Research article

Characteristics of Ion Components in River Water with Multivaraite Analysis and Piper Diagram in Agricultural Area

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Abstract The Tokachi and Nemuro areas are large-scale agricultural land, and are located in Eastern Hokkaido. Increases in nitrogen concentrations in the river water caused by the outflow of excess nitrogen from an agricultural land in the Tokachi and Nemuro area have been reported. Here we considered the characteristics of the origin of river water quality with multivariate analysis and piper diagram in the Tokachi and Nemuro areas with different agricultural land use. The main agricultural land uses in the Tokachi area are upland and dairy farming. It is an area mainly of dairy farming in the Nemuro area. The investigation was carried out in late August 2005. We analyzed the following ion parameters: Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, HCO_3^-, CO_3^-, PO_4^{3-}, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} by liquid chromatography. NO_3^- and SO_4^{2-} were higher in the Tokachi area; the values of NO_3^- and SO_4^{2-} were 0.71-31 mg/L and 1.9-39 mg/L in the Tokachi area and 0.44-9.7 mg/L and 2.0-19 mg/L respectively. On the other hand, HCO_3^- and Na^+ were higher in the Nemuro area; 6.4-31 mg/L and 3.3-9.9 mg/L in the Tokachi area and 13- 42 mg/L and 5.8-15 mg/L in the Nemuro area respectively. The plot in piper diagram showed that most of the river water samples in the Tokachi area fall in the field of mixed Ca-Mg-Cl type of water. Some samples are also representing Ca-Cl and Ca-HCO_3 types. The most of the samples in the Nemuro area fall in the field of Ca-HCO_3 types, and some samples also representing Na-Cl types. This result suggests that the outflow of excess nitrogen from the agricultural land affected river water quality in the Tokachi area while the mixing of seawater and geological component affected river water quality in the Nemuro area.

Keywords agricultural area, river water quality, ion components, multivariate analysis, piper diagram

INTRODUCTION

Large-scale agriculture is practised under harsh climatic conditions in Eastern Hokkaido, Japan, and nitrate pollution of river water and ground water in this region has been reported (Tabuchi et al., 1995; Matsumoto and Tou, 2006). Studies on several watersheds have shown that nitrogen concentrations in the river water are strongly correlated with the proportion of upland areas

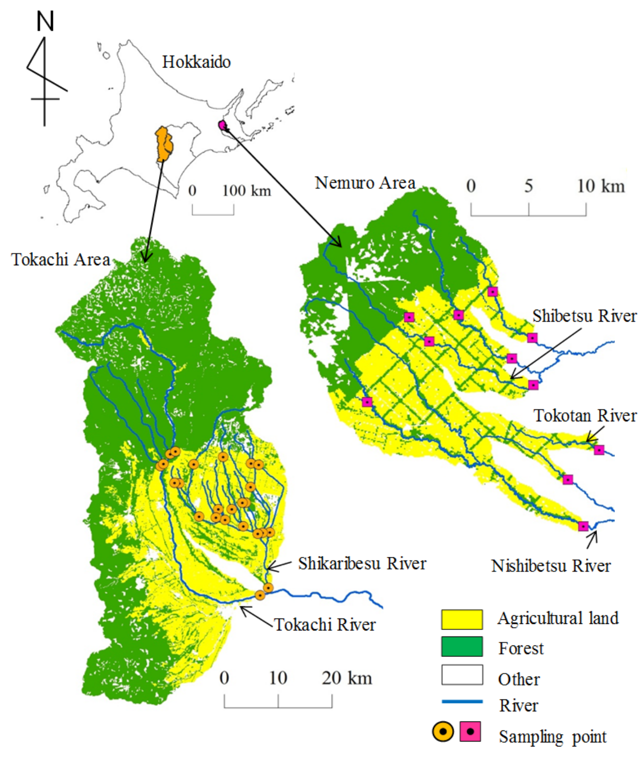
(Tabuchi et al. 1995; Nagumo and Hatano 2000; Woli et al. 2004).

