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A Natural Analogue Approach for Discriminating Leaks of CO_2 Stored Underground Using Groundwater Geochemistry Statistical Methods, South Korea

Kwang-Koo Kim [1], Se-Yeong Hamm [2,*], Jae-Yeol Cheong [3], Soon-Oh Kim [4] and Seong-Taek Yun [5]

1 Water & Transportation Center, Environmental Technology Division, Korea Testing Laboratory, Seoul 08389, Korea; kcubic@ktl.re.kr
2 Department of Geological Sciences, Pusan National University, Busan 46241, Korea
3 Research & Development Institute, Korea Radioactive Waste Agency, Daejeon 34129, Korea; jjy@korad.or.kr
4 Department of Geology and Research Institute of Natural Sciences(RINS), Gyeongsang National University, Jinju 52828, Korea; sokim@gnu.ac.kr
5 Department of Earth and Environmental Sciences, Korea University, Seoul 02841, Korea; styun@korea.ac.kr
* Correspondence: hsy@pusan.ac.kr; Tel.: +82-51-510-2252; Fax: +82-51-516-7767

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Abstract: Carbon capture and storage (CCS) is one of several useful strategies for capturing greenhouse gases to counter global climate change. In CCS, greenhouse gases such as CO_2 that are emitted from stacks are isolated in underground geological storage. Natural analogue studies that can provide insights into possible geological CO_2 storage sites, can deliver crucial information about the safety and security of geological sequestration, the long-term impact of CO_2 storage on the environment, and the field operation and monitoring requirements for geological sequestration. This study adopted a probability density function (PDF) approach for CO_2 leakage monitoring by characterizing naturally occurring CO_2-rich groundwater as an analogue that can occur around a CO_2 storage site due to CO_2 dissolving into fresh groundwater. Two quantitative indices, (QI_{tail} and QI_{shift}), were estimated from the PDF test and were used to compare CO_2-rich and ordinary groundwaters. Key geochemical parameters (pH, electrical conductance, total dissolved solids, HCO_3^-, Ca^{2+}, Mg^{2+}, and SiO_2) in different geological regions of South Korea were determined through a comparison of quantitative indices and the respective distribution patterns of the CO_2-rich and ordinary groundwaters.

Keywords: CO_2-rich groundwater; quantitative index for distribution pattern (QI_{tail}); quantitative index for distribution shift (QI_{shift}); natural analogue; probability density function (PDF)

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1. Introduction

Global climate change resulting from anthropogenic greenhouse gas emissions will accelerate if fossil fuel use increases in the future. Various technologies have been proposed and investigated for the purpose of preventing, reducing, and using the greenhouse gases that result from fossil fuel combustion. Carbon capture and storage (CCS) technology is perhaps one of the most attractive technologies for mitigating global climate change. CCS works by capturing greenhouse gases such as CO_2 that are emitted from stacks and isolating that CO_2 in underground geological storage. Geochemical and geophysical technologies are used alongside CCS for environmental monitoring. Natural analogue studies related to geological storage can: (1) Provide insight into future geological CO_2 storage sites; (2) Provide essential information about the safety and security of geological sequestration; (3) Help identify possible long-term impacts to the environment from CO_2 storage; (4) Help determine the field operations and monitoring required for geological sequestration. However, natural analogue studies such as NASCENT (Natural Analogues for the Storage of CO_2 in the Geological Environment) in the European Union (EU) and NASC (Natural Analogs for Geologic CO_2 Sequestration) in the USA require significant financial resources for building facilities, installing boreholes and monitoring systems, and for performing periodic monitoring.

Many studies and surveys using geochemical parameters (pH, alkalinity, heavy metals, and trace elements) have identified geochemical changes caused by injecting CO_2 at a shallow depth of 2–50 m and monitoring subsequent leakage at CO_2 storage sites and their surroundings [1] (Table 1). As a result of CO_2 injection in the Frio Formation, Texas, pH showed a sharp drop from 6.5 to 5.7 and pronounced increases resulted in HCO_3 concentration (100–3000 mg/L) and Fe concentration (30–1100 mg/L) at the observation well [2]. The monitoring of CO_2 injection in the Weyburn field, Saskatchewan, Canada, resulted in an increase in HCO_3 concentration and a decrease in $\delta^{13}C$ values of HCO_3 and CO_2 [3] and the $\delta^{13}C$ values revealed more than 18‰ lower than the average $\delta^{13}C$ values of dissolved inorganic carbon in baseline brines (−1.8‰) and carbonate minerals of reservoir rock (+4‰) [4]. Geochemical and stable isotope monitoring of CO_2 injection has been demonstrated as a useful tool for detecting the presence of CO_2 at the Pembina Cardium site, Canada [5]. For the Weyburn CO_2 monitoring and storage project, the International Energy Agency (IEA) has developed a probabilistic risk assessment (PRA) model of the geological storage of CO_2 using a probability distribution function (PDF) to reduce the uncertainty of input data in the PRA model [6]. However, geochemical approaches to groundwater-quality monitoring rarely detect near-surface CO_2 leakage from underground storage effectively or sufficiently because the geochemical parameters depend significantly on differences between the periods pre- and post injection [7,8]. In addition, most of these studies and surveys were executed over only a short period. Furthermore, geological and environmental complexity such as multiple bedrock types, various groundwater–rock interactions, and complex fault and joint geometries makes it difficult to explain geochemical change after CO_2 injection into a deep geological formation, and difficult to identify dramatic change in the target elements. Moreover, global and local risks from underground geological CO_2 storage, such as CO_2/CH_4 release into the air, CO_2 dissolution in groundwater, earthquakes, ground movement, brine displacement, and human/animal activities, are incompletely understood [9]. Finally, the several key parameters suggested for monitoring CO_2 substantially depend on the local natural environment [10].

Korea aims to reduce CO_2 emissions by 37% (314.7 Mt CO_2) from the expected 2030 level (850.6 Mt CO_2) [11]. The Ministry of Trade, Industry, and Energy, the Ministry of Science, ICT and Future Planning, and the Ministry of Oceans and Fisheries implement inland underground CO_2 storage sites in Korea. In this context, in 2014 Korea's Ministry of Environment launched the Korea CO_2 Storage Environmental Management Research Center (K-COSEM) in order to monitor, assess, predict, and manage the pre-determined CO_2 storage sites. Yun et al. [12] studied the results of underground CO_2 storage in Korea and concluded that improved prediction methods and enhanced approaches are necessary to better understand heterogeneous underground environments.

The objective of this study was to discriminate underground leaks from CO_2 storage using a natural analogue approach based on the PDF coupled with two quantitative indices (*QIs*)—QI_{tail} and QI_{shift}. For the natural analogue, the existing geochemical data of CO_2-rich and ordinary groundwaters in South Korea was analyzed by the PDF approach (Figure 1). The CO_2-rich groundwater mostly occurs in the Gangwon, Gyeongsang, and Chungcheong Provinces in South Korea [13,14].

Table 1. Key parameters for CO_2 monitoring [12].

Site	Date	CO_2 Injection Depth (m)	Monitoring Parameters	Change Trend	Key Parameters for CO_2 Monitoring
Svelvik, Norway	September 2011	20	pH, temp., EC, alkalinity Ca, Na, SO_4, Cl, Mg, Al, Ba, Mn, Ni, Co, B, Li Isotope	pH: decrease EC: increase Alkalinity: increase Ca, Li, Si, Sr: increase (Based on 10 m) Isotopes: decrease	pH EC Alkalinity Ca, Li, Si, Sr
Bozeman, Montana, USA	June–July 2008	2.5	pH, temp., EC, alkalinity, DO Al, As, Co, B, Li, Cd, Cr, Cu, Mo, Pb, Se, U, Zn HCO_3, Na, K, Mg, Ca, Sr, Ba, Mn, Fe, F, Cl, Br, NO_3, PO_4, SO_4, SiO_4, SiO_2, TDS Benzene, toluene, ethyl-benzene, xylene	pH: decrease EC: increase Alkalinity: increase Ca, Mg, Mn, BTEX: increase	pH EC Alkalinity Ca, Mg, Mn, BTEX
Wittstock, Brandenburg, Germany	March–April 2011	18	TIC/TOC Cl^-, NO_3^-, SO_4^{2-}, K, Na, Mg, Ca, Fe, Mn, Si BTEX, ammonium, chlorinated carbons, ethane, ethene, methane Isotope Basic groundwater, parameters (pressure, pH, EC, O_2, alkalinity, temp.)	pH: decrease EC: increase Alkalinity: increase TIC: increase Anions: decrease Ca, Mg, Sr, Ba, U: stable after increase Mn: increase	pH EC Alkalinity Ca, Mg, Mn, Sr, Ba, U
Colorado River, Austin, Texas	February 2012	3.7	Dissolved O_2, pH Ca, Mg, Sr, Ba, Mn, U, Si, K, As, Mo, V, Zn, Se, Cd, Co, Ni	pH: decrease (field test) Ca, Mg, Sr, Ba, Mn, U: stable after increase Si, K: increase	pH EC Alkalinity Ca, Mg, Mn, Sr, Ba, U, Si, K
Daniel Electric Generating Plant, Escatawpa, Mississippi	October 2011–March 2012	47.9	pH Resistivity Phase responses	pH: decrease Resistivity: decrease Phase responses: decrease	pH Resistivity Phase responses
Daniel Electric Generating Plant, Escatawpa, Mississippi	October 2011–March 2012	30.5	pH, EC, alkalinity Ba, Ca, Fe, Mg, Mn, Sr, Cl, Cr, Mo	pH: decrease EC: increase Alkalinity: increase Ba, Ca, Fe, Mg, Mn, Sr, Cl, Cr: decrease after increase Mo: decrease and increase	pH EC Alkalinity Ba, Ca, Fe, Mg, Mn, Sr, Cl, Cr

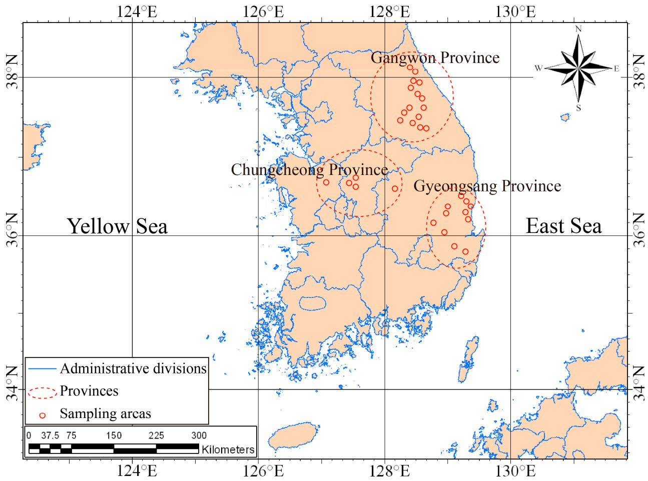

Figure 1. Sampling regions of carbonated water in South Korea [13].

2. Geological Setting

The study area includes Gangwon and Gyeongsang Provinces and Chungcheong Province in South Korea (Figure 1). CO_2-rich groundwater and natural carbonated springs occur mainly in north-east Gangwon Province, north Gyeongsang Province, and in the Chungcheong Province [13]. The CO_2-rich water emerges from natural springs in granitic areas of Gangwon and Gyeongsang Provinces and is extracted from deep wells for bathing in Chungcheong Province. The CO_2-rich water occurs in sedimentary rock areas of Gyeongsang Province, unlike Gangwon and Chungcheong Provinces [13].

The bedrock in Gangwon Province consists of various types of granite (Jurassic biotite granite, muscovite granite, and graphic granite) and banded gneiss [15–17]. Chungcheong Province is composed largely of granite, but with a wide variety of additional rock compositions. The Chojeong area consists of metamorphic rocks derived from sedimentary protoliths, Jurassic biotite granite, and chalk, with mineralized acidic dikes containing sphalerite, scheelite, chalcopyrite, and pyrrhotite, as well as Quaternary rocks. The Jungwon area consists mainly of biotite granite, consisting of 27.4% quartz, 26.3% K-feldspar, and 38% plagioclase, along with gneiss. The Munkyeong area features Quaternary rocks, biotite granite, and chalk karst terrain. In the Cheongsong area, Jurassic granite is the main lithology (Table 2).

