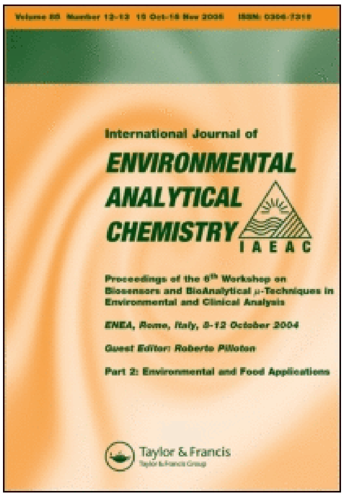

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Determination of Major and Trace Elements in Mushroom, Plant and Soil Samples Collected from Japanese Forests

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DETERMINATION OF MAJOR AND TRACE ELEMENTS IN MUSHROOM, PLANT AND SOIL SAMPLES COLLECTED FROM JAPANESE FORESTS

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Inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) were used to measure many major and trace elements in plant, mushroom and soil samples collected in Japanese forests. Sample preparation and analytical conditions were investigated to set up a simple routine procedure for measuring a large range of elements. Fifty elements were determined for soil samples. For plant and mushroom samples, 25 elements were determined.

Concentrations of some trace elements such as Zn, Pb, Cd, Bi, Sn and Sb in forest soils tended to be the highest in the surface soil layer, indicating the importance of atmospheric deposition on the total contents in the soils of these elements. In comparison with the element contents of plants, the mushroom contents could be characterized by low Mg, Ca, Sr and Ba amounts. Transfer factors (TFs) were estimated from the ratio of "concentration in plant or mushroom on dry weight basis" to "concentration in the surface soil on dry weight basis". The TFs of lanthanide elements, Th and U were very low in all plant and mushroom samples. Mushrooms tended to accumulate Cu, Zn, Rb, Cd and Cs. The TFs of Cs for mushrooms were one or two orders higher than those for other plants growing in the same forest. This result was consistent with the high concentrations of radiocesium in mushrooms reported by researchers in many countries.

Keywords: ICP-MS; trace elements; mushroom; plant; soil; forest

INTRODUCTION

Measurements of major and trace elements in biological and soil samples within a forest are needed to expand our knowledge of the elemental composition of the forest ecosystem and to predict migrations and effects of chemical elements.

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Most research efforts concerning the elemental migrations in forest ecosystems have concentrated on the major nutrient elements (e.g. K, Ca, Mg, P)[1] and some heavy metals (e.g. Cu, Zn, Pb, Cd)[2–4]. Although the lanthanide elements in plants have also been measured in some forests[5–6], the data were limited. Therefore, the distribution and transfer of many trace elements are still unknown.

Analytical methods commonly used in the determination of trace elements are neutron activation analysis (NAA), atomic absorption spectrometry (AAS), X-ray fluorescence (XRF) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Recently, inductively coupled plasma-mass spectrometry (ICP-MS) has been used for accurate and precise determination of trace elements in a variety of materials including environmental samples[7]. Due to its low detection limits, analytical speed, relative lack of chemical interferences, and multi-element capability, the method has been applied to more than 50 elements in environmental samples[8–12].

In the present study, ICP-MS was used to measure many trace elements in mushroom, plant and soil samples collected from Japanese forests. Major elements were measured using ICP-AES. Sample preparation and analytical conditions were investigated to set up a simple routine procedure for measuring a large range of elements. Distribution of the trace elements in the forests and specific accumulation of some trace elements by plants and mushrooms were discussed based on the analytical results.

MATERIALS AND METHODS

Plant samples were collected from a pine forest in Tokai, Ibaraki in September 1990. Mushroom samples were collected in the same forest from 1989 to 1991. Soils at different depths were sampled in the same forest and another forest at Tsukuba, Ibaraki for comparison. Plant and mushroom samples were freeze-dried and pulverized with a cooking blender. Soil samples were air dried, sieved (1 mm) and ground to powders.

Mushroom and plant (0.2–1 g) and soil (0.1 g) samples were digested in Teflon™ PFA pressure decomposition vessels or Teflon™ beakers with acids (HNO_3, HF and $HClO_4$). A microwave digester (CEM, MDS–2000) or hot plate (at about 150°C) was used for heating the samples. After digestion, the samples were evaporated to dryness. Then, the residues were dissolved in 1–2% HNO_3 to yield the sample solutions.

