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GROUNDWATER METAL AND NITROGEN CONTAMINATIONS CAUSED BY NITROGEN FERTILIZER IN TEA PLANTATION CATCHMENT, THE CENTER OF SHIZUOKA, JAPAN

By

Toyokazu TANAKA

Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan

Hiroyuki Ii

Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan

Tatemasa HIRATA

Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan

Masataka NISHIKAWA

National Institute for Environment Studies, 16-2 Onogawa, Ibaragi 305-0053, Japan

Kouichi UMEHARA

Shizuoka Prefecture Institute of Health and Environment, 87 Higashida, Shizuoka 430-0915, Japan

and

Yumi OGAWA

Tsukuba University, 1-1-1 Tennoudai, Ibaragi 305-8573, Japan

SYNOPSIS

Groundwater chemistry was studied in order to determine the effects of fertilizer used in tea plantations on groundwater quality. The groundwater character, in particular pH values, depended not only on the amount of nitrogen fertilizer used but also on the amount of (Ca, Mg)CO_3 neutralizer used. Acidification caused by nitrogen fertilizer increased Al, Ni, Zn and Mn concentrations of groundwater and they reached 50, 0.1, 1.0 and 5 mg/l respectively. The Mn and Fe ion concentrations also depended on Eh values and increased with each decrease of Eh values. However, concentrations of nitrate and metals in groundwater have decreased for several years because the amount of nitrogen fertilizer used has decreased from 112 kgN/10a in 1993 to 65 kgN/10a in 2000 and the amount of carbonate used has increased from 80 kgCO_3/10a in 1993 to 130 kgCO_3/10a in 2000. Therefore, the amount of nitrogen fertilizer and carbonate used was a very important factor in controlling nitrate and metal concentrations in groundwater.

INTRODUCTION

Nitrate contamination caused by nitrogen fertilizer is a serious issue because nitrate is a harmful substance in drinking water and acidification accompanied with nitrate contamination brings out metal contamination (T. Hirata (1), H. Ii et al. (2), (3), (4)). In particular, the use of nitrogen fertilizer in tea plantations per unit area is highest of all Japanese agricultural lands (Association of Agriculture and Forestry Statistics (5)). Shizuoka Prefecture, in the center of Honshu Island, is famous for its green tea. However, it was reported that fish had died in ponds derived from tea plantation catchments (Shizuoka Press (6)). Groundwaters near tea plantations in Shizuoka prefecture were investigated, and it was found that most spring water originating from tea plantations cannot be used as drinking water sources as it contains in excess of 10 mg/l NO_3-N (the Japanese drinking water standard) (Shizuoka Press (6)). In particular, Ii et al (2)