Table 2. The location of CO_2-rich water in Korea (Kim et al., 2002).

Province	Area	Geology
Gangwon	Yangyang	Granite
	Injae	Granite
	Gangneung	Granite
	Pyeongchang	Granite
	Hongchon	Granite
	Jeongsun	Granite
Gyeongsang	Youngcheon	Sedimentary
	Youngdeok	Sedimentary
	Cheongsong	Granite & Sedimentary
	Gunwe	Sedimentary
	Gyeongju	Sedimentary
Chungcheong	Chojeong	Granite
	Jungwon	Granite
	Cheonan	Granite
	Munkyeong	Granite
	Daepyeong	Granite
	Bugang	Granite
	Cheongju	Granite

Unlike Gangwon and Chungcheong Provinces, Gyeongsang Province consists mainly of sedimentary bedrock from the Gyeongsang Supergroup, which has a thickness of 8–10 km and includes conglomerate, sandstone, shale, mudstone, marl, and other lithologies, along with volcanic rocks and thin layers of limestone above and below the supergroup [13,14]. In Gyeongsang Province, the CO_2-rich groundwater occurs in the sedimentary rocks of this supergroup [18].

3. Methods

Water samples were collected at wells and springs in Gangwon, Gyeongsang, and Provinces [13]. The pumped water samples were collected after being purged at the wells. Physico-chemical data such as temperature, pH, oxidation–reduction potential (Eh), electrical conductivity (EC), and dissolved oxygen (DO) were measured in situ using a multi-parameter meter (model: Orion 1230) by Gumi Water Quality Analysis Center, according to Korea's water quality standard [14]. The major cation and trace element concentrations of the water samples were analyzed by ICP-AES (Shimadzu ICPS-11000 III, Kyoto, Japan) and ICP-MS (FISONS PlasmaTrace, Winsford, UK) at the Korea Basic Science Institute and anions were analyzed by ion chromatography (Dionex 500, Conquer Scientific Lab Equipment, San Diego, CA, USA) at the Korea Atomic Energy Research Institute (KERI) [14]. Tritium and stable isotopes were analyzed by using a liquid scintillation analyzer (Model Parkard Tricarb 2770TR/SL, Packard Instrument Co., Inc., Meriden, CT, USA) and the stable isotope analyzer (Model VG SIRA II, VG, Middlewhic, Cheshire, UK and Micromass Optima, USGS, Reston, VA, USA) at KAERI, respectively.

3.1. Statistical Procedure

Many factors can contribute to uncertainty in geochemical monitoring data, including the accuracy and precision of sampling and analysis, the representativeness of sample size and timing, and the proficiency of the participants. A probabilistic approach in statistics means to obtain the likelihood of occurrence of a certain number of events using a random variable. A probabilistic approach is useful for processing and expressing potentially uncertain geochemical data. In this study, the PDF test, a statistical probability technique, was implemented in order to examine and compare geochemical characteristics between CO_2-rich and ordinary groundwaters, and then to discriminate key parameters for CO_2 monitoring.

The procedure employed for discriminating CO_2-rich versus ordinary groundwater is as follows: (1) Select the chemical components of the CO_2-rich and ordinary groundwaters; (2) Fit the chemical components through Kolmogorov–Smirnov, Anderson–Darling, and Chi-square tests; (3) Determine the statistical distributions of the respective chemical components; (4) Execute a Monte Carlo simulation to generate a PDF.

3.2. Goodness of Fit Test for Distribution

3.2.1. Kolmogorov–Smirnov Test

The Kolmogorov–Smirnov (K–S) test compares the empirical cumulative distribution function of the sample data and the predicted cumulative distribution function. The test rejects the predicted cumulative distribution function with the greatest deviation, D, between the predicted cumulative distribution function and the empirical cumulative distribution function. At least 1000 samples are needed for accurate judgment of the K–S test. D is determined by

$$D = \max\left|F(X_j) - \frac{n(j)}{N}\right| \tag{1}$$

Here, the sample size is N, $F(X_j)$ is the predicted cumulative density function, and $\frac{n(j)}{N}$ is the empirical cumulative density function. In other words, D means the maximum distance between

$F(X_j)$ and $\frac{n(j)}{N}$. At a certain confidence level (e.g., 95%), the null hypothesis (H_0) is rejected if D is greater than the critical value. One advantage of the K–S is that the test statistic does not depend on the theoretical distribution type (i.e., logarithmic normal, exponential, etc.) nor the sample size, but one disadvantage is that the test is susceptible to D at the central part of the distributions.

3.2.2. Anderson–Darling Test

The Anderson–Darling (A–D) test is a modified K–S test. The null hypothesis (H_0) is rejected if AD is greater than the critical value, with a certain confidence level (e.g., 95%). That is, the sample distribution does not mean the same population as the theoretical distribution. The A–D test is the tightest method among the statistical tests. AD is determined by

$$AD = -N - S \tag{2}$$

Here, $S = \sum_{i=1}^{N} \frac{1-2i}{N}[InF(X_i) + \ln(1 - F(X_{N+1-i}))]$. The A–D test is more advantageous than the K–S test when both tails have a better fit than the central part, while it is disadvantageous due to dependence of the critical value on the specific distribution type. Consequently, the A–D test has the disadvantage of calculating the critical values for each theoretical distribution.

3.2.3. Chi-Squared Test

The Chi-squared (χ^2) test is a method of determining χ^2 by dividing the square of the absolute values of the observed data and the expected values by the number of class sections.

$$\chi^2 = \sum_{i=1}^{n} \frac{[O(i) - E(i)]^2}{E(i)} \tag{3}$$

where $O(i)$ and $E(i)$ denote the observed data and the expected values, respectively, and n is the number of class sections. A smaller χ^2 is means a better fit.

3.3. *Probability Density Function*

Probability density functions use a continuous random variable X that can take a certain real number x. A continuous random variable (X) has infinite possible real numbers, with almost zero probability of taking any real number, and is determined by the probability, P, that X belongs to two real number intervals, x_0 and x_n.

$$P(x_0 \leq X \leq x_n) = \int_{x_0}^{x_n} f(x)dx \tag{4}$$

Here, n is the number of class sections and $f(x)$ is the average rate of change of the probability in the interval (x_k, x_n). The probability $P(X \leq x_k + \Delta x) - P(x_k)$ that X belongs to an arbitrarily small interval (x_k, $x_k + \Delta x$) is equal to the area of the kth interval, $f(x)\Delta x$:

$$f(x_k)\Delta x \cong P(X \leq x_k + \Delta x) - P(x_k) \tag{5}$$

or

$$f(x_k) \cong \frac{P(X \leq x_k + \Delta x) - P(x_k)}{\Delta x} \tag{6}$$

where $f(x_k)$ is the average rate of change of the probability in the interval (x_k, $x_k + \Delta x$).

3.4. *Monte Carlo Simulations*

Monte Carlo simulations involve random sampling and computer simulation to obtain approximate solutions to mathematical or physical problems, especially those with a certain range of probability values. This study adopted a Monte Carlo approach to determine the predicted chemical component values of the random variable through repeated simulation. For a Monte Carlo simulation, a stochastic model should be established based on the relationship between the chemical component variables. The Monte Carlo method was effectively applied in this study of a highly uncertain, non-Gaussian distributed, complex function, with relationships existing between variables.

3.5. Comparing the PDFs of the CO_2-Rich and Ordinary Groundwaters

The generated PDF can supply quantitative statistical results, including median, mean, and standard deviation, and qualitative results (i.e., distribution patterns), such as normal, exponential, or uniform. These quantitative and qualitative results were used to compare the geochemical characteristics of the CO_2-rich and ordinary groundwaters. To effectively compare the different geochemical characteristics, two QIs (QI_{tail} and QI_{shift}), estimated from the PDF test, were compared with the results of the Wilcoxon test and the *t*-test that determined non-parametric and parametric estimations. QI_{tail}, a quantitative index for the distribution pattern, and QI_{shift}, an index for distribution shift, respectively, are expressed as:

$$QI_{tail} = \frac{|MD_b - MN_c|}{|MD_b - SD_b|} \tag{7}$$

$$QI_{shift} = \frac{|MD_b - MD_c|}{|MD_b - SD_b|} \tag{8}$$

Here, MD_c and MN_c are the median and mean of comparative values, respectively, MD_b is the mean of background values, and SD_b is one standard deviation (1σ) of background values. If the indices are greater than one, the pair being compared is judged different. The larger the difference between the median and mean values, the bigger QI_{tail} becomes. This indicates that the concentration of the water-quality parameter has been partially increased due to the effects of CO_2-rich groundwater, resulting in a distribution that has a long and shallow tail to the right. If the concentration increases overall, QI_{shift} increases and the distribution simply shifts with a similar pattern.

One standard deviation (1σ) was used because it is more sensitive than two standard deviations (2σ) when discriminating object values from background values. Additionally, because the concentration of a water-quality parameter is typically increased when rock reacts with CO_2-rich groundwater, only the values higher than one standard deviation (>+1σ) located beyond the right side of the distribution were used.

4. Results and Discussion

4.1. Gangwon Province

In Gangwon Province, the CO_2-rich groundwater is classified into Na-type, Ca-type, and Ca-Na-type, whereas the shallow ordinary groundwater contains approximately equal concentrations of Na and Ca, as well as K and Mg. The temperature and pH of the CO_2-rich water were 10.4–19.4 °C and 5.5–6.4, respectively. The electrical conductance (EC) values of 454–2220 μS/cm indicate a large amount of dissolved ions. The partial pressure of CO_2 in the CO_2-rich water in Gangwon Province was $10^{-0.37}$–$10^{0.31}$ atm, calculated by SOLVEQ [18] using data on temperature, pH, and alkalinity [13] (Table 3). Seventeen components (temperature, pH, Eh, EC, DO, alkalinity, $\log P_{CO_2}$, TDS, Na^+, K^+, Mg^{2+}, Ca^{2+}, SiO_2, Cl^-, SO_4^{2-}, NO_3^- and F^-) were used for the PDF test. By quantitative comparison, the PDF distributions of the CO_2-rich and ordinary groundwaters were clearly distinguished by the 15 items other than temperature and Cl^-, with QI_{shift} larger than 1, and by the 16 items other than temperature, with QI_{tail} larger than 1 (Figure 2, Table 4). The comparison of the PDF test with the *t*-test and the Wilcoxon test showed the same result as the monitoring items except for the cases of Eh and NO_3^- (Table 5). In addition, the PDF test had more effective discrimination capability than the *t* and Wilcoxon tests by the criteria of skewness and kurtosis. A similar distribution of the parameters for the groundwaters was also identifiable by the criterion of a median within one standard deviation (Table 4).

