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Behavior of soil nitrogen and leaching of metal elements from arable land

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In Japan, large amounts of fertilizer nitrogen are applied to tea plantations. We collected samples of tea plantation soil each season for a year. Samples were analyzed for their contents of various inorganic chemicals and total N. Nitrogen was present mainly in the top 0 to 30 cm of soil. However, at times the concentration of nitrate N in the soil water was more than 35 mg L⁻¹, even in the deepest layers. The contents of various metal elements in the soil were examined. Ba, Fe, Sr and Zn contents were high in the top 0 to 30 cm of soil. But Al and Mn contents were not always high in the top 0 to 30 cm of soil. From the correlation analysis among contents of various inorganic chemicals, it was suggested that increased leaching of Al, Mn, and Zn from tea plantation soil occurred with increased nitrate N concentration.

Keywords: Nitrate; Heavy metal; Soil nitrogen; Fertilizer nitrogen; Groundwater

1. Introduction

Particularly over the last 30 years, high concentrations of nitrate N have been reported in surface waters and groundwaters in and around agricultural areas [1–4]. And furthermore, not only nitrate N leaching and acidification in the surface water or groundwater, but also leaching of heavy metal elements, has been reported in tea plantation areas in Japan [5–7]. These pollutions by nitrate N and metal elements change the quality of water resources, and it is possible that these changes influence the drinking water supply or ecological system in the water. Therefore it is important to know how nitrate N and metal elements were leached from tea plantation. However the detailed process for leaching of metal elements and leaching of nitrate N from arable land have not been studied in Japan. So we investigated vertical distributions of various inorganic chemicals in the soil in tea plantation area.

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Large amounts of fertilizer N are applied to tea plantation soils in Japan. Every season for a year, we monitored the chemical properties of the soil of a tea plantation at Shizuoka, Japan. To identify the processes of N-transformation and leaching of metal elements occurring in the soil, we examined fluctuations in the vertical profiles of various forms of N and other inorganic chemicals. It was suggested that an increase in the nitrate N concentration of the soil water causes the increased leaching of other metal elements.

2. Experimental

2.1 Study site

The study site was in a tea plantation with an area of about 1.3 ha in a mountainous region with soils dating to the Tertiary period (figure 1). The altitude is 280 m to 290 m. The average yearly precipitation is 2340 mm, and the average yearly temperature over the previous 20 years has been 16°C. The site was a satsuma plantation until about 1978; between 1978 and 1983 it was changed to a tea plantation. After this production change, the nitrate N concentration of spring water around the site is thought to have increased gradually. Currently the concentration of nitrate N of spring water around the site is more than the national environmental standard, which is 10 mg L⁻¹ N as the sum of nitrite N and nitrate N. Fertilizer N at more than 1000 kg ha⁻¹ was applied to the tea plantation every year until 1997, but since then the quantity of fertilizer N applied has gradually decreased: the quantity of fertilizer N applied in 2002 was 553 kg ha⁻¹. There are no stock breeders or residences in the catchment

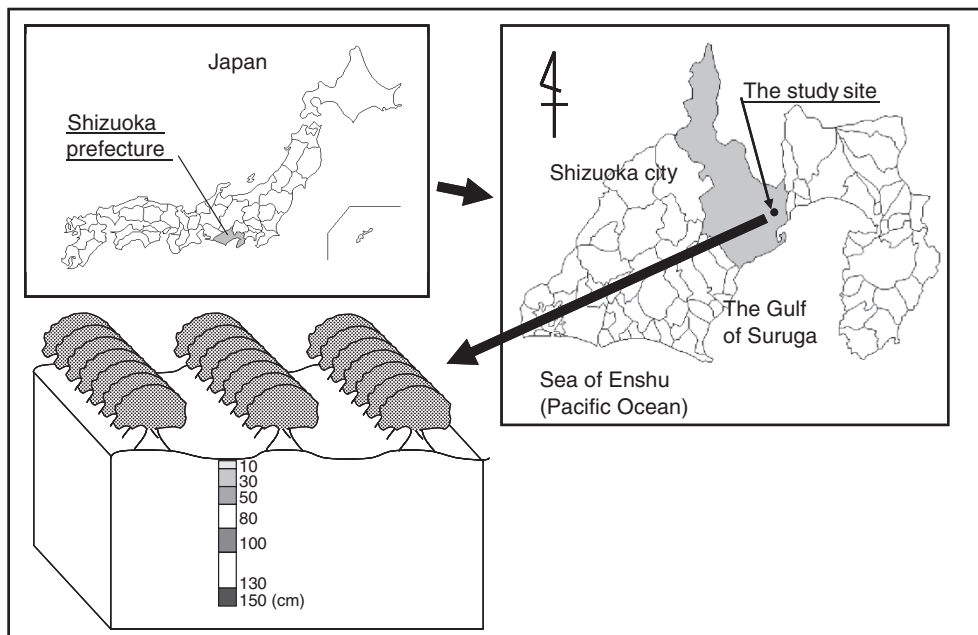


Figure 1. The map of the study site and conceptual illustration for cross-section of a typical sampling point.

area including the study site, so we considered that the sources of N were precipitation and the fertilizer applied to the tea plantation.

