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Fractionation of sedimentary arsenic from Port Kembla Harbour, NSW, Australia

Glennys A. O'Brien
University of Wollongong, gobrien@uow.edu.au

William E. Price
University of Wollongong, wprice@uow.edu.au

Bryan E. Chenhall
University of Wollongong, bryanc@uow.edu.au

muhammad damris

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Abstract

The binding of arsenic in sediments of the heavily industrialised Port Kembla Harbour, NSW, Australia, has been investigated. Both dredge and core samples have been used to develop a sieving/sequential extraction (SE) procedure. Dredge samples included oxic surficial and deeper anoxic sediment. The main core sample analysed was 18 cm deep, sliced at 2 cm intervals. Sediment was sieved to three size ranges (250 microm) and each of these was then subjected to a four step SE, sequentially solubilizing arsenic as ion exchangeable, 1 M HCl soluble, $\text{NH}_2\text{OH}\cdot\text{HCl}$ soluble, and strong oxidising acid soluble. Concentrations of 50-500 mg As kg^{-1} were found, elevated well above local background values. The core sample showed elevated concentrations of arsenic within the top 6-8 cm (300-500 mg As kg^{-1}), relative to the deeper sediment (100-200 mg As kg^{-1}). Substantial portions of the total arsenic present in the 0-8 cm sediments of core and dredge samples, were found to be soluble in 1 M pH 5 phosphate buffer or 1 M HCl. Arsenic in the lower 8-18 cm of the core displayed different solubility, the fourth stage SE strong acid digestion being required to solubilize >90% of the deep sediment arsenic. It appears that diagenesis had resulted in remobilisation of weakly bound arsenic with subsequent diffusion and deposition in surficial layers. Strong acid soluble arsenic present in deeper sediments has two possible origins: sedimented as strongly bound remaining untouched by diagenetic events, or subjected to diagenetic reactions such as pyritization, which lead to more stable crystalline forms of minerals.

Keywords

Fractionation, sedimentary, arsenic, from, Port, Kembla, Harbour, NSW, Australia, CMMB

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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Fractionation of sedimentary arsenic from Port Kembla Harbour, NSW, Australia

Muhammad Damris,^{ab} Glennys A. O'Brien,^{*a} William E. Price^a and Bryan E. Chenhall^c

^a Department of Chemistry, University of Wollongong, Northfields Avenue, Wollongong, 2522 NSW, Australia. E-mail: gobrien@uow.edu.au

^b Universitas Jambi, Kampus Mandalo Darat Jambi, 23129 Sumatera, Indonesia

^c School of Earth and Environmental Sciences, University of Wollongong, Northfields Avenue, Wollongong, 2522 NSW, Australia

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The binding of arsenic in sediments of the heavily industrialised Port Kembla Harbour, NSW, Australia, has been investigated. Both dredge and core samples have been used to develop a sieving/sequential extraction (SE) procedure. Dredge samples included oxic surficial and deeper anoxic sediment. The main core sample analysed was 18 cm deep, sliced at 2 cm intervals. Sediment was sieved to three size ranges (< 63 μm , 63–250 μm , > 250 μm) and each of these was then subjected to a four step SE, sequentially solubilizing arsenic as ion exchangeable, 1 M HCl soluble, $\text{NH}_2\text{OH} \cdot \text{HCl}$ soluble, and strong oxidising acid soluble. Concentrations of 50–500 mg As kg^{-1} were found, elevated well above local background values. The core sample showed elevated concentrations of arsenic within the top 6–8 cm (300–500 mg As kg^{-1}), relative to the deeper sediment (100–200 mg As kg^{-1}). Substantial portions of the total arsenic present in the 0–8 cm sediments of core and dredge samples, were found to be soluble in 1 M pH 5 phosphate buffer or 1 M HCl. Arsenic in the lower 8–18 cm of the core displayed different solubility, the fourth stage SE strong acid digestion being required to solubilize >90% of the deep sediment arsenic. It appears that diagenesis had resulted in remobilisation of weakly bound arsenic with subsequent diffusion and deposition in surficial layers. Strong acid soluble arsenic present in deeper sediments has two possible origins: sedimented as strongly bound remaining untouched by diagenetic events, or subjected to diagenetic reactions such as pyritization, which lead to more stable crystalline forms of minerals.

1. Introduction

Arsenic is a toxic metalloid, ubiquitous in the environment and of significant environmental concern even when present at $\mu\text{g L}^{-1}$ concentrations; and yet it is strangely familiar to people for its past therapeutic use and for its notoriety. In aquatic environments, sediments have been found to exert control over the distribution of arsenic.^{1,2} Sediments can act as both a sink and source of the contaminant and thus pose a threat to aquatic organisms.^{3,4} The most significant current human threat from this element is the contamination of drinking water where supplies are drawn from groundwater containing elevated levels of arsenic. Tens of millions of people living in the West Bengal and Bangladesh Ganges–Meghna–Brahmaputra Delta region are threatened by this circumstance; other areas of the world are known to experience similar problems.⁵

Arsenic ranks 20th in abundance of the elements in the Earth's crust with an average concentration of 3 mg kg^{-1} ⁶ and arsenic is ubiquitous—spread throughout the hydrosphere, the biosphere and the lithosphere. In the terrestrial environment, arsenic occurs as a component of more than 245 minerals, mostly ores containing sulfide, along with copper, nickel, lead, cobalt, gold or other metals and their alteration/weathering products.^{5,7} Arsenopyrite (FeAsS) is the most abundant arsenic mineral. A number of naturally occurring processes mobilize arsenic, including volcanic, geothermal and geological (weathering) processes and microbial activity.

Large quantities of arsenic are released into the environment by anthropogenic activity, mainly through mining operations, industrial processing of minerals containing arsenic, biocidal formulations and fossil fuel burning. These sources contribute approximately 30 000 t of arsenic per year, about 60% of which

is generated from two major sources, copper smelting and coal combustion.⁸

Port Kembla Harbour, NSW, Australia, supports Australia's largest industrial complex (Fig. 1), which comprises a number of heavy metallurgical industries with a long contamination history.⁹ The first industry, a copper smelting plant, established in the area in 1908, paved the way for other industries to be concentrated in the area, e.g. fertilizer production, steelworks, coal and grain port handling facilities. Numerous minor industries associated with the fabrication of copper and steel and the production of industrial refractories and fertilizer were also established. The copper smelter operated continuously until the mid 1990s, then briefly in 2002–2003.