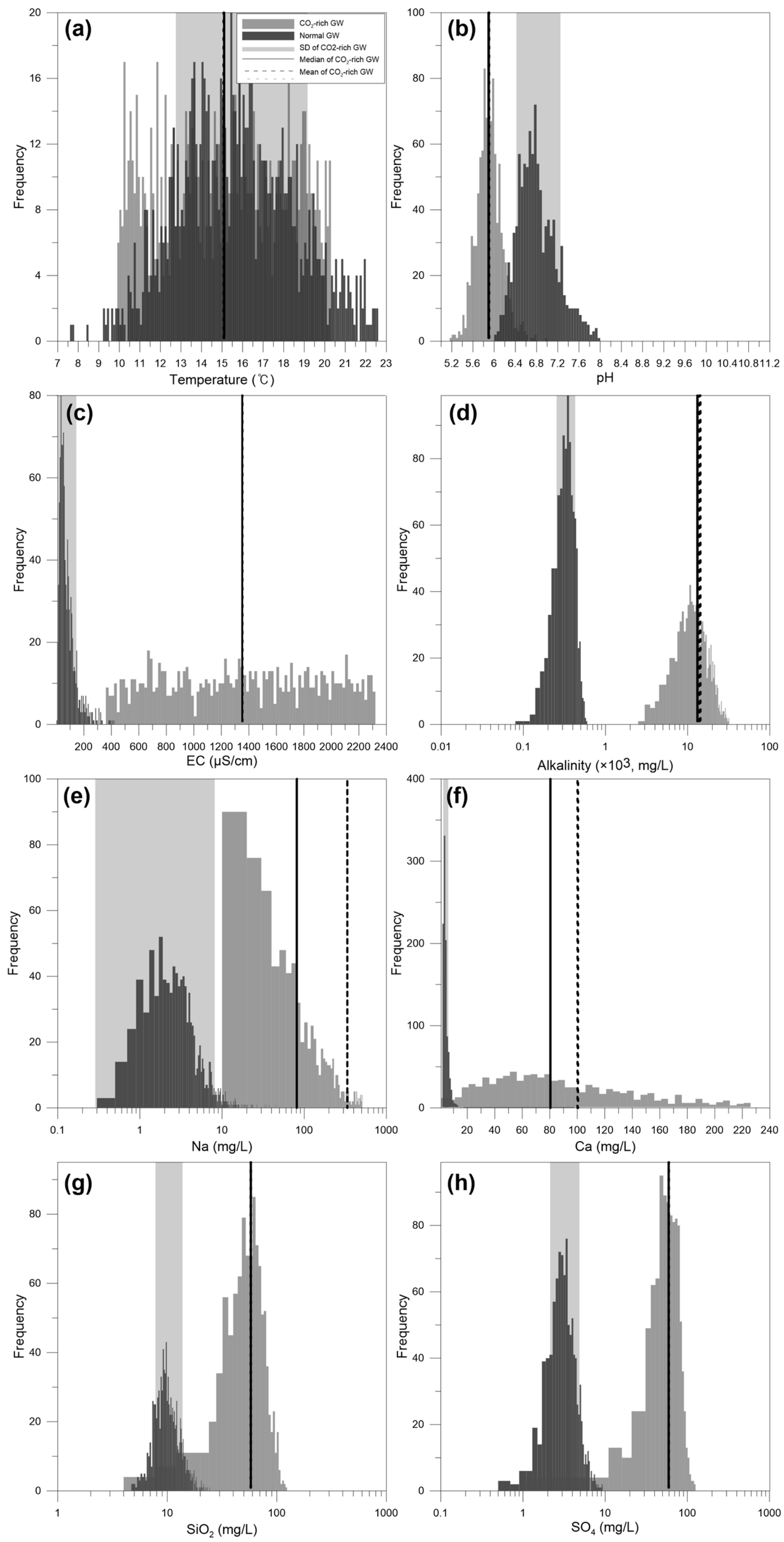

Figure 2. Probability density distributions of major parameters of CO_2-rich (gray) and ordinary (dark gray) groundwaters in the Gangwon Province. (**a**) Temperature, (**b**) pH, (**c**), EC, (**d**) Alkalinity, (**e**) Na, (**f**) Ca, (**g**) SiO_2, (**h**) SO_4.

Table 3. Geochemical data of water samples from Gangwon Province [13].

Water Type	Temp.	pH	Eh	EC	DO	Alkalinity	$logP_{CO_2}$ *	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	NO_3	F
	°C		mV	uS/cm	mg/L	* 10^3	atm	mg/L									
CO_2 rich water (Na-type)	19.4	6	113	1345	2.6	18.3	0	1628	345	23	1.6	31.5	79.6	7	12.9	0.1	7.5
	18.5	6.2	121	1348	3.1	19	−0.2	1773	419	25	2.1	44.6	87.7	8.3	13.8	0.1	7.7
	18.7	5.9	125.2	1268	3.8	21.3	0.15	2013	496	27.3	2.2	53.1	89	9.5	21.8	0.1	7.1
	18.2	6.2	131	2220	3.3	30.5	0	2624	544	32.1	2.6	57.1	93.1	2.5	22.4	0.1	7.1
	15.8	5.9	109.3	864	3.1	10.5	−0.15	1020	267	7.2	0.5	10.7	71.9	5	5	0.1	9.3
	15.4	6.1	132	1058	2.8	11.5	−0.32	1089	271	6.1	0.5	11	74	5.6	5.1	0.1	9.5
	13.4	5.9	124.5	1956	1.2	20.2	0.1	1845	455	13	5.2	54	61	8.3	8	0.1	4.9
	19.8	6.4	138	1871	1.5	21.5	−0.34	1921	457	10.5	5.1	53.2	60.1	8.6	7.3	0.1	4.8
CO_2 rich water (Ca-Na-type)	14.5	5.5	44.5	725	2.4	8	0.12	713	71.4	4.5	7.3	76.1	32.5	6.7	16.1	0.3	2.4
	16.2	5.7	150	778	2.1	8.5	−0.05	775	91.8	4	8.6	88.4	37.9	2.1	12.7	0.1	2.6
	17.6	5.9	154.1	1205	1.8	11	−0.14	1104	113	3.8	21.3	152	38.1	20.9	13.2	65.1	1.6
CO_2 rich water (Ca-type)	14.4	6	115.2	1528	3.5	16.2	−0.11	1463	32.3	4.2	25.7	293.8	76.1	2.9	21.1	0.1	0.9
	13.3	5.5	165	454	3.8	4.1	−0.17	419	6.6	0.5	9.7	72.5	54	3.3	13.6	0.1	1.7
	10.7	5.9	195	677	5.1	6.7	−0.37	642	15	2.7	11.9	109.7	60.8	2.6	10.5	0.3	1.5
	11.4	5.9	118	1034	1.6	12.5	−0.12	1055	37	2.3	35.4	162	36	2.3	4.3	0.1	0.6
	16.2	5.8	135.1	873	0.8	9.8	−0.1	855	14.8	1.6	36.1	140	35.1	2.1	9.2	0.1	0.2
	10.4	5.8	181	915	0.6	11.5	−0.06	964	15.5	4.6	37.2	140	39.2	2.3	7.8	0.1	0.3
	14.1	5.8	108	921	2.1	10	−0.1	834	15.2	2.9	46.1	93	30.2	2.1	7.6	0.1	0.4
	12.4	5.5	164	1098	3.6	13.2	0.31	1140	35.9	3.3	20.9	198.1	48.4	2.9	8.2	0.1	0.8
Shallow GW	20.2	6.6	173.5	125	5.8	0.5	−2.17	86	15.1	1.1	1.5	5.3	12.3	11.2	8	1.4	2.3
	13.7	6.5	242.5	69	7	0.4	−2.15	63	6	0.7	1.6	3.7	19.4	4.8	1.4	0.4	0.4
	19.5	6.3	144	271	6.5	0.3	−2.06	47	3.4	0.5	0.6	3.1	13.9	1.5	2.8	2.7	0.3
	17.1	6.3	171	35	6.3	0.3	−2.14	39	3.1	0.5	0.6	3.5	10.1	0.9	2.5	2.3	0.2
Surface W	20.5	6.7	177.2	34	8.7	0.2	−2.61	34	2.3	0.5	0.5	2.5	9.2	1	3.3	1.7	0.3
	15.3	6.8	118.4	57	7.5	0.3	−1.51	46	2	0.6	0.5	2.8	10.3	0.9	2.8	0.9	0.4
	13.4	7.8	144	53	9.4	0.4	−3.44	52	2.1	0.5	0.9	6.8	9.9	1	4.1	1.4	0
	13	7.5	174	47	9.1	0.3	−2.27	46	3.3	0.6	0.7	5.1	10.1	1.2	4.3	1.4	0.1
	10.2	6.9	177	60	9.6	0.4	−2.63	47	1.9	0.5	0.1	8.1	8.4	0.9	4.5	1	0.1
	14.5	6.8	157.1	94	9.4	0.4	−2.45	56	6.9	1.7	1.4	3.7	7.5	3.7	3.4	2.4	0.5
	15.2	6.9	157.2	29	6.4	0.2	−2.96	29	1.8	0.4	0.6	3.3	6.4	0.7	2.2	4.2	0.1
	17.2	6.9	151	46	8.7	0.4	−2.5	54	3.6	0.9	1.7	3.6	11.8	1.7	2.8	1.5	0.1

Note: * Calculated from measured alkalinity and pH data, using computer code SOLVEQ [19].

Table 4. Result of probability density function (PDF) verification for CO_2-rich and ordinary groundwaters in Gangwon Province.

Statistical Value	Temp.	pH	Eh	EC	DO	Alkalinity	$logP_{CO_2}$	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	NO_3	F
MD_b	15.6	6.8	165.4	59.7	7.7	0.3	−2.4	48.4	3.4	0.6	0.8	3.8	10.1	1.8	3.2	1.7	0.3
MD_c	15.1	5.9	134.1	1348.5	2.5	12.8	−0.1	1505.0	82.9	5.8	6.8	80.2	58.5	4.3	58.3	0.1	2.5
MN_c	15.2	5.9	132.9	1321.2	2.6	14.2	−0.1	1448.4	273.8	10.2	18.3	99.0	59.2	5.5	58.1	0.2	3.7
$1SD_b$	12.7 (below)	6.4 (below)	138.8 (below)	155.4 (above)	6.4 (below)	0.4 (above)	−1.9 (above)	62.9 (above)	8.0 (above)	1.1 (above)	1.4 (above)	6.7 (above)	13.5 (above)	4.6 (above)	5.0 (above)	0.9 (below)	0.7 (above)
QI_{shift} (Crit = 1)	0.2	2.3	1.2	13.5	4.0	125.0	4.6	100.5	17.3	10.4	10.0	26.3	14.2	0.9	30.6	2.0	5.5
QI_{tail} (Crit = 1)	0.1	2.	1.2	13.2	3.9	139.0	4.6	96.6	58.8	19.2	29.2	32.8	14.4	1.3	30.5	1.9	8.5

Table 5. Result of comparing PDF test with *t*-test and Wilcoxon test in Gangwon Province (0 means acceptance = no difference; 1 means rejection = difference).

Test	Temp.	pH	Eh	EC	DO	Alkalinity	$logP_{CO_2}$	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	NO_3	F
t-test (two tails)	0	1	0	1	1	1	1	1	1	1	1	1	1	1	1	0	1
Wilcoxon test (rank sum)	0	1	0	1	1	1	1	1	1	1	1	1	1	1	1	0	1
PDF test	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

As such, the 15 items of pH, Eh, EC, DO, alkalinity, log P_{CO_2}, TDS, Na^+, K^+, Mg^{2+}, Ca^{2+}, SiO_2, SO_4^{2-}, NO_3^-, and F^- were determined to be effective markers for CO_2 monitoring in the granite and banded gneiss areas of Gangwon Province.

4.2. Gyeongsang Province

In Gyeongsang Province, pH of CO_2-rich groundwater ranges from 5.9 to 6.4 with mean value of 6.23, slightly lower than the 6.5–6.7 (mean value of 7.21) of ordinary groundwater and the 6.6–7.6 of surface water. EC is high, 1406–3030 μS/cm. P_{CO_2} ranges from $10^{-0.40}$ to $10^{0.15}$ atm (the median of $10^{-0.18}$ atm) in carbonated groundwater, compared with $10^{-2.52}$–$10^{-2.09}$ atm in ordinary groundwater and $10^{-2.75}$–$10^{-1.54}$ atm in surface water [13,14]. The median P_{CO_2} of the CO_2-rich groundwater is $10^{-0.18}$ atm. (Table 6). Na^+ is dominant in high temperature and deep areas and Ca^{2+} is dominant in relatively lower temperature and natural groundwater areas [20,21]. Additionally, Ca^{2+} becomes dominant with the progress of carbonization. These phenomena in the Gyeongsang area imply that the natural environment is at relatively low temperature, or that the surrounding rocks are highly affected by gneiss, calcite, and dolomite, among others.

In Gyeongsang Province, the PDF test was performed using 21 components (Table 7). Most of the components of the ordinary and CO_2-rich groundwaters appeared distinctly as effective markers for CO_2 monitoring by the PDF test and by the *t* and Wilcoxon tests. However, the components of DO, Cl^-, SO_4^{2-}, Sr^{2+}, Na^+, and Li^+ were not suitable for use as markers (Figure 3, Table 8).

As such, 12 items (temperature, pH, Eh, EC, HCO_3^-, TDS, K^+, Mg^{2+}, Ca^{2+}, SiO_2, NO_3^-, and F^-) were determined as useful markers for CO_2 monitoring in the sedimentary rock areas of Gyeongsang Province. Trace elements such as Al^{3+}, Fe^{2+}, and Mn^{2+} were also discriminating, but were excluded because their concentrations were very low and because they were not analyzed at the other two provinces.

