FLUORIDE EXPOSURE FROM BURNING COAL-CLAY IN GUIZHOU PROVINCE, CHINA

Daishe Wu,[a,b,c] Baoshan Zheng,[a] Aimin Wang,[d] Guangqian Yu[a,b]
Guiyang, China

SUMMARY: The very high prevalence of dental and skeletal fluorosis in relation to the fluorine content of local coal and clay was investigated in two rural regions with low water fluoride (Hualuo Village and Majianzhuang Village) of Guizhou Province, China. The fluorine content of coal in the two regions is considerably lower than the total fluorine content of the commonly used coal-clay (a mixture of coal and clay). The fluorine released from combustion of the coal itself accounts for less than 15% of the total fluorine emissions during the combustion of coal-clay, thereby indicating that the fluorine source that contaminates the food and air is mainly from the clay rather than the coal.

Keywords: China; Coal-clay; Dental fluorosis; Endemic fluorosis; Fluoride in corn; Fluoride in hot pepper; Fluorine in coal; Guizhou Province; Hualuo Village; Majianzhuang Village; Skeletal fluorosis.

INTRODUCTION

Coal-burning fluorosis, a specific endemic disease discovered in mainland China at the end of the 1970s, is a general chronic fluorosis overtly affecting mainly bones and teeth. For example, according to the 2001 Statistical Record of Guizhou Province, coal-burning caused 10,484,540 cases of dental fluorosis and 666,065 cases of skeletal fluorosis. Previous studies found that this type of fluorosis is caused by the intake of elevated levels of fluoride emitted through domestic combustion of high fluorine coal, often without stoves or chimneys in the house.[1-8] In many places, the major source of fluorine is from the high fluorine content of coal in the endemic regions. However, most of the local residents usually mix 30% clay with the coal to make a longer-burning coal-clay and to stabilize the combustion. Therefore the question arises: Does clay affect the emission of fluoride during the combustion of coal-clay? This work is directed to answer this question.

MATERIALS AND METHODS

Two mountainous regions severely affected by endemic fluorosis, Hualuo Village and Majiazhuang Village in Zhijin County, Guizhou Province, China, were chosen to be surveyed. The local residents generally use poorly vented or unvented stoves for cooking, heating, and drying by burning coal-clay.

[a]For Correspondence: Daishe Wu, State Key Laboratory of Environmental Chemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Guizhou 550002, China; E-mail: wudaishe@hotmail.com; [b]Graduate School of CAS, Beijing 100039, China; [c]East China Institute of Technology, Fuzhou, Jiangxi 344000, China; [d]Center for Disease and Prevention of Zhijin County, Zhijin, Guizhou 552100, China.

Corn is the staple food, and hot (chili) pepper is the favorite vegetable. The local (low-fluoride) springs provide drinking water for the villagers. There are no other pathogenic fluoride sources in or around the two villages.

Normally in China, a village includes several groups or teams. Three village groups from the two villages were randomly selected. The total populations of adult villagers in the examined village groups are 1071 and 107 in Hualuo Village and Majiazhuang Village, respectively, while only 696 and 76 were found, respectively, to be in residence. We surveyed all school children 8 to 12 years old and examined all adult villagers who were at home. The severity of dental fluorosis of the children and adults and the degree of skeletal fluorosis among the adults were determined. Dental fluorosis was diagnosed according to Dean's scale.[9] The symptoms of skeletal fluorosis were classified into four degrees based on the Four Types Method.[10]

Coal, clay, coal-clay, coal-clay ash, drinking water, corn, and hot pepper were sampled to measure the fluorine content. Analytical calibrations were made against standard reference materials (GBW11121 and GBW11123). To determine the fluorine content of the coal, clay, coal-clay, and coal-clay ash, we used pyrohydrolysis followed by ISE analysis for fluoride ion, while the ISE method was applied directly to the drinking water.[11] Fluoride in corn and hot pepper was extracted by 1.0 M hydrochloric acid and then analyzed by the ISE method.[12] In order to minimize random error of sampling, the content of fluorine in coal, clay, coal-clay, and coal-clay ash in the two villages was averaged on a weighted basis, yielding 107 mg/kg, 4500 mg/kg, 697 mg/kg, and 537 mg/kg, respectively, for Hualuo Village and Majiazhuang Village. The mean percentage of clay in coal-clay was calculated to be 13.36%.

