

# Water quality studies in an aquatic environment of disused tin-mining pools and in drinking water

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## Abstract

Large areas of abandoned tin-mining pools have found secondary uses which provide natural habitats for aquaculture activities where most freshwater fishes are bred. Soils from tin-mining areas are rich in uranium and thorium. A study has been conducted on the status of waters and aquatic habitats in disused tin-mining pools and at water intake points for public drinking water supply to assess the presence of natural radionuclides and arsenic which are potential health hazards. The concentrations of uranium and thorium were determined by gamma spectrometry. Arsenic species were preconcentrated with ammonium pyrrolidinedithiocarbamate in chloroform and were later irradiated in a neutron flux of  $5.1 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  of a TRIGA Mk.II nuclear reactor to induce radioactivity due to the  $^{76}\text{As}$  radionuclide. The concentrations of uranium were found to be relatively lower than thorium whereas the As(III) species have almost similar concentrations with the oxidized form of As(V). The determination of radium from water samples taken from water intake points as well as treated water was done by co-precipitation separation with mixed barium carrier followed by reprecipitation using sulphuric acid. Results obtained showed that the average concentration of  $^{226}\text{Ra}$  for raw water is  $3.34 \text{ pCi l}^{-1}$  compared to about  $0.89 \text{ pCi l}^{-1}$  for treated water samples. These figures are well below the maximum permissible level of  $5 \text{ pCi l}^{-1}$  for drinking water. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The practice of open-cast and pit mining for tin has left large tracts of land with pools of immense

depths sometimes covering areas of more than 50 ha. Abandoned over long periods of time, these pools have found secondary land uses in the form of aquaculture and vegetable cultivation plots. Most tin-mining areas in Malaysia are rich in monazite and xenotime, the two minerals rich in natural radionuclides, particularly uranium, thorium and potassium. Rivers passing through these

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areas would carry in their load traces of these radionuclides plus a host of other toxic compounds such as the inorganic arsenic species, heavy metals and also radium. Most of these rivers are used as water intake points with the raw water treated later, prior to distribution to the consumers. Arsenic is not only toxic but also known to be carcinogenic and in the environment has both natural and anthropogenic origin. In the environment (La Touche and Mix, 1982), arsenic is found in minerals and ores, such as tin-ore, and could be released into the aquatic environment by dissolution and erosion. The levels of dissolved arsenic in unpolluted rivers are of the same magnitude as in seawater with a global average concentration of between 1 and 2  $\mu\text{g dm}^{-3}$  (Maher and Butler, 1988). Uranium and thorium present in the monazite- and xenotime-rich sand could enter the food chain in the aquatic system which involves the phytoplankton (algae), zooplankton (microorganism) and other aquatic life such as the species *Tilapia nilotica* and *Tilapia mossambica*, two types of freshwater fish commonly and abundantly found in disused mining pools. Radium is considered a Class A carcinogen by the Environmental Protection Agency (EPA) in the US and in 1976 the Safe Drinking Water Act (SDWA) has set a maximum contaminant level for combined  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  at 5 pCi  $\text{dm}^{-3}$ . Bio-accumulation of radium of the order of 100 has been observed in some aquatic organisms like the blue algae (Marple, 1980), and irrespective of biological necessity, plants have been observed to take up many cations, including radium, present in their root regions.

This study attempts to look at the distribution levels of various contaminants due to natural radioactivity and heavy metals in the waters of disused tin-mining pools and in river waters used for public drinking water. The determination of inorganic species present is often necessary in biological and environmental studies because they play toxic roles in living organisms, especially when they are passed on to human beings through the consumption of foodstuffs and drinking water. An evaluation of the water quality from prescribed sampling sites can be done based on the quantity of these contaminants present in the

water samples and compared to accepted standards.

