FLUORINE IN CHINESE COALS

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SUMMARY: Three hundred and five coal samples were taken from the main coal mines of twenty-six provinces, autonomous regions, and municipalities of China. The method of pyrohydrolysis was applied to measure the fluorine content in the samples, which exhibit logarithmic normal frequency distributions. The range of fluorine content in dry coal varies from 25 to 1230 mg/kg with a geometric mean of 136 mg/kg. The fluorine content decreases gradually from sub-bituminous through bituminous coal to anthracite. However, such varying tendency of fluorine content is not due to the presence of organic fluorine in coal. The geological age also apparently has no effect on the fluorine content. Even though the fluorine content of most coals in China is not high, much more attention should be given to the fluoride pollution caused by improper (unvented) coal-burning and the widespread household use of high-fluoride coal-clay.

Keywords: Chinese coal, Fluoride in coal.

INTRODUCTION

With a concentration scope of 20–500 mg/kg and an average value at 150 mg/kg, fluorine is one of the abundant trace elements in coal.[1] Because of its presence in the daily diet at varying levels, fluorine often has an extraordinary significance in health and environments. During the combustion of coal, fluorine is released into the fume in the form of HF, most of which enters the atmosphere. The largest man-made source of fluoride pollution in the United States comes from emissions of coal-burning power plants. According to recent statistical data, coal-burning power plants produce 82% of the total fluoride in air in the United States.[2]

China is the biggest coal-producer and coal-consumer in the world, and its energy structure, with coal being the major energy source, is not expected to change significantly over the next several decades.[3] About 84% of coal is burned directly as fuel in China.[4] By proper cleaning, the fluorine content of coal can be reduced by 50%.[5] Unfortunately, however, as of 1999, only 9% of primary steam coal in China is washed to remove fluoride.[6]

Statistical data collected by the Chinese Ministry of Health in 2001 from 201 counties of 14 provinces, autonomous regions, and municipalities in

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China indicates that coal-burning fluorosis led to 18,138,780 cases of dental fluorosis and 1,594,799 cases of skeletal fluorosis. Coal-burning fluorosis in China is therefore one of the most serious health problems resulting from environmental pollution anywhere in the world.

Because only limited information is available about the fluorine content and geochemistry of coals in China, this research was undertaken to help remedy this gap in such knowledge.

MATERIALS AND METHODS

Our nationwide sampling program was designed according to the resources distribution and yield of coal as well as the consideration of ranking by coal type and coal-forming periods. Using the National Standard GB 481-93, we collected 305 coal samples from the main coal mines of 26 provinces, autonomous regions, and municipalities of China. The principal locations of the sampling sites are shown in Figure 1.

