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Uranium isotope ratios in the environmental samples collected after a criticality accident in the uranium conversion facilities of JCO

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Abstract

Soil and botanical (grass and leaf) samples collected inside and in the vicinity of the uranium conversion facilities, in which a critical accident occurred on September 30, 1999, were analyzed for uranium concentration and $^{235}\text{U}/^{238}\text{U}$ isotope ratio by inductively coupled plasma mass spectrometry. Extractable uranium showed high $^{235}\text{U}/^{238}\text{U}$ ratios in contrast to uranium in the silicate fractions which had the natural isotope ratio. One of the leaf samples gave the highest $^{235}\text{U}/^{238}\text{U}$ ratio of 2.2 which limits the minimum isotope ratio of the contaminant. The impact of the enriched uranium was estimated using the observed $^{235}\text{U}/^{238}\text{U}$ ratios and uranium concentrations by assuming the mixing of two components (natural and enriched uranium). The impact systematically increased with decreasing distance of the sampling site from the laboratory where the accident occurred, providing a clue to source identification of the enriched uranium. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: ICP mass spectrometry; Uranium-235; Isotope ratio; JCO criticality accident; Tokai-mura; Environmental samples

1. Introduction

A criticality accident occurred on September 30, 1999 at the uranium conversion facilities of JCO Co. Ltd. (Tokai Plant, Tokai-mura, Japan; JCO hereafter). The outline of the accident was reported by the IAEA (1999) and urgent recommendations were issued by the Nuclear Safety Commission of Japan (1999). An excessive amount

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of uranyl nitrate solution (about 16.6 kg U) prepared from enriched uranium oxide (18.8% enrichment) was added to a precipitation tank causing criticality (Nuclear Safety Commission, 1999). The Citizens' Nuclear Information Center, 1999 also reported in a scientific journal from the viewpoint of nuclear safety. A collaborating scientific investigation team was organized and started collection and analysis using common samples (Sakanoue, 1999). In the course of the initial measurements, the emission of fission products and their daughters (^{131}I , ^{133}I , ^{134}Cs etc.) and in situ neutron activation (^{24}Na , ^{46}Sc , ^{198}Au , etc.) were observed (Sakanoue, 1999). The exhaust of the ventilation system from the uranium conversion building where the criticality accident took place was sealed and a charcoal filter was fitted in order to prevent gaseous radionuclides from spreading outside (Nuclear Safety Commission, 1999). Before this treatment, particulate matter should have been trapped on the HEPA filters fitted on the exhaust and only volatile substance should have been discharged through them.

In the past, when radioactive releases have occurred in related circumstances, uranium isotope ratios as well as ^{99}Tc , ^{236}U and ^{237}Np have been monitored in water samples, e.g. around a nuclear facility where radioactive waste had been discharged into an aquifer (Beasley, Dixon & Mann, 1998). ^{137}Cs and ^{90}Sr were utilized to estimate the impact caused by an accident involving stack-discharge of irradiated uranium (Chamberlain, 1987). The material used at the accident in JCO was uranium oxide containing moderately enriched uranium (18.8% ^{235}U) and the uranium isotope ratio must be a good indicator by which to judge whether or not particulate matter was emitted from the building.

Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive and rapid elemental and isotopic analytical method and has been applied to the determination of long-lived radionuclides such as Pu (Muramatsu, Uchida, Tagami, Yoshida and Fujikawa, 1999), U, Th, (Becker, Dietze, McLean and Montaser, 1999), ^{99}Tc (Becker & Dietze, 1999) and ^{129}I (Farmer III, Barinaga & Koppelaar, 1998). The typical precision of isotope measurement by an ICP-MS fitted with a quadrupole mass filter (ICP-QMS) is worse than 0.1% but the sensitivity and precision can be improved by using a sector-type ICP-MS (Becker & Dietze, 1999). In this study, environmental (soil and plant) samples were analyzed for uranium and its isotopic ratio by ICP-QMS in order to monitor rapidly the status around JCO and the impact of enriched uranium in the aftermath of the criticality accident.

