温泉科学（J. Hot Spring Sci.），72，38-47（2022）

短　　報

Simple group assessment for relationship between dissolved carbon dioxide concentration and compound factors of temperature and pH on springs in the Niseko area, western Hokkaido, Japan

Keishi TAKANO[1)*], Naoki AOYANAGI[1)], Kazuto OHMORI[2)], Takahiro SUZUKI[2)] and Makoto TAMURA[2)]

(Received Mar. 6, 2022, Accepted May 10, 2022)

北海道西部ニセコ地域に湧出する温泉群における遊離二酸化炭素濃度および泉温と pH の複合要因の関係に対する簡易な集団評価

高野敬志[1)*]，青柳直樹[1)]，大森一人[2)]，鈴木隆広[2)]，田村　慎[2)]

要　　旨

北海道西部に位置するニセコ地域に湧出する温泉群の遊離二酸化炭素（CO_2）濃度を測定し，CO_2 濃度と泉温および pH の 2 要因との複合的関係を評価した．CO_2 濃度が 10 mmol/kg 以上であった試料は全45試料中16% を占め，最高濃度は29.8 mmol/kgであった．CO_2/泉温（x 軸）と CO_2/pH（y 軸）の散布図から，比較的高い相関係数（r）である 0.7209 の回帰直線を得た．3 データが 95% 予測値範囲から外れた．2 データは高泉温かつ低 pH で高すぎる CO_2 濃度を示し，1 データは中性の pH で高すぎる CO_2 濃度を示したと考えられた．これら 3 つのデータを除いた散布図から得た回帰直線の r は 0.9616 に修正された．ニセコ地域の温泉における回帰直線の傾きの数値は，同様に求めた北海道全体の温泉の回帰直線の傾きよりも 2 倍ほど高かった．我々はこの理由として，回帰直線の傾きの数値は火山性の温泉地で高くなり，北海道全体の温泉の中には非火山性の温泉が多く存在することもあるためと推測した．さらに，回帰直線の傾きは CO_2 の起源に関係すると考え，温泉地ごとに固有の数値を持つと推測した．

キーワード：遊離二酸化炭素，pH，泉温，ニセコ地域

[1)] Hokkaido Institute of Public Health, Kitaku Kita 19 Nishi 12, Sapporo 060-0819, Japan. [1)] 北海道立衛生研究所　〒060-0819　札幌市北区北 19 条西 12 丁目．*Corresponding author：E-mail takakei@iph.pref.hokkaido.jp, Tel 011-747-2735, Fax 011-736-9476.

[2)] Hokkaido Research Organization, Industrial Technology and Environment Research Institute of Energy, Environment and Geology, Kitaku Kita 19 Nishi 12, Sapporo 060-0819, Japan. [2)] 地方独立法人北海道立総合研究機構産業技術環境研究本部エネルギー・環境・地質研究所　〒060-0819　札幌市北区北 19 条西 12 丁目．

Abstract

CO_2 concentrations were determined and the relationships between CO_2 concentrations and compound factors of temperature and pH were evaluated for springs in the Niseko area of western Hokkaido, Japan. CO_2 concentrations above 10 mmol/kg were observed in 16% of a total of 45 spring samples. The maximum concentration was 29.8 mmol/kg. The scatter plot of CO_2/temperature (x axis) and CO_2/pH (y axis) showed a regression line with a relatively high correlation coefficient (r), 0.7209. The three data were outside the 95% prediction interval. The two data sets might have a too high CO_2 concentration in relation to the observed temperature and pH and one data might have a too high CO_2 concentration in relation to the observed neutral pH. The regression line when these data were excluded was modified to $r = 0.9616$. The value of the regression line slope for springs in the Niseko area was higher than the value determined by the same method for springs across the whole of Hokkaido. This reason was speculated that the volcanic springs have high value of slope because many non-volcanic springs are present across the whole of Hokkaido. In addition, we also speculated that the values of the slopes vary by spring area due to the source of CO_2.

