Bull Environ Contam Toxicol (2009) 82:384–388
DOI 10.1007/s00128-008-9621-4

Determination of Toxic Trace Elements in Foodstuffs, Soils and Sediments of Bangladesh Using Instrumental Neutron Activation Analysis Technique

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Received: 12 December 2007 / Accepted: 11 November 2008

Abstract The concentrations of arsenic (As), chromium (Cr) and iron (Fe) were determined in the foodstuffs, soils and sediments from various areas in Bangladesh and new data for these toxic trace elements were given. The arsenic pollution problems in the most of the areas of Bangladesh are of geological origin. The high level of As in foodstuffs, soils and sediments, except for tannery sediments is probably positively correlated to the Fe concentration. An excessive amount of chromium was found in the sediments from the tannery area of Bangladesh.

Keywords As, Cr, Fe contamination · Foodstuffs · Soils · Sediments · Research reactor

Environmental pollution in Bangladesh has been becoming worse day by day. The ground water of many countries is contaminated with arsenic (As). Smedley and Kinniburgh (2002) reported that the scale of problem in terms of the population exposed to high As concentration is the greatest in the Bengal Basin, where more than 40 million people are drinking water with an excessive As concentration. The arsenic contamination of ground water has now become a serious threat to public health in Bangladesh, as over 97% of its population is dependent upon ground water for drinking purposes (Ahmed 2002). Ground water is free from bacteria and it does not need any treatment whereas the surface water needs to be boiled for drinking. Until the discovery of arsenic in the ground water, tube-well water was recommended as being safe for drinking but now the tube-well water in the most of districts in Bangladesh is highly polluted with arsenic. There is a great possibility that contamination of vegetables and crops is occurring as the water containing arsenic is used for their cultivation. The elevated concentration of As found in the groundwater of Bangladesh used for drinking purposes is of geological origin. Unfortunately the cause of ground water arsenic contamination in Bangladesh has not yet been clearly detected. Frisbie et al. (2002) reported that the most significant health risk from drinking water from tube-wells in Bangladesh is chronic arsenic poisoning. Furthermore, their study also revealed the unsafe concentrations of manganese (Mn), lead (Pb), nickel (Ni) and chromium (Cr) in the water.

There is a great chance of chromium contamination in the tannery industrial areas of Bangladesh. The chromium is a toxic element and it causes adverse effects on human health. Long-term exposure to arsenic via drinking water causes cancer of the skin, lungs, urinary bladder and kidney, as well as other skin changes such as pigmentation changes and thickening. In order to prevent millions of people from being attacked by developing the different types of cancer associated with these pollutants, their sources must be determined, especially for the As in the groundwater of Bangladesh. To assess the potential sources, particularly of As, a parallel study of ground water, surface water, foodstuffs, sediments and soils was conducted.

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Though field test kits can detect high levels of As in ground water but they are typically unreliable for assessing the lower concentrations of concern that affect human health nor can they detect As in foodstuffs, soils and sediments. Moreover, reliable arsenic pollution data are needed in order to designing of arsenic mitigation techniques. Calorimetric and gravimetric methods can be used for the determination of As levels, but these methods are either semi-quantitative or lack sensitivity. In recent years, AAS and ICP-MS have been used for the determination of As and Cr levels, as they offers very high sensitivity but both methods are very expensive.

Instrumental neutron activation analysis (INAA) is one of the most extensively used methods for environmental studies due to its high sensitivity, precision, versatility and multi-elemental character. Latif et al. (2002) showed that the level of As can be easily determined in the ground water of Bangladesh at ppb levels using INAA. In continuation of that research work in this study the INAA method has been applied to determine the levels of toxic trace elements (As and Cr) in foodstuffs, soils and sediments of Bangladesh. In addition, the concentrations of Fe in these earlier mentioned materials was determined so as to see if there might be any correlation with the toxic element As.