Trace elements (Cs, Sr, Zn, Cu, Cd, La, Ce, Th, U, etc.) were measured by ICP-MS (Yokogawa PMS–2000). The instrumental parameters are summarized in Table I. Under these conditions, the oxide formation level of Ce was found to be 0.5–2% (CeO^+/Ce^+). Internal standards such as Rh, In, and Bi were used to compensate for changes in analytical signals during the operation. Major elements, Na, Mg, Al, P, K, Ca, Ti, Mn and Fe, were analyzed by ICP-AES. Standard solutions were prepared from SPEX Multi-Element Plasma Standards (SPEX Industries Inc., XSTC–1, 7, 8 and 13) and used to get calibration curves. Several standard reference materials were used to validate the analytical procedure. A rock reference sample, JB- 1 (basalt) issued by the Geological Survey of Japan, was used for soil analysis. The details of soil analysis were described in Yoshida *et al*, [12]. Tomato Leaves (1573a) and Orchard Leaves (1571) issued by the National Institute of Standards & Technology, were used for plant and mushroom analyses.

RESULTS AND DISCUSSION

Validation of Analytical Procedure

Low background counts and the high sensitivity of ICP-MS provided extremely low detection limits for most elements (ng/l level in sample solution). Good agreements between the certified and measured values were observed for standard reference materials (see Figure 1). In the case of JB-1, errors of measured values were less than 10% of the certified values[13] for 36 elements, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Ga, Sr, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu, Hf, Pb, Bi, Th and U. The errors were less than 20% for 12 elements, Mn, Li, Be, Zn, Y, Cd, Sn, Sb, Cs, Ho, Ta and W. And the errors were less than 30% for Rb and Mo. Precisions calculated using three independent runs were typically better than 5% RSD (relative standard deviation) for most elements. For the plant reference samples, elements which are certified are limited. Errors were less than 30% of the certified or additional information values for 25 elements, Na, Mg, Al, P, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Cd, Cs, Ba, La, Ce, Sm, Gd, Pb, Th and U. For most elements, precisions for plant and mushroom samples were worse than those for soil samples due to high concentrations of matrix elements in sample solutions. Precisions calculated using three independent runs of Tomato Leaves were better than 5% RSD for Na, Mg, Al, P, Ca, Mn, Fe, Ba, La, Sm and Pb, 5–10% RSD for K, Cr, Cu, Zn, Rb, Sr, Cd and U, and 10–20% RSD for Co, Cs, Ce, Gd and Th. Precision for Ni was 24%. The high precision for Ni (Ni–60) might be attributable to an interference with CaO molecule.

TABLE I Instrumental parameters for the ICP-MS

Plasma	
Frequency (MHz)	27.12
RF power (kW)	1.20
Argon flow (L/min)	
Plasma	14.00
Auxiliary	1.20
Carrier	0.83
Sampling distance (mm)	4.80
Sample uptake rate (mL/min)	0.80
Data Acquisition	
Mode	Peak jumping mode
No. points per peak	3
No. sweeps	20
Dwell time per point (s)	0.1–0.5
No. replicates	3

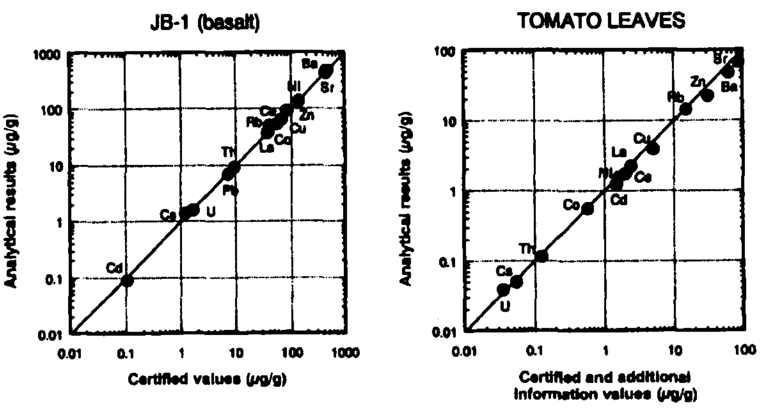

FIGURE 1 Binary plots of analytical results of selected trace elements, Co, Ni, Cu, Zn, Rb, Sr, Cd, Cs, Ba, La, Ce, Pb, Th and U versus their certified and additional information values for basalt (JB–1) and tomato leaves samples. Solid line: slope unity

