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Original Research

Arsenic Speciation in Marine Sediment Samples from the 26.12.2004 Tsunami Area in Thailand

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Abstract

Our paper reports results of speciation analysis of arsenic(III) and (V) in the exchangeable fraction of the marine sediments from the Andaman Sea. The sediments were collected from the coastal zone at the coast of Thailand affected by the 2004 tsunami waves. The samples were extracted with phosphate buffer and then subjected to determination of inorganic species of arsenic by HPLC-HG-AAS. A correlation between the contents of arsenic and grain size of the sediments was found. Higher content of As(III) established in fine grain fraction of the sediment can suggest its deposition by tsunami.

Keywords: marine sediments, arsenic, exchangeable fraction, tsunami

Introduction

Marine sediments deposited in the coastal zone contain great amounts of geogenic pollutants such as heavy metals, arsenic or mercury (rock weathering, decomposition of organic matter) and from anthropogenic sources (mine industry, municipal wastes, industrial wastes). The pollutants can migrate to water ecosystems and undergo bioaccumulation in the trophic chain, posing a threat to humans and other living organisms. The pollutants contained in the marine sediments in the coastal zone can also be harmful for land ecosystems in the case of its deposition by strong storms or tsunami waves on land, and becomes a base for the humus layer [1].

One element particularly toxic for humans and animals is arsenic. From among different species of arsenic occurring in the environment the most toxic are inorganic species of As(III) and As(V) [1, 2]. Therefore, besides total content of arsenic it is important to know the presence of its most toxic species [6]. In determination of the content of arsenic in sediments of great significance is the method of determination and the reagents used for extraction. Estimation of the real threat of the arsenic species present in the sediments requires determination of their content in the mobile: bioavailable or exchangeable fractions [3-5]. This paper presents results of the speciation analysis of As(III) and As(V) in the exchangeable fraction of marine sediments from the coastal zone of the Andaman Sea on the coast of Thailand. The extraction of the exchangeable fraction was performed with the use of phosphate buffer of pH=6±0.2 [7]. The speciation analysis of As(III) and As(V) was performed with the use of the hyphenated technique HPLC-HG-AAS [7, 8].

Experimental

Instrumentation

Construction of the hyphenated HPLC-HG-AAS system was described in the previous article [7, 8]. The HPLC instrument was a Shimadzu liquid chromatograph (LC-10A) with an HPLC pump (LC-10AT), vacuum degasser unit (GT-104) and thermostated by a column oven (CTO-10ASvp) anion-exchange column Supelco LC-SAX1

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Table 1. Marine bottom profiles data in transect I to VI.

Profile number	**GPS coordinates**		**Water depth [m]**	**Grain size***	**As(V)/As(III)**
	N	E			
I	8.8338	98.2611	2.5	well sorted MS	As(V) only
	8.8341	98.2403	8.5	well sorted CS	As(V) only
	8.8333	98.2189	12.0	G	As(V) only
	8.8334	98.2053	14.0	well sorted CS	As(V) only
	8.8334	98.1801	21.5	well sorted CS	As(V) only
	8.8334	98.1593	18.5	G	As(V) only
II	8.8500	98.2609	3.5	well sorted FS	6.21
	8.8500	98.2408	8.5	well sorted FS	6.66
	8.8501	98.2202	11.5	G	27.9
	8.8497	98.2060	13.5	well sorted CS	As(V) only
	8.8498	98.1806	18.5	well sorted CS	As(V) only
	8.8501	98.1602	20.5	well sorted MS	As(V) only
III	8.8669	98.2607	2.5	well sorted MS	8.43
	8.8665	98.2403	9.0	mud, MS, coral pieces	8.33
	8.8667	98.2198	12.0	mud, MS, coral pieces	11.3
	8.8663	98.2055	14.5	mud, MS, coral pieces	6.77
	8.8665	98.1804	17.0	well sorted CS	As(V) only
	8.8656	98.1610	21.5	well sorted MS	As(V) only
IV	8.8836	98.2606	2.5	well sorted MS	5.16
	8.8836	98.2398	6.0	well sorted MS	5.11
	8.8835	98.2059	14.0	mud, MS, coral pieces	6.92
	8.8820	98.1815	19.0	well sorted MS	12.61
	8.8823	98.1609	19.5	well sorted MS	11.56
V	8.9002	98.2399	3.5	well sorted MS	5.57
	8.8996	98.2197	3.0	well sorted MS	11.22
	8.9003	98.2050	9.5	Coral detrytus with CS	19.78
	8.8999	98.1798	19.5	well sorted MS	10.87
	8.9004	98.1598	19.5	well sorted MS	10.79
VI	8.9167	98.2406	2.5	well sorted MS	5.44
	8.9180	98.2228	1.5	Coral detritus with CS	As(V) only
	8.9166	98.1806	18.5	well sorted MS	16.11
	8.9167	98.1596	18.5	well sorted MS	9.95