Materials and Methods

The environmental samples (foodstuffs, soils and sediments) were collected from different areas of Bangladesh. The foodstuffs grown with tube-well water as well as samples of the same tube-well water were collected for comparison. The foodstuffs, soils and sediments were collected in polyethylene bags, which were previously cleaned with dilute nitric acid, pure water, acetone, and then dried. The foodstuffs were weighted using a micro-balance and then dried at 60°C for 30 h. The soil and sediment samples were at first naturally dried at room temperature in a clean room. The samples were then dried in an oven at 50°C for 7 days. The samples were then crushed into a 200 microns particle size powders in an agate mortar. About 50 mg of each sample was put in the clean polyethylene bags and the bags were doubly heat-sealed, and used it for the purpose of irradiation. About 50 μL of each chemical standard (As, Cr and Fe) was absorbed on the five folds of filter paper (Advantec (5A) ≅ 1.0 cm diameter) and then completely dried under room temperature. It was then put in polyethylene bags for irradiation. For the quality assurance of the analytical process about 50 mg of International Atomic Energy Agency (IAEA) certified reference materials (CRM) IAEA-soil-7, soil-5 and Lake sediment, SL-1 were also put in polyethylene bags for irradiation.

The samples and standards were simultaneously irradiated using the 3.5 MW research reactor, JRR-4 at the Japan Atomic Energy Agency (JAEA). The irradiations were performed at the TB pipe for 20 min. At the irradiation position the thermal neutron flux was 5.3×10^{13} n cm^{-2} s^{-1}.

After irradiation the cover bag was removed and the radioactive sample-containing bag was again covered with a new clean polyethylene bag in order to avoid contamination during gamma-ray measurements. The activities of the irradiated samples and standards were measured non-destructively using a high purity germanium (HPGe) detector coupled with a pulse-height multi-channel (4,096 channels) analyzer. The γ-rays emitted from both the samples and standards were measured at the same geometry. The dead time of the detector was kept below 3%. The cooling time was 72 h for the measurement of γ-rays emitted from ^{76}As and 15 days for ^{51}Cr and ^{59}Fe. The counting time was around 4,000 s for As and 12–24 h for Cr and Fe. Target and daughter nuclides, as well as other nuclear data pertinent to this study are listed in Table 1. In this study the elemental concentrations in the environmental samples were calculated using the comparative method.

Results and Discussion

Using the INAA technique the level of arsenic is determined by measuring the gamma-rays from the decay of ^{76}As, which is produced by the radiative neutron capture reaction, ^{75}As (n, γ)^{76}As. As ^{76}As can also be produced by ^{79}Br (n, α)^{76}As if bromine is present in the sample. To evaluate this possible interference effect we performed a simultaneous experiment with a potassium bromide (KBr) solution. The peak at 559 keV was not observed due to the

Table 1 Decay data for the investigated radionuclides and contributing reactions

Element	Isotopic abundance (%)	Contributing reaction	Cross section (barn)	Half-life	γ-ray energy (keV)	Branching ratio (%)
As	100	^{75}As(n, γ)^{76}As	4.5	26.30 h	559	45.0
Cr	4.35	^{50}Cr(n, γ)^{51}Cr	15.8	27.70 days	320	10.1
Fe	0.28	^{58}Fe(n, γ)^{59}Fe	1.28	44.51 days	1,099	56.5

^{79}Br(n, α)^{76}As reaction. But the peak at 559 keV for arsenic was well resolved.

The γ-rays emitted from ^{51}Cr at 320 keV were not interfered by other short-lived radioactive nuclides since the samples were measured after a long (15 days) cooling time. But ^{51}Cr can also be produced via the ^{54}Fe (n, α)^{51}Cr reaction in the sample. To evaluate this interference effect a simultaneous experiment with an iron (chemical) standard was performed. The typical γ-ray spectrum of the iron (chemical) standard is shown in Fig. 1 and there is no peak at 320 keV, which indicates that the ^{54}Fe(n, α)^{51}Cr reaction did not occurred in the present experiment.

The detection limit of an element depends on the matrix compositions and the amounts of the element present in the matrix. The most easily controlled parameter that influences the detection limit is the counting time. Indeed, it is important to maximize the peak-to-background ratio, the net counting rate in the peak, and the counting time to achieve the lowest detection limits. In this study, the detection limits for arsenic and chromium using INAA were determined. The detection limits were calculated for a sample size (soil) of 50 mg, using a typical sample spectrum. The actual detection limits were calculated as three times the standard deviation of the background count (3σ) in the region corresponding to the γ-ray lines of the specified elements. The detection limits determined for arsenic and chromium in the soil samples were 0.34 and 1.0 µg/g, respectively.