Port Kembla Harbour receives atmospheric depositions¹⁰ and stormwater from local industrial plants. Cooling water and other waste streams from industrial operations have also been discharged to the harbour.¹¹ Rights of discharge continue to be exercised today (NSW EPA, 2004, on-line public register¹²). Not surprisingly, given the long operating history of the copper smelter, elevated concentrations of metals in the harbour sediments have been reported.¹³

Studies of arsenic contamination in Port Kembla Harbour sediments to date have focused on bulk concentrations^{13–16} and have indicated the presence of a 'hot spot' of elevated arsenic levels immediately off the southern harbour shore, near the outlet of the main stormwater drain from the copper smelter area (Fig. 1). However, information on the association of arsenic with various sediment solid phases and particular grain size is not available. This is important because heavy metal contaminants of anthropogenic origin have often been found to be concentrated in fine grain sediments^{17,18} and

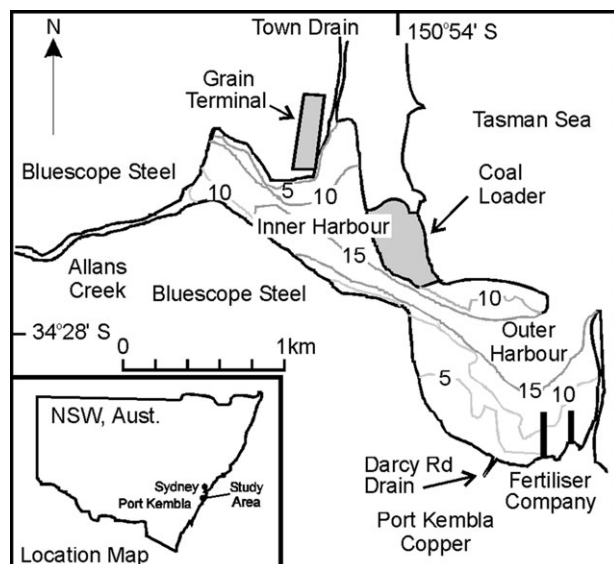


Fig. 1 Port Kembla Harbour and industrial complex (bathymetry in m).

attached to a variety of solid phase sediment components. Furthermore various diagenetic processes, bioturbation, other physical disturbances or reoxygenation can all alter the sediment chemistry of contaminants, changing their bioavailability. The distribution and partitioning of arsenic among different phases and particle sizes in these sediments will determine the nature and magnitude of the threat posed by this element to the Port Kembla Harbour environment.

Sequential extraction (SE) or fractionation is one possible method for establishing the mode and strength of binding of arsenic to the sediment. In this study bulk sediments from the outer harbour, collected without disturbance using a dredge sampler, were divided into surficial and subsurface samples that represented oxic and anoxic layers of the sediment, respectively. Both sediment types were used to optimise a sequential extraction procedure to elucidate the mode of arsenic binding. The method was then applied to sectioned sediment core samples collected from the same site using a hand corer.

Sequential extractions (SE or fractionation) have become accepted as useful and widely applicable methods for assessing various aspects of the sediment chemistry of toxic metals and metalloids. These are operationally defined methods that do not strictly identify individual specific phases as would XRD or identify particular molecular bindings and oxidation states as would XAS. Rather, samples are subjected to a series of increasingly strong extractants to solubilize different mineralogical fractions thought to be responsible for retaining the element of interest in the solid matrix. Then the extracts are analysed for the elements of interest, yielding the proportion of element in each operationally defined pool. The SE methods have the advantage that the element of concern is removed from the solid phase into solution and methods of solution quantitation are available, which have enough sensitivity to quantify the contaminant at mg kg^{-1} levels in the different pools. The SE methods do have disadvantages, which need to be recognised and accounted for in the interpretation of the information gained. These disadvantages are usually grouped into two main areas: (1) lack of specificity for a particular phase or phases, and (2) possible readsorption and redistribution of the element during the SE process as sediment equilibria adjust to the applied chemical conditions.¹⁹

The SE method developed in this study is adapted from the method of Keon *et al.*²⁰ Four stages of extraction are applied to size fractionated sediments to distinguish (i) ion exchangeable arsenic; (ii) arsenic associated with acid volatile sulfides

(AVS), carbonates, manganese oxides and amorphous iron oxyhydroxides; (iii) arsenic associated with crystalline reducible iron and manganese hydrous oxides and finally (iv) residual arsenic extractable with strong oxidising acids which would include organic components, crystalline sulfides and other mineral forms.

This study reports the optimised sequential extraction procedure for arsenic in the sediment solids and the partitioning of arsenic among the four operationally defined phases. This partitioning is reported to vary as a function of both grain size and sediment depth. The implications of the observed size partitioning for sediment quality monitoring are discussed in terms of grain size normalization.

2. Material and methods

2.1. Sediment sampling techniques

Two sampling devices were used for sampling harbour sediments from a boat in water up to 6 m depth. The first samples were collected with a dredge, yielding samples of approximately $20 \text{ cm} \times 22 \text{ cm} \times 10 \text{ cm}$ deep. The second sampler was a simple coring device operated by hand *via* a long pole. The core sample tubes were polycarbonate, 69.5 mm id, acid washed before use. This coring device allowed the collection of undisturbed cores in the shallow harbour waters.

In June 2001, two sediment samples were collected by dredge from the southern end of the Outer Harbour of Port Kembla about 100 m offshore in that area known to contain elevated levels of arsenic. Upon retrieval, the bulk of the samples were undisturbed sediment, retaining layering and structure. Using a plastic scoop, layers were scraped from the bulk sample to give a surficial oxic (0–2 cm) sample and a deeper (2–6 cm) anoxic sample. These samples were stored in airtight centrifuge tubes (50 mL), with air excluded by overflowing the tube. The two dredge samples (PK2, PK5) were kept separate, thus yielding two surface (PK2TL, PK5TL) and two subsurface samples (PK2BL, PK5BL) in total. The samples were stored chilled in an icebox during transport to the laboratory.

Later in July 2002, three undisturbed core samples were collected close to the same sampling site (Core 1, Core 2 and Core 3). A GPS was used to fix the position of sampling as close as possible to the previous dredge sampling point. Three additional cores were also collected from nearby sediment closer to the harbour shore (Core 4, Core 5 and Core 6). The collected sediment cores extended to 20–22 cm of depth. Once a core sample was obtained and brought back on board, the tube was capped at both ends with acid washed rubber stoppers to minimise exposure to oxygen. Core samples were maintained chilled in an icebox in a vertical position to avoid mixing or resuspension of surficial sediments during transportation to the laboratory.

2.2. Sediment processing

Dredge samples were centrifuged ($2500 \text{ rev min}^{-1}$, 10 min) immediately on return to the laboratory (same day) to separate the sediment solid phase and interstitial water. Following centrifugation interstitial water samples were filtered ($0.45 \mu\text{m}$) in a nitrogen glove box, acidified and analysed for total arsenic (Section 2.5).

Core samples were extruded and cut to yield 2 cm layers in an oxygen free atmosphere, immediately on return to the laboratory (same day). Sediment samples were commonly soft and the top layers unstable if tilted, so these cores had to be extruded while upright. In addition, except for the very top 0–2 cm at most, the sediments were generally anoxic, varying in colour between grey–black silty sands and soft black sulfidic gels. All processing was carried out in an oxygen free atmosphere. A system allowing upright extrusion of sediments in the nitrogen glove box was developed by modifying the base of our

glove box to allow it to sit over the extruder, hence anoxic conditions could be maintained during the extrusion/sectioning operation. Extruded sediment layers were collected into centrifuge tubes and then centrifuged to separate interstitial water. The interstitial water samples were filtered, acidified and analysed immediately for As(III) and later for total As (Section 2.5).

In the case of the six cores collected in June 2002, Core 1 was sectioned in its entirety and processed as below. The other five core samples (Cores 2–6) were sectioned to yield a surface layer (0–2 cm depth), a mid layer (6–8 cm depth) and a deep layer (12–14 cm depth).

Redox potential (E_h) and pH were measured on each core layer and each bulk sample by directly applying electrodes into a separate subsample of the sample, this subsample was later discarded. The values were recorded after stable readings had been established. The electrodes were rinsed and kept in Milli-Q water between successive measurements. Calibration of the electrodes was checked after every eight—ten sediment measurements. The reported values of absolute E_h in mV are corrected for the standard Ag/AgCl electrode potential.