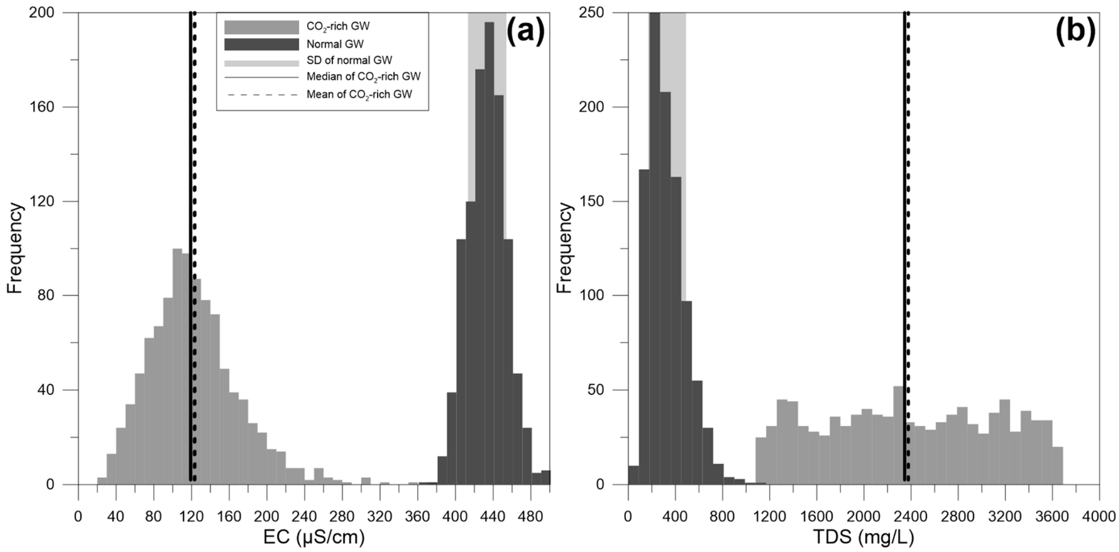

Figure 3. *Cont.*

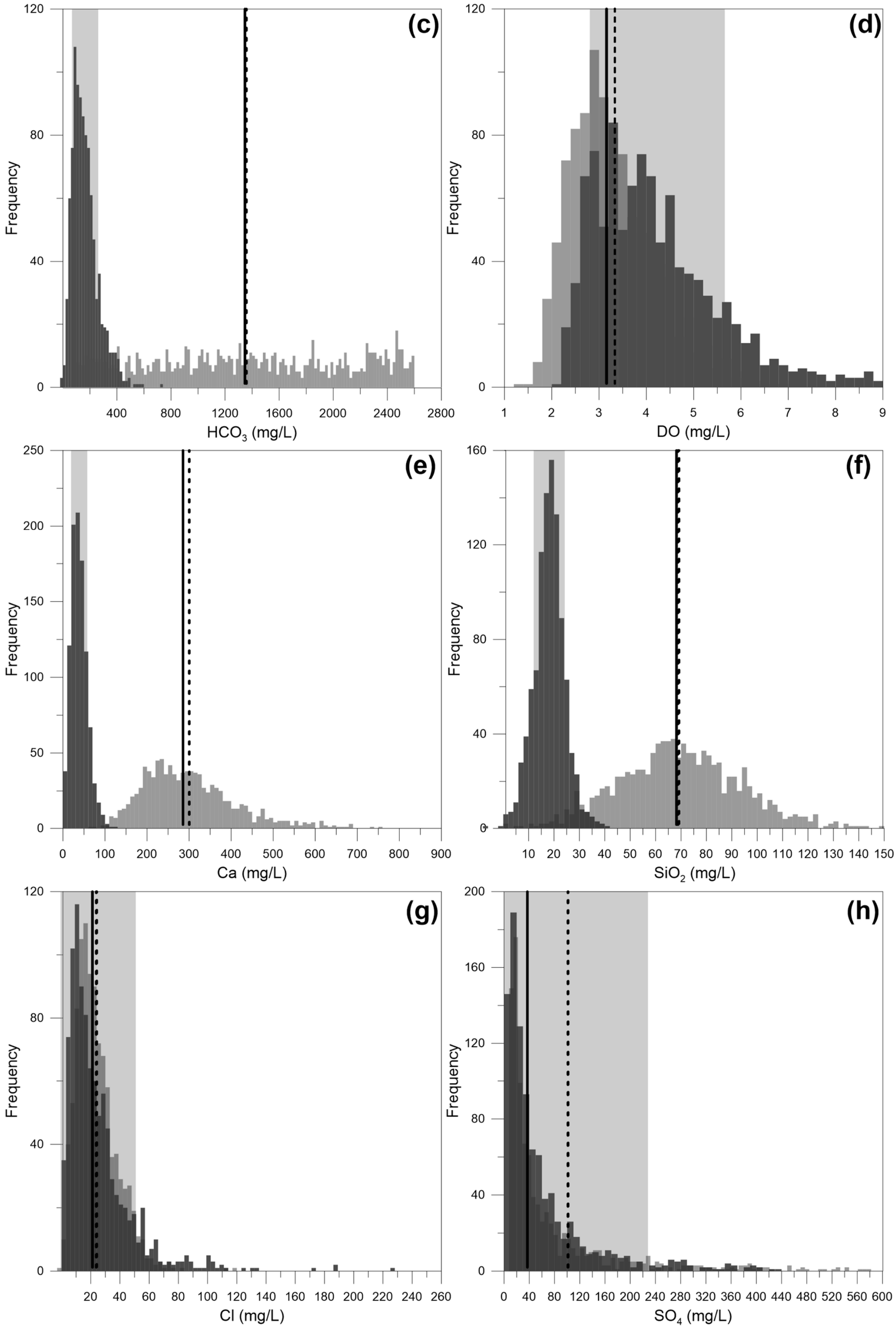

Figure 3. Probability density distributions of major parameters of CO_2-rich (gray) and ordinary (dark gray) groundwaters in Gyeongsang Province. (**a**) EC, (**b**) TDS, (**c**), HCO_3, (**d**) DO, (**e**) Ca, (**f**) SiO_2, (**g**) Cl, (**h**) SO_4.

Table 6. Geochemical data of water samples from Gyeongsang Province [13,14].

Water Type	Temp.	pH	Eh	EC	DO	$logP_{CO_2}$	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	HCO_3	F	NO_3	Sr	Fe	Mn	Al	Li
	°C		mV	µS/cm	mg/L	atm	mg/L															
CO_2 rich water	17.2	6.17	127.0	1554	2.7	−0.27	1409	60.6	3	43	231	56.5	41.4	49.4	919	1	0.2	1.49	1.23	0.89	0.22	0.23
	8.6	6.17	185.0	2340	4.2	0.09	3544	114.3	13.9	89.3	673.5	116.5	13.1	46.8	2469	0.6	0.3	3.04	0.12	3.22	0	0.37
	14.4	6.26	151.0	1961	2.5	−0.26	1713	80.9	4.3	65.2	252	73.6	9.7	13.5	1204	0.6	0	4.69	3.69	1.32	0.01	0.21
	17.1	6.25	65.0	1663	3	−0.25	1651	71	2.2	51.7	258	50.9	8.4	19.2	1169	0.9	0	14	4.73	1.07	0.02	0.38
	14.6	6.36	171.0	2620	3	−0.25	2273	76.8	4.8	70.8	378	95.2	12.5	17.3	1601	1.3	0	3.72	10.7	1.18	0.06	0.92
	16	6.33	93.0	2860	2.3	−0.11	2945	154	7.5	108	450	96.9	27	33.8	2045	2.3	0	4.67	14.6	1.43	0.01	0.37
	14.9	6.27	149.0	1722	4.5	−0.31	1575	67.8	4.2	44.6	253	61.8	14.1	22.6	1101	1.8	0	2.57	0.02	1.27	0.01	1.01
	12.9	6.55	171.0	3016	4.5	−0.4	2562	133	8.1	91.6	368	100.3	29.4	34.4	1789	2.4	0	4.6	0.02	1.47	0.02	0.75
	12.1	6.32	120.0	2770	2.9	−0.21	2340	115	7.3	84.4	343	76.2	22.3	31.4	1645	1.9	4	3.33	4.97	1.66	0	0.12
	20.9	6.70	174.0	1406	7.3	−1.44	1235	71.5	2.6	24.4	255	21.6	5.9	635.2	202	0.7	4.8	11	0.03	0.02	0	1.12
	19.1	6.03	108.0	1999	3.9	−0.13	2025	168	10.3	67.2	288	52	30.1	479.1	923	0.6	0.2	1.64	2.14	3.14	0.24	0.25
	16.9	6.31	183.0	1697	4	−0.36	1519	184	6.8	45.3	153	35.9	19.8	34.1	1033	1.1	0.9	2.61	1.82	0.48	0.06	0.64
	15.4	5.94	98.0	2280	2.4	0.15	2218	210	8.8	61.3	273	77.2	37.5	34.2	1498	1.6	0	3.24	12.4	1.47	0.06	1.18
	15.2	6.04	34.0	1864	2.3	−0.04	1761	154	7.4	46.5	205	66.1	51.6	31.3	1182	1.4	0	2.36	11.8	1.79	0.05	0.84
	16.2	5.96	65.0	1459	2.3	−0.11	1325	101	6.1	34.8	140	50.5	33.3	36.4	910	1.1	0	1.65	9.17	2.11	0.04	0.57
	12.8	6.33	167.0	3030	3.1	−0.1	3144	318	9.7	79.1	391	82.6	24.6	43.4	2167	2.1	0	4.42	19.8	2.1	0.22	1.86
	16.6	6.16	63.0	1911	2.8	−0.13	1852	172	5.5	56.5	230	59.9	20.9	30.2	1263	1.4	0	2.29	8.7	1.49	0.1	1.05
Acidic water	22.5	2.74	495.0	1342	3.8		566	16.6	0.5	15.1	19.3	111.3	7.1	327.5		0.3	1.5	0.08	62.8	4.08	33.3	0.02
	18.5	2.40	641.0	5520	2.7		5684	5.4	1.3	48.3	85	154.2	14.5	3680		39	0	0.27	1650	6.42	0.0005	0.21
GW	16.6	6.66	145.0	77	4.1	−2.09	64	4.4	0.9	1.6	6.3	12.1	0.1	0.1	39	0	0	0.04	0.02	0.02	0.389	0.0001
	22.4	6.50	158.0	41	6.5	−2.52	42	3.8	0.7	0.7	2.2	13.6	4.8	5.9	9	0.3	0.5	0.02	0.02	0.02	0.01	0.0006
	20.4	6.69	118.0	126	5.4	−2.14	107	6.5	4.4	2.9	12.5	13.6	9.2	9.6	36	0.3	11.9	0.1	0.02	0.02	0.002	0.0061
Surface W	20.2	6.58	275.0	148	5.9	−1.88	118	8.8	1.3	2.2	13.7	17.3	5.8	15.9	52	0.2	1.4	0.06	0.03	0.02	0.012	0.0003
	22.3	7.64	198.0	388	7.1	−2.75	191	13.5	3.6	8.5	23.4	19.7	9.9	25.6	79	0.3	7.6	0.17	0.02	0.02	0.003	0.0013
	5.6	6.70	170.0	279	7.8	−1.54	294	16.1	2.5	11.5	45.6	16.7	9.5	11.7	176	0.1	4	0.3	0.02	0.02	0.001	0.0006

Table 7. Result of PDF verification for CO_2-rich and ordinary groundwaters in Gyeongsang Province.

Statistical Value	Temp.	pH	Eh	EC	DO	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	HCO_3	NO_3	F	Al	Fe	Mn	Sr	Li
MD_b	17.0	7.2	429.0	573.5	3.6	455.5	33.0	1.9	15.4	67.4	19.7	24.6	32.8	265.2	18.4	0.2	5.0	34.6	8.5	13,630	26.4
MD_c	15.5	6.3	121.0	2212	3.4	2454	120.9	6.5	60.0	279.2	68.5	20.9	31.7	1360	0.0	1.2	44.0	9783	1623	7493	474.0
MN_c	15.5	6.2	126.8	2202	3.3	2406	130.5	6.4	62.2	299.1	68.7	23.5	97.2	1338	0.9	1.3	64.7	9710	1581	7615	676.8
$1SD_b$	15.7	6.8	325.0	1658	0.9	1303	162.7	3.9	51.2	112.7	24.1	5.9	149.8	539.2	0.0	0.8	29.2	94.5	109	5483	912.4
QI_{shift} (Crit = 1)	1.2	2.1	3.0	1.5	0.1	2.4	0.7	2.3	1.2	4.7	11.2	0.2	0.0	4.0	1.0	1.7	1.6	163.0	15.9	0.8	0.5
QI_{tail} (Crit = 1)	1.2	2.1	2.9	1.5	0.1	2.3	0.8	2.3	1.3	5.1	11.2	0.1	0.6	3.9	1.0	1.9	2.5	161.7	15.5	0.7	0.7

Table 8. Result of comparing PDF test with *t*-test and Wilcoxon test in Gyeongsang Province (0 means acceptance = no difference; 1 means rejection = difference).

