake (in µM) at 5, 10, and 20 µM spikes

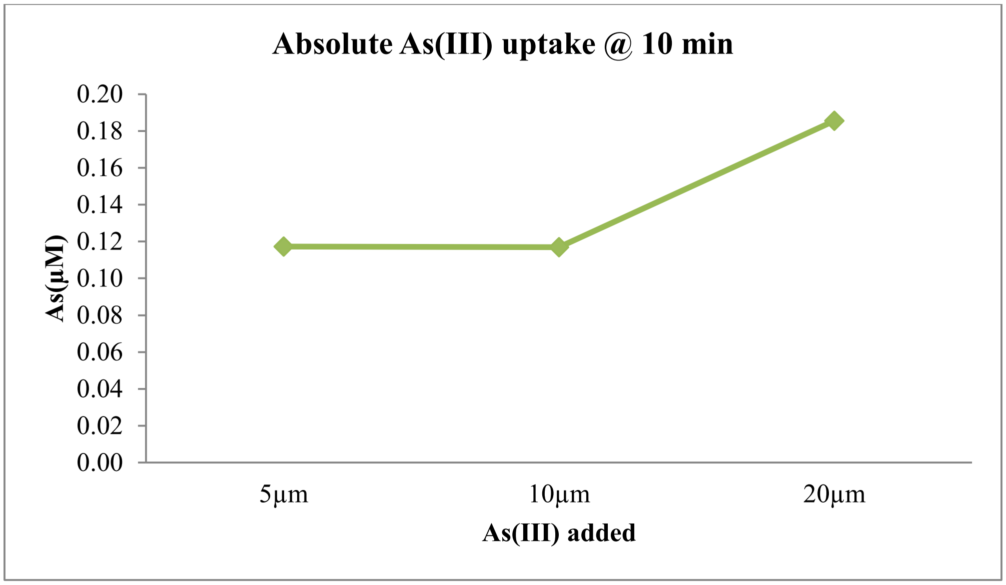


Figure 20: Absolute As uptake (in µM) at 5, 10, and 20 µM spikes

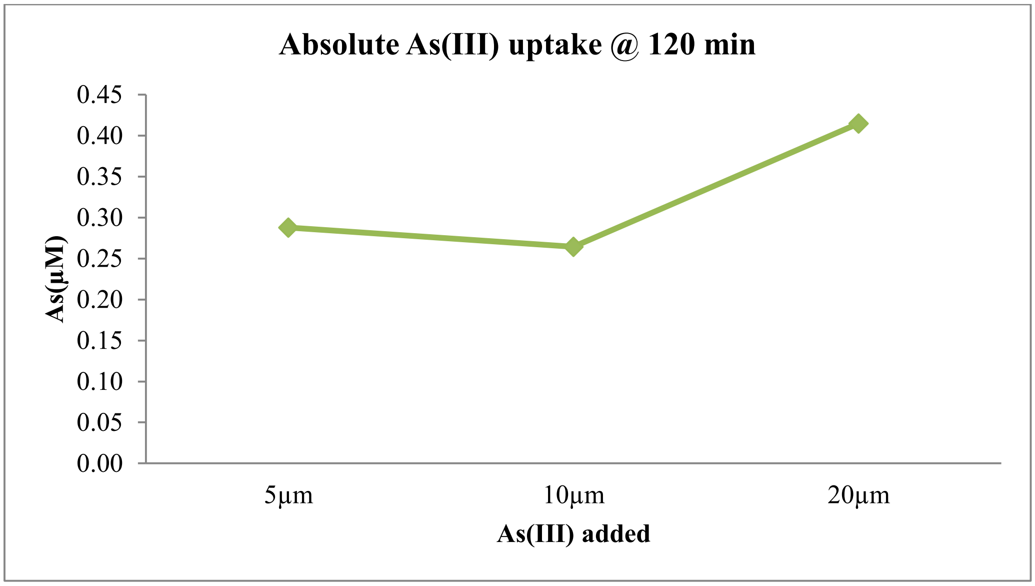


Figure 21: Absolute As uptake (in µM) at 5, 10, and 20 µM spikes

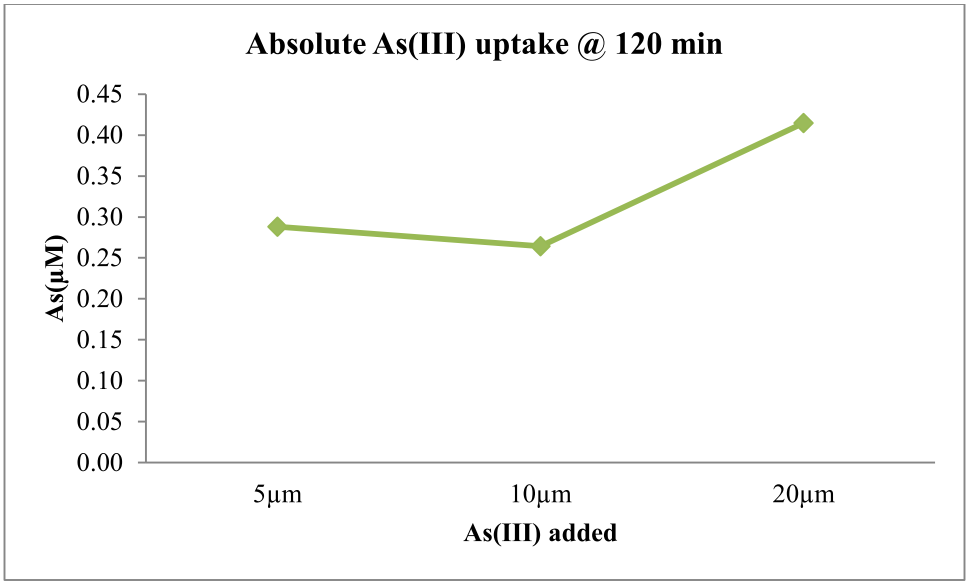


Figure 22: Absolute As uptake (in µM) at 5, 10, and 20 µM spikes

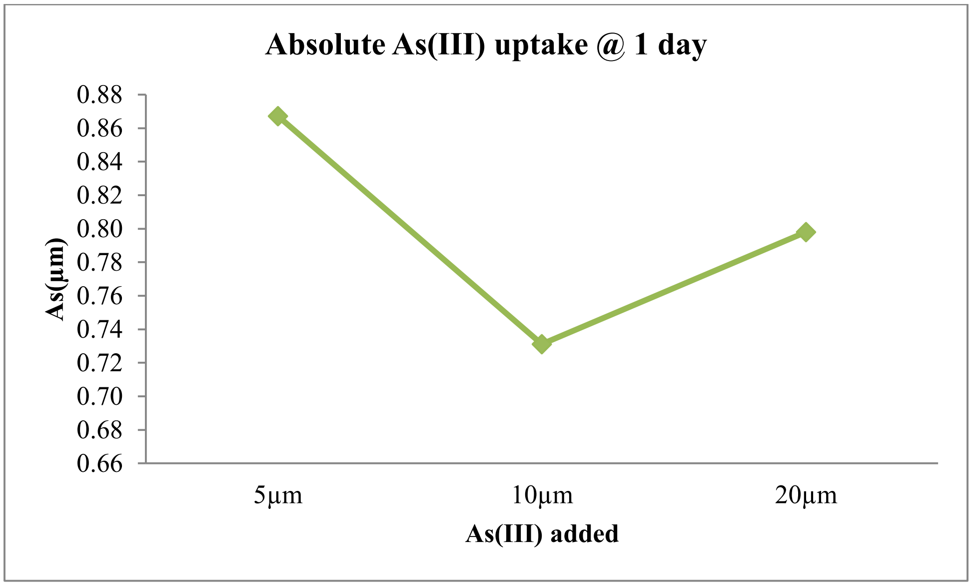


Figure 23: Absolute As Uptake (in µM) at 5, 10, and 20 µM spikes

Figure 24 depicts the average absolute amount of As that is sorbed as a function of time for the various concentration spikes investigated in this study. This plot shows an increase in the amount of As that partitions onto the solid phase with time. The standard deviation for each point in Figure 24, however, generally increases with time. The increasing standard deviation of the later sample times may provide evidence of the first stages in saturation of the solid phase in the higher As spikes (10 µM and 20 µM), although additional experiments with longer sample times are needed to fully support this interpretation.