Analytical Results of Soils

Analytical results of soil samples collected from a pine forest (Sand-dune Regosol) in Tokai, Ibaraki and a deciduous broad-leaved forest (Andosol) in Tsukuba, Ibaraki are shown in Table II. Fifty elements were determined for soil samples. Vertical profiles of the elements differed among elements and soil types. Concentrations of Zn, Pb, Cd, Bi, Sn and Sb in the Andosol are highest in the F+L or 0–5 cm soil layer and lower in the deeper soil layers. These elements are known to be accumulated in anthropogenic particulates. These observations indicate that a significant portion of these elements in the soil is derived from atmospheric deposition. The accumulation of Zn, Pb and Cd in the surface forest soils has also been observed in many forests contaminated by atmospheric pollution[3,14,15]. The concentrations of Al, Fe, Ti, Li, V, Cr, Ni, Cu, lanthanide elements, Th and U etc. were high in the deeper soil layers. These elements were mainly supplied from the bed rock or the original material of the soil, i.e. volcanic ash for the Andosol. The concentrations of most elements in the Sand-dune Regosol were lower than those in the Andosol, except for Na, Mg, K, Ca, Rb, Sr, Nb, Cd, Sb and Ba. In the Sand-dune Regosol, only Cd had its highest concentration in the surface soil layer (0–2 cm). The concentrations of the other elements did not change with depth or had a broad peak in the subsurface layers (2–10 cm). Sandy soils do not sorb these trace elements well because of the lack of any sorption site such as organic materials and sesquioxides of Al and Fe. Therefore, no accumulations of most trace elements in the surface layer were observed.

Analytical Results of Plants and Mushrooms

Analytical results of plants and mushrooms collected from the pine forest in Tokai, Ibaraki for 25 elements are summarized in Table III. The highest concentration in the mushrooms was found for K followed by P, Mg, Na and Ca. On the other hand, the highest concentration was observed for Ca in many plant samples. In comparison with the elemental content of plants, the contents of mushrooms could be characterized by low Mg, Ca, Sr and Ba concentrations.

In order to estimate the accumulation of each element by plants and mushrooms, transfer factors (TFs) from soil to plants and mushrooms were calculated by using the element concentrations in the surface soil (average of 0–2 cm and 2–5 cm layers) collected in the forest. It was defined as the ratio of "concentration in plant or mushroom on dry weight basis" to "concentration in the surface soil on dry weight basis". The calculated TFs for 14 trace elements, Co, Ni, Cu, Zn, Rb, Sr, Cd, Cs, Ba, La, Ce, Pb, Th and U, are summarized in Table IV.

The TFs of Co, Ba, La, Ce, Pb, Th and U were very low for all plants and mushrooms. On the other hand, those of Cu, Zn, Rb and Cd were relatively high. Mushrooms tended to accumulate Cu, Zn, Rb, Cd and Cs, although the TFs varied within the species. The TFs of Cs for mushrooms were one or two orders of magnitude higher than those for plants growing in the same forest. High concentrations of radiocesium discharged through nuclear weapons testing and nuclear accidents have been reported in many countries[16–20]. The high TFs for stable Cs obtained in this study indicated that mushrooms are important Cs accumulators and radiocesium is taken up from soils together with stable Cs.

TABLE II Concentration of major and trace elements in soils collected from two different forests (μg/g, dry wt)