## 2. Methods

### 2.1. Samples and standards

Water samples from disused mining pools were collected from seven different locations throughout the Malaysian peninsula, as shown in Fig. 1, with one location chosen as a control. Samples from water treatment plants were collected from 27 sampling sites chosen in the state of Johore, as depicted in Fig. 2, in an effort to evaluate the treatment process at the plants. The nature of activities in the vicinity of the reservoirs or rivers feeding the treatment plants has a profound effect on the arsenic and radium concentrations in the water samples depending on the locality of the raw water intake points. A 1.5 l polyethylene bottle was used to scoop water samples which were filtered through a 0.45  $\mu\text{m}$  Millipore membrane in a laminar flow hood to minimize external contamination. Preparation of samples for analysis was done within 72 h to avoid any changes in the metal species. Synthetic drinking water used as a reference sample was prepared by spiking with 100  $\mu\text{g dm}^{-3}$  of As(III) and As(V) each according to a prescribed method (Lo et al., 1982). To ensure minimum mineral contamination and loss of metal species from the water samples, all instruments and apparatus used in the sample collection and their manipulations prior to analysis were acid-washed and rinsed with doubly distilled water (DDW). Thorium ore SRM S-15 used in the determination of U and Th was obtained from the International Atomic Energy Agency (IAEA).

### 2.2. Reagents

All reagents were analytical-grade and purified prior to use. Concentrated hydrochloric acid (10 M) and nitric acid (16 M) were first distilled in a quartz still and aqueous stock solutions of As(III) and As(V) were prepared by first dissolving arsenic trioxide ( $\text{As}_2\text{O}_3$ ) in 1 M HCl and sodium



Fig. 1. Locations of disused tin-mining pools for water sampling.

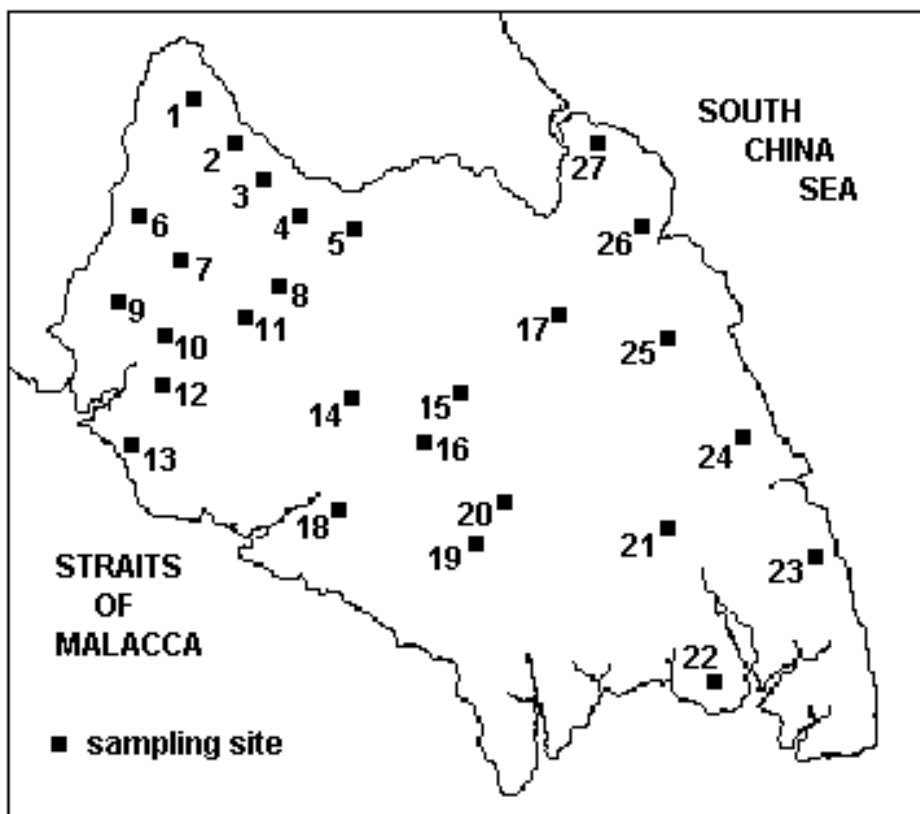


Fig. 2. Treatment plants for raw and treated water sampling.

arsenate ( $\text{Na}_2\text{AsO}_3$ ) in concentrated sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and subsequently diluted to the mark with DDW, respectively. The extracting solution of ammonium pyrrolidine-carbodithioate (APCDT) was purchased from Sigma (St. Louis, MO), the chloroform and sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) used in the extraction procedure was supplied by Fluka. Ethylene diaminetetraacetic acid (EDTA), obtained from Fluka, was used as a masking agent during the extraction step. Acetic acid (17.4 M), glacial acetic acid, ammonium sulphate, hydrated barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ), lead nitrate, sodium hydroxide (NaOH) and citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) used in the determination of radium were all obtained from Fluka.

