Research Article

Evidence of Multiple Sources of Soil Gas in the Tangshan Fault Zone, North China

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The sources of soil gases in the Tangshan fault zone, North China, were discussed, based on the soil gas compositions and isotopic ratios obtained by measurement in the field and sample analysis in the laboratory. Soil gas compositions and isotopic ratios indicate that air (A) end-member, limestone (L) end-member, and sediment (S) end-member are the major end-member components contributing to the soil gas in our study area, with fractional contributions in the range of 2-15 vol.%, 23-36 vol.%, and 62-65 vol.%, respectively, to CO2 from the gas wells. According to the relationship among the $^{3}$He/$^{4}$He, average CO2 concentration, and He concentration of soil gas, the deepest depth the fault cut downward and the most developed fractures in the segment where the Heibeiligong (HBLG) well located were inferred, and the shallower depth the fault cut downward and the more developed fractures in the fault segments where the Weifengshan (WFS), Siwangzhuang (SWZ), Tianjingyice (TJYC), and Douhetai (DHT) wells located were inferred. Significant variations in CO2 concentration were observed in soil gases sampled in DHT, HBLG, and WFS soil gas wells in concomitance with a local seismic sequence by 2018 confirming for the first time a possible source of carbon dioxide generated in underlying limestones.

1. Introduction

Earthquakes are caused by tectonic evolution accompanied by matter and energy exchange deep inside the earth [1–3], which is mainly transmitted by fluid being released through active faults and fractures at different depths [4], owing to that fault and fracture are preferential migration pathways for gases (CO2, Rn, He, etc.) in the deep crust to migrate upward to the surface, due to their enhanced permeability and porosity relative to the surrounding rocks [5–7]. General overviews of the geochemical, structural, and seismic features in tectonically active areas have shown some evidence of correlation between soil gas geochemistry anomalies and tectonic activities, and soil gas discharge through fault and fracture in the active fault zones can be influenced by fault and earthquake activity (Wakita et al., 1980; Toutain et al., 1992; [8–11]). As such, analyzing the origins and geochemical variations of soil gas in the seismically active areas could be a potential way to study faults and seismic activity [12–14]. At present, soil gas concentration and flux surveys along active fault zones have been widely undertaken for earthquake research and prediction (Caracausi et al., 2003; [11, 15]).

Recent studies of soil gas geochemistry within fault zones and its relationship with earthquake activity further indicate that it can potentially be used to monitor earthquakes [10, 11, 16, 17]. Soil gas geochemical surveys in seismically active areas have been carried out across the world [5, 6, 18, 19], and some anomalies appearing before earthquakes have been identified [11, 20]. In the Arax Basin (Armenia), radon volume activities have been observed to vary before and after earthquakes [21]. Similarly, anomalously high radon volume activity fluctuations were observed several hours to a few days before an earthquake (Ml > 3) that occurred in northern Taiwan [7].

Soil gas anomalies are usually complex as they are subject to multiple influences (atmospheric, biogenic, organic, and from the deep crust and mantle; [11, 22–24]) and occasionally
their relationships with seismic events may be ambiguous [4, 7, 25, 26]. Accordingly, if the observation of soil gas in fault zones is to become a useful method of fault activity assessment and seismic forecasting, further analysis of their relationships is required and the source identification for soil gas in the seismically active areas is a prerequisite.

The Tangshan fault is the main shock fault in which occurred the 1976 Tangshan Ms 7.8 earthquake, one of the most destructive earthquakes ever recorded and caused 240000 deaths and property losses of over $1.4 billion [27]. In this region, earthquakes have occurred with increasing frequency (more than 20 earthquakes of Ms ≥ 3.0 per year since 2016) and high concentrations of soil gas components have been observed [5, 28].

In the present study, we aim to (1) investigate the origins of soil gas emitted from the Tangshan fault zone based on gas compositions and isotope ratio values, (2) analyze correlations between variations of soil gas component concentrations and earthquakes in the Tangshan fault zone, and (3) identify methods and components that are potential for earthquake monitoring in the Tangshan area of Northern China.