For each sediment layer sample, the solid phase remaining after interstitial water separation was then wet sieved into three grain size fractions: <63 μm , 63–250 μm , and >250 μm . Stones, shell fragments, plant material and litter (>2 mm) found in any individual sample were discarded. Sieving was carried out using harbour seawater that had been deoxygenated. A portion of the sieving water was analysed to check for leaching of arsenic, less than 1% of total arsenic was found to have leached out of the sediment during sieving. The entire sieving procedure was conducted under nitrogen in the glove box.

Sediment dry weight was determined following sieving, on a separate subsample of each fraction, by drying at 60 °C to constant mass.

2.3. Sequential extraction of solid phase

The sequential extraction methodology used was adapted from the fractionation procedure reported by Keon *et al.*²⁰ Each grain size fraction was subjected to the four-stage sequential extraction as outlined in Table 1. The ion exchangeable fraction (symbol: IEx) was derived from an extraction with NaH_2PO_4 (1 mol L^{-1}) for 18 h at room temperature.²⁰ Various other extractants have been reported for this step aimed at ion exchangeable arsenic, for example NH_4OAc or MgCl_2 or $\text{Mg}(\text{NO}_3)_2$.^{19,21,22} The phosphate system was chosen here for the similarity of the phosphate ion to As(V) and As(III) as oxoanions.²¹ The residue from this first fraction was then extracted with HCl (1 mol L^{-1}) for 1 h ('AVS' type extraction; Di Toro *et al.*²³) to derive arsenic associated with carbonates, amorphous oxyhydroxides of Fe and Mn and the acid volatile sulfide fraction^{20,24,25} (symbol: HCl). The residue from the second extraction was then extracted with $\text{NH}_2\text{OH} \cdot \text{HCl}$

(1 mol L^{-1}) for 2 h to derive arsenic associated with the more crystalline oxyhydroxides of Fe and Mn, which are solubilized by reduction^{22,26} (symbol: REd). This reductive dissolution has been carried out with other reducing agents, for example Keon *et al.*²⁰ used Ti^{3+} . Finally the residual forms of arsenic were obtained by strong acid digestion (symbol: AD). In our initial studies, the strong acid digestion was a covered $\text{HNO}_3\text{--H}_2\text{SO}_4$ hot plate digestion; later a microwave assisted HNO_3 digestion (200 °C, 60 minutes) was used for this step. A variety of strong acid digestions have been reported,^{20–22} the reagents used depending on whether complete dissolution was intended. In this study, strong acid dissolution did not include a final HF step to ensure dissolution of all silicates. The strong oxidizing conditions used here would completely dissolve the target phases which were crystalline sulfides, including pyritic species,²⁷ organic components including any organoarsenical compounds not extracted in previous steps, and other oxyhydroxide minerals, but not silicates. Residue from this digest was discarded.

Open manipulations of samples were carried in the glove box; all extractant solutions were deoxygenated with a nitrogen stream prior to use. All sequential extractions except the fourth strong acid digestion stage were carried in a nitrogen atmosphere. Thus sediments were not exposed to the atmosphere from collection until after the $\text{NH}_2\text{OH} \cdot \text{HCl}/\text{HOAc}$ extraction had been completed.²⁸

To carry out the sequential extraction, between 0.3–0.6 g of wet sample was placed in a preweighed centrifuge tube (50 mL) which was then accurately weighed. Next the first extractant was added, the tube closed and the extraction allowed to proceed (Table 1). After agitation the tubes were centrifuged at 3000 rev min^{-1} for 10 min, returned to the glove box, and supernatants were poured off and filtered (0.45 μm). The filtered extracts were stored with acid preservation for total arsenic analysis. Milli-Q water (20 mL) was added to the remaining residue and the suspension was agitated for 20 min, the water wash was separated by centrifugation, filtered and added to the previously collected supernatant. The next extractant was then applied in its turn. The residue from extraction stage 4 was discarded.

2.4. Reagents

All reagents used for this study were analytical grade. All solutions were prepared using Milli-Q water. Reagent blanks were analysed for all solutions and found to contain less than detectable amounts of arsenic.

2.5. Determination of arsenic

All arsenic determinations were carried out using a SpectrAA 200, Varian atomic absorption spectrophotometer. The continuous flow vapour generation accessory (model VGA-76) was used for hydride generation and atomisation was achieved

Table 1 Sequential extraction reagents, agitation time, target phase and possible releasing mechanisms of the sequential extraction procedure modified from Keon *et al.*²⁰

Stage and symbol	Extracting agent	Target phases	Possible dissolution mechanism
1 IEx	40 mL 1 M NaH_2PO_4 , pH 5. 18 h agitation, 50 rev min^{-1}	Weakly bound ion exchangeable As	Anion exchange of PO_4^{3-} for AsO_4^{3-} and AsO_3^{3-}
2 HCl	40 mL 1 M HCl 1 h agitation, 50 rev min^{-1}	Amorphous hydrous oxides of Fe and Mn, amorphous metal sulfides (AVS), carbonates	Acid dissolution, Fe–Cl complexation
3 REd	40 mL 1 M $\text{NH}_2\text{OH} \cdot \text{HCl}$, 25% (v/v) HOAc, 2 h agitation, 50 rev min^{-1}	More crystalline oxides of Fe and Mn	Reductive dissolution
4 AD	Conc. $\text{HNO}_3\text{--H}_2\text{SO}_4$, or microwave HNO_3	Organic, crystalline sulfides and other minerals	Oxidation of organic matter, strong acid dissolution of oxide/sulfide minerals

in a flame heated quartz tube. A variety of hydride generation conditions were used, depending on the desired analysis.

Interstitial water:

1. As(III) analysis. Hydride generation conditions: sample made up to 5 mol L⁻¹ HCl, 0.05% w/v NaBH₄ in 0.05% w/v NaOH.^{29,30}

2. Total As analysis. Hydride generation conditions: sample made up to HCl 8 mol L⁻¹ and KI 1% pre-treatment; 0.8% w/v NaBH₄ in 0.5% w/v NaOH.

3. As(V) by difference (other As species, see below).

Sediment solid extracts:

4. Extract stage 1 or 2 or 3: total As analysis. Hydride generation conditions: sample made up to HCl 8 mol L⁻¹ and KI 1% pre-treatment; 0.8% w/v NaBH₄ in 0.5% w/v NaOH.

5. Extract stage 4: total As analysis. Hydride generation conditions: sample made up to HCl 8 mol L⁻¹, KI 1%, and urea 2% w/v pre-treatment; 0.8% w/v NaBH₄ in 0.5% w/v NaOH.