### 2.3. Extraction and determination of arsenic species

Aliquots of at least 200 ml were needed in the extraction procedure. A fresh batch of APCDT solution was prepared by dissolving 5 g of the salt in 100 ml DDW. Insoluble materials were filtered off and bromine and other impurities removed by shaking with chloroform. A 1% solution of EDTA was prepared as the masking agent to enhance the extraction procedure. A first batch of 100 ml water sample to be used in the As(III) extraction was adjusted to pH 1.5 with 1 M  $\text{HNO}_3$ , followed by the addition of 2 ml of APCDT solution, 4 ml EDTA and 100 ml  $\text{CHCl}_3$  in an Erlenmeyer flask. The mixture was shaken

for 10 min with the aid of a mechanical wrist action shaker before being allowed to settle for 10 min for phase separation. The organic phase was washed several times with a 5 ml batch of DDW. Then 8 ml of the organic phase was transferred to a flask and 2 ml of 50% HNO<sub>3</sub> was added for back-extraction of the As(III) species. To achieve maximum extraction of the As(III) species, the procedure was formed four times and finally after phase separation 1 ml of the final solution was transferred into a flip-top polyethylene vials (10 mm × 20 mm) supplied by Olympia and heat-sealed for irradiation in the final determination of arsenic species. A second batch of 100 ml of water sample, adjusted to pH 1.0 with 1 M HNO<sub>3</sub>, was required in the As(V) species determination. The As(V) was reduced to the As(III) by the addition of 1 ml of 1% sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution followed by 1 min of shaking. The total As(III) formed was extracted using the same procedure described earlier for the As(III) extraction. The difference in the two As(III) concentrations represents the total As(V) in the water sample.

#### 2.4. Irradiation and counting

Special care was taken in sealing the vials since the liquid samples could leak out during the irradiation step. Irradiations were performed on 1 ml of the final extraction solution in a neutron flux of  $4 \times 10^{16} \text{ n m}^{-2} \text{ s}^{-1}$  for 6 h at 750 kW power from a TRIGA Mk.II reactor at the Malaysian Institute for Nuclear Technology Research (MINT) followed by 3 days of cooling. A large-volume coaxial HPGe detector with a resolution of 1.9 keV at 1332 keV <sup>60</sup>Co was used to count the 559 keV  $\gamma$ -rays of <sup>76</sup>As in the liquid samples over a period of 3600 s. Amplification and analysis of signals were done using an ADC ND592 (Nuclear Data) analyzer connected to a ND6000 (Nuclear Data) multichannel analyzer.

#### 2.5. Determination of uranium and thorium

About 50 ml of water samples previously filtered were placed in 150 ml polyethylene bottles and then sealed to prevent leakage of <sup>222</sup>Rn out of the container. The samples were left to equilibrate over

a period of 30 days for the <sup>238</sup>U and <sup>232</sup>Th progenies to reach equilibrium. To achieve uniform counting geometry, the polyethylene container was carefully positioned at the end-cap of a high resolution HPGe  $\gamma$ -ray detector and counted for 10 800 s. The efficiency of the detector was determined experimentally by using standard sources in the same counting geometry as the samples. The concentrations of <sup>238</sup>U were calculated from the net peak area of interest in the spectrum from the sample relative to the same peak area in the corresponding 353 and 609 keV peaks due to <sup>214</sup>Pb and <sup>214</sup>Bi, respectively, while for <sup>232</sup>Th from the 583 and 911 keV peaks due to <sup>228</sup>Ac and <sup>208</sup>Tl, respectively. Corrections for decay of the activity during the delay between the standard and sample counting intervals were done taking into account the dead times and background in the peak energy region of interest of the corresponding peaks.

#### 2.6. Determination of radium

Radium from water samples is normally extracted and the method for the determination of isotopic radium follows that given by Baratta and Herrington (1960), American Public Health Association (1965) and Milvy and Cothorn (1990). The water samples, acidified previously by adding 2 ml concentrated HNO<sub>3</sub>, were filtered using a 0.45  $\mu\text{m}$  Millipore membrane in a laminar flow hood. This was followed by the addition of 5 ml of citric acid, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> · H<sub>2</sub>O, 1 M and a few drops of methyl orange indicator for each batch of 1000 ml of water samples. The addition of a few drops of concentrated HNO<sub>3</sub> until the solution turns red is only necessary if the initial solution is yellow. About 1 ml of lead carrier and 2 ml of radium carrier was added to the solution before heating it to almost boiling for 30 min, followed by carefully adding 20 ml of 18 N H<sub>2</sub>SO<sub>4</sub> and stirring it for about 10 min. The mixture of barium and lead sulphate was allowed to settle overnight, decanted and the supernatant discarded. The precipitate formed was transferred to a centrifuge tube containing about 1 ml of 0.1 N H<sub>2</sub>SO<sub>4</sub> and centrifuged for about 5 min. The supernatant solution was discarded and the precipitate was dissolved in 15 ml of EDTA, heated in a water bath and followed by the addition of