2. Materials and methods

2.1. Samples

Surface soil samples were collected from unoccupied land adjacent to JCO, in the southwest direction from the uranium conversion building, on October 5 (8 m-1 and 20 m) and 26 (8 m-2, 50 m, 100 m and 200 m), 1999. Each sample name indicates the distance in meters from JCO (Fig. 1). A grass sample was also collected from the same area. Soil samples, which were collected from the JCO campus on October 26, 1999,

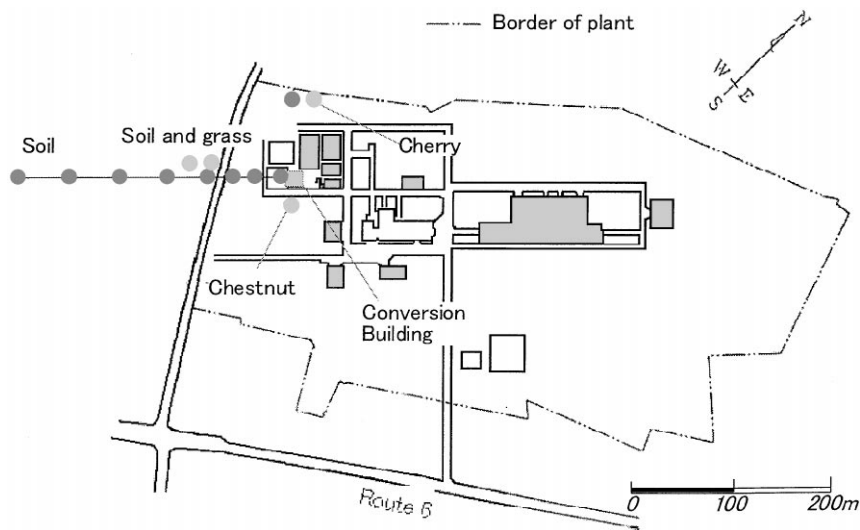


Fig. 1. Sampling locations of soil and botanical samples and border of JCO. Nuclear fuel processing buildings are shaded.

were provided to us after gamma-ray spectrometric measurements. Three samples that lay on the same line as the outside samples and one in the northwest direction were selected for analysis. The leaves of two deciduous trees (chestnut and cherry) growing on the JCO campus were sampled. Rock reference materials produced at the Geological Survey of Japan (JA-1, JB-1a, JG-1a and JR-1) and chestnut and cherry leaves collected at the National Institute for Environmental Studies (NIES), which is located 60 km southwest of JCO, were also analyzed as control samples.

2.2. Analytical Procedures

Sequential extraction procedures were applied to the soil samples from outside JCO in order to distinguish the features of uranium binding to the soil particles. The extraction procedures were as follows: Step 1; ultrasonification with water for 10 min at room temperature: step 2; ultrasonification with 0.1 mol/l nitric acid for 10 min at room temperature: step 3; extraction with 2 mol/l nitric acid for 2 h at 120°C: step 4; decomposition with a mixture of nitric acid and hydrofluoric acid at 140°C. Step 3 alone was applied to the soil samples from the JCO campus and step 2 was applied to the grass and leaf samples. Extracts and digests were centrifuged (2500 rpm, 20 min) and filtered through a disposable membrane filter (0.45 µm pore size, Sartorius, Minisalt) prior to the measurements. Purified water (Millipore, Milli-Q SP-TOC or SP ICP-MS) was used throughout the experiments. All acids used were of analytical grade (Kanto Chemicals, electronics industry grade or ultrapure grade). Beakers used for the hot extractions were made of Teflon and sample tubes were pre-washed with nitric acid and rinsed thoroughly with purified water.

2.3. Isotope measurements

Uranium isotopes of mass 235 and 238 were measured by ICP-QMS (Agilent Technologies, HP4500). The integration times for m/z 235 and 238 were 2 and 0.2 s, respectively. Three channels around the peak top of each mass were integrated. The number of repetitions was 10 and the total measurement time for one sample solution was about 60 s. Mass discrimination was corrected for using a 10 ng/g solution of UO10 (abundance of ^{235}U is 1%) issued by New Brunswick Laboratory, USA. The typical mass discrimination correction factor for $^{235}\text{U}/^{238}\text{U}$ was 3%.

