RELEASE OF HYDROGEN FLUORIDE FROM CLAY USED FOR COAL-COMBUSTION IN ZHIJIN COUNTY, GUIZHOU PROVINCE, PEOPLE’S REPUBLIC OF CHINA

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ABSTRACT: In the present study, we investigated the chemical composition of the clay topsoil from Hehua Village, Zhijin county, Guizhou province, People’s Republic of China, which is used as a clay binder in coal-combustion and has a high content of fluorine. We found the mean concentration of the fluoride ion (F⁻) of the topsoil was 1284 µg/g, the mean apparent acidity (pHa) was 4.92, and the mean total bisulfate (hydrogen sulfate) ion [mT(HSO₄⁻)] concentration was 4465 µg/g. The apparent acidity and the total sulfate ion (SO₄²⁻) content were found to be positively correlated ($r^2 = 0.7920$). It was concluded that sulfuric acid hydrate (H₂SO₄·H₂O) was present in the sulfated clay and that under certain circumstances, such as with heating or burning, this acid (H₂SO₄·H₂O) would decompose the fluorine in the clay and produce volatile hydrogen fluoride (HF). It was estimated that the mean HF production was 455 µg of HF/g of Hehua village topsoil. We found the amount of HF released was closely related to the soil acidity and confirmed that HF is preferentially released during the burning of coal using a clay topsoil binder with a high apparent acidity, a high total sulfate content, and a high fluoride content.

Key words: Acidity; Endemic fluorosis; Hehua village; Hydrogen fluoride; Sulfation.

INTRODUCTION

The endemic fluorosis in Zhijin county, Guizhou province, People’s Republic of China, 1-5 is caused by the intake of elevated levels of the fluoride ion (F⁻) emitted through the daily domestic burning coal to which high F⁻ clay has been added.6-10 Clay is added as an adhesive to powdered coal to form clay-coal briquettes which burn better than powdered coal does through there being better air flow between the briquettes. However, there are few studies on the chemical forms of fluorine in coal or clay, and the fluorine species that occur during the transfer of the fluorine between the coal or clay, the food being dried or stored for human consumption, and the human body. Liang et al. demonstrated that hydrogen fluoride (HF) is released from burning coal and suggested that it was also released when burning blended fuel.11 It was not clear whether or not this phenomenon also occurred with clay when it was used as a binder. The form in which fluorine is released from clay has been investigated but there is no direct experimental evidence.12 The so-called binder clay in previous studies is actually topsoil with a certain viscosity, which can be easily obtained in many areas.

The present study was undertaken in Hehua village in Zhijin county, Guizhou province, to ascertain whether the burning of the topsoil in the village releases HF. This study focuses on an area of fluorosis from a chemical equilibrium perspective, and makes a comparison with the topsoil in areas where there is no
fluorosis, in order to gain a better understanding of the properties of the binder clay used in the fluorosis areas.

**MATERIALS AND METHODS**

*Sample collection:* Topsoil (BT1-BT37) was collected from hillside fields within Hehua village that had not been cultivated. It was sampled at 20 cm below the surface in order to avoid the surface vegetation effect. In addition, binder clay (RHT1-RHT8) was also collected from the sloping fields behind the farm buildings of a random selection of local farmers. A total of 110 control topsoil samples were also taken from 16 adjacent areas (Jinping county in Guizhou province, the Daxing district in Beijing, Chizhou in Anhui, etc.). All the samples were taken in accordance with the principles of sampling.

* Determination of the total topsoil F content:* The total F content in the soils was determined by the combustion-hydrolysis fluoride ion-selective electrode method in accordance with the Chinese National Standards (GB4633-1997). For quality control, standard reference materials (GBW07403 [soil, China], GBW07406 [soil, China]) were randomly analyzed with each batch of soil samples.

* Determination of the topsoil pH:* The acidity of the clay used for binding the coal was determined by a pH electrode (Model METTLER-SG2), which, before taking measurements, was corrected using three standard pH buffer solutions, provided by Mettler-Toledo International, Inc., with pHs of 4.01, 7.00, and 9.02.

* Determination of the topsoil sulfate ion content:* The total sulfate ion in the soil was determined by ion chromatography (DX-120), equipped with a Dionex AS14 (250×4 mm) anion exchange column and a conductivity detector. The mobile phase was composed of 6.3 mM Na₂CO₃ and 1.7 mM NaHCO₃ at a rate of 1.9 mL/min. The samples were filtered through 0.25 mm filters before injection. For quality control, the standard reference material (GSB04-2080-2007), with a reference value of 1000 µg/g and a determination value of 948 ± 69 µg/g (n = 11) was used.

