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# Effects of Fertilization, Crop Year, Variety, and Provenance Factors on Mineral Concentrations in Onions

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Mineral concentrations of onions (*Allium cepa* L.) grown under various conditions, including factors (fertilization, crop year, variety, and provenance), were investigated to clarify how much each factor contributes to the variation of their concentrations. This was because the mineral concentrations might be affected by various factors. The ultimate goal of this study was to develop a technique to determine the geographic origins of onions by mineral composition. Samples were onions grown under various conditions at 52 fields in 18 farms in Hokkaido, Japan. Twenty-six elements (Li, Na, Mg, Al, P, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Y, Mo, Cd, Cs, Ba, La, Ce, Nd, Gd, W, and Tl) in these samples were determined by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry. Fertilization conditions and crop years of onions caused variations of P, Ni, Cu, Rb, Sr, Mo, Cs, and Tl concentrations in onions; different onion varieties also showed variations in numerous element concentrations. However, the variations of mineral compositions of onions by these factors were smaller than the differences between production places with a few exceptions. Furthermore, Na, Rb, and Cs in group IA of the periodic table, Ca, Sr, and Ba in group IIA, and Zn and Cd in group IIB showed similar concentration patterns by group; this result demonstrated that elements in the same periodic groups behaved similarly in terms of their absorption in onions.

**KEYWORDS: Onion; mineral; geographic origin; fertilization experiment; correlation; element concentration**

## INTRODUCTION

Nowadays laws in many countries enforce labeling of the geographic origin of agricultural products due to demands for more information on foods by consumers and also to maintain domestic agricultural production. It therefore becomes important to find ways of preventing deceptive labeling of the geographic origin. The development of scientific techniques to determine the geographic origin of agricultural products is needed to cope with this issue. Numerous techniques based on organic constituents (*1*, *2*), mineral contents or composition (*3*, *4*), light (*7*, *8*) or heavy element (*9*, *10*) isotope ratios or their combination (*11*, *12*) have already been reported. The technique based on mineral composition is the most commonly applied nowadays because inductively coupled plasma atomic emission spectrometer (ICP-AES) and inductively coupled plasma mass spectrometer (ICP-MS) have comparatively prevailed and can acquire considerable data simultaneously. We have been studying methods for using this technique to determine the geographic origin of onions (*Allium cepa* L.) from the experience of a previous study on the geographic origin of Welsh onions (*3*, *4*). Mineral compositions in agricultural products, however, might vary by various factors such as fertilization, climatic condition in the cultivated year, differences in soil types, history of fields and variety—even within a single farm field. This issue makes the development of reliable techniques of place-of-origin determination using mineral composition difficult. Therefore, it is important to know what elements are affected easily and how much those element concentrations vary by various factors. The objective of this study was to investigate the range and pattern of variance of mineral composition of onions grown under different conditions such as fertilization, crop year, variety, and provenance. This information was expected to be helpful in the development of methods for determining the geographic origins of onions by mineral composition. Onions from fields within Hokkaido, Japan, were used as provenance factors in this study because clearer differences between far-apart regions are expected if differences between near regions are observed.

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**Table 1.** Cultivation Conditions and Varieties of Onion Samples in 52 Fields

| sample | type of expt | | tentative name of farm | place of production | crop year | variety (abbreviation) | soil type | fertilization for fertilizing expt |
|---|---|---|---|---|---|---|---|---|
| 1 | Zn 1 (nonfertilized) | crop year[d] 1 | exptl farm 1 | Wakaba, Kunneppu town | 1 | Super-kitamomiji (SKM) | gray lowland | |
| 2 | Zn 2 (nonfertilized) | | exptl farm 2 | Yayoi, Kunneppu town | 8 | Super-kitamomiji (SKM) | black volcanic | |
| 3 | | | Kitami 1 | Hirosato, Kitami city | 29 | Super-kitamomiji (SKM) | gray highland | |
| 4 | | | Kitami 2 | Toyochi, Kitami city | >20 | Super-kitamomiji (SKM) | brown lowland | |
| 5 | | | Tanno 1 | Kawamukai, Tanno town | 15 | Super-kitamomiji (SKM) | brown lowland | |
| 6 | | | Tanno 2 | Kawamukai, Tanno town | >20 | Super-kitamomiji (SKM) | brown lowland | |
| 7 | | | Kunneppu 1 | Kashiwaoka, Kunneppu town | >20 | Super-kitamomiji (SKM) | gray highland | |
| 8 | | | Kunneppu 2 | Jitsugo, Kunneppu town | 16 | Super-kitamomiji (SKM) | brown lowland | |
| 9 | | | Bihoro 1 | Tyohoro, Bihoro town | >50 | Super-kitamomiji (SKM) | brown forest | |
| 10 | | | Bihoro 2 | Akino, Bihoro town | 7 | Super-kitamomiji (SKM) | brown lowland | |
| 11 | | | Bihoro 3 | Akino, Bihoro town | >30 | Super-kitamomiji (SKM) | brown lowland | |
| 12 | | | Bihoro 4 | Mihukita, Bihoro town | >30 | Super-kitamomiji (SKM) | peat | |
| 13 | | | Furano 1 | Kitaonuma, Furano city | 15 | Super-kitamomiji (SKM) | peat | |
| 14 | | | Furano 2 | Kamigoku, Furano city | >40 | Super-kitamomiji (SKM) | brown lowland | |
| 15 | | | Furano 3 | Gakudasanku, Furano city | >30 | Super-kitamomiji (SKM) | brown lowland | |
| 16 | | | Iwamizawa 1 | Nishikawacho, Iwamizawa city | 27 | Super-kitamomiji (SKM) | peat | |
| 17 | | | Iwamizawa 2 | Nencho, Iwamizawa city | 30 | Super-kitamomiji (SKM) | gray lowland | |
| 18 | | | exptl farm 1 | Wakaba, Kunneppu town | 1 | Kitamomiji2000 (KM) | gray lowland | |
| 19 | provenance[a] | | Kitami 2 | Toyochi, Kitami city | >20 | Kitamomiji2000 (KM) | brown lowland | |
| 20 | provenance | | Tanno 2 | Kawamukai, Tanno town | >20 | Kitamomiji2000 (KM) | brown volcanic | |
| 21 | provenance | | Kunneppu 3 | Koen, Kunnepp town | >20 | Kitamomiji2000 (KM) | gray highland | |
| 22 | provenance | | Bihoro 3 | Akino, Bihoro town | >30 | Kitamomiji2000 (KM) | brown lowland | |
| 23 | provenance | | Bihoro 2 | Akino, Bihoro town | 7 | Kitamomiji2000 (KM) | brown lowland | |
| 24 | provenance | | Furano 1 | Kitanuma, Furano city | 4 | Kitamomiji2000 (KM) | gray lowland | |
| 25 | provenance | | Iwamizawa 1 | Nishikawacho, Iwamizawa city | 27 | Kitamomiji2000 (KM) | peat | |
| 26 | variety[b] | crop year 1 | exptl farm 1 | Wakaba, Kunneppu town | 6 | Super-kitamomiji (SKM) | gray lowland | |
| 27 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Kitamomiji2000 | gray lowland | |
| 28 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Kamui | gray lowland | |
| 29 | variety | crop year 2 | exptl farm 1 | Wakaba, Kunneppu town | 6 | Kairo'ohotsuku1 (KO1) | gray lowland | |
| 30 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Salari | gray lowland | |
| 31 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Wolf | gray lowland | |
| 32 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Iomante | gray lowland | |
| 33 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Kitahayate2 (KH2) | gray lowland | |
| 34 | variety | | expyl farm 1 | Wakaba, Kunneppu town | 6 | Kitamikou38 (KMI38) | gray lowland | |
| 35 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Kitamikou39 (KMI39) | gray lowland | |
| 36 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Kitawase3 (KW3) | gray lowland | |
| 37 | variety | | exptl farm 1 | Wakaba, Kunneppu town | 6 | Ohotsuku222 (O222) | gray lowland | |
| 38 | N[c] (0 kg/a) | | exptl farm 1 | Wakaba, Kunneppu town | 1 | Kitamikou39 (KMI39) | gray lowland | $(NH_4)_2SO_4$: 0.0 kg/a |
| 39 | N (0.5 kg/a) | | exptl farm 1 | Wakaba, Kunneppu town | 1 | Kitamikou39 (KMI39) | gray lowland | $(NH_4)_2SO_4$: 2.3 kg/a |
| 40 | N (1.0 kg/a) | | exptl farm 1 | Wakaba, Kunneppu town | 1 | Kitamikou39 (KMI39) | gray lowland | $(NH_4)_2SO_4$: 4.7 kg/a |
| 41 | | | exptl farm 1 | Wakaba, Kunneppu town | 1 | Kitamikou39 (KMI39) | gray lowland | $(NH_4)_2SO_4$: 7.0 kg/a |
| 42 | N (2.0 kg/a) | | exptl farm 1 | Wakaba, Kunneppu town | 1 | Kitamikou39 (KMI39) | gray lowland | $(NH_4)_2SO_4$: 9.3 kg/a |
| 43 | N (3.0 kg/a) | | exptl farm 1 | Wakaba, Kunneppu town | 1 | Kitamikou39 (KMI39) | gray lowland | $(NH_4)_2SO_4$: 14 kg/a |
| 44 | Ca (fertilized) | | exptl farm 2 | Yahoi, Kunneppu town | 1 | Super-kitamomiji (SKM) | black volcanic | |
| 45 | Mg (fertilized) | | exptl farm 2 | Yahoi, Kunneppu town | 8 | Super-kitamomiji (SKM) | black volcanic | |
| 46 | Ca + Mg (non-fertilized) | | exptl farm 2 | Yahoi, Kunneppu town | 8 | Super-kitamomiji (SKM) | black volcanic | particle-shaped $CaCO_3$ coated with lignin $MgSO_4$: 6.0 kg/a |
| 47 | Zn 1 (fertilized) | | exptl farm 1 | Wakaba, Kunneppu town | 8 | Super-kitamomiji (SKM) | gray lowland | Azumin (fertilizer including 60% humus acid and zinc): 10 kg/a |
| 48 | Zn 2 (fertilized | | exptl farm 2 | Yahoi, Kunneppu town | 1 | Super-kitamomiji (SKM) | black volcanic | |
| 49 | | crop year 1 | exptl farm 1 | Wakaba, Kunneppu town | 24 | Super-kitamomiji (SKM) | gray lowland | |
| 50 | | | exptl farm 1 | Wakaba, Kunneppu town | 24 | Kitamomiji2000 (KM) | gray lowland | |
| 51 | | crop year 2 | exptl farm 1 | Wakaba, Kunneppu town | 24 | Kairo'ohotsuku1 (KO1) | gray lowland | |
| 52 | | crop year 2 | exptl farm 1 | Wakaba, Kunneppu town | 8 | Kairo'ohotsuku1 (KO1) | gray lowland | |