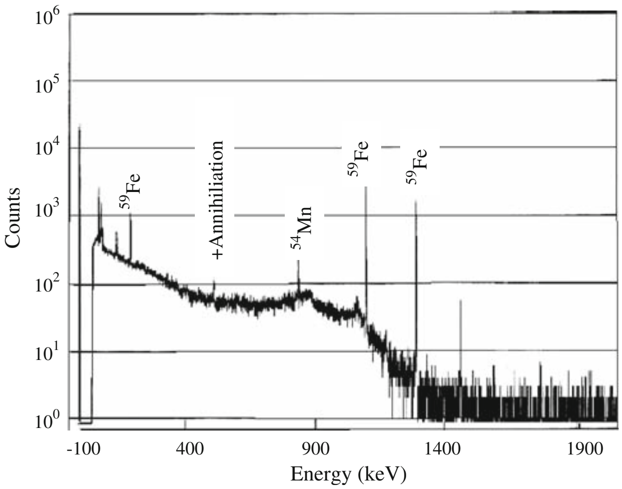

Fig. 1 Typical gamma-ray spectrum of an iron (chemical) standard

In order to evaluate the accuracy of this method three IAEA certified reference materials, IAEA-CRM-soil-7, soil-5 and SL-1 were analyzed. The analytical results are shown in Table 2. The measured concentrations of arsenic in the IAEA certified reference materials (soil-5, soil-7 and SL-1) are very consistent with the certified values. The measured concentration of chromium in the IAEA-CRM-soil-5 is deviated 4.6% from the certified value. The difference between measured chromium concentration and certified value for IAEA-CRM-soil-7 was significantly large (±17.7%). The range of Cr concentrations in IAEA-CRM-soil-7 was 49-74 µg/g. The measured concentration of the Cr in the lake sediment of IAEA-CRM-SL-1 is deviated 10% from the certified value.

The concentrations of the toxic trace elements- arsenic and-chromium in the soils and sediments collected from different areas of Bangladesh were determined using INAA and the obtained results are shown in Tables 3 and 4. The concentration of As in agricultural surface soils collected from Bailjuri, Gheore, Manikgong is very high (83.3 µg/g). This high concentration of As may be due to the direct exposure of the shallow tube well water, which is used for the purpose of cultivation. A high concentration level (168 µg/g) of As was also obtained from one of the sediments collected from the tannery area in Dhaka. This high level of As may be due to the anthropogenic contamination. An excessive amount (15,295 µg/g) of Cr was found in one of the sediments collected from the tannery area of Dhaka. The elevated level of Cr is probably due to the anthropogenic contamination because the tannery industry uses huge amounts of Cr salts for leather processing. The effluents that directly come from the tannery industry go directly to the sewage system and thus contaminate the environment. It is observed that the concentrations of As in the soil and sediment of the investigated areas of Bangladesh are very high compared to the uncontaminated soils of the different countries of the world (Shacklette and Boerngen 1984; Sadler et al. 1994; Nakadaira et al. 1995; Temple et al. 1977; Amonoo-Neizer et al. 1988; Ismael and Roberts 1992; Harako 1986; Chutke et al. 1995; Merry et al. 1983; Chang et al. 1999; Steinne et al. 1989; Esser 1996; Sanok et al. 1995; Merwin et al. 1994; Table 4).

Table 2 Comparison of elemental concentrations (in µg/g) determined in this study with certified values

Element	IAEA-CRM-soil-5			IAEA-CRM-soil-7			IAEA-CRM-SL-1		
	This study	Certified values	RSD (%)	This study	Certified values	RSD (%)	This study	Certified values	RSD (%)
As	91.9 ± 3.5	93.9 ± 7.5	2.05	13.2 ± 0.5	13.4 ± 0.9	1.29	27.7 ± 1.1	27.5 ± 2.9	0.77
Cr	30.2 ± 0.6	28.9 ± 2.8	4.6	70.6 ± 0.9	60.7 ± 1.8	17.7	114 ± 1.5	104 ± 9	9.6
Fe	41,260 ± 311	44,500 ± 1900	7.3	22,611 ± 176	25,700	12	58,848 ± 466	67,400 ± 1,700	12.7