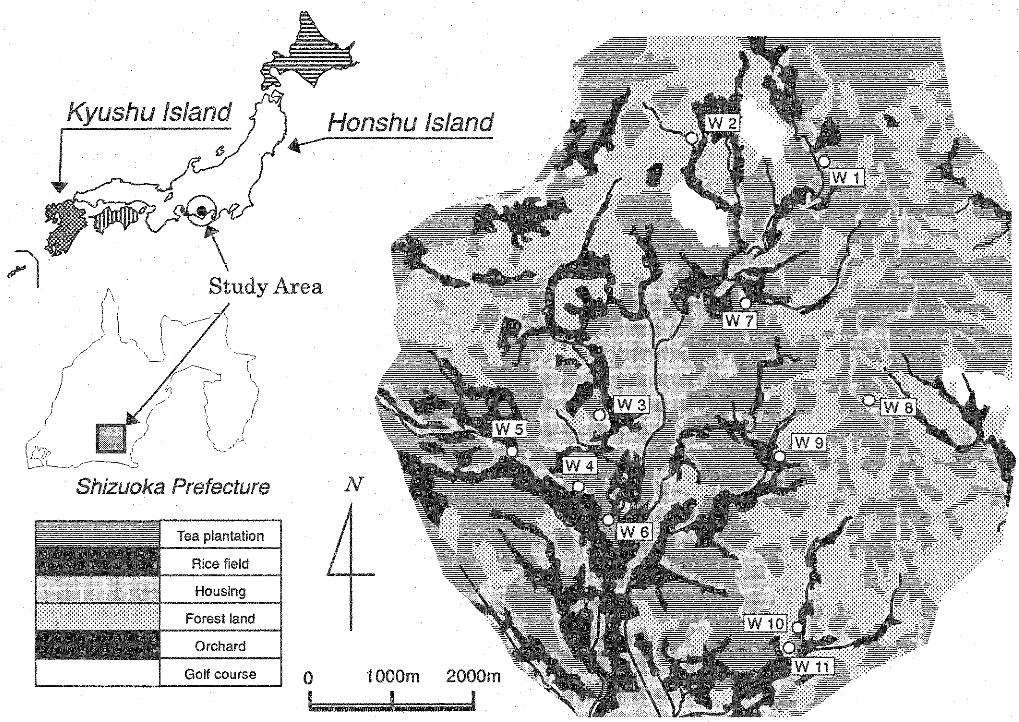

Fig.1 Study area

investigated the influence of fertilizer on pond water and river water near tea plantations in northern part of Kyushu Island and Shizuoka areas in Japan. It was found that at tea plantations in Kyusyu, excess amounts of nitrogen fertilizer used brought out both nitrate and Al contamination. Furthermore in tea plantations in Shizuoka prefecture, spring, river and pond waters from the tea plantations displayed low pH values and high nitrate concentrations. Al, Zn, Ni and Mn were detected as pH values decreased (H. Ii et al (4)). It was reported that fish had died because of acidification or Al contamination. As a result, farmers made efforts to decrease the amount of nitrogen fertilizer used in tea plantations from 110 kgN/10a in 1993 to 65 kgN/10a in 2000 and to increase the used amount of carbonates from 80 $kgCO_3$/10a in 1993 to 130 $kgCO_3$/10a in 2000 in order to neutralize the groundwater and to decrease nitrate concentration. Therefore, the influence of reduced amounts of fertilizer and increased amounts of carbonate on groundwater near tea plantations in the center of Shizuoka prefecture was examined.

STUDY AREA

The area studied is located near Shizuoka city in central Honshu, which is famous for its green tea. There were 11 wells in this area as shown in Fig.1. This is an area where plains are used for rice fields and housing, and plateaus and hillsides are used for tea plantations. The major land uses of catchment of sampling wells are tea plantations. Geologically, Quaternary terrace deposits covered Tertiary rock such as mudstone and siltstone are distributed at the plateaus and hillsides. Alluvial sediments are distributed at plains. The average annual precipitation is 2100 mm and average annual temperature is 16 degrees C.

INVESTIGATION

The groundwater was sampled from 11 wells in tea plantations once a month from April 1998 to April 2001. The wells are shown in Fig.1. The pH, EC and Eh values of the sampled waters were measured in situ using portable field kits. Samples were stored at 4 degrees C and concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-} and Cl^- were measured by ion exchange chromatography in the laboratory. Water samples were filtered (0.45 μm) before chemical analyses. HCO_3^- concentration was measured by titration in laboratory. After samples of heavy metal analysis were acidified (pH>3) with a spice of concentrated HNO_3, heavy metal

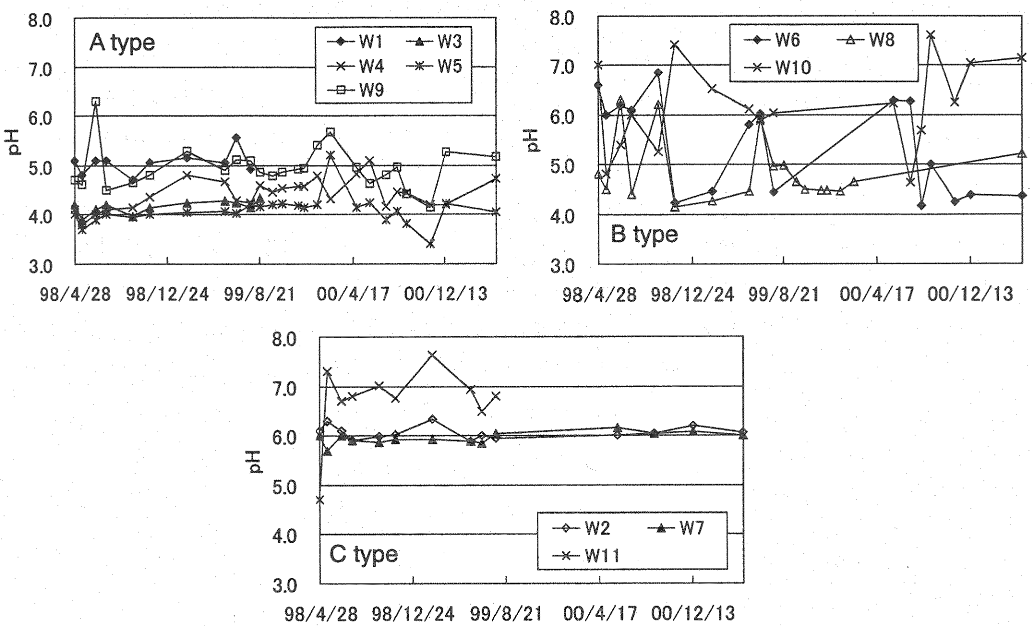

Fig.2 Time series of pH values

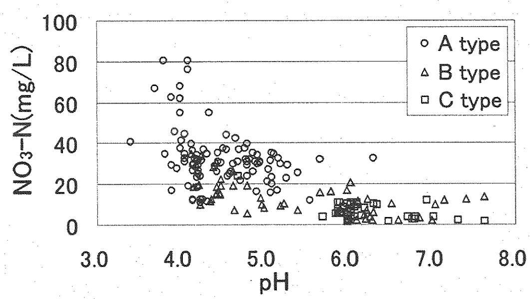

Fig.3 Relation between nitrate nitrogen concentration and pH values

concentrations were measured by ICP-AES method. It was found that the measured Al, Zn, Ni, Mn and Fe showed total metal concentrations in water.