2.2 Field sampling and analytical procedures

Soil samples were collected 4 times between January 2002 and February 2003. Samples were taken at 3 sites, each at the base of a furrow, and the sampling depths were 0 to 10 cm, 10 to 30 cm, 30 to 50 cm, 80 to 100 cm, and 130 to 150 cm (figure 1). Soil color and soil texture was observed. The soil at 0 to 10 cm layer was brownish black and consisted of almost all plant residue. The 10 to 30 cm layer was brown and sandy loam. The 30 to 50 cm layer was brown and sandy loam containing fine gravel. 80 to 100 cm consisted of brown and silty clay. The 130 to 150 cm layer was brown and sandy loam.

After collection, samples were preserved in plastic bags and kept cold. Landowners were asked what kind of fertilizer they applied, as well as how much and when. Information on precipitation and temperature was obtained from the Japan Meteorological Agency. The observing station was AMeDAS (Automated Meteorological Data Acquisition System) station at Shimizu which is about 2 km away from the study site. Soil samples were shaken for 6 h with water at a 1:10 w/w soil to extractant ratio. Soil extract were filtered with membrane filter (FM-45, FUJIFILM, Tokyo, Japan). The concentrations of eluted chemical components in the filtered soil extract were then determined. pH was measured with pH meter (PH-81, Yokogawa, Electric, Tokyo, Japan). Anion concentrations (F^- , Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-}) were measured with an ion chromatograph (DX-AQ, DIONEX, Sunnyvale, USA). Column for analysis was Ionpac CS-12 (DIONEX, Sunnyvale, USA), eluent was 20 mM MSA (methansulfonic acid) and flow rate was 1.0 mL min^{-1} . Concentrations of NH_4^+ were also measured with an ion chromatograph (DX-100, DIONEX, Sunnyvale, USA). Column for analysis was Ionpac A25S (DIONEX, Sunnyvale, USA), eluent was 2.7 mM $Na_2CO_3/0.3 \text{ mM NaHCO}_3$ and flow rate was 1.0 mL min^{-1} .

Eluted metal elements were measured by ICP (Inductively Coupled Plasma) optical emission spectrophotometry (ICAP750, Nippon Jarrell-Ash, Uji, Japan). Soil N contents were measured with an elemental analyzer (EA 1108, FISON'S INSTRUMENTS, Miran, Italy).

3. Results and discussion

3.1 Seasonal fluctuations in soil N

Figure 2 shows the quantities of fertilizer, fertilizer application dates, precipitation, temperature and soil sampling dates at the study site. Between January 2002 and February 2003, monthly average temperature peaked in August (27.7°C) and monthly precipitate peaked in June (304 mm). In July, September and October, precipitate was also much. In February and April, precipitate was little. Yearly average temperature was 15.3°C and yearly total precipitate was 2244 mm between January 2002 and February 2003. Fertilizer was applied between February and May (a to e and h in figure 2), in August and in September. For fertilizations a, b, c, and h, compound fertilizer containing ammonium N and nitrate N as inorganic N was used.

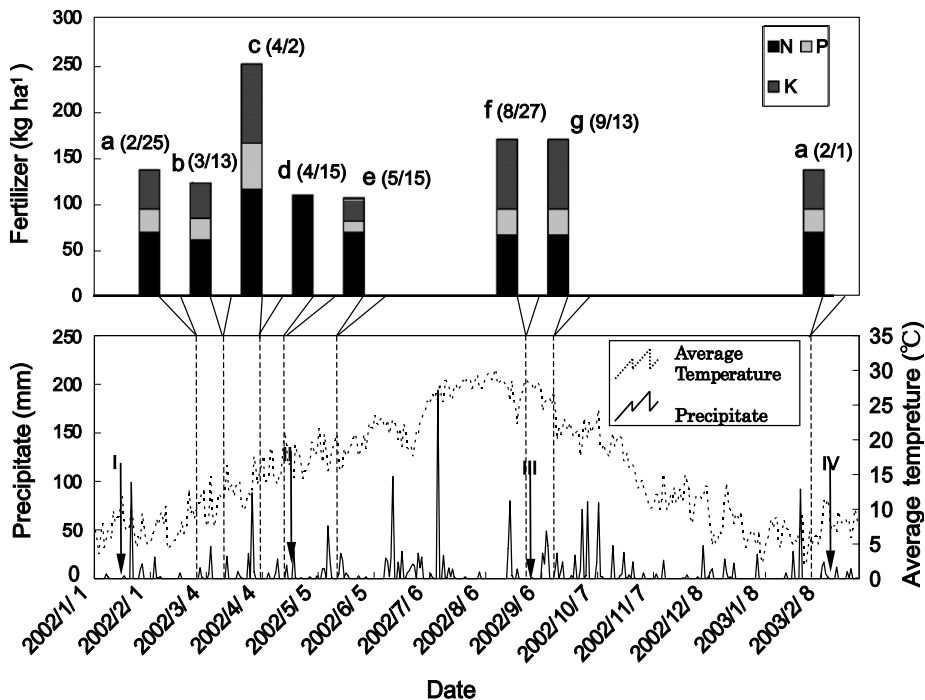


Figure 2. Precipitation, fertilizer application dates, and soil sampling dates at the study site. Sampling times indicated by roman numerals. a–c, h: Compound fertilizer containing nitrate N and ammonium N as inorganic N, d: Ammonium sulfate fertilizer, e: Compound fertilizer containing magnesia, lime, and ammonium N as inorganic N, f, g: Compound fertilizer containing ammonium N as inorganic N.