* G-gravel, CS- coarse sand, MS- medium sand, FS- fine sand
(after Szczuciński et al. submitted)

(250mm, 4.6mm i.d.). The chromatographic run was isocratic at 3 mL min^{-1} of phosphate buffer (50 mmol/l Na_2HPO_4 and 5mmol/l $KH_2PO_4·2H_2O$) with an injection volume of 200µl. PEEK transfer tubing of the eluent from the LC column to the hydride generation unit was inserted into a Tygon sleeve. The continuous hydride generation system (VGA-77, Varian) consisted of a manually controlled peristaltic pump with Tygon tubing (0.6 mm i.d.), one reaction coil (PTFE tubing 0.8 mm i.d., 75cm length) and three-way connectors. As a detector in the hyphenated system we used a model SpectraAA 220FS spectrometer (Varian, Australia) with atomization of arsenic hydrides (detected at 193.7nm, slit 0.5nm) in a quartz tube heated electrothermally to 900ºC (ETC-60, Varian).

Reagents

Compressed argon gas BOC GAZY (Poland) was employed as the carrier gas. Water was redistilled and further purified with a Milli-Q water purification system (Millipore, USA). Standard solutions (1000 mgl^{-1}) of arsenite and arsenate were prepared by dissolving appropriate amounts of sodium arsenite ($NaAsO_2$) and disodium hydrogenarsenate ($Na_2HAsO_4·7H_2O$), respectively, obtained from Sigma-Aldrich (USA). The standard stock solutions were stored in glass bottles kept at 4ºC in the dark. Low concentration standards prepared by dilution of the stock solutions were prepared daily. Sodium tetrahydroborate (III), used as reducing solution was prepared daily by dissolving $NaBH_4$ (Merck, Germany) in high-purity water and stabilizing with 1% (w/w) NaOH (Merck) solution to decrease its rate of decomposition, and was used without filtration. The HCl was of the highest quality grade (Suprapure, Merck). The buffer and buffered mobile phase (50 mmol l^{-1} Na_2HPO_4 and 5 mmol l^{-1} $KH_2PO_4·2H_2O$ at pH 6.0±0.2) were prepared by mixing disodium hydrophosphate (Na_2HPO_4) and potassium dihydrophosphate ($KH_2PO_4·2H_2O$) obtained from Merck.

Samples

The samples of marine sediments were collected from a boat with the help of a grab sampler, at 6 transects perpendicular to the coast (Fig. 1). Each sample was tagged with information on the depth and site of collection (Table 1). Wet sediments were dried by lyophilization and dry samples were stored in a refrigerator at –30ºC.

Extraction Procedure

For buffer extraction, a portion of 0.2 to 1.0 g of the sediment sample was put into a glass flask with reflux with 10 ml of phosphate buffer and extracted in water bath (at ca. 80ºC temperature). The arsenic species in buffer extracts were determined by a hyphenated HPLC-HG-AAS system immediately after the extraction procedure.

Results and Discussion

The content of arsenic species As(III) and As(V) was determined in the samples collected along transects I to VI. Results are presented against a background of the sea bottom profile for individual transects (Fig. 2). Table 1 presents the values of the ratio As(V)/As(III) evidencing the greater content of As(V) species than As(III) ones.

