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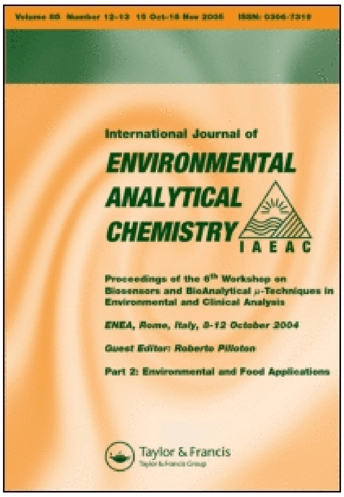

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The methodology and results of determination of inorganic arsenic species in mobile fractions of tsunami deposits by a hyphenated technique of HPLC-HG-AAS

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A method of extraction has been proposed for the determination of inorganic species of As(III) and As(V) in the exchangeable fraction of sediments left by the 2004 tsunami. The method combines the fractionation of solid samples with speciation analysis by high performance liquid chromatography with hydride generation and atomic absorption spectrometry (HPLC-HG-AAS). The proposed extraction liquid is a phosphate buffer of Na_2HPO_4 and KH_2PO_4, with different concentrations of phosphate ranging from 5 to 50 mmol L^{-1}. This method has been tested for different masses of samples as well as for different times of extraction, pH, temperature, and the presence or absence of mixing. The optimum conditions of extraction have been obtained by the use of buffer (50 mmol L^{-1} under pH from 5.8 to 6.2) at 80°C. The new technique was applied for the analysis of tsunami deposits left on land and sampled shortly after the tsunami (2005) and after the first (2006) and second rainy seasons (2007). The obtained results show that the exchangeable fraction of tsunami deposits was enriched in arsenic in comparison to reference soil samples. The major changes after the rainy seasons were not in the total concentration of inorganic As species, but in the ratio of As(III) to As(V). More toxic As(III) was removed from the deposits or oxidised, and after two years was hardly detectable in the tsunami deposits.

Keywords: arsenic; speciation; buffer extraction; tsunami deposits

1. Introduction

Arsenic is one of the toxic elements harmful to the health of living organisms, including humans. Inorganic compounds of this element containing As(III) or As(V) have the highest toxicity, such as the derivatives of arsenic(III) acid H_3AsO_3 and arsenic(V) acid H_3AsO_4 [1,2]. Therefore, the determination of the concentration of these species in surface and ground water and in soil is of the greatest interest. The speciation analysis of arsenic species most often employs hyphenated techniques, e.g., liquid chromatography in combination with different methods of spectrometric detection [3–8].

The use of hyphenated techniques for the analysis of solid state samples requires a preliminary extraction of arsenic species. The extraction procedures can be divided into single-stage procedures and sequential procedures. In the single-stage extraction, the

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extracting liquids can be acids (e.g., HCl, HNO_3, aqua regia), chelating agents, buffer solutions (e.g., $CH_3COONH_4 + CH_3COOH$), or salts (e.g. $CaCl_2$, $NaNO_3$) [9]. In sequential extractions, Tessier's extraction [10] and its modifications are most commonly used, involving a number of stages at which subsequent fractions are extracted with reagents of different extracting power; starting from salts, through weak acids, to reducing and oxidizing reagents, and finally up to strong acids (HF and $HClO_4$), leading to the total dissolution of a sample [9,11]. The application of extraction procedures in the analysis of solid material (e.g., soil or sediments) also provides information about the availability of a given pollutant and its mobility, and thus provides information on possible contacts, for instance with groundwater. The most important information to find from the point of view of a potential threat to human health is the content of a given pollutant (such as a form of arsenic) in potentially bio-available fractions.

Unfortunately, the majority of procedures for sequential extraction cannot be applied to arsenic speciation analysis because the agents used do not permit the application of the HPLC (high performance liquid chromatography) technique. A series of studies have reported methods for arsenic extraction from the soil or sediments recommended to precede analysis by liquid chromatography. One agent used to extract arsenic from the soil and sediments is hydrochloric acid [12], and it can also be used in combination with nitric acid and the application of microwave energy [8]. Another frequently used agent is orthophosphoric acid(V) H_3PO_4, which can be used either as a single extracting agent at different concentrations (0.1 to $1\,\mathrm{mol\,L^{-1}}$) [13–16], with $0.1\,\mathrm{mol\,L^{-1}}$ ascorbic acid [3,5,17], or with $0.1\,\mathrm{mol\,L^{-1}}$ hydroxylamine hydrochloride to stabilise the redox system [6]. Extraction is often performed in a microwave oven [3,4,6,13,14]. Good results have also been obtained with extractions using water and phosphate buffer at $\mathrm{pH} = 5.5$ to 6.5 with shaking [18] or ultrasound mixing [19].

In environmental studies, it is important to establish the likelihood that a given element or species will migrate from a soil or sediment. The procedures used for speciation analysis of arsenic in the mobile fraction of the solid state environmental samples can be generally classified as: the extraction of the water-soluble fraction with water, the extraction of the exchange fraction with buffer systems [19,20], and the extraction of the acid leachable fraction with acids [21]. Water, an eluent of low ionic strength, does not give information on the actual mobility of the metalloids from soils and sediments, which have ion-exchange properties. Water can only be used for the determination of the mobility of highly water-soluble compounds, e.g., salts. The use of buffer systems allows us to reproduce the actual mobility of the exchange fraction and also enables the best modelling of the processes taking place in the environment. In the speciation analysis of mobile fractions with the use of liquid chromatography, extraction with buffer systems ensures agreement between the eluent and the mobile phase, limiting possible interferences and necessary preliminary steps.