2. Geological Setting

The Tangshan fault zone is located in a fold depression region where the Northern China and Yanshan uplifts converge. It is considered to be a strain accumulation structure comprising three active faults, which are as follows, from north to south: Douhe fault (F₁), Weishan-Changshan fault (F₂), and Tangshan-Guye fault (F₃). All three are normal faults with right lateral strike-slip and have NE trending (25°-35°) and NW dipping with high dip angles (70°-80°; Liu et al., 2011). The 1976 Tangshan Ms 7.8 earthquake occurred in the middle segment of the Tangshan fault zone and was followed by 54 aftershocks of Ms ≥ 5.0 (Figure 1). This was interpreted as a complex tectonic process of strike-slip, thrust, and normal-fault events caused by detachment, fault propagation in the middle crust, and stress accumulation in the base of the upper crust [14].

The basement of the Tangshan area is composed of pre-Sinian metamorphic rocks with varying metamorphic grades whose outcrops rarely occur in the study area covered by the thick sediments of the Holocene (Q₄) and upper Pleistocene (Q₃), but Ordovician, Cambrian, and Proterozoic strata consisting mainly of limestone are widely exposed in the northern segment of the Tangshan fault zone, with δ¹³C (PDB) and δ¹⁸O (PDB) in the range of -0.65–1.40‰ and -12.34–7.47‰, respectively [29]; Mesozoic and Tertiary sediments are missing in the study area, and the thickness of Pleistocene and Holocene sediments increases from about 100 m in the north to 800 m in the south [14, 30, 31]. The total carbon contents of soil in the northern and southern segments of the Tangshan fault zone were 1.63% and 0.85%, respectively, and the Ra contents were 27.2 Bq kg⁻¹ and 20.4 Bq kg⁻¹, respectively [32]. Geological, seismic, and electrical surveys show that the active faults have dislocated the strata of the Cenozoic Era [14, 33]. The target area for the soil gas measurement in the field was about 2100 km² with the length of about 70 km and width of about 30 km, covered the three active faults and seven soil gas wells (Figure 1).

3. Methods

3.1. Soil Gas Measurements. Soil gas measurements were performed in the field at 388 measurement points covering the Tangshan fault zone (Figure 1). The CO₂ concentration and Rn (radon) activity were measured at approximately 1–1.5 km intervals between every two measurement points. In order to avoid possible meteorological effects on the soil gas concentrations (Hinkle, 1994), the soil gas survey was carried out during a period of stable meteorological conditions from 8 April to 7 May 2010. At this time (spring), the air temperature (mean = 7.1 – 19.6°C) and wind velocity (mean = 3 – 5 m s⁻¹) remain relatively stable and the mean rainfall over the study period (approximately 1 month) is 21.3 mm, which is relatively low given that the mean monthly rainfall for the Tangshan area is 50 mm (http://data.cma.cn). The CO₂ concentrations and Rn volume activity were measured by inserting a stainless steel sampling tube with a 3 cm diameter into the ground to a depth of 0.8 m [34]. The sampling tube was connected by rubber tubes to a radon detector (RAD 7, for Rn volume activity) and a portable infrared CO₂ monitor (GXH-3010-E, for CO₂ concentration; Figure 2). Rn activity was measured 15 min after sampling (the time necessary for Po and Rn nuclei to reach equilibrium, which is about five times the half-life of 219Po). The detection limit and measurement error of the RAD 7 radon detector were 3.7 Bq m⁻³ and ±5%, respectively. An inlet filter and molecular sieve were used to protect the detector from dust and soil moisture. The detection limit and measurement

![Figure 1: A map of the study area, with inset showing its location in NE China. F₁: Douhe fault; F₂: Weishan-Tangshan fault; F₃: Tangshan-Guye fault.](image-url)
error of the GXH 3010-E CO2 monitor were 0.01% and ±2%, respectively. An inlet filter was used to protect the detector from dust.