3. Results and discussion

3.1. Uncertainty of analysis

The four-step sequential extraction was applied to four rock reference materials prepared from different rock types in Japan and having different uranium contents. The analytical results for uranium in each fraction, together with the isotope ratio from step 4 (silicate fraction), are shown in Table 1. Less uranium was extracted in fractions 1 and 2 and most uranium was found in fraction 4 (JA-1, JB-1a and JR-1) or 3 (JG-1a). The sum of the uranium contents in each fraction was comparable to the reference value (Govindaraju, 1994) compiled from data obtained by various analytical methods. It is known that the matrix effect in ICP-MS measurement is high. The producer of these reference materials also reported analytical results for U measured by ICP-MS (Imai, 1990). The results corrected for matrix effect were 0.37 (JA-1) and 8.4 ng/g (JB-1), also comparable to our data. Sequential extractions are usually constructed by changing ionic strength, acidity, reduction ability (Martínez-Aguirre, García-León & Ivanovich, 1995). However, in this experiment, only acidity was changed in order to determine the extraction acidity sufficient to recover the uranium added to the environment. Accuracy and precision of isotope measurements by ICP-MS are dominated mainly by statistical errors and plasma fluctuation and depend on the concentration of the analyte and particularly of the less abundant isotope. The results for $^{235}\text{U}/^{238}\text{U}$ in fraction 4 correspond to the natural isotopic ratio, within error (1–5%). The statistical error for ^{235}U in a 1 ngU/g solution, which is equivalent to the concentration in the test solutions JB-1a and JG-1a, was about 2%, proving that the statistics dominate the precision.

3.2. Extraction behavior and uranium isotope ratio (outside the JCO campus)

The extraction behavior of the soil samples from outside the JCO campus is indicated by the relationship between uranium concentration and isotope ratio (Fig. 2). An error bar indicates the standard deviation of 10 repeated measurements. All the samples appearing in Fig. 2 were analyzed in duplicate and therefore the plot shows the reproducibility of the extraction and measurement processes. An obvious trend in the extraction behavior can be seen in Fig. 2. The uranium concentrations in

Table 1
Sequential extraction results for uranium in Japanese rock reference materials

	JA-1	JB-1a	JG-1a	JR-1
<i>Concentration (ng/g)</i>				
Step 1	0.001	0.001	0.005	0.005
Step 2	0.035	0.16	0.59	0.072
Step 3	0.034	0.14	2.50	0.089
Step 4	0.28	1.28	1.28	8.38
Sum	0.35	1.58	4.37	8.55
Reference Value ^a	0.34	1.6	4.7	9
<i>Isotope ratio</i> (²³⁵ U/ ²³⁸ U)				
Step 4	0.00699 ± 0.00035	0.00721 ± 0.00014	0.00730 ± 0.00012	0.00727 ± 0.00006
Natural isotope ratio		0.00725		

^aGovindaraju (1994).