Test	Temp.	pH	Eh	EC	DO	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	HCO_3	NO_3	F	Al	Fe	Mn	Sr	Li
t-test (two tails)	0	1	1	1	0	1	1	1	1	1	1	0	0	1	1	1	1	1	1	0	1
Wilcoxon test (rank sum)	1	1	1	1	0	1	1	1	1	1	1	0	0	1	1	1	0	1	1	0	1
PDF test	1	1	1	1	0	1	0	1	1	1	1	0	0	1	1	1	1	1	1	0	0

4.3. Chungcheong Province

The CO_2-rich water in Chungcheong Province is characterized by very low pH (~4.0) and low TDS, lower than adjacent ordinary groundwaters [13] (Tables 9 and 10). In Chungcheong Province, 18 components (temperature, pH, Eh, EC, DO, alkalinity, log P_{CO_2}, TDS, Na^+, K^+, Mg^{2+}, Ca^{2+}, SiO_2, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, and F^-) were used for the PDF test. Figure 4 shows the comparative result of the PDF of the components between the CO_2-rich and ordinary groundwater in the province.

The temperature distribution is very similar, both quantitatively and qualitatively, whereas the pH distribution has identical shape but is shifted to the left due to lower pH in the CO_2-rich groundwater than in the ordinary groundwater. The distributions and the statistical values of TDS and EC were identical between the CO_2-rich and ordinary groundwaters based on the correlation between TDS and EC (Figure 4).

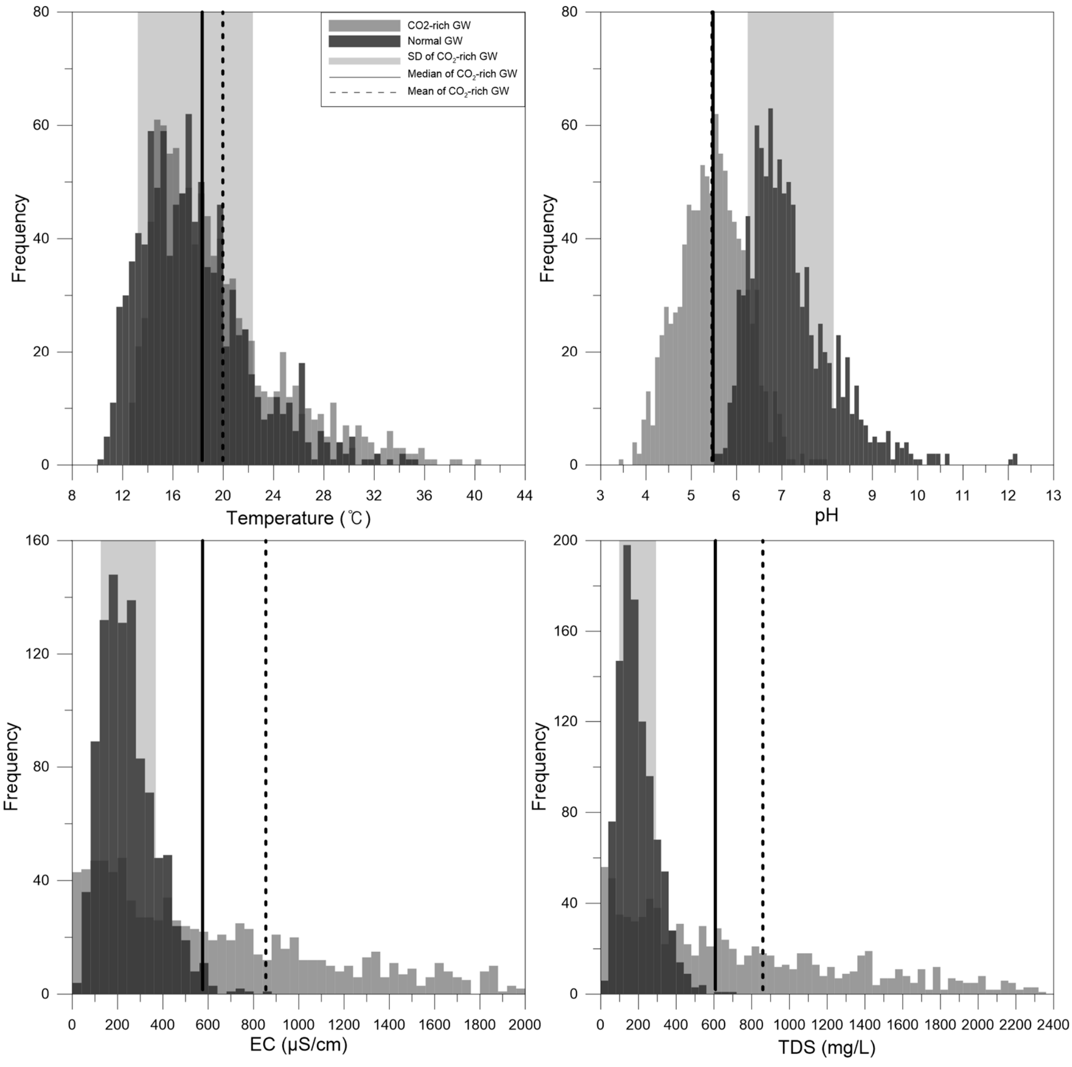

Figure 4. Comparison of temperature, pH, TDS, and EC of CO_2-rich (**gray**) and ordinary (**dark gray**) groundwaters in Chungcheong Province.

Table 9. Geochemical data of CO_2-rich water samples from Chungcheong Province [13].

Location	Temp. (°C)	pH	Eh (mV)	EC (μs/cm)	DO (mg/L)	$logP_{CO_2}$(atm)	Alkalinity (meq/L)	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	HCO_3	F	NO_3
								mg/L										
Chojeong	19.7	6.54		280	7	−1.62	1.44		18.4			27.3	39.6	26.3	12.8			14.9
	15.9	6.48		151	7.1	−1.67	1.13		5.5			13.4	20.1	2.1	1.9			2.4
	14.6	5.68		184	7.9	−0.96	0.95		12.2			17.1	24.7	11.2	24			0
	15.7	7.26		109	6.3	−2.61	0.79		9			10.2	32.2	2.9	1.6			4
	14.8	6.32		467	6.5	−0.9	5.27		13.4			73.6	47.1	6.3	1.9			5.3
	14.9	6		261	6.2	−0.84	2.75		11.7			34.9	43.8	6.2	1.6			5.2
	16.4	6.47		649	2.3	−0.9	7.38		27.2			108	71.5	1.9	4			0
	14.2	7.16		260	5.3	−2.06	2.46		20.4			30.4	29.6	7.5	12.4			0
	14	6.86		206	5.7	−1.9	1.67		4.8			29	14.3	6.2	3.3			14.2
	13.9	6.32		152	3.3	−1.43	1.4		6.7			21.8	15.4	5.7	5.6			10.2
	18.7	6.79		188	6	−2.06	0.95		7.1			15.9	22.5	4.2	3.5			7.3
Jungwon	24.9	9.5	−128	296	2.8	−4.56		254	68.4	0.3	0.1	1.9	17.2	6	6.4	95	12.4	0
	24.7	9.1	−136	167	6.3	−4.23		168	31	0.5	0.2	7.4	19.4	1.9	7.2	72	6.6	0.3
	23.5	7.5	−20.8	288	0	−2.33		287	40.3	1.9	4.2	22.5	25.4	24.5	15.9	150	1.9	0
	20.5	7	−29.5	489	0	−1.94		221	11.5	3.1	2.9	30.5	25.4	7.2	17.2	120	0.2	3.1
	17.5	6.7	36.4	198	0	−1.74		185	11.8	1.8	3.3	24.1	16	9.4	14.4	98	0.8	5.6
	15	7.2	−21.2	205	2.7	−2.61		138	8.9	0.9	2.4	18.7	20.1	5.2	16.3	56	0.3	8.9
	16.6	7.5	−13.6	179		−2.65		160	13.8	1.4	2.3	17.9	17.1	6	13.3	76	0.9	11.3
	19	7.7	−15.6	182	3.3	−2.95		152	9.1	0.9	3.5	18.2	28.5	4	16.9	59	0.5	10.3
	23.7	6.9	34.9	68	7.1	−2.44		78	5.4	0.5	1	7.9	22.3	1.3	3.5	28	0.7	7.5
Munkyeong	30.4	9.1	−125	135	0	−4.62		104	23.4	0.2	0	8.6	19.5	5.3	5.3	27.1	11.5	0.7
	24.1	9.4	−128	158	2.4	−4.84		116	31.7	0.2	0	4	18	5	5.5	35.6	9.4	0.8
	26.6	10.39	−84	151	9.4	−6.41		72	23.6	0.3	0	5.7	0.8	3.3	6.4	11.8	8.6	0
	30.2	9.46	−122	132	2.3	−4.97		107	23.2	0.3	0	6.5	22.3	4.1	7.2	27.9	10.8	0.1
	13.9	7.48	−118	571	1.6	−2.13		471	63.8	2	5	49	34	27.2	6.2	255.1	15.8	0
	11	7.58	−133	522	2.7	−2.28		447	66.9	1.1	4.3	44.5	31.7	27.6	7.6	236.8	16.2	0
	15.4	6.87	−90.5	487	2.7	−1.48		437	25.9	3	16.5	53.5	33	19.5	3.2	272.4	1.8	6.6
	15.4	6.79	12.8	477	3.9	−1.4		434	28.9	1.9	15.8	52.8	29.5	19.1	2.7	274.1	1.8	6.8
	12.8	8.03	−80.2	184	5.6	−3.24		174	9.3	1.6	4.9	18.5	30.2	12	1.9	68.7	0.3	25.3
	14.4	7.31	−20.4	365	6.4	−2.93		311	10.9	3.2	14.9	44	31.9	4.9	163	27	0.1	10.8
	14.1	6.93	−10.4	367	7.4	−2.46		296	13	2	9.9	44.6	28.7	4.5	149.5	33.6	0.1	9.2
	13.4	7.13	−58.4	81	6.6	−2.79		80	7.8	1.8	0.5	6.7	25.3	3.1	3.2	23.9	1.8	6.2