[a] Provenance experiment. [b] Variety experiment. [c] N, Ca, Mg, and Zn indicate the fertilization experiment of each element. [d] Crop year experiment.

This study also examined from several other viewpoints how differences in cultivation conditions or varieties affect contents of the 26 elements in onions.

## MATERIALS AND METHODS

**Samples.** Samples were onions (*A. cepa* L.) grown under various conditions from 52 fields on 18 farms in Hokkaido, Japan, in 2004 (**Table 1**). About 20 kg of onions were collected from five spots in each field, dried, and processed in the same manner as onions for marketing, randomly sampled as 10 onions from each field and made into composites for analyses. The number of onions for a composite was decided by a previous examination (*13*) as follows. As a model case, 10 onions were randomly sampled from a field, and each onion was analyzed three times repeatedly to obtain sampling and analytical variations. The element that had the largest sampling variation was Ni, and the variation coefficient by one-onion sampling was 39%. The variation coefficient by 10-onion sampling was calculated as 12%; this variation level was low enough to be considered representative from a field.

Four individual onions were also sampled from 34 fields, in which onions for fertilization, crop year, variety, and provenance examples were cultivated, and each of the four individuals was used for mineral analysis to include individual differences within onions from the same field with an analytical variation. In fact, these samples were used for analyses of both 10-onion composite and 4 individual-onion concentrations. The details of samples from these 34 fields are described as follows.

Onions from five fields fertilized with $(NH_4)_2SO_4$ at 0, 0.5, 1, 2, and 3 kg of N/are (the normal level is ~1.2 kg of N/a) were collected for the N fertilization experiment. Onions from fields fertilized and not-fertilized with particle-shaped $CaCO_3$ (mixed with lignin to prevent

**Table 2.** Operating Conditions for ICP-AES and ICP-MS Instruments

| ICP-AES | | ICP-MS | |
|---|---|---|---|
| plasma condition | | plasma condition | |
| RP power | 1.15 kW | RP power | 1.4 kW |
| plasma gas | 14 L/min | plasma gas | 14.2 L/min |
| auxiliary gas | 0.5 L/min | auxiliary gas | 0.97 L/min |
| nebulizer gas | 0.22 MPa | nebulizer gas | 1.22 L/min |
| solution uptake rate | 1.4 mL/min | solution uptake rate | 0.7 mL/min |
| signal acquisition | | signal acquisition | |
| integration time | | data point | 3 points/peak |
| axial | 20 s | integration time | 0.1 s/point |
| radial | 10 s | integration | 3 times |
| integration | 1 time | | |

| element | wavelength (nm) | observation direction | element | *m*/*z* |
|---|---|---|---|---|
| Na | 589.592 | radial | Li | 7 |
| P | 213.618 | axial | Al | 40 |
| K | 766.490 | radial | Co | 51 |
| Mg | 279.553 | radial | Ni | 59 |
| Ca | 184.006 | axial | Cu | 60 |
| Mn | 257.610 | axial | Rb | 63 |
| Fe | 238.204 | axial | Y | 85 |
| Zn | 213.856 | axial | Mo | 89 |
| Sr | 407.771 | radial | Cd | 98 |
| Ba | 455.403 | radial | In | 111 |
| | | | Cs | 115 |
| | | | La | 133 |
| | | | Ce | 139 |
| | | | Nd | 140 |
| | | | Gd | 146 |
| | | | W | 157 |
| | | | Tl | 205 |

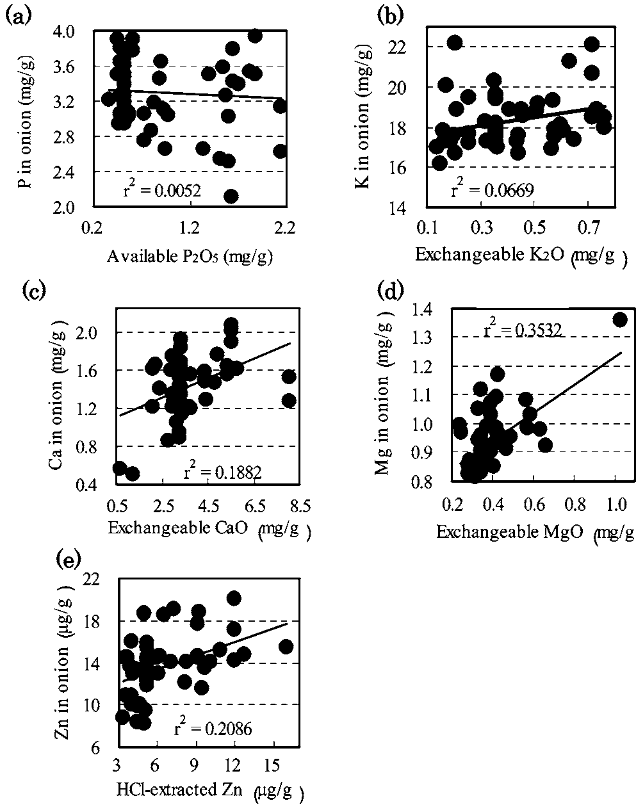


**Figure 1.** Correlations between P, K, Mg, Ca, and Zn concentrations in 52 onion samples and these element concentrations extracted from soils.

scattering) were collected for the Ca fertilization experiment. Onions from fields fertilized and not-fertilized with $MgSO_4$ were collected for the Mg fertilization experiment. Onions from fields of two kinds of soil types, fertilized and not fertilized with 60% humus acid including Zn, were collected for the Zn fertilization experiment. For these fertilization experiments, fertilizers were applied 2 or 3 days before onions were planted, as is the common procedure for onion cultivation in Hokkaido. Fertilizers used for fertilization experiments of Ca, Mg, and Zn are applied if soil diagnosis indicates that such fertilization is required. The amounts of applied fertilizer in these experiments were within ordinary levels. The fields of onions compared in fertilization experiments had the same cultivation conditions except for fertilization and were planted in adjoining fields on an experimental farm in the town of Kunneppu.