Tsunami waves are large seismic sea waves usually caused by earthquakes, volcano eruption or landslides. As the waves approach the coastline, they amplify their height and flood coastal areas. One of the biggest tsunamis in recorded history was the one caused by the 26 December 2004 earthquake west of Sumatra [22]. This deadly tsunami hit the coasts of Indonesia, Thailand, Sri Lanka, India, and other countries around the Indian Ocean. The death toll from the tsunami reached about 230,000. The tsunami also caused significant destruction of buildings and infrastructure, and had a major environmental impact. In Thailand alone, more than 20,000 ha of land was flooded [23] and deposits were left over most of that area – mostly in the form of sands and silts of marine origin [20,24].

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These deposits have had a significant impact on ecosystems. For instance, the sand deposits covered the former soil and are up to more than 0.5 m thick. They are now the major source of macro and microelements for newly developing plants and the geochemistry of the deposits may significantly influence these plants. Studies that have been conducted on the possible impact of tsunami deposits have pointed to the high content of ‘salts’, as well as the presence of heavy metals in bio-available fractions [20,21,25] and organomercury fractions [26]. Large amounts of exchangeable arsenic were also found in the tsunami deposits in Thailand [20,21]. In order to estimate the possibility of migration of the arsenic species from the sediments left by the tsunami into groundwater and the food chain, we propose extraction with phosphate buffer ($5\,\mathrm{mmol\,L^{-1}}$ K (KH_2PO_4) and $50\,\mathrm{mmol\,L^{-1}}$ Na (Na_2HPO_4) at $pH = 6.0 \pm 2$). This type of extraction of the mobile fraction of arsenic from sediments has previously been used successfully [19,20]. The aims of this study were to connect the fractionation and speciation analysis, and to determine the changes in concentration of arsenic species As(III) and As(V).

The samples were collected one month, one year, and two years after the tsunami, from the same locations. Between sampling surveys, rainy seasons occurred, with rainfall as high as 3000 mm. These data permit not only the assessment of the composition of tsunami deposits, but also its evolution in the terrestrial environment and potential long-term impact.

2. Experimental

2.1 *Instrumentation*

Construction and optimisation of the HPLC-HG-AAS system was described in a previous article [27]. In the present work, the analytical system was used in single element mode for arsenic determination. The HPLC instrument was a Shimadzu (Kyoto, Japan) liquid chromatograph (LC-10A) equipped with a pump (LC-10AT), a vacuum degasser unit (GT-104), and a thermostated column oven (CTO-10ASvp) anion-exchange column (Supelco, Bellefonte, PA, USA) LC-SAX1 (250 mm, 4.6 mm i.d.). The chromatographic run was isocratic at $3\,\mathrm{mL\,min^{-1}}$ of phosphate buffer ($50\,\mathrm{mmol\,L^{-1}}$ Na_2HPO_4 and $5\,\mathrm{mmol\,L^{-1}}$ $KH_2PO_4 \cdot 2H_2O$) with an injection volume of 200 µL. PEEK (polyetheretherketone) tubing was inserted into a Tygon sleeve for transfer of the eluent from the LC column to the hydride generation unit. The continuous hydride generation system (VGA-77, Varian; Techtron, Australia) consisted of a manually controlled peristaltic pump with Tygon tubing (0.6 mm i.d.), one reaction coil (polytetrafluoroethylene (PTFE) tubing 0.8 mm i.d., 75 cm length) and three-way connectors. The gas-liquid separator was made of glass, and the interior dead volume was about 3 mL. The detector was the spectrometer model SpectraAA 220FS (Varian, Techtron, Australia), with atomisation of arsenic hydrides (detected at 193.7 nm) in a quartz tube heated electrothermally to 900°C (ETC-60, Varian, Techtron, Australia).

2.2 *Gases and reagents*

Compressed argon gas (BOC GAZY, Poznan, Poland) was employed as the carrier gas for arsenic vapour to the quartz cell without further purification. Water was redistilled and purified with a Milli-Q water purification system (Millipore, Milford, MA, USA).

Standard solutions (1000 mg L^{-1} of As) of arsenite and arsenate were prepared by dissolving appropriate amounts of sodium arsenite ($NaAsO_2$) and disodium hydrogenarsenate ($Na_2HAsO_4 \cdot 7H_2O$) respectively, obtained from Sigma-Aldrich (Milwaukee, USA). The standard stock solutions were stored in polyethylene bottles and kept at 4°C in the dark. Low concentration standards prepared by dilution of the stock solutions were prepared daily. Sodium tetrahydroborate, used as reducing solution, was prepared daily by dissolving $NaBH_4$ (Merck, Darmstadt, Germany) in high-purity water and stabilising with 1% (w/w) NaOH (Merck) solution to decrease its rate of decomposition, and was used without filtration. The HCl solution used was of the highest quality grade Suprapure (Merck, Darmstadt, Germany). The buffer and buffered mobile phase were prepared by mixing disodium hydrophosphate (Na_2HPO_4) and potassium dihydrophosphate ($KH_2PO_4 \cdot 2H_2O$), which were obtained from Merck.

2.3 *Extraction procedure*

The extraction procedure was an attempt to reconstruct the environmental conditions in order to estimate the real risk posed to the ecosystem by the sediments left by the tsunami.