Fertilization d used ammonium sulfate. Fertilization e, in summer, used a compound fertilizer containing magnesia, lime, and ammonium N as inorganic N. Fertilizations f and g were performed in autumn and used compound fertilizers containing ammonium N as inorganic N. Organic fertilizers such as lees of rape seeds, chrysalis, crab shell, oyster shell, animal organic and ground fish were also applied in fertilization b, c, e, g and h. Sampling time I (at the end of January) was before the spring fertilization. Sampling time II (in mid-April) was just after the spring fertilization. Sampling time III (at the end of August) was just after the first autumn fertilization. Sampling time IV (in mid-February) was after the next year's first spring fertilization.

Soil N is transformed to nitrate N by nitrification [8] and is thought to be the source of nitrate N in groundwater. Therefore, it is important to know the quantities and chemical forms of soil N that are present.

Figure 3 shows the seasonal fluctuations in N content at each sampling depth in the soil. Most of the soil N was present in the top 0 to 30 cm, and there was very little below 30 cm. In the topsoil (0 to 10 cm) the N content was highest at the April sampling. In April and August, the range of data was broad because fertilizer was frequently applied. In January and in February of the following year, the range of data was narrow because fertilizer had been applied less frequently at around the time of sampling. The increase in N content in the top soil (0 to 10 cm) in April was most likely due to fertilizer application. Temperatures were high between April and August, and precipitation was high in June. Furthermore, fertilizer was not applied in June or July. Under these conditions,

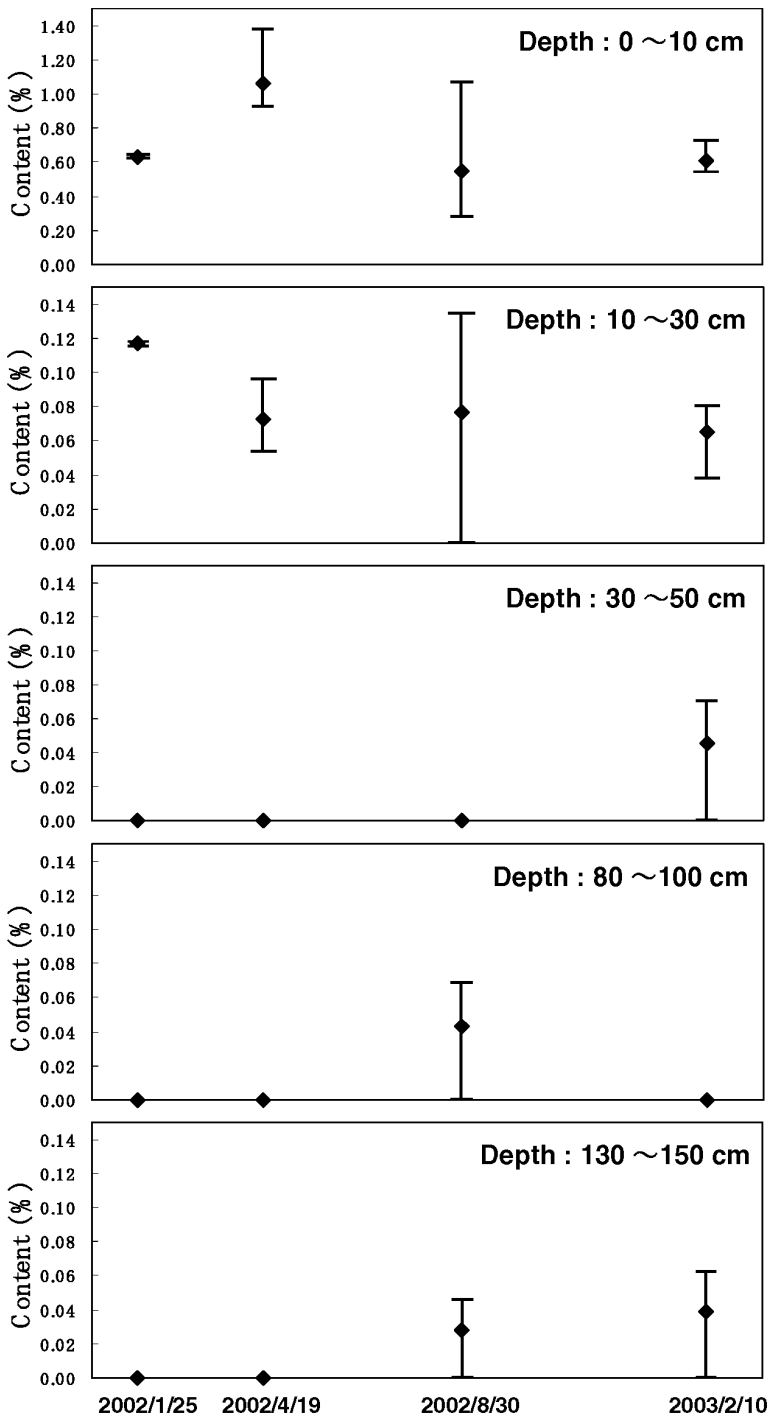


Figure 3. Seasonal fluctuations in contents of soil N in each soil layer.