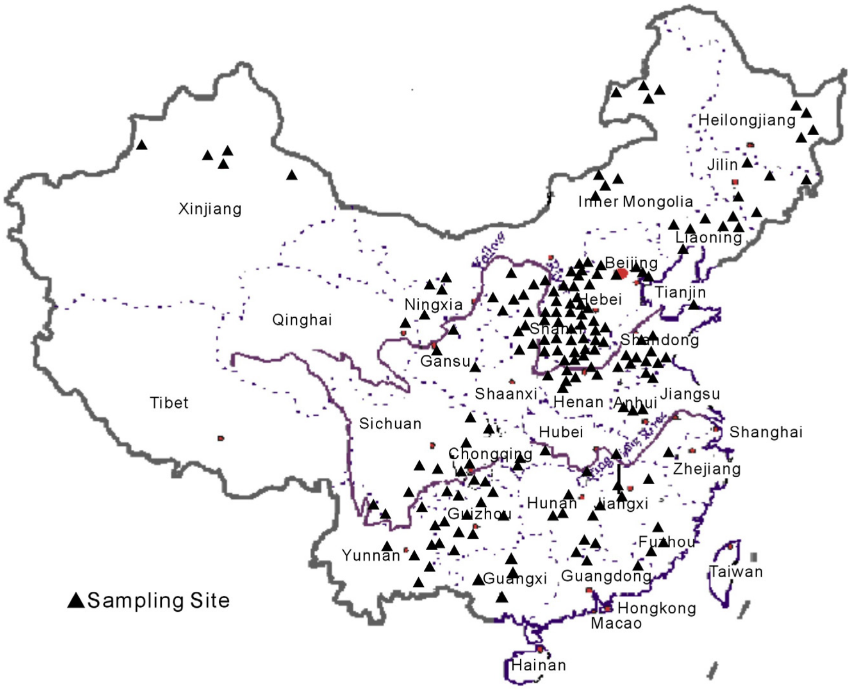

Figure 1. Map of China showing distribution of coal samples.

To prevent contamination and weathering, all samples were stored in plastic bags. Sample preparation was conducted according to the National Standard

GB 474-1996. The determination of fluorine in the samples used the pyrohydrolysis method.[7] Analytical calibrations were made against standard reference materials (GBW11121 and GBW11123).

RESULTS AND DISCUSSION

In China, lignite occurs mainly in Yunnan Province and is seldom mined as a fuel due to its poor quality. As shown in Table 1, the fluorine content decreases with increasing coal ranking. Fluorine in coal is basically associated with inorganic substances.[1,8-11] Although some organic combinations of fluorine exist in coal, the low chemical reactivity of fluoride ion (F^-) for forming covalent carbon bonds makes it difficult for fluorine to be incorporated into organic material in coal.[8] Therefore, organically combined fluorine occupies a very small part of the total fluorine in coal. Fluorine associated with the mineral matter is also not affected when coal is evolved from sub-bituminous coal to anthracite.[12] The decreasing fluorine content in passing from sub-bituminous coal through bituminous coal to anthracite, however, is not directly related to coal ranking.

Table 1. Fluorine content in sub-bituminous coal, bituminous coal, and anthracite (mg/kg)

Coal rank[a]	Range	AM[b]	GM[c]	Standard deviation	No. of samples
Sub-bituminous	71-889	229	184	172	25
Bituminous	30-855	166	141	111	213
Anthracite	25-1230	147	109	165	67

[a]Coal rank was classified by ASTM's standard ASTM, 1996.
[b]Arithmetic mean. [c]Geometric mean.

Our samples are from ten coal-forming periods, namely, Early Carboniferous (C_1), Middle Carboniferous (C_2), Late Carboniferous (C_3), Early Permian (P_1), Late Permian (P_2), Late Triassic (T_3), Early Jurassic (J_1), Middle Jurassic (J_2), Late Jurassic (J_3), and Tertiary (R). As shown in Table 2, the fluorine content increases in the order: C_1, J_2, J_1, P_1, C_3, C_2, P_2, J_3, R, T_3.

The concentration of trace elements in coal is strongly influenced by geological factors such as sedimentary environment, character of source rock, tectonic setting, and hydrogeological conditions.[12,13] Most of these parameters have regional characteristics,[13] whereas China's abundant coal resources are spread over widely distributed coal fields with large variations in coal-forming periods. Therefore, it is most unlikely that any consistent and meaningful relationship can be found between the fluorine content and the coal-forming period for the nation as a whole.

Table 2. Contents of fluorine in coals with different geological ages (mg/kg)

Geological age	Range	AM	GM	Standard deviation	No. of samples
Early Carboniferous	53-112	83	77	30	2
Middle Carboniferous	-	147	-	-	1
Late Carboniferous	40-439	158	143	78	60
Early Permian	25-382	137	119	72	85
Late Permian	37-1230	195	147	193	63
Late Triassic	34-377	249	202	120	11
Early Jurassic	40-258	132	115	66	13
Middle Jurassic	30-855	130	99	139	34
Late Jurassic	71-889	231	189	170	22
Tertiary	71-411	225	200	103	14