For the buffer extraction, a known (described in the text) mass of the sediment sample was put into a glass flask with a condenser containing 20 mL of phosphate buffer and extracted in a water bath (at ambient or ca 80°C temperature), ultrasonic bath, or a heated magnetic stirrer. The arsenic species in the buffer extracts were determined by HPLC-HG-AAS immediately after the extraction procedure. The final buffer concentration and pH were adjusted by phosphate buffer to the same conditions (pH, ionic strength) used for chromatographic analysis.

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2.4 *Samples*

Samples of tsunami deposits left on land (from 15 locations) and soil (1 location) were collected during three field surveys in the south-western part of Thailand: in January–February 2005 (two months after the 26 December 2004 tsunami), in February 2006 and in February 2007. Between the tsunami and the first survey, no rainfall occurred. The surveys one and two years later were conducted after rainy seasons, with precipitation of up 3000 mm per season. The samples were collected each time from the same locations with a possible error of several tens of metres (based on GPS coordinates). Tsunami deposits were collected from areas surrounding Patong Bay, (Phuket Island) and from areas close to the villages of Bang Mor and Nam Khem, located about 100 to 125 km northward in the Phang Nga province. In the latter region, a soil sample of similar grain size composition, but from a location not flooded by the tsunami, was collected as a reference. That was a big problem to find correct reference samples during field investigation and only one reference sample was used in these studies. The samples were subjected to complex analysis including sediment grain size, salinity (level of salts in the water soluble fraction), the presence of heavy metals in the acid leachable fraction, metalloids in the exchangeable fraction and fractionation of mercury [20, 21, 26]. The present study extends this work into speciation analysis of arsenic in the exchangeable fraction. The details of sampling locations were presented in previous works [20, 21]. Table 1 shows basic information including the coordinates, distance from the shoreline, the sediment type, and the thickness of the tsunami deposit layer.

Table 1. Basic data on sampling sites and tsunami deposits.

Sample	Location	Latitude N	Longitude E	Thickness of tsunami deposits layer [cm]	Distance from shoreline [m]	Mean grain size
1	Patong Bay	7° 53.09′	98° 16.44′	2	75	Coarse silt
2	Patong Bay	7° 53.01′	98° 16.44′	1	315	Very coarse silt
3	Patong Bay	7° 52.92′	98° 17.31′	5	430	Fine sand
4	Patong Bay	7° 52.91′	98° 17.32′	2	480	Fine sand
5	Patong Bay	7° 52.89′	98° 17.33′	2	520	Fine sand
6	Patong Bay	7° 52.86′	98° 17.35′	1	545	Fine sand
7	Patong Bay	7° 52.95′	98° 17.33′	2	390	Medium sand
8	Patong Bay	7° 52.94′	98° 17.34′	20	410	Fine sand
9	Nam Khem	8° 51.47′	98° 15.93′	20	60	Very fine sand
10	Nam Khem	8° 51.42′	98° 15.95′	15	100	Very coarse silt
11	Nam Khem	8° 51.41′	98° 16.31′	18	570	Very fine sand
12	Nam Khem	8° 51.55′	98° 15.94′	2	50	Medium sand
13	Nam Khem	8° 51.62′	98° 16.53′	5	1100	Very fine sand
14	Bang Mor	8° 49.97′	98° 16.13′	11	300	Very fine sand
15	Bang Mor	8° 49.91′	98° 16.27′	14	590	Very fine sand
16	Thung Tuk	8° 53.77′	98° 16.69′	Soil sample	1500	Medium sand

Source: Based on [20,24].

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The samples were collected from the upper 5 cm of the tsunami deposit layer or soil. In cases when the layer was thinner, the sample was taken from the total thickness of the tsunami deposits. Collected samples were exposed to UV radiation in order to inhibit biological processes. Wet sediments were dried by lyophilization and homogenised by rubbing and sieving through a 0.02 mm sieve. The dry samples were stored in a freezer at −30°C.

3. Results and discussion

3.1 *Optimisation of extraction procedures*

An extraction procedure has been performed for the tsunami sediment sample (from sampling point number 15 from Table 2, collected in 2005) in two modes with phosphate buffer; one mode at room temperature in an ultrasonic bath, and the second at elevated temperature (80°C) in a water bath with no stirring. For comparison, an extraction was performed at elevated temperature with stirring, as well as an extraction at room temperature with no stirring. A number of parameters that could influence the process were examined: the concentration of the extracting agent, pH, the duration of the process, and the mass of the sample to be extracted.

3.1.1 *Extraction at elevated temperature (in water bath)*

3.1.1.1 *Buffer concentration.* The course of extraction, taking place at 80°C in a buffer at a phosphate concentration in the range of 5 to 50 mmol L^{-1}, was studied at a constant pH of 6.0 ± 0.2 (Figure 1). For As(III) species, the yield of extraction slightly increased with increasing buffer concentration. For As(V) species, the yield of extraction decreased when

Table 2. Proposed conditions for extraction of exchangeable fraction of sediments for inorganic arsenic speciation study.

Conditions	Values
Buffer concentration as PO_4	25–50 mmol L^{-1}
Buffer pH	5.8–6.2
Temperature	80°C
Sediment mass (for 20 mL of buffer)	Max. 500 mg, optimal 200–300 mg
Extraction time	30 min.

