



Title	Spatial trends of nitrate pollution and groundwater chemistry in Shimabara, Nagasaki, Japan
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3 1 **Spatial trends of nitrate pollution and groundwater chemistry in Shimabara,**
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44 16 **Abstract**
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47 17 Groundwater nitrate contamination in agricultural areas is a common problem in many parts of
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50 18 the world. The important agricultural district Shimabara in Nagasaki, Japan, is also
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53 19 experiencing this problem. The general source of drinking water here is groundwater and
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56 20 consequently the nitrate contamination is a big problem. For this reason, a groundwater
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21 investigation was performed and water samples were collected at 40 locations including
22 residential areas, public water supply wells, springs, and rivers from August 2011 to November
23 2013. Results showed that nitrate nitrogen ($\text{NO}_3\text{-N}$) concentration exceeds the Japanese
24 drinking water quality standards (10 mg L^{-1}) at 15 locations. Maximum $\text{NO}_3\text{-N}$ concentration
25 was 26.6 mg L^{-1} . Nitrate (NO_3^-) is strongly correlated with Cl^- ($r = 0.96$), K^+ ($r = 0.68$), SO_4^{2-}
26 ($r = 0.66$), and Ca^{2+} ($r = 0.59$), respectively. The high correlations with Cl^- and K^+ are related to
27 livestock waste. Corresponding correlation with SO_4^{2-} is related to chemical fertilizers and Ca^{2+}
28 to calcareous material to neutralize acidic soil. Both the first and second components in
29 principal component analysis reflect ion dissolution from aquifer matrix during groundwater
30 flow along the mountain side towards the lower reaches of the alluvial fan. Using hierarchical
31 cluster analysis, chemical characteristics of groundwater were classified into four clusters. One
32 cluster was related to nitrate contaminated groundwater and the other clusters reflected the
33 origin of the major ions in the groundwater.

35 **Keywords**

36 Groundwater, Water chemistry, Nitrate pollution, Principal component analysis, Hierarchical
37 cluster analysis

39 **Introduction**

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40 Nitrate contamination of groundwater from agriculture is a common problem in many
41 countries (e.g., Robins 2002; Kaown et al. 2009; Hansen et al. 2012; Nemčić-Jurec et al. 2013;
42 Esmaeli et al. 2014; Rina et al. 2014). Nitrate polluted drinking water may cause health
43 problems such as methemoglobinemia for infants and cancer for adults. World Health
44 Organization (WHO 2011) maximum recommended nitrate ion concentration (NO_3^-) in drinking
45 water is 50 mg L^{-1} . Common pollution sources for nitrate are chemical fertilizers, manure, and
46 domestic wastewater. In Japan nitrate pollution in groundwater is often related to intensive
47 agriculture. The northern part of Shimabara City, Nagasaki Prefecture, has during recent years
48 experienced problems with elevated nitrate concentrations in public water supply wells. In
49 2005 a committee was established to discuss ways to reduce nitrate pollution for the Shimabara
50 Peninsula (Committee on nitrate reduction in Shimabara Peninsula 2006). The committee
51 recommended changes in agricultural fertilization practices and livestock waste control in the
52 affected regions. However, nitrate nitrogen concentration ($\text{NO}_3\text{-N}$) of drinking water is still
53 exceeding recommended maximum values in 23% of all public water supply wells in
54 Shimabara City (Committee on nitrate reduction in Shimabara Peninsula 2011). The Japanese
55 maximum recommended nitrate nitrogen concentration in water supply is 10 mg L^{-1} . In order to
56 better understand the sources and transport patterns of groundwater pollutants we studied the
57 spatial distribution of nitrate pollution together with major chemical elements. For this purpose
58 we collected and analyzed water samples at 40 locations with different area use from August
59 2011 to November 2013. At specific locations, relationships between precipitation,

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60 groundwater levels, and nitrate concentrations were assessed. Principal component analysis
61 (PCA) and hierarchical cluster analysis (HCA) were used to decipher factors controlling water
62 quality and spatial characteristic of water chemistry.

64 **Materials and Methods**

65 Figure 1 shows the study area and sampling locations. Shimabara City is located in
66 the northeast part of Shimabara Peninsula, Nagasaki, Japan. The area of Shimabara City is 82.8
67 km² occupying about 18% of Shimabara Peninsula. Shimabara City lies on the alluvial fan that
68 spreads on the gentle slopes of Mt. Hugendake in the center of Shimabara Peninsula. Four
69 geological formations represent the Paleogene period. These are, in ascending order, Kazusa,
70 Kitaarima, Tatsuishi (pre-Unzen volcanic rocks), and Unzen volcanic rocks. Kazusa and
71 Kitaarima formations are a part of Kuchinotsu formation, which was shaped in Early
72 Pleistocene. Kazusa formation is composed of deposits including mainly silt, sand, mud, and
73 tuff breccia and Kitaarima formation is composed of marine deposits including mainly sand and
74 sandy silt. Tatsuishi covered Kuchinotu formation, is covering large areas and composed by
75 olivine basalt and two-pyroxene andesite. This formation constitutes the foot of the mountain.
76 Unzen volcanic rock is mainly composed by hornblende andesite dacite (Murakami 1975;
77 Sugimoto 2006).

78 Figure 2 shows the altitude and land use of Shimabara City. Generally, forest is
79 covering high altitude areas while livestock farms are distributed along mid-slopes of the hills.

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80 Urbanized areas are located at lower altitudes. Agricultural areas are concentrated to the
81 northern parts of Shimabara City. Cultivated areas represented 18.8 km² and 23% of Shimabara
82 City in 2010 (Ministry of Agriculture, Forestry and Fisheries, Statistics Bureau 2012). Chinese
83 cabbage, radish, and carrots are major cultivated crops. Double-cropping is conducted by
84 cultivating crops such as potatoes, tomatoes, and onion all year around. Livestock represented
85 4200 cattle, 30000 pigs, and 937700 chicken in 2010 (Ministry of Agriculture, Forestry and
86 Fisheries, Statistics Bureau 2012). The stock of chicken in Shimabara, e.g., represented 70% of
87 the poultry in Nagasaki Prefecture.

88 The mean annual precipitation during the observation period was 2541 mm. The
89 highest monthly precipitation was 844.5 mm in July and the lowest monthly precipitation was
90 27.5 mm in January, 2012 (Japan Meteorological Agency 2014). The average annual
91 temperature is about 17°C. The highest monthly temperature was 28.3°C in August and the
92 lowest monthly average temperature was 6.3°C in February, 2012 (Japan Meteorological
93 Agency 2014).

94 Sampling locations are shown in Fig. 1. The “RW” represents residential wells, “W”
95 public water supply wells, “O” observation well, “S” springs, and “R” rivers, respectively. The
96 samples for RW-8, 9, 13 and O-1, 2 were collected using a bailer sampler. Other samples were
97 collected from the water tap at locations where wells were not accessible. These water samples
98 were collected after flushing to remove old water in the pipe. For all water sampling
99 polyethylene bottles were used and stored in the refrigerator. Bottles were rinsed thoroughly

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100 with sample water before collecting samples. Main cation and anions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- ,
101 NO_3^- , and SO_4^{2-}) were analyzed by ion chromatography of suppressor type (Metrohm 861
102 Advanced Compact IC). HCO_3^- was determined by acid-base titration. pH, electrical
103 conductivity (EC), and oxidation-reduction potential (ORP) were measured by a handheld
104 electrode (HORIBA D-52). For this instrument, pH and EC were measured by glass electrode
105 method and dipole electrode method, respectively. The ORP was measured by glass composite
106 electrode including Pt and Ag/AgCl electrodes. The inside of the glass electrode for pH and
107 ORP was filled with 3.33 mol L^{-1} KCl. Dissolved oxygen (DO) was measured by
108 luminescence-based sensor HQd portable meter (HACH HQ30d). Principal component analysis
109 (PCA) and hierarchical cluster analysis (HCA) were used in combination to analyze patterns of
110 chemical elements in the groundwater (e.g., Yidana et al. 2008; Yakubo et al. 2009; Li et al.
111 2013; Omonona et al. 2014).