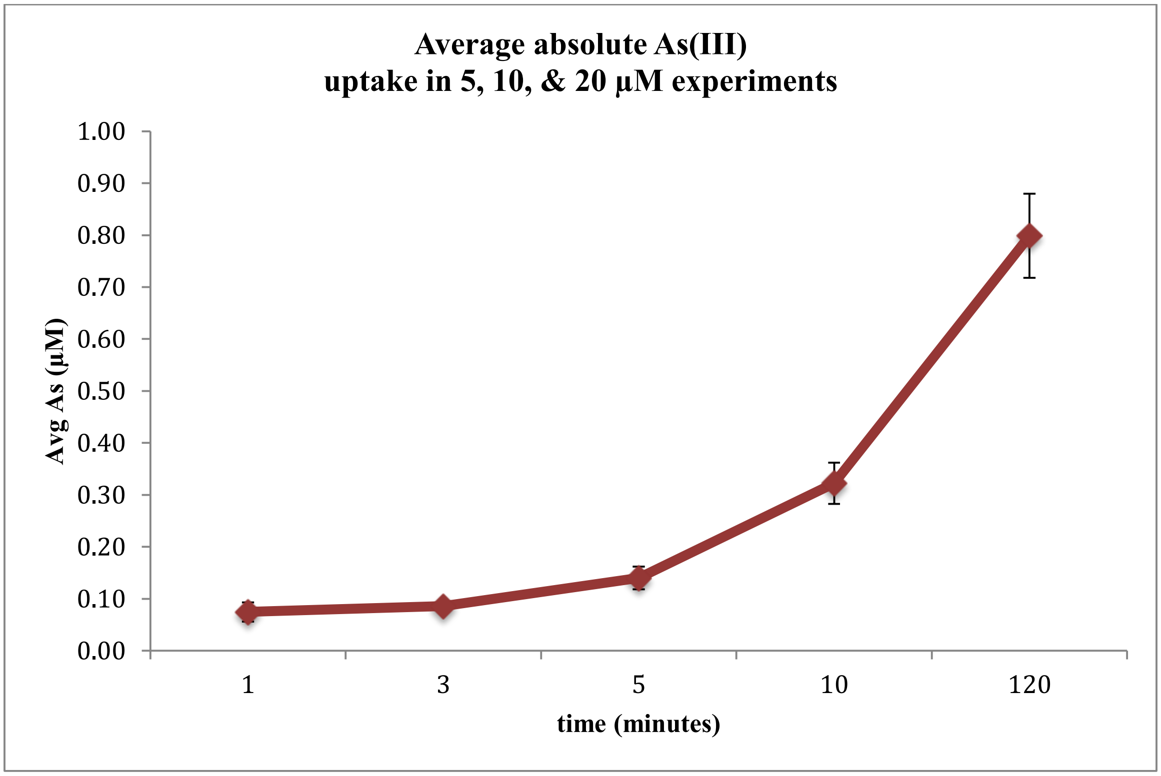


Figure 24: Average absolute uptake over time for 5, 10 & 20 µM experiments

Estimation of As Uptake at Equilibrium

The absolute amount of As adsobed was plotted against the inverse square root of time to evaluate whether the experiments in this study reached equlibrium (Figures 24 - 32). If the experiments reached equilibrium, the y intercept of the regression line, which respresents the amount sorbed at inifinite time, should be close to the uptake observed at the end of the experiment (7 days). Because the observed and predicted values are not the same, equilibrium was not reached. For example, in experiment 7 (Figure 27), the R^2 of

0.999 demonstrates a good fit to the data and suggests that the experiment followed equilibrium thermodynamics. Yet, the y intercept of absolute As uptake of 0.7925 µM, the predicted equilibrium uptake value is greater than the observed As uptake at the end of this experiment of 0.54 µM. This indicates that the experiment did not reach equilibrium. The results obtained through this data manipulation indicate that the equilibrium uptake of As(III) in the various experiments should range from a low of about 0.20 µmole of As to a maximum of about 3.68 µmole. It should be borne in mind, however, that the shape of the experimental uptake plots (i.e., versus time) suggest that a continued uptake of As would occur, even though the value observed at the end of the experiments was generally well below the assumed equilibrium uptake value derived from the inverse square root of time plots.

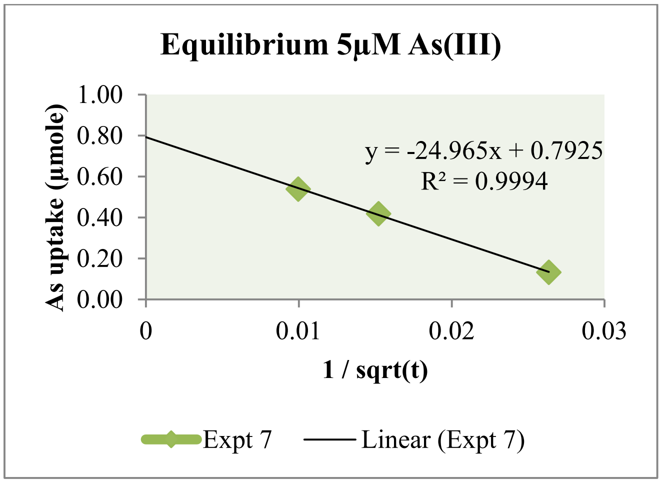


Figure 25: As uptake at equilibrium for experiment 7

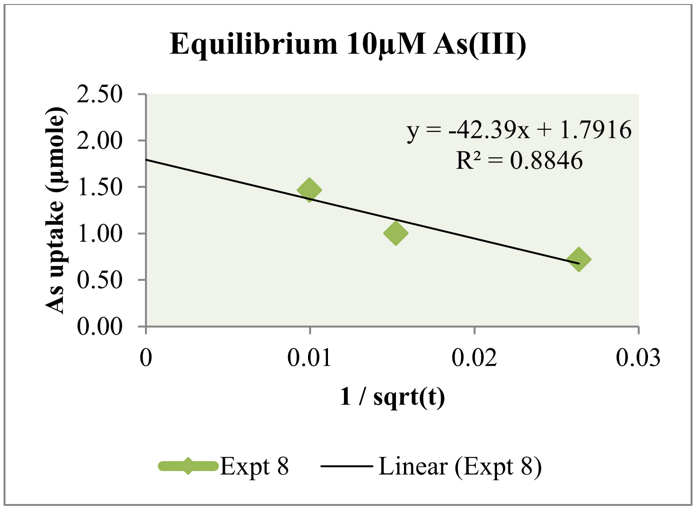


Figure 26: As uptake at equilibrium for experiment 8

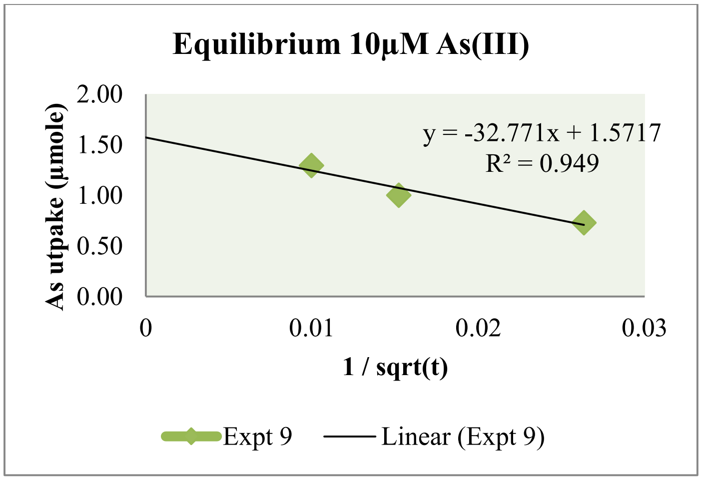


Figure 27: As uptake at equilibrium for experiment 9

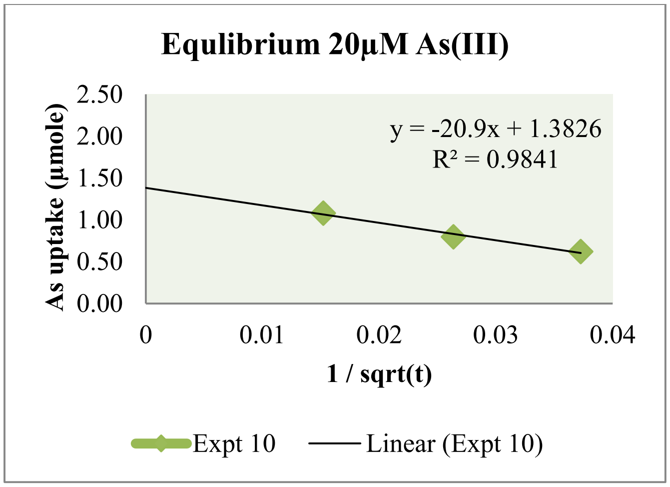


Figure 28: As uptake at equilibrium for experiment 10

The same approach, when applied to uptake experiments with As(V) shows greater amounts of As adsorbed onto the suspended sediments at infinite time than was observed for any of the As(III) experiments. The plots for the two 5 μ M As(V) duplicate experiments display R^2 values of 0.97251 and 0.98121, respectively and the predicted equilibrium uptake is similar (~2.24 µmole and ~2.64 µmole, respectively). As observed during the As(III) experiments, the actual uptake plots (i.e., versus time) show that uptake of As(V) at the end of the experiments was still below the assumed equilibrium uptake value (figure 33). Again, this is indicative of relatively slow uptake kinetics as and that equilibrium would be reached at a time beyond the seven day duration of the experiments conducted in this study.