In the samples collected along transect I only the presence of the less toxic As(V) species was detected. The content of arsenic varied from 226 ng g^{-1} to 839 ng g^{-1}, and was the highest in the sample collected in the central part of transect I. The three samples collected along transect II, nearest to the coast, contained As(III) and As(V) species in the amounts 807 and 130 ng g^{-1}, 502 and 3342 ng g^{-1} and 23 and 650 ng g^{-1}. In the other samples collected along this transect only As(V) species were found in amounts of 185 - 326 ng g^{-1}.

For the samples from transect III the situation was similar to those of transect II, but the total content of arsenic was much higher. In the samples collected at the greatest distance from the coast only As(V) was detected, while in the other samples As(III) occurred in concentrations from 89 to 234 ng g^{-1}, while As(V) in concentrations from 824 to 1597 ng g^{-1}. The greatest content of As(III) and As(V) was found in the samples from the middle section of the transect. All samples collected along transect IV revealed the presence of As(III) in concentrations 20-533 ng g^{-1} and As(V) in concentrations 233-2724 ng g^{-1}. Similarly, as for the samples from transect III, the highest contents of As(III) and As(V) were found in the middle section of the transect. A similar pattern was observed for the samples from transect V. The two species of arsenic occurred in all samples, As(III) concentration varied from 20 to 120 ng g^{-1}, while As(V) concentration ranged from 217 to 1222 ng g^{-1}. The highest concentrations of both species were found in the middle section of the transect.

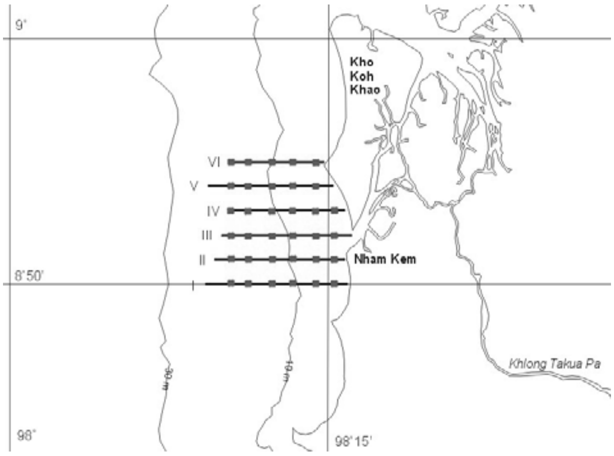

Fig. 1. Transects I to VI [11].