Key words : dissolved carbon dioxide, pH, temperature, Niseko

1. Introduction

The Niseko area is a major resort area in western Hokkaido, Japan, with many companies related to the leisure industry gathered in the area. Several volcanos such as Mt. Niseko Annupuri and Mt. Iwaonupuri are found in this area. The volcanic activity is considered to have begun from the early Pleistocene age, and increased markedly in the late Pleistocene (Oba, 1960 ; Igarashi and Yokota, 1970). A lot of springs are therefore found around the volcanos and are utilized as recreational spas. Recently, the drilling of hot spring has been actively pursued accompanied by the construction of many accommodation facilities. Due to concerns regarding this potential drain on spring resources, the Hokkaido government specified parts of the Niseko area as a protected area or a semi protected area from spring resource development in 2020 (Hokkadido, 2020).

The quality of the spring water and dominant element components vary by spring in the Niseko area. There are several types of spring water such as Na-Cl, Mg-SO_4, Ca-SO_4 and Na-HCO_3 (Ohmori and Suzuki, 2020). In addition, dissolved carbon dioxide (CO_2) is a component that has received much interest. Although there are few reports with detailed information of CO_2 for individual springs in the Niseko area, fans of hot springs have noted the existence of some CO_2 rich springs (e.g. the Kogane spring or Yakushi spring). It was also reported that a high terrestrial carbon dioxide concentration (94%) was detected from a spring in Niseko and it was suggested that the carbon dioxide originated from magma derived from the mantle (Ono *et al.*, 1993).

Although gaseous carbon dioxide has harmful effects on the human body at high concentrations (Langford, 2005), CO_2 in spas has been recognized historically as a useful therapy for patients with arteriopathies (Brandi *et al.*, 2001). Springs with ＞22.8 mmol/kg (1000 mgCO_2/kg) are regarded a medical treatment springs, “carbon dioxide springs” according to Japanese spring regulations. They are expected to be effective in the improvement of cuts, circulatory disorders, poor circulation and autonomic dysfunction (Maeda, 2015).

CO_2 interacts with various physico-chemical factors. For example, it was reported that the partial pressure of CO_2 could be derived from a formula using alkalinity, pH and Henry's law constant according to the survey of groundwater including some springs (Macpherson, 2009). Temperature causes changes in the solubility of CO_2 in water (Li and Tsui, 1971), and pH changes the chemical form of CO_2 and is shifted according the amount of CO_2 present (Cole and Prailie, 2009). Thus, CO_2 in springs is likely to be related to both temperature and pH. However, it is uncertain whether that a general law can be identified for the actual relationship between the CO_2 concentration and both temperature and pH in springs in which the environment differs from surface waters and groundwaters. In this study, we tried to clarify the CO_2 concentration in springs in the Niseko area and evaluate the relationships between CO_2 and compound factors of temperature and pH in the springs. In addition, we tried to compare the relationships among springs across Hokkaido.

2. Materials and methods

The sampling was conducted at a total of 45 sites (43 sites were working or abandoned springs and 2 sites a brook/ swamp) from July to September in 2017–2019. The map of the sites is shown in Fig. 1. The sampling area covered Kutchan, Niseko, Rankoshi, Kyowa and Iwanai towns.

The measurements of temperature, pH, CO_2 and electric conductivity (EC) were performed