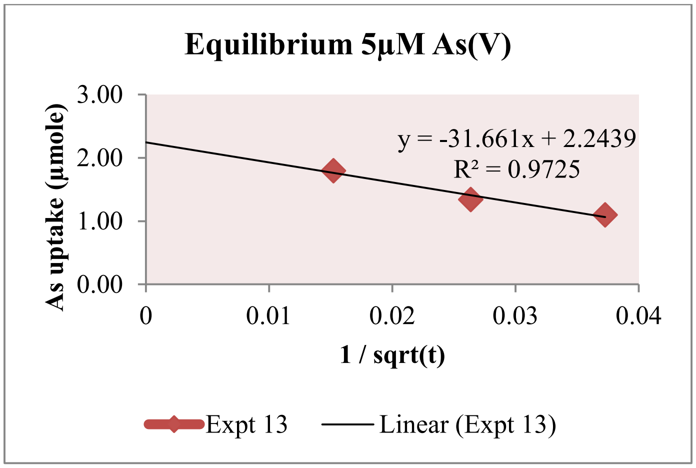


Figure 29: As uptake at equilibrium for experiment 13

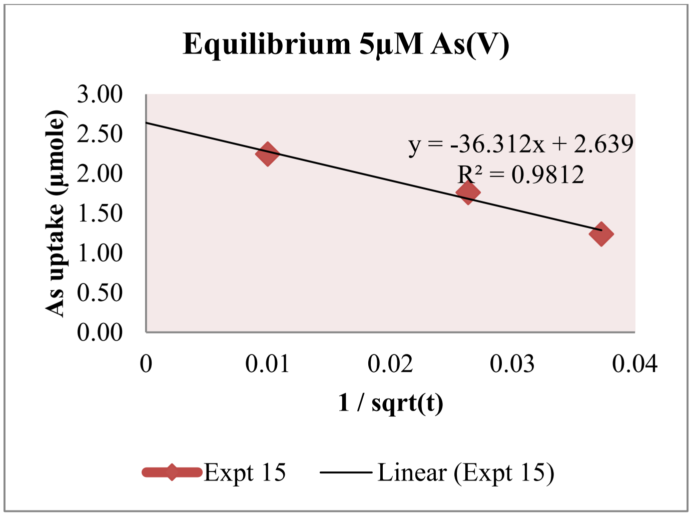


Figure 30: As uptake at equilibrium for experiment 15

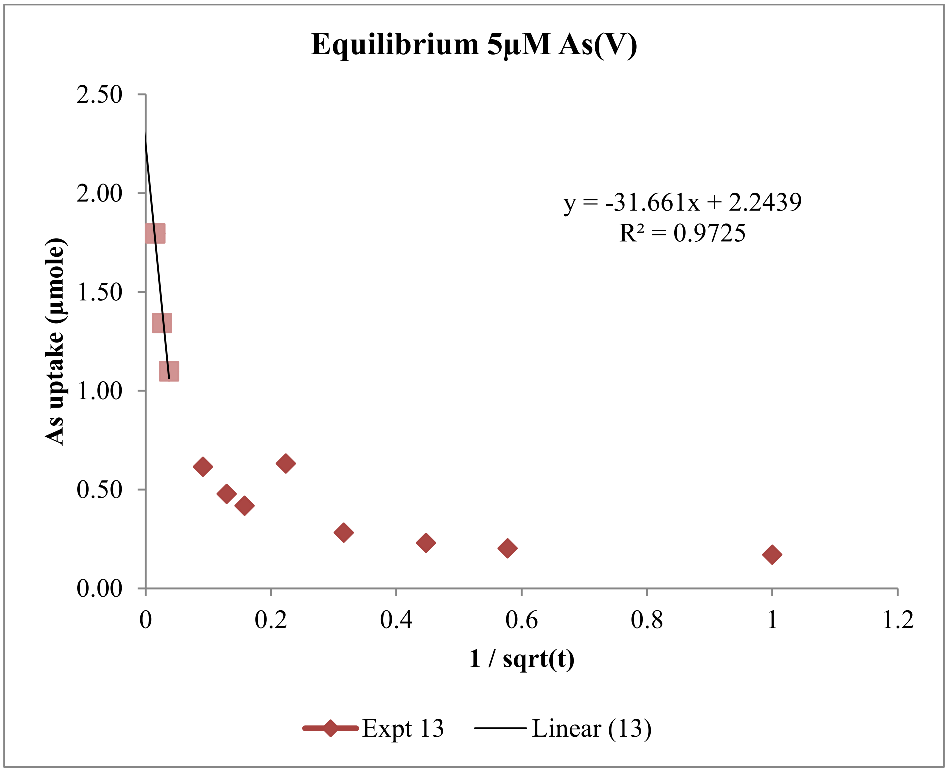


Figure 31: As uptake at equilibrium over a whole uptake plot for experiment 13 to show how equilibrium plot was projected

Real World Implications

The data collected in this study, in addition to known CWM site details, can be utilized in real world implication scenarios to predict a worse case scenario if Lewisite contained in CWM around Hawaii were to breach catastrophically and release their entire content to the environment at one time. In making such a prediction, the the highest As uptake, of about 30% observed in these experiments, was used to calculate the fractions of As derived from CWA that would be released to the sediments and seawater. As mentioned in the background, according to U.S. Military records, nearly 300 T (U.S.) (272,155 kg) of Lewisite were dumped off southern Oahu, with the majority of those DMM reported spread over an area of about 40 km^2. Analysis of the HUMMA sediment determined that As concentrations, were near 6 ppm throughout the HUM001-HUM007 sediment sample area. Calhoun (1999) estimated deep ocean sediment around Hawaii to have a general density of 2.0 Mg m^{-3}. Furthermore, Lewisite contains 39% As by weight.

Assuming an area of 40 km^2 and that sediment will be affected down to a depth of 10 cm below the seawater-sediment interface and that seawater will be affected throughout about 10 m above the seawater-sediment interface, we can estimate the impact Lewisite derived-As has on sediment and seawater as follows:

- Total amount of As = 272,155 kg Lewisite x 0.39 As/Lewisite = 106,140 kg As
- Sediment
    - As retained by sediment = 106,140 kg As x 0.30 = 31,842 kg As
    - Volume of sediment = 40 km^2 x 10 cm = 40 x 10^5 m^3
      = 40 km^2 x 1000 m km^{-1} x 1000 m km^{-1} x 0.1 m

    - Mass of sediment = 40 x 10^5 m^3 x 2 Mg m^{-3}
      = 80 x 10^6 Mg x (1 x 10^3 kg Mg^{-1}) = 80 x 10^9 kg

    - Added As in sediment over the natural concentration
      = 31,842 kg s (80 x 10^9 kg) = 3.98 x 10^{-6} Mg = 0.4 mg kg^{-1} (ppm)

- Seawater

    - As released in seawater = 106,140 kg As x 0.70 = 74,298 kg
      = 7.4298 x 10^{10} mg As

    - Volume of seawater = 40 x 10^6 m^2 x 10 m x 1000 L m^{-3} = 4 x 10^{11} L

    - Concentration of As added to seawater
      = (7.4298 x 10^{10} mg As) ÷ (4 x 10^{11} L) = 0.186 mg L^{-1} (ppm)

The hypothetical calculation above shows that the amount of As added to the sediment would only be 0.4 ppm if 30% of the As from the Lewisite went into the sediment. The amount of As added to the sediments represents only a small increase to the natural concentration of As that was previously observed in these sediments (6 ppm). In other parts of the HUMMA study area, however, concentrations of As reached near 20 ppm, and the amount of As added to the sediment based on the above calculations would be even less significant. Furthermore, Lewisite bombs dumped around the HI-05 site are relatively small when compared to the 40 km^2, and if the As did not disperse far amongst the sediment, then we might assume that only 10% of the area would be affected. Under this more conservative scenario the concentration of As added to sediments near DMM would be higher at about 4 ppm. The latter, however, is still not very large as concentrations of As in sediments around Hawaii range from below 10 ppm to several orders of magnitude higher values, in areas subject to human activities (De Carlo and Anthony, 2002; De Carlo et al., 2004; 2005; Cutler 2006, De Carlo et al., submitted). The concentration of As in other marine environments may range from 0.38 ppm to 1270 ppm in industrially polluted intertidal areas to 48 – 361 ppm in shale at mid-ocean ridges & Kinniburgh, 2011).

Calculations of the amount of As that would be added to seawater under the theoretical scenario described above indicate an increase of 0.186 ppm to the seawater across the 40 km^2 HUMMA area and over the bottom10 m of the ocean. Natural As concentrations in deep ocean water average about 1.7 ppm, which leads to an increase of less than 10% of total As. At about 500 m depth (within the thermocline), the depth range of the HUMMA study area, the concentration of As is only about 1.1 ppm. Hence the As added from catastrophic release of Lewisite would only represent about an 18% increase over existing levels of As. It is also very likely that the As released from Lewisite would not be limited to a ten meter depth range. Strong bottom currents observed at at the HUMMA site would likely spread the dissovled As into a greater volume, thereby commensurately decreasing its concentration and its impact on bottom water concentrations.

The calculation of the As released into the area surrounding CWM described is an absolute worst-case scenario, as all the Lewisite from DMM would be released into the environment at once. This is highly unlikely as is the volume of sediments or seawaer over which the As would be distributed. Yet the calculations reveal a rather minimal effect of such a catastrophic scenario on local As concentrations. As a result, it is much more likely that any leakage of Lewisite at a site such as the HUMMA area, the ensuing hydrolysis of the CWA to As(III) and its partitioning between sediment and seawater would only have a very limited impact on the environment and would not likely represent an environmental problem.

CHAPTER 5. CONCLUSION

This study investigated the adsorption of dissolved As in seawater onto deep-sea marine sediments. The rationale for the study was to evaluate the potential mobility of this toxic element that is released by the hydrolysis of Lewisite, of a constituent of chemical agents found in certain sea-disposed military munitions. This research determined the extent to which dissolved As(III) and As(V) are taken up by hemipelagic sediments under ambient conditions and the partitioning of As between the aqueous and solid phases. It was hypothesized that sediments around CWM had a high propensity for adsorbing and retaining Lewisite derived As, and that the uptake reaction would occur quickly once As was released from hydrolyzed Lewisite in the environment. Such a reaction would effectively immobilize As and prevent its transport through the water column. The final objective of the study was to use study results to estimate concentrations of As that would be found in the marine environment upon catastrophic release from CWM in order to address some of the public concerns regarding potential ecological and human health risks associated with discarded CWM.

The results of laboratory experiments partially disproved the working hypothesis, demonstrating that the adsorption of As did not occur as rapidly as hypothesized, and that equilibrium between As in the aqueous and solid phase was not reached even after 7 days. The maximum uptake of As onto the sediment at the end of the experimental procedures was found to be a function of the initial concentration of As in solution, but that the absolute amount of As taken up by the solid phase was more constant (i.e., the product of the % uptake of As and the initial solution concentration was nearly constant. Evaluation of the data and extrapolation of uptake curves to infinite time yielded "equilibrium" concentrations that were greater than those observed at the conclusion of the experiments, confirming that equilibrium was not reached by the end (7 days) of the experiments conducted in this study. The data demonstrate, that the adsorption of As onto the sediments found at the CWM sites occurs to a much lesser extent than anticipated, consequently the amount potentially released to the water column upon rupture of CWM is greater than expected.