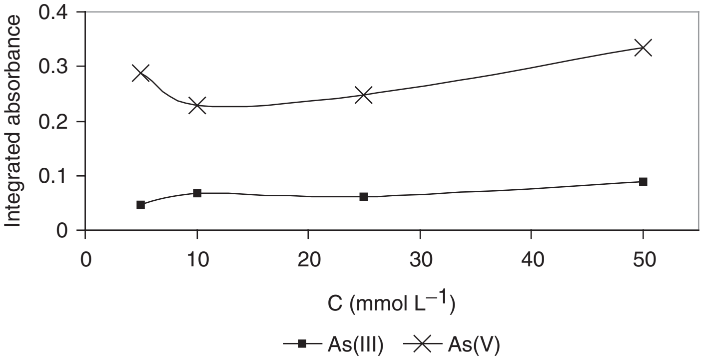

Figure 1. Effect of changes in the buffer concentration during extraction of tsunami sediment sample at 80°C (peak area for As(III) and As(V) from the HPLC-HG-AAS system).

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the concentration of the extracting liquid was changed from 5 mmol L^{-1} to 10 mmol L^{-1}. With a further increase in its concentration, the yield also increased. It should be emphasised that these changes are not very large, so the choice of the extracting liquid can also be made by adjusting the eluent to the mobile phase used for the analysis in the hyphenated HPLC-HG-AAS system.

3.1.1.2 *pH of the extracting liquid.* The extraction was performed over a range of pH (4.5 to 6.8), at a constant concentration of the extracting liquid of 50 mmol L^{-1} (Figure 2). For the analysed samples, a decrease in the extraction yield was observed (small for As(V)) with an increase in pH. These changes point to the crucial role of pH as a parameter in determining the type of fraction extracted. Due to the character of the environmental processes encountered in nature, a restriction of the pH range in the studies to 6.0 ± 0.2 seems to be justified. The pH values in this range would also ensure the consistency of the composition of the extracting liquid with that of the potential chromatographic mobile phase.

3.1.1.3 *Mass of the sediment sample.* From the point of view of the extraction efficiency, an important parameter to be adjusted is the mass of the sample used, which would permit quantitative evaluation of the process. It is obvious that with an increased mass of the sediment sample, the amount of arsenic species extracted by the same volume of the extracting liquid increases (Figure 3). Changes in the concentration of As(V) species in the extract are greater than those in the concentration of As(III) species. The actual yield

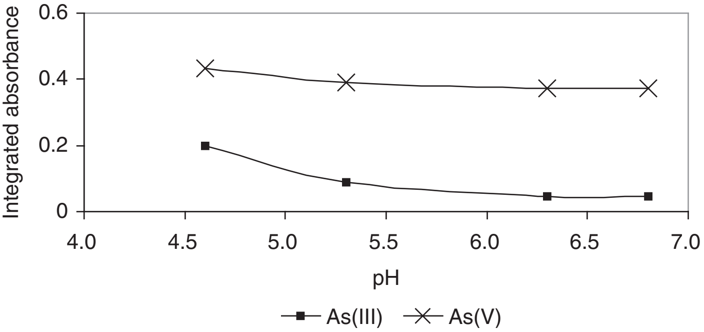

Figure 2. Effect of changes in pH during extraction of tsunami sediment sample at 80°C (as analytical signal – peak area for As(III) and As(V) in HPLC-HG-AAS system).

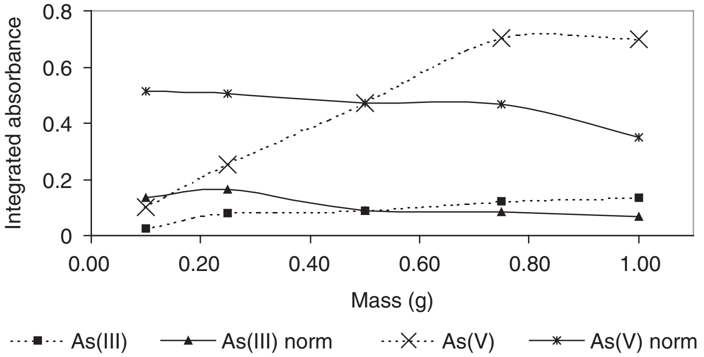

Figure 3. Effect of changes in sediment mass during extraction of tsunami sediment sample; (as analytical signal – peak area for As(III) and As(V) in HPLC-HG-AAS system) at 80°C and normalised as 0.50 g (norm).

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of extraction is described by the concentration values normalised with respect to a certain mass of the sample (0.50 g has been assumed, the results for different mass have been recalculated for 0.50 g) (Figure 3). An increase in the mass of the sample above 0.30 g leads to a decrease in the yield of extraction This is greater for As(III) than for As(V) species.

3.1.1.4 *Time of extraction*. Another element determining the course of extraction is its duration (Figure 4). The effect of duration on the yield of extraction was studied in the range of 30 to 120 min. Extraction times below 30 min are too short for quantitative extraction and give incomparable results. A small decrease in the yield of extraction was observed, with an increasing duration for the studied sediments.