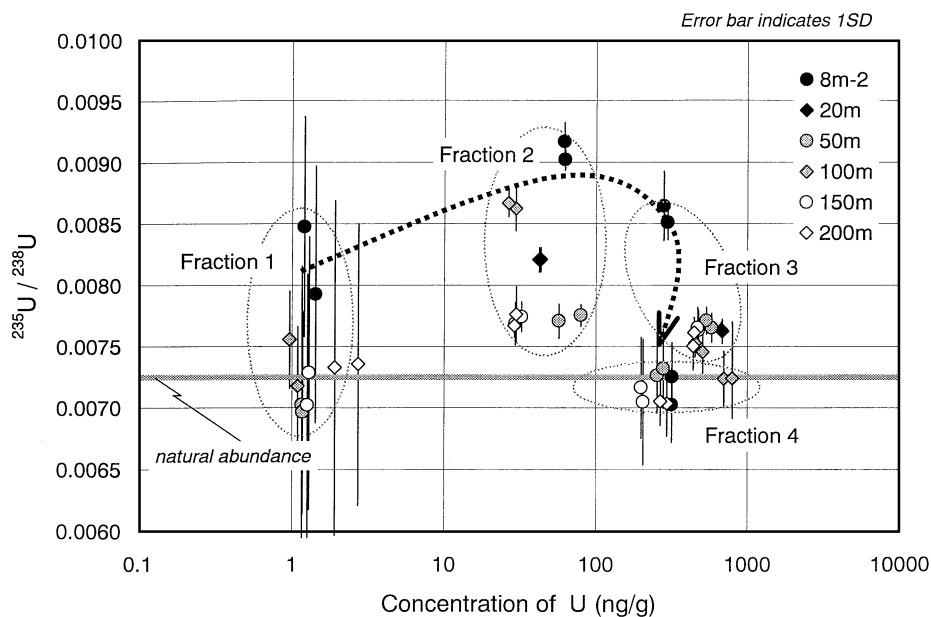


Fig. 2. Sequential extraction results for uranium and its isotopic ratio for the soil samples outside JCO.

fraction 1 are quite low and the isotope ratios are similar to the natural value except for 8 m-2. A moderate amount of uranium was generally extracted in fraction 2 and the isotope ratios were also high but varying from site to site. In most cases, the concentration of uranium was highest in fraction 3 but the isotopic ratio came closer

Table 2
Uranium concentration and isotope ratio for soil and botanical samples in and around JCO

Sample and extraction step	U (ng/g)	RSD (%)	$^{235}\text{U}/^{238}\text{U}$	1SD	
<i>Soil sample</i>					
8m-1	Step 1	0.35	3.0	0.0128	0.0013
		0.39	3.7	0.0118	0.0010
	Step 2	423	2.1	0.01447	0.00018
		425	1.0	0.01434	0.00015
	Step 3	881	1.0	0.01196	0.00007
		951	0.8	0.01199	0.00014
Sta. 12	Step 3	1220	1.0	0.00907	0.00016
Sta. 13	Step 3	1340	1.2	0.01103	0.00015
Sta. 19	Step 3	819	0.5	0.01069	0.00018
Sta. 20	Step 3	1020	0.6	0.00896	0.00016
<i>Botanical sample</i>					
Grass	Step 2	14.4	2.3	0.0080	0.0007
Chestnut (JCO)	Step 2	2.24	2.1	0.0218	0.0011
Cherry (JCO)	Step 2	0.33	6.5	0.0167	0.0017
Chestnut (NIES)	Step 2	1.51	2.3	0.0067	0.0008
Cherry (NIES)	Step 2	0.49	3.3	0.0071	0.0012

to the natural value except for 8 m-2. The isotope ratios in fraction 4 are the same as the natural value for all samples. As for the rock reference materials, most uranium contained in the silicate minerals was released into fraction 4 and its isotope ratio was the natural value. Although it cannot be concluded that fraction 4 does not contain contaminated uranium, the enriched uranium was completely extracted in fractions 1–3 as it has weak bonding with soil particles. Extraction 3 is sufficient to reach all the enriched uranium added to the soil, making data interpretation simple. Sample 8 m-1 showed a similar extraction pattern to the other soil samples (Table 2). The uranium isotope ratio of 8 m-1 is so high that it is beyond the range of Fig. 2. The grass sample did not show a significantly anomalous isotopic ratio (Table 2).

3.3. Uranium isotope ratio (inside the JCO campus)

Only extraction 3 was applied to the soil samples from within the JCO campus area and extraction 2 was applied to the leaf samples. The analytical results are listed in Table 2. The uranium concentrations in the JCO campus were higher than those outside and high $^{235}\text{U}/^{238}\text{U}$ ratios were obtained. The content of uranium in the leaf samples was lower than 3 ng/g. The isotopic ratio of the chestnut leaf from inside the JCO campus was the highest of the samples analyzed, in contrast to the natural values for the NIES samples. Sampling of leaves from living branches and weak acid treatment (step 2) may minimize the influence of wind-blown soil and of uranium taken from soil solution and stored inside leaf cells. Because chestnut and cherry trees

renew their leaves every year, the fact that the most enriched uranium was found in leaf samples implies the contamination occurred between spring 1999 and sample collection.