Calculations of the partitioning of As between sediment and seawater under a worst case scenario and based on the experimental data, reveal that that the impact on the environment would be minimal, even if 300 T (U.S) of CWA were to leak simultaneously out of the CWM during a catastrophic rupture and release of all CWA within a 40km^2 area of the seafloor. In spite of this somewhat comforting conclusion, it should be kept in mind that, although "dilution is a solution to pollution" in this case, the best situtation is one where no CWA/CWM is disposed of in the deep ocean. Short of the latter, however, one might conclude that the old military decisions to dispose of unwanted munitions in the ocean may not have been as ill thought out as many might believe.

In order to gain a greater understanding of the conditions controlling the adsorption of As on marine sediments, additional experiments will be needed to supplement the findings in this study. First, the temperature of the seawater in the batch reactor should mimic the temperature in the deep-sea areas CWM are often found (10-14^{0}C), as temperature has been reported to have an effect on speciation of As in the marine environment (Leermakers, et al., 2006) and because kinetics of reactions are known to be temperature dependent. Second, greater sediment loadings than used in this study should be utilized to reflect better conditions that will exist within the porewater of deep sea sediments at CWM sites. Additional experiments will also need to evaluate uptake as a function of redox state, which varies tremendously within the water column and sediment porewater. Finally, because equilibrium was not reached within the 7 day experimental period, further experiments will need to employ to be carried out for longer durations. After concluding further abiotic reactor experiments and more fully characterizing the behavior of Lewisite derived As under seafloor conditions, the impacts of As retained by sediments on benthic infauna can then be assessed.

APPENDIX A: Data for all experiments

Run	ID	Time	75As	147Sm	Mass Solid	Mass Soln	Time	1/t(1/2)	**Solid Sample As**	**Sample-Original**	**Sediment mass added to expt**	% uptake	pH of seawater
			ppb	ppb	mg	g	(min)		**µg total**	**µg total**	**g**		
Expt 1	(Discarded)												
	Mean of 1-1	5/7/12 14:01	11.1	1.103	10.9	9.44	1	1	96.43	90.66	1.0031	12.08830595	
	SD of 1-1		0.102	n/a									
	%RSD of 1-1		0.921	n/a									
	Mean of 1-3	5/7/12 14:06	23.76	1.283	28.5	8.58	3	0.577350269	71.75	65.98	1.0031	8.797869812	
	SD of 1-3		0.197	n/a									
	%RSD of 1-3		0.83	n/a									
	Mean of 1-5	5/7/12 14:12	23.28	1.345	33	8.32	5	0.447213595	58.88	53.11	1.0031	7.081059202	
	SD of 1-5		0.101	n/a									
	%RSD of 1-5		0.432	n/a									
	Mean of 1-10	5/7/12 14:16	24.81	1.403	31.9	8.4	10	0.316227766	65.53	59.77	1.0031	7.968680905	
	SD of 1-10		0.325	n/a									
	%RSD of 1-10		1.308	n/a									
	Mean of 1-20	5/7/12 14:21	23.04	1.403	36	8.5	20	0.223606798	54.57	48.80	1	6.506775333	
	SD of 1-20		0.134	n/a									
	%RSD of 1-20		0.58	n/a									

	Mean of 1-40	5/7/12 14:36	17.71	1.44	36.3	11.43	40	0.158113883	55.94	50.17	1.0031	6.689278739	
	SD of 1-40		0.045	n/a									
	%RSD of 1-40		0.255	n/a									
	Mean of 1-120	5/7/12 14:45	208.5	1.449	41.8	8.24	60	0.129099445	412.29	406.52	1.0031	54.20275648	
	SD of 1-120		0.767	n/a									
	%RSD of 1-120		0.368	n/a									
Expt 2	(discarded)												
	Mean of 2-1	5/7/12 15:11	122.4	1.727									
	SD of 2-1		0.956	n/a									
	%RSD of 2-1		0.781	n/a									
	Mean of 2-3	5/7/12 15:16	21.04	1.524									
	SD of 2-3		1.209	n/a									
	%RSD of 2-3		5.749	n/a									
	Mean of 2-5	5/7/12 15:20	18.9	1.548									
	SD of 2-5		0.264	n/a									
	%RSD of 2-5		1.398	n/a									
Expt 3 (3µm As(III))													
	Mean of 3-1	8/13/12 13:00	7.338	0.954	8.7	9.14	1	1	81.68	75.59	1.0595	33.59376541	
	SD of 3-1		0.199	n/a									
	%RSD of 3-1		2.71	n/a									

	Mean of 3-3	8/13/12 13:04	8.111	0.974	8.6	9.32	3	0.577350269	93.13	87.04	1.0595	38.68380695	
	SD of 3-3		0.241	n/a									
	%RSD of 3-3		2.974	n/a									
	Mean of 3-5	8/13/12 13:08	8.604	1.033	8.7	9.16	5	0.447213595	95.98	89.89	1.0595	39.94985611	
	SD of 3-5		0.11	n/a									
	%RSD of 3-5		1.277	n/a									
	Mean of 3-10	8/13/12 13:12	9.933	1.031	8	8.87	10	0.316227766	116.68	110.59	1.0595	49.15238875	
	SD of 3-10		0.253	n/a									
	%RSD of 3-10		2.548	n/a									
	Mean of 3-20	8/13/12 13:29	11.53	1.161	8.6	8.84	20	0.223606798	125.57	119.48	1.0595	53.10104491	
	SD of 3-20		0.277	n/a									
	%RSD of 3-20		2.402	n/a									
	Mean of 3-40	8/13/12 13:33	12.92	1.147	8.4	8.81	40	0.158113883	143.57	137.48	1.0595	61.10074836	
	SD of 3-40		0.358	n/a									
	%RSD of 3-40		2.773	n/a									
	Mean of 3-60	8/13/12 13:37	14.81	1.178	10.7	10.25	60	0.129099445	150.31	144.22	1.0595	64.09809969	
	SD of 3-60		0.462	n/a									
	%RSD of 3-60		3.122	n/a									
	Mean of 3-120	8/13/12 13:42	19.85	1.279	10.7	8.81	120	0.091287093	173.16	167.07	1.0595	74.2534567	
	SD of 3-120		0.496	n/a									

	%RSD of 3-120		2.496	n/a									
	Mean of 3-1d (1x2)	8/13/12 13:46	30.46	1.291	13.1	9.4	720	0.0372678	231.57	225.48	1.0595	100.2136028	
	SD of 3-1d (1x2)		1.01	n/a									
	%RSD of 3-1d (1x2)		3.315	n/a									
	Mean of 3-7d 10x	8/15/12 14:15	13.86	0.902	17.6	8.96	10080	0.009960238	74.76	68.67	1.0595	30.51830889	
	SD of 3-7d 10x		0.103	n/a									
	%RSD of 3-7d 10x		0.741	n/a									
Expt 4 (blank)													
	Mean of 4-1	7/11/12 16:37	14.6	1.339	20.8	9.97	1	1	70.23	64.46	1.0035		
	SD of 4-1		0.073	n/a									
	%RSD of 4-1		0.499	n/a									
	Mean of 4-3	7/11/12 16:42	16.23	1.571	22.6	9.27	3	0.577350269	66.80	61.03	1.0035		
	SD of 4-3		0.274	n/a									
	%RSD of 4-3		1.691	n/a									
	Mean of 4-5	7/11/12 16:47	16.63	1.695	23.9	10.29	5	0.447213595	71.85	66.08	1.0035		
	SD of 4-5		0.078	n/a									
	%RSD of 4-5		0.472	n/a									
	Mean of 4-10	7/11/12 17:07	20.67	1.977	29.6	10.11	10	0.316227766	70.85	65.08	1.0035		
	SD of 4-10		0.05	n/a									
	%RSD of 4-10		0.244	n/a									

	Mean of 4-20	7/11/12 17:12	22.4	2.177	29.9	9.8	20	0.223606798	73.68	67.90	1.0035		
	SD of 4-20		0.135	n/a									
	%RSD of 4-20		0.602	n/a									
	Mean of 4-40	7/11/12 17:17	12.61	2.109	15	9.78	40	0.158113883	82.50	76.73	1.0035		
	SD of 4-40		0.153	n/a									
	%RSD of 4-40		1.214	n/a									
	Mean of 4-60	7/11/12 17:22	27.97	2.431	35.5	9.05	60	0.129099445	71.55	65.78	1.0035		
	SD of 4-60		0.088	n/a									
	%RSD of 4-60		0.316	n/a									
Expt 5 (3µm As(III))													
	Mean of 5-1	8/13/12 13:54	24.96	1.467	31.6	9.58	1	1	16.36	10.14	1.0807	4.507227307	
	SD of 5-1		0.411	n/a									
	%RSD of 5-1		1.645	n/a									
	Mean of 5-3	8/13/12 14:11	27.75	1.697	25.7	9.1	3	0.577350269	21.24	15.02	1.0807	6.677165456	
	SD of 5-3		0.851	n/a									
	%RSD of 5-3		3.066	n/a									
	Mean of 5-5	8/13/12 14:15	28.75	1.624	27.9	8.37	5	0.447213595	18.64	12.43	1.0807	5.523577778	
	SD of 5-5		0.623	n/a									
	%RSD of 5-5		2.166	n/a									

	Mean of 5-10	8/13/12 14:19	37.89	1.849	40.4	10.08	10	0.316227766	20.43	14.22	1.0807	6.319686311	
	SD of 5-10		1.287	n/a									
	%RSD of 5-10		3.398	n/a									
	Mean of 5-20	8/13/12 14:23	41.99	1.806	34.5	8	20	0.223606798	21.05	14.83	1.0807	6.591608702	
	SD of 5-20		0.904	n/a									
	%RSD of 5-20		2.154	n/a									
	Mean of 5-40	8/13/12 14:27	41.44	1.92	38.1	11.33	40	0.158113883	26.64	20.42	1.0807	9.076183153	
	SD of 5-40		1.487	n/a									
	%RSD of 5-40		3.587	n/a									
	Mean of 5-60	8/13/12 14:32	39.44	1.842	32.3	10.83	60	0.129099445	28.58	22.37	1.0807	9.941479378	
	SD of 5-60		1.385	n/a									
	%RSD of 5-60		3.513	n/a									
	Mean of 5-120	8/13/12 14:44	48.91	2.155	38.9	12.67	120	0.091287093	34.43	28.22	1.0807	12.54123673	
	SD of 5-120		1.326	n/a									
	%RSD of 5-120		2.712	n/a									
	Mean of 5-12h 10x	8/15/12 14:19	10.24	0.947	37.4	9.1	720	0.0372678	26.93	20.71	1.0807	9.205406453	
	SD of 5-12h 10x		0.101	n/a									
	%RSD of 5-12h 10x		0.983	n/a									
	Mean of 5-1d 10x	8/15/12 14:23	10.25	0.912	46.3	12.09	1440	0.026352314	28.93	22.71	1.0807	10.09379506	