RESULTS AND DISCUSSION

Change in pH values

pH values of the sampled groundwaters ranged from 4 to less than 8 for about three years as shown in Fig.2. As pH values were varied, groundwaters were classified into 3 groups, A, B, C types, according to pH values. A type indicated low pH values (4 to 5). B type showed variable pH values (4 to 7). C type pointed out high pH value (6 to 7). Since the main land use of the catchments of the wells is tea plantation and the geological and geographical conditions within tea plantations are the same, the classification by pH values was thought to have been influenced by fertilizer. Nitrogen fertilizer used in Japan is usually $(NH_4)_2SO_4$ which transforms into NO_3^-, H^+, and SO_4^{2-} by the following nitrification process(H. Ii et al. (2), (3), (4)).

$$(NH_4)_2SO_4 + 4O_2 = 2NO_3^- + 4H^+ + SO_4^{2-} + 2H_2O \quad (1)$$

Fig.3 shows the relationship between pH values and nitrate concentrations of each type as H^+ is produced with

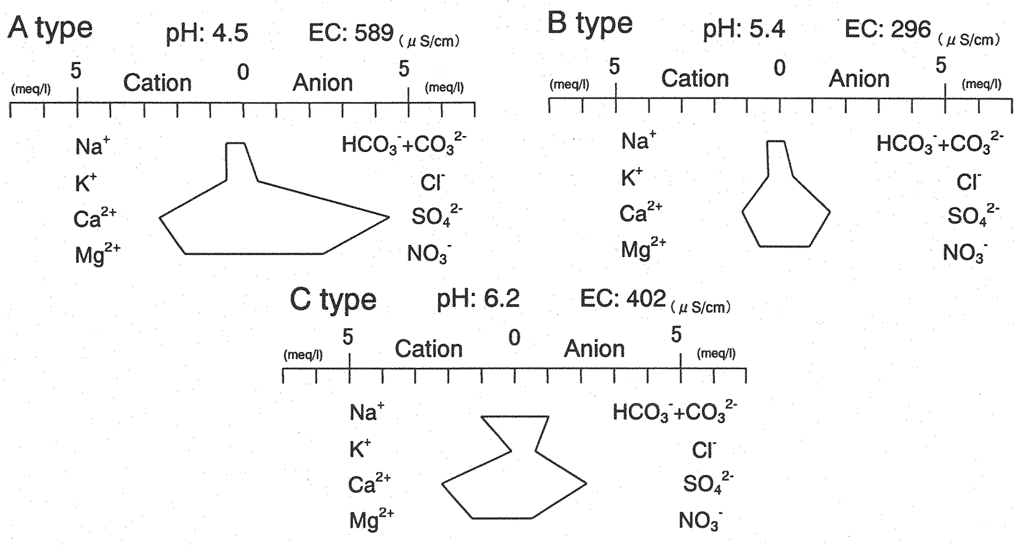

Fig.4 Stiff-diagrams of each type

nitrate. Nitrate concentrations increased with each decrease in pH values from C type through B type to A type. As A type wells have high nitrate concentrations and low pH values and C type wells have low nitrate concentrations and high pH values, it was thought that nitrate and hydrogen originating from nitrogen fertilizer had an influence on groundwater. Fig.3 suggests that these differences in types were caused by different amounts of nitrogen fertilizer used on the catchments; that is, A type was influenced by large amounts of nitrogen fertilizer and the amounts of fertilizer used in catchments of B and C type wells were smaller than A type.

Major components

Other main components were analyzed and stiff-diagrams are shown in Fig.4. These diagrams show average value of pH, EC and concentrations of each type of sampled water. Ca^{2+}, Mg^{2+}, NO_3^- and SO_4^{2-} were the main components in all types of wells. After nitrogen fertilizer is added, calcium and magnesium carbonates are also added into soil in order to neutralize acidic soil water because the pH values of soil water decrease. As a result, Ca^{2+} and Mg^{2+} concentrations of sampled water were very high and the following equation was considered (Eq. 2) (H. Ii et al. (2), (3), (4)).

$$2H^+ + (Ca, Mg)CO_3 = CO_2 + (Ca^{2+}, Mg^{2+}) + 2H_2O \qquad (2)$$

Therefore, high concentrations of Ca^{2+}, Mg^{2+}, NO_3^- and SO_4^{2-} were thought to have originated from fertilizer as well as from the chemical $(NH_4)_2SO_4$ and $(Ca, Mg)CO_3$. There was an increase in NO_3^- concentrations and a decrease in pH values in water from C type through B type to A type wells. The difference in pH values of the three types was thought to depend on the amount of nitrogen fertilizer used. But if the amount of nitrogen fertilizer used in C type is smaller than that in the B type, EC value and Ca^{2+}, Mg^{2+} and SO_4^{2-} concentrations of C type should be smaller than the samples taken from B type wells. However, comparing B and C type, EC value and Ca^{2+}, Mg^{2+} and SO_4^{2-} concentrations in C type were found to be higher than those in B type and particularly Ca^{2+} and Mg^{2+} concentrations in A and C type were found to be almost the same. Therefore, the difference in pH values of the three types of wells did not only depend on the amount of nitrogen fertilizer but also the amount of carbonate present.