3.1.1.5 *Temperature of extraction and sediment mixing*. Temperature had a significant effect on the extraction yield (Figure 5). Greater changes in the yield of extraction were observed for As(III) than for As(V). Mixing on a magnetic stirrer at ambient temperature (described as *dynamic*) had a much smaller effect on the extraction yield in comparison with not mixed sample (described as *static*). A higher yield was observed for mechanical stirring of the sample on a heating plate at 50°C or 80°C (described as *dynamic*), but the difference

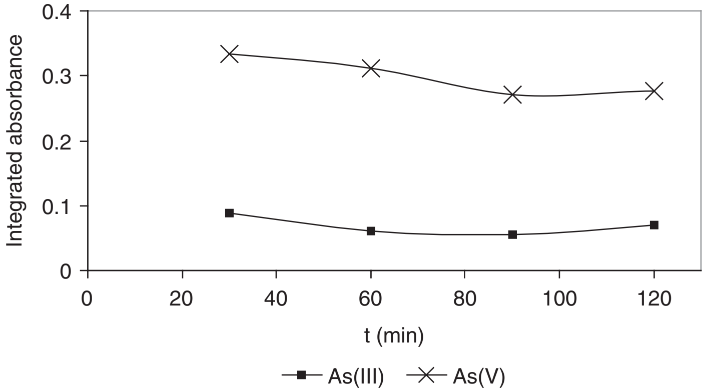

Figure 4. Effect of changes in extraction time during extraction of tsunami sediment sample at 80°C (as analytical signal – peak area for As(III) and As(V) in HPLC-HG-AAS system).

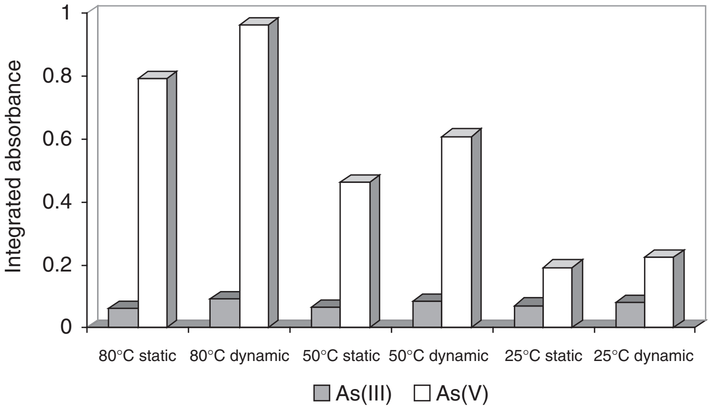

Figure 5. Effect of changes in extraction temperature and mixing (static or dynamic) for tsunami sediment sample (as analytical signal – peak's area for As(III) and As(V) in HPLC-HG-AAS system).

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varied by up to 20% in comparison with extraction provided on water bath (described as *static*). The effect of mixing was smaller on the extraction of As(III) than As(V).

3.1.2 *Extraction at room temperature*

3.1.2.1 *The buffer concentration.* When the extraction was conducted without mixing, changes in the extraction yield with increasing buffer concentration (Figure 6) followed the same trend as when the extraction was conducted at elevated temperature (Figure 1). When the extraction was ultrasound assisted, the effect of buffer concentration was different (Figure 6). The extraction yield slowly increased with the increase of buffer concentration to 25 mmol L^{-1}, and then it slowly decreased. The course of the extraction was similar for both arsenic species.

3.1.2.2 *Duration of the extraction.* When no mixing method was used, no changes in the extraction yield were found with increasing duration, whereas for the ultrasound-assisted

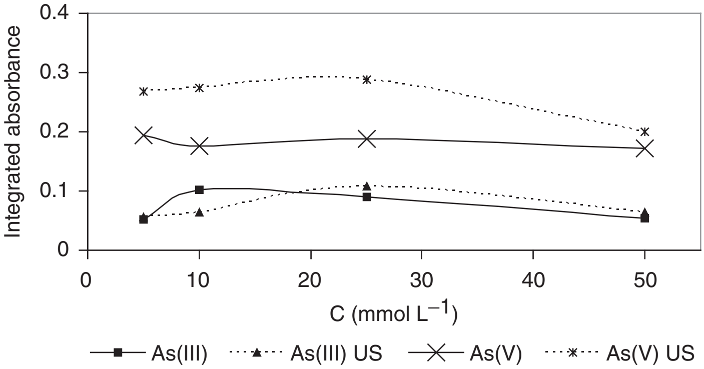

Figure 6. Effect of changes in buffer concentration during extraction of tsunami sediment sample at ambient temperature and at ambient temperature with sonication (US) (as analytical signal – peak area for As(III) and As(V) in HPLC-HG-AAS system).

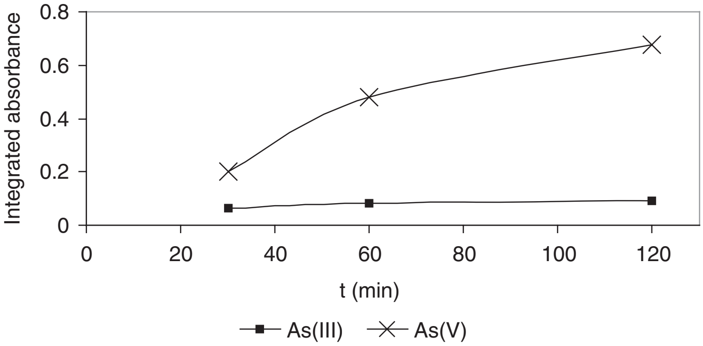

Figure 7. Effect of changes in extraction time during extraction of tsunami sediment sample at ambient temperature with sonication (as analytical signal – peak area for As(III) and As(V) in HPLC-HG-AAS system).

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extraction, the duration had a significant effect (Figure 7). The amount of the extracted As(V) species increased, but the difference in the amount of the extracted As(III) species was insignificant. However, in contrast to the extraction at elevated temperature, when the extraction lasted over 60 minutes, an increase in the concentration of As(V) was observed.