The concentration range used for analyses, over which response was linear, was 0–40 µg As L⁻¹. Spiked additions and analysis of synthetic samples showed that As(V) present in concentrations of 0–40 µg As L⁻¹, did not generate arsine and thus gave no signal under the conditions listed in 1 above for the analysis of As(III).²⁹

Other arsenic compounds of interest were monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Other organic forms of arsenic may have been present, but they are not generally found to constitute a substantial fraction of total arsenic in sediments.³¹ Our first interstitial water investigations indicated that the levels of methylated arsenic species were below detection. Determination of interstitial water MMA and DMA individually in the presence of inorganic arsenic was achieved by manipulation of the acidity of the hydride generation medium (DMA 0.05% NaBH₄, 0.10 mol L⁻¹ HCl, MMA 0.05% NaBH₄, 1.0 mol L⁻¹ HCl).^{29,30}

In sediment extracts, total arsenic was determined without speciation or transformation of all arsenic species into one form. Thus hydride generation conditions under which all four possible forms of arsenic present gave the same sensitivity were established. Because different chemical matrices were involved for the different extractant solutions, matrix effects on hydride generation were checked by spiked recovery. No matrix effects were indicated to be affecting hydride generation in the diluted extracts under the generating conditions used (HCl and KI added, final concentrations 8 mol L⁻¹ and 1%, respectively).

Total arsenic recovery: the accuracy and precision of the total analysis was evaluated by applying the total digestion procedure to a CRM, an estuarine sediment Certified Refer-

ence Material 277 (Community Bureau of Reference, Commission of the EC, Belgium, 1988). Recovery of arsenic was 88% of the certified value and relative standard deviation was within 10%. It is anticipated that incomplete dissolution of the solid phase accounts for the discrepancy; complete dissolution of the solid phase by the acid digestion used was not achieved or intended.

Recovery of arsenic species from the strong acid digestion (AD) was assessed by sediment spiking with each of As(III), As(V), MMA and DMA individually at three different concentrations. Total arsenic determination of these spiked sediment samples following digestion by conc. HNO₃-H₂SO₄, gave recoveries in the range of 94–100%, with a mean of 97%.

Detection limit: the method detection limit, calculated as (blank + 3σ), was 0.1 µg L⁻¹ As, for As(III) in any of the four extraction media. This detection limit applies to As(V), MMA and DMA as well, as the sensitivity for these arsenic forms was the same under the hydride generation conditions used. This detection limit translated to a sediment detection limit of 1–2 µg As g⁻¹, depending on final volumes.

3. Results and discussion

3.1. Sequential extraction methodology

The sequential extraction procedure was carried out on the dredge samples to yield the concentration of arsenic associated with each extractant group (IEx, HCl, REd, AD) for each particle size range (<63 µm, 63–250 µm, >250 µm). The fraction of total arsenic associated with each extractant group and size range was then calculated. Arsenic was found in sediment from all three particle size fractions and found in all four chemical fractions. Data are summarised in Table 2.

The reproducibility of the SE procedure for these sediments was established by carrying out a five-fold replication of the SE procedure on one particular sample, a <63 µm fraction. RSD values for [As] in each of the separate extracts of the SE showed good reproducibility to be achieved, for [As] > 50 µg g⁻¹, RSD <2%; for [As] 20–50 µg g⁻¹, RSD <4%.

Reproducibility of SE over time, reflecting possible changes on storage, was also examined. SE was generally carried out within 4–7 days of sampling, as soon as could be achieved following sample collection and processing. The sieved samples were stored in chilled conditions (4 °C) with a nitrogen headspace. In the case of the dredge samples, these samples were extracted within a week of sampling then again two more times over a period of a month. Changes in the fractionation of arsenic, which were significantly greater than sample variation, were observed in most of the sieved sediment samples extracted

Table 2 Dredge sample data. All arsenic concentrations are given in mg As kg⁻¹ dry weight of that fraction

Sample	Size fraction/µm	Size fraction (%)	[As] _{IEx}	[As] _{HCl}	[As] _{REd}	[As] _{AD}	Summed [As] _T ^a	Acid digest [As] _T	[As] _T
PK2TL	<63	44.2	95	80	15	119	309	309	
	63–250	43.3	69	76	11	67	224	217	
	>250	12.5	32	49	9	78	168	176	
	Whole sediment								
PK2BL	<63	49.3	338	357	26	462	1183	1201	
	63–250	35.4	114	79	2	232	428	390	
	>250	15.2	59	73	6	136	273	266	
	Whole sediment								
PK5TL	<63	46.5	70	51	9	57	188	190	
	63–250	45.5	94	87	13	51	246	247	
	>250	8.0	56	50	7	32	146	143	
	Whole sediment								
PK5BL	<63	39.9	52	76	16	67	210	204	
	63–250	48.1	101	78	20	74	273	213	
	>250	12.0	49	56	8	43	158	163	
	Whole sediment								

^a ∑(IEx + HCl + REd + AD).

three times during the month of storage. The summed total amount of arsenic did not change. The extraction showing most variation with storage time was the RED extract (RED: 1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, 25% HOAc). The proportion of total arsenic found in this extract was always minor, but generally found to increase with time of storage. The increase in arsenic in this extract was accompanied by reduction in arsenic in any of the other extracts. Because the portion of total arsenic held in this phase was always found to be low, changes on storage showed a large relative impact. The nature of the change was not further investigated, rather subsequent sample processing was done so as to achieve SE as soon after sampling as possible, with chilled storage used where needed. Chilled storage was chosen in preference to freezing so as to minimise solution changes that could have impacted on those solid phases especially associated with a high proportion of water.

The summed recovery of arsenic from different extracts ($\sum\text{SE}$) was found to be close to total arsenic as determined by acid digestion (AD) only. Total arsenic concentration was determined by both $\sum\text{SE}$ and AD on twelve sediment samples, compare columns 8 and 9 in Table 2. The mean difference between summed arsenic and arsenic from acid digest was 2.8% (σ 2.4%, one outlier, 22% diff.) with neither measurement method giving consistently higher arsenic results. Generally closer agreement was achieved with the fine fraction sediments. Thus arsenic determined under conditions where different forms could have been present, yielded the same quantity as when all forms present were converted to As(v) by digestion with strong acids. Thus organic forms of arsenic that do not yield volatile hydrides on hydride generation and so escape detection, or offer lower sensitivities, were present below detection limits.

3.2. Interstitial water chemistry: arsenic, E_h and pH

Interstitial water from the dredge samples was found to contain levels of arsenic (varying between 51 and 135 $\mu\text{g L}^{-1}$) that were elevated compared to overlying seawater and varied with depth. A higher concentration of dissolved arsenic was found in the subsurface anoxic layers (below 2 cm depth) of both dredge samples.

The vertical profile of interstitial water arsenic, $[\text{As}]_{\text{iw}}$, for the core sample Core 1, displays a trend of well-defined subsurface maximum centred 3 cm below the sediment/water interface (SWI) (Fig. 2). This vertical profile reflects those reported from other studies of marine sediments^{2,21,32} where an interstitial water concentration peak is observed within the top few cm. In the upper part of the core, dissolved As concentration increased with depth and reached a maximum value at (196 $\mu\text{g L}^{-1}$) 2–4 cm below the SWI. The concentration decreased rapidly then gradually at lower layers to a minimum value of 33 $\mu\text{g L}^{-1}$ at 12–14 cm depth, indicative

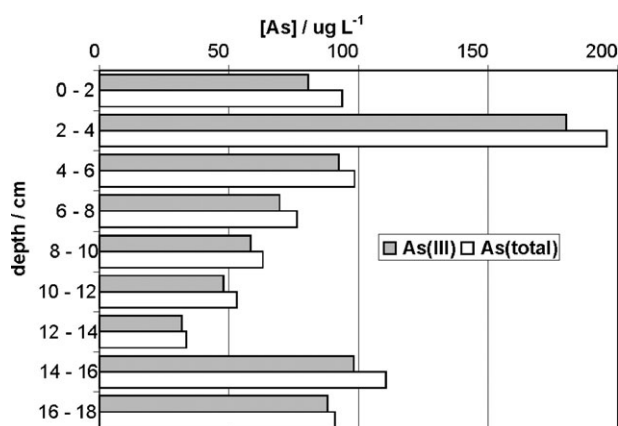


Fig. 2 Core 1 interstitial water [As] profile.

of solid phase incorporation.³² A second smaller peak occurs at 14–16 cm depth. Interstitial water from sampled layers of other sediment cores (DRD 2–6) showed a wide range of total arsenic concentrations, 15–206 $\mu\text{g L}^{-1}$, and generally showed higher concentrations below the surface sediment.