113 **Results and Discussion**

115 **Water chemistry**

116 Table 1 shows mean of major ion concentrations, $\text{NO}_3\text{-N}$, DO, ORP, EC, pH, and well
117 type. DO represents dissolved oxygen concentration in the water that ranged from 6.5 to 9.8 mg
118 L^{-1} with a mean of 9.1 mg L^{-1} . Standard deviation of DO ranged from 0.2 to 1.8 mg L^{-1} with a
119 mean of 1.0 mg L^{-1} . The DO for all sampling sites were above 2 mg L^{-1} which is suitable for

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3 120 aerobic bacteria. The ORP represented redox status ranging from 172.5 to 282.0 mV with a
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6 121 mean of 216.0 mV. Standard deviation of ORP ranged from 12.0 to 91.4 mV with a mean of
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9 122 61.2 mV. The ORP was positive, indicating that all collected water samples are in oxidation
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11 123 state. The EC depending on ion quantity ranged from 7.7 to 49.7 mS m⁻¹ with a mean of 28.8
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14 124 mS m⁻¹. Standard deviation of EC ranged 1.2 to 14.6 mS m⁻¹ with a mean of 6.5 mS m⁻¹. EC had
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17 125 high positive correlation with total ion concentration (mmol_c L⁻¹) (*r* = 0.95). pH ranged from
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20 126 6.4 to 7.8 with a mean of 7.0. Standard deviation of pH ranged from 0.0 to 0.6 with an average
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23 127 of 0.3. pH varied from slightly acidic to slightly alkaline.

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25 128 A trilinear diagram for all 277 water samples is shown in Fig. 3. All samples except
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28 129 RW-b were classified into Ca-HCO₃ (area I) or Ca-(SO₄+NO₃) (area III). Samples such as
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31 130 W7-9 and S-1, collected from a forest area, were classified into Ca-HCO₃ type. Samples from
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34 131 W-14~20, S-2, 3 and RW-1~3, collected from suburban and urban areas, were also classified
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37 132 into Ca-HCO₃. The Ca-HCO₃ type is the most common for shallow groundwater in Japan.
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40 133 Samples from RW-7~9, 11, 13 and 14, O-1, 2, R-2 and W-1~5 were collected from agricultural
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43 134 areas and here NO₃-N concentration exceeded Japanese recommended drinking water quality
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46 135 standard (10 mg L⁻¹) for most of these locations. These samples were classified into
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49 136 Ca-(SO₄+NO₃). According to the above results, the original groundwater is classified into
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52 137 Ca-HCO₃ while nitrate polluted groundwater is classified into Ca-(SO₄+NO₃).

53 138 Figure 4 shows stiff diagrams for the 40 sampling locations. At sampling locations
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56 139 with altitude from 300 to 400 m, the ion concentration was very low and the smaller the area of
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140 the polygonal shape because of the location close to mountainside recharge areas. As altitude
141 decreases, ion concentrations tend to increase. This indicates that ion dissolution from the
142 matrix occurs during groundwater flow. Ca^{2+} was the most common cation for most locations.
143 A few locations had higher contents of $\text{Na}^{+}+\text{K}^{+}$ or Mg^{2+} . Probably, cation exchange or other
144 kinds of mineral dissolution occur in these locations.

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146 **Spatial and temporal trends of $\text{NO}_3\text{-N}$ concentration**

147 Mean and standard deviation of $\text{NO}_3\text{-N}$ concentrations are shown in Fig. 5. $\text{NO}_3\text{-N}$
148 concentration ranged from 0.1 to 25.8 mg L^{-1} with an average of 8.8 mg L^{-1} . Maximum standard
149 deviation was 3.52 mg L^{-1} at O-2. Large standard deviations were found at RW-8, 9, 13, O-1, 2,
150 and W-3. RW-13 and W-3 are located halfway up on the mountainside. Other locations
151 represent discharge areas close the sea shore. The $\text{NO}_3\text{-N}$ concentration at 15 locations
152 exceeded Japanese drinking water quality standards (10 mg L^{-1} ; maximum at RW-11 with 25.8
153 mg L^{-1}). However, $\text{NO}_3\text{-N}$ concentration at 21 locations exceeded the threshold 3 mg L^{-1}
154 considered as contaminated by human activity (Eckhardt and Stackelberg 1995).

155 The variation in groundwater chemistry is mainly due to groundwater recharge,
156 pumping, and geochemical reactions. Rajmohan et al. (2005) reported that an increasing
157 groundwater level affected by rainfall means a nitrate concentration increase and decrease with
158 receding groundwater level. A comparison between groundwater table elevation, $\text{NO}_3\text{-N}$
159 concentration, and daily precipitation for RW-8, RW-9, and RW-13 is shown in Fig. 6. The

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160 figure shows that groundwater table increase resulted in NO₃-N concentration decrease at RW-8
161 on June 19, 2012. The NO₃-N concentration decreased due to dilution from groundwater
162 recharge and large amounts of precipitation (275.5 mm) from June 15 to 16, 2012. A significant
163 groundwater table increase was observed at RW-8 in August 5, 2013, which was a result of 35.5
164 mm precipitation the day before. In this case, NO₃-N concentration increased. This was due to
165 the flushing of nitrate by recharging groundwater. The groundwater table elevation in June 19,
166 2012, was lower than that in August 5, 2013. Probably the peak concentration in the
167 groundwater was not sampled for this event. On June 19, 2012, and August 5, 2013, the
168 groundwater table increased and the NO₃-N concentration decreased simultaneously at RW-9.
169 This was due to dilution by groundwater as well as for the case of RW-8. A rise in the
170 groundwater table at RW-13 was observed in August 22, 2012. This was a result of 100.5 mm
171 precipitation from August 8 to 14, 2012. The NO₃-N concentration decreased by dilution
172 related to the precipitation. According to the above results, recharging precipitation is the most
173 important factor controlling groundwater table changes and NO₃-N concentration in this area.

174 The spatial distribution of NO₃-N concentration is shown in Fig. 8. High NO₃-N
175 concentrations (above 10 mg L⁻¹) are mainly observed in the northern parts of Shimabara City.
176 When comparing to Fig. 2, high NO₃-N concentrations coincide with the spatial distribution of
177 agricultural areas. Sampling locations in forested, urban, and suburban areas do not show high
178 NO₃-N concentration. This reveals that agricultural activities are related to nitrate pollution in
179 the study area. Using statistical data on agriculture and forestry (Ministry of Agriculture,

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180 Forestry and Fisheries, Statistics Bureau, 2007), we analyzed nitrate load potential for each
181 village in 2005 (Nakagawa et al. unpublished). The area cover of each village is shown in Fig.
182 1. Nitrate load potential was estimated from the amount of livestock waste and applied
183 chemical fertilizer according to these statistics. High potential of nitrate load from livestock
184 waste was estimated for villages at 300-400 m altitude. The location of these villages are close
185 to S-1 and W-6~10. Estimated maximum nitrate load potential was 305041 kg N/year. The
186 nitrate load potential from livestock waste (1442043 kg N/year) was much higher than that
187 from chemical fertilizers (258520 kg N/year), at the city total. Therefore, livestock waste can
188 be assumed to be a main source of nitrate pollution in the area. This is confirmed by observed
189 high NO₃-N concentration downstream potential high load nitrate villages.

191 **Correlation of major ions**

192 Correlation coefficients between major ions for all 277 samples are shown in Table 2.
193 NO₃⁻ was positively correlated with Cl⁻ (correlation coefficient $r=0.96$), K⁺ ($r=0.68$), SO₄²⁻
194 ($r=0.66$), and Ca²⁺ ($r=0.59$). Livestock waste includes Cl⁻ and essential nutrients such as N, P,
195 and K. Jalali (2011) reported that high NO₃⁻ and Cl⁻ contamination in groundwater indicates
196 effects applied manure and livestock waste. Thus, positive correlation with Cl⁻ and K⁺ may
197 reflect application of manure and leakage of livestock wastes from composting facilities.

198 The positive correlation between NO₃⁻ and SO₄²⁻ may reflect application of chemical
199 fertilizers such as (NH₄)₂SO₄ (Babiker et al. 2004). Babiker et al (2004) reported that high

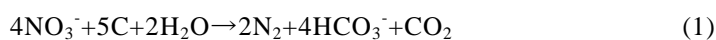
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200 positive correlation was found between NO_3^- , Mg^{2+} , and Ca^{2+} , which indicates their origin from
201 chemical fertilizers such as CaCO_3 and MgCO_3 . In this study, the positive correlation between
202 NO_3^- and Ca^{2+} indicates the use CaCO_3 in the area.

203 In Japan, calcareous material is often used for neutralization of pH against soil
204 acidification. The positive correlation between NO_3^- and Ca^{2+} may indicate application of
205 calcareous material in connection to crop production.

206 The correlation between NO_3^- and Mg^{2+} was 0.32 only. However, the correlation
207 became 0.80 at the NO_3^- concentration above 13 mg L^{-1} . The relationship is related to use of
208 MgCO_3 as a chemical fertilizer. The threshold of NO_3^- concentration when considering
209 contamination due to human activity is about 13 mg L^{-1} (Eckhardt and Stackelberg 1995). For
210 conditions of low NO_3^- concentration (below 13 mg L^{-1}), dissolution of minerals which are
211 included in biotite, amphibole, plagioclase, and olivine may contribute to the increasing K^+ ,
212 Ca^{2+} , and Mg^{2+} . These components are highly correlated with each other.