	SD of 5-1d 10x		0.113	n/a									
	%RSD of 5-1d 10x		1.105	n/a									
	Mean of 5-3d 10x	8/15/12 14:27	21.54	0.992	47.5	7.25	4320	0.015214515	35.53	29.32	1.0807	13.02932367	
	SD of 5-3d 10x		0.268	n/a									
	%RSD of 5-3d 10x		1.243	n/a									
	Mean of 5-7d 10x	8/15/12 14:31	11.35	0.975	54.9	11.57	10080	0.009960238	25.85	19.64	1.0807	8.727139154	
	SD of 5-7d 10x		0.194	n/a									
	%RSD of 5-7d 10x		1.71	n/a									
Expt 6 (5µm As(III))													
	Mean of 6-1 5x	8/15/12 14:48	4.054	0.956	18.7	8.77	1	1	10.19	4.03	1.0723	1.07410284	
	SD of 6-1 5x		0.031	n/a									
	%RSD of 6-1 5x		0.766	n/a									
	Mean of 6-3 5x	8/15/12 14:52	4.36	1.035	20	8.88	3	0.577350269	10.38	4.21	1.0723	1.123541643	
	SD of 6-3 5x		0.032	n/a									
	%RSD of 6-3 5x		0.738	n/a									
	Mean of 6-5 5x	8/15/12 14:56	4.58	1.047	20.6	10.15	5	0.447213595	12.10	5.93	1.0723	1.582215087	
	SD of 6-5 5x		0.056	n/a									
	%RSD of 6-5 5x		1.212	n/a									
	Mean of 6-10 5x	8/15/12 15:01	6.183	1.113	25.4	9.24	10	0.316227766	12.06	5.89	1.0723	1.571632678	
	SD of 6-10 5x		0.048	n/a									

	%RSD of 6-10 5x		0.776	n/a									
	Mean of 6-20 5x	8/15/12 15:05	9.194	1.182	37.4	9.2	20	0.223606798	12.13	5.96	1.0723	1.589328272	
	SD of 6-20 5x		0.176	n/a									
	%RSD of 6-20 5x		1.91	n/a									
	Mean of 6-40 5x	8/15/12 15:09	4.353	1.172	44.4	13.53	40	0.158113883	7.11	0.95	1.0723	0.252331511	
	SD of 6-40 5x		0.047	n/a									
	%RSD of 6-40 5x		1.07	n/a									
	Mean of 6-60 5x	8/15/12 15:13	6.633	1.176	44.9	11.5	60	0.129099445	9.11	2.94	1.0723	0.784745281	
	SD of 6-60 5x		0.088	n/a									
	%RSD of 6-60 5x		1.325	n/a									
	Mean of 6-120 5x	8/15/12 15:21	11.36	1.323	45.8	7.17	120	0.091287093	9.53	3.37	1.0723	0.898459411	
	SD of 6-120 5x		0.245	n/a									
	%RSD of 6-120 5x		2.152	n/a									
	Mean of 6-12h 5x	8/15/12 15:26	16.93	1.345	43.9	7.61	720	0.0372678	15.73	9.57	1.0723	2.551774375	
	SD of 6-12h 5x		0.314	n/a									
	%RSD of 6-12h 5x		1.855	n/a									
	Mean of 6-1d 5x	8/15/12 15:30	15.71	1.287	41.8	9.82	1440	0.026352314	19.79	13.62	1.0723	3.632555632	
	SD of 6-1d 5x		0.301	n/a									
	%RSD of 6-1d 5x		1.915	n/a									

	Mean of 6-3d 5x	8/15/12 15:34	16.25	1.337	47.6	8.92	4320	0.015214515	16.33	10.16	1.0723	2.709584958	
	SD of 6-3d 5x		0.28	n/a									
	%RSD of 6-3d 5x		1.722	n/a									
	Mean of 6-7d 5x	8/15/12 15:38	23.86	1.398	59.1	10.36	10080	0.009960238	22.42	16.26	1.0723	4.335759472	
	SD of 6-7d 5x		0.183	n/a									
	%RSD of 6-7d 5x		0.768	n/a									
Expt 7 (5µm As(III))													
	Mean of 7-1 5x	8/15/12 15:59	3.155	1.226	27.9	16.93	1	1	9.59	3.83	1.00	1.021352846	7.93
	SD of 7-1 5x		0.03	n/a									
	%RSD of 7-1 5x		0.947	n/a									
	Mean of 7-3 5x	8/15/12 16:03	2.756	1.226	26.3	21.09	3	0.577350269	11.07	5.31	1.00	1.41621283	7.92
	SD of 7-3 5x		0.03	n/a									
	%RSD of 7-3 5x		1.094	n/a									
	Mean of 7-5 5x	8/15/12 16:07	3.178	1.291	32.2	23.19	5	0.447213595	11.47	5.71	1.00	1.521372904	7.92
	SD of 7-5 5x		0.063	n/a									
	%RSD of 7-5 5x		1.973	n/a									
	Mean of 7-10 5x	8/15/12 16:12	4.006	1.291	31.7	20.25	10	0.316227766	12.82	7.06	1.00	1.882474574	7.92
	SD of 7-10 5x		0.113	n/a									
	%RSD of 7-10 5x		2.816	n/a									

	Mean of 7-20 5x	8/15/12 16:16	4.94	1.36	33.5	20.07	20	0.223606798	14.83	9.07	1.00	2.417593696	7.93
	SD of 7-20 5x		0.068	n/a									
	%RSD of 7-20 5x		1.368	n/a									
	Mean of 7-40 5x	8/15/12 16:20	6.194	1.381	37.8	20.27	40	0.158113883	16.64	10.88	1.00	2.90111269	7.95
	SD of 7-40 5x		0.078	n/a									
	%RSD of 7-40 5x		1.259	n/a									
	Mean of 7-60 5x	8/15/12 16:24	5.992	1.33	35.9	20.76	60	0.129099445	17.36	11.60	1.00	3.09285563	7.97
	SD of 7-60 5x		0.115	n/a									
	%RSD of 7-60 5x		1.918	n/a									
	Mean of 7-120 5x	8/15/12 16:28	6.287	1.363	33.6	20.92	120	0.091287093	19.61	13.85	1.00	3.693246352	8.02
	SD of 7-120 5x		0.098	n/a									
	%RSD of 7-120 5x		1.551	n/a									
	Mean of 7-12 10x	4/2/13 15:33	5.501	0.98	36.7	10.47	720	0.0372678	15.72	9.96	1.00	2.656926862	8.13
	SD of 7-12 10x		0.042	n/a									
	%RSD of 7-12 10x		0.763	n/a									
	Mean of 7-1d 10x	4/2/13 15:37	4.411	0.927	40.2	14.31	1440	0.026352314	15.70	9.95	1.00	2.653824876	8.14
	SD of 7-1d 10x		0.126	n/a									
	%RSD of 7-1d 10x		2.859	n/a									
	Mean of 7-3d 10x	4/2/13 15:42	17.28	0.977	40.9	8.79	4320	0.015214515	37.14	31.39	1.00	8.36992339	8.36

	SD of 7-3d 10x		0.395	n/a								
	%RSD of 7-3d 10x		2.287	n/a								
	Mean of 7-7d 10x	4/2/13 15:46	17.43	0.993	45.2	11.99	10080	0.009960238	46.24	40.49	1.00	10.79620649	8.3
	SD of 7-7d 10x		0.172	n/a								
	%RSD of 7-7d 10x		0.988	n/a								
Expt 8 (10µm As(III))												
	Mean of 8-1 10x	4/2/13 15:50	2.203	0.949	40.4	20.48	1	1	11.98	5.81	1.07	0.774656457	7.94
	SD of 8-1 10x		0.056	n/a								
	%RSD of 8-1 10x		2.522	n/a								
	Mean of 8-3 10x	4/2/13 16:07	1.929	0.938	41.3	26.34	3	0.577350269	13.16	7.01	1.07	0.934841814	8
	SD of 8-3 10x		0.057	n/a								
	%RSD of 8-3 10x		2.975	n/a								
	Mean of 8-5 10x	4/2/13 16:11	1.597	0.926	38	29.78	5	0.447213595	13.39	7.24	1.07	0.965202323	8.01
	SD of 8-5 10x		0.03	n/a								
	%RSD of 8-5 10x		1.879	n/a								
	Mean of 8-10 10x	4/2/13 16:15	1.598	0.906	36.9	32.47	10	0.316227766	15.05	8.89	1.07	1.185778833	8.03
	SD of 8-10 10x		0.038	n/a								
	%RSD of 8-10 10x		2.374	n/a								
	Mean of 8-20 10x	4/2/13 16:19	2.835	0.95	42.9	26.63	20	0.223606798	18.83	12.68	1.07	1.690335618	8.07
	SD of 8-20 10x		0.048	n/a								