Speciation analysis of interstitial water in core sample indicates that arsenite (As(III)) was the dominant species (Fig. 2) with As(v) being present as a minor fraction. The relative proportion of As(III) increased with depth up to 97% of total dissolved As on average, a lower proportion was found within the uppermost layer. In core samples DRD 2–6, the same trend was seen, *i.e.*, As(III) generally dominated interstitial water, with the As(v) making up a substantial portion of the total As only in the surface layer especially where this layer was visibly oxidised.

It needs to be emphasised that the analytical technique and conditions used in this study measured total arsenic as the sum of inorganic As(III + v) and methylated (DMA + MMA) species. Separate analysis used to measure only the methylated species confirmed that both MMA and DMA were below the detection limit. This is typical for marine sediments where methylated arsenic represents <5% of total dissolved arsenic.³³ Therefore, we assumed that the difference between total dissolved As and As(III) was As(v).

Redox potentials, measured for core samples Core 1 and Core 4, are shown in Fig. 3. Measured redox potentials show a steep decline over the top 6 to 8 cm of sediment, to a plateau around -200 mV. The absolute potentials measured can be seen to differ between Core 1 and Core 4, but the depth profiles show the same steep gradient. This gradient reflects the redox transition zone due to sediment diagenesis. This transition zone is an important horizon in early diagenesis as it controls the distribution of redox sensitive species.²

The more oxidising condition in the surface layer is consistent with the slightly increased ratio of As(v) : As(III), but the oxidising condition is not strong enough to convert substantial amounts of As(III) to As(v). At lower depths the continued presence of As(v), albeit in small concentrations, suggests that the redox potential developed in the sediment system is not the only factor that controls distribution of dissolved As species in the sediment interstitial water. Penetration of overlying oxic water and bioturbation^{21,33} may create some local oxic micro-environments resulting in resistance to As(v) reduction. Additionally, interconversion of As(III)–As(v) in the sediment systems may be kinetically limited.

The interstitial water profile suggests that dissolved As may originate from reductive dissolution of amorphous iron oxyhydroxides at the redox transition zone. This transition zone, marked by the steep potential gradient, was coincident with the maximum dissolved arsenic concentration, suggesting that the dissolution of arsenic is closely related to diagenetic events, such as the dissolution of amorphous iron oxyhydroxides. This observation is of importance because of the implied availability of arsenic bound to this phase. Dissolution of arsenic from more persistent minerals such as more crystalline Fe-oxides and sulfides²¹ and organic matter mineralisation³² is indicated

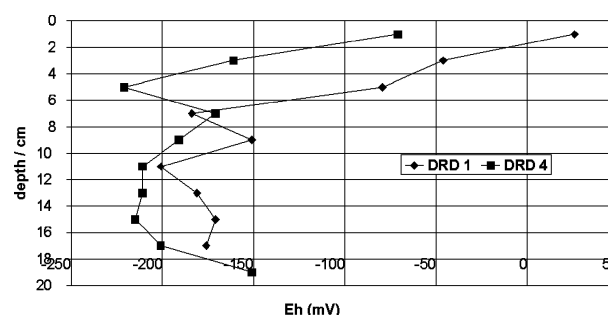


Fig. 3 Redox potential profile.

to occur under reducing conditions at greater depth giving rise to the second peak further down the vertical profile.

Measured pH values over the whole sediment core length of Core 1 ranged between 7.6 and 7.8 and stabilized at value of 7.8 at depth of 8–10 cm downwards. The profile of Core 4 showed a slightly wider pH range, 7.45–8.05, but no distinct profile. This narrow pH range and mildly alkaline conditions are typical of marine sediment.

3.3. Solid phase arsenic distribution in dredge samples

Data for arsenic found in the dredge samples are summarised in Table 2. Highly variable amounts of arsenic were found in these four samples; total arsenic in whole sediment (calculated from sieved fractions) between 200 and 250 mg As kg⁻¹ for three of the four samples, and 772 mg As kg⁻¹, for the fourth sample PK2BL. These concentrations of arsenic are elevated relative to the background of 15 mg As kg⁻¹ for this locality,³⁴ and are well in excess of the current ANZECC³⁵ interim guideline value (effects range-median, ERM) of 70 mg As kg⁻¹.

Arsenic found in these dredge samples was shown to be present in all particle size ranges (Table 2). However, the contribution of each particle size range to total arsenic burden varies, with the largest particles (> 250 µm) accounting for the least amount of arsenic. This distribution is illustrated in Fig. 4 where the % of total arsenic present in each size fraction is shown. Not only do the large particles make up a small fraction of these sediments (refer column 3, Table 2), but also the concentration of arsenic in these particles is relatively low. In contrast, the arsenic content of the intermediate size range particles is notable, e.g. in the PK5 dredge sample, sediments of this size range hold approximately 50% of the total arsenic. The size range contributing the most arsenic in the PK2 sediments is the fines.

The total amount of arsenic present in the solid phase was greatly in excess of that present in the interstitial water, which was calculated to account for less than 0.1% of total arsenic. This observation typifies most sediment metals and metalloids, the bulk of which are associated with the solid phase.

The chemical fractionation of arsenic in these dredge samples, given as divisions in the histograms of Fig. 4, shows substantial amounts of arsenic to be present in the IEx and HCl fractions. The REd fraction was consistently the smallest fraction. It is notable that although sample PK2BL contained a substantially greater amount of arsenic, the chemical fractionation was approximately the same as that found in the other three samples, viz. IEx, HCl and AD fractions each accounting for about 1/3 of the total arsenic. No one chemical fraction dominated the distribution of arsenic. Additionally, no outstanding difference in chemical fractionation was apparent between the surface (0–2 cm) and lower (2–6 cm) sediment layers for either dredge sample.

3.4. Solid phase arsenic distribution, Core 1

The sediment core samples collected in July 2002, yielded more information on the association of arsenic in terms of chemical and particle size fractionation as a function of depth. These cores extended to depths of 18–22 cm, thus sampling deeper sediment than had been collected with the dredge.