Onions of two varieties (Super-kitamomiji and Kairyo-ohostuku 1) from fields of crop years 1, 6, and 24 (years onions have been cultivated continuously in the field) were collected for crop-year experiments in this study. The fields for crop year 1 and 6 samples were adjoining, and these fields were located only ∼100 m from the crop year 24 field. Otherwise, each field had the same cultivation conditions. Continuous cropping is a common practice for onion cultivation in Hokkaido, and fields of 10 crop years or more are common in most of the main production regions.

Onions of 12 varieties cultivated under the same conditions were collected from a field on an experimental farm in the town of Kunneppu for the variety experiment.

Onions for the provenance experiment were collected from seven fields in six cities or towns representative of the production areas in Hokkaido.

Soils were sampled by a total of 2 kg from plow layers of four corners and the midpoint of ∼100 m square sections showing average onion growth and soil conditions in onion-sampled fields and were homogenized.

**Determination of Onion Mineral Contents.** Analyses were basically carried out according to the method reported by Ariyama et al. (*4*, *5*), with some minor modifications. Each of 52 samples was prepared by homogenizing 10 onions, and 26 elements were determined. The target part of an onion sample was the bulb excluding the orange or brown outer skins, the top edge, and the region within 1 cm from the base. To homogenize 10 onions, each target part of 10 onions was evenly cut into 16 or 24 along the axis, and the diagonal parts were placed in beakers; finally, they were pulverized by a mixer with ceramic cutting blades (B400, Nihon Büchi, Tokyo, Japan). A test portion, ∼5 g (corresponds to ∼0.5 g in dry weight), of each pulverized sample was transferred to a Teflon beaker. Acid digestion was carried out in an open vessel by $HNO_3$, $HClO_4$, and HF. Acids used were 61% $HNO_3$ (electronics industry grade, Kanto Kagaku, Tokyo, Japan), 60% $HClO_4$ (atomic absorption spectroscopy grade, Tokyo, Kanto Kagaku, Japan), and 50% HF (semiconductor grade, Daikin, Osaka, Japan). Moisture was obtained by drying 5−6 g of a pulverized sample in an Al foil cup at 70 °C for 24 h under atmospheric pressure. This series of procedures was triplicated, and blank analyses without the test portion were also performed three times together with sample analyses.

To investigate differences in mineral concentrations between samples with different factors (fertilization, crop year, variety, and provenance), 34 samples corresponding to types of experiments assigned in **Table 1** were prepared by pulverizing one onion. This preparation was repeated with four onions. In these experiments, the entire target part of the onion was pulverized by a mixer with ceramic cutting blades. The following procedure was the same as the analysis of a sample prepared with 10 onions. This series of procedures, however, was not repeated but performed just once, and blank analyses without the test portion were performed three times together with sample analyses.

Ten elements (Na, Mg, P, K, Ca, Mn, Fe, Zn, Sr, and Ba) were simultaneously determined by inductively coupled plasma atomic emission spectrometry (ICP-AES; IRIS Advantage, Thermo Electron, Waltham, MA). Sixteen elements (Li, Al, Co, Ni, Cu, Rb, Y, Mo, Cd, Cs, La, Ce, Nd, Gd, W, and Tl) were simultaneously determined by inductively coupled plasma mass spectrometry (ICP-MS; HP4500, Agilent Technologies, Palo Alto, CA) using In as an internal standard. Measurement conditions are shown in **Table 2**.

**Soil Analysis.** Each soil sample was dried in air at ∼15 °C for 3 weeks, after passing through a 2-mm sieve, and analyzed according to the standard method in Hokkaido (*14*). Soil pH ($H_2O$) was measured by glass electrode. Exchangeable cations of MgO, $K_2O$, and CaO were

**Table 3.** Detection Limits, Results of N Fertilization Experiment, Averages of Element Concentrations in Four Onions from Each of the N-Fertilized Fields, Significance by ANOVA and *t* Tests, and Results of Soil Analyses

| | | concn in onion ($\mu$g/g)[c] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | DL[a] ($\mu$g/g)[c] | 0 kg/a, sample 38 | 0.5 kg/a, sample 39 | 1 kg/a, sample 40 | 2 kg/a, sample 42 | | 3 kg/a, sample 43 | variation in groups[b] |
| Li*[d] | 0.001 | 0.005 | 0.005 | 0.004 | 0.003 | Li*[e] | 0.009 | 0.001 |
| Na | 14 | 330 | 430 | 440 | 330 | Na*[e] | 70 | 145 |
| Mg | 2 | 811 | 921 | 940 | 1000 | Mg*[e] | 1020 | 688 |
| Al | 0.6 | ND | ND | ND | 0.8 | Al | ND | 0.5 |
| P | 11 | 3090 | 3480 | 3610 | 3550 | P | 3800 | 430 |
| K | 41 | 18700 | 18900 | 17200 | 18900 | K | 22000 | 2810 |
| Ca | 4 | 923 | 887 | 1090 | 1330 | Ca | 1140 | 329 |
| Mn | 0.1 | 9.7 | 12.2 | 11.6 | 13.3 | Mn**[e] | 8.0 | 1.9 |
| Fe | 2 | 11 | 23 | 18 | 19 | Fe*[e] | 25 | 6 |
| Co | 0.001 | 0.014 | 0.019 | 0.015 | 0.015 | Co | 0.036 | 0.012 |
| Ni | 0.04 | 0.07 | 0.15 | 0.19 | 0.13 | Ni | 0.14 | 0.06 |
| Cu | 0.6 | 3.2 | 3.6 | 4.1 | 4.0 | Cu | 3.2 | 0.9 |
| Zn | 1 | 13.1 | 16.4 | 13.3 | 13.2 | Zn | 17.4 | 2 |
| Rb*[d] | 0.04 | 29.0 | 32.5 | 32.5 | 40.4 | Rb*[e] | 35.3 | 3.5 |
| Sr | 0.1 | 2.9 | 2.7 | 3.5 | 3.2 | Sr | 3.1 | 1.1 |
| Y | 0.001 | 0.005 | 0.001 | 0.001 | 0.001 | Y | 0.001 | 0.003 |
| Mo | 0.002 | 0.026 | 0.021 | 0.024 | 0.025 | Mo**[e] | 0.008 | 0.003 |
| Cd | 0.001 | 0.056 | 0.077 | 0.069 | 0.059 | Cd**[e] | 0.130 | 0.012 |
| Cs | 0.001 | 0.064 | 0.098 | 0.100 | 0.094 | Cs*[e] | 0.051 | 0.020 |
| Ba | 0.2 | 1.5 | 1.4 | 1.1 | 0.9 | Ba | 0.7 | 0.6 |
| La | 0.001 | ND | ND | ND | ND | La | 0.002 | 0.002 |
| Ce | 0.001 | 0.002 | 0.005 | 0.002 | 0.002 | Ce | 0.002 | 0.004 |
| Nd | 0.001 | ND | ND | ND | ND | Nd | 0.001 | 0.001 |
| Gd | 0.001 | ND | ND | ND | ND | Gd | ND | |
| W | 0.001 | ND | ND | ND | ND | W | ND | |
| Tl**[d] | 0.001 | 0.031 | 0.029 | 0.026 | 0.017 | Tl | 0.016 | 0.004 |
| | | results of soil analyses (pH) | | | | | | |
| | | 5.8 | 5.8 | 5.8 | 6.1 | | 5.5 | |
| | | exchangeable MgO (mg/g) | | | | | | |
| | | 0.47 | 0.41 | 0.42 | 0.39 | | 0.39 | |
| | | phosphatic acid availability in soil (mg/g) | | | | | | |
| | | 0.57 | 0.49 | 0.48 | 0.60 | | 0.45 | |
| | | exchangeable $K_2O$ (mg/g) | | | | | | |
| | | 0.19 | 0.14 | 0.16 | 0.17 | | 0.21 | |
| | | exchangeable CaO (mg/g) | | | | | | |
| | | 3.25 | 2.75 | 3.17 | 3.24 | | 2.99 | |
| | | HCl-extracted Zn ($\mu$g/g) | | | | | | |
| | | 4.3 | 3.5 | 3.7 | 4.0 | | 5.0 | |

[a] Detection limit; caluculated as 3 times the standard deviation of concentrations obtained by 12 blank analyses. [b] Square root of total variance within all groups divided by degree of freedom. [c] Concentration units shown on a dry weight basis. [d] Significance between samples 38, 39, 40, and 42: *, 5% significant; **, 1% significant. [e] Significance between samples 42 and 43: *, 5% significant; **, 1% significant.

extracted by batch method with ammonium acetate (pH 7) and determined by atomic absorption spectrometry. Available phosphoric acid was measured according to the Truog method (includes 0.001 mol/L sulfuric acid extraction for 30 min). Zinc was extracted in 0.1 mol/L HCl and determined by atomic absorption spectrometry.