Table 9. *Cont.*

Location	Temp. (°C)	pH	Eh (mV)	EC (μs/cm)	DO (mg/L)	$\log P_{CO_2}$(atm)	Alkalinity (meq/L)	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	HCO_3	F	NO_3
								mg/L										
Deajung	16.8	7.67	141	250	5.6	−2.59		236	10.5	2.5	5.3	33.4	28.3	3.6	8.8	142	1.4	0
	17.8	7.55	185	255	5.8	−2.52		172	11	2.6	5.7	29	0	3.5	2.2	116	0.5	0.6
	13.9	6.23	208	180	6.1	−1.3		174	11.2	2	5.4	16.1	34	5.3	3.6	88	0.4	7.8
	16	6.52	161	222	5.6	−1.54		189	11	2.4	6.3	22	34.2	4.9	1.7	104	0.5	2.3
	16.8	6.56	264	244	6.6	−1.53		256	59.1	0.7	0	0.1	33.4	4.8	4.8	152	0.8	0.7
	14.8	6.43	228	200	7.2	−1.44		185	11.5	1.7	5.3	21.1	31.9	5.2	4.7	98	0.3	5.4
	21.6	6.63	146	262	5.5	−1.6		87	11	2	6.6	26	30	5.1	3.7	110	0.4	4.3
	17.5	6.72	272	205	5.8	−1.73		187	11.4	1.8	5.4	21.5	31.7	5	5.2	99	0.3	5.1
	16	6.36	266	126	3.9	−1.69		113	7.6	0.9	3.7	11.3	21.6	4.7	3.4	55	0.1	4.3
	18.4	5.88	156	184	4.7	−1.16		128	9.8	1.5	4.2	12.3	30	6.3	1.6	55	0.3	6.9
Bugang	15.5	7.08	128	314	8.4	−1.99		266	14.9	1.8	3.9	37.7	24	13.9	16.1	143	1.2	8.7
	17.6	6.52	90	313	5.8	−1.44		247	16	1.8	4.3	43	25.7	14.5	5.5	131	1.1	3.5
Myeongam	11.2	7.1	128	234	9.9	−2.08		204	8.9	1.4	4.8	29.6	20.1	6	5.3	122	0.7	4.9
	22.9	6.67	139	300	4.7	−1.47		87	11	1.9	7.4	42	25.7	5.3	2	162	0.4	1.7
Daepyeong	16.4	6.65	313	77	4.9			115	8.7	0.7	2.2	11.7	24.5	4.2	3.6	46	1.1	18.2
	20.2	6.46	153	207	4.5	−1.48		166	10.8	1.6	5	18.3	17.1	9.5	6.1	96	1.5	0.1
	20.4	6.78	121	195	6.5	−1.88		151	11.8	2.6	4.7	17.1	19.4	8.6	2.6	82	0.1	0.9
	27	8.23	67	118	5.7	−3.5		93	7	2.7	3.2	11.2	8.9	5.3	1.5	52	0.6	0.4
	12.4	6.94	66	261	11.2	−1.92		212	14.5	3.7	4	25.8	13.6	11.6	17.6	110	0.8	10.2
	16.2	7.01	19	341	4.9	−1.91		260	21.2	4.8	5.7	38.5	20.8	20.1	5.8	140	0.4	1.6
	12.7	7.3	58	130	8.65	−2.78		97	6.3	1.2	2.2	13	13.3	10	6.4	37	0.6	7
	17.8	7.75	95	139	5.47	−3.21		87	7.6	1.5	2.5	14	17.6	6.3	2.3	52	0.4	1.3

Table 10. Geochemical data of ordinary water samples from Chungcheong Province [13].

Location	Temp. (°C)	pH	Eh (mV)	EC (μS/cm)	DO (mg/L)	$logP_{CO_2}$ (atm)	Alkalinity (meq/L)	TDS	Na	K	Mg	Ca	SiO_2	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-
								mg/L										
Chojeong	18.9	5.35		710	8.1	0.26	7.54		30.7			115	41.5	33.3	16.3			4.8
	20.8	5.08		350	3.6	−0.09	1.67		29.3			40.8	45.6	36.7	18.4			55
	17.8	5.13		258	4.6	−0.24	1.36		24.4			28.1	35.1	26.4	20.5			22.7
	16.6	5.82		429	4.5	−0.53	3.58		17.2			57.8	39.8	31.2	15.2			15.9
	17.6	5.28		467	3.6	−0.04	3.17		28.5			65.5	49.4	29.3	10.7			50.7
	19.4	5.75		600	2.6	−0.22	6.48		13.2			102	63.3	19.5	12			0.2
	15.2	5.55		1012	0.8	0.21	11.3		28			170	56	5.8	4.9			0.8
Jungwon	28.4	6.3	34.5	2830	2.1	−0.03		2721	245	11.3	39.5	363	96.9	20.1	17.7	1895	4	0
	19.5	5.7	24.5	1823	0.2	0.38		2009	118	2.6	36.3	276	81.3	12.1	4.8	1464	4.8	0
	26.2	6	84.9	1748	1.6	0.09		1859	111	2	49	246	69.1	8.4	6.4	1355	2.2	0
	23.9	6.1	50.4	1250	2.3	−0.23		1173	80	2.2	20	154.7	92.1	12.2	9.5	799	3.5	0
Munkyeong	30.2	6.4	47.8	2260	0	−0.27		1976	86.6	3.2	41.8	364.4	24.8	10.9	73.3	1365	1.4	0.9
	26	6.3	−9.7	2280	1.1	−0.15		2516	77.8	3.8	37.6	491.6	148	9	190.8	1544	1	0.1
	26.9	5.91	−20.6	980	2.2	−0.33		769	34.7	1.7	21	127	44.9	13.5	132.4	383	2.9	2
	24.9	6.17	−40.1	2035	3.4	−0.1		1969	74.2	2.6	43.8	344	111.5	12.7	79.3	1280	1.2	8.3
	18.6	6.44	−90.5	466	5.7	−1.06		400	20.7	1.3	10.2	53.2	37.2	9.2	6.4	256.6	0.9	0
	29.2	5.91	−49.7	1765	0.2	0.17		1831	80.5	2.6	35.3	316	127.8	33.9	3.1	1217	3.8	0
	21.2	6.21	−42.8	1825	2.9	−0.17		1810	79.8	2.8	33.6	307	116.6	16.6	2.3	1233	1.5	0
	25.9	6.39	−96.9	2450	1.4	−0.14		2682	81.1	3.4	47.3	398	131.6	11.9	5.1	1843	3.1	0
	22.5	6.46	−97.8	2426	2.5	−0.24		2588	85.5	3.1	41.8	394	133.5	10.7	3.7	1779	2.2	0
	32.7	5.85	−70	2150	2.3	0.35		2286	88.5	3.1	42.9	404	145.7	10.7	2.8	1571	2.3	0
	25	6.32	−30.3	775	3.1	−0.66		738	31.1	1.3	10.5	129	51.4	4.3	35.1	466.4	2.7	0
	25.8	6.16	−84	717	2	−0.59		585	29.9	1	8.6	95.9	49.7	3.3	16.6	374.1	3.2	0
	26	6.22	−35	2110	5.8	−0.06		2260	79.9	2.7	43.7	408	127.5	8.3	1.2	1570	2.5	0
	28.9	5.83	−82	1362	1.7	0.11		1359	61.6	2.9	18.5	230	114.9	21.4	5.9	882.4	5.7	0
Deajung	15.8	5.14	135	306	0.8	0.3		332	9.5	1.6	12.6	44.5	14.3	18.2	3.3	220	0.9	0
	15.6	5.16	358	337	2.5	0.22		374	10	2.6	15	47	15.1	16.8	1.7	253	0.4	2.2
	13.9	4.69	307	130	1.6	0.01		119	5.7	3.4	2.3	15.4	27.2	5.7	2.1	56	0.3	0.4
	16.3	4.04	148	67	4	0.01		57	5.3	1.8	1.5	8.7	32.1	4.8	1.9	55	0.4	0.3
	15.7	4.33	242	120	0.5	0.09		89	9.2	1.4	1.7	4.5	28.9	10.2	4.1	26	0.4	1.5
	15.6	4.35	252	105	2.9	−0.16		78	9.8	1.6	1.7	4.3	15.4	9.7	3.3	30	0.4	1.3
	14.6	4.43	350	82	4.5	−0.11		87	7.6	0.9	1.1	5	37.5	5.6	1.4	21	0.6	5.4
	16.5	4.73	209	91	4.5	−0.28		89	7.9	0.9	1.2	5.3	38.5	5.4	0.9	24	0.6	3.9
	16.8	4.46	267	95	2.7	−0.13		84	8.3	1	1.6	4.1	32.1	6.8	4.6	24	0.4	0.5
	17.5	4.33	252	98	3.7	0.01		93	8.5	1	1.9	7.3	34.2	5.9	4.4	29	0.5	0.2
	14.9	4.36	261	97	1	−0.2		74	7	1.9	1.3	2.4	31.5	7.3	0.7	17	0.4	3.5
	15.3	4.35	151	83	3.5	−0.05		84	7.7	2.3	1.5	2.8	34.2	4.6	0.2	28	0.4	1.5

Table 10. *Cont.*

Location	Temp. (°C)	pH	Eh (mV)	EC (μS/cm)	DO (mg/L)	$\log P_{CO_2}$ (atm)	Alkalinity (meq/L)	TDS	Na	K	Mg	Ca	SiO_2	Cl^-	SO_4^{2-}	HCO_3^-	F^-	NO_3^-
								mg/L										
Daepyeong	16.6	5.03	176	138	0	0.27		132	10	2.2	3.1	9.8	36.8	18.9	0.6	31	0.1	18.5
	14.2	4.95	164	146	0	0.5		144	11.2	2.6	2.9	11.1	47	10.3	1.5	50	0.2	6.8
	15.2	4.85	185	128	0	0.61		125	10.3	2.3	2.6	10.3	40.4	3.8	0.7	49	0.2	4.8
	14.5	4.8	175	101	0	0.39		89	9.6	1.4	1.6	5.1	27.2	6	1.8	27	0.1	8.5
	16	4.95	353	71	2.1			123	9.1	1.4	2.1	8	35.9	4.4	0.9	55	0.4	3.6
	15.7	5.07	368	88	1.9			147	10.5	1.7	2.6	9.4	44.5	7.6	1.1	67	0.3	4.5
	14.9	4.99	299	62	3.6			96	8.7	1	1.6	5.4	25.3	5.4	2	39	0.3	6.4
	17.2	5.29	261	78	3.8			163	10.8	1.3	5.9	8.4	36.5	7.4	3.6	71	0.4	3.1
	19.3	5.04	312	92	4.3			130	10	1.6	2.9	9.1	38.1	11.9	0.4	48	0.6	15.1
	14.5	6.03	60	1579	6.1	−0.06		1547	71.8	2.4	17.5	261	73.8	6.2	7.5	1098	2.2	0
	15.8	5.9	180	1613	2.6	0.04		1471	69	2.6	19	230	74.9	4.8	2.5	1059	2.7	0
	12.8	6.04	107	586	6.1	−0.6		468	54.6	3.2	11.5	48	22.3	11.9	15.4	295	0.8	0.1
	15.8	5.47	105	612	4.9	−0.03		535	60	3.5	14	57	25.7	11.4	5.1	353	1	0

Na^+, Ca^{2+} and Mg^{2+} show a similar tendency between the CO_2-rich and ordinary groundwaters. In this case, the median concentration is often located between the lower and upper limits of one standard deviation of the background values. Therefore, it is better to use the mean instead of the median for distinct quantitative identification when the tail (normally right side) of the probability distribution extends in one direction. Even though the probability distribution of K^+ in the CO_2-rich groundwater shifts slightly to the right (i.e., the direction of high concentration), those of the CO_2-rich and ordinary groundwaters cannot be distinctly distinguished, neither qualitatively nor quantitatively (Figure 5).

By comparing the QI_{shift} and QI_{tail} of the PDF test with the *t*-test and Wilcoxon test in Chungcheong Province, nine effective markers (pH, EC, log P_{CO_2}, TDS, Na^+, Mg^{2+}, Ca^{2+}, SiO_2, and HCO_3^-) were identified (Tables 11 and 12).