	Tokai (Sand-dune Regosol)						Tsukuba (Andosol)					
Code	*FR-23*	*FR-24*	*FR-25*	*FR-26*	*FR-27*	*FR-28*	*O-12*	*O-13*	*O-14*	*O-15*	*O-16*	*O-17*
Depth (cm)	***L***	***0-2***	***2-5***	***5-10***	***10-20***	***20-30***	***L***	***F + H***	***0-5***	***10-20***	***20-30***	***40-55***
Na	416	15300	16500	17000	17000	17500	150	4030	5540	6420	6730	4370
Mg	410	5180	7400	9460	5930	8200	1040	3670	6760	8770	8460	5770
Al	893	44400	52400	51700	50400	50600	2200	47700	79200	90100	89200	131000
K	614	18400	21800	17500	21400	19100	960	2470	3690	3700	3600	5550
Ca	2050	11400	12300	14900	13700	16300	1640	2970	3400	3510	3590	1520
Ti		1840	2910	3950	2260	2960	120	4440	5800	6810	6970	8330
Mn	98	564	536	647	506	613	310	920	1090	1130	1120	1170
Fe	407	15400	20200	24300	17200	21300	1410	39200	55600	65700	67800	82200
Li	0.32	12.2	13.8	13.5	12.5	13.2	0.54	16.0	20.5	22.4	23.3	32.5
Be	0.022	0.88	0.97	1.02	0.94	0.96	0.02	0.80	1.07	1.15	1.17	1.65
Sc	0.15	3.10	5.97	6.79	3.66	5.01	0.60	16.9	22.9	27.0	27.1	33.1
V	1.62	36.3	46.0	58.8	44.1	53.0	7.11	193	252	294	300	354
Cr	1.53	14.6	14.6	34.1	10.6	16.5	8.72	51.2	64.6	72.8	72.8	89.5
Co	0.43	4.07	5.19	6.40	4.77	5.39	1.06	19.5	25.1	29.2	30.0	35.0
Ni	0.79	6.34	6.43	7.65	5.91	7.00	4.35	27.2	33.9	38.0	38.5	45.2
Cu	1.62	7.69	6.06	5.40	7.27	4.48	6.80	70.9	87.2	96.6	98.4	122
Zn	9.51	42.9	47.5	49.4	35.1	38.6	40.4	133	133	117	102	118
Ga	0.26	8.75	10.6	10.6	10.1	9.97	0.31	15.1	19.7	22.4	23.0	28.0
Rb	1.75	42.7	65.0	43.8	45.3	46.4	3.71	28.3	37.7	36.7	36.2	62.0
Sr	10.8	78.0	146	127	94.8	109	25.9	72.4	87.7	94.0	96.1	64.9
Y	0.15	3.17	6.82	7.35	4.51	5.91	0.52	13.6	18.6	21.3	21.3	24.8
Zr	0.48	24.0	24.1	22.1	22.5	24.3	2.86	72.6	94.7	110	111	139
Nb	0.099	4.08	5.13	6.66	5.16	5.03	0.47	4.60	5.07	6.47	6.26	8.99
Mo	0.044	0.44	0.21	0.24	1.66	0.18	0.17	1.32	1.52	1.48	1.43	1.93

TABLE II Continued

	Tokai (Sand-dune Regosol)						Tsukuba (Andosol)					
Code	*FR-23*	*FR-24*	*FR-25*	*FR-26*	*FR-27*	*FR-28*	*O-12*	*O-13*	*O-14*	*O-15*	*O-16*	*O-17*
Depth (cm)	***L***	***0-2***	***2-5***	***5-10***	***10-20***	***20-30***	***L***	***F + H***	***0-5***	***10-20***	***20-30***	***40-55***
Cd	0.12	0.24	0.12	0.13	0.10	0.10	0.07	0.27	0.29	0.23	0.18	0.12
Sn	0.11	1.19	1.19	1.24	1.02	1.02	0.50	3.73	2.86	2.46	1.98	2.41
Sb	0.050	1.33	0.78	0.78	0.50	0.39	0.23	1.03	0.95	0.78	0.61	0.77
Cs	0.047	1.28	1.28	1.33	1.05	1.23	0.12	2.71	3.52	3.62	3.73	5.33
Ba	8.50	241	381	286	245	263	19.3	140	169	174	181	198
La	0.23	2.32	9.55	13.9	2.94	2.94	0.90	10.9	13.9	15.1	15.7	16.2
Ce	0.46	5.90	19.6	30.6	7.11	7.96	1.28	23.1	29.8	32.0	32.7	43.2
Pr	0.056	0.64	2.03	3.00	0.78	0.83	0.24	2.95	3.85	4.19	4.34	5.01
Nd	0.19	2.41	7.28	10.3	2.97	3.30	0.80	12.0	15.5	16.9	17.6	20.7
Sm	0.042	0.58	1.44	1.99	0.74	0.87	0.22	2.74	3.61	3.95	4.08	4.94
Eu	0.011	0.27	0.49	0.47	0.29	0.34	0.11	0.83	1.10	1.19	1.22	1.44
Gd	0.048	0.61	1.48	1.86	0.84	1.02	0.23	2.91	3.75	4.16	4.29	5.13
Tb	0.005	0.09	0.20	0.24	0.11	0.14	0.09	0.51	0.68	0.72	0.73	0.88
Dy	0.026	0.55	1.14	1.29	0.73	0.90	0.19	2.64	3.49	3.84	3.95	4.88
Ho	0.005	0.12	0.24	0.26	0.15	0.19	0.08	0.59	0.80	0.86	0.87	1.05
Er	0.015	0.35	0.72	0.77	0.48	0.59	0.12	1.60	2.17	2.41	2.49	2.99
Tm	0.002	0.06	0.11	0.11	0.07	0.09	0.06	0.28	0.38	0.40	0.39	0.48
Yb	0.015	0.38	0.74	0.78	0.52	0.69	0.11	1.52	2.06	2.30	2.33	2.88
Lu	0.002	0.06	0.11	0.12	0.08	0.10	0.05	0.25	0.36	0.38	0.37	0.46
Hf	0.016	1.98	1.77	1.77	1.78	1.80	0.12	2.14	2.76	3.12	3.17	4.00
Ta	0.010	0.48	0.50	0.68	0.53	0.55	0.03	0.96	1.74	2.25	1.67	2.45
W	0.033	0.51	0.55	0.55	0.55	0.49	0.19	1.17	1.31	1.22	1.12	1.54
Pb	1.56	12.2	19.0	12.7	8.75	8.47	3.27	26.7	27.6	19.2	14.1	15.6
Bi							0.03	0.39	0.44	0.34	0.27	0.31
Th	0.094	1.14	3.66	5.23	1.36	1.77	0.21	3.65	4.69	4.62	4.58	6.49
U	0.024	0.18	0.51	0.34	0.17	0.20	0.02	0.88	1.15	1.13	1.10	1.49