213 Negative correlation between NO_3^- and HCO_3^- ($r=-0.53$) is one of the factors that is
214 indicating the occurrence of denitrification (e.g., Mohamed et al. 2003). Denitrification occurs
215 in the presence of organic carbon and in a reducing environment with little oxygen. The
216 denitrification process can be expressed as:



218 This means that HCO_3^- increases with decreasing NO_3^- . However, the observations did not
219 indicate this relationship. Moreover, the DO and ORP data (Table 1) suggests that the

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220 groundwater in this area is not under redox condition. Thus, it may be concluded that
221 denitrification is not an important process for the investigated area.

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223 **Principal component analysis and hierarchical cluster analysis**

224 The input of 8 variables (major ions Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , Na^+ , K^+ , Mg^{2+} , and Ca^{2+})
225 was used to perform a combined analysis using principal components analysis (PCA) and
226 hierarchical cluster analysis (HCA). The input data was standardized before analysis. The
227 correlation between the variables were used to calculate eigenvalue, factor loading, and
228 principal component scores. HCA was based on Ward's method with squared Euclidean
229 distance (e.g., Yakubo et al. 2009; Omonona et al. 2014). The results of the PCA are shown in
230 Table 3. The total number of components (common factors) in the PCA was determined based
231 on the Kaiser criterion (Cloutier et al. 2008). In this criterion, only the components with
232 eigenvalues greater than 1 are retained. Two principal components were extracted, accounting
233 for most of total variance (87%). Hereafter, the first principal component is called Factor 1 and
234 the second Factor 2, respectively.

235 Factor 1 has high positive loading for Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+}
236 (0.73~0.92), and represents 60% of total variance. Figure 8 shows the relationship between the
237 two principal components (Factor 1 and 2) and the ion concentration. Factor 1 represents
238 increasing NO_3^- concentration due to livestock waste, application of manure, and chemical
239 fertilizer (Fig. 8a~c). There are low concentration horizontal distribution of NO_3^- and Cl^-

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240 associated with Factor 1. However, SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations related to
241 this distribution are plotted to show the increasing general trend. Thus, the increase of ion
242 concentration associated with Factor 1 except for NO_3^- and Cl^- is also related to contribution
243 from the same origin and ion dissolution during groundwater flow (Fig. 8a~c). Factor 2 has
244 negative loading for Cl^- and NO_3^- (-0.50 and -0.60, respectively) and positive loading for
245 HCO_3^- , Na^+ , and Mg^{2+} (0.53~0.97), representing 27% of the total variance. Although Factor 2
246 has negative correlation with NO_3^- and Cl^- , almost no relationship can be seen in Fig. 8d.
247 Increase in concentration for HCO_3^- , Na^+ , and Mg^{2+} associated with Factor 2 (Fig. 8e) is due to
248 ion dissolution during groundwater flow. Both Factor 1 and 2 represent ion dissolution from
249 aquifer matrix during groundwater flow from the mountain side to downstream. Additionally,
250 Factor 1 also explains the effect of nitrate pollution.

251 For the HCA, all 277 water samples were classified into four clusters. Hereafter,
252 these clusters are called Group 1 to 4. Averaged major ion concentration for each group is
253 shown in Table 4. Group 1, 2, and 3 show low NO_3^- concentration below 13 mg L^{-1} . When
254 comparing ion concentrations for Group 1-3, all ions except for Cl^- and NO_3^- concentration
255 were in order Group 2>1>3. The difference for all ion concentrations belonging to each group
256 except for Cl^- and NO_3^- is clear and shows the pristine water chemistry. Group 4 shows high
257 NO_3^- concentration due to nitrate pollution ($\text{NO}_3\text{-N}$ exceeding 10 mg L^{-1}). Therefore, the
258 groups can be divided into two main water types. Group 1, 2, and 3 thus represent
259 not-contaminated water and Group 4 nitrate polluted water.

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260 When we look at group association over time and depending on spatial location,
261 water samples keep the same cluster over the entire study period except for water samples at
262 W-17. These can be classified either into Group 1 or 3 depending on the sampling time.
263 However, W-17 does not show any seasonal changes. Figure 9 shows the spatial distribution of
264 the groups based on the latest data in the study period. Group 1 and 2 cover the urban and
265 suburban areas. Group 3 covers mainly forested areas at higher altitude. Finally, Group 4
266 covers agricultural areas.

267 Figure 10 shows all samples in a trilinear diagram divided into the groups. As seen
268 from the figure Group 1 and 2 can be classified into Ca-HCO_3 (area I) and Group 4 into
269 $\text{Ca-(SO}_4\text{+NO}_3\text{)}$ (area III). Group 3 is classified into both Ca-HCO_3 (area I) and
270 $\text{Ca-(SO}_4\text{+NO}_3\text{)}$ (area III). Although water samples such as W-12 and W-13 are classified into
271 Group 3, this water is probably changing chemical characteristics over time so as to transit
272 from pristine to polluted water. The sampling locations W-12 and W-13 were close to polluted
273 samples classified into Group 4 (see Fig. 9)

274 Figure 11 shows a scatter plot of all water samples against principal components
275 (Factor 1 and 2) and divided into groups. If the factor score is greater than 0, the processes
276 represented by the component have significant influences on the water chemistry at the location.
277 On the other hand, if the factor score is less than 0, the processes represented by the factor
278 probably do not have any significant influence on the water chemistry at that location (e.g.,
279 Yakubo et al. 2009). According to the figure, Group 4 is influenced by Factor 1 only. Most

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280 samples of Group 1 are influenced by Factor 2 (dissolution of ions). Some samples of Group 1
281 and all samples of Group 2 are influenced by common effects (dissolution of ions), Factor 1
282 (dissolution of ions and nitrate pollution), and Factor 2 (dissolution of ions). These two factors
283 do not have significant influence on the samples of Group 3. Thus, all groups except Group 3
284 must be controlled by ion dissolution and/or nitrate pollution.

286 **Conclusion**

287 To understand present status of nitrate contamination and determine the factors
288 controlling the water chemistry in Shimabara, water samples were collected and analyzed
289 regarding major ion component in private and public water supply wells, springs, and rivers.
290 The main findings were as follows: (1) According to the average $\text{NO}_3\text{-N}$ concentration 15 out
291 of 40 locations (38% of all sampling locations) exceeded 10 mg L^{-1} (Japanese drinking water
292 quality standard). The concentration at 21 locations (53% of all sampling locations) exceeded
293 the threshold value of 3 mg L^{-1} and can be considered as contaminated due to human activity.
294 The contaminated sampling positions are all located downstream of potential high nitrate load
295 areas, (2) Water samples were classified into Ca-HCO_3 or $\text{Ca-(SO}_4\text{+NO}_3)$ type, and water
296 quality changed from Ca-HCO_3 to $\text{Ca-(SO}_4\text{+NO}_3)$ type due to nitrate pollution, (3) The positive
297 correlation between NO_3^- and ions such as Cl^- , K^+ , and SO_4^{2-} indicate that nitrate pollution in
298 groundwater is caused by livestock waste and over-application of manure and chemical
299 fertilizers, (4) At some locations, the water table in water supply wells was clearly influenced

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300 by infiltrating precipitation. Thus, nitrate concentration was diluted by the recharge from
301 infiltration, (5) The PCA indicated that water chemistry is controlled by two main factors. Both
302 factors are related to ion dissolution during groundwater flow. One of these factors is also
303 influenced by nitrate pollution, and (6) According to the HCA, water samples can be classified
304 into four spatial groups. The water chemistry in one of these is controlled by nitrate pollution
305 and ion dissolution, whereas two groups are affected by only ion dissolution. The factors
306 obtained from PCA have no significant influence on the final group.

307 To conclude, our study shows the characteristics of groundwater chemistry in
308 Shimabara is divided into four clusters. Especially, the nitrate polluted cluster is clearly
309 different from the other clusters. The nitrate polluted areas are confined to the northern parts of
310 Shimabara City. Therefore, the contaminant sources must be located upstream of this area.
311 Countermeasures should be performed to improve the water quality. This can be done by more
312 detailed groundwater flow and contaminant transport analyses. Results from this paper can be
313 used to design such a groundwater flow and contaminant transport analysis.