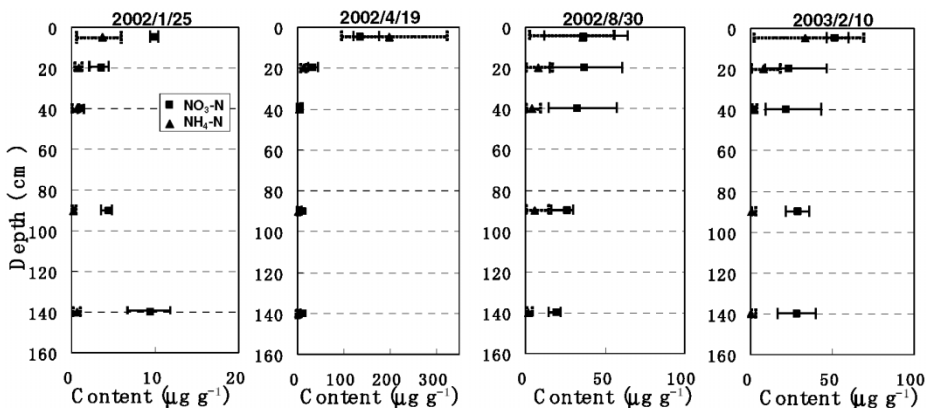


Figure 4. Vertical profiles of nitrate N and ammonium N contents of soil at the study site.

the N content of the topsoil was most likely reduced (figure 3) because of mineralization of organic N, plant uptake, and leaching of nitrate N. We examined the ammonium N and nitrate N contents of the soil to elucidate the mechanism by which fertilizer N is transformed and lost from the 0 to 150 cm layer. Figure 4 shows the vertical profiles of the contents of ammonium N and nitrate N in the soil. Ammonium N was present mainly in the 0 to 30 cm layer of soil throughout the year. Nitrate N was present mainly in the 0 to 30 cm layer of soil in April and in the 0 to 50 cm layer in August. However, in January, the nitrate N content increased with soil depth of 80 cm or more. In February of the following year, the nitrate N content in soil at 80 cm or more was higher than in soil in the 10 to 50 cm layer. These results are explained by following reasons: Fertilizer was frequently applied in April and August. Therefore nitrate N mineralized from fertilizer N was mainly present in the upper layers of soil. However, in January and February, fertilizer was not frequently applied and nitrate N in the upper layers of the soil was reduced by leaching. Nitrate N leached from upper layers moved to deeper layers in soil. Therefore it was thought that nitrate N in deeper layers was observed to be higher than in upper layers in soil in winter. These phenomena as above were thought to be observed in the area where climate conditions and fertilizing are similar to the study site.

3.2 Nitrate nitrogen in the soil water

Nitrate is not subject to adsorption by soil and dissolves easily in water. If water containing nitrate N percolates through the soil, the nitrate N concentration of the groundwater will increase. Thus, the increase in the nitrate N concentration of the groundwater depends on the quantity of the infiltrated water and its nitrate N concentration. Figure 5 shows the vertical profiles of nitrate N concentration in the soil water, as calculated from the soil nitrate N content and the water content of the soil. In April and August in the 0 to 50 cm layer the nitrate N concentration peaked, but in January, and in February of the following year, the values were lower in this layer. Below 80 cm depth there was little fluctuation in nitrate N concentration, and in the 130 to 150 cm layer the nitrate N concentration of the soil water was more than 35.5 mg L^{-1} throughout the year. In contrast to soil N, which occupied mainly

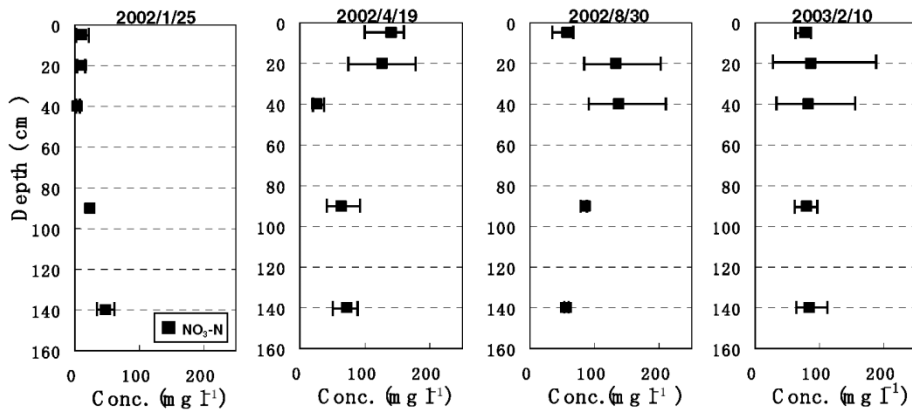


Figure 5. Vertical profiles of nitrate N concentration in the soil water.

the 0 to 30 cm layer of the soil (see figure 3), the nitrate N concentration of the soil water was above the environmental standard in the deepest layers of the soil throughout the year. Therefore, it appears that N in the surface soil was transformed to nitrate N and, with rainfall, infiltrated the deeper layers toward the water table. This is presumably the mechanism of nitrate N pollution of groundwater. The nitrate N concentration of the infiltrated water, the quantity of infiltrated water mixed into the groundwater, and the retention time of the groundwater are all determinants of the N concentration in the groundwater.

