Chemical removal of radionuclides in contaminated spinach derived from the Fukushima nuclear accident

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We examined a simple and effective removal method for contaminated farm products to ensure the relief of farmers and the security of consumers. Removal of radionuclides from spinach by chemical methods was investigated. The result of chemical removal showed that antioxidant agents removed radionuclides from spinach by 70–80% for 131I and more than 80% for radiocesium. In particular, ascorbic acid is promising as a safe and versatile option.

Key words: radioactive contamination, Fukushima nuclear accident, chemical decontamination, Iodine-131, Cesium-134, Cesium-137

Introduction

Huge amounts of radionuclides derived from the Fukushima nuclear accident were dispersed in the atmosphere. In five prefectures, various vegetables were shipment restriction due to contaminated with 131I and radiocesium14]. A simple and effective removal method for contaminated farm products was examined to ensure the relief of farmers and the security of consumers.

Methods

Various kinds of vegetables contaminated after the Fukushima nuclear accident were sent to us from March 28 through April 9 by five members of the Japanese Society of Radiation Safety Management who lived in Fukushima prefecture or a prefecture next to Fukushima prefecture. The distribution image of radioactivity in spinach was obtained using an imaging plate (IP) BAS-SR2025 and a Bioimaging Analyzer (BAS 5000; FUJIFILM). Radioactivity of spinach was measured by a Geiger-Mueller (GM) survey meter (TGS-136; Aloka) and a high purity germanium semiconductor (HPGe) detector (GMX-40195; Seiko).

1) Chemical removal of radioactivity from contaminated spinaches

After pre-washing under running water, the contaminated spinach was dipped in 1 L of various antioxidant agent solutions for 24 h. After dipping in antioxidant agent solution, the spinach was washed by hand under running water for 5 min. As antioxidant agents, 1% sodium thiosulfate (Na2S2O3 · 5H2O), 1% sodium hyposulfite (Na2S2O4), 1% sodium metabisulfite (Na2S2O5), 1% sodium sulfite (Na2SO3) and 1% ascorbic acid, were investigated. Distilled water was used as a control. Radioactivity of a bundle of spinach was measured by a HPGe detector and a GM survey meter for 1200–1800 sec.

The radioactivity removal rate (RRR) was calculated using the following formula.

\[ \text{RRR(\%)} = \left( \frac{A_0 - A}{A_0} \right) \times 100 \]

A0: Radioactivity before washing
A: Radioactivity after washing
2) A distribution image of the radioactivity of contaminated spinach

Contaminated spinach leaves before and after treatment by antioxidant agents were exposed to an imaging plate (IP) BAS-SR2025. After 12–24 hr, an image of the distribution of radioactivity was captured and analyzed by a Bioimaging Analyzer BAS5000. The resolution of the image obtained by IP was 100 μm.

Results and Discussion

Table 1 shows the removal of radioactivity, which was measured by a GM survey meter, by various antioxidant agents after pre-running water washing from contaminated spinach leaf. Five antioxidant agents showed a superior removal effect of radioactivity (60–82%) to distilled water as a control (45%). In particular, 1% sodium metabisulfite (Na2S2O5) (81%), 1% sodium sulfite (Na2SO3) (79%) and 1% ascorbic acid (82%), which are relative mild antioxidant agents, showed a high radioactivity removal rate. Table 2 shows the removal effect of 131I, 134Cs and 137Cs, which was measured by a Ge semiconductor detector, by various antioxidant agents from a bundle of contaminated spinach. The removal rate of 131I by pre-running water washing showed marked variations 12–41% by a Ge semiconductor detector. The removal rate of 131I was two times poorer than that of 137Cs. This might be because radioactivity derived from the Fukushima nuclear accident included 131I, which was not only water-soluble, I− and IO3− etc.2,3), but also water-insoluble. About 50% of 131I released by the Three Mile Island nuclear accident consisted of the water-insoluble type4,5). Sumiya6) reported that for spinach contaminated by exposing to gaseous I2, it was difficult to remove the radioactivity compared to iodide ion (I−). Thus, the removal effect of 131I depended on the chemical property and structure of 131I. The chemical structures of radioactive iodine released by the Three Mile Island nuclear accident (USA) were reported as follows: the rate of I2, HIO, CH3I and particle iodine was 25%, 18%, 29% and 27%, respectively4,5). According to this information, the rate of water-insoluble materials in 131I was more than 50%. The antioxidant materials having a reducing ability, some sulfites and ascorbic acid, are thought to change iodine molecules (I2), hypiodous acid (HIO) to I−, which is water soluble. We tried to use those antioxidant agents to remove 131I from contaminated spinach effectively. As a result, in Table 2, the antioxidant treatment showed the superior removal effect of 131I in comparison with pre-running water washing. Furthermore, 1% sodium metabisulfite showed radioactivity removal of about 80% for 131I in comparison with 49% with distilled water on antioxidant treatment after pre-running water washing. The radioactivity removal of all five antioxidant agents compared to 137Cs was about 80%.

