Fluorine Concentrations in Greenhouse Soils Sampled from Farms in Southern Kyushu, Japan

Isao AKAGI, Yoshitaka SATOH and Naoya CHISHAKI

Department of Biochemical Science and Technology, Faculty of Agriculture, Kagoshima University
(1-21-24 Korimoto, Kagoshima, Kagoshima 890-0065, Japan)

[Received September 3, 2014; Accepted December 24, 2014]

Summary

Phosphate fertilizer is thought to be the major source of F input in agricultural soils. We consider that F accumulation in Japanese agricultural soil is caused by excessive application of phosphate fertilizer, because Japan is one of the major chemical fertilizer consumer nations in the world. In this study, we analyzed the F concentration in greenhouse soils sampled from farms in southern Kyushu, Japan, and investigated the possibility of the F accumulation in the soils by comparing the concentrations in the greenhouse soils with those in neighboring non-cultivated soils. The total F concentration in non-cultivated soils and greenhouse soils ranged from 53 to 248 mg/kg and from 163 to 471 mg/kg, respectively. Almost all greenhouse soils had a higher total F concentration than the neighboring non-cultivated soils, which indicates that total F concentrations were generally higher in almost all greenhouse soils. The water-soluble F concentrations in non-cultivated soils and greenhouse soils ranged from 0.15 to 4.89 mg/kg and from 1.75 to 20.3 mg/kg, respectively. As well as total F concentration, almost all greenhouse soils had a higher water-soluble F concentration than the neighboring non-cultivated soils. A positive correlation was observed between the total F and the total P concentrations in greenhouse soils, which indicates that the F in the greenhouse soils is derived from phosphate fertilizers. The above results indicate that soil F accumulation is due to excessive application of phosphate fertilizers that are widely used on greenhouse soils throughout Japan, and water-soluble F concentrations are correspondingly elevated in these soils.

Key words: Soil fluorine concentration, Greenhouse soil, Application of phosphate fertilizer

INTRODUCTION

Phosphate fertilizer is an indispensable agricultural material for stable crop production. Phosphate fertilizers are frequently used to improve soil fertility, especially in Japan where Andosols, which have a high phosphorus (P) fixing capacity, are distributed widely. Because phosphate fertilizers contain around 10–20 g/kg fluorine (F) depending on the origin of the phosphate rock used¹⁾, they are thought to be the major source of F in agricultural soils^{2, 3)}. Recently, in New Zealand and Australia, it has become clear that F accumulation in pasture soils is caused by the continuing phosphate fertilizer application. Loganathan et al.⁴⁾ reported that the F concentrations in New Zealand pasture soils that had received phosphate fertilizer were 1.3–2.2 times higher than in soils that had not been fertilized.

Japan is one of the major chemical fertilizer consumer nations in the world. In 2005, chemical fertilizers containing phosphate were applied at a rate of 99 kg P/ha/year in Japan⁵⁾. The continuing excessive use of phosphate fertilizer has recently been reported to have caused accumulation of P in agricultural soils in Japan⁶⁾. According to monitoring survey data of soil properties from 1979 to 1997, from 54% to 78% of greenhouse soils in Japan showed extremely high concentrations of available P (0.001 mol/L sulfuric acid-extractable phosphate) exceeding the recommended level⁷⁾. Given the above facts, we consider that F accumulation in agriculture soils in Japan is caused by

excessive application of phosphate fertilizers. However, a few studies have investigated F concentrations in Japanese agricultural soils⁸⁾, but no information is available on the effects of the application of phosphate fertilizer on F accumulation in agricultural soils.

In this study, we analyzed the F concentrations in greenhouse soils sampled from farms in southern Kyushu, Japan, and investigated the possibility of the F accumulation in the soil by comparing the F concentrations of the greenhouse soils with those of the neighboring non-cultivated soils.