314

315 **Acknowledgements**

316 This work was supported by JSPS KAKENHI Grant Number 24360194.

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382 **Figure Captions**

- 383 **Fig. 1** Location of the study area and sampling points
- 384 **Fig. 2** Land use map of the study area; (a) Altitude, and (b) Land use
- 385 **Fig. 3** Trilinear diagram for 277 samples in the study area
- 386 **Fig. 4** Distribution of stiff diagrams for 40 sampling points
- 387 **Fig. 5** Mean values and standard deviation of NO₃-N for 40 sampling points
- 388 **Fig. 6** NO₃-N concentration and water table elevation at RW-8, RW-9 and RW-13 and daily
389 precipitation during the study period
- 390 **Fig. 7** Distribution of NO₃-N concentration
- 391 **Fig. 8** Relationship between two principal components and ion contents; (a) Factor 1 vs.
392 SO₄²⁻, Cl⁻, and NO₃⁻, (b) Factor 1 vs. Na⁺ and K⁺, (c) Factor 1 vs. Mg²⁺ and Ca²⁺, (d)
393 Factor 2 vs. Cl⁻ and NO₃⁻, and (e) Factor 2 vs. HCO₃⁻, Na⁺ and Mg²⁺
- 394 **Fig. 9** Distribution of respective clusters
- 395 **Fig. 10** Trilinear diagram of 277 samples divided into clusters
- 396 **Fig. 11** Scatter plot for two principal components and respective clusters
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398 **Table captions**

399 **Table 1** Mean values of anions, cations, NO₃-N, DO, ORP, EC, pH, and well type

400 **Table 2** Correlation between eight ion contents

401 **Table 3** Results of principal component analysis

402 **Table 4** Mean concentrations of respective clusters

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Table 1 Mean values of anions, cations, NO₃-N, DO, ORP, EC, pH, and well type

	Number of samples	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	HCO ₃ ⁻ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Ca ²⁺ (mg L ⁻¹)	NO ₃ -N (mg L ⁻¹)	DO (mg L ⁻¹)	ORP (mV)	EC (mS m ⁻¹)	pH	Well type
RW-1	1	16.4	25.9	15.2	118.5	30.9	4.8	4.4	30.3	5.9	N.M.	N.M.	38.0	6.8	S
RW-2	1	6.0	8.1	8.3	138.4	10.7	7.1	12.4	22.3	1.8	N.M.	N.M.	33.0	6.5	D
RW-3	1	9.3	0.5	16.7	111.9	22.3	4.7	7.6	21.7	0.1	N.M.	N.M.	30.0	7.3	S
RW-7	8	23.9	104.5	37.0	24.6	16.3	10.5	10.8	34.6	23.6	7.9	195.5	48.7	6.9	D
RW-8	11	18.2	67.0	40.0	37.4	12.7	12.8	6.9	35.7	15.1	6.5	242.3	37.3	6.7	S
RW-9	10	16.6	68.9	23.9	29.4	13.2	8.2	9.6	23.9	15.6	8.5	228.9	42.9	6.6	S
RW-11	2	18.9	114.4	9.8	23.2	13.0	13.2	8.7	22.3	25.8	N.M.	N.M.	33.0	6.5	D
RW-12	1	10.8	20.0	5.5	27.8	6.8	2.9	3.8	12.7	4.5	N.M.	N.M.	9.9	6.6	D
RW-13	11	23.2	97.2	57.3	12.1	11.3	8.9	11.4	42.1	22.0	9.3	211.7	49.7	6.5	S
RW-14	2	18.3	62.5	38.1	37.9	21.7	5.5	10.8	23.4	14.1	8.8	172.5	32.1	7.3	D
RW-a	8	24.7	99.1	22.5	26.7	16.7	8.2	11.9	29.0	22.4	8.9	211.1	48.0	7.1	
RW-b	1	10.3	21.4	32.2	64.8	23.3	10.3	4.8	14.0	4.8	9.5	212.0	30.7	7.2	
O-1	6	24.2	81.4	33.6	39.7	16.4	9.1	11.9	36.1	18.4	7.4	188.0	46.1	7.1	-
O-2	6	23.4	79.9	31.3	42.4	17.0	8.5	11.7	35.1	18.1	7.9	174.5	47.0	7.2	-
R-1	1	7.5	26.2	15.6	32.6	5.3	7.2	4.0	19.5	5.9	N.M.	N.M.	21.0	6.7	-
R-2	1	19.1	74.8	36.3	47.0	15.5	9.4	9.8	31.9	16.9	9.7	272.0	45.0	7.8	-
S-1	5	3.3	1.1	1.8	37.6	6.3	3.4	1.7	6.1	0.2	9.3	26.8	12.9	7.0	D
S-2	1	5.4	11.7	6.3	83.0	8.5	4.9	7.6	16.1	2.6	9.0	282.0	23.6	6.4	-
S-3	1	5.7	11.5	6.1	77.2	8.6	4.8	6.8	15.2	2.6	9.0	233.0	20.5	6.4	-
S-4	1	13.0	11.6	9.9	128.3	11.5	6.6	15.4	27.6	2.6	N.M.	N.M.	N.M.	N.M.	-
W-1	10	15.8	55.6	25.4	44.2	12.3	5.8	10.3	22.8	12.6	9.5	221.3	32.2	7.4	D

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6	W-2	10	14.4	36.4	25.8	34.8	11.5	4.8	8.1	18.6	8.2	9.2	208.4	25.9	7.3	D
7	W-3	10	18.2	61.1	40.3	27.7	14.0	6.4	10.5	25.9	13.8	9.4	217.3	34.9	7.2	D
8																
9	W-4	9	24.4	77.6	50.6	25.0	16.5	7.4	12.9	30.0	17.5	9.6	208.8	41.2	7.1	D
10	W-5	10	21.0	77.0	44.0	20.9	15.8	7.6	11.3	28.0	17.4	9.5	207.0	37.5	7.0	D
11																
12	W-6	10	3.9	6.3	2.2	45.1	6.5	3.4	3.4	8.3	1.4	9.4	216.3	11.0	7.4	D
13	W-7	9	3.8	2.2	0.9	42.1	6.2	3.7	2.8	7.4	0.5	9.4	227.1	9.1	7.4	
14																
15	W-8	10	3.7	1.2	0.7	35.3	5.8	3.1	2.3	5.7	0.3	9.6	222.4	7.9	7.3	D
16	W-9	10	3.6	0.5	0.6	36.9	6.5	2.9	2.3	5.7	0.1	9.6	216.7	7.7	7.3	
17																
18	W-10	10	5.1	13.5	3.0	32.0	6.3	4.1	3.0	8.0	3.1	9.8	211.9	11.2	7.2	D
19	W-11	10	18.8	64.5	18.9	35.9	13.4	8.6	8.9	22.3	14.6	9.7	202.9	31.0	7.0	D
20																
21	W-12	10	6.8	18.8	7.8	38.7	8.1	4.1	4.7	12.2	4.2	9.6	205.5	14.9	7.4	D
22	W-13	10	10.0	39.0	8.2	31.1	9.8	4.6	5.5	13.9	8.8	9.8	205.2	19.4	7.1	D
23																
24	W-14	10	6.0	9.1	10.0	103.7	12.0	5.1	9.2	18.6	2.0	9.4	228.0	23.5	6.8	
25	W-15	10	5.9	6.1	8.9	132.5	12.2	5.5	12.8	22.9	1.4	9.4	221.6	25.4	6.7	
26	W-16	10	6.9	15.6	11.7	76.9	9.7	5.0	7.6	18.2	3.5	9.1	221.5	21.4	6.7	
27	W-17	10	5.9	9.2	8.8	103.3	10.7	4.3	9.7	20.3	2.1	9.4	228.1	23.3	6.6	
28	W-18	10	7.5	13.5	11.4	101.3	12.8	4.5	10.2	19.7	3.1	9.4	215.1	24.2	6.7	
29	W-19	10	7.1	5.0	51.5	214.8	33.0	9.0	20.4	43.4	1.1	8.7	222.9	46.8	6.4	
30	W-20	10	6.9	7.4	31.9	136.9	18.8	6.7	16.6	26.8	1.7	8.8	217.8	34.4	6.6	
31																
32	Average		12.3	38.9	21.7	57.8	12.6	6.3	8.9	22.1	8.8	9.1	216.0	28.8	7.0	
33																
34																
35																

36 "N.M." = not measured.

