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ORIGINAL PAPER

Fluorosis caused by indoor coal combustion in China: discovery and progress

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Abstract In this study, investigations into endemic fluorosis were conducted and fluorine concentration in environmental samples determined. In an indoor coal-combustion-type fluorosis area, local clay was used to mix with coal for indoor combustion. There are two key steps in the procedure of the indoor transition of fluorine: indoor wet corns and vegetables strongly absorbed fluorine from indoor air; and fluorine strongly accumulated in clay, which was mixed with coal for combustion. Therefore, with the increasing of the percentage of clay in the clay-mixed coal as well as corn in foodstuff, the ratio of fluorosis will be increased.

Keywords Coal · Clay · Fluorosis

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Introduction

Fluorosis caused by indoor coal combustion—the situation in China

Fluorosis, both dental and skeletal, caused by indoor coal combustion is the only type of endemic disease in China that still lacks effective methods of prevention and control. By the end of 2000 there were almost 34 million people living in regions in China where fluorosis is endemic. There are almost 18 million patients suffering from dental fluorosis, and almost 1.5 million patients suffering from skeletal fluorosis. Although exposure to excess fluorine is generally from high concentrations in drinking water, in Guizhou Province most of the fluorosis is caused by indoor coal combustion. More than 52% of the total population of Guizhou Province, about 19.6 million people, including almost 9.9 million dental fluorosis patients, were living in indoor coal-combustion fluorosis areas in Guizhou Province (NSB, 2000).

History of indoor coal-combustion-type fluorosis

Research on indoor coal-combustion fluorosis has been conducted for more than 50 years. According to Lyth (1946) L. G. Kilborn in 1934 noticed dental fluorosis in the north east of Yunnan

Province and in the north west of Guizhou Province. Lyth, a missionary from England, first reported fluorosis in Shimenkan Village, Weining County, Guizhou Province (Lyth, 1946). In his report he described four cases of typical skeletal fluorosis and reported on fluorine concentrations in two water samples from the Shimenkan Village. Fluorine concentration in water coming from a coal mine was 6.9 mg/l, and in water coming from a local fountain the fluorine content was 5.9 mg/l. But now, we do not think these results are correct. In the 1970s, dozens of water samples in Shimenkan Village were collected and analyzed and no fluorine concentration was found to be higher than 0.3 mg/l.

Thirty years after Lyth's report, an investigation of fluorosis in the Bijie Region in Guizhou Province was conducted by the collaboration of the Guiyang Medicine College and the Institute of Geochemistry in Guiyang and proved that local endemic fluorosis was not induced by excessive concentrations of fluorine in drinking water, but rather it was caused by fluorine in foods that were being eaten. Therefore, it was thought that excessive fluorine in the plants was coming from local soils and rocks (Guiyang Medical College, 1979; Liu, Chen, & Yu 1980; Group of Environmental Hygiene, Guiyang Medical College, 1981).

The local Station of Sanitation and Disease Prevention (Enshi CDC, 1980) was the first to report excessive fluorine in food derived from volatization of fluorine during coal combustion in the Enshi region of Hubei Province. This report did not reject the possibility of plants absorbing excessive fluorine from soils. In 1981, the Guiyang Station of Sanitation and Disease Prevention also published a similar report (Guiyang Center for Disease Control, 1981).

During the period 1980–1984, investigations into fluorosis in Guizhou, Yunnan, Sichuan, Hubei, Hunan, Hebei, and Beijing Provinces, and experiments in Zhijin County, Guizhou Province were conducted by the Institute of Geochemistry of the the Chinese Academy of Sciences.

The following results were demonstrated:

- There is no positive relationship between fluorine concentration in foodstuff and in soils and rocks.
- Fluorine absorbed from the indoor combustion of coal resulted in high fluorine contents in foods such as corn. The fluorine emitted from the coal combustion was acid-soluble.
- Of the two factors that induced fluorosis, the method used to dry and store foodstuff was more significant than the concentration of fluorine in coal. If there was indoor coal combustion without any protection, if the main foodstuff of the local people was corn, and if the fluorine concentration of coal was only a few tens of mg/kg, fluorosis would occur. But in the same conditions, the higher the fluorine concentration in coal, the more severe the fluorosis would be. In the most severe fluorosis areas, fluorine concentrations were all higher than 500 mg/kg (Li et al., 2002; Zheng & Huang, 1984; Zheng, Huang, & Wang, 1984; Zheng & Huang, 1985, 1986, 1987; Zheng & Hong, 1988; Zheng & Huang, 1989; Zheng, 1992; Zheng & Wang 1994; Zheng, Zhang, & Ding, 1999).