3.3 Vertical distributions of metal elements in the soil

Table 1 shows the soil contents (w/w of dry soil) of various chemical components. Except for the chemical components in table 1, we measured the soil contents of Pb, As, Cd, Cr and Cu, and all of them were less than detection limits. The contents of most chemical components were high in the topsoil and decreased with depth, although the Al content was highest in the 80 to 100 cm layer. The Mn content was high not only in the topsoil but also in the 80 to 100 cm and 130 to 150 cm layers. To know the process of leaching of metal elements, it is important to investigate their vertical distributions and their seasonal fluctuations in the soil. Figure 6 shows the vertical profiles of metal elements except alkali and alkali earth metal applied as fertilizer.

The Al content was lowest in April and peaks were recognized in the 30 to 100 cm layer in April, August and February of the following year (figure 6a). Because the Al content was relatively low in the upper layers, Al was presumably not supplied as fertilizer but was leached from the soil.

Fluctuations of Mn content were minor throughout the year, and peaks were apparent not only in the topsoil in January and April, but also in the 80 to 150 cm layer in August and February of the following year (figure 6a).

The Fe content is high and its range of data was broad in the top soil, while it was very low in January and was below the limit of detection in April, August and February under 30 cm layer (figure 6c). This suggests that Fe is mainly supplied from fertilizer and is hard to move with the infiltrated water.

Table 1. Contents of various chemical components of soil at the study site.

Depth (cm)	F ⁻ ($\mu\text{g g}^{-1}$)			Cl ⁻ ($\mu\text{g g}^{-1}$)			PO ₄ ³⁻ ($\mu\text{g g}^{-1}$)			SO ₄ ²⁻ ($\mu\text{g g}^{-1}$)			NO ₃ -N ($\mu\text{g g}^{-1}$)			NH ₄ -N ($\mu\text{g g}^{-1}$)		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
0–10	6.5	13.3	1.9	20.8	82.9	1.5	438.9	1395.5	76.5	638.9	1621.6	35.8	63.1	152.9	9.5	73.9	276.2	1.2
10–30	2.1	4.4	0.7	8.1	28.7	1.1	19.3	50.6	0.0	241.0	444.2	96.4	26.2	62.4	2.5	8.2	18.9	0.2
30–50	1.9	3.3	0.6	7.9	28.0	2.0	1.4	5.4	0.0	285.9	613.0	133.7	16.5	58.5	0.9	2.6	8.9	0.2
80–100	1.6	2.7	0.4	5.7	11.4	1.7	0.3	1.5	0.0	231.9	384.3	104.5	19.1	36.3	3.7	2.1	14.3	0.2
130–150	1.4	2.2	0.5	5.1	7.5	2.1	0.1	1.3	0.0	190.7	385.0	91.1	18.0	40.3	6.9	1.0	3.6	0.1

Depth (cm)	Na ($\mu\text{g/g}$)			Mg ($\mu\text{g/g}$)			K ($\mu\text{g/g}$)			Ca ($\mu\text{g/g}$)			TN (%)			pH		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
0–10	7.9	19.4	3.8	28.3	90.9	6.9	85.0	155.4	22.7	115.4	489.7	44.9	0.87	1.29	0.28	3.8	4.2	3.3
10–30	2.8	5.4	1.4	10.7	34.8	2.5	47.9	106.6	16.8	23.0	47.4	12.1	0.08	0.14	0.00	3.9	4.4	3.6
30–50	3.4	7.7	1.1	10.8	21.4	2.8	46.3	102.6	12.0	25.9	59.1	5.8	0.01	0.07	0.00	4.2	4.6	3.9
80–100	3.5	5.9	1.2	12.3	19.8	3.8	38.4	64.9	8.3	25.1	57.8	6.0	0.01	0.07	0.00	5.1	6.7	4.3
130–150	3.5	5.6	1.0	11.1	26.4	2.8	29.9	55.6	8.0	22.0	66.0	3.7	0.02	0.06	0.00	4.4	4.8	4.1

Depth (cm)	Al ($\mu\text{g g}^{-1}$)			Ba ($\mu\text{g g}^{-1}$)			Fe ($\mu\text{g g}^{-1}$)			Mn ($\mu\text{g g}^{-1}$)			Sr ($\mu\text{g g}^{-1}$)			Zn ($\mu\text{g g}^{-1}$)		
	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
0–10	7.73	18.40	1.70	0.34	0.71	<0.01	1.43	10.12	<0.01	3.56	15.81	1.47	0.31	1.36	<0.01	0.45	1.59	<0.01
10–30	8.66	32.53	1.79	0.12	0.30	<0.01	0.26	2.28	<0.01	1.10	2.44	0.50	0.06	0.19	<0.01	0.14	0.37	<0.01
30–50	11.43	42.19	1.03	0.11	0.27	<0.01	0.01	0.11	<0.01	1.54	3.72	0.23	0.09	0.20	<0.01	0.12	0.31	<0.01
80–100	13.17	24.69	1.52	0.13	0.27	<0.01	0.01	0.06	<0.01	3.40	10.46	0.34	0.08	0.21	<0.01	0.05	0.17	<0.01
130–150	9.56	23.10	1.93	0.15	0.27	0.07	0.01	0.08	<0.01	3.47	9.36	0.63	0.10	0.27	<0.01	0.03	0.10	<0.01

