

# Content of 27 Selected Elements in the Potentially Mobile Fraction of Tsunami Sediments

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## Abstract

Our paper reports results of a study on the bioavailability of selected elements from sediments deposited by the tsunami event of 26 December 2004 in south Thailand. In January 2005, 15 samples of the sediments deposited by the tsunami were collected at four different localities. The reference sample was collected in an area not affected by the tsunami. In the acid leachable sediments fraction (the bioavailable fraction) the contents of 27 selected elements (Be, Ga, Bi, Rb, Cs, Sn, Mn, Re, Co, Rh, Ru, Mo, V, Nb, Ta, Zr, Sc, Th, Pt, La, Ce, Nd, Eu, Gd, Tb, Ho, Lu) were determined using ICP-MS. The measurements were repeated after one year to establish a potential effect of the rainy season on the content of these elements in this fraction.

**Keywords:** metals, fractionation, tsunami sediments, ICP-MS

## Introduction

On 26 December 2004 an earthquake of magnitude  $M=9.0$  took place northeast of the coast of Sumatra and generated tsunami waves. The waves, moving at a few hundred kilometres per hour, hit the Indian Ocean Coast, rising up to 30m and encroaching the land to a distance of up to 20 kilometres. The impact force of the waves destroyed buildings, roads, and ports, and caused the death of over 200,000 people. The greatest damage was along the coasts of Indonesia, Thailand, India and Sri Lanka. The environment of tsunami-affected areas suffered tremendously: ecosystems of the coastal coral reefs and the land near the coast were completely destroyed. The surface and ground waters were salinated, which meant that the inhabitants of the small islands were without drinking water. Waves moving into the land covered hundreds of hectares of land with a layer

of salty sediments, destroying the land ecosystems and agricultural land [1].

In January 2005, one month after the disaster, a group of geologists from A. Mickiewicz University, Poznań, in cooperation with the Department of Mineral Resources (Minister of Natural Resources and Environment, Thailand) collected 15 samples of tsunami sediments at four localities to subject them to geochemical analysis. A sample of soil from outside the land affected by the tsunami was also collected as reference. The chemical analyses concerned determination of the content of the water-soluble salts ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ), heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) in the hydrochloric acid soluble fraction and metalloids (As, Sb, Se) in the exchangeable fraction of the sediments [2]. The analysis proved high salinity of the tsunami sediments relative to that of the reference sample. Also, the contents of heavy metals and metalloids were higher in the tsunami sediments than in the reference sample.

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Table 1. Spike recovery for hydrochloric acid extracts of environmental samples.

spike	Be	Sc	V	Mn	Co	Ga	Rb	Zr	Nb	Mo	Ru	Rh	Sn	Te	Cs	La	Ce	Nd	Eu	Gd	Tb	Ho	Lu	Re	Pt	Bi	Th	
<b>sample 1/05</b>																												
25 mg/kg	24	24	25	25	24	25	25	25	27	26	25	25	26	22	25	29	28	26	26	26	27	27	27	27	27	25	23	27
recovery %	96	96	100	101	95	99	98	101	108	102	101	100	103	86	100	116	111	105	104	105	109	109	109	109	107	102	93	110
50 mg/kg	47	48	51	51	48	50	51	51	54	53	51	53	53	42	51	56	55	54	53	53	58	58	58	58	54	52	49	59
recovery %	94	95	101	103	96	100	101	102	108	106	102	106	105	85	102	112	110	107	105	106	117	116	117	108	104	97	117	
<b>sample 15/05</b>																												
25 mg/kg	25	26	26	27	24	25	25	24	26	25	25	25	25	22	25	25	25	26	26	26	27	27	27	27	26	25	23	28
recovery %	101	102	103	107	96	99	101	98	104	101	101	100	100	86	102	98	100	103	103	104	107	107	107	108	105	100	94	111
50 mg/kg	49	51	52	52	49	50	51	52	52	53	51	53	51	44	51	52	53	52	52	52	57	57	57	57	53	51	48	59
recovery %	97	102	104	103	97	100	102	103	104	105	102	106	102	88	102	105	107	104	103	104	114	114	114	114	105	101	97	117

The determinations were repeated in 2006 on the 15 new samples of the sediments and a reference sample collected outside the reach of the tsunami. The collection of new samples and the repetition of the determinations were aimed at evaluating the influence of the rainy season on the geochemical composition of the sediments [3]. As the above-mentioned elements could be released to ground water (bioavailable fraction) they were potentially threatening to the environment.