3.2. Soil Gas Measurement in Selected Wells. Seven sites were selected for soil gas measurements and equipped with shallow depth wells in November 2017 (Figure 1). These sites were selected because they are characterized by (1) relatively high CO2 concentration and Rn activity, (2) distance < 2.0 km from the fault, and (3) a lack of possible artificial sources of contamination. An inverted polytetra-fluoroethylene (PTFE) circular accumulation hemispherical chamber with a volume of $1.68 \times 10^2$ m$^3$ and a radius of 0.2 m was fixed 5.0 m below the ground. A 6-channel deconcentrator was installed on the inner wall of the chamber to reinject the circulating gas in order to ensure the immediate and homogeneous mixture of gas in the chamber. Two exhaust tubes (PTFE, 5.0 m in length, 10 cm in diameter) were used, with their lower ends connected to the top of the chamber and their other ends connected to the inlet and outlet of the detector. These devices form a closed circuit for the analysis of gases present in the first five meters of sediments (Figure 3). Gas measurements were performed repeatedly in the field at the end of each month from June to November 2018. Gas samples were also collected from the outlet of the apparatus following the methods described by Chen et al. [5] and Zhang et al. [35] in September 2018.

3.3. Laboratory Analysis. Gas compositions (CO2, CH4, Ar, H2S, N2, and O2) and isotopic ratios ($\delta^{13}C_{CO2}$, $^3$He/$^4$He (R/Ra), CO2/$^4$He, and $^4$He/$^{20}$Ne) were all measured in the Laboratory of Gas Geochemistry (Lanzhou, China), Institute of Geology and Geophysics, Chinese Academy of Sciences. Gas compositions were determined by a mass spectrometer (MAT 271) and characterized by relative standard deviations of <5%. The $^3$He/$^4$He (reported as R/Ra, Ra = 1.4 $\times 10^{-6}$) and $^4$He/$^{20}$Ne values were determined by a different mass spectrometer (VG 5400), while $\delta^{13}$ C values were analyzed by a gas chromatography-pyrolysis-isotope ratio mass spectrometer (HP 6890-Delta Plus XL) with uncertainties of ±0.3‰. Analysis of all the samples was completed from December 5 to December 7, 2018, within 10 days of sampling. Air on the Gaolan Hill in the south of Lanzhou was used to calibrate the instrument [35].

3.4. Population Identification and Spatial Distribution Analysis. The graphical statistical method (GSA) of Sinclair [36] was used as described by Chiodini et al. [22] to distinguish different populations of soil gas from the Tangshan fault zone. This method involves plotting CO2 concentrations or Rn volume activity values against a cumulative probability and identifying inflection points within each dataset. The inflection points signify partitions among different statistical populations, which may represent discrete sources of soil gas [37]. The data obtained at the mobile measurement points were processed using the Kriging interpolation method in the SURFER 8.0 package; then, the contour maps were built with the data set to analyze the spatial distributions of CO2 concentrations and Rn volume activity. Kriging is a general approach for stochastic spatial interpolation in which the continuous regionalized variable of interest $Z(s)$, sometimes referred to as the primary variable, is predicted at any unsampled location $s$ of the study area $D$ using the values of $Z$ measured at different locations; $Z(s), i = 1, \cdots, n$, the predicted value at location $s$, $Z(s)$, is calculated as an affine linear combination of the $n$ observed values in such a way that it is a best linear unbiased prediction predictor [38].

4. Results

The CO2 concentrations and Rn activities obtained at the 388 measurement points were in the ranges of 514.0–10318.1 ppm and 882.4–17283.5 Bq m$^{-3}$, respectively, with means of 2438.6 ppm and 4730.5 Bq m$^{-3}$, respectively (Table 1).