The vertical profile of arsenic concentration for Core 1, the sediment core sectioned and analysed in its entirety, is shown in Fig. 5, where total arsenic per kg of whole sediment (dw) is plotted as a histogram with size fractionation. The most prominent feature of this profile is the elevated levels of arsenic present in the top 6 to 8 cm of the core and the steep decline of arsenic concentration over the 6–12 cm depth. This overall profile of elevated concentrations in surficial sediments has been a pattern reported for arsenic in a variety of sediment investigations.^{2,3,36} The concentration of arsenic found in the

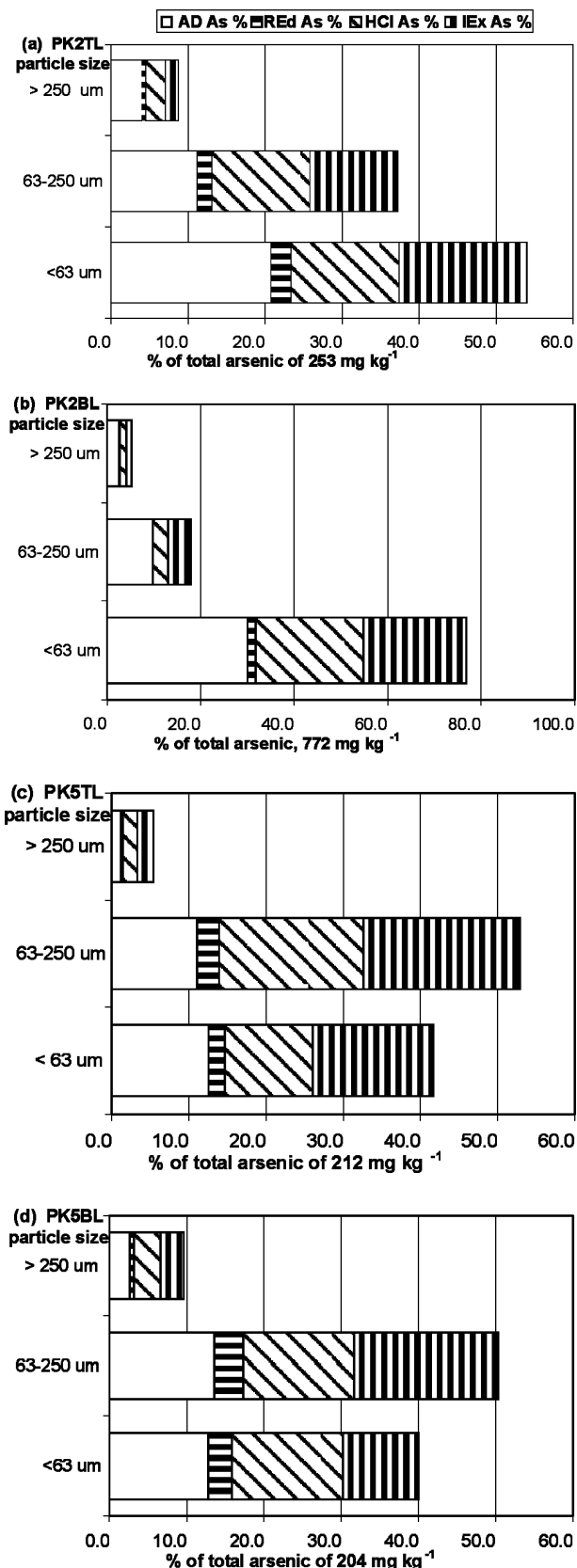


Fig. 4 Dredge samples, PK2 and PK5: % total arsenic distributed over particle size classes and SE fractions.

top 6 cm, 400–500 µg g⁻¹, falls within the range of arsenic concentration found in the dredge samples.

The fractionation of arsenic with particle size shows that approximately 60–80% of arsenic is associated with the fine fraction, and 4–11% is associated with the largest particle size group. Similar to findings in the dredge samples, the largest size

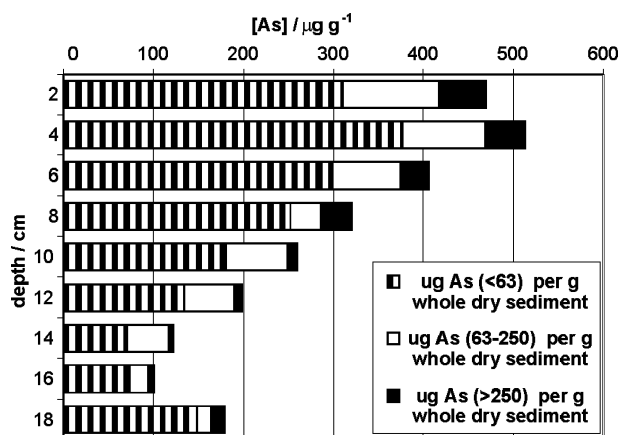


Fig. 5 Solid phase arsenic concentration depth profile, $\mu\text{g As kg}^{-1}$ whole sediment (dw), fractionated according to particle size classes.

fraction contained the smallest amount of arsenic. In addition the fractionation showing 60–80% of all arsenic present to be associated with the ‘fines’, reflects the size fractionation observed for arsenic in the most highly contaminated dredge sample PK2BL, *i.e.* where arsenic levels were found to be above the 200–300 mg As kg^{-1} concentration range, a high proportion is contained in the fines.

The variation of particle size distribution with depth for this core is shown in Fig. 6. Particle size distribution is a function of incoming material, current patterns and flow speed in the overlying water at the time of settling. In addition, post-depositional mobilisation and sorting may occur due to bioturbation or an unusual flow associated with a flood event or resuspension with a storm or shipping traffic. The sampling site in Port Kembla Harbour is offshore from a major stormwater channel (locally known as the Darcy Rd Drain) and so the nature of the deposited material will depend on what material is carried in suspension by storm flow from the drain, and where this is deposited as determined by flow. Thus the particle size distribution of the sediment is not expected to be uniform. The catchment of Darcy Rd drain includes several industries besides the copper plant, extensive road and rail infrastructure and some areas of bare land with a previous history of industrial use. Thus incoming sediment at the sampling site would have borne a variable arsenic load, depending on its origin.

Chemical fractionation of the arsenic associated with the different particle size ranges is shown in the histograms in Fig. 7. Here, arsenic concentration is expressed as mg As per kg of size fractionated sediment. For example, in the 0–2 cm layer of core DRD 1, 310 mg As per kg whole dry sediment is associated with the $<63 \mu\text{m}$ sized particles, this is equivalent to a concentration of 1000 mg As per kg $<63 \mu\text{m}$ particles. Of this 1000 mg As kg^{-1} , IEx bound arsenic contributes 195 mg , HCl

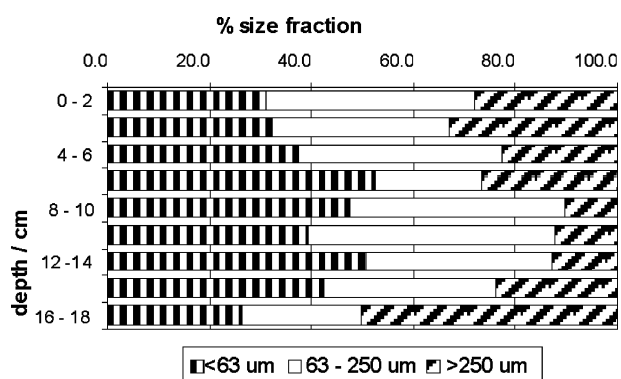


Fig. 6 Core 1: particle size distribution.

