論　文

Seasonal Changes in Nitrate Ion Concentration in the Headwater Area of the Ishite River

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石手川源流部における硝酸イオン濃度の季節的変化

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要　旨　愛媛県下の石手川源流部において二つの小集水域（伐採跡地と造林地）を選び，1年間，降水量と流出水量の連続観測を行うとともに，流出水中の硝酸イオンと塩類一般の代表としてのカルシウムイオンの濃度を約10日間隔で測定した。その結果，両イオン濃度に季節的変化が認められ，そのさいに，伐採跡地において変動幅が大きいことが認められた。また，両イオンと両集水域に共通して，降水量の少ない冬季に，イオン濃度と流出水量との間に正の関係が認められた。さらに，カルシウムイオン濃度については，連続的な降雨が直接的間接的に影響する場合，すなわち，雨が多い春や初夏の梅雨時期，梅雨後の乾燥した夏に，両集水域に共通して流出水量との間に負の関係が認められた。しかし，硝酸イオンについては，冬から初春にかけてカルシウムイオンと同様の流出様式が認められたのみであり，カルシウムイオンとは異なった，一層複雑な流出環境下にあるとみられた。

Summary: In two small catchments (cutover and afforested) in the headwater area of the Ishite River, Ehime Prefecture, Japan, NO_3^- and Ca^{2+} concentrations in the drainage streams were examined at *ca.* 10 day intervals for one year, and continuous gaugings of precipitation and discharge were carried out. The concentrations of both ions showed seasonal changes, with a wider variation in the cutover catchment. Positive relationships were found between ion concentration and discharge during the winter season under light precipitation, for both ions in the two catchments. Under the direct and indirect influence of successive rainfalls, Ca^{2+} showed negative relationships with discharge in both catchments, *i.e.* during the rainy spring and the early rainy summer periods, and the following dry summer. NO_3^- seemed to behave in the same transport mode as Ca^{2+} only from the winter through early spring. The situations seemed to be more complicated in the case of NO_3^-.

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I INTRODUCTION

In a previous paper (KAGAWA *et al.,* 1985), the authors reported a positive relationship between annual precipitation and annual mean nitrate ion (NO_3^-) concentration of river water after a monthly 7-year observation. This relationship involved an exception during two successive heavy rainy years, when the NO_3^- concentration decreased against an increase in precipitation. The authors intended to clarify the mechanism which caused this relationship, including the exception, and in this report investigated seasonal changes in NO_3^- concentration in the headwater area of the Ishite River where the above relationship was found.

II METHODS

1. *Study area*

In the headwater area of the Ishite River, Ehime Prefecture, Japan, two neighboring catchments, named Kaname-no-tani and Kijigoya, were used for the water quality ex-