The geochemical parameters of soil gases sampled in the seven shallow depth wells (DHT, TJYC, HBLG, LHD (Luhuadai), HET (Haiertun), SWZ, and WFS) in the Tangshan fault zone are listed in Table 2. The concentrations of CO2, CH4, Ar, H2S, N2, and O2 in soil gas sampled in the seven constructed shallow depth wells were in the ranges of 0.09–6.23%, 31–113 ppm, 0.92–1.15%, 0–631 ppm, 78.64–97.81%, and 0.45–19.90%, respectively. The Rn volume activities were in the range of 4.59–33.00 Bq m$^{-3}$. The atmospheric concentrations of CO2 and He in the study area were 0.04% and 5.35 ppm, respectively. The $^3$He/$^4$He (R/Ra), CO2/$^4$He, and $^4$He/$^{20}$Ne ratios of soil gas sampled in the seven shallow depth wells varied from 0.99 to 1.13, 3.68 $\times 10^8$ to 3.18 $\times 10^9$, and 0.28 to 0.31, respectively. The $\delta^{13}$ C values of CO2 were in the range of $-19.9$ to $-18.9$‰. The $^3$He/$^4$He (R/Ra), $\delta^{13}$ C$_{CO2}$, CO2/$^4$He, and $^4$He/$^{20}$Ne ratios of air in the study area were 0.99, $-8.3$‰, 5.40 $\times 10^7$, and 0.29, respectively (Table 2).

5. Discussion

5.1. Sources of Soil Gas Sampled in the Tangshan Fault Zone. The probability plots of both CO2 concentration and Rn activity of soil gas collected at the 388 sampling points displayed three-segment distributions, characterized by the
partial overlap of a low population (A), a medium population (B), and a high population (C; Figures 4 and 5). There were two inflection points at CO$_2$ concentrations of 3692 ppm and 8269 ppm, indicated by arrows in the figures, which delineate the fractions of 80% for Population A, 16% for Population B, and 4% for Population C (Figure 4). There were also two inflection points at Rn volume activities of 7588.2 Bq m$^{-3}$ and 13749.8 Bq m$^{-3}$, delineating the fractions of 83% for Population A, 12% for Population B, and 5% for Population C (Figure 5). The means and 95% confidence intervals of CO$_2$ concentration and Rn volume activity and the fractions of the three populations listed in Table 3 were determined using the GSA method [39].

Contour maps of soil gas CO$_2$ concentrations and of Rn activities found in the 388 mobile measurement points were mapped in Figures 4 and 5. A consistent spatial coincidence of CO$_2$ concentrations and of Rn activities was found (Figures 6 and 7), which may indicate common sources of CO$_2$ and Rn, as CO$_2$ can act as a carrier gas for Rn [4, 40]. In addition, almost all the CO$_2$ and Rn values from Population C are concentrated near the fault zone; in contrast, almost all CO$_2$ and Rn values from Population A are distributed outside the fault zone. Moreover, most of the CO$_2$ and Rn values from Population B are located near the fault zone but with some outside it (Figures 6 and 7). Gases migrating from deep geological formations towards the surface through faults are usually characterized by enrichment in one or more components compared to atmospheric composition and are expected in fault zones. Outside the fault zones, gases are diffused in the superficial soil and show lower concentrations.

Table 1: CO$_2$ concentrations and Rn activities in soil sampling points.

<table>
<thead>
<tr>
<th>Gas component</th>
<th>No.</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rn (Bq m$^{-3}$)</td>
<td>388</td>
<td>4730.5</td>
<td>882.4</td>
<td>17283.5</td>
<td>3465.3</td>
</tr>
<tr>
<td>CO$_2$ (ppm)</td>
<td>388</td>
<td>2438.6</td>
<td>514.0</td>
<td>10318.1</td>
<td>2068.0</td>
</tr>
</tbody>
</table>

Figure 3: A sketch of the constructed soil gas well.
Table 2: Geochemical compositions of gases sampled in shallow depth wells.