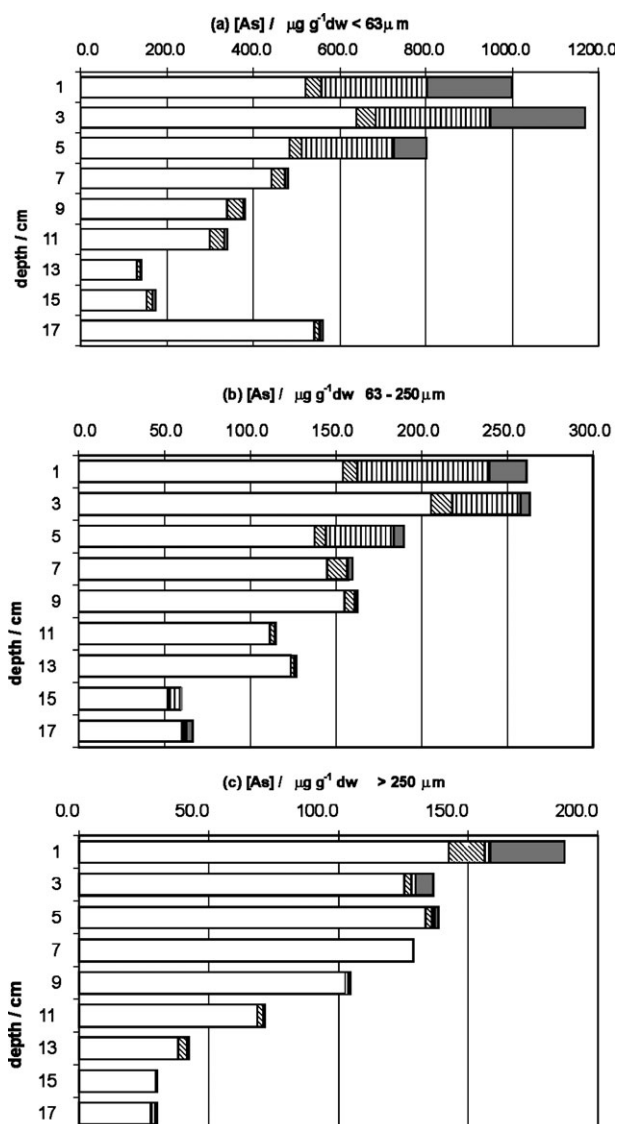


Fig. 7 SE fractionation of (a) $<63 \mu\text{m}$ particles arsenic, (b) 63–250 μm particles arsenic, (c) $>250 \mu\text{m}$ particles arsenic. AD arsenic (□), REd arsenic (▨), HCl arsenic (▧) and IEx arsenic (■).

bound arsenic contributes 246 mg , REd bound arsenic 37 mg and AD bound arsenic 521 mg .

The outstanding feature of the profiles shown in Fig. 7 is the change in chemical fractionation of arsenic with depth. In the top 6 cm of sediment, 40–48% of arsenic attached to $<63 \mu\text{m}$ particles was associated with the extractant groups IEx, HCl, and REd. Deeper in the sediment core, the proportion of arsenic associated with these extractant groups was much lower, ranging between 3 and 12%. The same pattern is observed for arsenic attached to the larger size range particles. This pattern was not observed in the dredge samples, because the sediment below 6 cm depth was not sampled.

The observed changes in chemical fractionation of arsenic with depth/anoxia points to changes in arsenic binding in response to diagenesis. The maximum pore water arsenic concentration was found to occur at the depth of maximum change in redox potential. Reduction of iron(III) minerals is expected to be associated with this redox change. In particular the readily accessible amorphous oxyhydroxides of iron, often present as particle coatings, would be the form of iron most susceptible to reduction. Arsenic associated with this iron is released into solution by the reductive dissolution of the iron, giving rise to elevated pore water arsenic. Once dissolved, this arsenic is free to move in response to the concentration gradient. Because $[\text{As}]_{\text{iw}}$ is at a peak at 2–4 cm depth, diffusion

may occur in either direction, upwards or downwards. Upwards movement would be expected to result in reprecipitation within the sediment at higher redox potential, or loss to the overlying water. The arsenic concentration in the overlying water was always found to be below the detection limit of the analytical technique. This possibly indicates that upwards diffusion of dissolved arsenic out of the sediment into the overlying water is limited, although to verify such loss out of the sediment requires appropriate experimentation. Precipitation within the oxidised sediment will lead to surficial concentration enrichment. Removal of arsenic from the pore water to the solid phase can occur by adsorption to iron(III) oxyhydroxides in the oxidised sediments, or by coprecipitation with diagenetically cycling iron, freshly precipitating as amorphous oxyhydroxides. This iron species is considered as the most important binding phase for arsenic under oxic conditions.³⁷⁻⁴⁰

Previous studies on coastal marine and freshwater sediments by several authors have shown that iron(III) oxyhydroxides control early diagenetic behaviour of arsenic.^{3,21,25,36} This chemical behaviour is related to a high affinity of inorganic As(III) or As(V) towards iron. Iron oxyhydroxides can absorb/coprecipitate up to 0.7 mole As per mol Fe.^{38,39} The sediments of Port Kembla Harbour contain up to 10% iron,¹³ so this species is not limited. Enrichment of the solid phase arsenic in surficial sediments is therefore closely linked to the diagenetic cycle of Fe, which controls the distribution of dissolved arsenic. Reductive dissolution of Fe oxyhydroxides results in upwards diffusion of dissolved Fe and As to the oxic sediment where iron precipitates as iron oxides, coprecipitating or adsorbing arsenic.

The comparison of vertical profiles of different parameters needs to be made taking into account the core sectioning carried out. It is conceivable that the positions of maximum $[As]_{iw}$, $[As]_{IEx+HCl+REd}$, and maximum $\Delta E_h/\Delta d$ do not precisely coincide, but this is hidden due to sectioning of the core into 2 cm sections which were homogenised. Such broad partitioning of sediment will mask the details of vertical profiles.

Arsenic associated with IEx and HCl extractions is amenable to reductive dissolution where the binding phase is amorphous oxyhydroxides of iron, so these fractions are expected to be the source of pore water arsenic. Other binding phases, which yield arsenic to these extractions, do not necessarily release arsenic during diagenesis. Arsenic associated with the AD fraction is expected to be non-active with respect to these diagenetic reactions, and not dissolve into the pore water.

Possible downward movement of dissolved arsenic is also indicated by the pore water arsenic concentration profile, where reprecipitation or adsorption to other solid phases must be responsible for the decrease in $[As]_{pw}$. The binding of arsenic below 8 cm depth, was found to be largely to the residual phases. In the chemical fractionation used here, this arsenic will be covalently bound in organic matter, in crystalline oxyhydroxides or sulfides or in siliceous material. A small fraction was observed to be associated with hydroxylamine reducible components which points largely to the more crystalline oxyhydroxides of iron and manganese. These oxides have two sources. It is possible that authigenic amorphous oxyhydroxides of iron, reprecipitated in the upper sediment, age and therefore become more crystalline before reaching the redox boundary, and are then able to pass below the diagenetically active zone without reduction. It is also anticipated that a portion of iron(III) oxyhydroxides does not become reduced as it passes the redox boundary. Iron(III) oxyhydroxides are not exclusive to the upper oxidised zones of sediments at all,³⁶ and their presence in sulfidic sediments indicates combinations of kinetically slow reduction and lack of accessibility to reductants due to crystalline nature or coatings of organic matter/amorphous oxyhydroxides/freshly deposited amorphous sulfides. Thus iron(III) and associated arsenic can be observed in sulfidic sediments.