Table 3 Measured concentrations of As, Cr and Fe in soils and sediments

Sl. no.	Sample name (depth, cm)	Location	Concentration (μg/g)		
			As	Cr	Fe
1	Soil (50)	Madhupur Tanghil	12.73 ± 0.3	112.5 ± 1.5	46,770 ± 388
2	Soil (200)	AERE, Savar, Dhaka	11.4 ± 0.3	125.2 ± 2.0	49,623 ± 490
3	Soil (surface)	Bailjuri, Gheore, Manikgang	83.3 ± 5.5	123.9 ± 1.6	45,627 ± 350
4	Soil (150)	Bailjuri, Gheore, Manikgang	31.8 ± 5.1	65.3 ± 1.7	29,061 ± 299
5	Soil (300)	Bailjuri, Gheore, Manikgang	19.4 ± 1.7	101.7 ± 2.1	28,266 ± 317
6	Pond sediment	Bailjuri, Gheore, Manikgang	40.2 ± 2.7	104.2 ± 1.4	39,047 ± 306
7	River sediment	Isamoti, Gheore, Manikgang	3.5 ± 0.4	84.7 ± 2.0	32,956 ± 372
8	Sediment	Tannery area, Dhaka	4.5 ± 0.4	15,295 ± 156	27,356 ± 658
9	Sediment	Tannery area, Dhaka	168 ± 9	107.4 ± 5.6	27,520 ± 502
10	Sediment	Tannery area, Dhaka	33.3 ± 2.8	217.6 ± 4.8	26,484 ± 483

Table 4 Measured concentrations of As, Cr and Fe in foodstuffs

Sl. no.	Sample name	Location	Concentration (μg/g)		
			As	Cr	Fe
1	Arum (root)	Panti, Muradnagar, Comilla	8.2 ± 1.1	1.8 ± 0.1	820 ± 12
2	Arum (trunk)	Panti, Muradnagar, Comilla	8.0 ± 0.3	1.4 ± 0.1	561 ± 10
3	Kalmilata (root)	Panti, Muradnagar, Comilla	5.0 ± 0.2	0.6 ± 0.05	264 ± 5
4	Kalmilata (trunk)	Panti, Muradnagar, Comilla	29.6 ± 1.3	19.1 ± 0.7	9,317 ± 135

The concentrations of As in the investigated foodstuffs collected from the Comilla district are very high as quoted in Table 4. This may be due to the direct exposure of the tube well water, which is also contaminated with a very high amount of arsenic. In most soil samples the elevated levels of As are positively correlated with Fe. In pond and river sediments As is also positively correlated with Fe but in tannery sediments it is varied. So the As concentrations in tannery sediments may be due to anthropogenic contamination. Thus there is no systematic correlation between As and Fe concentrations. However, in the case of foodstuffs As is positively correlated with Fe.

Conclusions

This study reveals that foodstuffs, soils and sediments from the different investigated areas of Bangladesh are highly contaminated with arsenic. A high concentration of arsenic was detected in one agricultural surface soil sample from the Manikgong district. It may have been due to its direct exposure to the shallow tube well water. An excessive amount of chromium was measured in the sediments from the tannery areas of Bangladesh that indicates these areas are polluted by it. From this preliminary study we can conclude that the arsenic pollution problem in most areas of Bangladesh is of geological origin. This study also shows that the higher levels of As in foodstuffs, soils and sediments, except for the tannery sediment samples, are positively correlated with the Fe concentrations. The quality assurance tests indicate the reliability of the analysis.

Acknowledgments The authors are grateful to Mr. Damien Andrews from Australia for his effort to improve this manuscript by checking English grammar and syntax. The authors wish to thank the reactor operations staff for performing irradiation at research reactor JRR-4 of the Japan Atomic Energy Agency (JAEA). The authors are highly grateful to Dr. Haruka Minowa of the Radioisotopes Research Facility, Research Center for Medical Science, Jikei University School of Medicine, Minato-ku, Tokyo, Japan for her kind cooperation during the experiment.

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