<table>
<thead>
<tr>
<th>No.</th>
<th>Site</th>
<th>CO₂ (%)</th>
<th>Rn (kBq m⁻³)</th>
<th>He (ppm)</th>
<th>N₂ (%)</th>
<th>O₂ (%)</th>
<th>H₂S (ppm)</th>
<th>Ar (%)</th>
<th>CO₂ (%)</th>
<th>CH₄ (ppm)</th>
<th>δ¹³ C (%)</th>
<th>He³²He/He³⁰He</th>
<th>CO₂/³He</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DHT</td>
<td>1.91</td>
<td>3.60</td>
<td>5.17</td>
<td>4.54</td>
<td>1.72</td>
<td>2.01</td>
<td>18.40</td>
<td>16.10</td>
<td>19.80</td>
<td>16.16</td>
<td>19.00</td>
<td>25.80</td>
</tr>
<tr>
<td>2</td>
<td>TJYC</td>
<td>3.76</td>
<td>4.40</td>
<td>3.83</td>
<td>3.30</td>
<td>2.08</td>
<td>2.11</td>
<td>9.69</td>
<td>9.14</td>
<td>8.20</td>
<td>6.17</td>
<td>6.06</td>
<td>6.80</td>
</tr>
<tr>
<td>3</td>
<td>HBLG</td>
<td>3.99</td>
<td>4.01</td>
<td>4.32</td>
<td>6.23</td>
<td>2.55</td>
<td>3.50</td>
<td>23.20</td>
<td>22.30</td>
<td>22.40</td>
<td>13.80</td>
<td>27.20</td>
<td>8.11</td>
</tr>
<tr>
<td>4</td>
<td>LHD</td>
<td>0.62</td>
<td>0.59</td>
<td>0.74</td>
<td>0.85</td>
<td>0.89</td>
<td>0.89</td>
<td>6.72</td>
<td>6.47</td>
<td>6.7</td>
<td>5.88</td>
<td>4.59</td>
<td>7.15</td>
</tr>
<tr>
<td>5</td>
<td>HET</td>
<td>0.14</td>
<td>0.12</td>
<td>0.09</td>
<td>0.13</td>
<td>0.15</td>
<td>0.18</td>
<td>8.53</td>
<td>9.31</td>
<td>5.34</td>
<td>5.93</td>
<td>4.37</td>
<td>7.86</td>
</tr>
<tr>
<td>6</td>
<td>SWZ</td>
<td>2.04</td>
<td>1.62</td>
<td>2.50</td>
<td>2.82</td>
<td>3.66</td>
<td>3.48</td>
<td>8.71</td>
<td>8.08</td>
<td>9.33</td>
<td>10.20</td>
<td>11.80</td>
<td>12.90</td>
</tr>
<tr>
<td>7</td>
<td>WFS</td>
<td>1.15</td>
<td>2.45</td>
<td>2.78</td>
<td>3.28</td>
<td>3.26</td>
<td>2.99</td>
<td>31.00</td>
<td>26.10</td>
<td>26.10</td>
<td>25.70</td>
<td>31.80</td>
<td>31.60</td>
</tr>
</tbody>
</table>

**Geofluids**
of nonatmospheric components [41–43]. Hence, it could be inferred that the CO₂ and Rn of Population A come from the superficial soil, while those of Population C uprise from deeper locations through faults. Meanwhile, the CO₂ and Rn of Population B could have a complex source due to biogenic, thermogenic, mechanochemical, or rock weathering origins [9, 44–46]. Accordingly, further investigations into eventual geochemical variations over time should be carried out chiefly in soil gases from Population C since they are more representative of the deep originating component.

Therefore, attention has been focused on identifying the origin of soil gases of Population C and seven soil gas wells with depths of 5.0 m were constructed along faults in November 2017 for soil gas measurement and sampling (Figures 1 and 3). As shown in Tables 1 and 2, the CO₂ concentrations (0.12–6.23%) and Rn activities (4.59–33.00 Bq m⁻³) of soil gas from the seven soil gas wells were much higher than those from the 388 mobile measurement points (514.0–10318.1 ppm for CO₂ concentration and 882.4–17283.5 Bq m⁻³ for Rn volume activity), suggesting that the new wells were relatively less exposed to diffusion processes of gases by the superficial soil gas and by the atmosphere.

The results of the total gas component analysis showed that the major chemical species of the soil gas samples were N₂, O₂, CO₂, and Ar. The He concentrations in the soil gas samples from the well were slightly higher than those of the atmosphere except for that of DHT (Table 2), according to the results of ³He/⁴He (R/Ra) and ⁴He/²⁰Ne analyses (Figure 8), which could indicate the minority contribution of gases upwelling from the deep earth to the soil gases of the Tangshan fault, although the soil gases could mainly derive from the atmosphere.