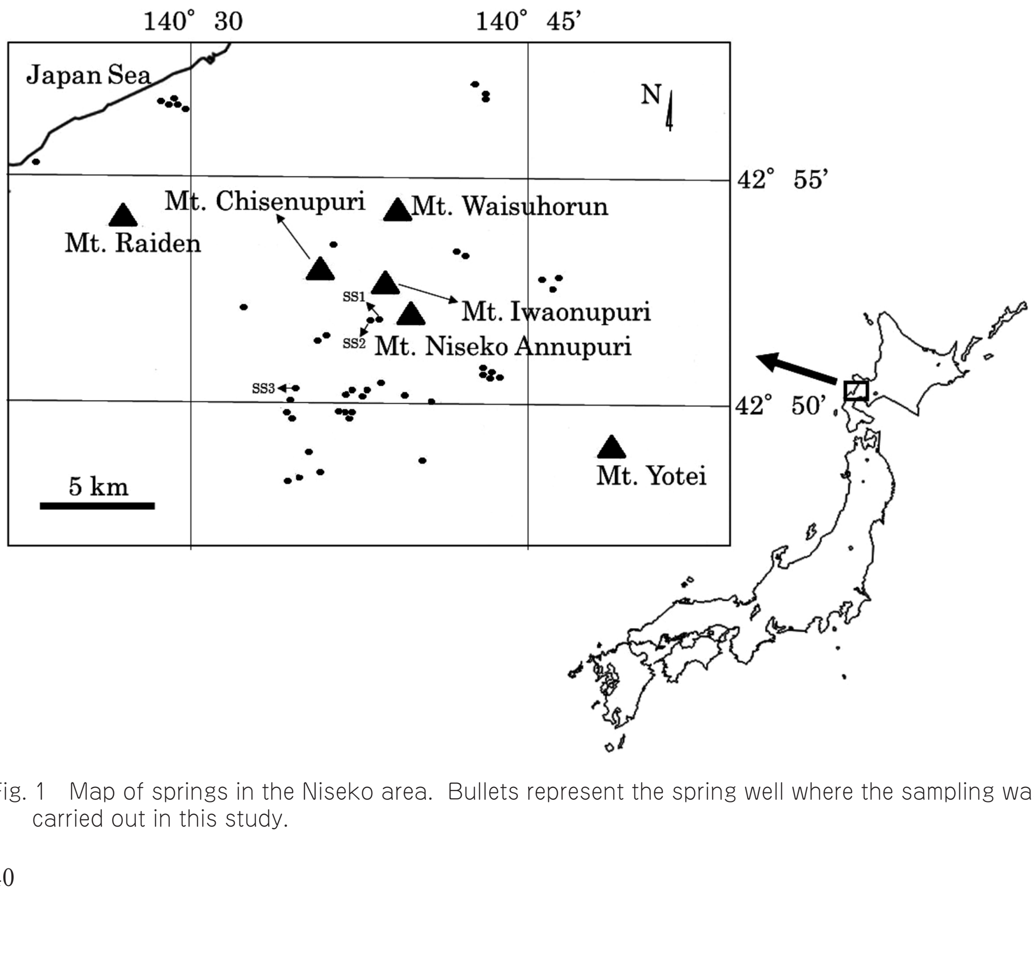

Fig. 1　Map of springs in the Niseko area. Bullets represent the spring well where the sampling was carried out in this study.

at sampling. Temperature, pH and EC were determined by hand-held measuring instruments calibrated beforehand. Major components and total hydrogen sulfide were measured by conventional methods (Ministry of the Environment Government of Japan, Natural Environment Bureau, 2014).

CO_2 was determined by the back titration method (see Crossno *et al*., 1996). After 10 ml of 0.25 mol/l NaOH, 5 ml of a mixed solution of 1 mol/l potassium sodium tartrate and 1 mol/l trisodium citrate, and small amount of phenolphthalein were added to Ehrenmeyer flask, a 160 ml sample was poured carefully into the flask,. The color of most sample turned red. In cases in which it did not, the volume of the sample was reduced until it remained a red color. Then, the titration procedure has performed using a volumetric pipet with 0.25 mol/l HCl until the red color vanished (pH 8.3). CO_2 concentration was calculated from the volume of the consumed 0.25 mol/l HCl. If the pH of the spring was below 4, the blank value was subtracted from the initial CO_2 concentration. The blank value was determined by the same back titration method after the CO_2 was completely removed by boiling.

CO_2, temperature and pH data for the whole of Hokkaido were referenced from the official analysis sheets of 1069 springs issued in 2010–2019. These analyses were prepared by 10 authorities registered with the Hokkaido government.

3. Results and discussion

3.1 CO_2 concentrations in springs in the Niseko area

Fig. 2 shows a histogram of CO_2 concentration in springs in the Niseko area. We found 31% of surveyed springs showed a value below 1 mmol/kg. The number of springs with a value 1–10 mmol/kg decreased with increased CO_2 concentration, although the proportion of springs with a value above 10 mmol/kg was relatively high at 16%. The spring with the maximum CO_2 concentration (29.8 mmol/kg) was categorized as a medical treatment spring.