In the samples collected in 2005 and in 2006 the contents of other elements in the potentially bioavailable fraction (leachable by 2M HCl) were also determined: lanthanides (La, Ce, Nd, Eu, Gd, Tb, Ho, Lu), noble metal (Pt) and Be, Ga, Bi, Rb, Cs, Sn, Mn, Re, Co, Rh, Ru, Mo, V, Nb, Ta, Zr, Sc, Th. The determinations were made using ICP-MS.

## Experimental

### Equipment and Reagents

The analysis was performed using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrument Agilent 7500ce following ISO 17294 procedure. All reagents used in the analytical procedures were analytical-pure and the water was redistilled and purified in a Milli-Q unit (Milipore). The multielemental standard for ICP analysis (Promochem) was used.

### Study Area and Samples

The samples were collected in southern Thailand. In 2005 they were collected at Phuket Island (Palong Bay, Kamala Beach), Nham Khem, and Bang Mor, while the reference sample was collected at Thung Tuk (sample 16). In 2006 the samples were collected from the same location as in the previous year. The samples were averaged and placed in polyethylene containers using plastic tools. To restrict the biological activity in the samples they were subjected to UV radiation. The samples were stored at about minus 30°C. Prior to analyses the samples were lyophilized and homogenized. A portion of 1g of each sample was subjected to extraction with 10 ml 2M HCl acid in water bath at 80°C. The time of extraction was 0.5h. The next step was a multielemental analysis by ICP MS.

Because of the lack of reference materials for fractionation of marine sediments, in order to establish the traceability of the chemical analysis, the method of the standard addition to the natural samples was used. For this procedure two samples collected in 2005 at sites 1 and 15, with a different content of macroelements, were used [2]. The obtained recovery of the standard added to the sample (Table 1) varies  $\pm 20\%$ , which is satisfactory for trace analyses.

## Results and Discussion

The contents of 27 elements in the samples of the tsunami sediments collected in 2005 and 2006 (samples 1-15) and in the reference samples (sample 16) were measured.



The numbers of analyzed samples are the same as for Szczuciński et al. 2005 [2] and Szczuciński et al. 2007 [3]. The results for the 27 elements from the hydrochloric acid leachable fraction are presented in Table 2; the results are ordered according to increasing atomic number of the elements.

### Beryllium

In the samples collected in 2005 the content of beryllium in the HCl leachable fraction of the tsunami sediments varied from 0.12 to 1.6 mg kg<sup>-1</sup>; the samples (1 and 2) with the highest content of this element were collected from Patong Bay area. In the other samples the content of beryllium was much lower, reaching a maximum of 0.65 mg kg<sup>-1</sup>. In 2006, after the rainy season, the content of beryllium decreased to 0.08-0.42 mg kg<sup>-1</sup>. However, these values were much higher than that determined in the reference sample (sample 16), in which the content of beryllium was below the detection limit of <0.01 mg kg<sup>-1</sup>. The level of beryllium content in the acid-leachable fraction of the tsunami sediments was similar to the total content of this element in the sandy sedimentary rocks, varying from 0.2 to 1 mg kg<sup>-1</sup> [4].

### Scandium

In the samples collected in 2005 the content of scandium in the potentially bioavailable fraction of the tsunami sediments varied in the range 0.10-0.65 mg kg<sup>-1</sup>, while in the samples collected in 2006 – from 0.06 to 0.53 mg kg<sup>-1</sup>. Similarly as for beryllium, the content of scandium in the reference sample was below the detection level of 0.01 mg kg<sup>-1</sup>. The content of scandium in the studied fraction of the sediment samples did not exceed the total content of this element in the sandy sedimentary rocks determined as about 1 mg kg<sup>-1</sup> [4].

### Vanadium

The content of vanadium in the analyzed fraction varied from 1.2 to 12 mg kg<sup>-1</sup> and 0.85 to 5.7 mg kg<sup>-1</sup> in the samples collected in 2005 and 2006, respectively. In the reference samples collected in 2005 and 2006 it was 1.5 and 1.1 mg kg<sup>-1</sup>, respectively. The content of vanadium in the acid leachable fraction of the tsunami sediments was much lower than the mean total content of this element in the sandy sedimentary rocks determined as 10-60 mg kg<sup>-1</sup> [4].