* Calculation of the correct acidity of the topsoil:* According to the above test results, the apparent acidity (pHₐ), the water volume, and the correct acidity (pHₑ) were calculated as follows, and the pHₑ was considered to represent the actual acidity of the topsoil found in a natural state within the study area:

\[
\text{pHₑ} = - \log ([\text{H}^+] )
\]

\[
[[\text{H}^+] ] = \frac{10^{-\text{pHₐ}} \times V}{V_1}
\]
Calculation of the topsoil bisulfate (hydrogen sulfate) content: The primary ionization constant $K_{a1}$ (1000) of sulfuric acid is far greater than that of the secondary ionization constant $K_{a2}$ (0.012), and therefore, only the secondary ionization of sulfuric acid was considered. The ions of sulfuric acid in a soil solution should exist in the forms of $\text{HSO}_4^-$ and $\text{SO}_4^{2-}$. The concentration of the bisulfate (hydrogen sulfate) ion was calculated using the following formula:

$$m(\text{HSO}_4^-) = \frac{[\text{H}^+]_1 \times C(\text{SO}_4^{2-})}{[\text{H}^+]_1 + K_{a2}} \times V(\text{H}_2\text{O}) \times 97 \times 10^6$$

where:
- $m(\text{HSO}_4^-)$ = the content of the bisulfate (hydrogen sulfate) ion ($\mu$g/g);
- $([\text{H}^+]_1)$ = the actual acid concentration (mol/L);
- $C(\text{SO}_4^{2-})$ = the total sulfate ion content (mol/L);
- $K_{a2}$ = the secondary ionization constant of sulfuric acid;
- $V(\text{H}_2\text{O})$ = the water content (L/L);
- 97 = the molar mass of the hydrogen sulfate root ($\text{H}=1$, $\text{S}=32$, $\text{O}_4^-$=64)
- $M_0$ = sample quantity (g).

RESULTS AND DISCUSSION

The $\text{pH}$, $\text{SO}_4^{2-}$, $\text{HSO}_4^-$, and $\text{F}^-$ content in topsoil: The $\text{F}^-$ content in the topsoil from the study area ranged from 621 to 2816 $\mu$g/g, with an average of 1284 $\mu$g/g ($n = 45$) (Tables 1A and 1B), which is higher than that in the control areas (117–721 $\mu$g/g, average 412, $n = 110$) (Table 2), but is close to the $\text{F}^-$ content of the binder clay in Hehua village reported by Dai et al., Liu et al., and Wang et al.13-15

The present study shows that most of the topsoil from Hehua village has a high $\text{F}^-$ content.

Table 1A. The content of water $[V(\text{H}_2\text{O})$, L/L], apparent acidity $[\text{pH}_a]$, correct acidity $[\text{pH}_c]$, total fluoride ion $[m(\text{F}^-)$, $\mu$g/g], total sulfate ion $[m(\text{SO}_4^{2-})$, $\mu$g/g], and bisulfate ion $[m(\text{HSO}_4^-)$ ($\mu$g/g)] of the topsoil in Hehua village ($n=45$, (n=12 in Table 1A and n=33 in Table 1B))