Li and Mo from fertilizers ($CaCO_3$ and $MgSO_4$) and soil samples 45 and 46 were extracted according to the extraction method of available Mo with acidic ammonium oxalate (*15*). Ca, Ni, Cu, Zn, and Sr from humus acid fertilizer and soil samples 1, 2, 47, and 48 were extracted by 0.1 mol/L HCl method. These elements in extracted solutions were determined by ICP-MS (HP4500, Agilent Technologies).

**Statistical Analysis.** Mineral data above and at detection limits were used for statistical analyses, but *t* test and analysis of variance (ANOVA) on the data less than quantitation limits are not shown. The significance of differences between two samples was judged by a two-sided test that did not hypothesize the homoscedasticity, and the significance of differences between more than two samples was judged by ANOVA using the application software Microsoft Excel 2002 (Microsoft, Redmond, WA). Data for these statistical analyses were element concentrations of 4 individual onions sampled from each of 34 fields.

Cluster analysis was carried out using the application software Statistica Pro 03J (StatSoft Japan, Tokyo, Japan). The elements used for cluster analyses were the 21 elements (Li, Na, Mg, Al, P, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Y, Mo, Cd, Cs, Ba, and Tl) having analytical results above the detection limits for onion samples in more than half of the 52 samples. Cluster analyses for classifying all production places clearly were also tried by choosing elements used for analyses from 21 elements. Element data used for cluster analysis were standardized concentrations in 10-onion composites from each of 52 fields. Euclidean distance was used as the scale to calculate differences between samples as simple distances without weighting. The linkage rule was the Ward method, generally regarded as efficient for significant clustering (*16*).

## RESULTS AND DISCUSION

**Correlation between Onions and Soils.** Twenty-six elements in 52 onion samples were determined, and soils from fields where these samples were grown were analyzed. **Figure 1** shows correlations between concentrations of 5 elements (P, K, Mg, Ca, and Zn) in 52 onion samples and those extracted from soil (available $P_2O_5$, exchangeable $K_2O$, exchangeable MgO, exchangeable CaO, and HCl-extracted Zn). Correlations of P and K were not significant at the 5% level. For Mg, Ca, and Zn,

**Table 4.** Results of Ca and Mg Fertilization Experiments: Averages of Element Concentrations in Four Onions from Each of the Nonfertilized and Fertilized Fields, Significance by ANOVA and *t* Tests, and Results of Soil Analyses

| | concn in onion[b] ($\mu$g/g) | | | |
|---|---|---|---|---|
| | nonfertilized, sample 46 | Ca expt, sample 44 | Mg expt, sample 45 | variation in groups[a] ($\mu$g/g)[b] |
| Li | ND | ND | ND | |
| Na | 70 | 70 | 70 | 6 |
| Mg | 933 | 839 | 860 | 76 |
| Al | ND | ND | ND | |
| P | 2760 | 2480 | 2570 | 203 |
| K | 17700 | 17600 | 17400 | 1020 |
| Ca | 1910 | 1800 | 1950 | 372 |
| Mn | 10.3 | 9.2 | 9.9 | 1.8 |
| Fe | 14 | 13 | 12 | 2 |
| Co | ND | 0.002 | 0.002 | 0.012 |
| Ni | 0.08 | 0.04 | 0.10 | 0.06 |
| Cu | 4.7 | 4.4 | 4.8 | 0.9 |
| Zn | 11 | 10 | 10 | 2 |
| Rb | 9.86 | 9.77 | 10.0 | 0.8 |
| Sr | 5.5 | 5.3 | 5.8 | 1.0 |
| Y | ND | ND | ND | |
| Mo | 0.110 | 0.152[c] | 0.166[d] | 0.026 |
| Cd | 0.059 | 0.059 | 0.069 | 0.009 |
| Cs | 0.004 | 0.003 | 0.003 | 0.006 |
| Ba | 2.3 | 2.7 | 2.7 | 0.5 |
| La | ND | ND | ND | |
| Ce | ND | ND | ND | |
| Nd | ND | ND | ND | |
| Gd | ND | ND | ND | |
| W | ND | ND | ND | |
| Tl | 0.003 | 0.002 | 0.003 | 0.001 |
| | results of soil analyses (pH) | | | |
| | 6.3 | 6.5 | | 6.4 |
| | exchangeable MgO (mg/g) | | | |
| | 0.29 | 0.28 | | 0.26 |
| | phosphatic acid availability in soil (mg/g) | | | |
| | 1.34 | 1.52 | | 0.95 |
| | exchangeable $K_2O$ (mg/g) | | | |
| | 0.58 | 0.60 | | 0.65 |
| | exchangeable CaO (mg/g) | | | |
| | 5.39 | 5.78 | | 4.92 |
| | HCl-extracted Zn ($\mu$g/g) | | | |
| | 4.0 | 4.7 | | 4.4 |

[a] Square root of total variance within all groups divided by degree of freedom. [b] Concentration units shown on a dry weight basis. [c] Significance between samples 46 and 44: *, 5% significant. [d] Significance between samples 46 and 45: *, 5% significant.

**Table 5.** Results of Zn Experiments at Two Types of Fields: Averages of Element Concentrations in Four Onions from Each of the Nonfertilized and Fertilized Fields, Significance by *t* Test, and Results of Soil Analyses

| | concn in onion ($\mu$g/g)[b] | | | | | | |
|---|---|---|---|---|---|---|---|
| | gray lowland soil, crop year 1 | | | | black volcanic soil, crop year 8 | | |
| | nonfertilized, sample 1 | fertilized, sample 47 | variation in groups[a] | | nonfertilized, sample 2 | fertilized, sample 48 | variation in groups[a] |
| Li | 0.005 | 0.007 | 0.003 | Li | 0.001 | 0.001 | 0.001 |
| Na | 190 | 160 | 6 | Na | 70 | 60 | 7 |
| Mg | 1030 | 1130 | 95 | Mg | 854 | 934 | 64 |
| Al | ND | ND | | Al | ND | ND | |
| P | 3220 | 3820 | 202 | P | 2410 | 2390 | 184 |
| K | 17500 | 19700 | 1600 | K | 18200 | 17700 | 673 |
| Ca*[c] | 1540 | 2080 | 304 | Ca | 1550 | 2070 | 328 |
| Mn | 14.0 | 16.5 | 2.0 | Mn | 8.9 | 11.1 | 1.8 |
| Fe | 18 | 21 | 3 | Fe | 16 | 14 | 4 |
| Co | 0.013 | 0.014 | 0.004 | Co | ND | 0.002 | 0.003 |
| Ni*[c] | 0.10 | 0.14 | 0.02 | Ni | 0.07 | 0.13 | 0.03 |
| Cu*[c] | 2.6 | 5.4 | 1.0 | Cu**[c] | 1.9 | 5.7 | 0.3 |
| Zn | 14 | 17 | 2 | Zn | 9 | 10 | 1 |
| Rb | 35.1 | 34.3 | 4.6 | Rb | 11.0 | 10.8 | 0.6 |
| Sr**[c] | 5.9 | 8.1 | 0.5 | Sr | 4.3 | 5.7 | 0.9 |
| Y | ND | 0.002 | 0.002 | Y | ND | ND | |
| Mo | 0.032 | 0.036 | 0.015 | Mo | 0.109 | 0.108 | 0.017 |
| Cd | 0.081 | 0.098 | 0.025 | Cd | 0.061 | 0.091 | 0.017 |
| Cs | 0.073 | 0.047 | 0.016 | Cs | 0.004 | 0.004 | 0.000 |
| Ba | 2.6 | 3.5 | 0.6 | Ba | 1.9 | 2.7 | 0.6 |
| La | ND | 0.002 | 0.001 | La | ND | ND | |
| Ce | ND | 0.002 | 0.002 | Ce | ND | ND | |
| Nd | ND | ND | | Nd | ND | ND | |
| Gd | ND | ND | | Gd | ND | ND | |
| W | ND | 0.002 | 0.002 | W | ND | ND | |
| Tl | 0.025 | 0.023 | 0.006 | Tl | 0.004 | 0.004 | 0.001 |
| | results of soil analyses (pH) | | | | | | |
| | 6.0 | 5.8 | | | 6.3 | 6.2 | |
| | exchangeable MgO (mg/g) | | | | | | |
| | 0.42 | 0.44 | | | 0.32 | 0.32 | |
| | phosphatic acid availability in soil (mg/g) | | | | | | |
| | 0.45 | 0.48 | | | 1.63 | 1.61 | |
| | exchangeable $K_2O$ (mg/g) | | | | | | |
| | 0.26 | 0.20 | | | 0.56 | 0.61 | |
| | exchangeable CaO (mg/g) | | | | | | |
| | 5.39 | 5.78 | | | 5.39 | 5.40 | |
| | HCl-extracted Zn ($\mu$g/g) | | | | | | |
| | 5.1 | 6.0 | | | 4.4 | 5.1 | |