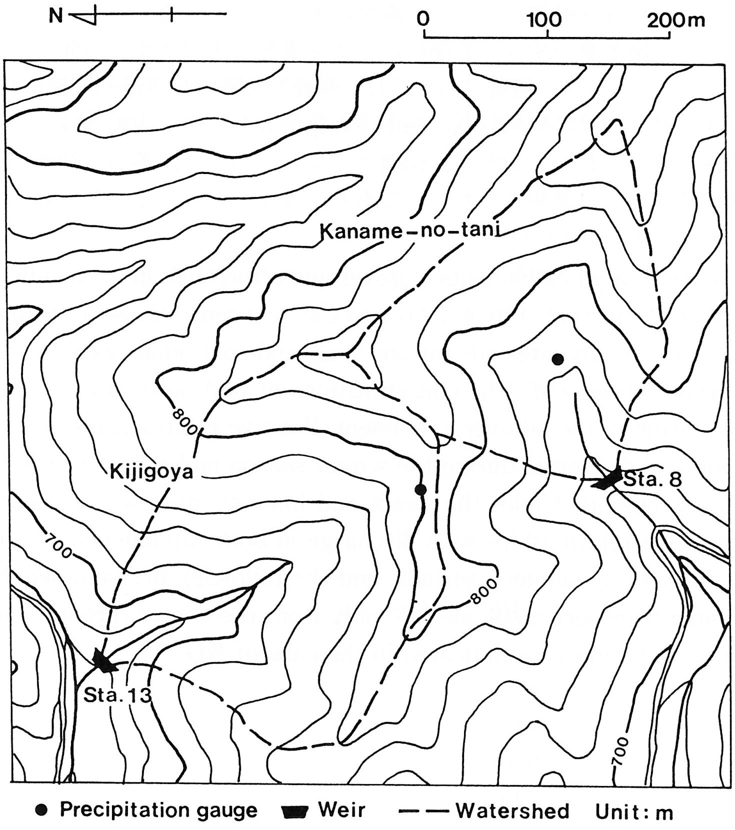

Fig. 1. Topographical map of study areas.

amination (see Fig. 1). In Kaname-no-tani, natural forest was logged from 1982 through 1983, and two species of coniferous trees *Cryptomeria japonica* D. DON and *Chamaecyparis obtusa* SIEB. et ZUCC. were planted in 1984. Kijigoya was reforested by planting these trees in 1973. The areas of the catchments are 4.48 ha in Kaname-no-tani and 6.40 ha in Kijigoya above V-notch measuring weirs. Weirs with water level recorders were constructed in June 1985 at 730 m above sea level in Kaname-no-tani and at 660 m in Kijigoya, which were the same sites as Nos. 8 and 13 of the previous paper (KAGAWA *et al.*, 1985), respectively. At station 8 (Sta. 8), where the elevation was high and the forest was cutover, the water level recorder was removed from December through March to avoid freezing, and the water level was measured by hand once a week and at each sampling time. Precipitation gauges were set in both catchments, as shown in Fig.1. These gauges were also removed from December through March, and the precipitation data during this period were provided by the Komenono Forest Research Center, the University Forest, Ehime University, which is located 2.6 km west of the study area. Further descriptions of the study area are given in the previous paper.

2. *Water quality examination*

Water samples for chemical analyses were taken from streams just above the weirs almost every ten days from 16 April 1985 to 27 May 1986. Sampling in the rain was avoided in principle, because the interesting positive relationship between annual mean NO_3^- concentration and annual precipitation in the previous paper was found near base flow.

Water samples were brought to the laboratory within 3 hours for chemical analyses. Although many chemical components were determined, only NO_3^- and calcium ion (Ca^{2+}) concentrations are reported in this paper. Ca^{2+} is reported as an index showing the behavior of salt in general in the catchment.

NO_3^-: After filtering through a 0.45 μm membrane filter, samples were treated by a cadmium-copper column in order to reduce NO_3^- to NO_2^-. NO_2^- concentrations in the treated and untreated samples were determined colorimetrically using GR reagent. The difference of these two determinations was used as the NO_3^- concentration in the original sample.

Ca^{2+}: Calcium concentrations in filtered samples were determined by an atomic absorption method using an addition of 1500mg/l of strontium in the final concentration to overcome interference. Although some calcium might have been in chemical forms other than Ca^{2+}, calcium was represented by the typical Ca^{2+} and the unit milliequivalents per liter (me/l) was used to show both NO_3^- and Ca^{2+} concentrations for the convenience of chemical comparison.

III RESULTS AND DISCUSSION

1. *Seasonal changes in precipitation and discharge in the study catchments*

Daily precipitation and discharge in the study catchments are shown in Figs. 2 and 3. Cumulative precipitations for about one year were 1590 mm in Kaname-no-tani (16 June-31 May) and 1725 mm in Kijigoya (6 June - 31 May), and 29.9% (476mm) in the former and 29.7% (512 mm) in the latter were recorded during one half month of successive rainy days (21 June - 4 July). The rest of the summer and the winter had light precipitation, and the autumn