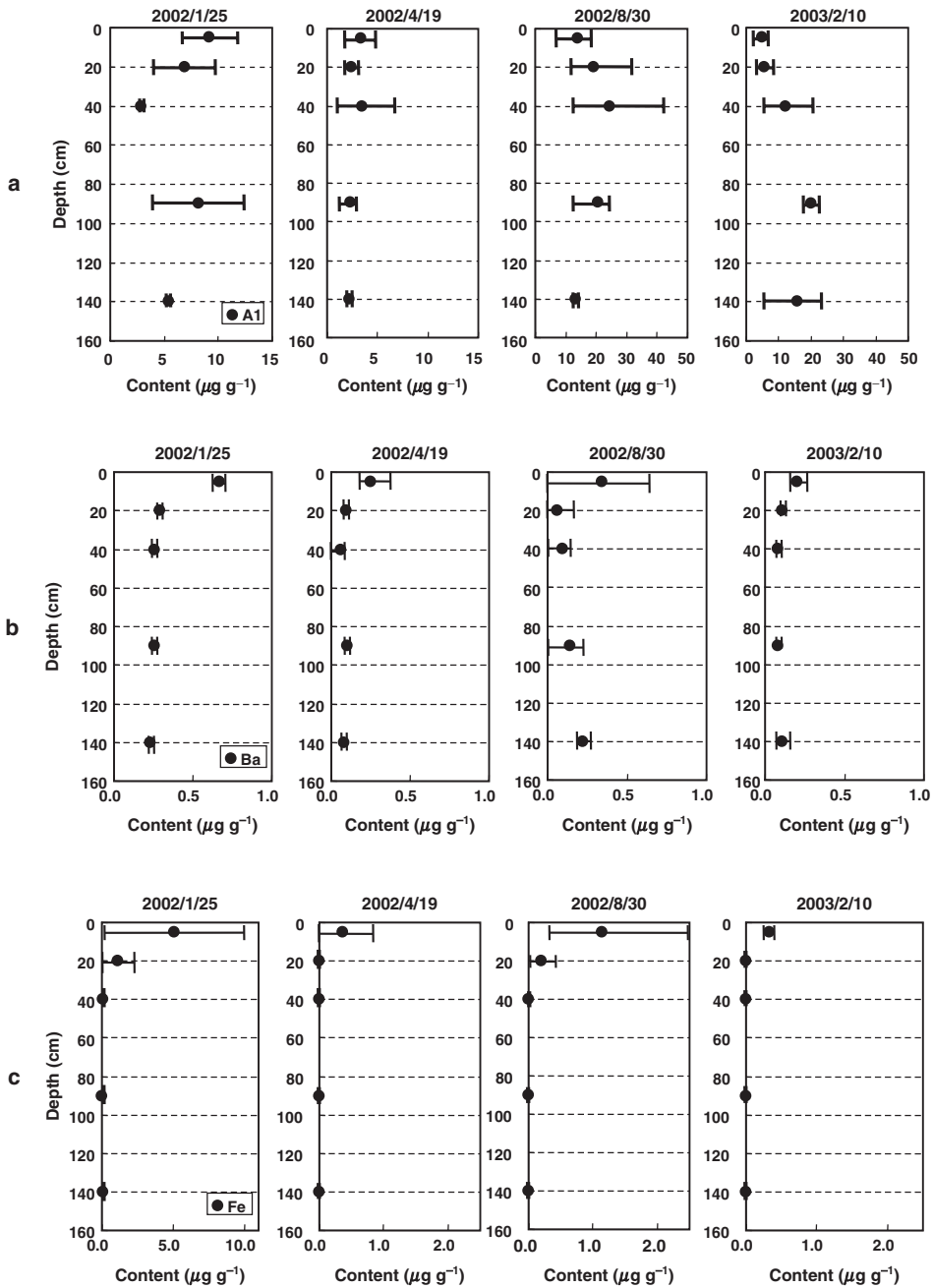


Figure 6. Vertical profiles of Al, Mn, Fe, Zn, Sr and Ba in the soil.

Fluctuations in Zn content were not noteworthy between January and February of the following year (figure 6d). In April and August, the Zn content was high in the topsoil and very low below 30 cm depth. These results indicate that Zn was supplied mainly as fertilizer and leached out gradually.