37 In well type, "S" means shallow well (<30 m deep) and "D" deep well (>30 m deep).

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Table 2 Correlation between eight ion contents

	NO_3^-	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
NO_3^-		0.96	0.66	-0.53	0.26	0.68	0.32	0.59
Cl^-			0.73	-0.44	0.37	0.68	0.41	0.67
SO_4^{2-}				0.00	0.64	0.66	0.67	0.81
HCO_3^-					0.51	-0.03	0.53	0.22
Na^+						0.52	0.78	0.66
K^+							0.51	0.74
Mg^{2+}								0.80
Ca^{2+}								

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Table 3 Results of principal component analysis

	Components	
	Factor 1	Factor 2
Cl ⁻	0.83	-0.50
NO ₃ ⁻	0.77	-0.60
SO ₄ ²⁻	0.90	-0.02
HCO ₃ ⁻	0.05	0.97
Na ⁺	0.73	0.53
K ⁺	0.83	-0.11
Mg ²⁺	0.78	0.53
Ca ²⁺	0.92	0.16
Eigenvalues	4.78	2.15
% of variance	59.7	26.8
Cumulative %	59.7	86.5

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Table 4 Mean concentrations of respective clusters

	Number of samples	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	HCO ₃ ⁻ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Ca ²⁺ (mg L ⁻¹)
Group 1	60	6.7	9.9	13.6	113.0	13.2	5.3	10.9	21.0
Group 2	11	7.1	5.2	49.7	209.2	31.7	8.8	21.4	44.6
Group 3	81	5.3	11.7	3.8	37.7	7.0	3.7	3.5	9.2
Group 4	125	20.0	73.4	34.7	31.0	14.3	8.3	10.4	28.9