Ammonium volatilization

Fig.5 shows the relationship between Ca^{2+}+Mg^{2+} concentrations and nitrate concentrations compared to amount of carbonate and nitrogen fertilizer. Ca^{2+}+Mg^{2+} concentrations increased as nitrate concentration

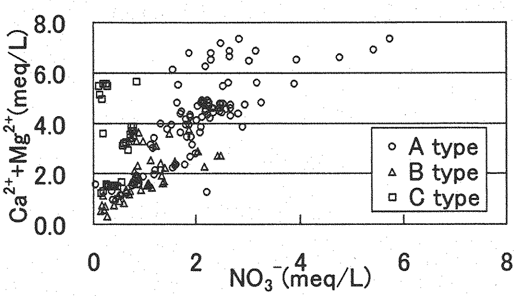

Fig.5 Relationship between $Ca^{2+}+Mg^{2+}$ and nitrate concentrations

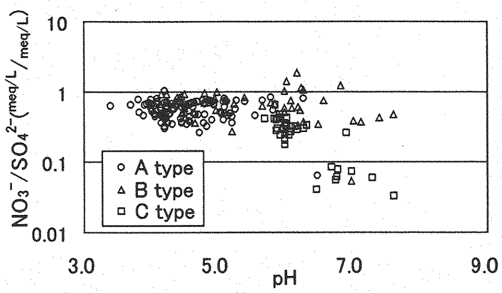

Fig.6 Relation between pH values and NO_3/SO_4 equivalent ratio

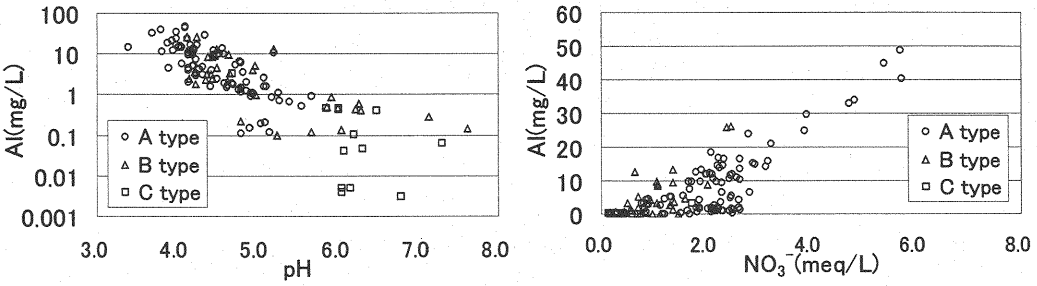

Fig.7 Relations between pH values and aluminum concentration and between nitrate and aluminum concentration

increased. In particular, $Ca^{2+}+Mg^{2+}$ concentration of C type was higher than nitrate concentration of A and B type. It was thought that in C type catchments, the amount of carbonates used was greater than A and B type and the amount of nitrogen fertilizer used was less than A and B type. Fig.6 shows pH values and NO_3/SO_4 equivalent ratio of A, B and C type, as the ratio of NO_3/SO_4 and pH values were controlled by fertilizer according to the Eq.1. As the nitrogen fertilizer used is the same type in each catchment of types, the ratio of NO_3/SO_4 equivalent ratio should be same. But the ratio of C type decreased with each increase of pH value even though the ratio of A and B type were uniform. Ammonium volatilization occurs depending pH values. This is shown in the following equation (Eq. 3) (S. Iwata (7)).

$$NH_4^+ + OH^- = NH_3 + 2H_2O \qquad (3)$$

This equation (Eq. 3) shows that ammonium ions released from nitrogen fertilizer changes into ammonium and volatilizes as pH values increases. As a result, nitrate is hardly produced from ammonium by nitrification as pH value becomes higher. Therefore, there were sufficient amount of carbonates in the catchment of C type. As a result of ammonium volatilization, it was thought nitrate concentration of C type was low and the ratio of NO_3/SO_4 became low. It was thought that carbonates decreased the nitrate and hydrogen concentration. As acidification of groundwater is known to cause metal contamination, the relationship between nitrogen fertilizer and metal concentrations were examined.

Metal contamination of the groundwater

Fig.7 shows two relationships: one between pH values and Al concentrations and another between nitrate and Al concentrations. Total Al concentrations in groundwaters depended on pH values. Total Al concentration in groundwaters increased from less than 0.01 to 50 mg/l with a decrease in pH and an increase in nitrate concentrations. Most groundwater contains an excess of 0.2 mg/L Al (the agreeable maximum concentration of Japanese drinking water). Generally Al minerals are stable under a neutral pH condition, but Al is dissolved from Al minerals of kaolinite ($Al_2Si_2O_5(OH)_4$) and $Al(OH)_3$ occurs due to weathering at low pH condition by the following process (H. Ii et al. (4)).

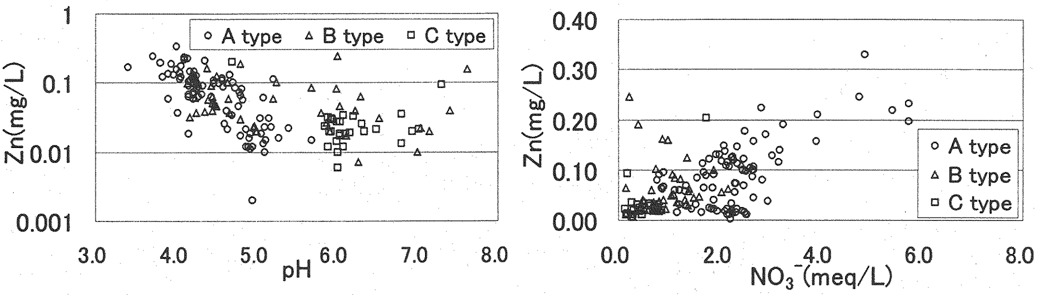

Fig.8 Relations between pH values and zinc concentration
and between nitrate and zinc concentration