We had previously investigated the long-term river water quality in the Tokachi and Nemuro areas, where the agricultural land use is mutually different (Yamazaki et al., 2013, 2014; Muneoka et al., 2013). It was shown that the nitrate-nitrogen concentration in the river water was higher in the Tokachi area and the electrical conductivity was higher in the Nemuro area, when the proportion of agricultural land was in the same range in each sampling point (Yamazaki et al., 2013). It was inferred that, apart from the nutrients run off from agricultural land, regional differences was the reason for such differences. The percentages of ionic components were also different in the Tokachi and Nemuro area (Yamazaki et al., 2014). It is necessary to elucidate not only the water quality but also the origin of the river water to reduce water pollution in the agricultural area.

In this study, we examined the characteristics of river water quality by multivariate analysis and piper diagram to analyse in detail the differences in ionic components within the river water in the Tokachi and Nemuro areas.

METHODOLOGY

The study sites are outlined in Fig. 1. The Tokachi area, which consists of a total of 24 watersheds in the Tokachi river system and in the Shikaribetsu river system (No. *1* to *24*), is in the north-western part within the jurisdiction of Tokachi General Sub-prefectural Bureau. It is an area of upland and dairy farming. The Nemuro area, which consists of a total of 11 watersheds in the Shibetsu, the Tokotan, and the Nishibetsu river systems (*A* to *K*), is located in the western part within the jurisdiction of Nemuro Sub-prefectural Bureau. It is mainly an area of dairy farming. In both these areas, large-scale farming has been pursued, and there have been no substantial changes in agricultural land use in either area since 1985.



Sampling Point	River name	Bridge name	Area (km^2)	Land use (%) Agricultural land	Forest
Tokachi area					
1	Tokachi	Oojika	632	1	94
2	Penkenai	Pennai	23	0	98
3	Penkenikorbetsu	Penkenikorobetsu	48	2	96
4	Penkenikoro	Minamiiwamatsu	72	2	97
5	Tokachi	Nakajima	1798	21	70
6	Shikaribetsu	Urimaku	217	4	91
7	Sikanosawa	Kikuchi	5	83	13
8	Kamihoronai	Kamihoronai	3	88	12
9	Shikaribetsu	Momiji	256	13	81
10	Minami1sen	Nakashikakann2gou	13	72	17
11	Iketo	Minamisawa	9	95	2
12	Pankebibaushi	Kousui	27	90	7
13	Urimaku	(no bridge)	9	13	66
14	Poronai	(no bridge)	3	90	7
15	Urimaku	Mutsu	49	58	32
16	Penkeutorei	Honmaki	3	88	11
17	Pankeutorei	(no name)	5	93	6
18	Pankeutorei	Komadome	17	65	25
19	Penkechin	Okuyama	26	22	49
20	Ponchin	Kamimaki	13	75	18
21	Penkechin	Isami	63	46	33
22	Pankechin	Sinnei	10	52	32
23	Pankechin	Taneuma	72	72	15
24	Shikaribetu	Kunimi	667	48	45
Nemuro area					
A	Kanjiushi	Yourouushi	11	4	71
B	Keneka	Minori	41	7	81
C	Keneka	Hakuyou	82	32	57
D	Shibetsu	Nagori	54	3	91
E	Shibetsu	Kamisibetu	82	22	72
F	Masu	Masukawa	10	32	64
G	Masu	Kenebetsu	28	49	46
H	Tokotan	Houtoku	12	81	14
I	Nishibetsu	Kousai	19	10	60
J	Nishibetsu	Nishisyunnbetsu	149	54	32
K	Ponomebetsu	Akashi	19	73	21

Fig. 1 Outline of the Tokachi and Nemuro areas

For the years 1981 to 2010, the annual mean air temperature and the yearly precipitation were 5.9 °C and 840.7 mm, respectively, at Komaba in the Tokachi area, and 5.4 °C and 1158.0 mm, respectively, at Nakashibetsu in the vicinity of the Nemuro area. Both areas have a relatively cold climate with less rainfall than other agricultural areas of Japan.