On the basis of coal-forming period, sedimentary facies, distribution of coal seam, geological structure, and geographical factors, five coal-cumulating areas can be identified in the mainland of China, namely, Permocarboniferous (C-P) coal-cumulating area in northern China, Late Permian (P_2) coal-cumulating area in southern China, Early-Middle Jurassic (J_{1-2}) coal-cumulating area in northwestern China, Late Jurassic (J_3) coal-cumulating area in northeastern China, and Mesozoic-Cenozoic (M-C) coal-cumulating area in Yunnan Province and Tibet.[14] The distribution of fluorine content in coals of these five coal-cumulating areas is shown in Table 3. The two coal-cumulating areas, C-P and J_{1-2}, occupy about 40% and 33.3%, respectively, of the entire national coal resource, corresponding to geometrical mean (GM) values of 121 mg/kg and 85 mg/kg. The M-C coal-cumulating area with a coal resource of less than 10 billion tons has been little exploited, and therefore only one coal sample was taken from it. It is interesting that the fluorine content of coals from the J_3 coal-cumulating area has a GM as high as 203 mg/kg.

Table 3. Contents of fluorine in coals from five coal-cumulating areas (mg/kg)

Coal-cumulating area	Range	AM	GM	Standard deviation	No. of samples
C-P in northern China	25-855	141	121	89	186
J_{1-2} in northwestern China	42-164	92	85	36	11
P_2 in southern China	37-1230	211	162	183	76
J_3 in northeastern China	71-889	239	203	152	31
M-C in Yunna and Tibet	-	120	-	-	1

As shown in Figure 2, the contents of fluorine in coals of China exhibit a logarithmic normal frequency distribution.

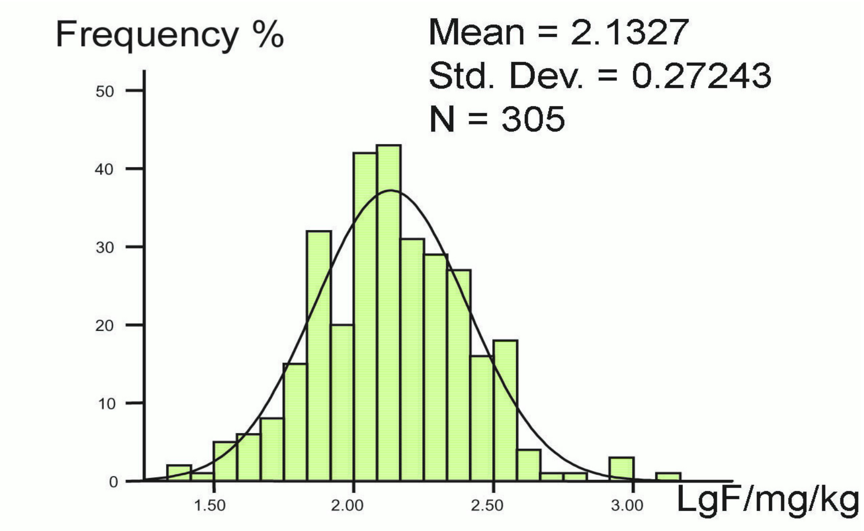

Figure 2. Distribution of the fluoride content in Chinese coals

Hence the most probable fluorine content in Chinese coals is the GM value of 136 mg/kg.[15] In order to avoid errors from abnormally high and low values, the arithmetic mean (AM) value of fluorine content over 90% of coals of China (152 mg/kg) is often adopted.[15] The AM fluorine content for all coal samples of China is 167 mg/kg. Weighted by the yield of each coal mine where the coal was sampled, it is calculated to be 166 mg/kg. The Guizhou Administration of Coal Geology (GACG) collected 616 samples over the whole province and deduced a value of 116 mg/kg for the AM fluorine content of the whole province.[16] Compared with these data, our results in Table 4 are in good agreement, thus indicating that our sampling was probably representative and reliable.