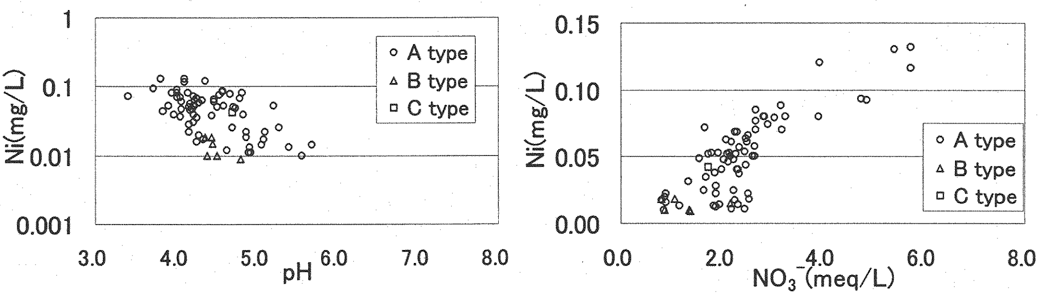

Fig.9 Relations between pH values and nickel concentration
and between nitrate and nickel concentration

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + 2H_2O \quad (4)$$
$$Al(OH)_3 + 3H^+ = Al^{3+} + 2H_2O \quad (5)$$

The equations (Eq. 4, 5) indicate that Al minerals dissolve with an increase of hydrogen ion concentration. Therefore, increases in hydrogen concentration originating from nitrogen fertilizer can increase Al concentrations.

Similarly, total Zn concentrations in groundwaters depended on pH values. Fig.8 illustrates two relationships: one between pH values and Zn concentrations and another between nitrate and Zn concentrations. All sampled groundwater contained less than 1.0 mg/L Zn (the Japanese drinking water standard). Total Zn concentration increased from less than 0.01 to 1 mg/l or more with a decrease from 6 to less than 4 in pH and an increase in nitrate concentrations. However, total Zn concentrations increased as pH values increased from 6 to over 7. ZnO is a production of weathered rock. ZnO dissolves easily into Zn ion under neutral to acidic condition and also ZnO dissolves into Zn hydrate ions under alkaline condition and this is shown by the following equations (Eq. 6, 7) (M. Taga, and S. Nasu (8)).

$$ZnO + 2H^+ = Zn^{2+} + H_2O \quad (6)$$
$$ZnO + 2H_2O = Zn(OH)_3^- + H^+ \quad (7)$$

This equation (Eq. 6) shows that Zn dissolves with an increase of hydrogen ion concentration. Therefore, it was thought that as nitrogen fertilizer was converted into nitrate and hydrogen ions, nitrate concentration increased with each decrease of pH values and Zn ion concentrations also increased. The total Zn concentrations did not decrease at the condition of over 6 in pH values. ZnO dissolution was thought to have been caused by the reaction of equation (Eq. 7) and total Zn concentrations were thought to increase with an increase of pH.

Similarly, total Ni concentrations in groundwaters also depended on pH values. Fig.9 indicates two relations between pH values and Ni concentrations and between nitrate and Ni concentrations. Ni concentrations in groundwaters increased from less than 0.01 to over 0.1 mg/l with a decrease in pH and an increase in nitrate concentrations. Most groundwater contained an excess of 0.01 mg/L Ni (the guiding concentration of Japanese drinking water). Ni ions were usually detected in the A type. However, they were not common in the B and C types. Ni ions are easily precipitated as $Ni(OH)_2$ produced by weathering.

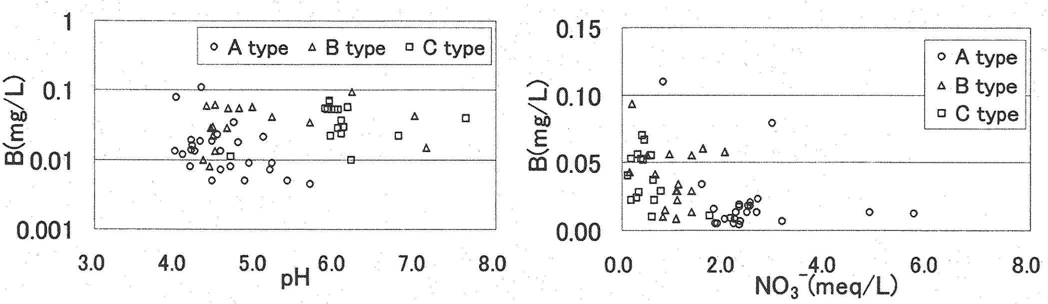

Fig.10 Relations between pH values and boron concentration and between nitrate and boron concentration