A distribution image of radioactivity in a spinach leaf before and after antioxidant agent was analyzed by a Bioimaging analyzer BAS 5000 (Figure 1 and 2). There were two types of contaminations, spot type and spread type, in vegetables. The radioactivity removal of each spot type contamination and spread type contamination by antioxidant agents was analyzed by Multi Gauge v3.0 software of imaging analyzer BAS 5000. The radioactivity removal (71%) by the antioxidant agent in the spot type of contamination was superior to that in the spread type of contamination (59%), because some of the spot type of contamination was caused by radionuclides invaded into damage parts of the spinach.

Conclusion

The removal of 131I from contaminated spinach leaf was difficult by only water washing, however, the antioxidant agent, which was safe for humans, may be a superior 131I removal agent. It is also effective for the removal of radiocesium. In particular, 1% ascorbic acid is probably promising as a safe and versatile option.

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Table 1 Removal of radioactivity from contaminated spinach leaf by antioxidant agents

| Antioxidant agents | Radioactive removal rate (%)\(\ast\) |
|-------------------|----------------------------------|
| 1% Na2S2O5·5H2O   | 60 ± 13                          |
| 1% Na2S2O4        | 74 ± 12                          |
| 1% Na2S2O5        | 81 ± 8                           |
| 1% Na2SO3         | 79 ± 9                           |
| 1% ascorbic acid  | 82 ± 8                           |
| Distilled water   | 45 ± 11                          |

\(\ast\) The values were measured by a GM survey meter.
Table 2  Removal of radioactivity from a bundle of contaminated spinach by antioxidant agent treatments.

| Antioxidant agents | Radioactivity removal rate (%)<sup>∗</sup> | Pre-running water washing** | Antioxidant treatment*** |
|--------------------|------------------------------------------|-----------------------------|-------------------------|
| 1% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O | 131I 31 ± 3 | 72 ± 6 | 134Cs 60 ± 4 | 80 ± 6 | 137Cs 55 ± 4 | 80 ± 8 |
| 1% Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> | 131I 39 ± 4 | 66 ± 4 | 134Cs 71 ± 6 | 78 ± 6 | 137Cs 69 ± 5 | 79 ± 6 |
| 1% Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> | 131I 39 ± 4 | 78 ± 4 | 134Cs 49 ± 3 | 85 ± 7 | 137Cs 48 ± 3 | 84 ± 8 |
| 1% Na<sub>2</sub>SO<sub>3</sub> | 131I 23 ± 2 | 69 ± 6 | 134Cs 49 ± 3 | 80 ± 6 | 137Cs 50 ± 3 | 81 ± 6 |
| 1% ascorbic acid | 131I 22 ± 3 | 67 ± 7 | 134Cs 57 ± 4 | 81 ± 7 | 137Cs 61 ± 5 | 80 ± 7 |
| Water | 131I 33 ± 4 | 49 ± 5 | 134Cs 59 ± 4 | 67 ± 4 | 137Cs 53 ± 4 | 68 ± 5 |

<sup>∗</sup> The values were measured by a HPGe detector.

<sup>**</sup> The values show the radioactivity removal rate after pre-running water washing before treatment with antioxidant agents.

<sup>***</sup> The values show the radioactivity removal rate after treatment with antioxidant agents.

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Fig. 1. A distribution image of radioactivity in spinach before pre-running water washing (No.1 and No.2).

Fig. 2. A distribution image of radioactivity in spinach after 1% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (No.1[A] and 1% ascorbic acid treatment (No.2)[B].
Chemical removal of radioactivity from vegetables.

References

1) Ministry of Health, Labour and Welfare. Japan. (2011) (In Japanese.) http://www.mhlw.go.jp/shinsai_jouhou/dl/shokuhin.pdf
2) Yoshida, S., Muramatsu, Y., Katou, S., Sekimoto, H. Determination of the chemical forms of iodine with IC-ICP-MS and its application to environmental samples. J Radioanal. Nucl. Chem. 273: 211–214 (2007).
3) Muramatsu, Y., Sumiya, M., Ohmomo, Y. Iodine-131 and other radionuclides in environmental samples collected from Ibaraki/ Japan after the Chernobyl accident. The Science of Total Environment. 67: 149–158 (1987).
4) Research Organization for Information Science & Technology. “ATOMICA” http://www.rist.or.jp/atomica/09-04-03-10.
5) Bellamy, R.P, Investigations into the air cleaning aspects of the Three Mile Island accident, 16th Air cleaning Conference, CONF-801038, Vol.2, 1427 (1981).
6) Sumiya, M.: Removal of radioiodine from leafy vegetables and algae by cooking "Chouli sousa niyou shokuhintyu no youso no jyokyokouka nituite (in Japanese)". 12th NIRS seminar “Housya-seikakusuyou nokagakukei gahibakusenyouhouyouka ni oyobosu eikyo (in Japanese)”. pp141–144, National Institute of Radiological Sciences, Chiba, Japan. (1986).