drops of NaOH 6 N until a clear solution is obtained. About 1 ml of  $(\text{NH}_4)_2\text{SO}_4$  ( $200 \text{ mg ml}^{-1}$ ) was added to the solution and stirred thoroughly. Acetic acid solution ( $\text{CH}_3\text{COOH}$  17.4 N) was added dropwise until a precipitate appeared, followed by another 2 ml of the acetic acid solution and later left for about 5–10 min. The  $\text{BaSO}_4$  precipitate formed was separated by centrifuging the mixture and the time reading commenced. The precipitate was washed with 15 ml DDW, centrifuged and the supernatant discarded. It was later transferred to a stainless steel planchet, moistened with a little DDW and dried under infrared light before counting using a Canberra 2404 alpha scintillation counter for 3600 s.

### 3. Results

The seven tin-mining pools chosen as sampling sites are shown in Fig. 1, while the 28 water treatment plants and intake points scattered over an area of about  $18950 \text{ km}^2$  are shown in Fig. 2. Both raw and treated water samples were taken to evaluate the efficiency of the conventional treatment process in terms of reducing the  $^{226}\text{Ra}$  concentration. The concentrations of arsenic species, uranium and thorium in water samples, expressed in  $\mu\text{g ml}^{-1}$ , taken from mining pools are presented in Table 1. Data gathered from test runs on water samples spiked with standard As(III) and As(V) to ascertain the percentage recoveries of the arsenic species by APCDT- $\text{CHCl}_3$  extraction are shown in Table 2. The data gave both the recoveries with and without EDTA as the masking agent

at room temperature. Table 3 shows some water quality parameters and concentrations of  $^{226}\text{Ra}$  determined in raw and treated water samples taken from water treatment plants. The figures are expressed in  $\text{pg ml}^{-1}$  for the arsenic species and in  $\text{pCi l}^{-1}$  for the  $^{226}\text{Ra}$  to designate the total activities. Wherever applicable, the range of errors associated with the quantitative determination was illustrated in the same units used to express the concentrations of the species and metal.

### 4. Discussion

Most of the mining pools chosen for the determination of U, Th and the inorganic arsenic species were abandoned for more than 10 years and have been converted to secondary land uses such as fish breeding and other aqua-culture activities. The concentrations of the  $^{238}\text{U}$  were calculated from the 353 and 609 keV peaks of the  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ , respectively, while those of  $^{232}\text{Th}$  from the 911 and 583 keV due to  $^{228}\text{Ac}$  and  $^{208}\text{Tl}$  and these radionuclides were assumed to be in secular equilibrium with their corresponding decay products. Jagam et al. (1993) made use of the  $^{239}\text{Np}$   $\gamma$ -rays for  $^{238}\text{U}$  and after prolonged delay the  $\gamma$ -rays from  $^{233}\text{Pa}$  were used for the  $^{232}\text{Th}$  determinations. The reliability of the concentration data for  $^{238}\text{U}$  and  $^{232}\text{Th}$  was checked against a thorium ore SRM S-15 supplied by IAEA where the concentrations were expressed in wt.% for Th and  $\mu\text{g g}^{-1}$  for U and excellent agreement was obtained using the relative method for counting the samples.