### Manganese

The content of manganese in the analyzed fraction varied from 13 to 124 mg kg<sup>-1</sup> and 7.1-53 mg kg<sup>-1</sup> in the samples collected in 2005 and 2006, respectively. In the reference samples it was 6.8 and 2.7 mg kg<sup>-1</sup> in the samples from 2005 and 2006, respectively. The content of manganese in the mobile fraction was much lower than the mean total content of this element in the sandy sedimentary rocks determined as 100-500 mg kg<sup>-1</sup> [4].

### Cobalt

In the mobile fraction of deposits cobalt occurred in the content from 0.18 to 3.2 mg kg<sup>-1</sup> and 0.14 to 1.1 mg kg<sup>-1</sup> in the samples collected in 2005 and 2006, respectively. In the respective reference samples the content of cobalt was 0.08 and 0.04 mg kg<sup>-1</sup>. Similarly as for manganese and vanadium, the content of cobalt in the acid-leachable fraction of the tsunami sediments was much lower than the mean total content of this element in the sandy sedimentary rocks equal to 0.3-10 mg kg<sup>-1</sup> [4].

### Gallium

The content of gallium in the analyzed fraction was similar to that of beryllium and was much higher in samples Nos. 1 and 2 collected at Patong Bay in 2005, of 6.1 and 6.7 mg kg<sup>-1</sup>, respectively. In the other samples from 2005 the content of gallium varied from 0.56 to 3.0 mg kg<sup>-1</sup>. In the samples from 2006, it varied from 0.56 to 1.9 mg kg<sup>-1</sup>, and was much reduced in the corresponding samples 1 and 2, to 2.2 and 2.6 mg kg<sup>-1</sup>, respectively. In the reference samples it was 1.1 and 1.2 mg kg<sup>-1</sup> in the samples from 2005 and 2006. The content of gallium in the acid-leachable fraction of the sediments studied was in the range of total content of this element in the sandy sedimentary rocks determined as 5-12 mg kg<sup>-1</sup> [4].

### Rubidium

Similarly as for beryllium and gallium, the content of rubidium in samples 1 and 2 collected in 2005 in Patong Bay was much higher than in the other samples, of 44 and 49 mg kg<sup>-1</sup>, respectively. In the corresponding samples collected after the rainy season in 2006 it was much reduced to 14 and 3.5 mg kg<sup>-1</sup>. In the other samples the content of rubidium varied from 0.44 to 9.6 mg kg<sup>-1</sup> in 2005 and from 1.0 to 9.4 mg kg<sup>-1</sup> in 2006. The content of rubidium at the reference sites was much lower, of 0.27 and 0.34 mg kg<sup>-1</sup> in 2005 and 2006. The content of rubidium in the acid leachable fraction of the sediments studied was close to the mean total content of this element in the sandy sedimentary rocks determined as 45 mg kg<sup>-1</sup> [4].

### Zirconium

In all of the samples, except sample 1 collected in 2005, no presence of zirconium was detected (<0.01 mg kg<sup>-1</sup>) in the fraction studied. In sample 1 from 2005 its content was 0.03 mg kg<sup>-1</sup>. The content of zirconium in the acid-leachable fraction of the sediments studied was much lower than the mean total content of this element in the sandy sedimentary rocks determined as 180-220 mg/kg [4].

### Niobium

As for beryllium, gallium and rubidium, also the content of niobium was much higher in samples 1 and 2 from 2005, reaching 1.8 and 2.3 mg kg<sup>-1</sup>. After the rainy season,

in the corresponding samples from 2006, its content was much reduced to 0.13 mg kg<sup>-1</sup> and below 0.01 mg kg<sup>-1</sup>, respectively. In the other samples from 2005 the content of niobium varied from below 0.01 mg kg<sup>-1</sup> in seven samples to 0.28 mg kg<sup>-1</sup>, while in the samples from 2006 it was below 0.01 mg kg<sup>-1</sup>. In the reference samples from 2005 and 2006 the content of niobium was below 0.01 mg kg<sup>-1</sup>. The content of niobium in the fraction studied, in a few samples from 2005 was much higher, while in all the samples collected in 2006 it was much lower than the mean total content of this element in the sandy sedimentary rocks determined as 0.05 mg kg<sup>-1</sup> [4].