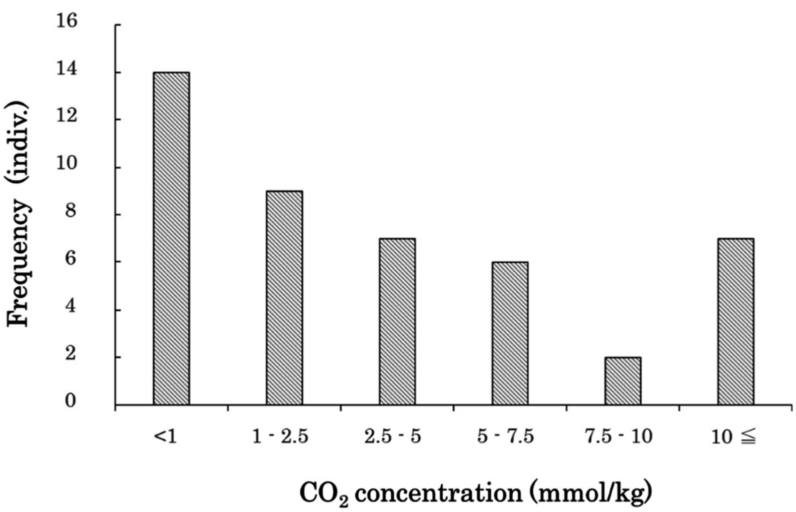

Fig. 2　The histogram of CO_2 concentrations of springs in the Niseko area.

3.2 CO_2 concentration and compound factors of temperature and pH

To evaluate the relationship between the CO_2 concentration and compound factors of temperature and pH, a scatter plot was made for CO_2/temperature and CO_2/pH (Fig. 3). The value of slope and y-intercept of regression line was 6.0294 and zero, respectively. The correlation coefficient was 0.7209, which seemed be a relatively high value. The relative high correlation coefficient value indicated that the CO_2 concentration was related to both temperature and pH for springs in the Niseko area. Three data sets (the sampling site (SS) 1, SS 2 and SS 3) were outside the 95% prediction interval (see Forthofer *et al.*, 2007). This indicated that CO_2 concentrations in the three sites were unexpected in relation to the pH and temperature conditions compared to the other springs in the Niseko area. SS 1 and SS 2 in Fig. 3 were characterized by low pH and high temperature (Table 1). Although CO_2 concentration tends to be high at a low pH, it may actually become low at a very low pH due to volatilization into the atmosphere. In addition, high temperature lowers the solubility of CO_2 in liquids. Therefore, the CO_2 concentrations may tend to be low under the condition of SS 1 and SS2. SS 3 in Fig. 3 was characterized by a neutral pH, low temperature and low conductivity (Table 1). Even though the solubility of CO_2 is high at low temperatures, the CO_2 concentration should fall through the exchange from

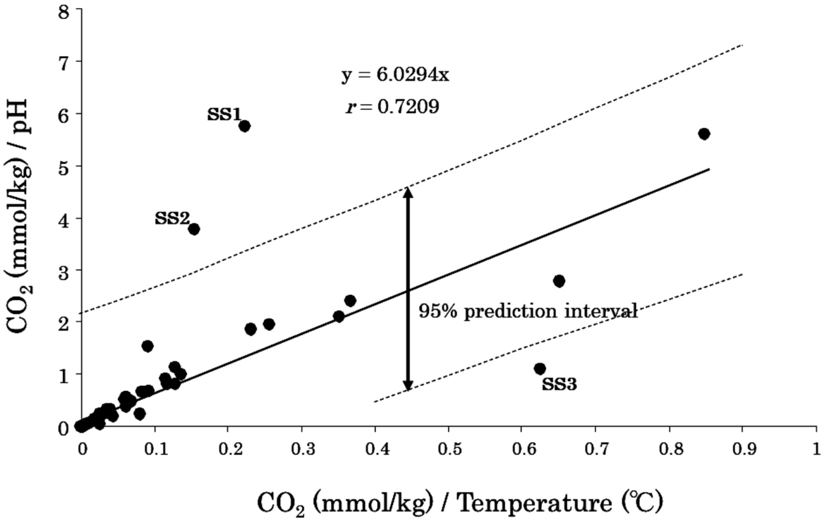

Fig. 3　The scatter plot of CO_2 concentration/pH to CO_2 concentration/temperature of springs in the Niseko area.

Table 1　Overview of the three sampling sites outside the 95% prediction interval in Fig. 3.

	Temp. (℃)	pH	Electrical conductivity (S/m)	CO_2 (mmol/kg)	H_2S+HS^- (mmol/kg)	Dominant ion
SS 1	67.2	2.6	0.57	15.0	0.43	Mg – SO_4
SS 2	58.9	2.4	0.72	9.1	0.11	Mg – SO_4
SS 3	12.9	7.3	0.16	8.1	0.27	Mg – SO_4

CO_2 to HCO_3^- besides CO_3^{2-} due to the effect of pH. Further, a high CO_2 concentration might cause a shift to a lower pH.