	%RSD of 8-20 10x		1.707	n/a									
	Mean of 8-40 10x	4/2/13 16:24	3.72	0.944	47.4	25.53	40	0.158113883	21.44	15.29	1.07	2.038164895	8.12
	SD of 8-40 10x		0.08	n/a									
	%RSD of 8-40 10x		2.155	n/a									
	Mean of 8-60 10x	4/2/13 16:28	3.392	0.943	39.6	27.66	60	0.129099445	25.35	19.20	1.07	2.559811798	8.16
	SD of 8-60 10x		0.046	n/a									
	%RSD of 8-60 10x		1.362	n/a									
	Mean of 8-120 10x	4/2/13 16:32	1.427	0.935	13.7	26.19	120	0.091287093	29.19	23.04	1.07	3.071564389	8.22
	SD of 8-120 10x		0.034	n/a									
	%RSD of 8-120 10x		2.412	n/a									
	Mean of 8-12h 10x	4/2/13 16:44	6.909	0.982	44.8	29.24	720	0.0372678	48.25	42.10	1.07	5.613014917	8.36
	SD of 8-12h 10x		0.167	n/a									
	%RSD of 8-12h 10x		2.416	n/a									
	Mean of 8-1d 10x	4/2/13 16:49	9.31	0.964	46.2	27.93	1440	0.026352314	60.22	54.07	1.07	7.209400606	8.38
	SD of 8-1d 10x		0.257	n/a									
	%RSD of 8-1d 10x		2.762	n/a									
	Mean of 8-3d 10x	4/2/13 16:53	17.43	0.982	59.2	25.8	4320	0.015214515	81.28	75.13	1.07	10.01688694	8.37
	SD of 8-3d 10x		0.349	n/a									

	%RSD of 8-3d 10x		2	n/a								
	Mean of 8-7d 10x	4/2/13 16:57	19.65	0.988	49.2	27.2	10080	0.009960238	116.24	110.09	1.07	14.67813821	8.35
	SD of 8-7d 10x		0.281	n/a								
	%RSD of 8-7d 10x		1.43	n/a								
Expt 9 (10µm As(III))												
	Mean of 9-1 10x	4/2/13 17:01	1.375	0.981	38.8	30.47	1	1	10.69	5.00	0.99	0.666201727	7.92
	SD of 9-1 10x		0.014	n/a								
	%RSD of 9-1 10x		1.04	n/a								
	Mean of 9-3 10x	4/2/13 17:05	1.451	0.99	35.4	28.58	3	0.577350269	11.60	5.90	0.99	0.787164267	7.93
	SD of 9-3 10x		0.023	n/a								
	%RSD of 9-3 10x		1.596	n/a								
	Mean of 9-5 10x	4/2/13 17:18	1.63	0.993	40.7	31.71	5	0.447213595	12.57	6.88	0.99	0.917159543	7.94
	SD of 9-5 10x		0.003	n/a								
	%RSD of 9-5 10x		0.167	n/a								
	Mean of 9-10 10x	4/2/13 17:22	1.897	0.996	39.1	30.11	10	0.316227766	14.46	8.77	0.99	1.169066703	7.96
	SD of 9-10 10x		0.021	n/a								
	%RSD of 9-10 10x		1.11	n/a								
	Mean of 9-20 10x	4/2/13 17:26	2.063	0.97	40.2	30.36	20	0.223606798	15.42	9.73	0.99	1.297333322	8
	SD of 9-20 10x		0.037	n/a								

	%RSD of 9-20 10x		1.811	n/a									
	Mean of 9-40 10x	4/2/13 17:30	2.695	0.991	39.2	27.83	40	0.158113883	18.94	13.25	0.99	1.766215617	8.06
	SD of 9-40 10x		0.041	n/a									
	%RSD of 9-40 10x		1.539	n/a									
	Mean of 9-60 10x	4/2/13 17:35	2.84	0.972	36.9	27.75	60	0.129099445	21.14	15.45	0.99	2.059803306	8.09
	SD of 9-60 10x		0.084	n/a									
	%RSD of 9-60 10x		2.952	n/a									
	Mean of 9-120 10x	4/2/13 17:39	3.998	1.012	43.6	28.12	120	0.091287093	25.52	19.83	0.99	2.644120846	8.16
	SD of 9-120 10x		0.051	n/a									
	%RSD of 9-120 10x		1.27	n/a									
	Mean of 9-12h 10x	4/2/13 17:43	7.544	1.004	39.6	29.98	720	0.0372678	56.53	50.84	0.99	6.778600976	8.3
	SD of 9-12h 10x		0.165	n/a									
	%RSD of 9-12h 10x		2.184	n/a									
	Mean of 9-1d 10x	4/2/13 17:47	8.37	1.023	40.8	29.81	1440	0.026352314	60.53	54.84	0.99	7.311895198	8.31
	SD of 9-1d 10x		0.107	n/a									
	%RSD of 9-1d 10x		1.279	n/a									
	Mean of 9-3d 10x	4/2/13 18:00	12.95	1.042	44.3	27.92	4320	0.015214515	80.78	75.09	0.99	10.01244144	8.3
	SD of 9-3d 10x		0.283	n/a									

	%RSD of 9-3d 10x		2.185	n/a									
	Mean of 9-7d 10x	4/2/13 18:04	17.53	1.042	46.2	27.36	10080	0.009960238	102.76	97.06	0.99	12.94183639	8.31
	SD of 9-7d 10x		0.277	n/a									
	%RSD of 9-7d 10x		1.579	n/a									
Expt 10 (20µm As(III))													
	Mean of 10-1 10x	7/19/13 12:53	1.901	1.148	37	25.31	1	1	12.88	7.19	0.9906	0.479045414	7.98
	SD of 10-1 10x		0.064	n/a									
	%RSD of 10-1 10x		3.359	n/a									
	Mean of 10-3 10x	7/19/13 12:57	1.127	1.095	25.3	28.61	3	0.577350269	12.62	6.93	0.9906	0.461913778	8
	SD of 10-3 10x		0.035	n/a									
	%RSD of 10-3 10x		3.101	n/a									
	Mean of 10-5 10x	7/19/13 13:02	2.147	1.116	39.1	28.4	5	0.447213595	15.45	9.75	0.9906	0.650135931	8.01
	SD of 10-5 10x		0.064	n/a									
	%RSD of 10-5 10x		2.976	n/a									
	Mean of 10-10 10x	7/19/13 13:06	2.01	1.111	30.7	30.24	10	0.316227766	19.61	13.92	0.9906	0.927784559	8.03
	SD of 10-10 10x		0.028	n/a									
	%RSD of 10-10 10x		1.405	n/a									
	Mean of 10-20 10x	7/19/13 13:10	2.556	1.081	36.8	31.13	20	0.223606798	21.42	15.72	0.9906	1.048174677	8.06
	SD of 10-20 10x		0.07	n/a									

	%RSD of 10-20 10x		2.73	n/a									
	Mean of 10-40 10x	7/19/13 13:22	3.005	1.126	37.9	29.92	40	0.158113883	23.50	17.80	0.9906	1.186926988	8.11
	SD of 10-40 10x		0.145	n/a									
	%RSD of 10-40 10x		4.811	n/a									
	Mean of 10-60 10x	7/19/13 13:27	3.398	1.177	37.6	31.33	60	0.129099445	28.05	22.35	0.9906	1.490103727	8.14
	SD of 10-60 10x		0.018	n/a									
	%RSD of 10-60 10x		0.519	n/a									
	Mean of 10-120 10x	7/19/13 13:31	4.843	1.176	41.5	31.83	120	0.091287093	36.80	31.10	0.9906	2.073340758	8.13
	SD of 10-120 10x		0.102	n/a									
	%RSD of 10-120 10x		2.101	n/a									
	Mean of 10-12h 10x	7/19/13 13:35	7.409	1.201	40.9	29.12	720	0.0372678	52.25	46.56	0.9906	3.103921658	8.28
	SD of 10-12h 10x		0.13	n/a									
	%RSD of 10-12h 10x		1.753	n/a									
	Mean of 10-1d 10x	7/19/13 13:39	9.168	1.215	41	29.59	1440	0.026352314	65.54	59.85	0.9906	3.989881016	8.33
	SD of 10-1d 10x		0.109	n/a									
	%RSD of 10-1d 10x		1.188	n/a									
	Mean of 10-3d 10x	7/19/13 13:43	12	1.212	38.1	27.82	4320	0.015214515	86.80	81.10	0.9906	5.40683	8.32
	SD of 10-3d 10x		0.26	n/a									

	%RSD of 10-3d 10x		2.169	n/a									
Expt 11 (5µm As(III))													
	Mean of 11-1 10x	6/12/13 14:58	1.781	1.35	45	25.2	1	1	10.95001544	4.64	1.0979	1.236557451	7.98
	SD of 11-1 10x		0.06	n/a									
	%RSD of 11-1 10x		3.373	n/a									
	Mean of 11-3 10x	6/12/13 15:03	1.946	1.34	42.5	25.49	3	0.577350269	12.81405331	6.50	1.0979	1.733634216	7.98
	SD of 11-3 10x		0.054	n/a									
	%RSD of 11-3 10x		2.78	n/a									
	Mean of 11-5 10x	6/12/13 15:07	1.954	1.318	44.3	27.4	5	0.447213595	13.26887739	6.96	1.0979	1.854920637	7.98
	SD of 11-5 10x		0.066	n/a									
	%RSD of 11-5 10x		3.36	n/a									
	Mean of 11-10 10x	6/12/13 15:11	2.367	1.366	44.6	25.94	10	0.316227766	15.11458252	8.80	1.0979	2.347108672	7.97
	SD of 11-10 10x		0.055	n/a									
	%RSD of 11-10 10x		2.331	n/a									
	Mean of 11-20 10x	6/12/13 15:15	3.266	1.402	39.6	21.45	20	0.223606798	19.42276592	13.11	1.0979	3.495957578	7.93
	SD of 11-20 10x		0.11	n/a									
	%RSD of 11-20 10x		3.359	n/a									