RESULTS

As summarized in Table 1, the fluorine content of corn in Hualuo and Majiazhuangwo is very high, 47.1 times and 51.7 times higher, respectively, than in fresh corn.[13] The fluorine content of hot pepper is 302 times and 202 times, respectively, than in fresh hot pepper.[12] The fluoride levels in drinking water of the two villages are both very low.Through our measurements, we found that the average ash content of the coal is 20%, the loss on ignition of the clay is 5% at 900 °C after 1 hr, and the fluorine in coal released by combustion is 90.4%.[14] The results of our health surveillances are shown in Tables 2 – 4. They indicate that the villagers are seriously afflicted by both dental and skeletal fluorosis. For example, 13.36% of the examinees in Hualuo Village and 18.42% in Majiazhuang Village were not able to undertake any physical labor work due to the disabling effects of their skeletal fluorosis. Villagers with advanced stages of skeletal fluorosis are so crippled that they

are unable to look after themselves. The incidence of this distressing condition is 8.6% in Hualuo Village and 13.16% in Majiazhuang Village.

Table 1. Fluorine content of coal, clay, coal-clay, coal-clay ash, drinking water, corn and hot pepper in two villages in Zhijin County, Guizhou Province, China

Sample type	Hualuo Village			Majiazhuang Village		
	No. of samples	F level (mg/kg)		No. of samples	F level (mg/kg)	
		Mean	Standard deviation		Mean	Standard deviation
Coal	11	108	80.2	5	104	65.5
Clay	10	6100	2450	6	1900	373
Coal-clay	10	805	211	5	481	119
Coal-clay ash	10	640	451	5	333	176
Drinking water	7	0.12	0.03	3	0.14	0.03
Corn	10	30.6	7.6	7	33.4	13.2
Hot pepper	9	513	389	6	343	238

Table 2. Dental fluorosis among 8- to 12-year-old children in Hualuo and Majiazhuang villages in Zhijin County, Guizhou Province, China (individual prevalence percentages in parentheses)

Village	Age	No.of examinees	Normal	Very mild	Mild	Moderate	Severe	Preval. rate%
Hualuo Village	8	55	1 (1.82)	3 (5.45)	10 (18.18)	19 (34.55)	22 (40)	98.18
	9	25	0 (0)	3 (12)	5 (20)	8 (32)	9 (36)	100
	10	33	0 (0)	0 (0)	5 (15.15)	12 (36.36)	16 (48.48)	100
	11	24	0 (0)	3 (12.5)	4 (16.67)	6 (25)	11 (45.83)	100
	12	88	0 (0)	5 (5.68)	12 (13.64)	24 (27.27)	47 (53.41)	100
	Sum	225	1 (0.44)	3 (5.45)	10 (18.18)	69 (30.67)	105 (46.67)	99.56
Majiazhuang Village	8	27	2 (7.41)	5 (18.52)	6 (22.22)	9 (33.33)	5 (18.52)	92.59
	9	10	0 (0)	0 (0)	1 (10)	5 (50)	4 (40)	100
	10	9	0 (0)	1 (11.11)	1 (11.11)	4 (44.44)	3 (33.33)	100
	11	13	0 (0)	0 (0)	1 (7.69)	1 (7.69)	11 (84.62)	100
	12	6	0 (0)	0 (0)	1 (16.67)	1 (16.67)	4 (66.67)	100
	Sum	65	2 (3.08)	6 (9.23)	10 (15.38)	20 (30.77)	27 (41.54)	96.92

Table 3. Dental fluorosis among adults in two villages in Zhijin County, Guizhou Province, China (individual prevalence rate percentages in parentheses)