The distribution of fluorine content in coals from 26 provinces, autonomous regions, and municipalities is shown in Table 4. The provinces of Jilin, Liaoning, and Heilongjiang in the northeastern China have coal with high GM fluorine content of 393, 252, and 225 mg/kg, respectively. The fluorine content in coals of the southern China, such as in the provinces of Jiangxi, Hubei, Guangxi, Guangdong, Fujian, and Sichuan, is also high. Their GM is, respectively, 324, 280, 260, 192, 191, and 190 mg/kg. Low fluorine content coals are found mainly in the northern and northwestern parts of China.

Table 4. Fluorine contents in coals from China as well as 26 provinces, autonomous regions and municipalities (mg/kg)

Province	Range	AM	GM	Standard deviation	No. of samples
Shanxi	25-333	138	120	62	85
Hebei	40-341	136	112	79	15
Beijing	-	103	-	-	1
Henan	40-382	131	116	73	23
Shandong	73-266	137	128	51	20
Shaanxi	30-855	165	100	216	12
Inner Mongolia	53-439	180	149	109	17
Anhui	47-234	134	123	55	11
Jiangsu	79-176	135	129	38	6
Xinjiang	42-164	94	81	49	5
Gansu	62-119	90	87	20	5
Ningxia	35-201	110	81	74	4
Qinghai	-	95	-	-	1
Heilongjiang	145-353	235	225	68	10
Liaoning	184-411	261	252	70	9
Jilin	274-889	437	393	230	5
Guizhou	37-305	111	99	58	20
Yunnan	82-296	136	124	65	8
Sichuan	47-377	233	190	120	9
Chongqing	56-347	192	165	91	8
Guangxi	71-1230	425	260	422	5
Guangdong	185-200	193	192	8	2
Fujian	149-255	196	191	44	3
Hunan	53-375	181	148	111	9
Hubei	237-347	283	280	43	5
Jiangxi	69-835	413	324	250	7
China	25-1230	167	136	131	305

Guizhou Province is the region most severely afflicted with endemic fluorosis caused by coal-burning. It has 44.91% of the total affected population in China with 57.14% of the total cases of dental fluorosis and 44.44% of the total cases of skeletal fluorosis.[17] High fluorine coal has been deemed to be the major fluorine source in the endemic areas,[3,18-24] and it was taken for granted that Guizhou Province must have much higher fluorine content in coal. However, the AM fluorine content of 16 coals sampled from households in the two villages in Guizhou that are most seriously affected by coal-burning fluorosis is only 107 mg/kg. As we have shown recently, the main fluorine source in these villages is not the coal but from the clay mixed with the coal to make coal-clay.[24] Thus it is extremely important that all sources of fluorine in coal-burning fluorosis be re-examined in other districts of China. (To avoid introducing an artifact into the national averaging of our study, these 16 household coal samples, which came from two mines already included in our national sampling, were excluded from the national averaging totals.)

By application of the same pyrohydrolysis method for analysis, the fluorine contents in coals of Australia,[9] the Asturian area of Spain,[10] and Canada[11] are shown in Table 5. From this table, it is clear that the fluorine content of most coals in China is relatively low in comparison with coal in other countries. Owing largely to the incorrect (unvented) manner in which it is conducted, household coal-burning, along with the widespread use of high-fluoride coal-clay,[25] remains a major source of endemic fluorosis in China.[3,18-31]

Table 5. Contents of fluorine in Chinese, Australian, Canadian, and Asturian coals (mg/kg)

Coal	Range	AM	GM	Standard deviation	No. of samples
Chinese coal	25-1230	167	136	131	305
90% of Chinese coal	47-347	152			305
Australian coal[a]	15-458	117	90	84	74
90% of Australian coal[a]	20-300	110			74
90% of Canadian coal[b]	31-580	154			57
Asturian run-of-mine coal[c]	130-582	343	308	147	23
90% of Asturian raw coal[c]	137-564	342			23

Note: [a]From Ref.9. [b]From Ref.11. [c]From Ref.10.

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