The investigation of the river water quality was conducted at the normal water level at 35 sampling points. The investigations were carried out in late August 2005. We analysed the concentrations of following ions as parameters: Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, HCO_3^-, CO_3^-, PO_4^{3-}, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} by liquid chromatography.

We used the cluster analysis and the piper diagram to classify the trend of ionic components in the river water. A cluster analysis is a group of multivariate techniques. It is often used to analyse water quality characteristics. We used the R package and Ward's method for cluster analysis. A piper diagram is a method for water quality classification by graphical representation. It is used for an observation of ground water and river water quality. A piper diagram shows the characteristics of water by the location of the plot in the key diagram from the proportion of equivalent concentration of cations and anions. In this study, we used the Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, Na^+, K^+, Ca^{2+} and Mg^{2+} for the piper diagram. The results are classified into five types: Cl-SO_4-NO_3 type, Ca-HCO_3 type, Na-HCO_3 type, Na-Cl type, and mixed type.

RESULTS AND DISCUSSION

Ion Concentrations in the Tokachi and Nemuro Areas

Table 1 shows the concentration of ionic components in the Tokachi and Nemuro areas. Ca_2^+ and HCO_3^- were the main ionic components in both areas. However, the trend of ionic components differed between the two areas. The concentrations of NO_3^- and SO_4^{2-} were 0.71–31 mg/L and 1.9–39 mg/L, respectively, in the Tokachi area and 0.44–9.7 mg/L and 2.0–19 mg/L, respectively, in the Nemuro area. The average concentrations of these components were found to be higher in the Tokachi area. On the other hand, concentrations of HCO_3^- and Na^+ were 6.4–31 mg/L and 3.3–9.9 mg/L, respectively, in the Tokachi area and 13.5–42.1 mg/L and 5.8–15 mg/L, respectively, in the Nemuro area. The average concentrations of these components were found to be higher in the Nemuro area.

Cluster Analysis

Cluster analysis was conducted to classify the tendency of ionic components in the river water. Figure 2 shows the results of cluster analysis for each sampling point in the Tokachi area (nos. *1–24*) and the Nemuro area (*A–K*) in a dendrogram. NH_4^+, NO_2^- and PO_4^{2-} were excluded from the cluster analysis because their values were too small. The dendrogram shows four major clusters. The sampling points in the Tokachi area were classified into clusters 1, 3 and 4. The sampling points in the Nemuro area were classified into clusters 1 and 2. The cluster 1 and 2 tended to include the sampling points that had high concentration of cationic components and the proportion of agricultural land use was less than 50%. Meanwhile, the cluster 3 and 4 tended to include the sampling points that had high concentration of anionic components and the proportion of agricultural land use was more than 50%. The river water quality was different between both areas except few sampling points from the cluster analysis. We verified the difference of the river water quality in the Tokachi and Nemuro areas by the piper diagram.

Piper Diagram

Figure 2 (a, b) shows the piper diagram of the ionic components in the two areas. The piper diagram was classified by the cluster 1–4 (a) and the proportion of agricultural land (b). Many sampling points in the Tokachi area belonged to the mixed type. In addition, the cluster 4 belonged to the Na-SO_4-NO_3 type, and it was confirmed that the proportion of (SO_4 + NO_3) and (Ca_2 + Mg) increased due to the agricultural activities in the cluster 4. In the Nemuro area, many sampling points belonged to the mixed type and to the Ca-HCO_3 type. Only *D* in cluster 2 belonged to the Na-Cl type, because of the commingling of the sea water or hot spring water into the ground water. Furthermore, as shown in Fig 2(b), which shows if the proportion of agricultural land use was less than or more than 50%, the sampling points in the Tokachi area, which had high proportion of the agricultural land, were located at upper part of the key diagram. On the other hand, it was not confirmed whether the clear difference of ionic components in the Nemuro area was due to the small or large proportion of agricultural land. From these results, the river water quality was found to be very different in the Tokachi and Nemuro areas. In addition, the ionic components of the river water in the Tokachi area were influenced by agriculture, whereas the ones in the Nemuro area were influenced by other geological features.