SS 1 and SS2 are natural volcanic springs with high temperature, low pH and high hydrogen sulfide concentrations, and are located in southern foothills of Mt. Iwaonupuri (Fig. 1). SS 3 is a natural brook (drifting spring) with low temperature, neutral pH and high hydrogen sulfide concentration, and is located near (about 1 km) the spring which had the highest CO_2 concentration in this study. It was suggested that the natural springs with dominant Mg-SO_4 concentrations in the Niseko area were a mixture of water from a volcanic hot spring source and rainwater (Shibata *et al.*, 2011). Although no detailed data were available to why the CO_2 concentrations were high at those three sites, we assumed that the source of those springs originally had high CO_2 concentrations derived from volcanic gas and the analyzed spring water showed the initial stage of a CO_2 concentration decrease in the case of SS 1 and SS 2, and a decrease in pH in the case of SS 3.

Fig. 4a and 4b show the relationships between CO_2 concentration and temperature and pH, respectively, in springs in the Niseko area. The springs with temperatures above 42℃ accounted for 76% of all surveyed springs. Regression analysis did not reveal any significant relation between temperature (x axis) and CO_2 concentration (y axis) ($p > 0.05$). The springs with a neutral pH from pH 6.0 to 7.5 accounted for 64% of all surveyed springs, and regression analysis revealed a significant relation between pH (x axis) and CO_2 concentration (y axis) ($p < 0.05$). These regression analyses indicated that pH rather than temperature was closely related with CO_2 concentration. As shown in Fig. 4a and 4b, none of SS 1, SS2 and SS3 were extraordinary as their data were within the 95% prediction interval. Therefore, relationships to consider were found in terms CO_2 concentration and the compound factors of temperature and pH, but reasonable relationship were present between CO_2 concentration and temperature and between CO_2 concentration and pH for the three data.

3.3 Comparison with springs across the whole of Hokkaido

The value of slope and correlation coefficient (r) were modified from 6.0294 to 6.1746 and from 0.7209 to 0.9616, respectively, on excluding the data for SS 1–3 (Fig. 5a). The regression line is also shown in Fig. 5a based on 918 springs in Hokkaido Prefecture, Japan, without 151 springs outside the 95% prediction interval. The regression line slope on the Niseko springs was about twice that for the springs across the whole of Hokkaido. This means that pH was lower and temperature was higher under the same CO_2 concentration conditions in the springs in Niseko area compared with those across the whole of Hokkaido. There are a lot of non-volcanic, deep drilled springs in Hokkaido. Such springs tend to have high pH and moderately high temperature, thus contributing to the low value of the regression line slope in Fig. 5a. The correlation coefficient of the regression line for the whole of Hokkaido was lower than that for the Niseko area. This indicated that the slope of the regression line varied for each spring area in Hokkaido.

In addition to the springs in Hokkaido, we tried to confirm the regression line of the springs in the Beppu spring area in southern Japan (Fig. 5b), calculated from data listed previously (Yang, 2021). The slope of the regression line was higher at 7.7972 ($n = 48$, $r = 0.9851$ when the