Arsenic in sulfidic sediments may also be removed from solution by sulfide interaction. This may be *via* precipitation as arseno-sulfides (AsS or As_2S_3) or association with authigenic iron monosulfides.^{21,41} The binding of arsenic to iron sulfides will be further influenced by pyritization, giving rise to crystalline phases, amenable to dissolution only in strong oxidising acids.

The medium and large grain fractions, although holding lesser quantities of arsenic, nevertheless have arsenic concentrations significantly elevated above background and above guideline values. The observed change in chemical fractionation with depth indicates diagenetic processes at work on these particles as well, most likely involving reactions of arsenic in surface coatings of particles. Arsenic is either dissolved from the solid phase by reductive dissolution and readsorbed elsewhere following diffusion, or subjected to pyritization changes. Both possible reactions would lead to the observed decreasing proportion of labile arsenic.

The potential for remobilisation of the arsenic present in this sediment core is indicated to be confined to arsenic in the top 6 to 8 cm layer of sediment. Sediment deeper in the core was found to contain arsenic >90% of which was soluble only in concentrated oxidising acids. The arsenic anticipated to be labile within the sediment would be that fraction which dissolves during diagenesis, that arsenic associated with the oxyhydroxides of iron. Up to 50% of arsenic in the surficial sediment may be in this category. Whether this labile arsenic is taken up by biota or released to the overlying seawater is not yet determined.

The pattern of diagenetic behaviour of the arsenic present in this sediment core was reflected somewhat in the other cores (Cores 2-6), however only three separate layers of these cores were analysed (0-2 cm, 6-8 cm, 12-14 cm). Two cores taken close to Core 1 indicated higher arsenic concentration nearer to the surface, arsenic associated with all particle sizes, but not such a clear-cut pattern of chemical association changes with depth. Three sediment cores taken from closer to the shore line showed no distinct elevation of concentration in surficial layers, arsenic associated with all particle sizes, and again, not such a distinct chemical fractionation change with depth as was observed in Core 1. So the 12-14 cm deep layer analysed in Cores 2-6 showed arsenic fractionated between IEx, HCl and AD fractions, but not dominated by AD to the same extent as in Core 1. Observations and E_h measurements indicate anoxia and diagenesis occurring in these other sediment cores, however other factors must be operating within these sediments, perhaps a lesser degree of diagenetic behaviour depending on various limiting factors. Arsenic, present at a level of approximately $0.005 \text{ mol kg}^{-1}$, is only a minor player here, responding to conditions, so its chemical behaviour is driven by the gross or bulk parameters, for example organic carbon or sulfur in its various forms.

The original source of the arsenic found in Port Kembla Harbour would have been the various copper ores and concentrates brought to the copper smelter over the decades of operation. Arsenic from this source would have been carried to the harbour by a variety of processes; atmospheric fallout of ore dusts and chimney dusts, especially in earlier years before dust control measures were employed, stormwater carriage of ore particles and processing particulates, discharge of (treated) process water. The arsenic that arrived at the sediment/water interface would have been present in a variety of chemical forms, which then responded variously to diagenetic events. Some forms of arsenic depositing in the sediment, for example, unprocessed ores where arsenic may be present as copper arsenopyrite, may not be labile, and not influenced by diagenesis. However other forms for example, arsenate or arsenite from process water deposited with iron(III) oxyhydroxides, may be redissolved by diagenesis. This variability is reflected in the arsenic chemistry represented by the sediment results reported here.

3.5. Sediment normalization

Various calculations of sediment contaminant loading involving normalization procedures are reported, where contaminant concentration is expressed as the amount of contaminant per unit of a fraction of the sediment. This fraction may be decided on the basis of, for example, particle size, chemical fractionation or conservative element concentration. Some normalization procedures are done with the physical exclusion of some portion of a sediment sample, usually by sieving for a particular particle size range, prior to any analysis. These normalizations are done for a variety of purposes, especially in the investigations of sources.^{42,43} Particle size normalization reflects the propensity of the fines, especially clays, oxyhydroxides of aluminium, iron and manganese, and organic matter, to act as the main accumulator of various contaminants.⁴⁴ The sediments investigated in this study showed that a considerable proportion of the total arsenic burden was carried in the >63 µm fraction. This finding demonstrates that procedures, which exclude a portion of sediment, should be undertaken only with considerable foreknowledge of the sediment being investigated. Before a decision to investigate only a particular fraction, say, the fines, can be taken, the concentration of the contaminants in the remaining, larger particle size, material should be ascertained. Only if this material can be shown to contain the contaminants at concentrations below defined levels of interest, can the exclusion be justified.⁴⁵

Conclusions

High concentrations of arsenic, elevated 10–50 fold over local background levels, are reported for sediments of the outer Port Kembla Harbour. Dredge samples collected in 2001 and core samples collected in 2002 were used to develop a sequential extraction procedure to elucidate the modes of arsenic binding and the potential for remobilisation. The sediment was sieved to three size ranges (<63 µm, 63–250 µm, >250 µm) and each of these was then subjected to a four step SE, sequentially solubilizing arsenic as ion exchangeable, 1 M HCl soluble, NH₂OH·HCl soluble and, finally, strong oxidising acid soluble. All sediment processing and extraction procedures except strong acid digestion were carried out in a nitrogen atmosphere with deoxygenated reagents. The reproducibility of the SE method was established by replication and by comparing total arsenic obtained from strong acid digestion with total arsenic obtained from the summed recovery of sequentially extracted arsenic for 12 sediment samples, both methods showing levels of variation within 2–4%.

The two dredge samples, extending to a depth of 6 cm, were divided into surface (0–2 cm) and subsurface (2–6 cm) layers. Arsenic was found in these sediments to be associated with all three particle size ranges. Although the largest particle size carried the lowest amount of arsenic, in one dredge sample the mid size range particles (63 µm to 250 µm) carried the largest concentration and amount of arsenic. The SE showed arsenic binding to be approximately 1/3 IEx, 1/3 HCl and 1/3 AD in all dredge samples. There was no apparent difference between the surface and subsurface layers in terms of arsenic binding.

The sediment core sample showed a vertical [As]_T profile with elevated concentration in the surficial 0–8 cm, (400–500 mg As kg⁻¹), relative to the deeper sediment (100–200 mg As kg⁻¹). Arsenic was found in all three particle size ranges, with the fines accounting for 60–80%. Sequential extractions of the core layers showed arsenic bound to IEx, HCl or RED groupings accounted for up to 50% of all arsenic in the top 6 cm. The deeper sediments were found to have not only lower concentrations of arsenic, but also markedly different binding of arsenic, with >90% of all arsenic present, bound in a form solubilised only by strong oxidising acid. Thus potentially available arsenic was found predominantly in the top 6 cm,

arsenic present at greater depths was strongly held. This pattern was not so clearly apparent in other core samples; however, of these core samples, only three slices from different depths were examined.

The variability in arsenic chemistry, found in the dredge and core samples, reflects the variable forms of arsenic arriving at the sediment surface, in terms of both attachment and particle size. This variability is further impacted by diagenetic events. Assessment of associations between arsenic and other chemical species, for example copper, organic carbon, forms of sulfur, iron, will further clarify the binding of arsenic in these sediments.

Abbreviations

Dw = dry weight, DMA = dimethylarsinic acid, MMA = monomethylarsonic acid, SE = sequential extraction, SWI = sediment/water interface, XRD = X-ray diffraction, XRF = X-ray fluorescence.

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