<table>
<thead>
<tr>
<th>Sample number (n=12)</th>
<th>$V(\text{H}_2\text{O})$ (L/L)</th>
<th>$\text{pH}_a$</th>
<th>$\text{pH}_c$</th>
<th>$m(\text{F}^-)$ (µg/g)</th>
<th>$m(\text{SO}_4^{2-})$ (µg/g)</th>
<th>$m(\text{HSO}_4^-)$ (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHT1</td>
<td>$6.22 \times 10^{-3}$</td>
<td>4.96</td>
<td>4.06</td>
<td>1091</td>
<td>3886</td>
<td>28.3</td>
</tr>
<tr>
<td>RHT2</td>
<td>$5.55 \times 10^{-3}$</td>
<td>4.8</td>
<td>3.85</td>
<td>1047</td>
<td>4653</td>
<td>54.8</td>
</tr>
<tr>
<td>RHT3</td>
<td>$4.82 \times 10^{-3}$</td>
<td>4.3</td>
<td>3.28</td>
<td>935</td>
<td>6797</td>
<td>282</td>
</tr>
<tr>
<td>RHT4</td>
<td>$5.40 \times 10^{-3}$</td>
<td>4.53</td>
<td>3.56</td>
<td>1736</td>
<td>5479</td>
<td>122</td>
</tr>
<tr>
<td>RHT5</td>
<td>$3.69 \times 10^{-3}$</td>
<td>5.47</td>
<td>4.34</td>
<td>718</td>
<td>3731</td>
<td>14.2</td>
</tr>
<tr>
<td>RHT6</td>
<td>$3.20 \times 10^{-3}$</td>
<td>5.23</td>
<td>4.04</td>
<td>855</td>
<td>3509</td>
<td>26.7</td>
</tr>
<tr>
<td>RHT7</td>
<td>$7.76 \times 10^{-3}$</td>
<td>4.6</td>
<td>3.79</td>
<td>1654</td>
<td>4686</td>
<td>62.3</td>
</tr>
<tr>
<td>RHT8</td>
<td>$6.86 \times 10^{-3}$</td>
<td>4.79</td>
<td>3.93</td>
<td>1433</td>
<td>3827</td>
<td>37.3</td>
</tr>
<tr>
<td>BT1</td>
<td>$6.44 \times 10^{-3}$</td>
<td>4.19</td>
<td>3.30</td>
<td>1998</td>
<td>5339</td>
<td>214</td>
</tr>
<tr>
<td>BT2</td>
<td>$5.81 \times 10^{-3}$</td>
<td>4.03</td>
<td>3.09</td>
<td>1320</td>
<td>6050</td>
<td>380</td>
</tr>
<tr>
<td>BT3</td>
<td>$0.90 \times 10^{-3}$</td>
<td>4.47</td>
<td>2.73</td>
<td>1178</td>
<td>5177</td>
<td>699</td>
</tr>
<tr>
<td>BT4</td>
<td>$1.11 \times 10^{-3}$</td>
<td>5.32</td>
<td>3.67</td>
<td>1736</td>
<td>2958</td>
<td>52.3</td>
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</tbody>
</table>
The pH\textsubscript{a} of the topsoil in Hehua village varied from 4.03–6.35, with an average of 4.92 (n=45). By determining the water content in the topsoil (0.42 × 10\textsuperscript{-3} L/L–
7.76 × 10⁻³ L/L) the pHc of the topsoil in Hehua village was obtained and the range for the soil in its natural state was found to be from 2.09–5.03, with an average of 3.67. Compared with the topsoil in the adjacent control areas, the topsoil in Hehua village was found to be more highly acidic (Table 2).

Table 2. The apparent acidity (pHₐ), total fluoride ion \([m(F^-), \mu g/g]\) and total sulfate ion \([m(T(SO_4^{2-}) \mu g/g)]\) content of topsoil in control areas within the People's Republic of China