Table 1  
Concentrations of As(III), As(V), uranium and thorium in water samples from mining pools

Site	pH	Temperature ( $^{\circ}\text{C}$ )	As(III) ( $\text{pg l}^{-1}$ )	As(V) ( $\text{pg l}^{-1}$ )	As(III)/As(V)	U ( $\mu\text{g l}^{-1}$ )	Th ( $\mu\text{g l}^{-1}$ )
1	7.54	30.5	$44.2 \pm 5.90$	$221.0 \pm 5.90$	0.20	$27.7 \pm 1.00$	$41.8 \pm 5.50$
2	7.30	29.0	$157.3 \pm 20.2$	$557.0 \pm 77.1$	0.28	$84.7 \pm 9.55$	$179.1 \pm 15.9$
3	7.54	30.3	$731.0 \pm 50.3$	$1017 \pm 41.5$	0.72	$39.0 \pm 2.90$	$88.5 \pm 5.00$
4	7.33	30.5	$255.8 \pm 31.0$	$235.5 \pm 23.3$	1.09	$41.7 \pm 6.70$	$114.6 \pm 15.0$
5	6.80	31.7	$689.3 \pm 66.0$	$595.0 \pm 45.2$	1.16	$110.5 \pm 9.00$	$297.2 \pm 32.0$
6	7.50	30.3	$238.1 \pm 34.3$	$2320 \pm 59.0$	0.10	$44.8 \pm 5.75$	$95.3 \pm 10.6$
7	7.65	29.0	$170.7 \pm 19.5$	$1115 \pm 120$	0.15	ND <sup>a</sup>	ND

<sup>a</sup> ND, not detectable.

Table 2

Percentage recoveries of APCDT-CHCl<sub>3</sub> extraction of As(III) and As(V) with and without EDTA

Sample	As(III) added ( $\mu\text{g l}^{-1}$ )	As(V) added ( $\mu\text{g l}^{-1}$ )	% recovery of As(III)	% recovery of As(V)
Seawater <sup>a</sup>	100	100	71.5 $\pm$ 1.7	75.5 $\pm$ 1.9
Well-water <sup>a</sup>	100	100	79.8 $\pm$ 1.8	87.9 $\pm$ 2.0
Seawater <sup>b</sup>	100	100	100.7 $\pm$ 2.5	96.5 $\pm$ 2.2
Well-water <sup>b</sup>	100	100	101.3 $\pm$ 2.7	98.7 $\pm$ 2.3

<sup>a</sup> Without EDTA, at room temperature.<sup>b</sup> With EDTA, at room temperature.

The extraction procedure used in this work to separate the inorganic arsenic species from natural waters was found to be effective, as depicted by the percentage recoveries in Table 2. The percentage recovery for standard As(III) species was 100.6% and is comparable to 100.4% obtained in another study by Yusof et al. (1994) and 102.2% by Subramaniam et al. (1984). This method enabled the elimination of interfering alkali metals especially <sup>23</sup>Na, and halogens, especially <sup>81</sup>Br. Both produce high-intensity  $\gamma$ -peaks from the <sup>24</sup>Na and <sup>82</sup>Br that results from the high neutron capture cross-sections during the irradiation step. With the elimination of bromine, possible overlapping of the 556 keV peak from <sup>82</sup>Br on the 559 keV peak from <sup>76</sup>As is overcome. The presence of other metal ions such as Pb<sup>2+</sup>, Cu<sup>2+</sup>, Sn<sup>2+</sup> and Sn<sup>4+</sup> which could affect the degree of extraction of As(III) with the dithiocarbamate due to competitions by these ions was eliminated by using EDTA as the masking agent. The As(III) is readily extractable from the aqueous solution compared to the As(V) species, hence it was more effective to reduce the As(V) to its lower oxidation state of As(III) using a suitable reducing agent such as Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, followed by extraction of the total As(III). The difference in the As(III) concentrations from the two water sample aliquots constitutes the As(V) present.

The efficiency of <sup>226</sup>Ra detection using the Canberra 2404 alpha scintillation counter was performed with UO<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O as the reference materials. It was found that the counting efficiency was about 10.03% and this figure was used throughout the work in the determination of <sup>226</sup>Ra through the short-lived radon progeny energies of 295 and 352 keV of <sup>214</sup>Pb and 609 keV of

<sup>214</sup>Bi. In line with the requirements set by most countries in the world and also the criteria set by the World Health Organization and USEPA Report (1976), the maximum permissible level for radium in drinking water is 5 pCi l<sup>-1</sup>; hence all figures for <sup>226</sup>Ra concentrations are expressed in pCi l<sup>-1</sup>.