MATERIALS AND METHODS

Soil samples

Thirty-four soil samples were collected from 11 areas in southern Kyushu (Fig. 1). Of these 34 samples, 23 were collected from farm greenhouses and 11 were collected from the non-cultivated fields adjacent to the greenhouses. Soils were taken using a stainless steel trowel from the 15 cm surface layer soil at each sampling site in mid-May to early June after the cultivation period. Soil samples were air-dried and passed through 2 mm mesh sieves before analysis. These soil samples were classified into three groups: Gray Lowland soils, Andosols, and Sand-dune Regosols according to "Classification of Cultivated Soils in Japan, Third Approximation"⁹⁾. The sample numbers, sampling areas, soil groups and land use are listed in Table 1.

Fig. 1 Map showing the locations of sampling sites in southern Kyushu, Japan

Table 1 Brief description of the sampling sites

Location	Soil group	Sample No.	Land use
A: Saito City, Miyazaki Pref.	Gray Lowland soils	A-0	Non-cultivated field
		A-1	Greenhouse field
		A-2	Greenhouse field
		A-3	Greenhouse field
		A-4	Greenhouse field
B: Higashimorokata District, Miyazaki Pref.	Gray Lowland soils	B-0	Non-cultivated field
		B-1	Greenhouse field
C: Nichinan City, Miyazaki Pref.	Gray Lowland soils	C-0	Non-cultivated field
		C-1	Greenhouse field
		C-2	Greenhouse field
		C-3	Greenhouse field
D: Kushima City, Miyazaki Pref.	Gray Lowland soils	D-0	Non-cultivated field
		D-1	Greenhouse field
		D-2	Greenhouse field
E: Koyu District, Miyazaki Pref.	Andosols	E-0	Non-cultivated field
		E-1	Greenhouse field
		E-2	Greenhouse field
		E-3	Greenhouse field
F: Shibushi City, Kagoshima Pref.	Andosols	F-0	Non-cultivated field
		F-1	Greenhouse field
G: Kimotsuki District, Kagoshima Pref.	Andosols	G-0	Non-cultivated field
		G-1	Greenhouse field
		G-2	Greenhouse field
H: Minamikyushu City, Kagoshima Pref.	Andosols	H-0	Non-cultivated field
		H-1	Greenhouse field
I: Miyazaki City, Miyazaki Pref.	Sand-dune Regosols	I-0	Non-cultivated field
		I-1	Greenhouse field
		I-2	Greenhouse field
		I-3	Greenhouse field
		I-4	Greenhouse field
J: Kimotsuki District, Kagoshima Pref.	Sand-dune Regosols	J-0	Non-cultivated field
		J-1	Greenhouse field
K: Minamisatsuma City, Kagoshima Pref.	Sand-dune Regosols	K-0	Non-cultivated field
		K-1	Greenhouse field

Analytical methods

Soil pH was measured with a glass electrode pH meter (F-51; Horiba) in a water suspension with the ratio of soil to distilled water adjusted to 1:2.5 weight/volume¹⁰⁾. The concentration of total C was measured using a dry combustion method (Macro corder JM1000CN; J-Science Lab)¹⁰⁾. Amorphous Al and Fe were extracted by shaking 0.5 g of soil with 50 mL of oxalate solution (0.2 mol/L oxalic acid and ammonium oxalate solution, pH 3.0) for 4 hours^{10, 11)}. Al and Fe in this extract were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SPS1700VR; Seiko Instruments). The concentration of total P was determined by the vanadomolybdate spectrophotometric method after digestion with a mixture of nitric and perchloric acids on a hot plate¹⁰⁾.

Total F was separated by steam distillation in the presence of sulfuric acid (H_2SO_4)¹²⁾. A 1-g soil sample was distilled at 145 ± 5 °C with 80 mL of 9 mol/L H_2SO_4 , 1 mL of phosphoric acid and 1 g of silicon dioxide. Approximately 200 mL of the distillate was collected at a rate of about 3–5 mL per minute. F in the distillate was determined by a spectrophotometric method with lanthanum-alizarin complexone (La-AC)¹³⁾. The La-AC reagent was prepared by dissolving Dotite Al-fusone (Dojin Chemical). To the distillate solution was added 2 mL of 1.0 mol/L acetate buffer (pH 5.0), 2 mL of acetyl acetone, 5 mL of 10 g/L La-AC reagent and 10 mL of acetone, and the solution was made up to 50 mL with distilled water^{14, 15)}. The absorption of the prepared solution was measured at 620 nm after 1 hour.