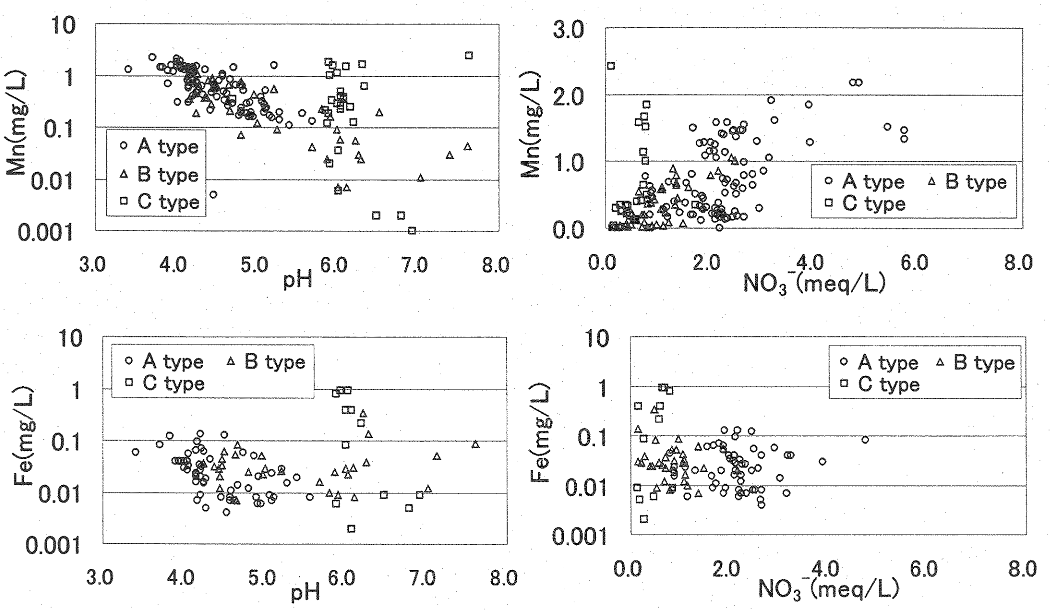

Fig.11 Relations between pH values and Mn and Fe concentration and between nitrate and Mn and Fe concentration

Thus, $Ni(OH)_2$ is quoted to be dissolved into Ni ion by using the following equation (Eq. 8) (T. Yamada (9)).

$$Ni(OH)_2 + 2H^+ = Ni^{2+} + 2H_2O \quad (8)$$

Eq.8 shows that Ni dissolves with an increase of hydrogen ion concentration. Therefore, it was thought that as nitrogen fertilizer was converted into nitrate and hydrogen ions, the nitrate concentration increased with a decrease of pH values and Ni ion concentration also increased.

B (Boron) is an important element in environmental issues because recently B has been added to the list of concentration limits for Japanese drinking water (Ministry of Environment (10)). As B is an essential element for a tea plantation, B is used with fertilization. Fig.10 shows two relationships: one between pH values and B concentrations and another between nitrate and B concentration. The concentration of B in groundwaters was from 0.002 mg/L to 1.27mg/L. All groundwater contained less than 0.2 mg/L B (the guiding concentration of Japanese drinking water). B did not depend on pH value and nitrate concentration. Therefore, it was thought that B was not affected by the change of pH values, and the B was supplied to each tea plantation and the supplying process was found to be different from nitrogen fertilizer.

Fig.11 shows two relationships: one between pH values and Mn concentrations and another between nitrate and Mn concentrations. Most groundwater contained an excess of 0.05 mg/L Mn (the Japanese

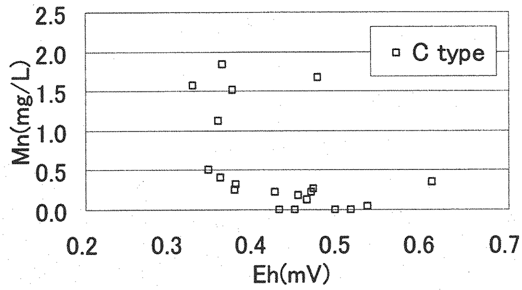

Fig.12 Relations between Eh value and Mn concentration of C type

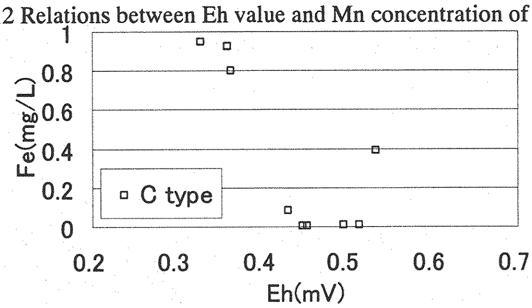

Fig.13 Relations between Eh value and Fe concentration of C type

drinking water standard). Mn ion concentrations increased from less than 0.001 to over 2.00 mg/l with a decrease in pH and an increase in nitrate concentrations. However, Mn ion concentrations in C types were variable with uniform pH values, about 6.0. As manganese is a redox-sensitive element in groundwater, Mn ion concentration depends on both pH and Eh values and Mn ions are easily precipitated as various kinds of Mn oxides, and Mn oxides are dissolved into Mn ion by means of the following equations (Eq. 9, 10, 11, 12) (N. Shikazono (11)).

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \quad (9)$$
$$Mn_2O_3 + 6H^+ + 2e^- = 2Mn^{2+} + 3H_2O \quad (10)$$
$$Mn_3O_4 + 8H^+ + 2e^- = 3Mn^{2+} + 4H_2O \quad (11)$$
$$Mn(OH)_2 + 2H^+ = Mn^{2+} + 2H_2O \quad (12)$$

Eq. 9, 10, 11 and 12 indicate that Mn dissolves with an increase of hydrogen ion concentration in a reductive condition. Manganese ion concentration in A and B type wells increased with hydrogen concentrations but Mn ion concentration in C type was thought to depend on Eh condition. So, Fig.12 shows the relation between Eh values and Mn ion concentration. As a result, Mn ion concentration in C type well increased with each decrease of Eh values and it depended on redox conditions.