[a] Square root of total variance within groups divided by degree of freedom. [b] Concentration units are shown on a dry weight basis. [c] *, 5% significant; **, 1% significant.

positive correlations at the 1% significance level were obtained. However, correlations of Ca and Zn were low; the $r^2$ values of these elements were 0.1882 and 0.2086, respectively, whereas the $r^2$ of Mg was 0.3532.

Correlations between 20 element concentrations in 52 onion samples and soil pH are shown in the Supporting Information. Concentrations of Mn and Cd had negative correlations with soil pH; $r^2$ values were above 0.3. It was demonstrated that absorption of Cd, which is harmful for humans, is more easily affected by soil pH than those of the other 19 elements. The elements that obtained correlations at the 5% significance level (except Mn and Cd) were Na, K, Zn, Mo, Ba, and Tl. Of these elements, Na, K, Zn, and Tl had a tendency of higher concentrations in onions with lower soil pH. On the contrary, Mo and Ba had a tendency of higher concentrations with higher soil pH.

As described above, correlations between element concentrations in onions and results of soil analyses were 1 or 5% significant only for some elements, so their correlations were not sufficient to estimate any element concentration in an onion from results of soil analyses.

**Fertilization Experiments.** *N Fertilization Experiment.* Detection limits of minerals in onions and analytical results of onions from fields N-fertilized at five levels (0, 0.5, 1, 2, and 3 kg of N/a) and soils from these fields are shown in **Table 3**. Onions from fields fertilized at 3 kg of N/acre showed greatly different element patterns from the others: Li, Mg, P, K, Mn, Fe, and Cd had higher concentrations but Na, Rb, Mo, Cs, and Ba had lower concentrations than ones fertilized at 2 kg of N/a at 1 or 5% significance levels. The soil pH was obviously low, and the low concentration of Mo and high concentrations of Mn and Cd might have been due to this. In addition, these onions' growth was suppressed, which is considered to be caused by overfertilization. This is likely why the element pattern differed greatly from those of onions at lower N levels of fertilization. In onions fertilized at <3 kg of N/a, the elements that attained significant differences were Li, Rb, and Tl; Li and

**Table 6.** Results of Crop-Year Experiments on Two Varieties: Averages of Element Concentrations in Four Onions from Each Field of Three Levels of Crop Year, Significance by ANOVA, and Results of Soil Analyses

| | concn in onion ($\mu$g/g)[b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Super-kitamomiji | | | | | Kairyo-ohostuku 1 | | | |
| | crop year 1, sample1 | crop year 6, sample26 | crop year 24, sample 49 | variation in groups[a] | | crop year 1, sample 52 | crop year 6, sample 29 | crop year 24, sample 51 | variation in groups[a] |
| Li | 0.005 | 0.004 | 0.003 | 0.001 | Li**[c] | 0.003 | 0.003 | ND | 0.001 |
| Na**[c] | 190 | 100 | 70 | 27 | Na**[c] | 210 | 80 | 70 | 36 |
| Mg | 1030 | 1060 | 1020 | 84 | Mg | 976 | 953 | 934 | 51 |
| Al | ND | ND | ND | | Al | ND | ND | ND | |
| P*[c] | 3220 | 3480 | 4030 | 270 | P**[c] | 2950 | 3020 | 3960 | 58 |
| K**[c] | 17500 | 19500 | 20500 | 870 | K | 17900 | 17700 | 19900 | 1070 |
| Ca*[c] | 1540 | 2160 | 2610 | 431 | Ca | 1470 | 1790 | 2190 | 180 |
| Mn | 14.0 | 14.9 | 15.1 | 2.2 | Mn**[c] | 15.5 | 12.8 | 10.6 | 12 |
| Fe | 18 | 20 | 23 | 4 | Fe**[c] | 22 | 20 | 19 | 4 |
| Co | 0.013 | 0.018 | 0.010 | 0.004 | Co | 0.020 | 0.015 | 0.016 | 0.005 |
| Ni**[c] | 0.10 | 0.14 | 0.06 | 0.02 | Ni | 0.13 | 0.19 | 0.08 | 0.07 |
| Cu**[c] | 2.6 | 3.5 | 4.7 | 0.6 | Cu | 3.0 | 3.9 | 3.4 | 0.6 |
| Zn | 14 | 15 | 17 | 2 | Zn | 15 | 13 | 15 | 2 |
| Rb**[c] | 35.1 | 18.5 | 7.95 | 2.9 | Rb**[c] | 33.5 | 18.3 | 7.40 | 1.4 |
| Sr | 5.9 | 7.3 | 7.8 | 1.1 | Sr | 5.0 | 5.9 | 6.0 | 0.7 |
| Y | ND | ND | ND | | Y | ND | ND | ND | |
| Mo*[c] | 0.032 | 0.048 | 0.100 | 0.025 | Mo**[c] | 0.012 | 0.085 | 0.119 | 0.01 |
| Cd | 0.081 | 0.066 | 0.070 | 0.013 | Cd**[c] | 0.098 | 0.037 | 0.047 | 0.014 |
| Cs**[c] | 0.073 | 0.018 | 0.003 | 0.011 | Cs**[c] | 0.055 | 0.016 | 0.003 | 0.010 |
| Ba | 2.6 | 2.6 | 3.8 | 0.6 | Ba | 1.9 | 2.5 | 2.1 | 0.3 |
| La | ND | ND | ND | | La | ND | ND | ND | |
| Ce | ND | ND | 0.011 | 0.006 | Ce | ND | ND | ND | |
| Nd | ND | ND | ND | | Nd | ND | ND | ND | |
| Gd | ND | ND | ND | | Gd | ND | ND | ND | |
| W | ND | 0.001 | ND | | W | ND | ND | ND | |
| Tl**[c] | 0.025 | 0.004 | 0.003 | 0.002 | Tl**[c] | 0.020 | 0.002 | 0.001 | 0.002 |
| | | | | results of soil analyses (pH) | | | | | |
| | 6.0 | 6.5 | 6.2 | | | 6.0 | 6.5 | 6.2 | |
| | | | | exchangeable MgO (mg/g) | | | | | |
| | 0.42 | 0.34 | 0.33 | | | 0.42 | 0.34 | 0.33 | |
| | | | | phosphatic acid availability in soil mg/g | | | | | |
| | 0.48 | 0.52 | 1.88 | | | 0.48 | 0.52 | 1.88 | |
| | | | | exchangeable $K_2O$ (mg/g) | | | | | |
| | 0.26 | 0.36 | 0.72 | | | 0.26 | 0.36 | 0.72 | |
| | | | | exchangeable CaO (mg/g) | | | | | |
| | 3.29 | 3.34 | 5.52 | | | 3.29 | 3.34 | 5.52 | |
| | | | | HCl-extracted Zn $\mu$g/g | | | | | |
| | 5.1 | 5.2 | 9.1 | | | 5.1 | 5.2 | 9.1 | |

[a] Square root of total variance within groups divided by degree of freedom. [b] Concentration units shown on a dry weight basis. [c] *, 5% significant; **, 1% significant.