Water-soluble F was extracted by shaking 1 g soil with 50 mL ultrapure water for 2 hours⁸⁾. After shaking, the suspension was filtered through no. 5C Advantec filter paper. F in the extract was determined by a spectrophotometric method with La-AC as described above.

RESULTS AND DISCUSSION

Total F concentration

The total F concentration in non-cultivated soils and greenhouse soils ranged from 53 to 248 mg/kg (median 169 mg/kg) and from 163 to 471 mg/kg (median 258 mg/kg), respectively (Table 2). These ranges lie within the ranges reported for world soils (8–990 mg/kg³⁾, 20–1,000 mg/kg¹⁶⁾). There were differences in the total F concentrations in the non-cultivated soils among the three soil groups ($p = 0.049$, Kruskal-Wallis test): the concentration ranges in the Gray Lowland Soils, Andosols, and Sand-dune Regosols were 168–247 mg/kg (median 207 mg/kg), 122–248 mg/kg (median 191 mg/kg), and 53–72 mg/kg (median 72 mg/kg), respectively. These differences may reflect differences in the parent materials and soil-forming processes.

All greenhouse soils except three (samples A-2, A-4, and D-1) had a higher total F concentration than the neighboring non-cultivated soils; for example, the total F concentrations in the greenhouse soils I-1 (203 mg/kg), I-2 (321 mg/kg), I-3 (246 mg/kg), and I-4 (282 mg/kg) were 2.8, 4.5, 3.4 and 3.9 times higher than those in the neighboring non-cultivated soil I-0 (72 mg/kg). This result shows that the total F concentration was elevated in almost all greenhouse soils. The total F accumulated in the greenhouse soils was estimated at 17–249 mg per kg of oven-dry soil by subtracting the total F concentration in the greenhouse soils from the total F concentration in the neighboring non-cultivated soils.

The F accumulated in the greenhouse soils is considered to be

derived from phosphate fertilizer, because phosphate fertilizer contains around 10–20 g F/kg¹⁾ and is frequently used for greenhouse culture in Japan. The chemical properties of the greenhouse soils and the non-cultivated soils are listed in Table 2. Total P concentrations in the greenhouse soils (2.59–10.3 mg/kg) were significantly higher than in the non-cultivated soils (0.07–1.39 g/kg). All greenhouse soils had a higher total P concentration than the neighboring non-cultivated soils; for example, the total P concentrations in the greenhouse soils I-1 (5.45 g/kg), I-2 (10.3 g/kg), I-3 (7.18 g/kg), and I-4 (4.61 g/kg) were 45, 86, 60 and 38 times higher than in the neighboring non-cultivated soil I-0 (0.12 g/kg). Phosphate fertilizer has been used almost exclusively as a source of P nutrition, although animal manure compost and other material containing some P have often been added at the sampling sites. Thus, the increase in total P concentration appears to be a result of the application of phosphate fertilizer.

Correlations between total F concentration in the soils and some chemical properties of the soils are shown in Table 3. Total F concentration showed a significant positive correlation with total P concentration (Spearman's rank correlation coefficient, $r_s = 0.683$, $p < 0.001$, Fig. 2). A positive correlation was also observed for each soil group separately (Gray Lowland soils, $r_s = 0.634$; Andosols, $r_s = 0.527$; Sand-dune Regosols, $r_s = 0.849$). Thus the elevation in F concentration was associated with elevation in P concentration due to excessive application of phosphate fertilizer. A similar relationship was observed in New Zealand pasture soils treated with phosphate fertilizer⁴⁾. Furthermore, total F concentration also showed a positive correlation with total C concentration ($r_s = 0.472$, $p = 0.005$), amorphous Fe concentration ($r_s = 0.491$, $p = 0.003$), and amorphous Al concentration ($r_s = 0.390$, $p = 0.023$). The correlations can be considered to be related to the strong F adsorption capacity of amorphous Al and Fe oxide/hydroxide and Al-humus complex^{17, 18)}. The correlation between total F and amorphous Al concentration in our soils was quite weak in comparison with that in New Zealand pasture soils ($r = 0.498$) reported Loganathan et al.²²⁾. This shows that a soil component other than Al, for example Ca capable of forming apatite, might play an important role in the retention of F in the soils studied here.