	Mean of 11-40 10x	6/12/13 15:22	2.869	1.378	41.9	24.64	40	0.158113883	18.52337052	12.21	1.0979	3.256118804	7.86
	SD of 11-40 10x		0.017	n/a									
	%RSD of 11-40 10x		0.608	n/a									
	Mean of 11-60 10x	6/12/13 15:26	3.954	1.379	47.6	25.47	60	0.129099445	23.22851479	16.92	1.0979	4.510823944	7.82
	SD of 11-60 10x		0.13	n/a									
	%RSD of 11-60 10x		3.289	n/a									
	Mean of 11-120 10x	6/12/13 15:30	4.973	1.384	47.5	24.28	120	0.091287093	27.90848856	21.60	1.0979	5.75881695	7.79
	SD of 11-120 10x		0.154	n/a									
	%RSD of 11-120 10x		3.091	n/a									
	Mean of 11-12h 10x	6/12/13 15:43	8.352	1.402	46.2	25.08	720	0.0372678	49.77815863	43.47	1.0979	11.59072897	7.84
	SD of 11-12h 10x		0.396	n/a									
	%RSD of 11-12h 10x		4.738	n/a									
	Mean of 11-1d 10x	6/12/13 15:47	13.18	1.413	53.6	26.43	1440	0.026352314	71.35272583	65.04	1.0979	17.34394689	7.93
	SD of 11-1d 10x		0.502	n/a									
	%RSD of 11-1d 10x		3.807	n/a									
	Mean of 11-3d 10x	6/12/13 15:51	21.4	1.449	58.8	25.18	4320	0.015214515	100.6131991	94.30	1.0979	25.14673976	7.84
	SD of 11-3d 10x		0.546	n/a									
	%RSD of 11-3d 10x		2.553	n/a									

	Mean of 11-7d 10x	6/12/13 15:55	25.82	1.443	66.7	28.18	10080	0.009960238	119.7661745	113.45	1.0979	30.25419987	7.93
	SD of 11-7d 10x		1.017	n/a									
	%RSD of 11-7d 10x		3.938	n/a									
Expt 12 (to be analyzed)													
Expt 13 (5µm As(V))													
	Mean of 13-1 10x	6/12/13 13:43	2.768	1.149	30.5	20.36	1	1	18.52557602	12.76	1.0026	3.402833604	7.98
	SD of 13-1 10x		0.088	n/a									
	%RSD of 13-1 10x		3.186	n/a									
	Mean of 13-3 10x	6/12/13 13:47	3.142	1.157	31.9	21.16	3	0.577350269	20.89579319	15.13	1.0026	4.034891517	7.98
	SD of 13-3 10x		0.078	n/a									
	%RSD of 13-3 10x		2.473	n/a									
	Mean of 13-5 10x	6/12/13 13:51	2.805	1.14	30.7	25.05	5	0.447213595	22.94721161	17.18	1.0026	4.58193643	7.99
	SD of 13-5 10x		0.128	n/a									
	%RSD of 13-5 10x		4.573	n/a									
	Mean of 13-10 10x	6/12/13 13:55	4.697	1.18	31.1	17.76	10	0.316227766	26.89247867	21.13	1.0026	5.634007646	7.99
	SD of 13-10 10x		0.158	n/a									
	%RSD of 13-10 10x		3.368	n/a									

	Mean of 13-20 10x	6/12/13 14:00	0.718	1.122	2.9	21.39	20	0.223606798	53.09638225	47.33	1.0026	12.62171527	8.02
	SD of 13-20 10x		0.015	n/a									
	%RSD of 13-20 10x		2.156	n/a									
	Mean of 13-40 10x	6/12/13 14:16	4.59	1.243	29.4	23.72	40	0.158113883	37.12852873	31.36	1.0026	8.363620996	8.05
	SD of 13-40 10x		0.206	n/a									
	%RSD of 13-40 10x		4.498	n/a									
	Mean of 13-60 10x	6/12/13 14:21	6.131	1.245	31.1	21.06	60	0.129099445	41.62526336	35.86	1.0026	9.562750228	8.1
	SD of 13-60 10x		0.153	n/a									
	%RSD of 13-60 10x		2.488	n/a									
	Mean of 13-120 10x	6/12/13 14:25	5.874	1.237	26.4	23.29	120	0.091287093	51.95498265	46.19	1.0026	12.31734204	8.12
	SD of 13-120 10x		0.205	n/a									
	%RSD of 13-120 10x		3.496	n/a									
	Mean of 13-12h 10x	6/12/13 14:29	12.01	1.26	29.5	21.59	720	0.0372678	88.12544723	82.36	1.0026	21.96279926	8.18
	SD of 13-12h 10x		0.392	n/a									
	%RSD of 13-12h 10x		3.264	n/a									
	Mean of 13-1d 10x	6/12/13 14:33	21.61	1.292	41.4	20.33	1440	0.026352314	106.39458	100.63	1.0026	26.83456801	8.31
	SD of 13-1d 10x		0.601	n/a									
	%RSD of 13-1d 10x		2.782	n/a									

	Mean of 13-3d 10x	6/12/13 14:37	25.76	1.318	41.8	22.73	4320	0.015214515	140.4419054	134.68	1.0026	35.91385477	8.32
	SD of 13-3d 10x		0.984	n/a									
	%RSD of 13-3d 10x		3.821	n/a									
Expt 15 (5µm As(V))													
	Mean of 15-1 10x	7/19/13 14:42	2.077	1.046	26.7	24.42	1	1	19.03057551	13.27	1.0018	3.538726803	8.31
	SD of 15-1 10x		0.043	n/a									
	%RSD of 15-1 10x		2.074	n/a									
	Mean of 15-3 10x	7/19/13 14:46	2.376	1.041	26.6	21.65	3	0.577350269	19.37330553	13.61	1.0018	3.630121476	8.31
	SD of 15-3 10x		0.044	n/a									
	%RSD of 15-3 10x		1.846	n/a									
	Mean of 15-5 10x	7/19/13 14:50	3.112	1.071	27.2	21.05	5	0.447213595	24.12702709	18.37	1.0018	4.897780557	8.32
	SD of 15-5 10x		0.063	n/a									
	%RSD of 15-5 10x		2.009	n/a									
	Mean of 15-10 10x	7/19/13 14:54	3.084	1.076	23.5	22.53	10	0.316227766	29.62025044	23.86	1.0018	6.362640118	8.32
	SD of 15-10 10x		0.051	n/a									
	%RSD of 15-10 10x		1.656	n/a									
	Mean of 15-20 10x	7/19/13 14:58	4.876	1.083	34.3	21.98	20	0.223606798	31.30244725	25.54	1.0018	6.811225933	8.34
	SD of 15-20 10x		0.057	n/a									

	%RSD of 15-20 10x		1.16	n/a									
	Mean of 15-40 10x	7/19/13 15:03	5.073	1.061	31.1	22.04	40	0.158113883	36.01613378	30.26	1.0018	8.068209008	8.38
	SD of 15-40 10x		0.079	n/a									
	%RSD of 15-40 10x		1.554	n/a									
	Mean of 15-60 10x	7/19/13 15:07	3.33	1.075	20.4	15.6	60	0.129099445	25.51054235	19.75	1.0018	5.266717961	8.4
	SD of 15-60 10x		0.091	n/a									
	%RSD of 15-60 10x		2.718	n/a									
	Mean of 15-120 10x	7/19/13 15:11	7.555	1.086	29.8	19.23	120	0.091287093	48.84032173	43.08	1.0018	11.48799246	8.43
	SD of 15-120 10x		0.172	n/a									
	%RSD of 15-120 10x		2.278	n/a									
	Mean of 15-12h 10x	7/19/13 15:24	14.11	1.127	37.6	22.05	720	0.0372678	82.89508668	77.13	1.0018	20.56926311	8.5
	SD of 15-12h 10x		0.345	n/a									
	%RSD of 15-12h 10x		2.443	n/a									
	Mean of 15-1d 10x	7/19/13 15:28	20.74	1.147	39.5	18.75	1440	0.026352314	98.62657595	92.87	1.0018	24.76432692	8.49
	SD of 15-1d 10x		0.438	n/a									
	%RSD of 15-1d 10x		2.11	n/a									
	Mean of 15-3d 10x	7/19/13 15:32	27.35	1.159	41.1	20.68	4320	0.015214515	137.8627923	132.10	1.0018	35.22731795	8.44
	SD of 15-3d 10x		0.315	n/a									

	%RSD of 15-3d 10x		1.153	n/a									
15-7d actually a 16 day sample	Mean of 15-7d 10x	7/19/13 15:36	42.14	1.203	56.3	23.23	23040	0.006588078	174.1872543	168.43	1.0018	44.91384116	8.49
	SD of 15-7d 10x		0.57	n/a									
	%RSD of 15-7d 10x		1.353	n/a									