Tl had lower concentrations at 5 and 1% significance levels, respectively, as the content of fertilizer increased, whereas Rb had a higher concentration at the 5% significance level as the content of fertilizer increased. It is considered that using ammonium sulfate as the N fertilizer negatively affected the absorption of Li and Tl into onions. The mechanism for this finding was not clarified, but the result itself is interesting, as Tl is harmful to humans, and its absorption into onions was decreased by applying ammonium sulfate. As for Rb, it is considered that ammonium sulfate positively affected its absorption into onions because Rb was not detected in the extract from this fertilizer.

*Ca Fertilization Experiment.* Analytical results of onions and soils from fields on which Ca fertilizer composed primarily of calcium carbonate was and was not applied are shown in **Table 4**. Mo had higher (5% significance) concentration in onions from the Ca-fertilized field than from the nonfertilized field. Because Mo was not detected in the fertilizer, it is considered that calcium carbonate positively affected the absorption of Mo into onions.

No difference at a 5% significance level was shown between calcium concentration in onions from Ca-fertilized and nonfertilized fields. The increase in exchangeable CaO concentration in soil by fertilization was small, and the correlation between Ca concentrations in onions and those in extracted solutions from soils was also low (**Figure 1d**). This suggests that the simple application of a fertilizer containing Ca does not automatically increase Ca concentration in onions.

*Mg Fertilization Experiment.* Analytical results of onions and soils from fields on which Mg fertilizer composed of magnesium sulfate was and was not applied are shown in **Table 4**. Mo had a higher concentration (5% significance) in onions from the Mg-fertilized field than from the nonfertilized field. Because concentrations of Mo in extracts from magnesium sulfate and the soil of fields were almost the same (data not shown), it is considered that magnesium sulfate positively affected the absorption of Mo into onions.

Although the exchangeable MgO concentration in soil was increased by fertilization, no significant difference was shown between onions from farm fields on which the fertilizer was

**Table 7.** Results of Variety Experiment: Averages of Element Concentrations in Four Onions from Each of 12 Varieties of Onions and Significances by ANOVA

| | concn in onion ($\mu$g/g)[b] | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SKM, sample 26 | KM, sample 27 | Kamui, sample 28 | KO1, sample 29 | Salari, sample 30 | Wolf, sample 31 | Iomante, sample 32 | KH2, sample 33 | KMI38, sample 34 | KMI39, sample 35 | KW3, sample 36 | O222, sample 37 | variation in groups[a] |
| Li*[c] | 0.004 | 0.003 | 0.003 | 0.003 | 0.004 | 0.005 | 0.002 | 0.002 | 0.004 | 0.003 | 0.004 | 0.004 | 0.001 |
| Na**[c] | 102 | 91 | 77 | 78 | 91 | 90 | 90 | 71 | 85 | 85 | 66 | 96 | 11 |
| Mg**[c] | 1060 | 851 | 915 | 953 | 969 | 847 | 872 | 886 | 915 | 928 | 900 | 878 | 57 |
| Al | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | |
| P**[c] | 3480 | 3660 | 3290 | 3020 | 3490 | 3340 | 3310 | 284 | 2940 | 3200 | 2860 | 2890 | 309 |
| K**[c] | 19500 | 18400 | 17100 | 17700 | 17900 | 16800 | 16900 | 17800 | 18300 | 19700 | 17300 | 16800 | 1000 |
| Ca*[c] | 2160 | 1810 | 1640 | 1790 | 1530 | 1630 | 1780 | 1560 | 1410 | 1300 | 1980 | 1870 | 302 |
| Mn | 14.9 | 9.7 | 13.5 | 12.8 | 12.7 | 11.9 | 11.2 | 13.3 | 11.7 | 11.6 | 13.2 | 12.6 | 2.0 |
| Fe**[c] | 20 | 16 | 14 | 20 | 20 | 15 | 15 | 24 | 28 | 21 | 24 | 26 | 4 |
| Co**[c] | 0.018 | 0.012 | 0.009 | 0.015 | 0.021 | 0.014 | 0.011 | 0.008 | 0.019 | 0.013 | 0.020 | 0.008 | 0.005 |
| Ni | 0.14 | 0.12 | 0.15 | 0.19 | 0.42 | 0.41 | 0.05 | 0.07 | 0.12 | 0.19 | 0.11 | 0.10 | 0.20 |
| Cu**[c] | 3.5 | 3.9 | 5.0 | 3.9 | 4.3 | 2.7 | 3.3 | 2.0 | 3.8 | 4.9 | 4.3 | 3.0 | 0.9 |
| Zn | 15 | 12 | 14 | 13 | 12 | 13 | 13 | 13 | 13 | 14 | 12 | 13 | 2 |
| Rb | 18.5 | 18.3 | 18.8 | 18.3 | 17.2 | 17.1 | 16.6 | 16.3 | 15.9 | 18.7 | 16.8 | 15.3 | 2.0 |
| Sr*[c] | 7.3 | 6.6 | 5.6 | 5.9 | 5.0 | 5.6 | 6.0 | 5.0 | 4.9 | 4.1 | 6.3 | 6.1 | 1.0 |
| Y | ND | ND | ND | ND | ND | ND | 0.001 | ND | 0.001 | ND | 0.001 | ND | 0.0006 |
| Mo**[c] | 0.048 | 0.069 | 0.039 | 0.085 | 0.054 | 0.055 | 0.070 | 0.061 | 0.076 | 0.090 | 0.086 | 0.042 | 0.016 |
| Cd | 0.066 | 0.025 | 0.052 | 0.037 | 0.053 | 0.045 | 0.039 | 0.050 | 0.056 | 0.029 | 0.050 | 0.045 | 0.018 |
| Cs*[c] | 0.018 | 0.014 | 0.013 | 0.016 | 0.019 | 0.026 | 0.023 | 0.022 | 0.017 | 0.015 | 0.024 | 0.021 | 0.006 |
| Ba**[c] | 2.6 | 2.2 | 3.1 | 2.5 | 1.4 | 1.7 | 1.9 | 1.8 | 1.8 | 1.8 | 2.2 | 2.4 | 0.5 |
| La*[c] | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | |
| Ce | ND | 0.003 | ND | 0.002 | ND | ND | ND | 0.004 | ND | 0.002 | ND | ND | 0.002 |
| Nd | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | |
| Gd | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | |
| W | 0.001 | ND | ND | ND | ND | ND | ND | ND | ND | 0.003 | ND | ND | 0.0007 |
| Tl**[c] | 0.004 | 0.003 | 0.003 | 0.002 | 0.004 | 0.009 | 0.007 | 0.003 | 0.003 | 0.003 | 0.006 | 0.005 | 0.002 |

[a] Square root of total variance within groups divided by degree of freedom. [b] Concentration units shown on a dry weight basis. [c] *, 5% significant; **, 1% significant.

**Table 8.** Results of Provenance Experiment: Averages of Element Concentrations in Four Onions from Each of Seven Fields in Hokkaido and Significance by ANOVA