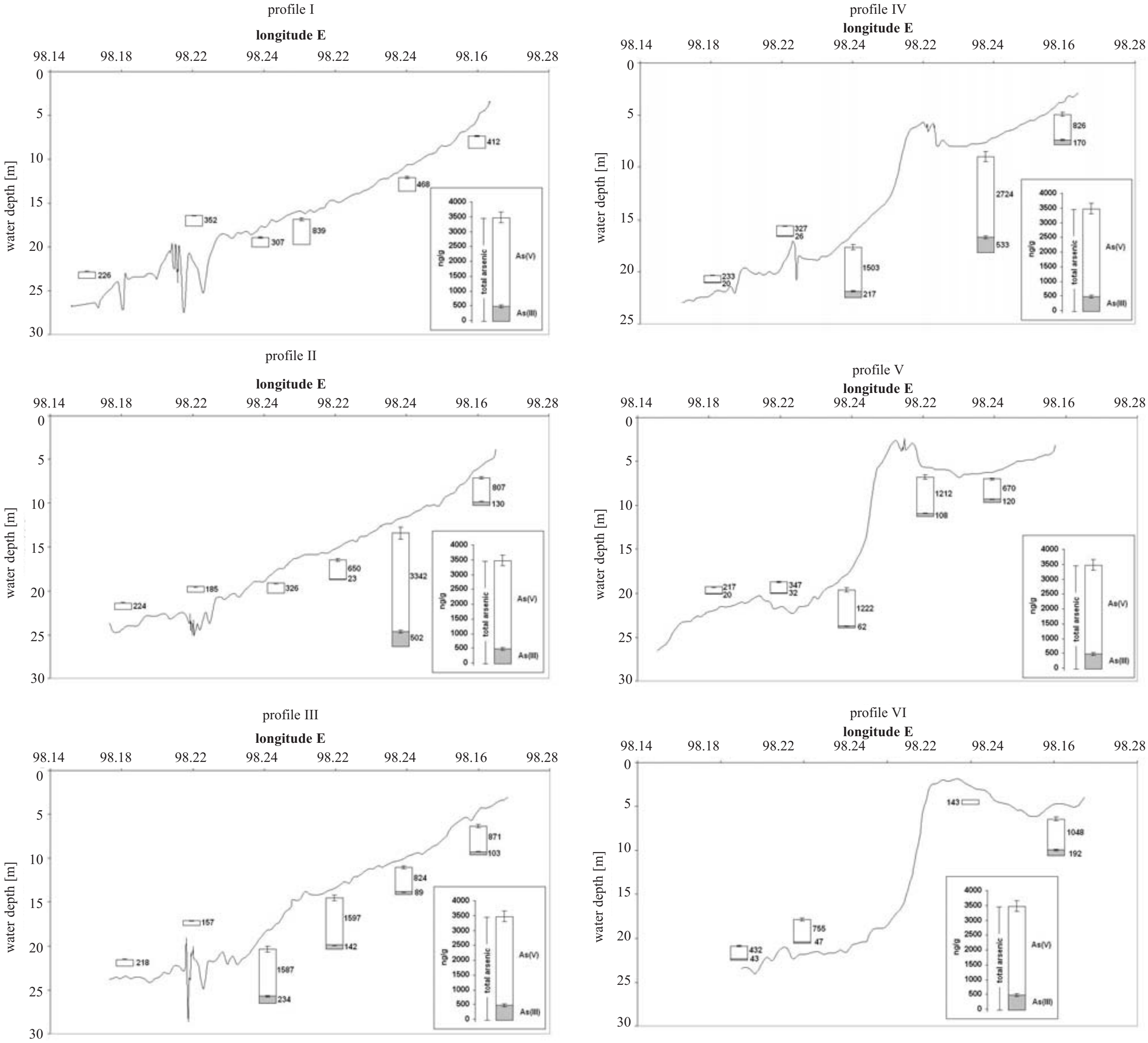

Fig. 2. Concentrations of arsenic species (ng g^{-1}) in marine sediment samples (bottom profiles in transects I to VI).

The samples collected along transect VI contained both species of arsenic, except one sample collected at site 98.2228ºE showing the presence of a coral reef and containing no As(III) and low As(V) content of 143 ng g^{-1}. In the other samples, both species of arsenic were found, As(III) in concentrations from 43 to 192 ng g^{-1}, and As(V) in concentrations from 432 to 1048 ng g^{-1}. In contrast to samples from the other transects, the sample with the highest contents of both species was collected at the site closest to the coast.

Analysis of the results has revealed a number of interesting tendencies. In general, samples collected at sites close to the coast contained the highest concentrations of As(III). The farther from the coast the collection site, the lower the content of As(III) species (Fig. 3). The highest concentrations of As(III) were determined in samples from the sites near the coast at transects II-IV, on strait separating Kho Khao Island from land. As(III) species were detected in samples containing fine and medium sand. In most of the samples made of coarse sand, gravel or coral reef fragments, only As(V) species was determined. It can be supposed that the tsunami sediments containing As(III) could have been deposited by the tsunami from 2004, as they could be an alien element of the marine bottom environment [8].