Fig.11 showed two relations between pH values and Fe concentrations and between nitrate and Fe ion concentrations. Fe ion concentrations in groundwaters did not increase with each decrease in pH and increase in nitrate concentrations against Mn ions and they were from less than 0.002 to 0.94 mg/l. Fe ions are precipitated easily as various kinds of Fe oxides, and Fe oxides are dissolved into Fe ion by the following equations (Eq. 13, 14, 15) (M. Taga, and S. Nasu (8)).

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \quad (13)$$
$$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O \quad (14)$$
$$Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+ \quad (15)$$

As Fe ion concentration depended on both pH and Eh values, Fe ion concentration was not thought to change with pH values and nitrate concentrations depending on Eh condition. In particular, Fe ion concentrations in C type varied considerably with the same pH values. Therefore, Fig.13 shows the relations between Eh values and Fe concentration of C type. As a result, Fe ion concentration decreased with each increase of Eh values and redox condition was found to be very important for Fe dissolution. Only some of

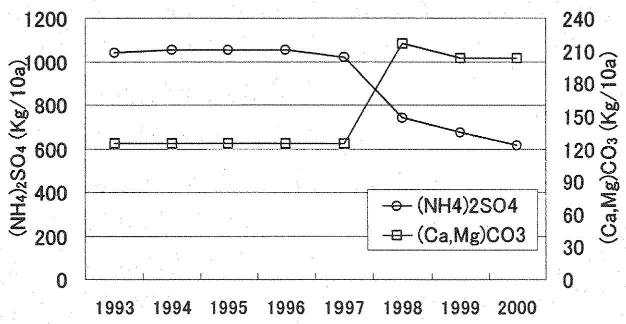

Fig.14 Time series of used amount of nitrogen fertilizer and carbonates of A type

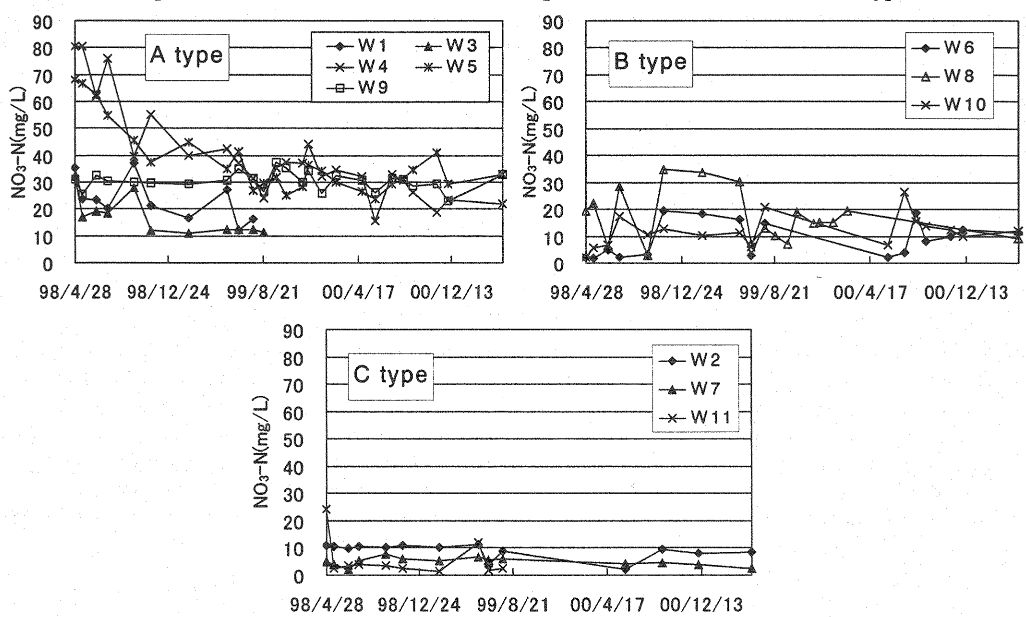

Fig.15 Time series of nitrate nitrogen concentrations

groundwater in C type contains in excess of 0.3 mg/L Fe (the Japanese drinking water standard)

Reduction in nitrogen fertilizer use

Nitrate and Al contamination of groundwater and the sudden death of fish in the pond derived from tea plantation catchment were recently reported in the media. In order to control nitrate contamination caused by nitrogen fertilizer, the amount of nitrogen fertilizer used has been decreased and the amount of carbonates has been increased. Fig.14 shows the time series of the average amount of nitrogen fertilizer and carbonates used. The amount of nitrogen fertilizer used on the catchments decreased from 110 kgN/10a in 1993 to 65 kgN/10a in 2000, and the amount of carbonate used increased from 80 $kgCO_3$/10a in 1993 to 130 $kgCO_3$/10a in 2000. Fig.15 shows the time series of NO_3-N concentration of each type. NO_3-N concentration in A type wells decreased gradually with the reduction in the amount of nitrogen fertilizer used. However, NO_3-N concentration of A type wells still exceeded 10 mg/L (the Japanese drinking water standard). Nitrate concentration in both B type and C type did not decrease. NO_3-N concentration in B type wells exceeded the Japanese drinking water standard and nitrate concentration in C type wells stabled about 10 mg/L. It was thought that as the amount of nitrogen fertilizer of A type was greater than B and C type originally, and the average decrease of amount of fertilizer used was thought to be caused by decrease of nitrogen fertilizer used in tea plantation containing A type well. In Japan, each farmer has a special method of growing tea plants because heavy tea competition determines tea prices. The difference in the amount of fertilizer used