Table 1 Ion concentrations in the Tokachi and Nemuro areas

Sampling point	Ion concentration (mg/L) Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	NO_2^-	HCO_3^-	SO_4^{2-}	PO_4^{3-}	Total
Tokachi area												
1	5.5	1.3	0.018	6.9	1.5	3.3	0.71	< 0.05	13.5	9.2	<0.001	41.9
2	3.3	1.4	< 0.01	3.3	0.9	1.6	0.75	< 0.05	9.3	4.0	<0.001	24.6
3	3.8	1.9	< 0.01	3.1	0.8	1.7	0.84	< 0.05	9.6	3.4	<0.001	25.2
4	3.7	1.7	< 0.01	3.2	0.9	1.8	0.89	< 0.05	6.4	3.2	<0.001	21.8
5	5.0	1.6	0.039	6.5	1.6	3.9	2.5	< 0.05	12.9	8.0	<0.001	42.0
6	8.7	1.6	< 0.01	7.6	1.8	6.1	2.1	< 0.05	29.2	7.0	<0.001	64.1
7	5.4	2.8	< 0.01	9.1	2.9	5.2	15.0	< 0.05	13.0	6.8	0.01	60.2
8	5.4	3.7	< 0.01	9.6	3.1	5.5	15.0	< 0.05	15.5	6.5	0.005	64.3
9	7.5	2.3	< 0.01	8.1	2.0	5.1	3.9	< 0.05	17.6	6.7	0.003	53.2
10	9.9	3.6	< 0.01	28.0	8.7	8.0	27.0	0.095	31.1	39.0	0.10	155.5
11	9.1	5.8	< 0.01	18.0	6.0	9.1	20.0	< 0.05	25.9	18.0	0.25	112.2
12	8.5	4.9	< 0.01	17.0	5.3	7.9	19.0	< 0.05	22.4	18.0	0.18	103.2
13	3.7	1.5	< 0.01	5.7	1.2	1.5	1.1	< 0.05	14.3	2.0	0.08	31.1
14	8.2	2.4	< 0.01	20.0	6.5	6.6	30.0	< 0.05	13.4	36.0	0.05	123.2
15	6.6	2.7	< 0.01	13.0	3.7	5.0	12.0	< 0.05	19.5	10.0	0.18	72.7
16	9.4	3.6	< 0.01	21.0	7.3	12.0	22.0	0.099	17.7	35.0	0.01	128.1
17	8.7	3.8	< 0.01	24.0	7.0	9.7	31.0	0.079	21.2	30.0	0.12	135.6
18	7.0	4.1	< 0.01	15.0	4.8	6.7	13.0	< 0.05	16.4	23.0	0.07	90.1
19	3.8	1.7	0.003	6.5	1.2	1.3	0.66	< 0.05	15.7	1.9	0.06	32.8
20	5.8	2.1	< 0.01	13.0	3.0	4.1	12.0	< 0.05	17.4	10.0	0.03	67.4
21	5.1	2.2	< 0.01	11.0	3.0	3.5	6.6	< 0.05	18.9	8.1	0.02	58.4
22	6.3	3.6	< 0.01	22.0	4.1	5.8	15.0	< 0.05	31.1	11.0	0.07	99.0
23	8.6	4.1	< 0.01	27.0	8.7	7.0	16.0	< 0.05	30.8	36.0	0.10	138.3
24	8.4	3.6	< 0.01	16.0	4.6	6.8	11.0	< 0.05	22.1	17.0	0.02	89.5
Average	6.6	2.8	0.020	13.1	3.8	5.4	11.6	0.091	18.5	14.6	0.08	76.4
Nemuro area												
A	5.8	0.6	< 0.01	4.3	1.3	2.3	0.44	< 0.05	13.5	2.0	0.05	30.3
B	7.1	0.9	< 0.01	5.4	1.3	3.4	1.0	< 0.05	15.3	2.5	0.11	37.0
C	8.9	1.7	< 0.01	11.0	2.5	5.6	4.2	< 0.05	23.8	3.6	0.09	61.4
D	13.0	0.9	< 0.01	6.6	1.3	9.6	< 0.05	< 0.05	12.6	11.0	0.07	55.1
E	13.0	1.2	< 0.01	9.3	2.1	8.6	1.8	< 0.05	17.9	8.8	0.04	62.7
F	8.6	1.3	< 0.01	6.1	1.9	3.7	2.2	< 0.05	17.5	2.5	0.11	43.9
G	9.9	2.2	< 0.01	13.0	3.5	6.4	5.3	< 0.05	28.2	2.4	0.08	71.0
H	12.0	2.4	< 0.01	23.0	6.0	11.0	9.7	< 0.05	42.1	5.4	0.03	111.6
I	15.0	1.6	< 0.01	9.9	3.1	5.7	0.58	< 0.05	20.5	19.0	0.22	75.6
J	13.0	1.9	< 0.01	13.0	3.3	6.6	3.7	< 0.05	24.7	13.0	0.19	79.4
K	12.0	3.6	< 0.01	20.0	4.7	11.0	8.9	< 0.05	34.0	6.3	0.08	100.6
Average	10.8	1.7	< 0.01	11.1	2.8	6.7	3.8	< 0.05	22.7	7.0	0.10	66.2