3.4. Estimation of the impact from the enriched uranium

As the uranium isotopic anomaly was high in the JCO campus in general and had been brought to the leaf surface within half a year, the source of the enriched uranium was assumed to be JCO and the impact from enriched uranium was estimated as follows. If the extractable uranium is composed of natural uranium and enriched uranium components, then the observed extractable concentration C_{ox} and its isotope ratio r_0 are expressed by the following equations:

$$C_{ox} = C_e + C_{nx}, \quad (1)$$

$$r_0 = \frac{C_e/A_e a_{e235} + C_{nx}/A_n a_{n235}}{C_e/A_e a_{e238} + C_{nx}/A_n a_{n238}}, \quad (2)$$

where r is the isotopic ratio, C is the concentration, A is the atomic weight, a is the abundance, mass is shown as 235 and 238, and the subscripts o, e, n and x stand for observed, enriched, natural and extractable, respectively. Here, A_e and A_n can be replaced by a combination of M (mass of isotope) and a :

$$A_e = M_{234} a_{e234} + M_{235} a_{e234} + M_{238} a_{e238} \quad (3)$$

$$A_n = M_{234} a_{n234} + M_{235} a_{n234} + M_{238} a_{n238} \quad (4)$$

Because the abundance of ^{234}U is small (< 0.001), a_{e234} and a_{n234} can in practical terms be taken to be 0. Consequently, by substituting Eqs. (1), (3) and (4) in (2), Eq. (2) can be solved for C_e :

$$\begin{aligned} C_e &= C_{ox} \frac{(r_0 - r_n)(M_{235} r_e + M_{238})}{(r_e - r_n)(M_{235} r_0 + M_{238})} \\ &= C_{ox} R. \end{aligned} \quad (5)$$

The contribution of the enriched fraction to the extractable uranium (R) is a function of r_e and r_0 . JCO usually treated nuclear fuel materials for light water reactors and rarely treated enriched uranium oxide with 18.8% ^{235}U . The annual use of uranium for light water reactors (4% enrichment on average) and 18.8% uranium were 440 t/y and 400 kg/y, respectively (JCO, 1999). Therefore, two r_e values are given for the calculation; namely $r_e = 0.235$ (18.8% ^{235}U in weight) used in the criticality accident and $r_e = 0.04$ for the typical light water reactor use. The former gives a minimum R value and the latter a maximum R . In the calculation, individual C_{ox} and r_0 values for fractions 1–3 were combined appropriately. The calculated R and C_e together with estimates of C_{ox} , C_{nr} (fraction 4, representing the residual natural content) and r_0 are shown in Table 3. When 18.8% of ^{235}U was assumed, the

Table 3

Estimation of the contribution from the enriched uranium component. Two values for the isotope ratio of the enriched component (r_e) were used to show the range of R and C_e .

Sample	Approximate sampling depth (cm)	C_{ox} (ng/g)	C_{nr} (ng/g)	r_0	$r_e = 0.235^a$		$r_e = 0.04$	
					R (%)	C_e (ng/g)	R (%)	C_e (ng/g)
8 m-1	0.5	1340	na ^b	0.0129	3.0	41	18	240
8 m-2	1	349	314	0.00878	0.82	2.9	4.8	17
20 m	0.5	719	na	0.00776	0.27	2.0	1.6	12
50 m	1	625	263	0.00778	0.29	1.8	1.7	11
100 m	1	469	278	0.00766	0.22	1.0	1.3	6.1
150 m	1	502	200	0.00774	0.26	1.3	1.6	7.8
200 m	1	503	747	0.00765	0.22	1.1	1.3	6.4
Sta. 12	10	1220	na	0.00907	0.98	12	5.7	70
Sta. 13	2	1340	na	0.0110	2.0	27	12	160
Sta. 19	10	819	na	0.0107	1.8	15	11	89
Sta. 20	10	1020	na	0.00896	0.92	9.4	5.4	55
Chestnut	—	2.2	—	0.0218	7.8	0.17	45	1.0
Cherry	—	0.3	—	0.0167	5.0	0.02	29	0.10

^aAbundance of ^{235}U was assumed to be 18.8 Wt%.