There is little variation in the temperature range recorded for water samples taken from mining pools but changes in the pH values would show some impacts on the quantity of dissolved uranium and thorium contents. This was evident in water samples taken from location 5, which showed a relatively low pH value of 6.80 compared to the rest of the samples with pH values ranging from 7.33 to 7.65. The high concentration of U (110.5  $\pm$  9.00  $\mu\text{g l}^{-1}$ ) and Th (297.2  $\pm$  32.0  $\mu\text{g l}^{-1}$ ) as compared to the rest of the samples ranging from 27.7  $\pm$  91.00 to 84.7  $\pm$  9.55  $\mu\text{g l}^{-1}$  for U and from 41.8  $\pm$  5.50 to 179.1  $\pm$  15.9  $\mu\text{g l}^{-1}$  for Th illustrated this phenomenon very well. Depending on the locations and the average pH of about 7.30–7.50, the amount of U and Th in the water samples remains the same. In fact, at a much higher pH value, as indicated by water samples taken at site 7, the amount of dissolved U and Th would seem negligible.

The overall concentrations of the inorganic arsenic species in water samples taken from mining pools range between a minimum of 265.2 pg l<sup>-1</sup> to a maximum of 2558.1 pg l<sup>-1</sup> that is between 0.265 and about 2.26  $\mu\text{g l}^{-1}$  and the average total inorganic arsenic for most surface waters is about 1.0  $\mu\text{g l}^{-1}$  (Wedepohl, 1978). In this study only three sites (5, 6, and 7) recorded total arsenic concentrations exceeding 1.0  $\mu\text{g l}^{-1}$  and this reflected the nature of the soil in these particular

areas as compared to the others. In terms of inorganic arsenic contents related to water quality, and under normal circumstances of an aquatic environment, the As(V) concentrations would far exceed the As(III) concentrations. However, several factors, such as the external introduction of arsenic species from the surrounding areas where the sites are located, competing processes which can modify the concentrations of the arsenic species in natural waters, such as lack of oxygen since most of the pools have depths of more than 30 m, leading to a low oxidizing environment and would shift the As(III)/As(V) ratio from less than 1.0 for a normal condition to more than 1.0 as illustrated by sites 4 and 5. The shift from a more dominant As(V) to one which is more dominant in As(III) can be found in certain reduced environments

especially for water samples taken from deep wells or from surface waters of tropical gyres where the high internal cycling of phosphorous-based compounds inputs results in the rapid uptake of As(V) by phytoplanktons in the warm waters and its excretion it as the As(III) reduced species (Andreae, 1986). Sites 4 and 5 could be comparable to a rather confined water body with little or no flow, thus depriving the aquatic environment of oxygen required to sustain life. In terms of water quality the dissolved oxygen in waters taken from these sites is relatively low, thus providing an environment not suitable for the formation of the more stable higher oxidation state of As(V). It can be inferred that water samples with As(III)/As(V) ratios of less than unity originate from a normal surface water environment suitable for aquatic life.

Table 3

Water quality data and  $^{226}\text{Ra}$  activities for raw and treated water samples taken from treatment plants

Site	Raw water samples			Treated water samples			Source
	pH	Temp. (°C)	$^{226}\text{Ra}$ act. (pCi l <sup>-1</sup> )	pH	Temp. (°C)	$^{226}\text{Ra}$ act. (pCi l <sup>-1</sup> )	
1	5.8	26.0	2.20 ± 0.27	7.1	26.4	0.44 ± 0.03	River
2	7.2	25.4	3.53 ± 0.44	7.2	25.5	0.22 ± 0.02	River
3	7.2	26.2	2.91 ± 0.33	7.2	26.5	0.48 ± 0.05	River
4	6.7	26.8	3.35 ± 0.33	7.1	26.4	0.04 ± 0.01	River
5	7.0	23.4	4.23 ± 0.38	7.2	25.3	0.71 ± 0.06	River
6	6.1	27.1	2.86 ± 0.22	7.1	27.1	0.22 ± 0.02	Reservoir
7	6.8	25.6	3.08 ± 0.36	7.4	26.8	0.88 ± 0.05	River
8	6.8	24.8	4.40 ± 0.37	7.0	25.0	0.88 ± 0.07	River
9	6.5	25.1	3.75 ± 0.38	6.8	24.0	0.88 ± 0.07	River
10	6.8	26.5	2.86 ± 0.25	7.0	26.5	0.66 ± 0.06	River
11	7.1	24.8	3.52 ± 0.32	7.3	25.4	0.22 ± 0.02	River
12	6.0	27.2	1.98 ± 0.18	6.8	26.8	0.66 ± 0.05	Reservoir
13	5.7	27.2	4.63 ± 0.38	7.0	25.0	0.44 ± 0.03	River
14	6.8	27.4	2.51 ± 0.22	6.8	27.4	0.53 ± 0.03	River
15	7.5	25.5	4.19 ± 0.39	7.5	26.0	1.32 ± 0.09	River
16	6.7	26.6	3.31 ± 0.39	7.0	26.4	0.66 ± 0.05	River
17	7.4	25.8	3.31 ± 0.29	7.8	27.5	2.20 ± 0.19	River
18	5.8	24.8	3.39 ± 0.27	6.8	25.8	1.19 ± 0.15	River
19	6.2	26.2	4.41 ± 0.38	6.2	26.0	0.44 ± 0.04	River
20	7.0	26.2	3.44 ± 0.33	7.5	26.5	0.57 ± 0.04	River
21	7.3	25.4	2.56 ± 0.28	7.3	26.0	0.13 ± 0.02	River
22	6.2	24.5	4.89 ± 0.49	6.8	25.3	0.71 ± 0.05	Reservoir
23	6.0	26.9	4.09 ± 0.37	6.5	27.0	1.45 ± 0.01	River
24	6.2	24.4	3.44 ± 0.39	7.0	25.5	1.01 ± 0.08	River
25	6.8	25.1	3.66 ± 0.43	7.0	25.5	0.79 ± 0.03	Mining pool
26	6.0	26.2	2.56 ± 0.36	6.5	23.5	0.57 ± 0.04	Reservoir
27	6.1	27.3	1.01 ± 0.09	6.6	27.4	0.35 ± 0.03	Reservoir