Figure 1



Figure 2

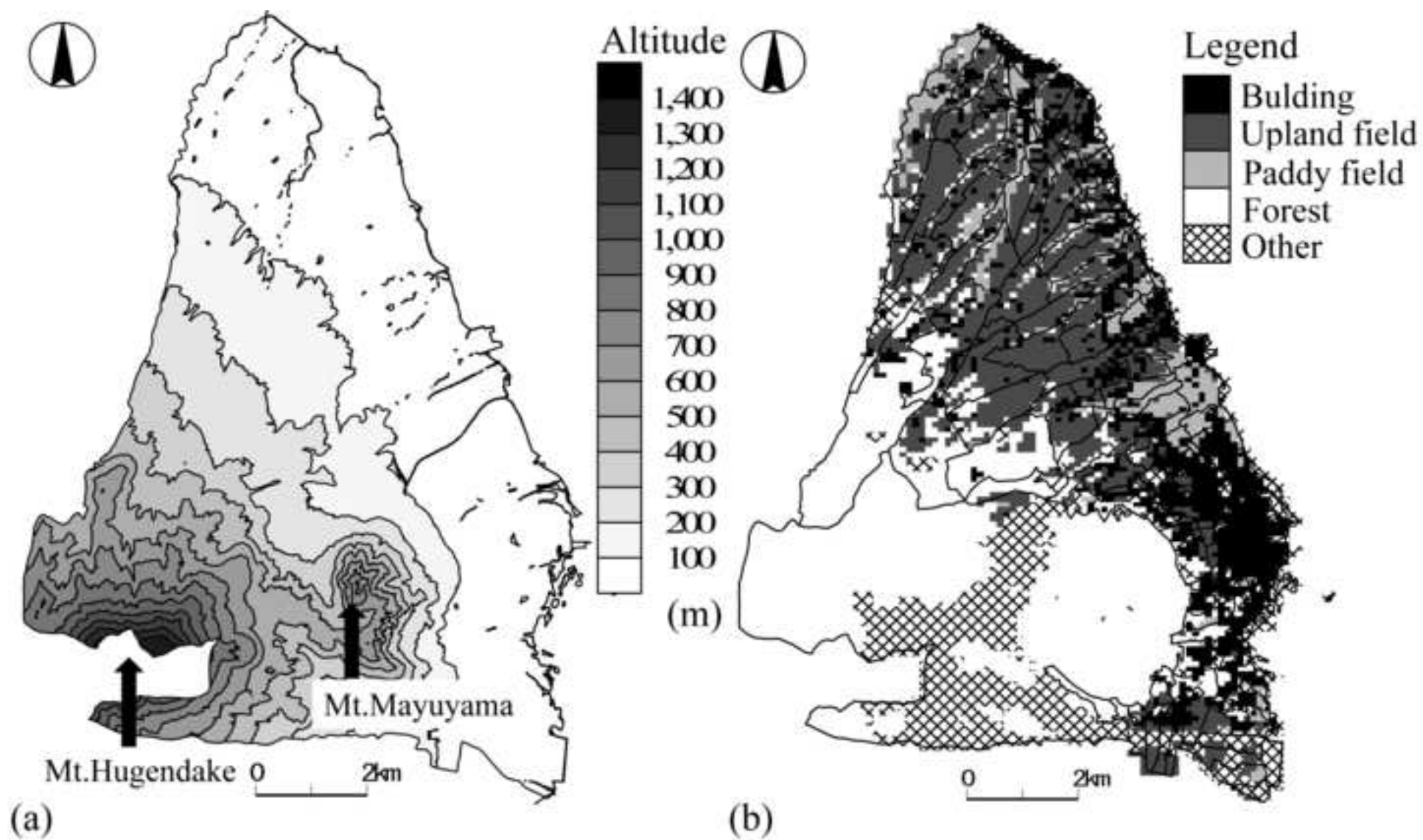


Figure 3

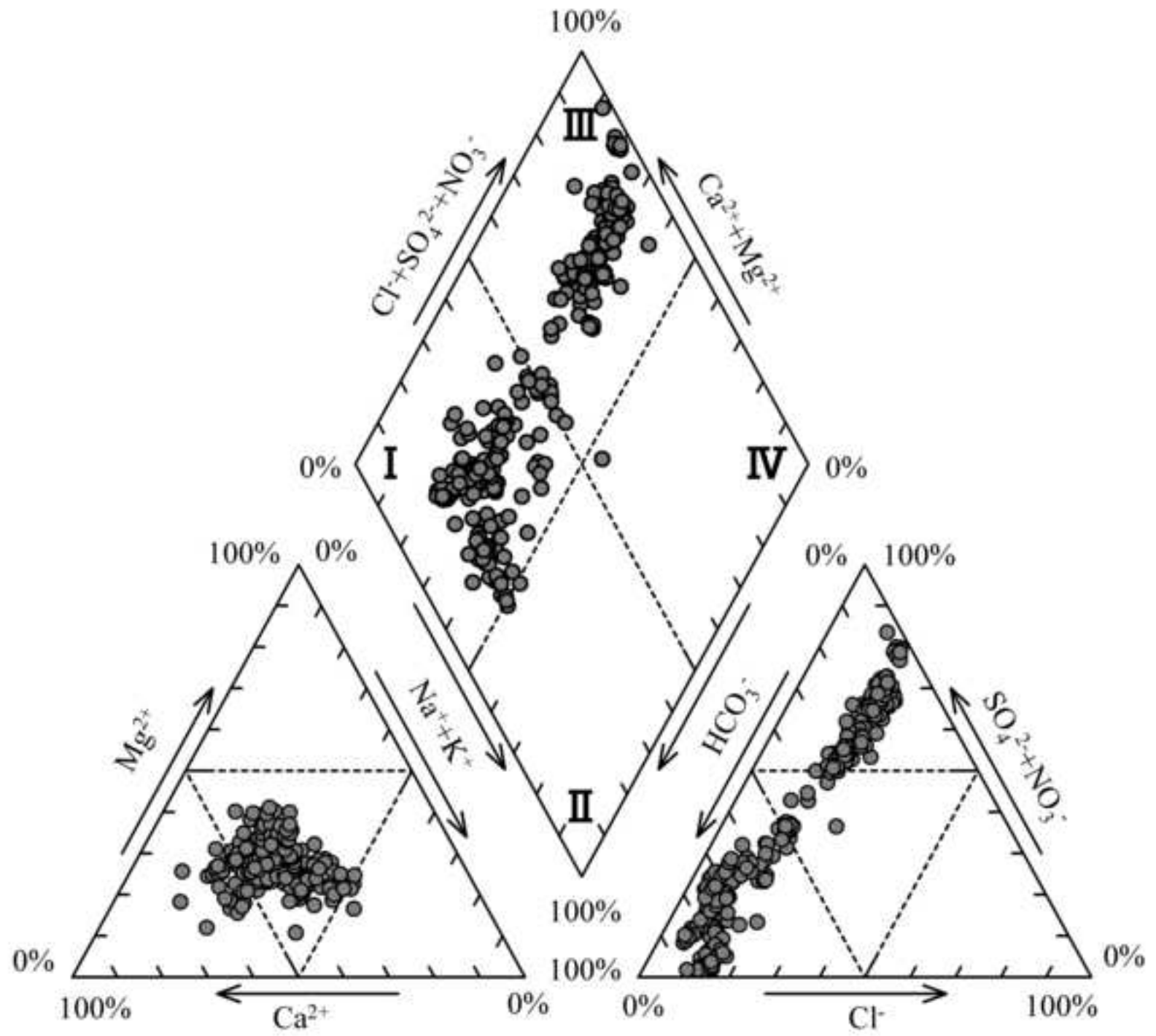


Figure 4

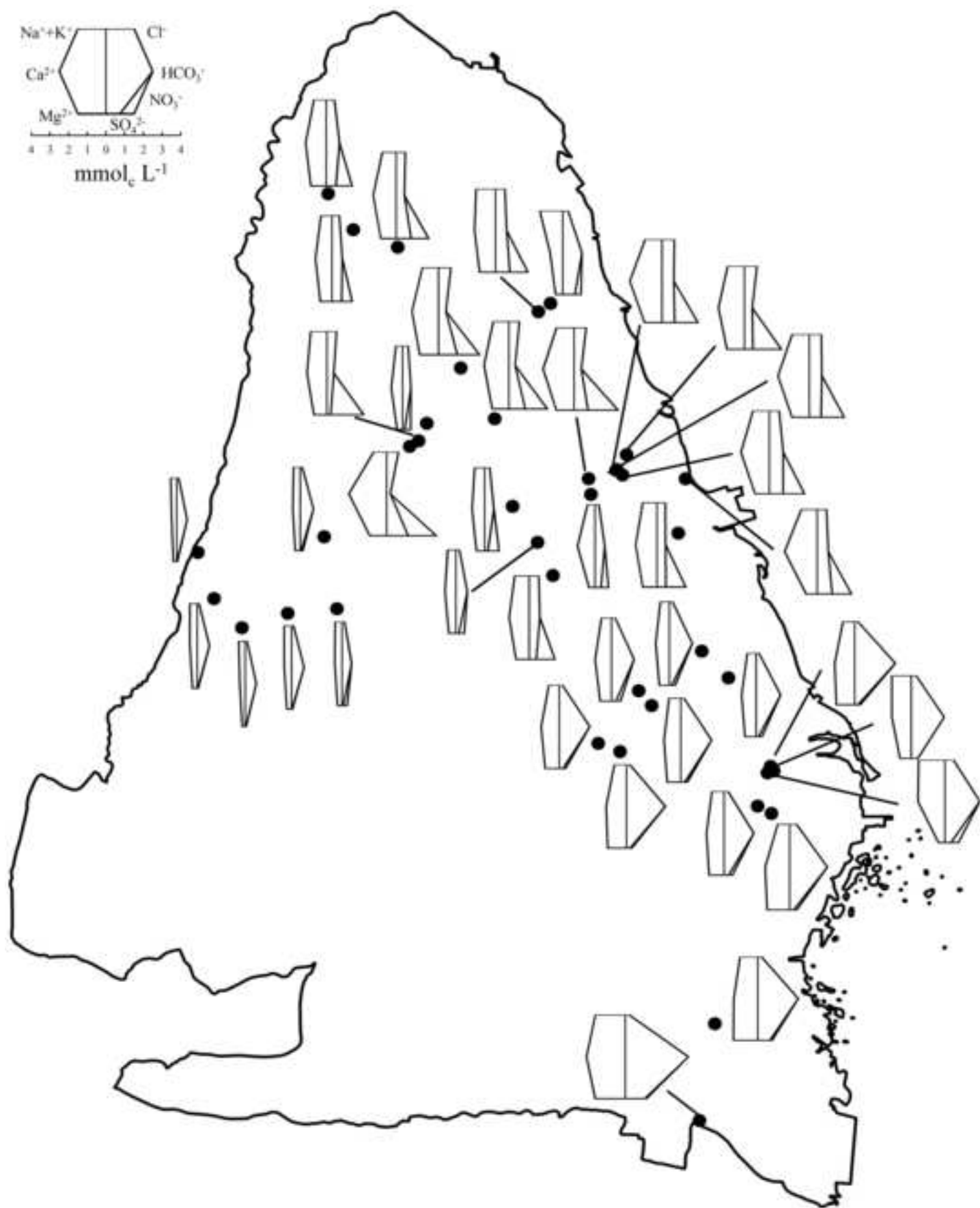