The above results indicate that soil F accumulation is due to excessive application of phosphate fertilizer that is widely used on greenhouse culture. This is the first finding in Japan, although it has often been pointed out that application of fertilizer may have caused F accumulation in agricultural soils. Robinson and Edgington¹⁹⁾ reported that the amount of F accumulated in soils that had received fertilizer for 40 years in New Jersey, USA, were up to 144 mg/kg. Loganathan et al.⁶⁾ reported that the amount of F accumulated in New Zealand pasture soils that had received fertilizer for 20 years was 143 mg/kg. In this study some greenhouse soils had accumulated up to 200 mg/kg, which indicates that the F accumulation has progressed more in Japanese greenhouse soils than in the soils investigated in the above two studies. The F content of phosphate fertilizer is known to vary depending on the fertilizer type and the origin of the phosphate rock used as raw material¹⁾. Thus, the degree of F accumulation in the soil may be affected by not only the amount but also the quality of the added fertilizer. It is impossible to evaluate this possibility at present because the fertilizer history of the sampling site is not accurately known.

Table 2 Fluorine concentration (total F and water-soluble F) and soil chemical properties in non-cultivated soils and greenhouse soils

Sample No.	Soil group ¹⁾	Land use ²⁾	F concentration				pH	Total C	Total P	Amorphous	
			Total F	Δ total F ³⁾	Water-soluble F	Δ water-soluble F ⁴⁾				Al	Fe
			(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)				(g/kg)	(g/kg)
A-0	G	NC	247	—	4.89	—	4.7	18.4	1.39	1.88	6.42
A-1	G	G	275	28	3.78	-1.11	5.4	16.8	3.60	2.88	5.19
A-2	G	G	239	-8	3.07	-1.82	6.4	33.6	4.57	3.71	4.86
A-3	G	G	292	45	4.02	-0.87	5.7	26.6	4.59	2.14	4.50
A-4	G	G	243	-4	2.06	-2.83	5.9	26.1	3.59	2.26	3.28
B-0	G	NC	213	—	2.14	—	5.3	21.3	0.43	2.24	5.98
B-1	G	G	435	222	20.3	18.2	6.8	44.0	6.65	36.4	12.4
C-0	G	NC	201	—	1.57	—	5.3	45.5	0.43	12.5	6.43
C-1	G	G	258	58	4.97	3.40	5.8	34.7	5.81	10.3	7.08
C-2	G	G	230	29	4.59	3.02	5.6	16.2	4.75	2.17	4.54
C-3	G	G	273	72	3.74	2.17	6.1	33.8	7.49	7.00	6.23
D-0	G	NC	168	—	2.94	—	4.8	21.6	1.08	4.47	4.48
D-1	G	G	163	-5	5.89	2.95	6.2	21.3	2.59	10.1	3.74
D-2	G	G	185	17	6.41	3.47	6.2	20.1	3.74	4.94	3.21
E-0	A	NC	248	—	0.15	—	4.8	75.8	0.71	39.0	16.6
E-1	A	G	471	223	2.00	1.85	5.3	93.1	5.42	55.9	17.6
E-2	A	G	391	143	1.75	1.59	5.4	87.6	4.48	53.1	18.5
E-3	A	G	353	105	1.98	1.83	5.1	119.	5.04	44.1	13.9
F-0	A	NC	169	—	0.39	—	5.3	52.6	0.40	69.9	15.7
F-1	A	G	251	82	14.6	14.2	6.6	43.7	5.17	38.4	10.4
G-0	A	NC	214	—	0.44	—	5.4	49.0	0.53	38.4	10.4
G-1	A	G	265	51	3.79	3.35	5.1	54.2	9.79	20.9	9.24
G-2	A	G	288	74	7.98	7.54	5.5	82.6	9.71	33.2	13.0
H-0	A	NC	122	—	1.31	—	5.5	47.5	0.77	35.6	14.4
H-1	A	G	217	95	5.54	4.22	5.5	50.5	6.51	27.6	14.8
I-0	S	NC	72	—	1.14	—	5.2	4.1	0.12	0.85	2.51
I-1	S	G	203	131	3.06	1.93	6.5	18.4	5.45	5.01	2.05
I-2	S	G	321	249	1.79	0.65	4.9	32.7	10.3	8.20	5.79
I-3	S	G	246	174	3.05	1.92	6.0	20.3	7.18	6.97	3.59
I-4	S	G	282	210	8.59	7.45	5.7	18.4	4.61	5.71	2.61
J-0	S	NC	72	—	1.15	—	5.5	2.9	0.07	1.42	1.58
J-1	S	G	170	98	3.09	1.95	4.7	24.7	4.15	9.59	4.54
K-0	S	NC	53	—	1.22	—	5.3	9.5	0.14	0.74	0.72
K-1	S	G	210	139	8.56	7.34	6.1	35.8	4.61	3.15	2.22