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Control area</th>
<th>Control area sample site</th>
<th>n</th>
<th>pHₐ</th>
<th>m(F⁻) (\mu g/g)</th>
<th>m(T(SO_4^{2-}) (\mu g/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mean Range</td>
<td>Mean Range</td>
<td>Mean Range</td>
</tr>
<tr>
<td>PA1–5</td>
<td>Pengan</td>
<td></td>
<td>5</td>
<td>7.73</td>
<td>7.39 – 8.19</td>
<td>480 – 643</td>
</tr>
<tr>
<td>WF1–5</td>
<td>Weifang</td>
<td></td>
<td>5</td>
<td>7.74</td>
<td>7.38 – 8.16</td>
<td>281 – 325</td>
</tr>
<tr>
<td>HC1–9</td>
<td>Hancheng</td>
<td></td>
<td>9</td>
<td>6.93</td>
<td>6.67 – 7.21</td>
<td>349 – 479</td>
</tr>
<tr>
<td>SJZ1–8</td>
<td>Shijiazhuang</td>
<td></td>
<td>8</td>
<td>7.13</td>
<td>6.98 – 7.35</td>
<td>399 – 499</td>
</tr>
<tr>
<td>SHG1–9</td>
<td>Qinhuangdao</td>
<td></td>
<td>9</td>
<td>7.82</td>
<td>7.11 – 8.38</td>
<td>456 – 579</td>
</tr>
<tr>
<td>DX1–6</td>
<td>Beijing</td>
<td></td>
<td>6</td>
<td>7.98</td>
<td>7.73 – 8.63</td>
<td>346 – 427</td>
</tr>
<tr>
<td>YQ1–5</td>
<td>Yangquan</td>
<td></td>
<td>5</td>
<td>7.94</td>
<td>7.70 – 8.09</td>
<td>427 – 503</td>
</tr>
<tr>
<td>CF1–5</td>
<td>Chifeng</td>
<td></td>
<td>5</td>
<td>8.23</td>
<td>8.13 – 8.32</td>
<td>430 – 487</td>
</tr>
<tr>
<td>JSYC1–6</td>
<td>Yancheng</td>
<td></td>
<td>6</td>
<td>7.01</td>
<td>6.85 – 7.36</td>
<td>321 – 454</td>
</tr>
<tr>
<td>AQ1–8</td>
<td>Anqing</td>
<td></td>
<td>8</td>
<td>8.20</td>
<td>7.93 – 8.48</td>
<td>567 – 583</td>
</tr>
<tr>
<td>CH1–5</td>
<td>Chaohu</td>
<td></td>
<td>5</td>
<td>6.93</td>
<td>6.95 – 7.06</td>
<td>303 – 319</td>
</tr>
<tr>
<td>CZ1–10</td>
<td>Chizhou</td>
<td></td>
<td>10</td>
<td>6.70</td>
<td>6.52 – 6.89</td>
<td>262 – 316</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>110</td>
<td>7.78</td>
<td>6.52 – 8.48</td>
<td>412 – 721</td>
</tr>
</tbody>
</table>
For example, the range for the pHc in the topsoil in the control areas which were sampled in our experiment in Jinping county, Guizhou province, was 6.93–7.57. Jinping has a healthier environment and there is apparently no pollution nor fluorosis. The higher acidity of the topsoil from Hehua village, compared to the topsoil in Jinping county, shows that it contains a considerable amount of soluble acidic substances.

Compared to the control areas, the amount $\text{SO}_4^{2-}$ in the topsoil of the study area in Hehua village was more than six times higher with a range from 1665–7003 µg/g and an average value of 4465 µg/g. As shown in Tables 1A and 1B, there were wide variations in the $\text{HSO}_4^-$ content within the topsoil at different sites within Hehua village with the values ranging from 1.3–2572 µg/g. The level of $\text{HSO}_4^-$ in samples BT16 and BT17 was more than 2500 µg/g. The results show that the topsoil in Hehua village contained variable amounts of $\text{HSO}_4^-$, and that the $\text{HSO}_4^-$ level was closely related to the apparent acidity pH$a$. Where the soil was more highly acidic, the content of $\text{HSO}_4^-$ was also relatively higher.

A positive correlation between the $\text{SO}_4^{2-}$ and pH$a$ was observed in the topsoil of Hehua ($r^2 = 0.7920$, Figure 1).

**Figure 1.** Relationship between the total sulfate ion ($\text{SO}_4^{2-}$) content and the apparent acidity (pH$a$) value of the topsoil in Hehua village. $r^2 = 0.7920$, $y = -2437.8x + 16624$. 

Total sulfate ion ($\text{SO}_4^{2-}$) content of the topsoil in Hehua village (µg/g)
No significant correlation between the $\text{SO}_4^{2-}$ and the $\text{pH}_a$ was found in the topsoil in the control areas in Jinping county, Guizhou province. This suggests that the acidic substance in the topsoil of Hehua is an acidic sulfate, and shows a similarity to the acidic buffer system $\text{HSO}_4^-/\text{SO}_4^{2-}-\text{nH}_2\text{O}$. Liang et al. studied the characteristics of the domestic coal in the fluorosis areas in Guizhou province using a time-of-flight secondary ion mass spectrometer (TOF-SIMS), and detected, in the coal samples, the ions $\text{H}_3\text{O}^+$, $\text{H}_2\text{SO}_4^+$, and $\text{HSO}_4^-$, which are the characteristic ions of sulfuric acid hydrate ($\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$). Our findings are consistent with these results and suggests that the topsoil in Hehua has been sulfating.