The maximum contaminant level for combined  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  set for drinking water is  $5 \text{ pCi l}^{-1}$  (USEPA Report, 1976), but it does not specify time or location of sample collection for radionuclides. However, in general radon formation from  $^{226}\text{Ra}$  exists in water distribution systems exposed to radium bearing water (Valentine and Stearns, 1994). This same setting is found in areas where the water intake points are from rivers and reservoirs as observed in this study. There may not be a major deposit sources but the general terrain of the Malaysian Peninsular, which consist mostly of granitic rocks may still because to radon release through the dissolution of  $^{226}\text{Ra}$  in river waters flowing through these rocks and fissures. Even though it may affect a small fraction of the population, the importance must be gauged by the proposed maximum contamination level (MCL) of  $5 \text{ pCi l}^{-1}$  for drinking water which has the tendency to accumulate and with time could exceed the MCL. From Table 3 it was observed that all the 27 treatment plants where raw and treated water samples were taken showed activities of  $^{226}\text{Ra}$  to be less than  $5 \text{ pCi l}^{-1}$ . Initially the  $^{226}\text{Ra}$  activities seemed comparatively higher in the raw water samples, but after treatment using the normal treatment process, the levels were brought down to as much as 10% of the original activities. It was observed that water samples taken from reservoir exhibited much lower levels of  $^{226}\text{Ra}$  compared to those originating from rivers. It was thought that the suspended particles in the water column incorporating the  $^{226}\text{Ra}$  would have ample time to settle to the bottom of the reservoir, thus leaving less total suspended particulate in the surface water. Raw water treated using the conventional method of flocculation should serve as an efficient means in eliminating the  $^{226}\text{Ra}$  trapped in the suspended particulates in the water column.

## 5. Conclusion

Some of the results presented in this study reflect the suitability and efficiency of certain analytical techniques used in the quantitative analysis, namely separation as in the case of inorganic

arsenic and  $^{226}\text{Ra}$  determination; neutron activation analysis to determine the inorganic arsenic species using the 559 keV  $\gamma$ -peak of  $^{76}\text{As}$  and alpha spectrometry to calculate the  $^{226}\text{Ra}$  activity. The efficiency of the separation process was also evaluated using spiked standards for As(III) and As(V) and the method proved to be useful in low levels arsenic species determination. Water quality for water samples taken from different aquatic environments was also examined by assessing the concentrations of dissolved species, which was also used as an indicator of the redox status of the water bodies. Finally health hazards related to radiation exposure were also investigated by assessing the  $^{226}\text{Ra}$  levels in raw and treated drinking water. Conclusions were drawn from all the observations to address issues pertaining to water pollution in different aquatic environments. Speciation studies can be extended to include quantitative determination of other toxic species such as methyl mercury and this could be critical to public drinking water quality assurance in view of pollution from point sources and non-point sources.

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