TABLE III Concentration of major and trace elements in plants and mushrooms collected from a pine forest in Tokai, Ibaraki (μg/g, dry wt)

	Tree leaves			Shrub					Mushroom				
Code	*Pinus thunbergii (C)* TL-2a*	*Pinus thunbergii (C+1&2)† TL-2b*	*Morus bombycis TL-4*	*Indigofera pseudo-tinctoria GR-5*	*Vitex rotundi-folia GR-6*	*Oenothera lamarck-iana GR-8*	*Miscanthus sinensis GR-9*	*Ophi-opogon japonicus GR-10*	*Suillus granu-latus MR-7*	*Lactarious hatsudake MR-24*	*Russula mariae MR-93*	*Amanita panther-ina MR-151*	*Tricholoma flavo-virens MR-211*
Na	93	331	6040	713	1850	900	892	670	308	228	1490	167	1782
Mg	1300	1100	3450	5660	1300	4710	1200	2290	1100	1040	976	682	1400
Al	293	506	305	7.9	188	201	62	254	310	222	323	218	943
P	984	697	1480	1540	1790	2150	608	1590	6470	4720	6900	4920	4300
K	6900	4250	15300	8890	8830	24500	3960	17900	32900	24900	37600	28700	51500
Ca	2574	6440	29800	58300	25900	28700	5820	6700	186	145	207	100	626
Mn	223	569	150	167	33	283	137	197	22	7.3	30	10	35
Fe	41	93	349	85	228	194	109	265	175	126	180	93	452
Cr	0.46	0.60	1.26	0.58	1.13	0.53	8.27	1.35	4.08	1.11	1.00	1.66	0.88
Co	0.10	0.18	0.15	0.17	0.25	0.14	0.10	0.099	0.42	0.12	0.20	0.072	0.17
Ni	0.97	0.56	1.46	1.45	0.75	0.94	3.31	0.92	1.07	1.09	1.08	0.65	0.84
Cu	2.81	2.37	6.81	9.48	3.05	5.23	2.37	8.80	27.8	6.79	40.4	22.7	23.9
Zn	18.8	30.7	19.0	13.6	9.28	25.0	18.0	37.4	77.0	116	69.9	74.3	216
Rb	8.24	2.96	10.3	14.9	7.94	31.8	3.98	15.9	101	95.7	46.6	73.2	254
Sr	13.7	27.3	108	151	99.3	113	38.2	42.3	1.48	1.10	1.89	1.07	5.59
Cd	0.34	0.40	0.082	0.18	0.042	0.17	0.039	0.21	0.28	1.18	4.32	9.89	1.55
Cs	0.024	0.017	0.048	0.10	0.037	0.11	0.022	0.052	2.39	2.23	0.34	0.31	20.3
Ba	2.72	6.39	15.3	13.5	8.19	13.6	8.68	15.0	2.97	1.98	2.02	2.02	8.02
La	0.020	0.082	0.46	0.76	0.22	0.41	0.077	0.15	0.10	0.048	0.043	0.019	0.16
Ce	0.029	0.10	0.37	0.34	0.23	0.27	0.069	0.23	0.20	0.088	0.090	0.034	0.32
Sm	0.002	0.010	0.068	0.17	0.032	0.057	0.007	0.019	0.016	0.007	0.009	0.003	0.030
Gd	0.002	0.008	0.028	0.028	0.015	0.024	0.005	0.016	0.015	0.007	0.009	0.003	0.030
Pb	0.39	0.82	2.64	0.56	1.28	1.24	0.85	1.48	0.60	0.33	1.42	0.21	1.52
Th	0.003	0.014	0.040	0.006	0.036	0.019	0.008	0.028	0.026	0.010	0.013	0.005	0.042
U	0.001	0.004	0.012	0.002	0.007	0.006	0.002	0.009	0.004	0.008	0.012	0.007	0.010