Figure 5

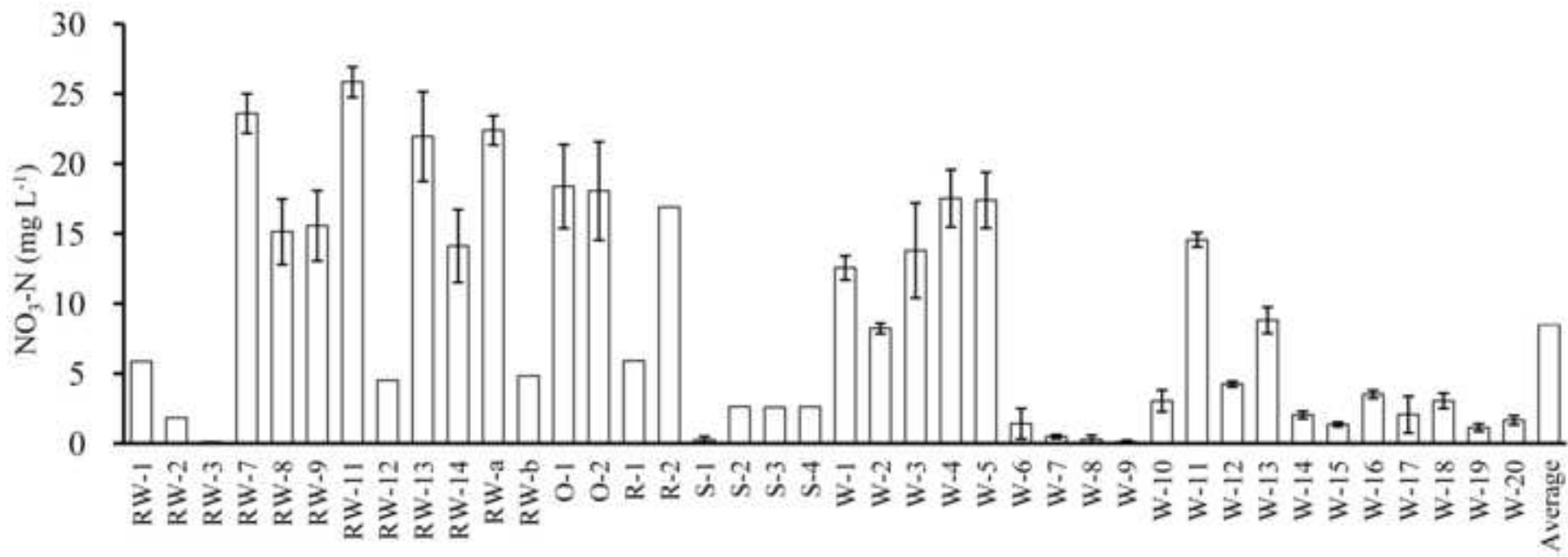


Figure 6

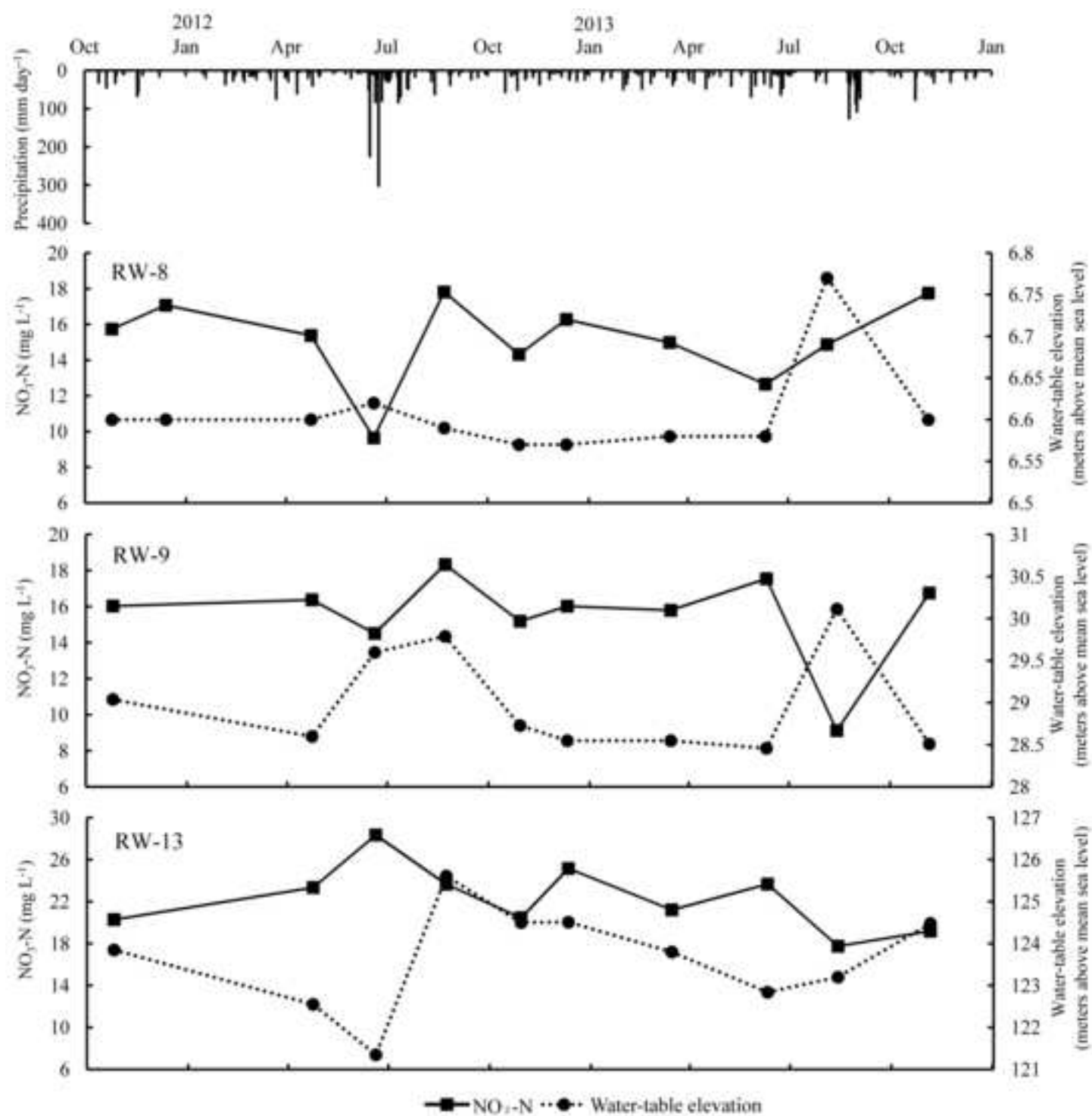


Figure 7

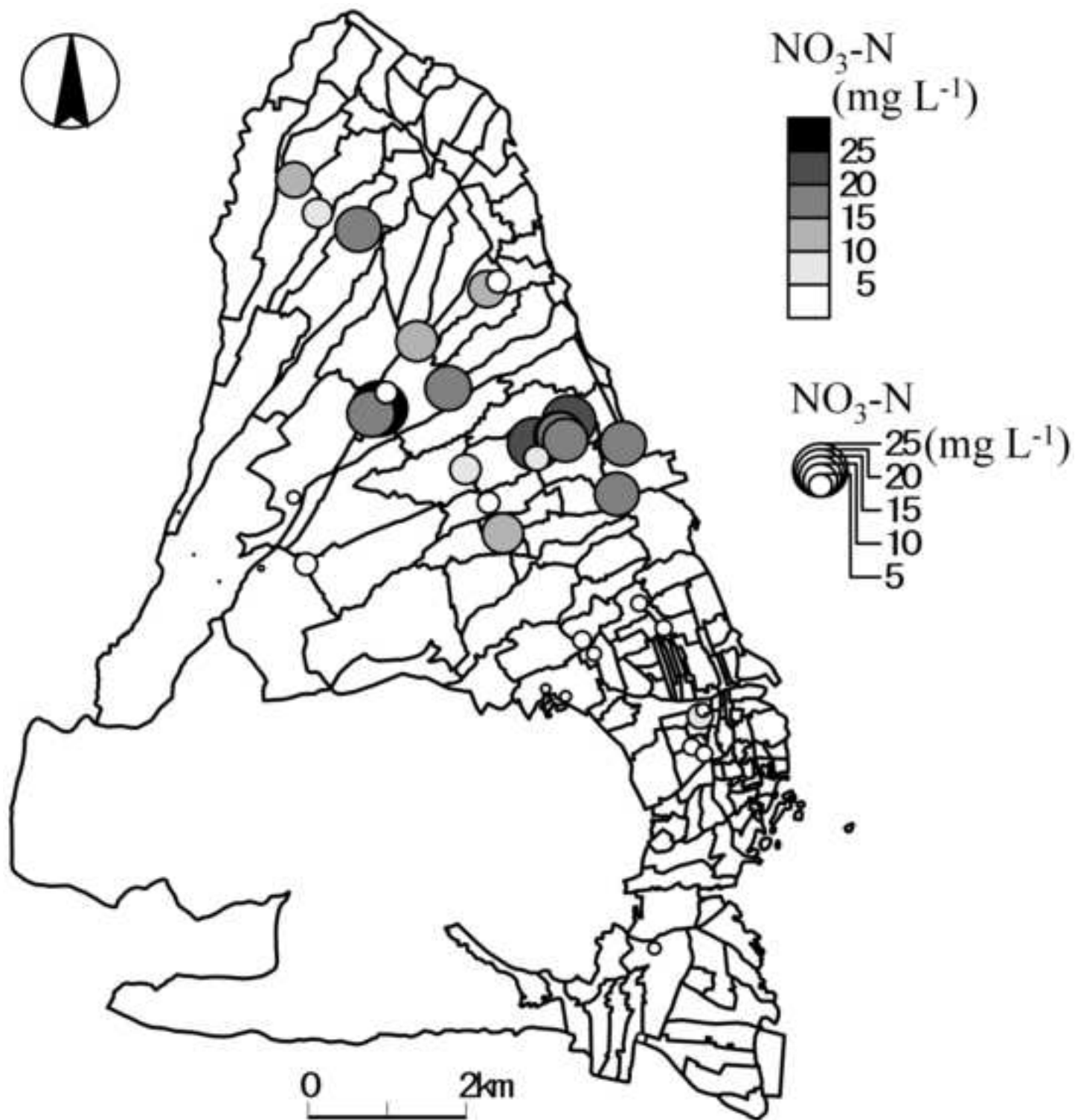