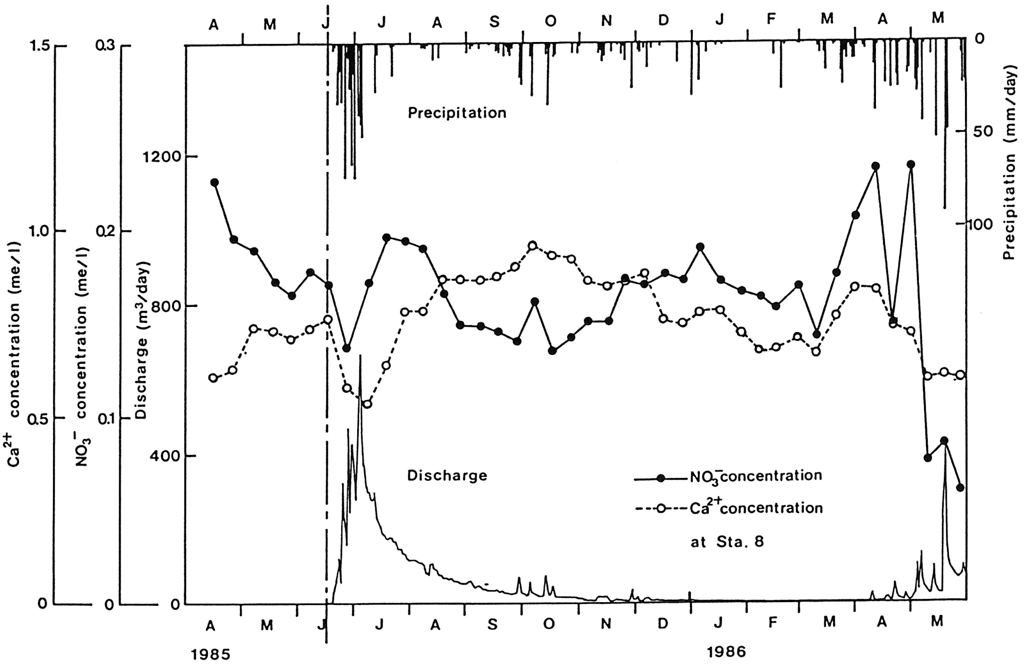

Fig. 2. Seasonal changes in NO_3^- and Ca^{2+} concentrations as well as precipitation and discharge in Kaname-no-tani catchment.

and the spring were relatively rainy.

The discharge varied very much according to precipitation. The highest discharge was recorded on 4 July, the last day of the summer rainy period, in both catchments, and it decreased with several low peaks until March. Some peaks might have been missed in Kaname-no-tani owing to relatively long intervals between water level measurings during the winter season. From April through May, the discharge increased again due to spring rainfalls. Hydrological aspects, such as the water balance in the study areas, will be reported in another paper.

2. *Seasonal changes in NO_3^- and Ca^{2+} concentrations in the drainage streams*

NO_3^- and Ca^{2+} concentrations in the drainage streams are shown in Figs. 2 and 3 together with precipitation and discharge. NO_3^- varied between 0.060 me/*l* (27 May) and 0.233 me/*l* (30 April) at Sta. 8 in Kaname-no-tani and between 0.022 me/*l* (27 June, 17 February) and 0.075 me/*l* (19 May) at Sta. 13 in Kijigoya. The higher NO_3^- concentration at Sta. 8, where the forest was cutover, was discussed in the previous paper (KAGAWA *et al.,* 1985). Ca^{2+} varied between 0.534 me/*l* (8 July) and 0.958 me/*l* (6 October) at Sta. 8 and between 0.425 me/*l* (8 July) and 0.623 me/*l* (16 October) at Sta. 13. Ca^{2+} as well as NO_3^- concentrations were higher at Sta. 8 than at Sta. 13 throughout the whole study period, and the ranges of variation were wider at Sta. 8 than at Sta. 13 for both ion concentrations.