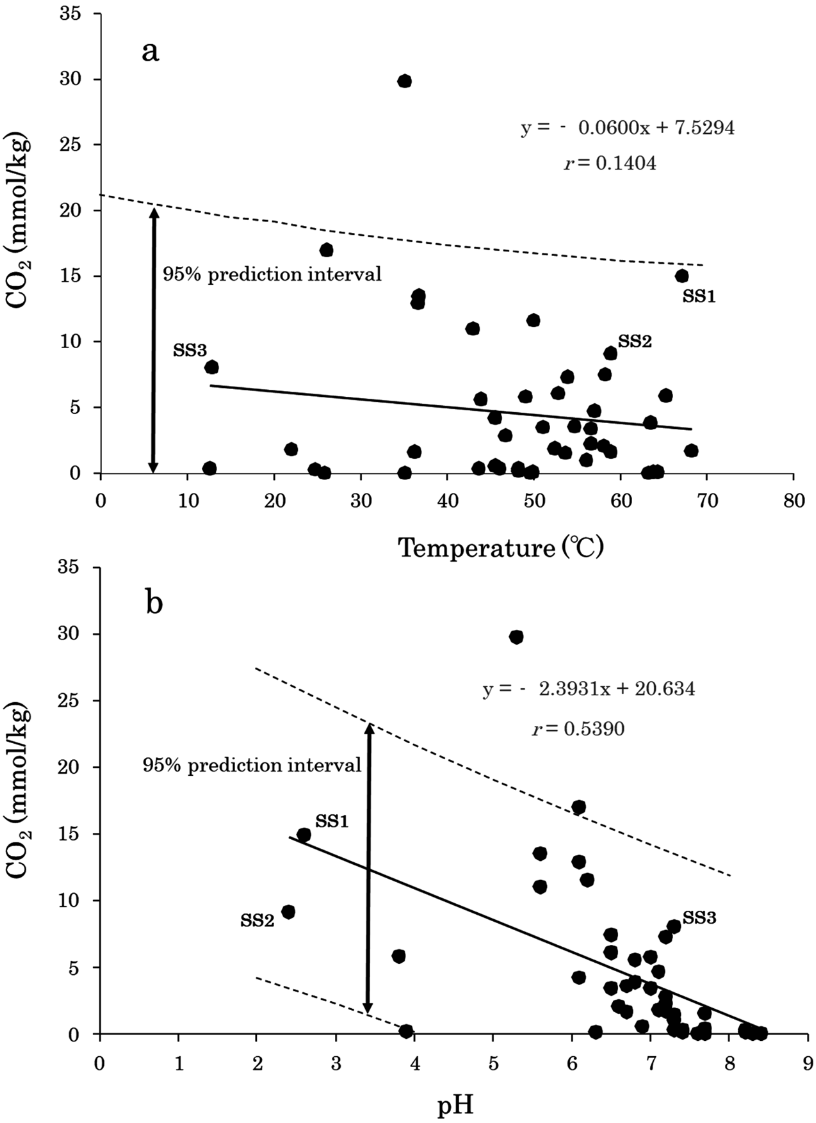

Fig. 4 The scatter plots of CO_2 concentration to temperature (a) and of CO_2 concentration to pH (b).

four springs outside the 95% prediction interval were excluded) than the springs in the Niseko area. The Beppu springs are volcanic and located in one of the largest geothermal fields in Japan (Komatsu *et al.*, 2012). The high value of the slope might relate with the origin of CO_2 such as magma. The high temperatures above 48℃ were recorded at the four sites outside 95% prediction interval, (Table 2). The three springs of those sites were acid and weak acid springs. The dominant ions were Mg and SO_4 at the two sampling sites. The data of spring site with the high temperature and acidity or weak acidity may often lie outside the 95% prediction interval from the examples in the Niseko and Beppu areas.