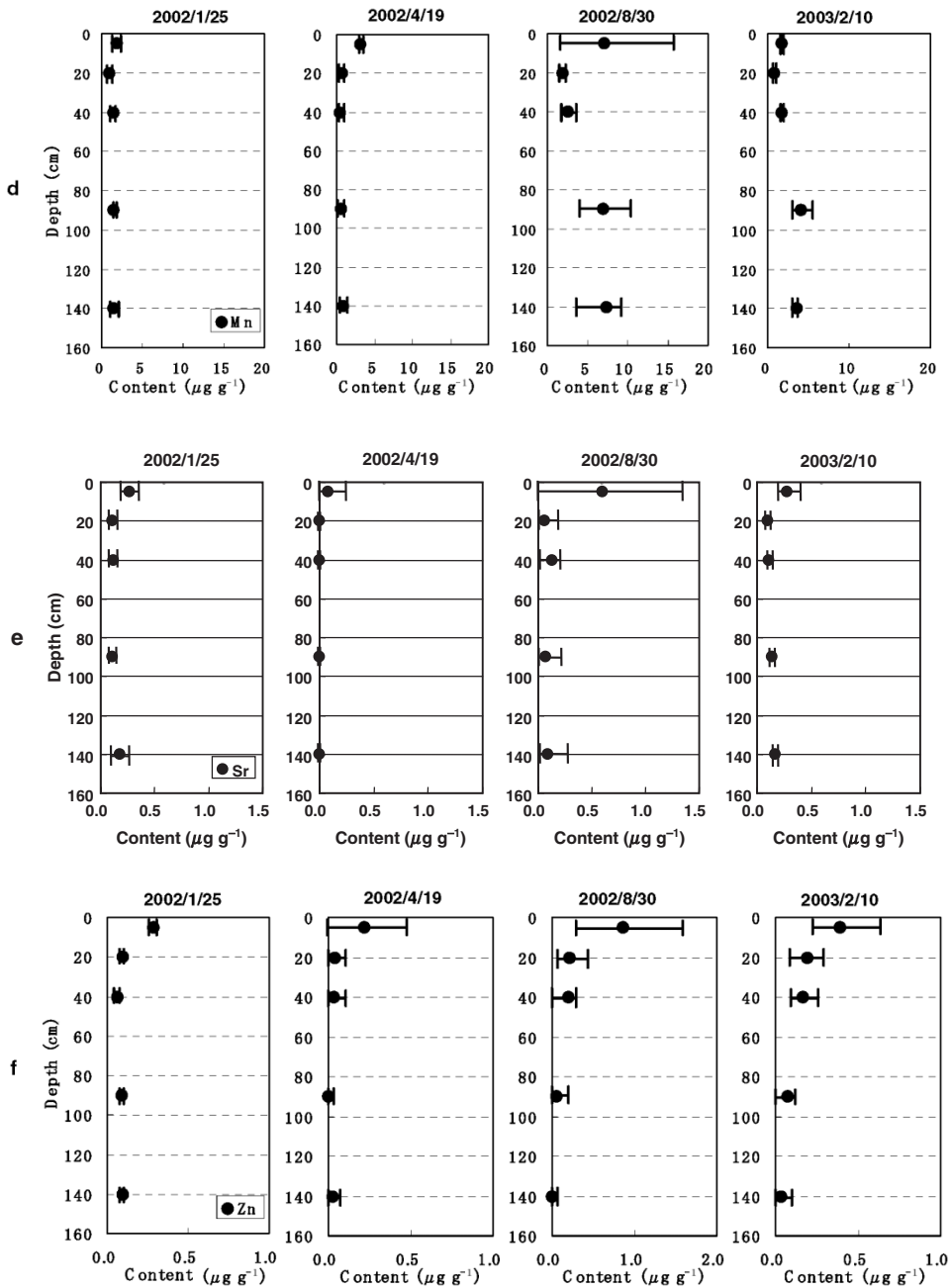


Figure 6. Continued.

The Sr content in the top soil was high and its range of data was broad in August, while it was low and the range of data was narrow in April (figure 6e). It was thought to be because that compound fertilizer containing lime was applied in May (fertilization e shown in figure 2). Sr belongs to the II A group on the periodic table of the elements,

the same as Ca and Mg. Ionic radius of Sr is similar to that of Ca. So substances containing Ca always contain Sr. In the soil below 10 cm, Sr content changes very little and doesn't change with depth.

The Ba content in the top soil was high and its range of data was broad compared with that under 10 cm layer (figure 6f). In August, Ba content increased with depth in soil at 10 cm or more depth. These results indicate that Ba was supplied from fertilizer and leached out gradually, but it is thought to be easier to move with the infiltration water than Zn and Fe.

The above results suggest that Zn, Fe, Mn, Ba and Sr are mainly supplied by fertilizer although Al is mainly supplied through soil. In the study site, magnesia, lime and organic fertilizers such as lees of rape seeds, chrysalis, crab shell, oyster shell, animal organic and ground fish were applied. These fertilizers thought to contain Zn, Fe, Mn, Ba and Sr. Peaks except in the top soil were recognized in Al and Mn contents. This suggests that, compared with other metal elements, Al and Mn are easy to move with infiltrated water, and also suggests that profiles of Al and Mn reflect their quantity in the soil and the ability of the infiltrated water to dissolve Al and Mn when the water percolates. Zn content decreases with depth and Fe content was very low under the 30 cm layer. This suggests that Zn and Fe are harder to move with infiltrated water than other metal elements. Ba and Sr contents do not decrease with depth. This suggests that Ba and Sr are easy to move with infiltrated water than Zn and Fe.

3.4 Leaching of metal elements with increased nitrate N concentration

We examined the relationships among the contents of various chemical components in the soil to discover what caused leaching of metal elements. When the data for all depths were used, no clear correlation was recognized. This is probably because in the topsoil the presence of large amounts of fertilizer made it hard to determine what chemical components influenced on the leaching of fertilizer. Therefore, we examined the data for the 30 to 150 cm layer. Table 2 is a correlation matrix of data on the various chemical components of the 30 to 150 cm layer. In this table, not only the contents of ammonium N, Ca, Mg and K applied as components of fertilizer but also the contents of Al, Mn, and Zn were positively correlated with the nitrate N content.