The potential release of hydrogen fluoride from the topsoil in Hehua village: As mentioned above, sulfuric acid hydrate ($\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$) is present in the soils in Hehua village. In addition, the $\text{F}^-$ content was also found to be high (average 1248 µg/g, Tables 1A and 1B). Because sulfuric acid hydrate and fluoride compounds are universally present in topsoil, chemical reactions under certain conditions are inevitable. Sulfuric acid hydrate ($\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$) is a typically strong acid. Consequently, heat or combustion promoted diffusion could easily lead to a neutralization reaction which would produce hydrogen fluoride (HF):

$$\text{F}^- + \text{H}_2\text{SO}_4\cdot\text{H}_2\text{O} = \text{HF} + \text{H}_2\text{SO}_4^- + \text{H}_2\text{O} \quad (4)$$

Liang et al. proposed that hydrogen fluoride (HF) is released from domestic coal in the fluorosis areas of Guizhou province, and this is similar to the findings of our study. In summary, our results indicate that the topsoil in the fluorosis areas of southwest China, as represented by Hehua village, could potentially be releasing hydrogen fluoride (HF).

The maximum amount of the hydrogen fluoride release from topsoil can be theoretically calculated according to equation 4, assuming that the fluoride minerals in the topsoil have all reacted and that other influencing factors (such as soil adsorption) are not taken into consideration. In the process of the forming hydrogen fluoride, two main dynamic balances are involved:

(i) Hydrogen ions react with fluoride ions in a soil solution to form HF:

$$\text{H}^+ + \text{F}^- = \text{HF} \quad (5)$$

(ii) The fluoride ion reacts with the bisulfate (hydrogen sulfate) ion ($\text{HSO}_4^-$) derived from sulfuric acid hydrate ($\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$), and forms HF.

$$\text{F}^- + \text{H}_2\text{SO}_4\cdot\text{H}_2\text{O} = \text{HF} + \text{HSO}_4^- + \text{H}_2\text{O} \quad (6)$$

Because the dissociation constant ($K_a$) of hydrogen fluoride (HF) ($K_a = 6.8 \times 10^{-4}$) is far less than the secondary ionization constant ($K_{a2}$) of sulfuric acid hydrate ($\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$) ($K_{a2} = 1.2 \times 10^{-2}$), only the $\text{H}^+ + \text{F}^- = \text{HF}$ balance was
considered and the impact of $\text{SO}_4^{2-}$ was ignored. The content of the HF released could thus be theoretically calculated as follows:

$$m(\text{HF}) = \frac{[\text{H}^+]_1 \times C(\text{F}^-)}{[\text{H}^+]_1 + K_a} \times V(\text{H}_2\text{O}) \times 20 \times 10^6 \quad (7)$$

where:
- $m(\text{HF})$ = the content of the hydrogen fluoride (HF) released (µg/g);
- $[\text{H}^+]_1$ = the actual acid concentration (mol/L);
- $C(\text{F}^-)$ = the total fluoride ion content (mol/L);
- $K_a$ = the ionization constant of hydrogen fluoride (HF) ($6.8 \times 10^{-4}$);
- $V(\text{H}_2\text{O})$ = the water volume of the original topsoil (L/L);
- $20$ = the molar mass of the hydrogen fluoride (H=1, F=19) (g/mol);
- $M_0$ = sample quantity (g).

**The estimation of the hydrogen fluoride emissions**: The estimates of the amount of HF able to be released from the soils at various sampling sites in the study area in Hehua village varied from 9.1–1643 µg/g, with an average of 455 µg/g (Table 3).

**Table 3.** Estimates of the maximum amount of hydrogen fluoride (HF) able to be released from the topsoil and the indoor-air HF concentrations in Hehua village

<table>
<thead>
<tr>
<th>Sample number</th>
<th>$m(\text{HF})$ (µg/g)</th>
<th>$C(\text{HF})$ (mg/m³)</th>
<th>Sample number</th>
<th>$m(\text{HF})$ (µg/g)</th>
<th>$C(\text{HF})$ (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHT1</td>
<td>132</td>
<td>0.26</td>
<td>BT16</td>
<td>797</td>
<td>1.60</td>
</tr>
<tr>
<td>RHT2</td>
<td>191</td>
<td>0.38</td>
<td>BT17</td>
<td>682</td>
<td>1.36</td>
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<tr>
<td>RHT3</td>
<td>426</td>
<td>0.85</td>
<td>BT18</td>
<td>376</td>
<td>0.75</td>
</tr>
<tr>
<td>RHT4</td>
<td>524</td>
<td>1.05</td>
<td>BT19</td>
<td>194</td>
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<tr>
<td>RHT5</td>
<td>47.8</td>
<td>0.096</td>
<td>BT20</td>
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<td>0.23</td>
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<td>RHT6</td>
<td>107</td>
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<td>BT21</td>
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<td>BT22</td>
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<tr>
<td>BT1</td>
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<td>BT15</td>
<td>1314</td>
<td>2.63</td>
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</table>