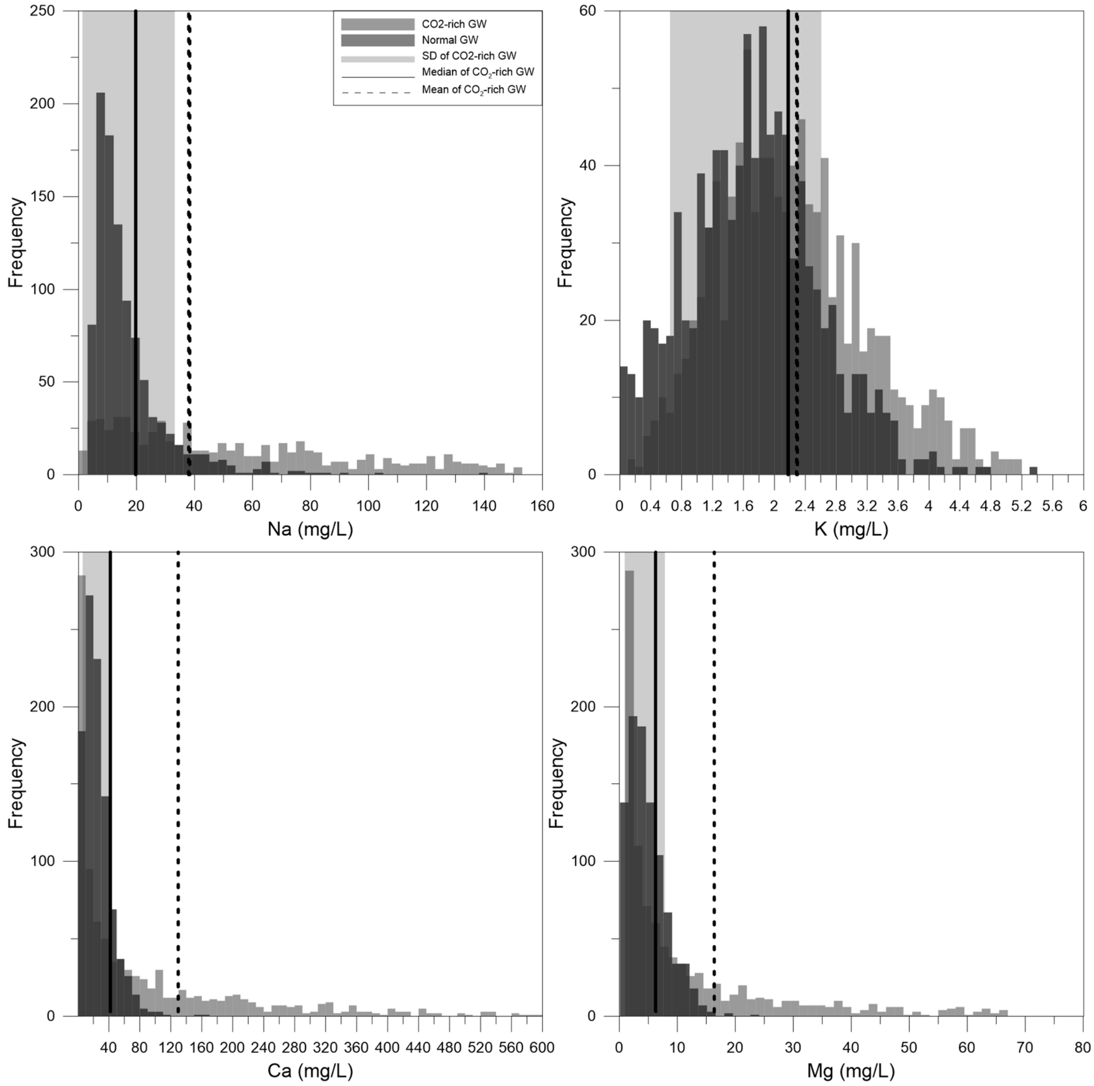

Figure 5. Comparison of Na^+, K^+, Ca^{2+}, and Mg^{2+} of CO_2-rich (**gray**) and ordinary (**dark gray**) groundwaters in Chungcheong Province.

Table 11. Result of PDF verification for CO_2-rich and ordinary groundwaters in Chungcheong Province.

Statistical Value	Temp.	pH	Eh	EC	DO	$\log P_{CO_2}$	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	HCO_3	F	NO_3
MD_b	16.52	7.02	45.61	223.0	5.33	−2.08	174.0	13.11	1.64	3.72	20.6	24.88	6.38	4.84	81.18	0.84	3.61
MD_c	18.01	5.44	120.97	576.0	2.63	−0.06	587.0	19.75	2.13	5.94	39.14	46.14	9.30	4.49	200.85	0.88	3.43
MN_c	20.03	5.43	127.80	825.25	2.60	−0.05	882.58	40.30	2.28	14.91	125.39	57.95	12.62	13.93	607.78	1.56	4.04
$1SD_b$	22.33	6.25	184.08	377.3	2.70	−1.26	286.77	37.84	2.70	7.57	46.80	34.23	151.27	41.85	168.88	8.21	10.59
QI_{shift} (Crit = 1)	0.3	2.1	0.5	2.3	1.0	2.5	3.7	0.3	0.5	0.6	0.7	2.3	0.0	0.0	1.4	0.0	0.0
QI_{tail} (Crit = 1)	0.6	2.1	0.6	3.9	1.0	2.5	6.3	1.1	0.6	2.9	4.0	3.5	0.0	0.2	6.0	0.1	0.1

Table 12. Result of comparing PDF test with *t*-test and Wilcoxon test in Chungcheong Province (0 means acceptance = no difference; 1 means rejection = difference).

Test	Temp.	pH	Eh	EC	DO	$\log P_{CO_2}$	Alkalinity	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	HCO_3	F	NO_3
t-test (equal variance)	0	1	1	1	1	1	0	1	1	1	1	1	1	1	0	1	0	0
t-test (heteroscedasticity)	0	1	1	1	1	1	0	1	1	0	1	1	1	1	0	1	0	0
Wilcoxon test (upper)	1	1	0	1	1	1	0	1	1		1	1	1	1	0	1	0	0
Wilcoxon test (lower)	0	1	1	1	1	1	-	0	1	0	0	1	1	0	1	0	0	0
PDF test (QI_{shift})	0	1	0	1	0	1	-	1	0	0	0	0	1	0	0	1	0	0
PDF test (QI_{tail})	0	1	0	1	0	1	-	1	1	0	1	1	1	0	0	1	0	0

4.4. Discussion

Groundwater becomes CO_2-enriched when it circulates to depth, where there is a supply of CO_2 gas in these deep places at high temperatures and/or water–rock interaction. The CO_2-rich water vigorously reacts with rocks like granite in these deep places and is mixed and/or diluted with local shallow groundwater as it ascends to the surface. In Korea, CO_2-rich water is governed by geochemical characteristics and geological settings that vary considerably across the country. In Gangwon Province, CO_2-rich water is tightly coupled with the large-scale fracture system. In Gyeongsang Province, CO_2-rich water looks like to be mostly produced by groundwater reacting with granite at depth and partly by reacting with sedimentary rocks. In Chungcheong Province, the occurrence of CO_2-rich water that is characterized by very low pH of ~4.0 and lower TDS than the surrounding ordinary groundwater can be explained by the direct supply of CO_2 gas to shallow groundwater without water–rock reactions in deep places [7]. In this case, the PDF technique was effectively applied for discriminating the leakage of CO_2 gas from underground storage, and the origins and water–rock reaction mechanisms of the natural CO_2-rich waters were essentially irrelevant.

Comparing the CO_2-rich groundwaters from different bedrocks and origins in Gyeongsang and Gangwon Provinces resulted in similar statistical shape and values for P_{CO_2}, Eh, DO, SiO_2, K^+, and Na^+ (Figure 6). In particular, for pH, TDS, and EC, the qualitative distributions were very similar, while the quantitative results were distinguishable, indicating that these parameters were affected by the bedrock types under the same P_{CO_2} conditions and reaction times of the CO_2-rich groundwater and rock (Figure 6).

Per the PDF test, the distinct indicator parameters for distinguishing CO_2-rich and ordinary groundwaters in South Korea are pH, TDS, EC, HCO_3^-, Mg^{2+}, Ca^{2+}, and SiO_2 (Table 13). However, NO_3^- reflects the characteristics of the regional anthropogenic environment rather than the natural influence of carbonic acid. Other items such as temperature, SO_4^{2-}, Cl^-, and others, were proven to be indistinct indicators (Table 13).

Table 13. Major parameters for identification for the three areas with distinct indicator (○) and indistinct indicator (×).

Province	Temp.	pH	Eh	EC	HCO_3	DO	TDS	Na	K	Mg	Ca	SiO_2	Cl	SO_4	NO_3	F
Gwangwon	×	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Gyeongsang	○	○	○	○	○	×	○	×	○	○	○	○	×	×	○	○
Chungcheong	×	○	×	○	○	○	○	○	×	○	○	○	×	×	×	×

The threshold of P_{CO_2} between CO_2-rich and ordinary groundwaters around the three provinces [13,14] is $10^{-0.79}$ atm with a confidence interval of 97.4% (Table 14, Figure 7). In the study areas, the P_{CO_2} threshold for CO_2-rich groundwater was higher than $10^{-0.5}$ atm and for ordinary groundwater was lower than $10^{-0.7}$ atm, similar to the results calculated by SOLVEQ and reported in [12]. In the three study areas, the median values of pH for CO_2-rich groundwater were such that Chungcheong < Gangwon < Gyeongsang (Figure 8). On the other hand, the median values of P_{CO_2} in the three areas were highly analogous (Figure 8).

Table 14. log P_{CO_2} of the CO_2-rich and ordinary groundwaters for the three areas.

Province	Gangwon		Gyeongsang *	Chungcheong	
Statistics of logP_{CO_2}	**CO_2-Rich**	**Ordinary**	**CO_2-Rich**	**CO_2-Rich**	**Ordinary**
Mean	−0.1	−2.4	−0.22	−0.05	−2.3
Median	−0.1	−2.4	−0.18	−0.05	−2.08
S.D	0.2	0.4	0.24	0.31	1.06
Minimum	−0.9	−3.9	−1.55	−1.98	−7.22
Maximum	0.6	−0.3	0.28	0.91	−0.36

Note: * Please note there is no P_{CO_2} data for ordinary groundwater from Gyeongsang Province.

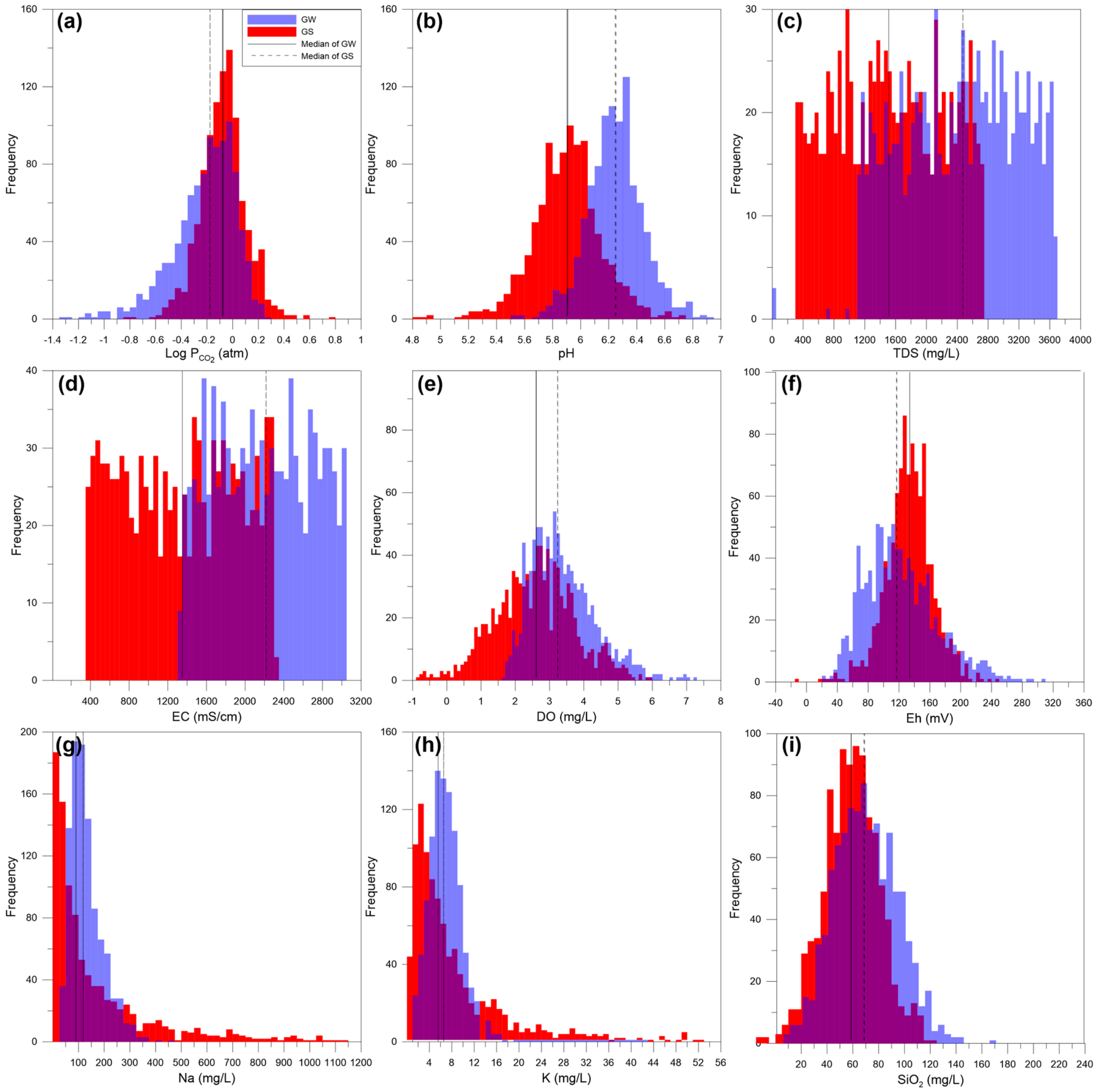

Figure 6. Comparison of probability density distributions of CO_2-rich groundwater for Gangwon (GW, blue) and Gyeongsang (GS, red) Provinces. (**a**) log P_{CO_2}, (**b**) pH, (**c**), TDS, (**d**) EC, (**e**) DO, (**f**) Eh, (**g**) Na, (**h**) K, (**i**) SiO_2.