1) Soil group: G, Gray Lowland soils; A, Andosols; S, Sand-dune Regosols.

2) Land use: NC, non-cultivated field; G, greenhouse field.

3) Δ total F: Amount of accumulated total F = total F concentration in the greenhouse soil - total F concentration in the neighboring non-cultivated soils

4) Δ water-soluble F: Amount of accumulated water-soluble F = water-soluble F concentration in the greenhouse soil - water-soluble F concentration in the neighboring non-cultivated soils

Table 3 Spearman's rank correlation coefficient (r_s) between F concentration (total F and water-soluble F) and soil chemical properties

	Total F	pH	Total C	Total P	Amorphous Al	Amorphous Fe
Total F	—	0.065 (0.715)	0.472 (0.005)	0.683 (< 0.001)	0.390 (0.023)	0.491 (0.003)
Water-soluble F	0.302 (0.083)	0.558 (0.001)	-0.094 (0.596)	0.585 (< 0.001)	-0.087 (0.623)	-0.131 (0.459)

Numbers in parentheses indicate p -value

Fig. 2 Relationship between total P concentration and total F concentration in non-cultivated soils and greenhouse soils

Fig. 3 Relationship between total P concentration and water-soluble F concentration in non-cultivated soils and greenhouse soils

Water-soluble F concentration

The water-soluble F concentrations in non-cultivated and greenhouse soils ranged from 0.15 to 4.89 mg/kg (median 1.22 mg/kg) and from 1.75 to 20.3 mg/kg (median 3.79 mg/kg), respectively (Table 2). Compared with total F concentration, water-soluble F concentrations were very low; the proportion of total F present as water-soluble F was 0.1–5.8 %. The result suggests that most F in soil is present in insoluble form, as already reported^{3, 17, 20}. As well as the total F concentration, there were differences in water-soluble F concentrations in the non-cultivated soils among the three soil groups ($p = 0.024$, Kruskal-Wallis test): the concentration ranges in Gray Lowland Soils, Andosols and Sand-dune Regosols were 1.57–4.89 mg/kg (median 2.59 mg/kg), 0.15–1.31 mg/kg (median 0.42 mg/kg) and 1.14–1.22 mg/kg (median 1.15 mg/kg), respectively.

All greenhouse soils except four (samples A-1, A-2, A-3, and A-4) had higher water-soluble F concentrations than the neighboring non-cultivated soils; for example, the water-soluble F concentrations in the greenhouse soils E-1 (2.00 mg/kg), E-2 (1.75 mg/kg) and E-3 (1.98 mg/kg) were 13, 12 and 13 times higher, respectively, than in the neighboring non-cultivated soil E-0 (0.15 mg/kg). This result shows that not only total F concentration but also water-soluble F concentration was elevated in greenhouse soils. However, there was no significant correlation either between the total F concentration and the water-soluble F concentration ($r_s = 0.302$, $p = 0.083$) or between the amount of accumulated total F and the amount of accumulated water-soluble F ($r_s = 0.219$, $p = 0.315$).