However, the CO₂ concentrations of gas samples from the seven new soil gas wells were much higher than the atmospheric concentration (Table 2), suggesting that there were other sources of CO₂. As reported in previous studies, underground CO₂ is a crucial link in the interactions among gas, water, rocks, and biological activities [46]. The two main origins of underground CO₂ are the microbial degradation of organic matter in sediment and limestone weathering, including water-limestone interactions and limestone decomposition [44, 45, 47, 48]. Thus, an approach analogous to that used for the identification and quantification of CO₂ in volcanic and geothermal regions was adopted [35, 49, 50]. The mantle (M) end-member was replaced with an air (A) end-member (Figure 9); then, three major end-member components involving an air (A) end-member, limestone (L) end-member, and sediment (S) end-member were selected to identify and quantify the various sources contributing to CO₂ from the seven new wells. The δ¹³C value of −8.3‰ and the CO₂/³He ratio of 5.4 × 10⁻³ for the (A) end-member were obtained by measuring air samples (Table 1). For the (L) and (S) end-members, δ¹³C values of 0‰ and −30‰, respectively, with a corresponding CO₂/³He ratio of 1.0 × 10⁻³, were suggested by Sano and Marty [49]. The fractions contributed by the (A), (L), and (S) end-members to the CO₂ at the seven new wells were estimated using the following mass balance equations:

\[
\delta^{13}C_{\text{observed}} = \delta^{13}C_A + f_L \delta^{13}C_L + f_S \delta^{13}C_S,
\]

\[
\frac{1}{(\text{CO}_2/\text{³He})_{\text{observed}}} = \frac{f_A}{(\text{CO}_2/\text{³He})_A} + \frac{f_L}{(\text{CO}_2/\text{³He})_L} + \frac{f_S}{(\text{CO}_2/\text{³He})_S},
\]

\[
f_A + f_L + f_S = 1,
\]

where \(\delta^{13}C\) is the fraction contributed by the (A), (L), and (S) end-members.

The results showed that 62–65% of the CO₂ from the seven wells was derived from the (S) end-member, 23–36% was derived from the (L) end-member, and the remaining 2–15% came from the (A) end-member (Figure 9 and Table 4).

This suggests that the major sources of CO₂ in the Tangshan fault zone are the microbial degradation of organic matter and the decomposition of carbonatic rocks in sediments. Furthermore, the higher N₂/O₂ ratios, together with the strong correlation between the depleted O₂ concentrations (compared to the atmosphere) and the CO₂ concentrations
in the wells (correlation coefficient of 0.90; Table 2 and Figure 10), indicate that CO\textsubscript{2} is mainly contributed by the microbial oxidation of organic matter in the sediments of the Tangshan fault zone. In particular, enriched N\textsubscript{2} (93.65% and 97.81%, respectively) and depleted O\textsubscript{2} (0.45% and 4.55%, respectively) were observed in soil gas wells LHD and HET (Table 2), which are located in the farmland. This should be attributed to the acceleration of nitrifying and denitrifying bacterial activity caused by artificial fertilization [51, 52].

The Tangshan fault zone is located in the well-known Bohai Bay sedimentary basin, where limestones are widely distributed in Ordovician, Cambrian, and Proterozoic strata [30, 53]. These limestones could release

<table>
<thead>
<tr>
<th>Population</th>
<th>Fraction Rn</th>
<th>Mean concentration CO\textsubscript{2} (ppm)</th>
<th>95% confidence interval</th>
<th>Mean activity Rn (Bq m\textsuperscript{-3})</th>
<th>95% confidence interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Population A</td>
<td>0.80 0.83</td>
<td>1513</td>
<td>1491-1643</td>
<td>3894.1</td>
<td>3549.0-4240.2</td>
</tr>
<tr>
<td>Population B</td>
<td>0.16 0.12</td>
<td>5415</td>
<td>5396-6109</td>
<td>10229.0</td>
<td>9655.5-10803.0</td>
</tr>
<tr>
<td>Population C</td>
<td>0.04 0.05</td>
<td>8893</td>
<td>8679-9328</td>
<td>15471.0</td>
<td>14861.0-16082.0</td>
</tr>
</tbody>
</table>