* current leaves

† one and two year old leaves

TABLE IV Transfer factors of trace elements from soil to plants and mushrooms

Sample	*Code*	*Co*	*Ni*	*Cu*	*Zn*	*Rb*	*Sr*	*Cd*	*Cs*	*Ba*	*La*	*Ce*	*Pb*	*Th*	*U*
Tree leaves															
Pinus thunbergii (C)*	TL-2a	0.022	0.15	0.41	0.42	0.15	0.12	1.9	0.019	0.009	0.003	0.002	0.025	0.001	0.003
Pinus thunbergii (C + 1&2)†	TL-2b	0.039	0.09	0.34	0.68	0.05	0.24	2.2	0.013	0.021	0.014	0.008	0.053	0.006	0.012
Morus bombycis	TL-4	0.032	0.23	0.99	0.42	0.19	0.97	0.5	0.037	0.049	0.077	0.029	0.170	0.017	0.034
mean		0.031	0.16	0.58	0.51	0.13	0.44	1.5	0.023	0.026	0.031	0.013	0.082	0.008	0.016
Shrub															
Indigofera pseudo-tinctoria	GR-5	0.037	0.23	1.38	0.30	0.27	1.35	1.0	0.078	0.043	0.128	0.026	0.036	0.003	0.006
Vitex rotundifolia	GR-6	0.053	0.12	0.44	0.21	0.15	0.89	0.2	0.029	0.026	0.037	0.018	0.082	0.015	0.021
Oenothera lamarckiana	GR-8	0.029	0.15	0.76	0.55	0.59	1.01	0.9	0.087	0.044	0.069	0.021	0.080	0.008	0.019
Miscanthus sinensis	GR-9	0.022	0.52	0.34	0.40	0.07	0.34	0.2	0.017	0.028	0.013	0.005	0.054	0.003	0.007
Ophiopogon japonicus	GR-10	0.021	0.14	1.28	0.83	0.29	0.38	1.2	0.041	0.048	0.026	0.018	0.095	0.012	0.026
mean		0.033	0.23	0.84	0.46	0.28	0.79	0.7	0.051	0.038	0.055	0.018	0.069	0.008	0.016
Mushroom															
Suillus granulatus	MR-7	0.091	0.17	4.0	1.7	1.9	0.013	1.6	1.86	0.010	0.018	0.016	0.039	0.011	0.011
Lactarious hatsudake	MR-24	0.026	0.17	1.0	2.6	1.8	0.010	6.6	1.74	0.006	0.008	0.007	0.021	0.004	0.022
Russula mariae	MR-93	0.043	0.17	5.9	1.5	0.9	0.017	24.0	0.27	0.006	0.007	0.007	0.091	0.005	0.034
Amanita pantherina	MR-151	0.016	0.10	3.3	1.6	1.4	0.010	55.0	0.24	0.007	0.003	0.003	0.013	0.002	0.020
Tricholoma flavovirens	MR-211	0.037	0.13	3.5	4.8	4.7	0.050	8.6	15.8	0.026	0.027	0.025	0.098	0.017	0.031
mean		0.043	0.15	3.5	2.4	2.1	0.020	19.1	3.99	0.011	0.013	0.012	0.052	0.008	0.024

* current leaves
† one and two year old leaves

The location of roots and mycelia is one of the important factors controlling trace element concentrations in plants and mushrooms. In this study, the surface soil (0–5 cm) was used for the calculation of TFs because most roots and mycelia grow in this layer. However, there are some variations in the location due to the species. For accurate determination of TFs, the appropriate soil layer should be used in accordance with the placing of the roots and mycelia.

Multi-element capability of ICP-MS can provide information on the distribution of many trace elements in forest ecosystems. The TFs estimated in this study tended to be lower than those estimated from radiotracer experiments for vegetables. Since the bulk soil samples were analyzed in this study, the TFs of elements combined with minerals might be underestimated. The *in situ* TFs provided in this study can be used for the estimation of species specific accumulation and plant-availability of the elements.

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