Seasonal changes were found in both ion concentrations, especially at Sta. 8. At Sta. 8, NO_3^- which was 0.226 me/*l* (16 April) decreased gradually to 0.170 me/*l* (17 June) just before the summer rainy period. It dropped down to 0.136 me/*l* in the rainy period, but rose up to 0.196 me/*l* on 18 July. NO_3^- decreased again gradually through the remaining dry summer to

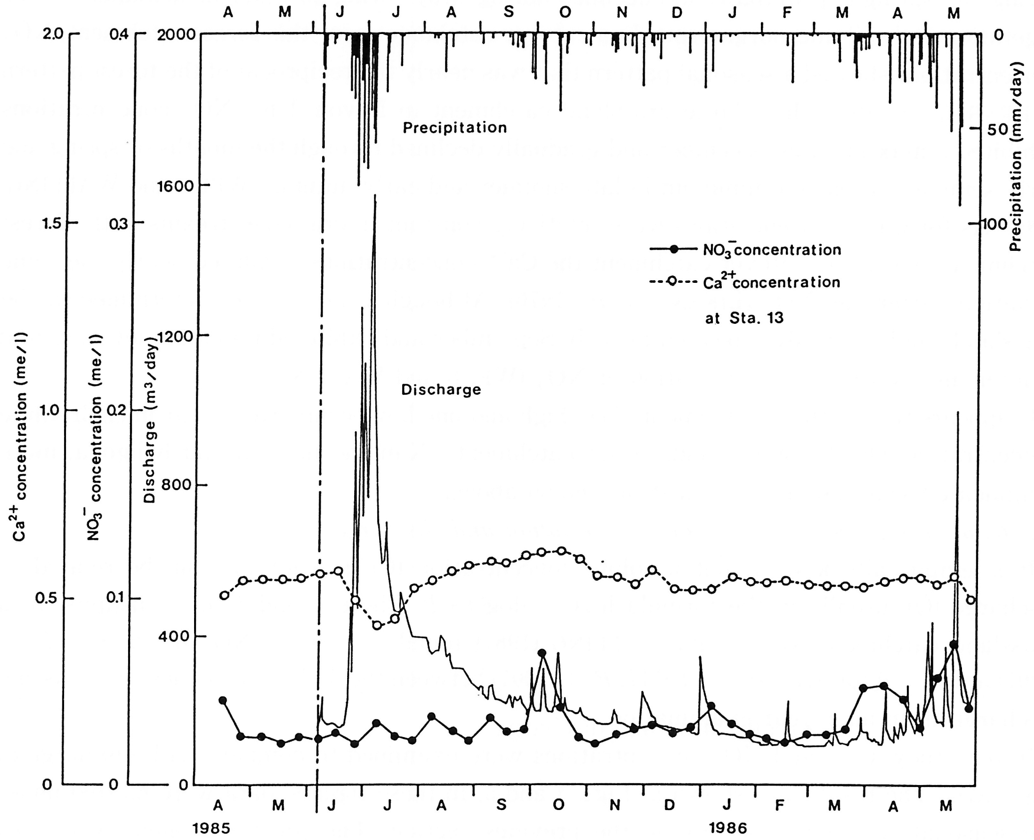

Fig. 3. Seasonal changes in $\mathrm{NO_3^-}$ and $\mathrm{Ca^{2+}}$ concentrations as well as precipitation and discharge in Kijigoya catchment.

0.140 me/*l* (27 September) and 0.135 me/*l* (16 October). Then it increased through the autumn under intermittent rains to 0.173 me/*l* (25 November) and 0.175 me/*l* (16 December). It decreased again through the winter under light precipitation to 0.142 me/*l* (10 March) and then varied widely up and down due to relatively heavy spring precipitation. Two peaks on 6 October and 6 January seemed to be on the recession periods of small storm events so they were omitted here from consideration.

On the other hand, $\mathrm{Ca^{2+}}$ concentration increased at first, in contrast to $\mathrm{NO_3^-}$. It dropped down once during the summer rainy period like $\mathrm{NO_3^-}$, but increased through the dry summer after the rainy period, and then decreased through the autumn, in contrast to $\mathrm{NO_3^-}$. In the winter it continued to decrease, and in the rainy spring it increased then decreased, like $\mathrm{NO_3^-}$.

At Sta. 13, the seasonal changes in $\mathrm{NO_3^-}$ concentration were obscure. No drop was observed during the summer rainy period, but increasing effects by rainfalls were found in the spring. On the other hand, $\mathrm{Ca^{2+}}$ showed seasonal changes similar to Sta. 8, although the variations were narrower.