### Molybdenum

The content of molybdenum in the acid-leachable fraction in the samples studied varied from below 0.01 to 1.49 mg kg<sup>-1</sup>. In the reference samples the content of molybdenum was much lower, below 0.01 and 0.03 mg kg<sup>-1</sup> in the samples from 2005 and 2006. In the analyzed fraction of the tsunami deposits the content of molybdenum was in the range of the total content of this element in the sandy sedimentary rocks determined as 0.2-0.8 mg kg<sup>-1</sup> [4].

### Ruthenium

In the analyzed sediment samples the content of ruthenium in the acid-leachable fraction was generally below 0.01 mg kg<sup>-1</sup>; only in two samples, Nos. 2 and 15 collected in 2005, it was higher, of 0.14 and 0.08 mg kg<sup>-1</sup>, respectively. The content of ruthenium in the rocks has not been well established, it is assumed to vary from 0.01 to 60 mg kg<sup>-1</sup> in the sandy sedimentary rocks [4].

### Rhodium

The content of rhodium in the acid leachable fraction of the tsunami sediment was below 0.01 mg kg<sup>-1</sup>. Similarly as for ruthenium, in samples 2 and 15 collected in 2005 the content of this element was higher, of 0.12 and 0.07 mg kg<sup>-1</sup>. The content of rhodium in the rocks is not well known and the total content of this element in the sandy sedimentary rocks is assumed to be 0.01-20 mg kg<sup>-1</sup> [4].

### Tin

Similarly as for beryllium, gallium, rubidium and niobium, the content of tin was much greater in samples 1 and 2 collected in 2005, in which it reached 8.7 and 9.0 mg kg<sup>-1</sup>. After the rainy season its content decreased to 1.9 mg kg<sup>-1</sup> and 0.19 mg kg<sup>-1</sup>, determined in samples 1 and 2 collected in 2006. In the other samples from 2005, the content of tin varied from below 0.01 mg kg<sup>-1</sup> to 3.5 mg kg<sup>-1</sup>, in the samples from 2006 it varied from 0.07 to 1.4 mg/kg. In the reference samples from 2005 and 2006 the content of tin was below 0.01 mg/kg. The content of tin in the analyzed fraction was much higher than the mean total content of this element in the sandy sedimentary rocks of 0.5 mg kg<sup>-1</sup> [4].

### Tellurium

The content of tellurium in the acid-leachable fraction of all samples of the tsunami sediments was below 0.01 mg kg<sup>-1</sup>. It is assumed that the total content of this element in rocks is below 0.01 mg kg<sup>-1</sup> [4].

### Caesium

Similarly as for beryllium, gallium, rubidium, niobium and tin, the content of caesium was much higher in samples 1 and 2 collected in 2005, reaching 13 and 14 mg kg<sup>-1</sup>, respectively. In the corresponding samples collected in 2006, after the rainy season, the content of caesium was much reduced to 3.8 mg kg<sup>-1</sup> and 0.97 mg kg<sup>-1</sup>, respectively. In the other samples collected in 2005, the content of caesium varied from 0.17 mg kg<sup>-1</sup> to 3.0 mg kg<sup>-1</sup>, while in the samples from 2006 – from 0.36 to 2.9 mg kg<sup>-1</sup>. In the reference sample from 2005 it was 0.22 mg/kg and in the reference sample from 2006 it was 0.15 mg kg<sup>-1</sup>. The content of caesium in the acid-leachable fraction of the deposits was much higher than the total content of this element in the sandy sedimentary rocks established as 0.5-2 mg kg<sup>-1</sup> [4].