In particular, the highest correlation coefficient was recognized between Al and nitrate N content. In the study area, much ammonia was applied as fertilizer and nitrate is thought to be generated through the oxidation of ammonia. In the process of the oxidation of ammonia to nitrate, hydrogen ion was generated [9] and it acidified the soil water. Leaching of metal elements with nitrate leaching was reported around the tea plantation area in Shizuoka prefecture, Japan [5–7]. In these study areas, compound fertilizers containing lees of rape seeds, chrysalis, crab shell, oyster shell, animal organic and ground fish were applied. pH levels in these study areas suggested acidification in the surface water or groundwater. In this study site, the pH level also suggested acidification in the soil water (table 1).

Therefore leaching of metal elements are thought to be because increased nitrate N concentration caused the acidification of soil water and metal elements such as Al, Mn, Zn dissolved in soil water.

Seasonal and vertical fluctuation of H^+ concentration was not correlated to that of metal elements such as Al, Mn, Zn as showed in table 2. But it was thought to be explained as follows: H^+ was utilized for reactions such as cation exchange, dissolution

Table 2. Correlation matrix for contents of chemical components of the soil at 30 to 150 cm at the study site.

	H ⁺ ***	NO ₃ -N	NH ₄ -N	SO ₄	Al	Ba	Ca	Fe	Mg	Mn	Na	K	Sr	Zn
NO ₃ -N	0.161	1.000	0.359*	0.127	0.900**	-0.425*	0.530**	-0.283	0.534**	0.469**	0.234	0.390*	0.265	0.356*
NH ₄ -N	0.349	0.359*	1.000	0.507**	0.453**	-0.156	0.402*	-0.173	0.231	0.381*	0.180	0.244	0.229	0.202
SO ₄	0.659	0.127	0.507**	1.000	0.202	-0.386*	0.355*	-0.166	0.251	0.080	-0.122	0.179	-0.012	0.265
Al	0.189	0.900**	0.453**	0.202	1.000	-0.264	0.669**	-0.240	0.717**	0.576**	0.462**	0.597**	0.409*	0.462**
Ba	-0.430	-0.425*	-0.156	-0.386*	-0.264	1.000	0.008	0.451**	0.102	0.171	0.465**	0.212	0.200	-0.090
Ca	0.132	0.530**	0.402*	0.355*	0.669**	0.008	1.000	-0.018	0.838**	0.596**	0.623**	0.744**	0.667**	0.477**
Fe	-0.424	-0.283	-0.173	-0.166	-0.240	0.451**	-0.018	1.000	-0.057	-0.205	0.033	0.215	-0.028	0.030
Mg	0.053	0.534**	0.231	0.251	0.717**	0.102	0.838**	-0.057	1.000	0.650**	0.709**	0.696**	0.647**	0.414*
Mn	-0.020	0.469**	0.381*	0.080	0.576**	0.171	0.596**	-0.205	0.650**	1.000	0.644**	0.208	0.398*	-0.144
Na	-0.223	0.234	0.180	-0.122	0.462**	0.465**	0.623**	0.033	0.709**	0.644**	1.000	0.534**	0.665**	0.212
K	0.004	0.390*	0.244	0.179	0.597**	0.212	0.744**	0.215	0.696**	0.208	0.534**	1.000	0.514**	0.758**
Sr	-0.225	0.265	0.229	-0.012	0.409**	0.200	0.667**	-0.028	0.647**	0.398*	0.665**	0.514**	1.000	0.326
Zn	0.237	0.356*	0.202	0.265	0.462**	-0.090	0.477**	0.030	0.414*	-0.144	0.212	0.758**	0.326	1.000

*Statistically significant by Student's *t*-test ($P < 0.01$).

**Statistically significant by Student's *t*-test ($P < 0.05$).

***H⁺ was calculated from pH data.

of hydroxide and carbonate of metal elements. Therefore, H^+ concentration of soil extract reflects the condition after H^+ was utilized for these reactions. On the other hand, nitrate is hard to be influenced by chemical reaction after H^+ was generated with the transformation of soil N to nitrate N. As a result, nitrate N concentration was thought to correlate to Al, Mn, Zn. Therefore it was thought that the leaching of Al, Mn and Zn was indirectly caused by the increase of the nitrate N concentration of the soil water. Ca and Mg contents also have fair correlations to contents of Al, Mn, Zn. It's because Ca and Mg are applied to the topsoil in the form of CaO, $Ca(OH)_2$, $CaCO_3$ and MgO in fertilizer and they are easy to dissolve in acidified water. Therefore Ca and Mg contents were high when soil water was acidified by the increase of nitrate N concentration in soil water and they were thought to have fair correlations to contents of Al, Mn, Zn.

In summary, these results show that metal elements such as Al, Mn, Zn were increasingly leached with increased nitrate N concentration in the 0 to 150 cm layer of soil. These phenomena are thought to be because increased nitrate N concentration causes the acidification of soil water and metal elements such as Al, Mn, Zn dissolve in soil water.

4. Conclusions

Nitrogen was present at high levels in the topsoil throughout the year. The nitrate N concentration of the soil water was at least 35 mg L^{-1} even in the deepest layers (130 to 150 cm) throughout the year. Examination of the contents of various metal elements in the soil suggested that high levels of nitrate N at depth are associated with high contents of water-soluble heavy metals. Nitrate N contamination of groundwater therefore has a secondary effect of increasing heavy metal contamination.

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