Figure 8

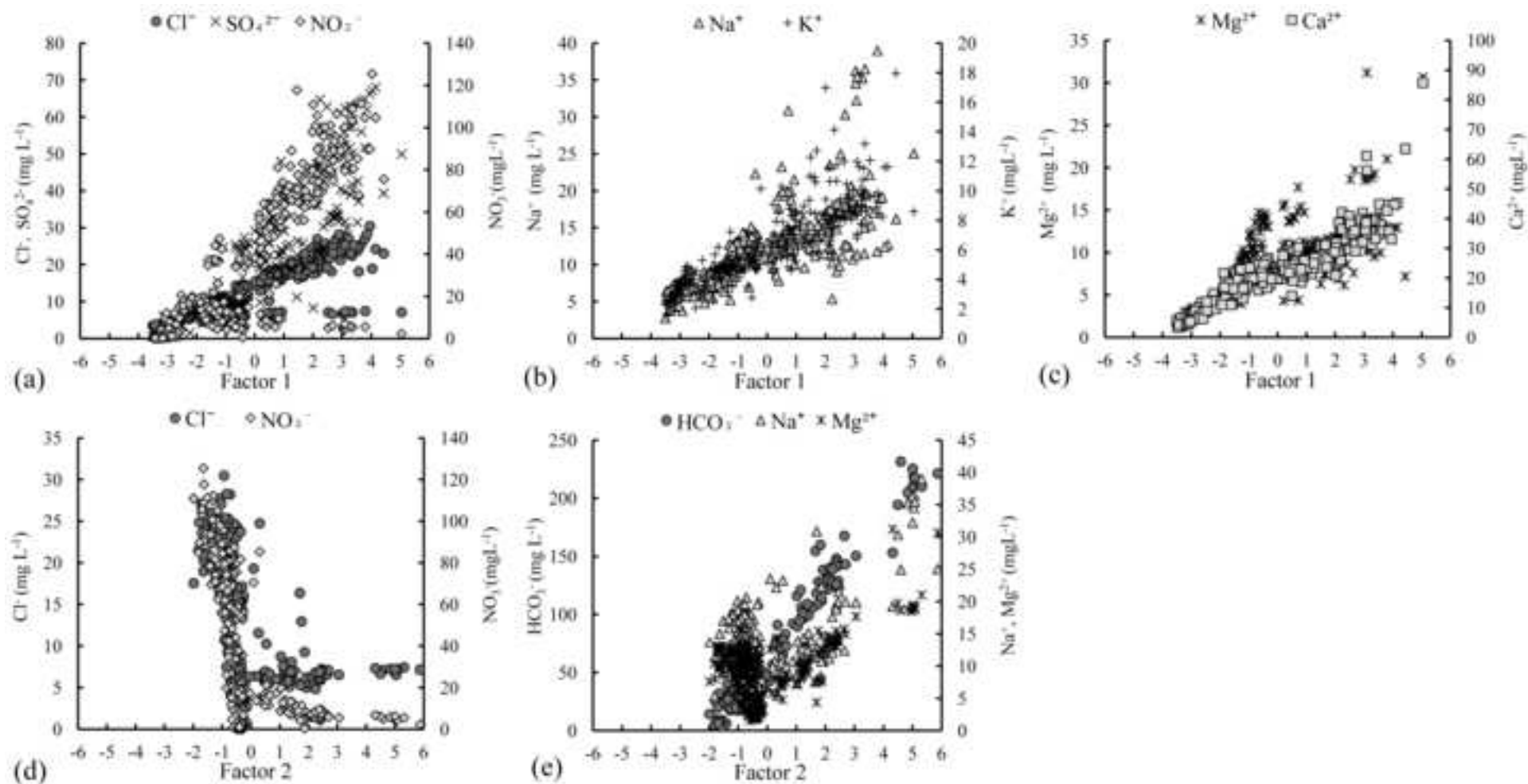


Figure 9

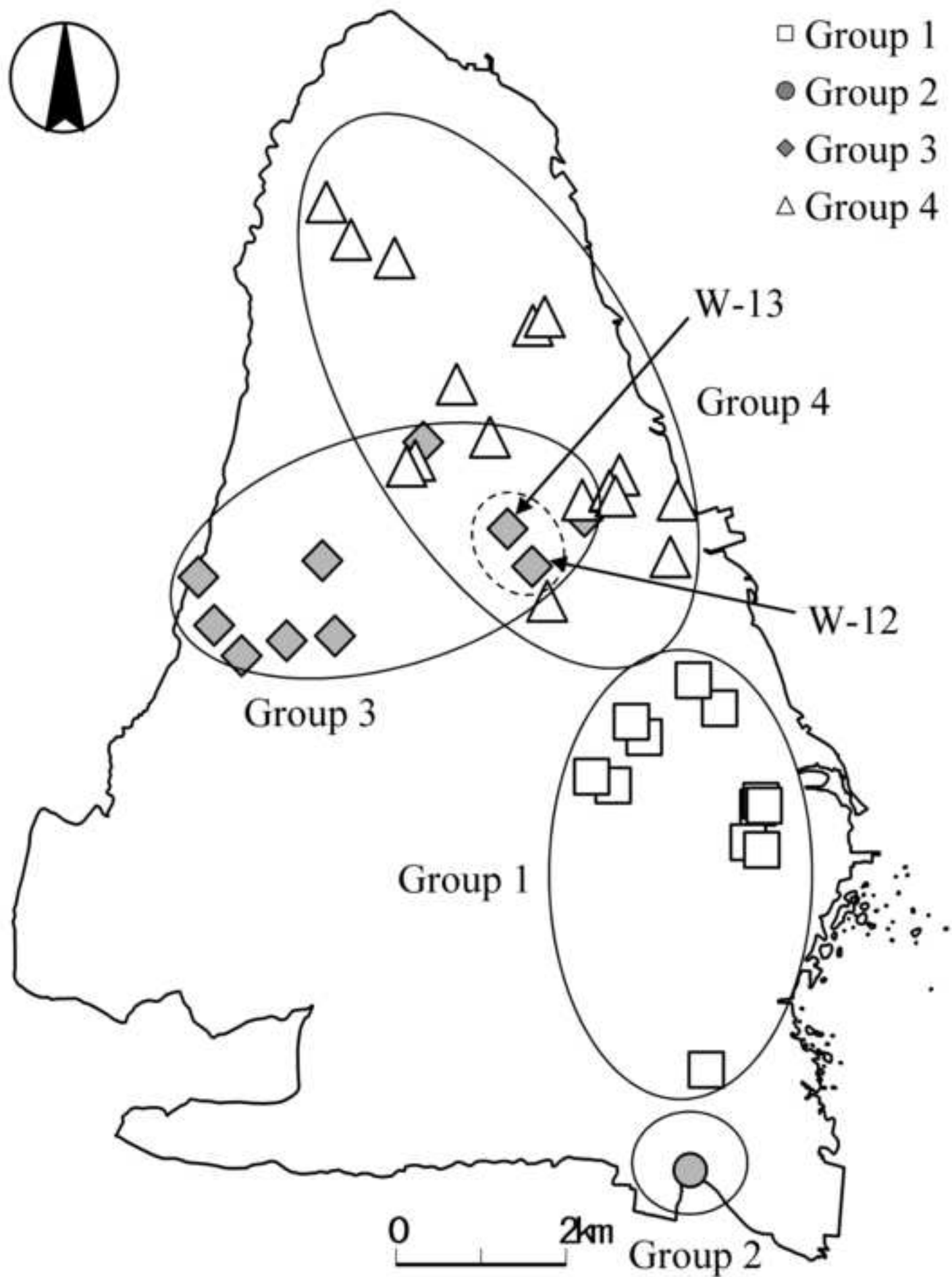


Figure 10

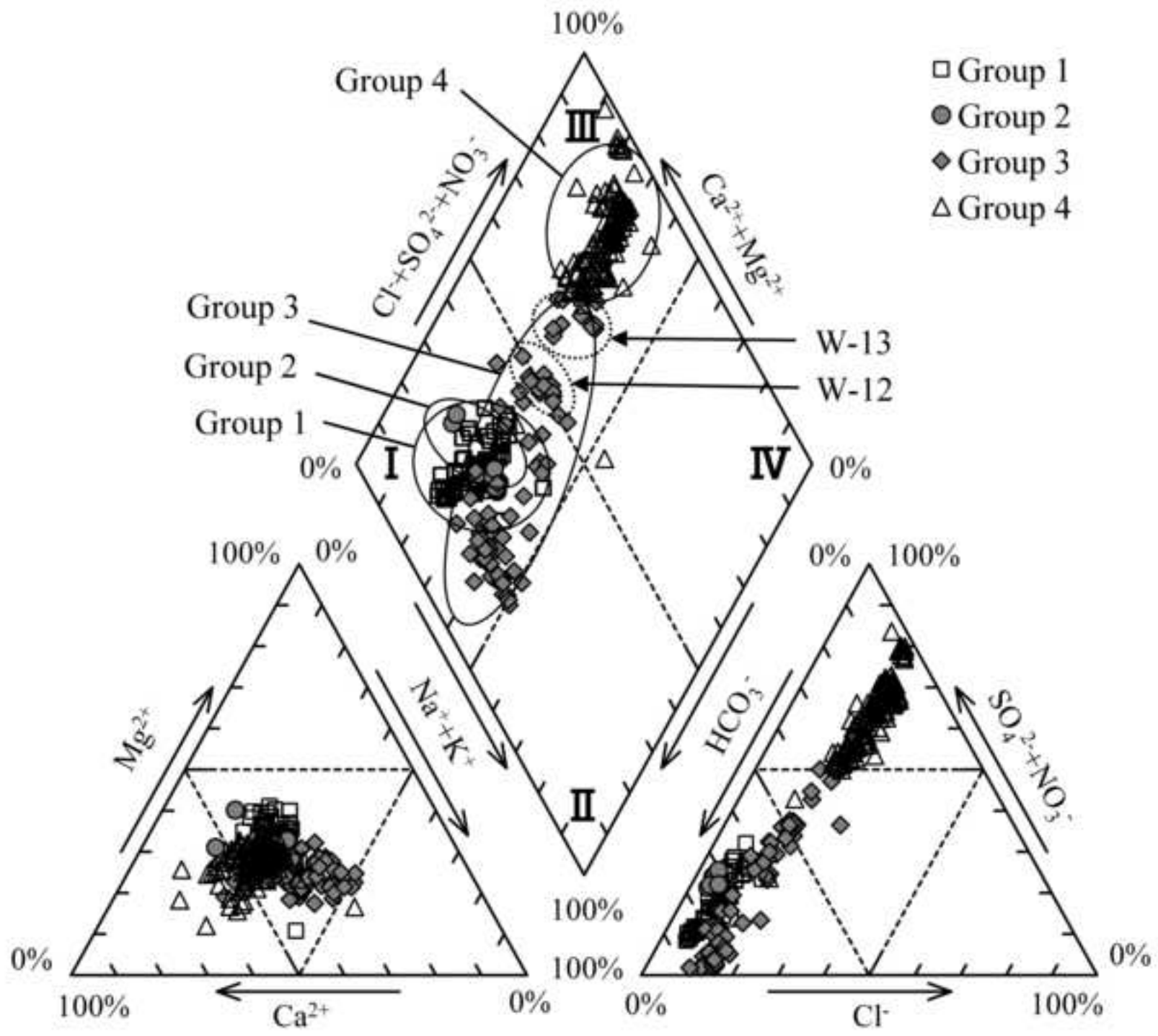


Figure 11