**Table 3: Statistical parameters of partitioned CO\textsubscript{2} concentrations and Rn volume activities at the mobile measurement points.**

![Figure 6: A contour map of soil gas CO\textsubscript{2} concentrations in the 388 sampling points.](image6)

![Figure 7: A contour map of soil gas Rn volume activities in the 388 sampling points.](image7)

![Figure 8: Plots showing \textsuperscript{3}He/\textsuperscript{4}He (R/Ra) versus \textsuperscript{4}He/\textsuperscript{20}Ne values for gas samples from the seven soil gas wells.](image8)

**Table 4: Fractional CO\textsubscript{2} contributions by different end-members to the soil gases.**

<table>
<thead>
<tr>
<th>Site</th>
<th>Proportions of A-derived CO\textsubscript{2} (%)</th>
<th>Proportions of L-derived CO\textsubscript{2} (%)</th>
<th>Proportions of S-derived CO\textsubscript{2} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHT</td>
<td>3</td>
<td>32</td>
<td>65</td>
</tr>
<tr>
<td>TJYC</td>
<td>5</td>
<td>31</td>
<td>64</td>
</tr>
<tr>
<td>HBLG</td>
<td>2</td>
<td>36</td>
<td>62</td>
</tr>
<tr>
<td>LHD</td>
<td>15</td>
<td>23</td>
<td>62</td>
</tr>
<tr>
<td>HET</td>
<td>8</td>
<td>28</td>
<td>64</td>
</tr>
<tr>
<td>SWZ</td>
<td>2</td>
<td>33</td>
<td>65</td>
</tr>
<tr>
<td>WFS</td>
<td>2</td>
<td>34</td>
<td>64</td>
</tr>
</tbody>
</table>

![Figure 9: Plot showing CO\textsubscript{2}/\textsuperscript{3}He versus \delta\textsuperscript{13} C values for gas samples from the shallow depth wells. A: air end-member; L: limestone end-member; S: sediment end-member.](image9)
CO₂ at high concentrations during its decomposition and reaction with groundwater and CO₂, as per Eq. (2) \[54–57\].

\[
\begin{align*}
\text{CaCO}_3 (g) & \rightarrow \text{CaO} (g) + \text{CO}_2 (g) \\
\text{H}_2\text{O} (l) + \text{CO}_2 (g) & \rightarrow \text{H}_2\text{CO}_3 (aq) \\
\text{H}^+ (aq) + \text{CaCO}_3 (s) & \rightarrow \text{Ca}^{2+} (aq) + \text{HCO}_3^- (aq) \\
-\text{HCO}_3^- (aq) + \text{H}^+ & \rightarrow \text{H}_2\text{O} (aq) + \text{CO}_2 (g) 
\end{align*}
\]

Above all, it should be noted that the decomposition of carbonates in limestone strata could be another important potential source for the CO₂ in the wells at the Tangshan fault zone.

In addition, it was shown in the relationship between \(^3\text{He}/\text{He}\) and the average values of CO₂ concentration and He concentration of soil gas from the seven soil gas wells (Figure 11). Population A included the soil gas well HBLG with relatively high He and CO₂ concentrations, population B included the soil gas wells LHD and HET with relatively low CO₂ concentration and medium He concentration, and population C included the soil gas wells TJYC, WFS, DHT, and SWZ with medium CO₂ concentration and relatively low He concentration (Figure 11);
higher fractional contributions of L-derived CO\textsubscript{2} is also present in TJYC, DHT, SWZ, and WFS wells, compared with LHD and HET wells, and with the highest one present in HBLG well (Table 4). Faults are preferred, and high-speed passage ways for uprising of gases from the deep earth [58], through which the escape of gases included in rocks of the deeper crust to the surface soil becomes relative easily [4, 59], and the gases migrating from the deeper earth usually have higher gas concentrations [15, 60]. This indicated the deepest depth the fault cut downward and the most developed fractures in the segment where the HBLG well located, and the shallower depth the fault cut downward and the more developed fractures in the fault segments where the WFS, SWZ, TJYC, and DHT wells located [8, 61, 62].