| | concn in onion ($\mu$g/g)[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | exptl farm 1, sample 18 | Kitami 2, sample 19 | Tanno 2, sample 20 | Kunneppu 3, sample 21 | Bihoro 3, sample 22 | Furano 1, sample 24 | Iwamizawa 1, sample 25 | variation in groups[a] |
| Li**[c] | 0.009 | 0.003 | 0.003 | 0.001 | 0.011 | 0.002 | 0.006 | 0.001 |
| Na**[c] | 70 | 290 | 70 | 100 | 220 | 80 | 150 | 59 |
| Mg**[c] | 1070 | 911 | 942 | 1090 | 934 | 989 | 783 | 65 |
| Al | ND | 0.6 | ND | ND | ND | ND | ND | 0.7 |
| P**[c] | 3680 | 3250 | 3540 | 3470 | 3220 | 3010 | 2660 | 300 |
| K | 17800 | 16800 | 19500 | 17200 | 17500 | 17100 | 18300 | 1220 |
| Ca | 1550 | 1200 | 1450 | 1330 | 1570 | 1460 | 1330 | 232 |
| Mn | 12.5 | 12.5 | 12.8 | 11.1 | 10.0 | 11.7 | 11.6 | 1.8 |
| Fe | 17 | 16 | 19 | 16 | 20 | 15 | 20 | 4 |
| Co**[c] | 0.012 | 0.016 | 0.004 | 0.000 | 0.004 | 0.015 | 0.027 | 0.006 |
| Ni**[c] | 0.48 | 0.15 | 0.17 | 0.14 | 0.47 | 0.29 | 0.80 | 0.15 |
| Cu**[c] | 2.5 | 5.9 | 3.5 | 4.6 | 3.7 | 4.6 | 3.2 | 0.8 |
| Zn**[c] | 13 | 15 | 14 | 13 | 15 | 12 | 18 | 1 |
| Rb**[c] | 5.43 | 27.1 | 5.83 | 10.1 | 13.2 | 4.88 | 4.44 | 1.5 |
| Sr | 3.8 | 4.5 | 4.4 | 4.0 | 3.4 | 3.5 | 3.5 | 0.7 |
| Y | ND | ND | ND | ND | ND | ND | ND | |
| Mo**[c] | 0.107 | 0.017 | 0.034 | 0.073 | 0.164 | 0.084 | 0.044 | 0.013 |
| Cd**[c] | 0.081 | 0.077 | 0.112 | 0.036 | 0.066 | 0.024 | 0.140 | 0.018 |
| Cs**[c] | 0.007 | 0.066 | ND | 0.010 | 0.020 | 0.003 | 0.002 | 0.008 |
| Ba**[c] | 0.4 | 1.6 | 0.9 | 1.2 | 0.2 | 1.8 | 0.6 | 0.4 |
| La | ND | ND | ND | ND | ND | ND | ND | |
| Ce | ND | ND | ND | ND | ND | ND | 0.004 | 0.004 |
| Nd | ND | ND | ND | ND | ND | ND | ND | |
| Gd | ND | ND | ND | ND | ND | ND | ND | |
| W | 0.002 | ND | ND | ND | ND | ND | ND | 0.02 |
| Tl**[c] | 0.005 | 0.022 | ND | 0.011 | 0.012 | 0.013 | 0.002 | 0.005 |

[a] Square root of total variance within groups divided by degree of freedom. [b] Concentration units shown on a dry weight basis. [c] **, 1% significant.

and was not applied. The correlation between Mg concentrations in onions and in extracts from soils exhibited 0.3532 correlation at $r^2$ (**Figure 1c**), but this was not enough to suggest an increase in the concentration in onions from increasing the exchangeable MgO concentration in soil. Therefore, it is considered that the simple application of a fertilizer including Mg does not automatically increase Mg concentration in onions.

*Zn Fertilization Experiment.* Analytical results of onions and soils from fields on which humus acid including Zn was and was not applied as a fertilizer are shown in **Table 5**. The Zn

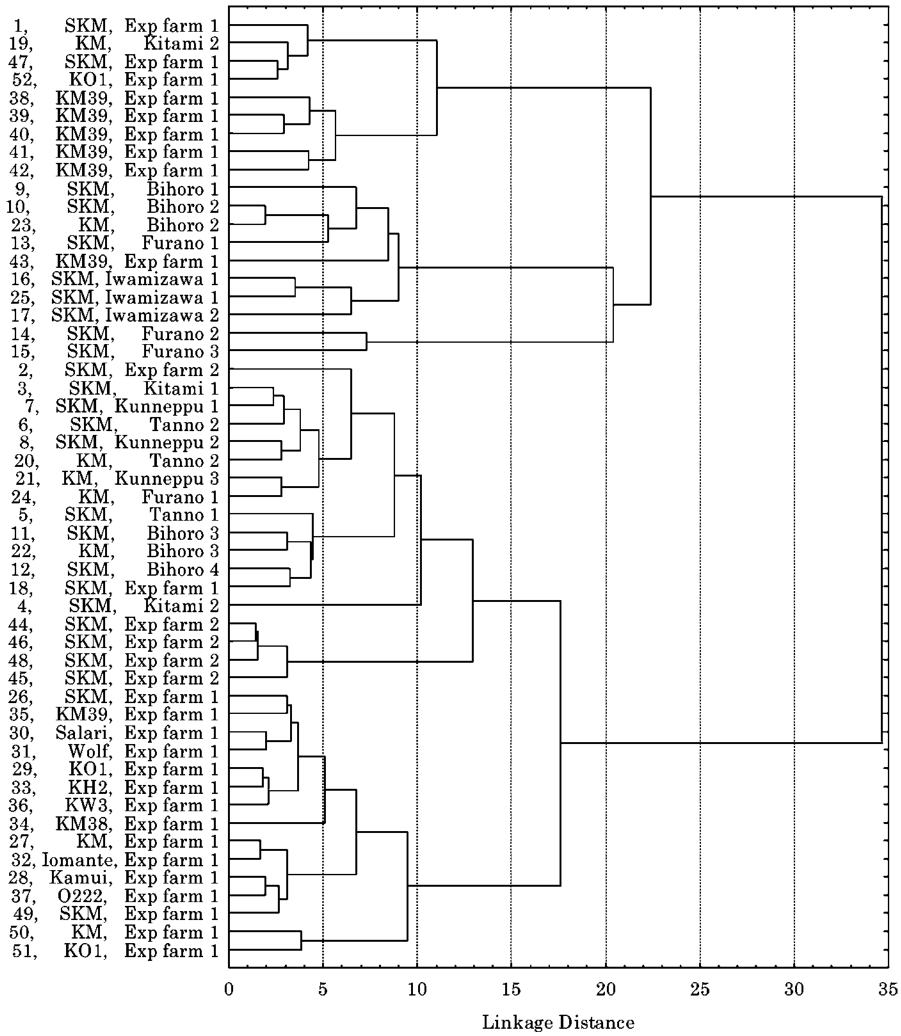


**Figure 2.** Dendrograms of 52 samples using the standardized data of 21 elements (Li, Na, Mg, Al, P, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Y, Mo, Cd, Cs, Ba, and Tl). Distance metrics is Euclidean distance; cluster analysis is by the Ward method. Sample numbers, abbreviations of varieties, and tentative names of experimental farms are represented as sample names in this order. Details of samples are shown in **Table 1**.

fertilization experiment was carried out to compare onions from fields with gray lowland soil (crop year 1) and black volcanic soil (crop year 8). It is known that gray lowland soil is appropriate for onion cultivation in Hokkaido, but that black volcanic soil, despite its high Zn content, easily causes Zn depletion in crops owing to its unavailability. Copper had higher concentrations in onions from the fertilized field than from the nonfertilized field at the two types of fields. It is considered that the humus acid positively affected absorption of Cu into onions because concentration of this element extracted from humus acid was lower than or almost the same as that from soils (data not shown). Onions fertilized in the gray lowland soil field (crop year 1) showed positively significant differences from the nonfertilized onions in Ca, Ni, and Sr concentrations. As one of the causes for increases of element concentrations by fertilization, it is considered that the humus acid positively affected the absorption of Ca into onions because concentrations of these elements extracted from humus acid were lower than or almost the same as those from soils (data not shown). As for Ni and Sr, increases in concentrations of elements existing in forms available to onions are thought to be one of the causes because concentrations of these elements extracted from humus acid were higher than those extracted from soils (data not shown). The crop year 1 field with gray lowland soil increased absorption of more elements by fertilization with humus acid than the crop year 8 field with black volcanic soil containing much more organic matter, although the absorption of Cu was largely increased by fertilization with humus acid at the field with black volcanic soil. As for Zn, no significant differences were observed in onions from the two fields, despite extracts from the fertilized soils showing higher Zn concentrations than those from nonfertilized soils (**Table 5**). Cultivation of onions in black volcanic soil with applied humus acid with Zn was found to be no less effective than cultivation in gray lowland soil in terms of absorption of Zn.

**Crop-Year Experiment.** Analytical results of two varieties of onions (Super-kitamomiji and Kairyo-ohotsuku 1) from fields with three "ages" in terms of crop years are shown in **Table 6**. Elements showing significant differences in concentrations by crop years for both varieties were Na, P, Ca, Rb, Mo, Cs, and Tl. Among these, Na, Rb, Cs, and Tl decreased in concentration at 1% significance in both varieties as crop years passed. It was considered that these elements were depleted from soil as crop years pass because it was thought these elements are not added into fertilizer or soil amendments as essential elements. On the contrary, elements for which concentrations increased as crop years passed were P, Ca, and Mo. These concentrations increased differently at 1 or 5% significance levels. In addition, K and Cu increased in concentrations for the Super-kitamomiji variety as crop years passed. It was considered that these elements, which are contained in fertilizers as the main elements or added into it as essential elements for crops, accumulate in soils as crop years passed because their supply by fertilization exceeds their absorption by onions. P, Ca, and K concentrations increased in both extracts from soils and onions as crop years passed, except for the onion Kairyo-ohotsuku 1. It was shown these elements accumulated in soils by continuous cropping, and this affected onions as well.