It is known that the water-soluble F concentration in soil reflects a number of factors affecting the solubility of F in soil¹⁸. Correlations between water-soluble F concentration in soil and some chemical properties of the soil are summarized in Table 3. Water-soluble F concentration showed a significant positive correlation with total P concentration ($r_s = 0.585$, $p < 0.001$, Fig. 3). This correlation indicates that there is a link between water-soluble F concentration in the soil

and the use of phosphate fertilizer, similar to the correlation found for total F concentration. Furthermore, water-soluble F concentration also showed a positive correlation with soil pH ($r_s = 0.558$, $p = 0.001$). This correlation is consistent with the finding of Gilpin and Johnson²¹ that F solubility in soils in Pennsylvania, USA, increased at pH values above 6. This result indicates that water-soluble F concentration in soil may be partly controlled by soil pH management. Loganathan et al.²² found that the water-soluble F concentration was positively related to total C concentration in New Zealand soils, but such a correlation was not found in this study.

The above results indicate that the water-soluble F concentration in greenhouse soils in Japan is elevated due to the application of phosphate fertilizer. It is recognized that the water-soluble F concentration closely reflects plant availability. Although it is known that excessive F uptake is detrimental to plant growth and yield^{23, 24}, the critical level of water-soluble F in soils above which plant growth is affected has not been fully clarified. Thus, we cannot evaluate the effect of the water-soluble F concentration in the greenhouse soils studied here on crop production. However, no visible injury due to F toxicity, which is seen as marginal necrosis on foliage, was observed on the cultivated plants (sweet pepper; *Capsicum annuum* L.) from the greenhouses. It is still necessary to investigate the effect of soil F accumulation due to the application of phosphate fertilizer on plant growth and yield in the future.

CONCLUSIONS

The total F concentration in non-cultivated soils and greenhouse soils ranged from 53 to 248 mg/kg and from 163 to 471 mg/kg, respectively. All greenhouse soils except three had a higher total F concentration than the neighboring non-cultivated soils, which indicates that the total F concentration was elevated in almost all greenhouse soils. The amount of F accumulated in the greenhouse soils was es-

timated at 17–249 mg per kg oven-dry soil by subtracting the total F concentration of the greenhouse soils from that of the neighboring non-cultivated soils. Total F concentration in the soil showed a significant positive correlation with total P concentration in the soil ($r_s = 0.683$, $p < 0.001$), which suggests that elevation in F concentration is associated with elevation in P concentration due to the excessive application of phosphate fertilizer. The water-soluble F concentrations in non-cultivated and greenhouse soils ranged from 0.15 to 4.89 mg/kg and from 1.75 to 20.3 mg/kg, respectively. These concentrations were significantly lower than the total F concentration, which indicates that most F in soil is present in insoluble form. All greenhouse soils except four had a higher water-soluble F concentration than the neighboring non-cultivated soils. This shows that not only total F concentration but also water-soluble concentration was correspondingly elevated in greenhouse soils.

ACKNOWLEDGEMENTS

This work was supported by a Grant-in-Aid for Challenging Exploratory Research from the Japan Society for the Promotion of Science (JSPS KAKENHI Grant Number 25660280).