Seasonal changes in solute concentrations in drainage streams are reported in some literature. In one forest catchment in New Hampshire, USA, $\mathrm{NO_3^-}$ concentrations were low throughout the summer growing season, increased in November, reached the maximum during the spring (April) thaw, and declined during May owing to nutrient demands by the vegetation and soil microorganisms. In a cutover catchment near this forest catchment, NO_3^- concentrations showed a seasonal pattern that was nearly the reciprocal of the forest pattern (LIKENS *et al.,* 1970). In a large grassland catchment in Devon, UK., NO_3^- concentrations exhibited a maximum in December and gradually declined through the months of spring and early summer to reach a minimum in late summer and early autumn (WEBB and WALLING, 1985). As for Ca^{2+}, concentrations were relatively constant in drainage streams in the forest catchment, but in the cutover catchment the Ca^{2+} concentrations exhibited nearly the same variation pattern as NO_3^- (LIKENS *et al.,* 1970). Although Ca^{2+} was not determined in the grassland catchment, Mg^{2+} peaked in early September and exhibited minimum levels in mid-winter just in a reciprocal variation of NO_3^- (WEBB and WALLING, 1985).

It appears that in these catchments, one high and one low occurs every year in each solute concentration. On the other hand, in our catchments, Kaname-no-tani and Kijigoya, more complicated seasonal changes exist, as shown above.

3. *Relationships between a solute concentration and discharge*

It is empirically known that a solute concentration (C) in a stream can be related to discharge (Q), usually in the formula $\log C = a \log Q + b$, where a and b are constants. In a grassland catchment, WEBB and WALLING (1985) found $a > 0$ for NO_3^- ($r = 0.7882$; $P < 0.001$) and $a < 0$ for Mg^{2+} ($r = -0.9117$; $P < 0.001$) between the daily mean concentrations and discharge from an 8-year examination.

In our study, Ca^{2+} and NO_3^- concentrations were examined to compare with discharge in log scales. The results are shown in Figs. 4 and 5. In these figures, data were plotted under the seasonal partition described in the previous section. The precise delineation of two seasons was difficult to decide, because the plots had compound properties in a variable ratio.

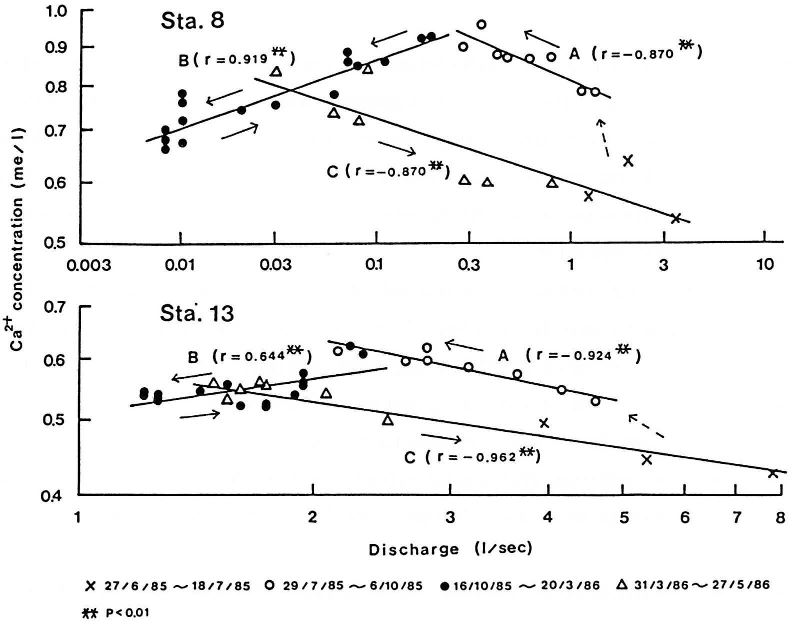

Fig. 4. Relationships between Ca^{2+} concentration and discharge.