As for Ca, the concentration in onions increased as crop years passed, although no significant difference was shown in the Ca fertilization experiment. Because Ca is an essential and often deficient element in human diets, cultivation of crops with high Ca content is desired. For the sake of that, fertilization with Ca in available forms is likely needed.

As described above, differences in element concentrations by crop years were large and had similar tendencies in the two varieties. In this study, obvious concentration differences were shown for many elements (Na, P, Ca, Rb, Mo, Cs, and Tl) because the fields used for these experiments differed widely in crop years, particularly because crop year 1 fields, which are rare in onion cultivation in Hokkaido, were included. It was interesting that Na and Tl had higher concentrations in onions from crop year 1 fields than in other fields, whereas the concentration differences between those from the crop year 6 and 24 fields were small. From this, it was expected that variations in element concentrations might diminish as crop years pass.

**Variety Experiment.** Analytical results of onions of 12 main varieties grown at the same fields and under the same conditions are shown in **Table 7**. Mineral concentrations of Li, Ca, Sr, Cs, and La in onions differed at a 5% significance level, and those of Na, Mg, P, K, Fe, Co, Cu, Mo, Ba, and Tl differed at a 1% significance level. There was no variety that showed a markedly different concentration pattern compared with others, although significant differences among varieties were shown in many individual elements.

**Provenance Experiment.** Analytical results of onions of the same variety but grown at seven different fields are shown in **Table 8**. Concentrations of Li, Na, Mg, P, Co, Ni, Cu, Zn, Rb, Mo, Cd, Cs, Ba, and Tl were different at a 1% significance level. Mineral concentrations were largely different between onions from different provenances.

**Cluster Analysis. Figure 2** shows a dendrogram by cluster analysis (Ward method) using standardized concentrations of 21 elements (Li, Na, Mg, Al, P, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Y, Mo, Cd, Cs, Ba, and Tl) in 52 samples. Onions from the city of Iwamizawa formed a cluster. Onions from the town of Bihoro formed clusters divided into two. Onions from the towns of Tanno and Kunneppu formed a mixed cluster. Onions from the experimental farms formed roughly crop year 1 fields and another two clusters. Sample 43, which was not included in these clusters, was over-N-fertilized, but samples 2 and 18 were not included in these clusters. Onions from the cities of Kitami and Furano did not form clusters. As for varieties, onions that were from the same provenance formed a cluster despite being different varieties (samples 26−37 and 49−51). This result demonstrated that the differences in a total of 21 elements were larger between provenances than between varieties. Onions used for the fertilization experiments on N (samples 38−40, 42, and 43), Ca (samples 44 and 46), Mg (samples 45 and 46), and Zn (samples 1 and 47) at fields of gray lowland soil formed clusters, respectively. These results also demonstrated that the difference within each of these experiments was smaller than that between provenances based

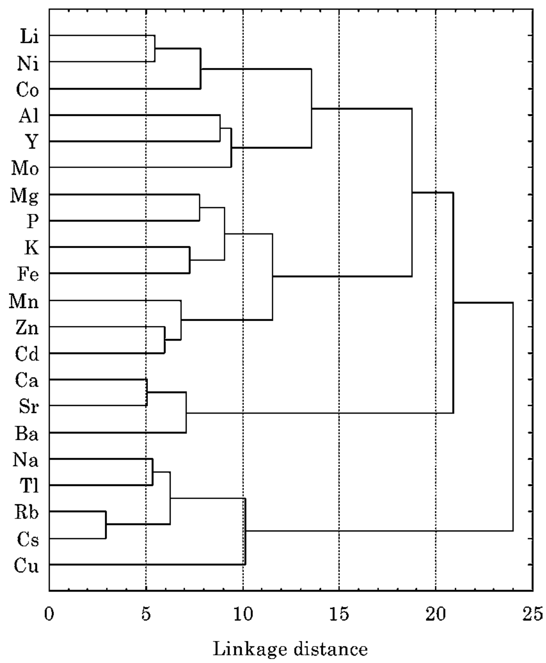


**Figure 3.** Dendrogram of elements using the standardized data of 21 elements (Li, Na, Mg, Al, P, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Y, Mo, Cd, Cs, Ba, and Tl) in 52 samples. Distance metrics is Euclidean distance; cluster analysis is by the Ward method.

on all 21 elements. However, onions used for the Zn fertilization experiment (samples 1 and 48) at fields of black volcanic soil showed large differences. Onions used for the crop-year experiments (samples 1, 26, 29, 49, 51, and 52) also did not form clusters. However, onions of crop years 6 and 24 (samples 26, 29, 49, and 51) were classified in the same cluster despite the large difference of crop years, and onions of crop year 1 (samples 1 and 52) were separated from the others in the dendrogram. Therefore, mineral intakes into onions are considered to become steady by continuous cropping, so the difference as judged from numerous elements' data is considered to be smaller than that between production places in Hokkaido, where most of the fields are beyond the crop year 10.

Cluster analyses for classifying all production places clearly were also tried by choosing elements used for analyses from 21 elements. However, this trial could not be achieved because effective elements for classifying all production places could not be specified.

**Figure 3** shows a dendrogram by cluster analysis (Ward method) of the elements using the same data. Na, Rb, and Cs in group IA (alkali metals) formed a cluster and included Tl instead of Li and K, which are in the same group in the periodic table. Ca, Sr, and Ba in group IIA (alkali earth metals) and Zn and Cd in group IIB also formed respective clusters; however, Mg did not form the cluster with other elements in group IIA. Overall, there was a tendency for elements in the same group in the periodic table to form clusters, with some exceptions. This is considered to have occurred because the behaviors of elements forming clusters were similar: in soils, between onions and soils, and in onions. Pairs of elements having high concentration correlations in onions were Zn−Cd, Ca−Sr, and Rb−Cs, as was also found in a study investigating element concentrations in soils of Japan (*17*). It is considered that these correlations in soils between elements were caused by similarities of behaviors in the soil genesis process, from formation of parent rock to the weathering of rock-forming minerals and the eluviation processes. Other pairs of elements for which high concentration correlations in soils were reported include K−Rb, Mg−Co, Ca−Mg, Fe−Mg, Fe−Co, K−Tl, Li−Rb, Li−Cs, etc. (*17*); these correlations were not reflected in onions. Particularly, no correlations in onions were obtained despite high correlations in soils of K−Rb, Li−Rb, and Li−Cs, all in the same group IA, perhaps because of physiological fractionations of elements in onions when these elements are absorbed.

In conclusion, although applications of typical fertilizers and varieties used for onion cultivation in Hokkaido varied the mineral compositions of onions, the variations by fertilization were smaller than the differences between production places when judged from an overview of numerous (21) elements. Mineral compositions in onions largely varied as the crop years passed, but the difference between crop year 6 and 24 onions was smaller than those between production places. Although it was shown that Na, P, Ca, Cu, Rb, Mo, Cs, and Tl concentrations in onions can be affected by fertilization and crop years, there was a tendency for differences between even nearby production places within Hokkaido to be larger than variations by fertilizztion or crop year when judged by numerous elements. Therefore, even clearer differences are expected between distant regions. In the development of a technique for determining the geographic origin based on mineral composition, it is important to choose a number of elements having large concentration differences between target places to establish the criteria of discrimination. Variations between varieties within a range where phenotypes are not greatly different or changes of cultivation conditions within an ordinal range will not largely affect geographic origin determination if appropriate elements are chosen are found.

Furthermore, Na, Rb, and Cs in group IA of the periodic table, Ca, Sr, and Ba in group IIA, and Zn and Cd in group IIB showed similar concentration patterns in 52 onion samples compared to those of other elements. These results demonstrated similarities in the behavior of elements belonging to the same periodic group.

**Supporting Information Available:** Correlations between 20 element concentrations in 52 onion samples and soil pH. This material is available free of charge via the Internet at http://pubs.acs.org.

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