3.1.3 *Sequential extraction*

In order to check whether the procedures applied lead to the extraction of the whole fraction, three cycles of sequential extraction were applied using the same agent (phosphate buffer) and the same extraction conditions. In this way, the actual yield of a single extraction cycle could be estimated (Figure 8). The increase in the yield of the extraction process due to elevated temperature was significantly greater than that due to ultrasound-assisted extraction. The yield of the second stage of extraction was 19% for As(III) and 13% for As(V), relative to the values obtained in the first stage.

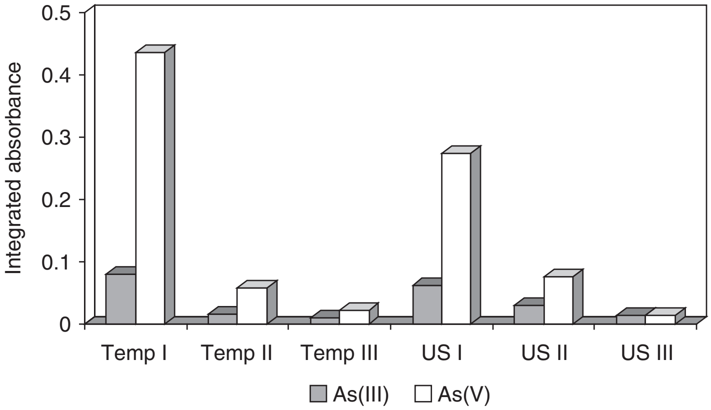

Figure 8. Sequential extraction of tsunami sediment sample at 80°C (Temp) and at ambient temperature with sonication (US).
Notes: I–first extraction, II–second extraction, III–third extraction.

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3.1.4 *Conclusions regarding extraction methodology*

As follows from the above results, in particular those on the effect of the extraction duration and sequential extraction, extraction with the buffer at 80°C permitted more effective separation of the exchange fraction of the sediment, although these conditions differ from environmental conditions. The ultrasound assisted extraction of the fraction studied is less effective. The effect of the buffer concentration on the yield of extraction is small, and the effect of mixing is smaller than expected, while that of the process temperature is significant. The pH of the extracting liquid is of critical importance. A small pH change from 4.5 to 5.8 leads to probable extraction of a different fraction of arsenic in the sediment. Therefore, the range of pH from 5.8 to 6.2 was selected because it is close to the natural environmental conditions.

It should be emphasised that this study was not meant to optimise the process (except in terms of the duration of extraction and the mass of the sample), but to gain a better understanding of the sediment fractionation in order to be able to isolate the exchange or mobile fraction. The conditions of extraction of the exchange fraction of sediment samples proposed in this work (Table 2) have been used in the work of Szczuciński *et al.* [20, 24]. The proposed analytical procedure could be of interest in inter-laboratory studies.

3.1.5 *Application to hyphenated system analysis*

The characteristics of the analytical performance were evaluated for both inorganic arsenic species As(III) and As(V). The content of arsenic species was proportional to the area and the height of the peak, which were determined in each analysis. However, because of the asymmetry and the variation of the peak shape (dispersion) in the samples, only the peak area was considered. Validation parameters characterising the analytical method are shown in Table 3. The detection limits (based on a $3\sigma_{\text{blank}}$ criterion) obtained, as well as the precision of the results (determined as RSD of the mean of six replicate measurements of arsenic species standards) can be compared with the results acquired by other authors using different sample separation systems (column–eluent) [28–30].

Table 3. Analytical figures of merit.

	As(III)	As(V)
Retention time(s)	78.0	141.2
Intercept	0.7818	0.6365
Slope	0.0541	0.0340
Correlation coefficient	0.9950	0.9941
For liquid (*standards*)		
Linear range of calibration curve/ng mL^{-1}	DL*–500	DL*–500
Detection limit (3σ)/ng mL^{-1}	0.5	0.7
Precision as instrumental RSD (at 100 ng mL^{-1})/%	6.5	5.8
For solid (*for* 0.50 g *of samples*)		
Linear range analysis/ng g^{-1}	DL*–10000	DL*–10000
Detection limit (3σ)/ng g^{-1}	10	10
Precision as RSD/%	8.5	7.8

Notes: *Detection limit; number of replicates = 6, peak area.

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Since it was impossible to check the traceability due to the lack of certified reference materials for the determination of inorganic arsenic species, the recovery of each species was determined by adding the standard to an environmental sample. The recovery of each form was found to be high (90%–105%). Therefore, the proposed hyphenated analytical method HPLC-HG-AAS allows for the determination of inorganic arsenic species As(III) and As(V) in fractions extracted from environmental samples.

3.2 *Results of tsunami deposits analysis*

The proposed method for the determination of inorganic arsenic species in the exchangeable fraction of sediments was applied to the analysis of tsunami deposits. The content of arsenic species and the total amount of potentially mobile inorganic arsenic vary considerably among samples. The complete results are presented in Table 4. In tsunami deposits left on land, the sum of As(III) and As(V) in the exchangeable fraction was in the range of 219 to 1820 ng g^{-1} in 2005, 87 to 1480 ng g^{-1} in 2006 and 178 to 2170 ng g^{-1} in 2007. In reference soil samples collected during the same surveys, the values were significantly lower: 110, 18 and 108 ng g^{-1}, respectively, in 2005 to 2007. There is no evident trend in the As content after successive rainy seasons. A trend was only observed in the case of As(III). The exchangeable fractions of sediments sampled two months after the tsunami contained As(III) in the range of 14 to 160 ng g^{-1}. After one year, the level was within the detection limit in two samples, and in 2007, all samples contained As(III) at a level lower than the detection limit (10 ng g^{-1}). Considering the geographical variation of tsunami deposits, different compositions can be seen for two different regions: areas surrounding Patong Bay, with an average sum of As in an exchangeable inorganic form between 350 and 500 ng g^{-1}, and lying more than 100 km to the north, the neighbourhood of Nam Khem village, where average values of 700 to 1200 ng g^{-1} were found. This difference can also be seen in terms of As(III) and As(V) concentrations, although the ratio between the inorganic forms of arsenic is similar in both regions.