In 2005 the concentration of arsenic species was determined in the exchangeable fraction in 15 samples of post-tsunami sediments deposited on land. The sediments were collected at four different sites and were found to contain both As(III) and As(V) species. The results revealed a correlation between the type of species distribution and the site of the sample collection. The measurements were repeated at the same sites in the years 2006 and 2007, and these results revealed a change in the arsenic speciation pattern and the dominant presence of only one species - As(V) [8]. A comparison of the results obtained from the land samples

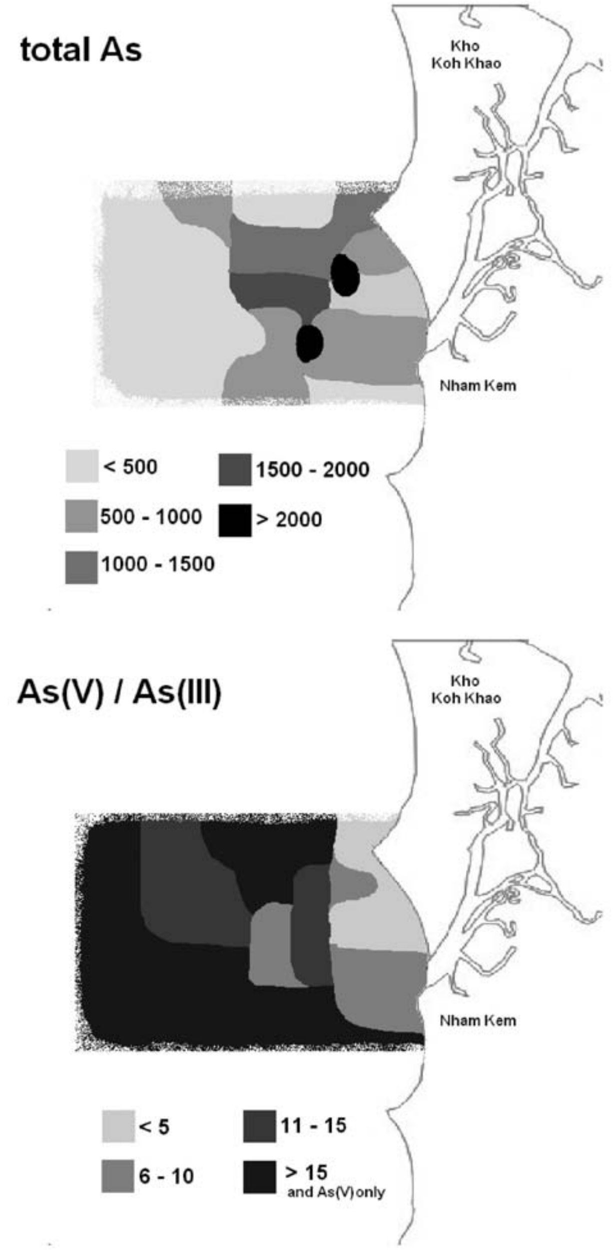

Fig. 3. Spatial distribution of arsenic (ng g^{-1}) and its species in exchangeable fraction of marine sediments.

with those presented in this paper permits putting forward a hypothesis explaining the origin of the sediments and the changes in the pattern of arsenic species in the exchangeable fraction of the sediments. The presence of As(III) can be related with the tsunami-deposited sediments (probably by the returning wave). These sediments are characterized by finer grains. The sediment of this type could be eroded from the tidal zone grown with mangrove vegetation. In this zone, anaerobic conditions favouring the presence of As(III) are often met. The sediments showing the presence of As(V) only are systematically moved by the waves or currents, so they are better oxidized and therefore the arsenic species dominant in them is As(V). The fine grain sediments can be more resistant to erosion than coarse sediments because of the cohesive forces. Conformation of this thesis in subsequent investigation of marine sediments [9] would be an interesting example of application of the speciation analysis in geological research.

Conclusions

The results of buffer extraction conducted in the conditions close to those in the natural environment have permitted evaluation of the actual threat related to the presence of metalloids in the environment. These results have proved the suitability of the applied technique for environmental analysis focused not only on the total content of the exchangeable fraction of a given element, but also on its inorganic species, which may, as in the case of As, differ significantly in their toxicity. Apart from providing information on the state of the marine bottom environment and the treat related to the migration of the toxic As(III) species, the speciation study of arsenic also brings data on the processes taking place in this environment.

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