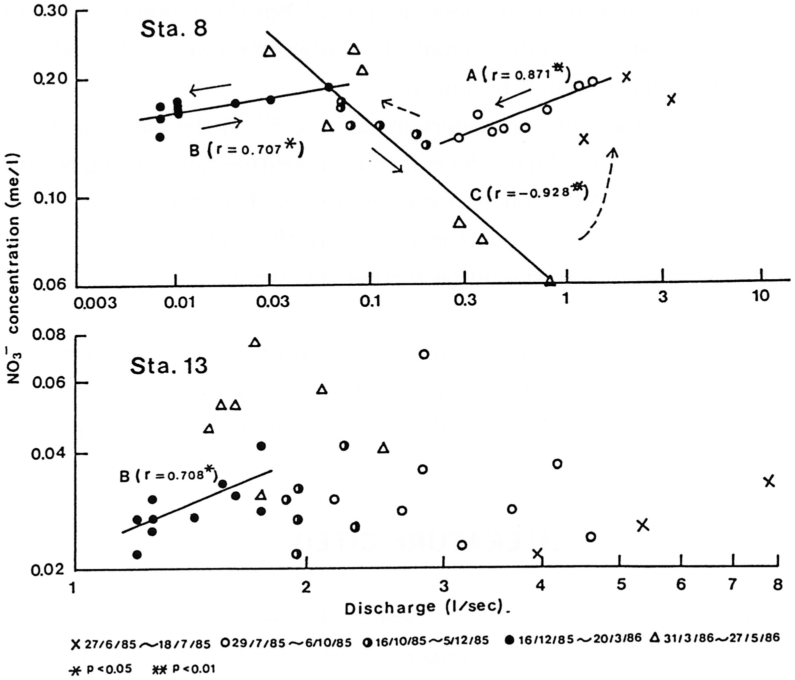

Fig. 5. Relationships between NO_3^- concentration and discharge.

In Figs. 4 and 5, the divisions were decided from the point of view of obtaining a higher correlation. Although the rainfalls were over, 18 July was put into the summer rainy period group. The sixth of October was included in the summer dry season and 20 March was included in the winter dry season, although it had already begun to rain in both cases.

In Fig. 4, Ca^{2+} shows a concentration-discharge pattern common with Stas. 8 and 13. Eight points in the summer dry season after the rainy period, 16 points in the composite autumn and winter season and 10 points in the rainy spring and rainy early summer, all indicated highly significant correlations at each station. These three groups were approximated by three straight lines, A, B and C in the formula $\log C = a \log Q + b$. In these, lines A and C had negative slopes ($a<0$) and B had a positive slope ($a>0$). Arrows in the figures show one of the hypothetic directions of seasonal variation. From these observations, principally of the base flow, successive rains seem to have led to the negative slopes. SEGUCHI *et al.* (1985) reported negative slopes for $Ca^{2+}+Mg^{2+}$ in some storm events. This report suggests that our conclusion is reasonable. WEBB and WALLING (1985), however, reported a negative slope for Mg^{2+} as an annual trend under relatively light precipitation. It is desirable to substantiate our hypothesis with much more observation.

As shown in Fig. 5, NO_3^- took different concentration-discharge patterns from the Ca^{2+} pattern in Fig. 4. In Fig.5, 6 points in the autumn and 10 points in the winter were separated into independent groups considering Figs. 2 and 3. At Sta. 8, 3 groups of points showed a significant correlationship and were approximated by three straight lines A, B and C. Line A indicated the pattern in the summer dry season, but the slope was positive ($a>0$) against the Ca^{2+} pattern. Line B in the winter season had a positive slope ($a>0$) as in the Ca^{2+} pattern, but the length of line was shorter than in Ca^{2+}, because the autumn season did not come on the same line. Line C showed a negative slope as in Ca^{2+} but three points in the rainy early summer left this line. At Sta. 13, only 8 points in the winter season showed a significant positive correlationship approximated by line B.

NO_3^- seems to behave in the same transport mode as Ca^{2+} in the catchments only in the winter through spring. In order to clarify the causes of a positive relationship between annual precipitation and annual mean NO_3^- concentration in a river (KAGAWA *et al.*, 1985), seasonal differences in the mechanism of NO_3^- transport and the different effects of seasonal precipitation on the NO_3^- transport should be further investigated.

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