Total range ($n=45$): 9.1 – 1643

Total mean ($n=45$): 455
Research report
Fluoride 50(1 Pt 2)182–192
January-March 2017

Release of hydrogen fluoride from clay used for coal-combustion in Zhijin County, Guizhou Province, People’s Republic of China

Hong, Liang, Lv

Zhang et al. analyzed the classification of the fluorine content in Chinese coal and determined that coal with a fluorine content of more than 200 µg F/g of coal to be high fluorine coal.\(^\text{16}\) If this is converted to hydrogen fluoride (210 µg HF/g of coal), then it can be seen to be less than the estimated mean amount of hydrogen fluoride content able to be released from the high fluoride topsoil in Hehua village (mean = 455 µg HF/g of topsoil, Table 3). When the high fluoride topsoil in Hehua village is used as a clay binder for coal-combustion, it causes greater harm to human health than does the burning of F\(^-\)-rich coal.\(^\text{17-22}\)

Southwest China has a damp climate. Local residents use open furnaces to dry corn, to cook, and to warm houses. The doors and windows are frequently closed in winter resulting in reduced ventilation and increased pollution. Households use, on average, 10 kg of coal slurry daily in the winter, and of this binder clay accounts for 30% (3 kg of the mass). The average kitchen area in the study households was about 50 m\(^2\), with an air exchange ratio of 20%. The daily average HF concentration is shown in Table 3, where only the HF release from the binder clay was calculated. The HF released from burning the powdered coal was not included. The daily average HF concentration indoors ranged from 0.018–3.29 mg/m\(^3\), with an average of 0.85 mg/m\(^3\). There are no established safety standards for gaseous fluoride indoors in China, but the atmospheric fluoride standard is established as a daily average of 0.007 mg/m\(^3\). However, atmospheric fluoride is not the main cause of coal-burning fluorosis. In this context, the atmospheric air was not polluted by anthropogenic indoor coal burning so that the atmospheric fluoride standard cannot be used for the indoor burning of coal. Liang et al.\(^\text{23}\) proposed that the maximum allowable daily concentration of gaseous fluoride should be 0.01 mg/m\(^3\). Based on this standard, the daily average concentrations of gaseous fluoride shown in Table 3 are all above the standard of 0.01 mg/m\(^3\) with the minimum of 0.018 mg/m\(^3\), the maximum of 3.29 mg/m\(^3\), and the average of 0.85 mg/m\(^3\) being 1.8-fold, 329-fold, and 85-fold, respectively, greater than the standard. This indicates that there is a serious risk of HF pollution in the kitchen air within Hehua village.

Figure 2 shows the relationship between the pH\(_a\) of the topsoil in the study area and the estimated amount of HF able to be released. The figure reveals a significant positive correlation: the stronger the acidity of the topsoil, the more the HF that was able to be released. It can therefore be concluded that acidic clay, containing H\(_2\)SO\(_4\).H\(_2\)O, contributes to the release of hydrogen fluoride (HF).

Release of hydrogen fluoride: HF has a boiling point of 19.5ºC and is volatile at ambient temperatures. The above analytical results were verified in further studies. Backup topsoil samples with different pH\(_a\) values were heated to about 200ºC in our laboratory and the headspace gas was analysed with a Picarro G1105 HF analyzer. The results confirmed that HF was released from topsoil and the strength of the hydrogen fluoride release was closely linked to the topsoil acidity. It can be concluded that fluoride will be preferentially released from topsoil in the form of HF.
The results obtained in this study in Hehua village, where endemic fluorosis is very serious and has been prevalent for a long time, indicate that the topsoil and the binder clay used in coal burning are extremely acidic or sulfated. It is, therefore, considered to be capable of releasing HF with heat or combustion, and the amount of HF released depends upon the acidity of the soils. Further study confirmed the release of HF from Hehua village topsoil after heating to 200°C. The cause of this phenomenon, and whether other endemic fluorosis areas have the same situation, requires further study.

ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (number: 41371449). We would like to give special thanks to Yin Zhang, Yue Xie, and Wenhai Zhang for their support in the underground sampling and the collection of soil.

REFERENCES