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Table 4. Concentrations (ng g^{-1}) of exchangeable As(III), As(V) and their sum in tsunami deposits and soil samples from 2005, 2006 and 2007 sampling surveys.

Sampling points	As(III)	As(V)	Total inorganic As	As(III)	As(V)	Total inorganic As	As(III)	As(V)	Total inorganic As
	2005			2006			2007		
1	112	754	866	<10	327	327	<10	248	248
2	104	388	492	<10	779	779	<10	665	665
3	22	222	244	<10	410	410	<10	396	396
4	16	203	219	<10	354	354	<10	178	178
5	14	358	372	<10	1480	1480	<10	293	293
6	20	354	374	<10	208	208	<10	386	386
7	19	210	229	<10	87	87	<10	244	244
8	24	403	427	<10	218	218	<10	301	301
9	101	969	1070	<10	139	139	<10	916	916
10	160	1100	1260	<10	687	687	<10	974	974
11	144	1110	1254	40	1150	1190	<10	1320	1320
12	19	384	403	<10	556	556	<10	743	743
13	145	1675	1820	139	609	748	<10	1350	1350
14	70	980	1050	50	1020	1070	<10	774	774
15	110	1200	1310	<10	706	706	<10	2170	2170
16	15	95	110	<10	18	18	<10	108	108

In the tsunami deposit samples from various locations, the content of exchangeable As was much higher than in reference soil samples. This may suggest that tsunami deposits, which are mostly of marine origin [24], are enriched in the bio-available fractions of heavy metals [20,21,25] and of arsenic. This result also suggests that in the case of other coastal hazards that transport marine sediments on land, like storms or hurricanes, the resulting deposits could also be expected to be enriched in the bio-available fractions of these potentially toxic elements.

A regional variability was observed among the tsunami deposits, which could partly be explained by differences in sediment type, since higher concentrations were generally found in finer sediment samples. However, this variability could be also related to a variable geological situation. For instance, the region of Nam Khem village and its surroundings are known to be mining areas (mainly for cassiterite). Mining could enhance the amount of arsenic bearing minerals subjected to weathering, and in this way, could cause an increase in mobile arsenic in the environment.

In tsunami deposits, rainy seasons do not lead to a simple increase or decrease of the total concentration of inorganic exchangeable arsenic species. One of the possible explanations is that the As content in this fraction is not only an effect of its removal from the tsunami deposits, but may also be related to the continuous recharge from more resistant fractions. However, a steady decrease in the As(III) fraction can be observed. The initial ratio between As(V) and As(III) reflects the ratio found in seawater [31]. The dominance of the As(V) form may also suggest that eroded marine sediments were oxygenated [31], so the tsunami eroded only surface sediments, and/or that the deposits very rapidly oxidised during transport and sedimentation. The ratio of As(V) to As(III) increased after the rainy season. This may suggest that As(III) species are more susceptible to removal from exchangeable fractions (both by wash and precipitation), or that this form is oxidised to the As(V) form.

The results obtained were also subjected to cluster analysis and statistical correlation analyses. Cluster analysis revealed that in the three series analysed (for 2005, 2006 and 2007), the variations of As(III) and As(V) species concentrations remained more constant than the sum of arsenic in the exchangeable fraction. This may suggest that the changes in arsenic speciation are caused by similar processes on a larger than local scale (e.g., tsunami, rainy season, dry season). As discussed above, these changes are mainly related to a decrease in As(III) caused by its removal or oxidisation. The cluster analysis also showed that the variations in results are larger in 2006 than in 2005 and 2007. This is also supported by correlation analysis, which showed that there is a high correlation ($r = 0.87$) between changes of the As(III) and As(V) forms in samples collected shortly after the tsunami. The variation of results from 2005 and 2007 is similar ($r = 0.79$), but was quite different in 2006 (for 2005–06 and 2006–07, $r = 0.39$). This may be due to the disturbance of the initial ratio of arsenic species in the exchangeable fractions of tsunami deposits after the first rainy season, and its stabilisation for new terrestrial conditions after the second rainy season.

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4. Conclusion

The obtained results show that the proposed procedure for extraction of the exchangeable fraction can be applied in an investigation of environmental objects aimed at the determination of the content of inorganic arsenic species As(III) and As(V) or other metalloids. The results of this extraction, which was conducted under conditions close to those observed in the natural environment, permits an evaluation of the actual threat related to the presence of metalloids in the environment. In the speciation analysis of inorganic species of arsenic, it is of great importance to use the same reagent as the extraction liquid and as the mobile phase in the HPLC-HG-AAS, which permits direct speciation analysis of the extracted fraction.