5.2. Relationship between Earthquakes and Soil Gas Chemical Variations. In the period August 5–19, 2018, a seismic sequence (four earthquakes of magnitude 2.0–4.0) struck the Guye region in the northern section of the Tangshan fault zone. The distances between the epicenter of the main shock (M\textsubscript{s} 3.7, focal depth = 7 km) and the soil gas wells ranged between 6 and 45 km (Figure 12).

Abnormal soil gas signals related to earthquakes have been recognized in previous studies [7, 17, 63]. In this study, considerable variations in CO\textsubscript{2} concentration were unexpectedly observed in the soil gas of the DHT, HBLG, TJYC, and WFS wells from July 28–September 28, 2018, during which time the seismic sequence occurred (Figure 13). Taking the mean values of CO\textsubscript{2} concentration observed in June, October, and December 2018 as background values, the maximum increases in CO\textsubscript{2} concentration were calculated to be 175%, 94%, 47%, and 33% at the DHT, HBLG, TJYC, and WFS wells, respectively. These variations of the CO\textsubscript{2} concentration were beyond the measurement error of the GXH 3010-E CO\textsubscript{2} monitor, which is ±2%.

The time series data of CO\textsubscript{2} concentrations in soil gas from the TJYC soil gas well, atmospheric pressure, and local rainfall from June 15, 2018, to December 15, 2018 are shown in Figure 14. It is indicated that the atmospheric pressure and rainfall have little impact on CO\textsubscript{2} concentrations in soil gas from the TJYC soil gas well, which may be attributed to the significant depth at which the accumulation chamber had been fixed (5.0 m below the ground).

Therefore, the abnormal variations in soil gas CO\textsubscript{2} concentration at wells DHT, HBLG, TJYC, and WFS could be responses to the seismic sequence. The peaks in CO\textsubscript{2} concentration could be attributed to increased contributions of gas from underlying limestones as observed in different geological contexts [24, 37].

6. Conclusions

The sources of soil gases in the Tangshan fault zone, North China, have been analyzed based on the soil gas chemical compositions and isotopic ratios obtained by measurement in the field and samples analysis in the laboratory.

The soil gases from the Tangshan fault zone were distinguished by three populations, based on the statistical analysis of CO\textsubscript{2} concentration and Rn volume activity of soil gas collected at 388 sampling points using graphical statistical methods. Carbon dioxide of group (A) originates in the superficial soil while carbon dioxide of group (C) comes from deeper geological formations through faults. Carbon dioxide from group (B) could have a complex source, such as biogenic, thermogenic, mechanochemical, or be due to rock weathering.

Further information about the origin of soil gases was obtained according to the geochemical investigations of soil gases sampled in seven soil gas wells, drilled at the sites where group (C) soil gases had been observed. Soil gas compositions and isotopic ratios indicated that air (A) end-member, limestone (L) end-member, and sediment (S) end-member were
identified as three major end-member components contributing to soil gas in the Tangshan fault zone; gas from the sediment (S) end-member was the primary source for the soil gases, and limestone (L) end-member was the secondary one.

The relationship between $^{3}$He/$^{4}$He and the average values of CO$_2$ concentration and He concentration of soil gas indicated the deepest depth the fault cut downward and the most developed fractures in fault segments were where the HBLG well was located and the shallower depth the fault cut downward and the more developed fractures in fault segments were where the WFS, SWZ, TJYC, and DHT wells were located.

Variations in CO$_2$ concentration in the DHT, HBLG, and WFS wells observed in concomitance with a local seismic sequence confirm for the first time a possible contribution of carbon dioxide probably generated in underlying limestones.

**Data Availability**

The data for this paper are available in the text.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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