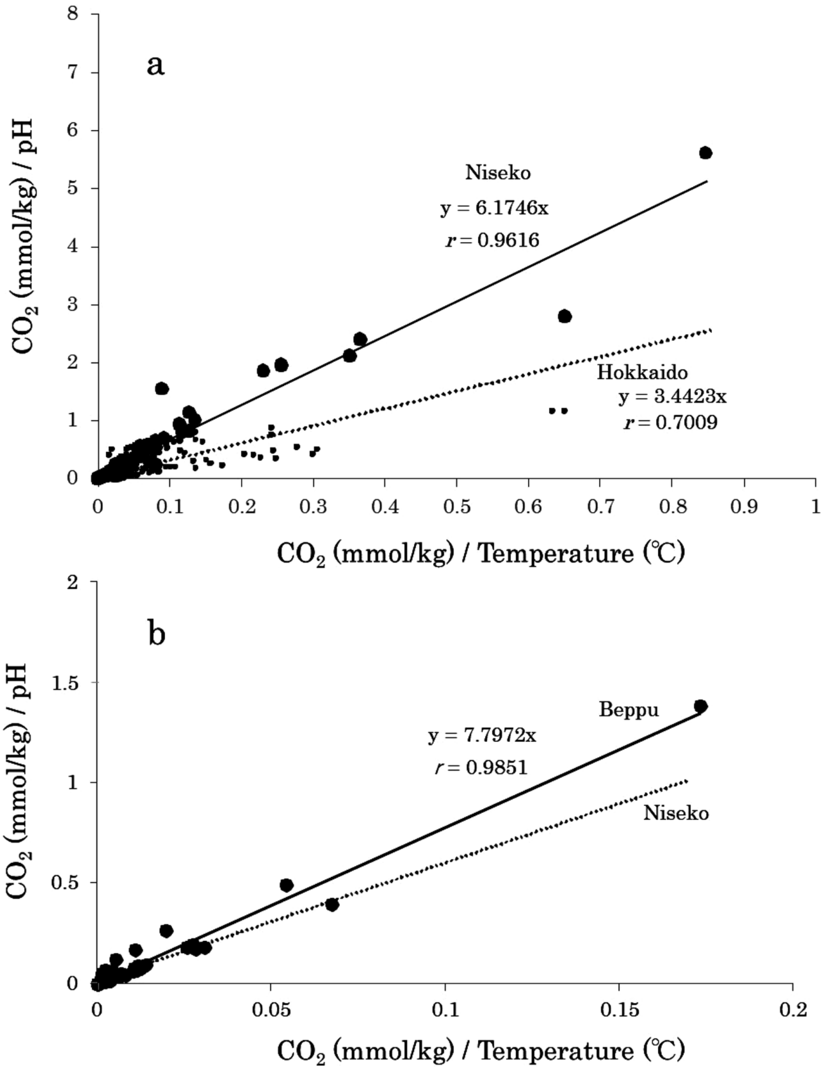

Fig. 5　The scatter plots of CO_2 concentration/pH to CO_2 concentration/temperature of springs without the three data outside the 95% prediction interval in the Niseko area and across the whole of Hokkaido. Large bullets : data of the Niseko area, small bullets : data of the whole of Hokkaido, solid line : regression line for springs in the Niseko area, dotted line : regression line for springs across the whole of Hokkaido (a). The scatter plots without the four data outside the 95% prediction interval. Bullets : data of the Beppu area, solid line : regression line for springs in the Beppu area, dotted line : regression line for springs in the Niseko area (b).

3.4　Notes for the group assessment in this study

The least square method determined the regression line generally requires to minimalize the residual sum of squares for the parameters in y axis regarding that the parameters in x axis is error-free. If the parameters in x axis and y axis replace each other, there is a little change in the correlation coefficient and the difference sometimes occurs with the data outside 95% predic-

Table 2　Overview of the four sampling sites outside the 95% prediction interval in the Beppu area (Fig. 4b). These data were noted by Yang (2021).

	Temp. (℃)	pH	Electrical conductivity (S/m)	CO_2 (mmol/kg)	Dominant ion
Site 1	48.2	7.8	0.12	4.7	$Na - HCO_3$
Site 2	49.7	2.9	0.10	0.9	$Mg - SO_4$
Site 3	97.2	4.4	0.75	1.6	$Na - Cl$
Stte 4	87.2	3.5	0.25	1.0	$Mg - SO_4$

tion interval. Therefore, which to select between x axis and y axis has to be considered for the parameters of CO_2/pH and CO_2/temperature.

4. Conclusion

CO_2 concentrations were determined for the springs in Niseko area. Relatively high concentration above 10 mmol/kg occupied 16% of 45 surveyed springs and the maximum concentration was 29.8 mmol/kg. A scatter plot was made for CO_2/temperature and CO_2/pH to clarify the relationship of CO_2 concentration and combined factor of temperature and pH. It showed a good correlation with 0.9616 of correlation coefficient on the exclusion of three data outside the 95% prediction interval. The value of regression line' s slope of springs in Niseko area was quite higher than springs in whole Hokkaido and was sometimes lower than springs in Beppu area.

In this study, the relationship among CO_2, and combined factor of temperature and pH could be assessed easily from a scatter plot without the simulations based on complicated calculations found in previous reports. In addition, the data with a too high CO_2 concentration in relation to temperature and pH was able to be found by the establishment of a 95% prediction interval.

We speculated that the slope of the regression lines had generally high values in the volcanic spring groups, although insufficient survey examples were available. As we speculated that the value of the slope is related to the CO_2 source, further investigation is needed to clarify the relationship between CO_2 concentration and compound factors of temperature and pH in various spring areas.

Acknowledgements

We thank to the administrators of spring well for collecting the spring water samples. In addition, we are also thankful to the anonymous referees for the valuable comments. This study was supported financially by the Hokkaido government.

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