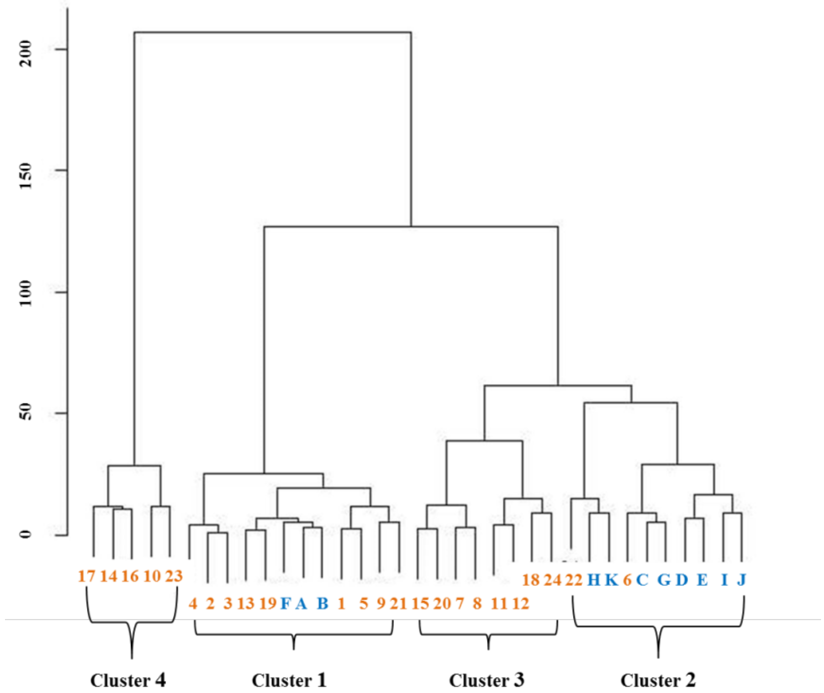


Fig. 2 Dendrogram from cluster analysis

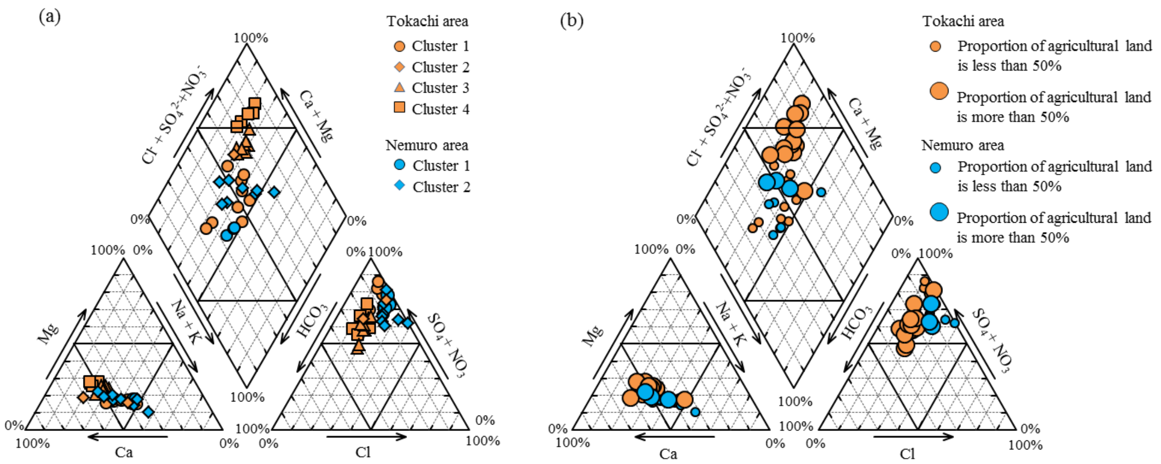


Fig. 3 Piper diagram of the ionic components in the Tokachi and Nemuro areas

Correlation Matrix of Ion Concentrations

Table 2 shows the correlation matrix of ion concentrations within the Tokachi and Nemuro areas. NO_3^- and SO_4^{2-} showed a strong correlation in the Tokachi area. It was recognized that the NO_3^- and SO_4^{2-} in the river water was derived from chemical fertilizer because an ammonium sulfate was mainly used for a nitrogen fertilizer in the Tokachi area. In the Nemuro area, Na^+ had a strong correlation with SO_4^{2-}. There is a hot spring in the upper part of the Nemuro area. The spring quality is sodium-sulfate spring. It was inferred that the proportion of Na^+ in the river water was increased due to the hot spring water mixed into the ground water. Especially, *D*, *E*, and *I* in the Nemuro area which was classified into cluster 2 (Fig. 2) and belonged to near Na-Cl type in the piper diagram (Fig. 3), showed high proportion of (SO_4+Na). Ca^{2+} and Mg^{2+} had a strong correlation with NO_3^- within the two areas, it was considered that these ionic components eluted easily due to use of fertilizer and soil acidification in the agricultural area.