REFERENCES

- 1) Swaine, D.J.; Fluorine, "The trace-element content of fertilizers", pp.102–131, Commonwealth Agricultural Bureaux, England (1962)
- 2) McLaughlin, M.J., Tiller, K.G., Naidu, R. and Stevens, D.P.: Review: the behaviour and environmental impact of contaminants in fertilizers. *Aust. J. Soil Res.*, **34**, 1–54 (1996)
- 3) Cronin, S.J., Manoharan, V., Hedley, M.J. and Loganathan, P.: Fluoride: a review of its fate, bioavailability and risks of fluorosis in grazed-pasture systems in New Zealand. *New Zealand Journal of Agricultural Research*, **43**, 295–321 (2000).
- 4) Loganathan, P., Hedley, M.J., Wallace, G.C. and Roberts, A.H.C.: Fluoride accumulation in pasture forages and soils following long-term applications of phosphorus fertilizers. *Environmental Pollution*, **115**, 275–282 (2001)
- 5) Mishima, S. and Kohyama, K.: The database and the methodologies to estimate recent trend of nitrogen (N) and phosphate (P) flows and residual N and P in Japanese national prefectural scales and examples their application. *Bull. Natl. Inst. Agro-Environ. Sci.*, **27**, 117–139 (2010) (in Japanese with English abstract)
- 6) Yoshiike, A.: The status of fertilized phosphate accumulation in agricultural land soil. *Jpn. J. Soil Sci. Plant Nutr.*, **75**, 255–261 (1983) (in Japanese)
- 7) Obara, H. and Nakai, M.: Available phosphate of arable land in Japan. Changes of soil characteristics in Japanese arable land (II). *Jpn. J. Soil Sci. Plant Nutr.*, **75**, 59–67 (2004) (in Japanese with English abstract)
- 8) Yamada, H., Hattori, T. and Fujita, T.: Distribution of fluorine on the cultivated land in Kameoka basin of Kyoto prefecture. *The Sci. Rep. Kyoto Prefect. Univ. Agric.*, **34**, 127–134 (1982) (in Japanese with English abstract)
- 9) Cultivated Soil Classification Committee: Classification of Cultivated Soils in Japan, Third Approximation. Miscellaneous publication of the National Institute of Agro-Environmental Science, No. 17, Tsukuba, Japan (1995) (in Japanese)
- 10) Soil Environmental Analysis Committee: Soil chemistry, pp.195–385, "Soil environmental analysis", Hakuyusya, Tokyo (1997) (in Japanese)
- 11) Blakemore, L.C. and Searle, P.L.: Extractable iron, aluminum and silicon. *New Zealand Soil Bur. Sci. Rep.*, **80**, 71–80 (1987)
- 12) Ministry of the Environment, Environmental Management Bureau: Fluorine, pp.88–98, "Survey method of bottom sediment", Ministry of the Environment (2012) (in Japanese)
- 13) Hashitani, H., Yoshida, H. and Muto, H.: Simple method for direct photometric determination of traces of fluoride with alizarin complexone, *Japan Analyst*, **16**, 44–46, (1967) (in Japanese with English abstract)
- 14) Hashitani, H., Yoshida, H. and Adachi, T.: Direct determination of fluoride in water by use of acetylacetone as a demasking agent. *Bunseki Kagaku*, **28**, 680–685 (1979) (in Japanese with English abstract)
- 15) Okumura, M., Yoshimura, T. Fujinaga, K. and Seika, Y.: Direct spectrophotometric determination of traces of fluoride in rain water. *Bunseki Kagaku*, **52**, 485–488 (2003) (in Japanese with English abstract)
- 16) Alina, K.P.; Fluorine, pp.385–393, "Trace elements in Soils and Plants" 4th ed., CRC, Florida (2011)
- 17) Bower, C.A. and Hatcher, J.T.: Adsorption of fluoride by soils and minerals. *Soil Science*, **103**, 151–154 (1967)
- 18) Pickering, W.F.; The mobility of soluble fluoride in soils. *Environmental Pollution*, **9**, 281–308 (1985)
- 19) Robinson, W.O. and Edgington, G.: Fluorine in soils. *Soil Science*, **61**, 341–353 (1946)
- 20) Omuetti, J.A.I and Jone, R.L.; Fluoride adsorption by Illinois soils. *Journal of Soil Science*, **28**, 564–572 (1977)
- 21) Gilpin, L. and Johnson, A.H.; Fluorine in agricultural soils of southern Pennsylvania. *Soil Science Society of America Journal*, **44**, 255–258 (1980)
- 22) Loganathan, P., Gray, C.W., Hedley, M.J. and Roberts, A.H.C.: Total and soluble fluorine concentrations in relation to properties of soils in New Zealand. *European Journal of Soil Science*, **57**, 411–421 (2006)
- 23) Hara, T. and Sonoda, Y. and Iwai, I.; Growth response of cabbage plants to sodium halides under water culture condition. *Soil. Sci. Plant Nutr.*, **23**, 77–84 (1977)
- 24) Bar-Yosef and Rosenberg, R.; Response of corn and tomato plants to fluorine concentration in solution culture. *Agron. J.*, **80**, 173–177 (1988)