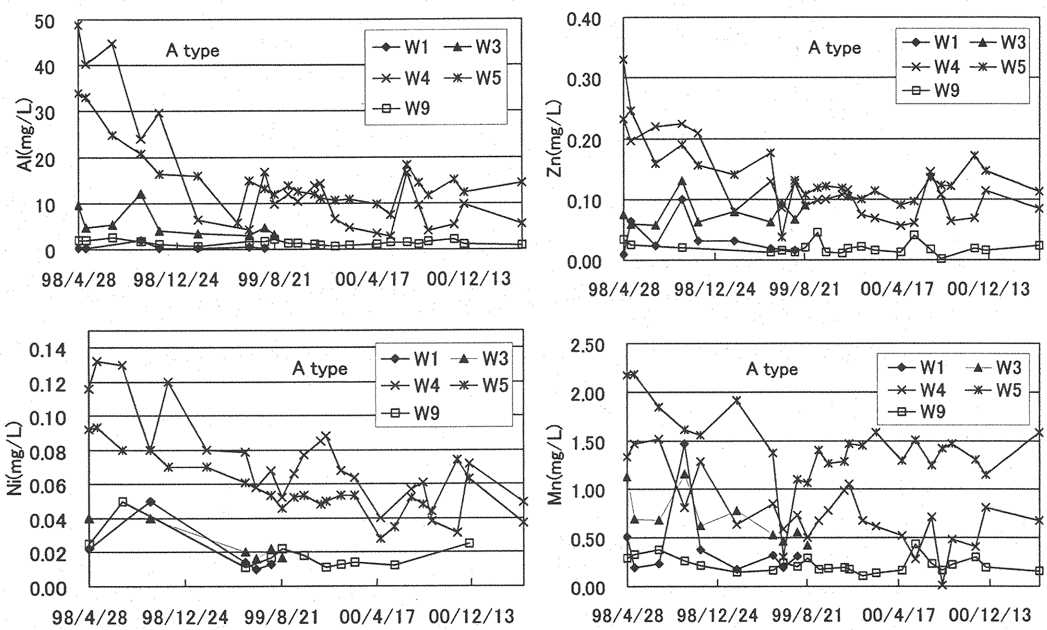

Fig.16 Time series of metal concentrations of A type

previously depended on a farmer's decision was thought to determine the groundwater quality A, B and C types. A type and B type wells contained an excess of 10 mg/L NO_3-N and NO_3-N concentration of C type wells stabled about 10 mg/L. As pH value of A type was low and many metals were detected, a variety of metal concentrations of A type were examined. Fig.16 shows the time series of metal concentrations of A type. Al, Zn, Ni, Mn concentrations decreased respectively. As the amount of nitrogen fertilizer decreased and the amount of carbonates increased, hydrogen ion concentration decreased and each metal concentration decreased. Therefore reduction in the amount of nitrogen fertilizer used on the catchments and an increase in carbonates can control nitrate and metal contamination in groundwater of plantations.

CONCLUSION

Groundwater chemistry was studied in order to determine the influence of fertilizer used in tea plantations on groundwater quality. Groundwater was sampled from wells in tea plantation catchments and amounts of used nitrogen fertilizer were studied. pH values and nitrate concentrations of the groundwater in tea plantation catchments ranged from 4 to 8 and from 50 to 350 mg/l, respectively. pH values decreased with each increase in nitrate concentrations because nitrogen fertilizer used in tea plantations eventually changed into hydrogen ion and nitrate. However, although nitrate concentrations in groundwater were not low, some groundwater indicated low pH values and high nitrate concentrations. As (Ca, Mg)CO_3 was also added into tea plantations, pH values were also thought to be influenced by carbonate neutralizer. Sufficient carbonate increased pH values of groundwater and this was thought to accelerate ammonium volatilization and reduce nitrate concentration. As a result, the ratio of NO_3/SO_4 in groundwater with high pH value was thought to become low. Low pH values, which originated from nitrogen fertilizer, also caused metal contamination of groundwater. Al, Ni, Zn and Mn ion concentrations of groundwater also increased with the decrease of pH values and the increase of nitrate concentrations. Their maximum values reached 50, 0.1, 1.0, and 5 mg/l, respectively. The Mn and Fe ion concentrations also depended on Eh values and increased with each decrease of Eh values. However, the use of sufficient carbonate and reduced amounts of nitrogen fertilizer used decreased nitrate concentrations and increased pH values. As a result, Al, Ni, Zn and Mn ion concentrations decreased. Therefore, pH control caused by the addition of carbonate and the reduction of nitrogen fertilizer was considered an important factor in lowering the nitrate and metal concentrations in groundwater.

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