### Lanthanides

Similarly as for a few other elements, the content of the lanthanides was much higher in samples 1 and 2 collected in 2005. In these two samples the content of lanthanum was 43 and 33 mg kg<sup>-1</sup>, that of cerium 62 and 49 mg kg<sup>-1</sup>, that of neodymium 48 and 36 mg kg<sup>-1</sup>, europium 0.87 and 0.81 mg kg<sup>-1</sup>, gadolinium 10 and 7.8 mg kg<sup>-1</sup>, terbium 1.5 and 1.2 mg kg<sup>-1</sup> and lutetium 0.47 and 0.50 mg kg<sup>-1</sup>. These values were considerably reduced in the corresponding samples collected after the rainy season. The contents of the lanthanides in the reference samples were much lower than in the samples of the tsunami sediments. The total contents of the lanthanides in the sandy sedimentary rocks has been established as: lanthanum 17-40 mg kg<sup>-1</sup>, cerium 25-80 mg kg<sup>-1</sup>, neodymium 16-38 mg kg<sup>-1</sup>, europium 0.7-2 mg kg<sup>-1</sup>, gadolinium 3-10 mg kg<sup>-1</sup>, terbium 1.6-2 mg kg<sup>-1</sup>, holmium 2 mg kg<sup>-1</sup>, lutetium 0.8-1.2 mg kg<sup>-1</sup> [4].

### Rhenium

The content of rhenium in the acid-leachable fraction of the sediment samples was below 0.01 mg kg<sup>-1</sup>. Similarly as for ruthenium and rhodium, only in two samples (2 and 15), collected in 2005, the content of this element was higher, reaching 0.15 and 0.11 mg kg<sup>-1</sup>, respectively. The content of rhenium in the rocks has not been well established. It is assumed to be of about 0.001 mg kg<sup>-1</sup> [4].

### Platinum

The content of platinum in the acid-leachable fraction of the tsunami sediment was below 0.01 mg kg<sup>-1</sup>. Similarly as for ruthenium, rhodium and rhenium, in two samples (Nos. 2 and 15, collected in 2005), the content of platinum

was higher, reaching 0.15 and 0.10 mg kg<sup>-1</sup>, respectively. It is assumed that the total content of platinum in rocks varies from 0.001 to 0.075 mg kg<sup>-1</sup> [4].

### Bismuth

Along with beryllium, gallium, rubidium, niobium, tin, caesium and the lanthanides, the content of bismuth was also much higher in samples 1 and 2 collected in 2005, reaching 1.7 and 1.4 mg kg<sup>-1</sup>, respectively. In the corresponding samples collected after the rainy season in 2006, the content of bismuth was considerably reduced to 0.10 mg kg<sup>-1</sup> and below 0.01 mg kg<sup>-1</sup>. In the other samples from 2005, it was below 0.01 mg kg<sup>-1</sup>, whereas in the samples from 2006 it varied from below 0.01 to 0.54 mg kg<sup>-1</sup>. In the two reference samples from 2005 and 2006 the content of bismuth was below 0.01 mg kg<sup>-1</sup>. The content of bismuth in the acid-leachable sediments fraction was in some samples much higher than the total content of this element in the sandy sedimentary rocks determined as 0.1-0.2 mg kg<sup>-1</sup> [4].

### Thorium

The content of thorium in the mobile fraction varied from 1.1 to 7.3 mg kg<sup>-1</sup> in the samples collected in 2005 and from 0.71 to 6.7 mg kg<sup>-1</sup> in those collected in 2006. In the reference samples it was below 0.01 mg/kg in that from 2005, and 0.32 mg kg<sup>-1</sup> in that from 2006. The content of thorium in the acid-leachable fraction of the sediments was close to the total content of this element in the sandy sedimentary rocks established as 1.7-3.8 mg kg<sup>-1</sup> [4].

### Conclusions

Analysis of the above-presented results of the chemical composition of the tsunami sediment samples has indicated two tendencies. Samples 1 and 2 collected at the two sites in Patong Bay in 2005 were characterized by elevated contents of a number of elements, such as beryllium, gallium, rubidium, niobium, tin, caesium, the lanthanides, and bismuth. The corresponding samples collected at the same

sites one year later revealed much-reduced contents of these elements, most probably as a result of washing out in the rainy season. Another group of interesting samples were Nos. 2 and 15 collected in 2005, in which the elevated contents of ruthenium, rhodium, rhenium and platinum were determined. These samples were collected at two sites some distance apart: Patong Bay and Bang Mor, but they were morphologically similar – the sediment at both sites occurred in the form of very thick mud. Thus, similarity in the chemical composition can be expected for samples collected at close sites (the same area) and for samples of similar morphology.

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