Table 2 Correlation matrix of ion concentrations in the Tokachi and Nemuro areas

	Tokachi area								Nemuro area							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-
Na^+	1.00								1.00							
K^+	0.68	1.00							0.37	1.00						
Ca^{2+}	0.81	0.72	1.00						0.43	0.89	1.00					
Mg^{2+}	0.84	0.75	0.96	1.00					0.43	0.86	0.98	1.00				
Cl^-	0.91	0.77	0.80	0.85	1.00				0.69	0.64	0.76	0.67	1.00			
SO_4^{2-}	0.80	0.57	0.89	0.95	0.79	1.00			0.86	0.04	0.07	0.11	0.29	1.00		
HCO_3^-	0.73	0.57	0.74	0.64	0.58	0.48	1.00		0.29	0.86	0.98	0.98	0.63	-0.06	1.00	
NO_3^-	0.74	0.70	0.87	0.89	0.82	0.84	0.45	1.00	0.16	0.89	0.95	0.92	0.63	-0.23	0.97	1.00

CONCLUSION

Based on our results, the proportion of (SO_4 + NO_3) and (Ca + Mg) increased due to chemical fertilizer in the Tokachi area. In contrast, many sampling points in the Nemuro area belonged to the Ca-HCO_3 type and to the mixed type, and it was not confirmed whether the difference in ionic components was due to a small or large proportion of agricultural land. Our results revealed that the river water quality in the Tokachi area was affected by the agricultural activity, whereas the river water quality in the Nemuro area reflected the impact not only of agricultural activity but also of other geological features and regional nature.

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