^bna: Not analyzed.

R value varied from 0.2 to 3%, while it ranged from 1.3 to 18% when an r_e of 0.04 was taken. The same approach is applicable to leaf samples. The contribution of enriched uranium to the leaves was higher than that to the soils and the maximum R obtained was 45%. As the minimum r_e value is limited by the maximum r_0 , searching for a sample having the highest $^{235}\text{U}/^{238}\text{U}$ ratio is one method of identifying a contamination source.

Another way to identify a source is to survey systematically and map the spatial distribution of C_e . Sampling depth directly affects C_e as well as R , if the contaminant occurs in the surface layer of soil. In this surveillance, several kinds of sampling methods were used, like coring, scraping with a trowel, etc. Therefore the sampling depth shown in Table 3 was not definitive in some cases. Assuming that the contamination remains on the uppermost surface of the soil, the effect of dilution with uncontaminated soil can be cancelled when the C_e value is divided by the sampling depth. In Fig. 3, the normalized C_e value for 18.8% enrichment is plotted. Most samples except Sta. 12 were sampled along a straight line and the normalized C_e values decrease systematically with distance from the conversion building. An exceptionally low C_e was found at Sta. 13 which was located just beside the building. Soil samples collected in the southeast direction also showed high $^{235}\text{U}/^{238}\text{U}$ ratios and a dependence on the distance from the conversion building (Komura, 1999). There is no building in which nuclear fuel was processed (shaded buildings in Fig. 1) between Stas. 19 and 13, and the ventilated air of the conversion building was led to the exhaust of another building. Therefore, if fine particles were emitted from the

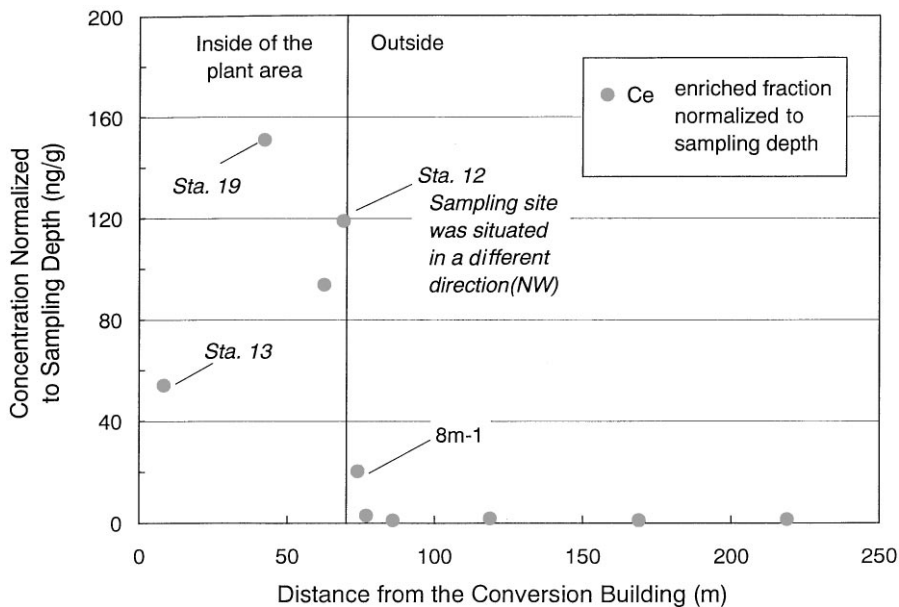


Fig. 3. Relation between the distance from the conversion building and C_e (enriched component normalized to sampling depth). The abundance of ^{235}U was assumed to be 18.8% for the calculation.

exhaust, the conversion building itself might physically have screened the particulate matter from settling out around Sta. 13. In the course of these collaborative studies, many soil samples which have not yet been analyzed for uranium have been collected and stored. The source of the enriched uranium has not been identified but the analyses of these samples and generation of a detailed spatial distribution will solve this ambiguity. When the isotopic composition of the contaminant is identified, the amount of enriched uranium discharged from the source can be estimated from the horizontal distribution of C_e . The amount of enriched uranium discharged might be small compared with the natural uranium inventory of the soil. However, it is significant that an anomalous $^{235}\text{U}/^{238}\text{U}$ ratio was found outside the uranium conversion facilities.