Village	Age Range	No. of examinees	Normal	Very mild	Mild	Moderate	Severe	Preval. rate%
Hualuo Village	16-25	96	2 (2.08)	0 (0)	9 (9.38)	31 (32.29)	54 (56.25)	97.92
	26-35	171	0 (0)	0 (0)	15 (8.77)	51 (29.82)	105 (61.40)	100
	36-45	125	0 (0)	0 (0)	9 (7.2)	19 (15.2)	97 (77.6)	100
	46-55	137	0 (0)	0 (0)	2 (1.46)	8 (5.84)	127 (92.70)	100
	> 56	167	0 (0)	0 (0)	3 (1.8)	20 (11.98)	144 (86.23)	100
	Sum	696	2 (0.29)	0 (0.29)	38 (5.46)	129 (18.53)	527 (75.72)	99.71
Majiazhung Village	16-25	19	0 (0)	0 (0)	0 (0)	4 (21.05)	15 (78.95)	100
	26-35	32	0 (0)	0 (0)	0 (0)	8 (25)	24 (75)	100
	36-45	11	0 (0)	0 (0)	0 (0)	1 (9.09)	10 (90.91)	100
	46-55	7	0 (0)	0 (0)	0 (0)	0 (0)	7 (100)	100
	> 56	7	0 (0)	0 (0)	0 (0)	0 (0)	7 (100)	100
	Sum	76	0 (0)	0 (0)	0 (0)	13 (17.11)	63 (82.89)	100

Table 4. Skeletal fluorosis among adults in two villages in Zhijin County, Guizhou Province, China (individual prevalence percentages in parentheses)

Village	Age Range	No.of examinees	Normal	Very mild	Mild	Moderate	Severe	Preval. rate%
Hualuo Village	16-25	96	67 (69.79)	28 (29.17)	0 (0)	1 (1.04)	0 (0)	30.21
	26-35	171	62 (36.26)	81 (47.37)	26 (15.20)	0 (0)	2 (1.17)	63.74
	36-45	125	28 (22.4)	35 (28)	49 (39.2)	8 (6.4)	5 (4)	77.6
	46-55	137	5 (3.65)	18 (13.14)	66 (48.18)	28 (20.44)	20 (14.6)	96.35
	> 56	167	9 (5.39)	17 (10.18)	52 (31.14)	56 (33.53)	33 (19.76)	94.61
	Sum	696	171 (24.57)	179 (25.72)	193 (27.73)	93 (13.36)	60 (8.62)	75.43
Majiazhung Village	16-25	19	15 (78.95)	3 (15.39)	0 (0)	0 (0)	1 (5.26)	21.05
	26-35	32	15 (46.88)	8 (25)	6 (18.75)	2 (6.25)	1 (3.13)	53.13
	36-45	11	0 (0)	1 (9.09)	4 (36.36)	3 (27.27)	3 (27.27)	100
	46-55	7	0 (0)	0 (0)	0 (0)	3 (42.86)	4 (57.14)	100
	> 56	7	0 (0)	0 (0)	0 (0)	6 (85.71)	1 (14.29)	100
	Sum	76	30 (39.47)	12 (15.79)	10 (13.16)	14 (18.42)	10 (13.16)	60.53

DISCUSSION

Gaseous and aerosol fluoride released inside the home by combustion of high fluoride coal-clay can be easily absorbed by uncovered food. This fluoride cannot be removed from the food by washing. Therefore the residents suffer from severe fluorosis after ingesting excessive fluoride by both respiratory and digestive routes.[4]

The climate in Zhijin County is of the subtropical humid monsoon type with plentiful rainfall. Thus the action of chemical weathering is strong, and the illuvial lower soil (B horizon) is rich in clay minerals. Clay contains large

amounts of fluorine because the fluoride ion (F^-) can replace hydroxyl groups or hydroxide ions in the lattice of clay minerals.[15] Fluoride-bearing minerals are weathered in cultivated surface soil (A horizon), and the free F^- is adsorbed and stored in B horizon, thereby making the fluorine content in B horizon is much greater than in A horizon. This explains why our reported fluorine levels of clay are significantly higher than those reported by others.[7,13,16-18] Because of its high viscosity, clay from B horizon is favored and adopted as the adhesive to make coal-clay.

Through the method mentioned above, the mean percentage of fluorine released from the coal in the burning of coal-clay can be calculated to be 15.6% of the total fluorine released during combustion. Our analyses also indicate that our sampling method has large deviations. In fact, fluorine released from coal accounts for less than 15% of the total fluorine emissions.

From the foregoing evidence and discussion, it is clear that the principal fluorine source in the endemic areas is from the clay rather than the coal. This discovery is consistent with several previous studies.[19-23] Because of the similar geochemistry and the essentially identical habits of coal-clay usage in Guizhou Province, the results deduced here from the Hualuo and Majiazhuang endemic regions can be extended to the whole of Guizhou Province.

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