The results obtained with the new extraction procedure in the HPLC-HG-AAS system for tsunami deposits left in coastal zone of Thailand revealed that the contents of As(III) and As(V) in the tsunami deposits of likely marine origin are much higher than in reference soil samples. Additionally, the ratio of As(III) to As(V) was relatively uniform in the fresh tsunami deposits, indicating a common source and geochemical processes regardless of sampling location. Changes in the total amount of inorganic arsenic in the exchangeable fractions reflect regional changes in geology and/or sediment grain size. Finally, after the first rainy season with a rainfall of about 3000 mm, the ratio between As species was modified and stabilised compared to after the second rainy season, when As(III) was below the detection limit in all samples.

The more general conclusion can be made that coastal flooding may transfer marine sediments onto land, and the new deposits may be enriched in As, in particular in its more toxic As(III) form, which is subjected to removal and/or oxidisation in the terrestrial environment. From the analytical point of view, these results prove 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.

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References

[1] F.C. Konowles and A.A. Benson, Trends Biochem. Sci. **8**, 178 (1983).
[2] D.J.H. Philips, Aquat. Toxicol. **16**, 151 (1990).
[3] M.J. Ruiz-Chancho, R. Sabe, J.F. Lopez-Sanchez, R. Rubio, and P. Thomas, Microchim. Acta **151**, 241 (2005).
[4] M. Vergara Gallardo, Y. Bohari, A. Astruc, M. Potin-Gautier, and M. Astruc, Anal. Chim. Acta **441**, 257 (2001).
[5] S. Garcia-Manyes, G. Jemenez, A. Padro, R. Rubio, and G. Rauret, Talanta **58**, 97 (2002).
[6] M.J. Ellwood and W.A. Maher, Anal. Chim. Acta **477**, 279 (2003).
[7] Z. Gong, X. Lu, M. Ma, C. Watt, and X.Ch. Le, Talanta **58**, 77 (2002).
[8] C. Demesmey and M. Olle, Fresenius J. Anal. Chem. **357**, 1116 (1997).
[9] G. Rauret, Talanta **46**, 449 (1998).
[10] A. Tessier, P.G.C. Campbell, and M. Bisson, Anal. Chem. **51**, 844 (1979).
[11] W.W. Wenzel, N. Kirchbaumer, T. Prohaska, G. Stingeder, E. Lombic, and D.C. Adriano, Anal. Chim. Acta **436**, 309 (2001).
[12] J. Chappell, B. Chisswell, and H. Olszowy, Talanta **42**, 323 (1999).
[13] P. Thomas, J.K. Finnie, and J.G. Williams, J. Anal. At. Spectrom. **12**, 1367 (1997).
[14] S. Rattanachongkiat, G.E. Millward, and E. Foulkes, J. Environ. Monit. **6**, 254 (2004).
[15] I. Pizarro, M. Gomez, C. Camara, and M.A. Palacios, Anal. Chim. Acta **495**, 85 (2003).
[16] L. Orero Iserte, A.F. Roig-Navarro, and F. Hernandez, Anal. Chim. Acta **527**, 97 (2004).
[17] J. Zheng, H. Hintelmann, B. Dimock, and M.S. Dzurko, Anal. Bioanal. Chem. **377**, 14 (2003).
[18] B.A. Manning and D.A. Martens, Environ. Sci. Technol. **31**, 171 (1997).
[19] A. Huerga, I. Lavilla, and C. Bendicho, Anal. Chim. Acta **534**, 121 (2005).
[20] W. Szczuciński, P. Niedzielski, G. Rachlewicz, T. Sobczyński, A. Zioła, A. Kowalski, S. Lorenc, and J. Siepak, Environ. Geol. **49**, 321 (2005).
[21] W. Szczuciński, P. Niedzielski, L. Kozak, M. Frankowski, A. Zioła, and S. Lorenc, Environ. Geol. **53**, 253 (2007).
[22] T. Lay, H. Kanamori, C.J. Ammon, M. Nettles, S.N. Ward, R.C. Aster, S.L. Beck, S.L. Bilek, M.R. Brudzinski, R. Butler, H.R. DeShon, G. Ekström, K. Satake, and S. Sipkin, Science **308**, 1127 (2005).
[23] UNEP, After the Tsunami. Rapid Environmental Assessment, 140 pp. (2005).
[24] W. Szczuciński, N. Chaimanee, P. Niedzielski, G. Rachlewicz, D. Saisuttichai, T. Tepsuwan, S. Lorenc, and J. Siepak, Polish J. Environ. Stud. **15**, 793 (2006).
[25] S. Srinivasalu, N. Thangaduurai, M.P. Jonathan, J.S. Armstrong-Altrin, T. Ayyamperumal, and V. Ram-Mohan, Environ. Geol. **53**, 1711 (2008).
[26] L. Boszke, A. Kowalski, W. Szczuciński, G. Rachlewicz, S. Lorenc, and J. Siepak, Environ. Geol. **51**, 527 (2006).
[27] P. Niedzielski, Anal. Chim. Acta **551**, 199 (2005).
[28] K. Van den Broeck, C. Vandecasteele, and J.M.C. Geuns, Anal. Chim. Acta **361**, 101 (1998).

[29] G. Samanta, U.K. Chowdhury, B.K. Mandal, D. Chakraborti, and C.N. Sekaran, Microchem. J. **65**, 113 (2000).

[30] M.C. Villa-Lojo, E. Alonso-Rodriguez, P. Lopez-Mahia, S. Muniategui-Lorenzo, and D. Prada-Rodriguez, Talanta **57**, 741 (2002).

[31] J.M. Neff, Environ. Toxicol. Chem. **16**, 917 (1997).

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