4. Conclusion

The accident at JCO was the first criticality accident that Japan has ever experienced. Rapid surveillance was required in such an emergency case. Although the precision of ICP-QMS is limited, it conforms to the requirement for quick action. Consequently, anomalous $^{235}\text{U}/^{238}\text{U}$ ratios in the easily extractable forms were found by ICP-QMS in soils and botanical samples. The impact from enriched uranium was dependent on distance from the conversion building. Further intensive analyses and

compilation of data obtained by other researchers are necessary to elucidate the complete detail of the impact of the accident.

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References

- Beasley, T. M., Dixon, P. R., & Mann, L. J. (1998). ^{99}Tc , ^{236}U , and ^{237}Np in the Snake River Plain aquifer at the Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho. *Environmental Science and Technology*, 32, 3875–3881.
- Becker, J. S., & Dietze, H. -J. (1999). Application of double-focusing sector field ICP mass spectrometry with shielded torch using different nebulizers and precise isotope analysis of long-lived radionuclides. *Journal of Analytical Atomic Spectrometry*, 14, 1493–1500.
- Becker, J. S., Dietze, H. -J., McLean, J. A., & Montaser, A. (1999). Ultratrace and isotope analysis of long-lived radionuclides by inductively coupled plasma quadrupole mass spectrometry using a direct injection high efficiency nebulizer. *Analytical Chemistry*, 71, 3077–3084.
- Citizens' Nuclear Information Center (1999). What happened at the uranium criticality accident. Kagaku (Iwanami), 69, 959–960, (in Japanese)
- Chamberlain, A. C. (1987). Environmental impact of particles emitted from the Windscale Piles, 1954–7. *The Science of the Total Environment*, 63, 139–160.
- Farmer III, O. T., Barinaga, C. T., & Koppenaal, D. W. (1998). Determination of ^{129}I in ambient air by inductively coupled plasma mass spectrometry (ICP/MS). *Journal of Radioanalytical and Nuclear Chemistry*, 234, 153–157.
- Govindaraju, K. (1994). 1994 compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter*, 18(special issue), 1–158.
- IAEA (1999). Report on the preliminary fact-finding mission following the accident at the nuclear fuel processing facility in Tokaimura, Japan. (p. 35).
- Imai, N. (1990). Multielement analysis of rocks with the use of geological certified reference material by inductively coupled plasma mass spectrometry. *Analytical Sciences*, 6, 389–395.
- JCO (1999). Private communications.
- Komura, K. (1999) Private communication.
- Martínez-Aguirre, A., García-León, M., & Ivanovich, M. (1995). U and Th speciation in river sediments. *The Science of the Total Environment*, 173/174, 203–209.
- Muramatsu, Y., Uchida, S., Tagami, K., Yoshida, S., & Fujikawa, T. (1999). Determination of plutonium concentration and its isotopic ratio in environmental materials by ICP-MS after separation using ion-exchange and extraction chromatography. *Journal of Analytical Atomic Spectrometry*, 14, 859–865.
- Nuclear Safety Commission, Japan (1999). Urgent recommendations — Interim report, World Wide Web site at http://atmimg.tokyo.jst.go.jp:8090/eng/report_e.html, Investigation Committee for Criticality Accident at Uranium processing Plant.
- Sakanoue, M. (1999). Action of chemists studying radioactivity — on two accidents which occurred this autumn. *Chemistry and Chemical Industry*, 52, 1485–1489 (in Japanese).