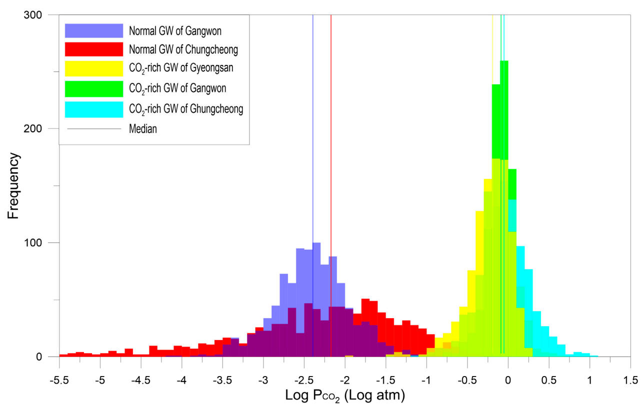

Figure 7. log P_{CO_2} threshold for separating CO_2-rich (blue, green, and yellow distributions) and ordinary (red and dark blue distributions) groundwaters in South Korea. Yellow box line indicates −0.97 and separates log P_{CO_2} of CO_2-rich groundwater from that of ordinary groundwater with the same confidence interval of 97.4%.

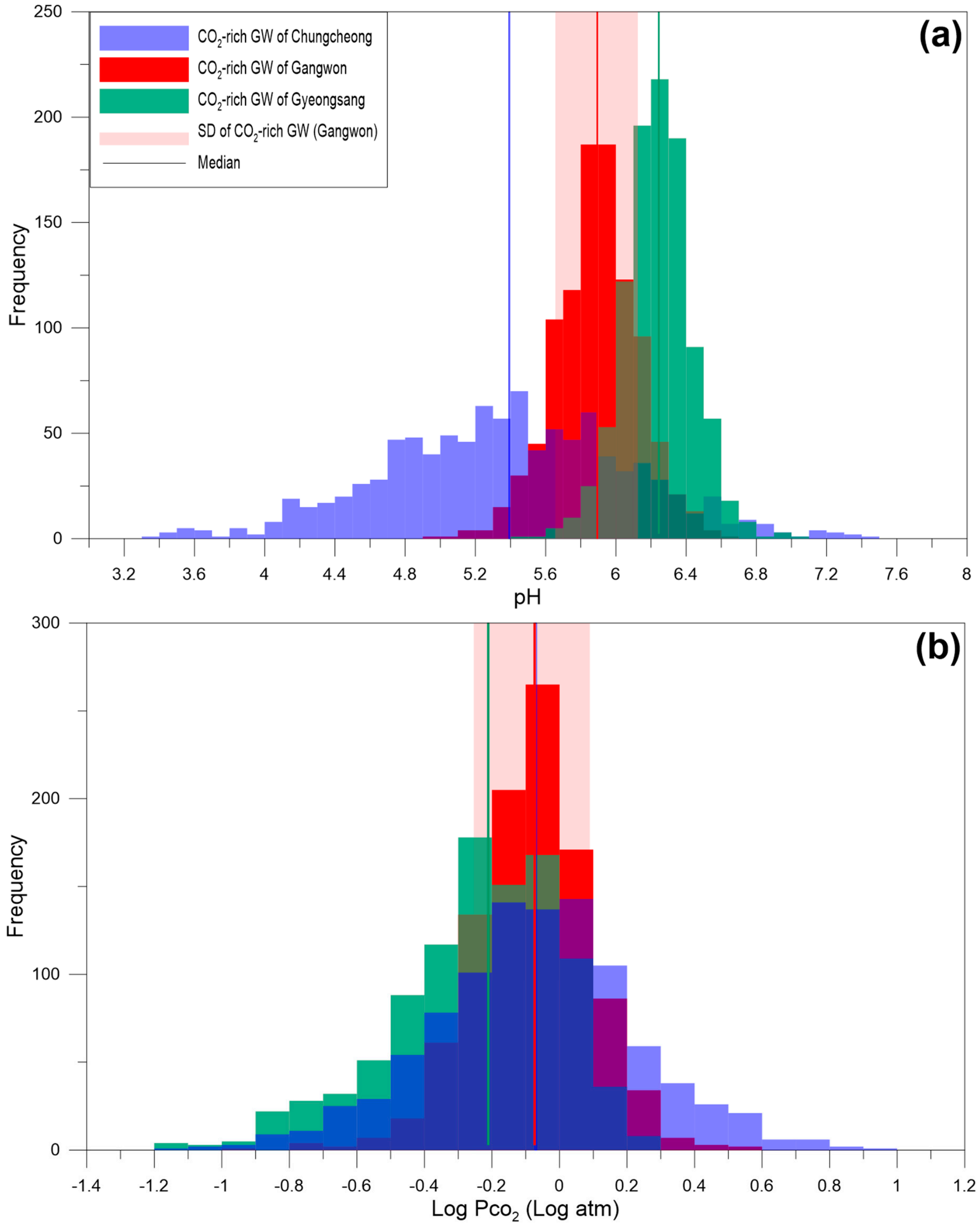

Figure 8. Comparison of Chungcheong (blue), Gyeongsang (green), and Gangwon (red) Provinces using probability density distributions of (**a**) pH and (**b**) P_{CO_2} in CO_2-rich groundwaters.

The EC and TDS of the CO_2-rich and ordinary groundwaters were such that Chungcheong < Gangwon < Gyeongsang and Gangwon < Chungcheong < Gyeongsang, respectively (Figure 9). This finding indicates that the chemical characteristics of the groundwaters are significantly affected by the geology. The different PDF distribution shapes appear as uniform for Gangwon and Gyeongsang Provinces and triangle-shaped for Chungcheong Province. The uniform shape indicates the similar density of the EC or TDS values in Gangwon and Gyeongsang Provinces while the triangle shape designates a great density at a certain range of EC or TDS values in Chungcheong Province. These distribution shapes might be related to different depths of CO_2 generation as well as the different geological characteristics of the three provinces that are based on the different reaction between CO_2-rich groundwater and bedrock by using isotopes (oxygen, hydrogen, carbon, sulfur, nitrogen, and strontium) analyses and water–rock interaction processes [12,13]. Kim et al. [13] reported that CO_2-rich groundwater originated in deep places in Gangwon and Gyeongsang Provinces, whereas the CO_2-rich groundwater took place at shallow depths in Chungcheong Province.

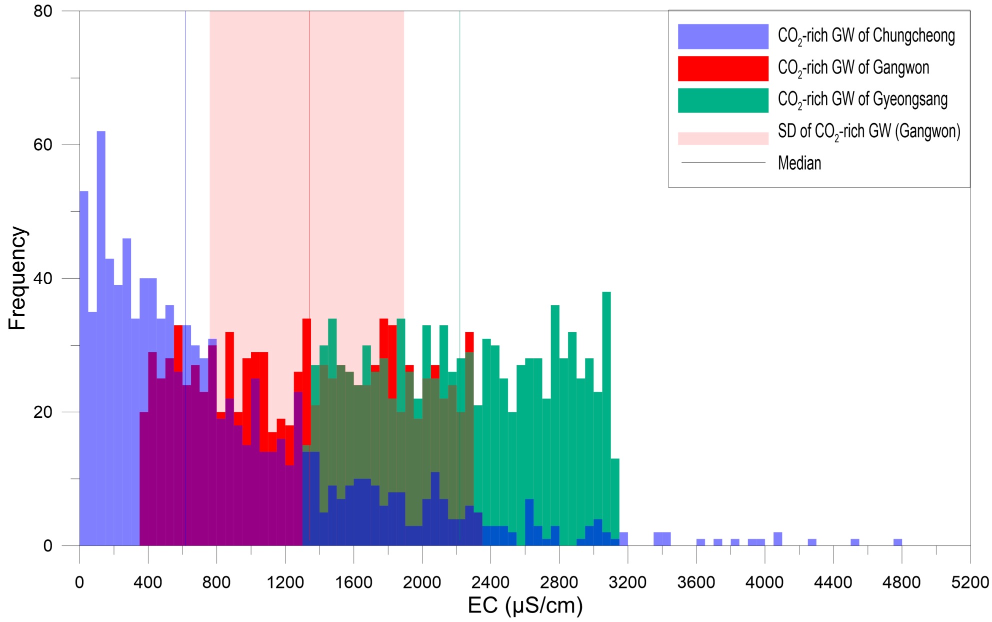

Figure 9. Comparison of EC PDFs of CO_2-rich groundwater in Gangwon (**red**), Chungcheong (**blue**), and Gyeongsang (**green**) Provinces.

5. Conclusions

The chemical components of naturally occurring CO_2-rich groundwater in Gangwon, Gyeongsang and Chungcheong Provinces of South Korea were effectively characterized by a new approach based on the PDF test. Twenty-three chemical components (temperature, pH, Eh, EC, DO, alkalinity, log P_{CO_2}, TDS, Na^+, K^+, Mg^{2+}, Ca^{2+}, SiO_2, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, F^-, Al, Fe, Mn, Sr, and Li) for CO_2-rich and ordinary groundwaters were analyzed using the PDF test for both quantitative and qualitative monitoring of CO_2, and useful monitoring parameters were identified, even in light of uncertainty based on geological complexity.

Through the comparison of CO_2-rich groundwater and ordinary groundwaters occurring in Gangwon Province, Gyeongsang Province, and Chungcheong Province, it was determined that pH, TDS, EC, HCO_3^-, Mg^{2+}, Ca^{2+}, and SiO_2 are the most effective markers for detecting leakage of CO_2 stored underground. In total, 15 markers (pH, Eh, EC, DO, alkalinity, log P_{CO_2}, TDS, Na^+, K^+, Mg^{2+}, Ca^{2+}, SiO_2, SO_4^{2-}, NO_3^-, and F^-) were identified in Gangwon Province, which features mostly granite and banded gneiss; 12 markers (temperature, pH, Eh, EC, alkalinity, TDS, K^+, Mg^{2+}, Ca^{2+}, SiO_2, NO_3^-, and F^-) were identified in Gyeongsang Province, which is composed of sedimentary rock; and 9 markers (pH, EC, log P_{CO_2}, TDS, Na^+, Mg^{2+}, Ca^{2+}, SiO_2, and HCO_3^-) were identified in Chungcheong Province, composed mostly of granite and metamorphic rock. The geological characteristics indicate that in Gangwon Province, CO_2-rich groundwater of deep origin underwent a substantial reaction period with the surrounding rocks, whereas in Chungcheong Province, CO_2-rich groundwater occurring at shallow depth had a relatively short reaction period. In Gangwon Province especially, P_{CO_2}, and alkalinity were identified as good markers for CO_2-leakage monitoring.

The P_{CO_2} threshold between CO_2-rich and ordinary groundwaters in the three study areas is $10^{-0.79}$ atm, with a confidence interval of 97.4%. The comparison of CO_2-rich and ordinary groundwaters in the three study areas showed that the median values of pH of the CO_2-rich groundwater are such that Chungcheong < Gangwon < Gyeongsang, while the median values of P_{CO_2} of the three areas are very similar.

In this study, the PDF test as a qualitative and quantitative tool was shown to sufficiently discriminate hydrochemical characteristics of different rock types in South Korea for CO_2 leakage monitoring, while minimizing the influence of sample site, size, and timing. Furthermore, the PDF test can be used effectively for comparing two or more items and provides a reasonable result by comparing the probability range, including uncertainty, which may occur during an investigation instead of a single representative value, such as mean or median. However, the applicability of the PDF approach can be confirmed by a subsequent study on relating the PDF results and chemical reaction.

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