APPENDIX B: HUMMA As analysis by ICPMS

Sample ID #	Arsenic (mg/kg)	date	Sample location
HUM 001	6.02	3-Mar-09	RC1
HUM 002	6.76	3-Mar-09	RC1
HUM 003	6.79	3-Mar-09	RC1
HUM 004	5.75	3-Mar-09	RC1
HUM 005	6.04	3-Mar-09	RC1
HUM 006	6.25	3-Mar-09	RC1
HUM 007	5.74	3-Mar-09	RC1
HUM 008	6.73	3-Mar-09	RC2
HUM 009	6.30	3-Mar-09	RC2
HUM 010	6.86	3-Mar-09	RC2
HUM 011	5.00	3-Mar-09	RC2
HUM 012	6.12	3-Mar-09	RC2
HUM 013	6.02	3-Mar-09	RC2
HUM 036	6.98	8-Mar-09	RC4
HUM 037	7.02	8-Mar-09	RC4
HUM 038	6.92	8-Mar-09	RC4
HUM 039	**7.69**	8-Mar-09	RC4
HUM 040	6.66	8-Mar-09	RC4
HUM 041	**7.68**	8-Mar-09	RC4
HUM 042	6.74	8-Mar-09	RC4
HUM 014	**13.29**	5-Mar-09	DS1
HUM 015	**14.05**	5-Mar-09	DS1
HUM 016	**13.91**	5-Mar-09	DS1
HUM 017	**12.41**	5-Mar-09	DS1
HUM 018	**13.41**	5-Mar-09	DS1
HUM 019	**12.87**	5-Mar-09	DS1
HUM 020	**12.40**	5-Mar-09	DS1
HUM 021	**12.17**	5-Mar-09	DS2
HUM 043	**33.86**	10-Mar-09	DS3
HUM 044	**35.64**	10-Mar-09	DS3
HUM 045	**31.72**	10-Mar-09	DS3
HUM 046	**36.78**	10-Mar-09	DS3
HUM 047	**35.11**	10-Mar-09	DS3
HUM 048	**31.73**	10-Mar-09	DS3
HUM 049	**34.66**	10-Mar-09	DS3
HUM 063	**14.11**	13-Mar-09	DS4
HUM 064	**13.63**	13-Mar-09	DS4
HUM 065	**13.41**	13-Mar-09	DS4

HUM 066	**13.49**	13-Mar-09	DS4
HUM 067	**12.25**	13-Mar-09	DS4
HUM 068	**13.60**	13-Mar-09	DS4
HUM 029	6.29	8-Mar-09	DMM1
HUM 030	6.83	8-Mar-09	DMM1
HUM 031	5.74	8-Mar-09	DMM1
HUM 032	6.98	8-Mar-09	DMM1
HUM 033	6.32	8-Mar-09	DMM1
HUM 034	3.41	8-Mar-09	DMM1
HUM 035	4.19	8-Mar-09	DMM1
HUM 050	**38.11**	11-Mar-09	DMM2
HUM 051	**38.65**	11-Mar-09	DMM2
HUM 052	**38.11**	11-Mar-09	DMM2
HUM 053	**36.62**	11-Mar-09	DMM2
HUM 054	**35.23**	11-Mar-09	DMM2
HUM 055	**40.15**	11-Mar-09	DMM2
HUM 069	7.12	16-Mar-09	DMM3
HUM 070	**7.69**	16-Mar-09	DMM3
HUM 071	**7.51**	16-Mar-09	DMM3
HUM 072	6.69	16-Mar-09	DMM3
HUM 073	6.19	16-Mar-09	DMM3
HUM 074	**7.31**	16-Mar-09	DMM3
HUM 075	5.95	17-Mar-09	DMM4
HUM 076	6.01	17-Mar-09	DMM4
HUM 077	4.76	17-Mar-09	DMM4
HUM 078	5.76	17-Mar-09	DMM4
HUM 079	5.92	17-Mar-09	DMM4
HUM 080	4.63	17-Mar-09	DMM4
HUM 081	5.82	17-Mar-09	DMM4
HUM 082	6.86	17-Mar-09	DMM5
HUM 083	6.66	17-Mar-09	DMM5
HUM 084	5.85	17-Mar-09	DMM5
HUM 085	7.23	17-Mar-09	DMM5
HUM 086	6.95	17-Mar-09	DMM5
HUM 087	6.74	17-Mar-09	DMM5
HUM 088	6.40	17-Mar-09	DMM5
HUM 089	6.10	17-Mar-09	DMM6
HUM 090	6.00	17-Mar-09	DMM6
HUM 091	6.22	17-Mar-09	DMM6
HUM 092	6.30	17-Mar-09	DMM6
HUM 093	5.88	17-Mar-09	DMM6
HUM 094	4.49	17-Mar-09	DMM6
HUM 095	3.90	17-Mar-09	DMM6

HUM 096	4.73	17-Mar-09	DMM7
HUM 097	5.40	17-Mar-09	DMM7
HUM 022	5.72	7-Mar-09	DMM_DS1
HUM 023	5.31	7-Mar-09	DMM_DS1
HUM 024	4.95	7-Mar-09	DMM_DS1
HUM 027	**7.94**	7-Mar-09	DMM_DS1
HUM 028	6.12	7-Mar-09	DMM_DS1
HUM 056	**22.20**	11-Mar-09	DMM_DS2
HUM 057	**32.23**	11-Mar-09	DMM_DS2
HUM 058	**32.70**	11-Mar-09	DMM_DS2
HUM 059	**29.53**	11-Mar-09	DMM_DS2
HUM 060	**34.60**	11-Mar-09	DMM_DS2
HUM 061	**32.86**	11-Mar-09	DMM_DS2
HUM 062	**32.80**	11-Mar-09	DMM_DS2
HUM 098	**21.48**	18-Mar-09	DMM_DS3
HUM 099	**20.73**	18-Mar-09	DMM_DS3
HUM 100	**22.27**	18-Mar-09	DMM_DS3
HUM 101	**18.21**	18-Mar-09	DMM_DS3
HUM 102	**21.18**	18-Mar-09	DMM_DS3
HUM 103	**17.22**	18-Mar-09	DMM_DS3
HUM 104	**19.86**	18-Mar-09	DMM_DS3
HUM 105	**19.19**	18-Mar-09	DMM_DS3

APPENDIX C: Lewisite Production and Chemical Behavior

LEWISITE

The preparation of Lewisite (L-1) by the original procedure is complicated and dangerous. It involves the reaction of acetylene with arsenic trichloride, by using aluminum chloride as a catalyst. The reaction yields three principal products (5-19):

$$\mathrm{HC{\equiv}CH + AsCl_3 \rightarrow}$$
$$\underset{\text{L-1}}{\mathrm{ClCH{=}CHAsCl_2}} + \underset{\text{L-2}}{\mathrm{(ClCH{=}CH)_2AsCl}} + \underset{\text{L-3}}{\mathrm{(ClCH{=}CH)_3As}} \qquad (5\text{–}19)$$

The optimum yield of Lewisite is about 20 percent, obtained along with L-2, L-3, tar, and an explosive material. Acetylene reacts with $AsCl_3$ in hydrochloric acid solution, with mercuric chloride as a catalyst, to give Lewisite in 80 to 85 percent yield (based on $AsCl_3$). Cuprous chloride and ethanolamine hydrochloride used together, however, constitute the best catalyst for the reaction.

The hydrolysis of Lewisite by water involves the following equilibria (5-20):

$$\mathrm{ClCH{=}CHAsCl_2} \overset{\text{(fast)}}{\rightleftarrows} \mathrm{ClCH{=}CHAs(OH)_2 +}$$
$$\mathrm{2HCl} \underset{\text{(slow)}}{\rightleftarrows} \mathrm{ClCH{=}CHAsO + H_2O} \underset{\text{(slow)}}{\rightleftarrows} \mathrm{(ClCH{=}CHAsO)_n} \qquad (5\text{–}20)$$

The only substance isolated is polymeric 2-chlorovinylarsinoxide, a white insoluble powder.

The cold aqueous media of pH = 0.5 Lewisite decomposes as follows (5-21):

$$\begin{aligned} &\mathrm{ClCH{=}CHAs(OH)_2 + OH^{\ominus} \rightarrow} \\ &\quad \mathrm{Cl^{\ominus} + HC{\equiv}CH + As(OH)_3} \qquad (5\text{–}21) \end{aligned}$$

The vesicant character of arsenicals such as Lewisite is not a property of the $AsCl_2$ group exclusively, since carefully prepared solutions of corresponding oxide or dihydroxide are equally vesicant. Lewisite reacts with sodium alkoxides to give derivatives that are volatile, vesicant liquids (5-22) that hydrolyze irreversibly on contact with water:

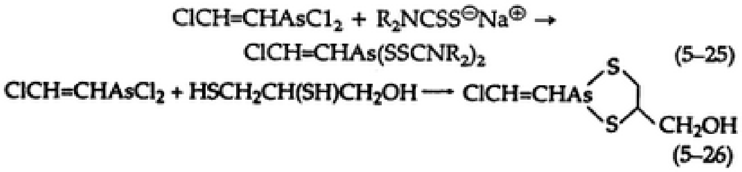
$$\begin{aligned} &\mathrm{ClCH{=}CHAsCl_2 + RO^{\ominus}Na^{\oplus} \rightarrow} \\ &\quad \mathrm{ClCH{=}CHAs(OR)_2 + 2NaCl} \qquad (5\text{–}22) \end{aligned}$$

Reaction with sodium mercaptides gives the analogous thioethers (5-23), which are only slightly soluble in water and in general are hydrolyzed reversibly, giving toxic and sometimes vesicant solutions, although the equilibrium generally favors thioether formation (5-24):

$$\begin{aligned} &\mathrm{ClCH{=}CHAsCl_2 + RS^{\ominus}Na^{\oplus} \rightarrow} \\ &\quad \mathrm{ClCH{=}CHAs(SR)_2 + 2NaCl} \qquad (5\text{–}23) \end{aligned}$$

$$\mathrm{ClCH{=}CHAs(SR) + 2H_2O = ClCH{=}CHAs(OH)_2 + 2RSH} \qquad (5\text{–}24)$$

Aqueous and alcoholic solutions of sodium dialkyldithiocarbamates react readily with Lewisite to give crystalline, sharp-melting solids that are useful for its characterization (5-25). These dithiocarbamates are much more stable than the simple thioethers. However, hydrolysis of cyclic thioethers, such as the reaction product of Lewisite and BAL (British Anti-Lewisite) (5-26) is negligible.



Alkali hydrolyzes all of these compounds with the evolution of acetylene (5-21). Hydrogen peroxide causes decomposition of the ethers and thioethers in neutral or acid solution, giving free arsenic acids.

Little information is available in the literature concerning the reactions of Lewisite with biologically important molecules, although it is reasonable to assume that, as with sulfur mustard, DNA is a major target.

(Pechura & Rall, 1993)

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