With the progress on fluorosis research in the 1980s, a policy of fluorosis prevention was carried out. In this policy, changing the indoor coal-combustion stove from open combustion to airtight combustion was the crucial factor.

Source of the fluorine causing indoor coal-combustion-type fluorosis

There were still some questions concerning the formation of fluorosis and the strategy of fluorosis prevention. Guizhou Province is the most severe province for indoor coal-combustion fluorosis. More than 29% of China's fluorosis-affected villages and 56% of China's fluorosis patients are in Guizhou Province. At the same time, according to an incomplete investigation by the Geological Coal Mining Bureau of Guizhou Province, the average fluorine concentration in 616 Guizhou coal samples was only 115.5 mg/kg, and the average fluorine concentration in 166 coal samples from Zhijin County and in 329 coal samples from Nayong County, the two areas most severely affected by fluorosis in Guizhou Province, was only 113.5 mg/kg and 111.4 mg/kg respectively. These concentrations are similar to the US and global averages (Bragg et al., 1998; Swaine, 1990). Furthermore, fluorosis was found in the area of Guizhou Province where the average fluorine concentration of local coal samples was only 15 mg/kg. Overall, fluorosis is severe in the Provinces where fluorine concentrations of the local coal are lower than the average for the whole country, and fluorosis is severe in the counties where the fluorine concentrations of local coal are lower than the average for the Province.

Not all scientists noticed this curious relationship. Li et al. (2002) believed that the fluorine concentration in coal was the crucial factor in the incidence of fluorosis (Li et al., 2002). From epidemiological investigations in Hunan, Jiangxi, Shanxi, Liaoning, Hebei and Beijing Provinces they found a positive linear correlation between fluorine in coal and the incidence of fluorosis. However, the local fluorosis patients did not use chimneys and they did not have the habit of drying and storing foodstuff using indoor combustion. As the fluorine concentration in coal and drinking water are all very low, the incidence of fluorosis in the region can hardly be explained by the theory expounded at that time.

Although in many experiments fluorine in the home and food sharply decreases by adding the chimney to the stove, in reality, a similar positive result could not be obtained. In fact, only 10% of the fluorine in indoor air is left when using a stove with a chimney, but more than 50% of the fluorine still remains in the foods dried by this process. Therefore, changing only the stove cannot diminish fluorosis. Furthermore, changing stoves will significantly reduce the efficiency of drying foods. Until now, health education and improving living conditions are more important for reducing fluorosis than changing the stove.

Clay and indoor coal-combustion-type fluorosis

Zhou Daixing from the Sanitation and Disease Prevention Station of the South West Area of Guizhou Province first noticed that clay was being used as a binder in coal briquettes (Zheng, 1992). He speculated that the difference in the incidence of fluorosis in the region was due to the difference in fluorine concentration in the clay that was mixed with coal to form the briquettes. It was recommended that people living in fluorosis-affected areas should not use clay with a high fluorine content to mix with coal for briquettes. In his research, 17 clay samples from southwest Guizhou Province were analyzed and the highest fluorine concentration found was 2,280 mg/kg (Zhou, Fu, & Wang, 1991). Similar results were also reported from Hunan and Yunnan Provinces (Li, Wen, & Lu, 1992; Li, Xu, & Wang, 1995).

In collaborative research between the US Geological Survey and the Institute of Geochemistry starting in 1996, fluorine and other elements were determined in coal from fluorosis-affected areas. A positive linear relationship between fluorine and potassium was found. Potassium mainly existed in clay minerals in coal, so it is likely that fluorine also exists in clay minerals in coal and the fluorine concentration in coal would increase with the increasing percentage of clay in coal (Finkelman et al., 2002).

In 2003, a second fluorosis investigation in Zhijin and Weining counties was conducted. In one sample, fluorine concentrations in clay were as high as 16,400 mg/kg. The average fluorine concentration in coal, clay, and clay in the coal was 108, 6,100, and 810 mg/kg respectively. The average percentage of clay in coal was about 20%. Therefore, the fluorine concentration in clay and clay in the coal was at least 14.2 and 5.5 times the fluorine concentration in coal respectively. Even the releasing coefficient of fluorine from coal and clay was different; fluorine coming from clay was much higher than that from coal.

Until the late 1990s the fact that clays used to make briquettes had high fluorine content was not considered a general phenomenon and the fluorine in coal was still considered to be the controlling factor in fluorosis.

New thoughts on fluorine source of indoor coal-combustion-type fluorosis

On the basis of the new research and investigations on fluorosis, it appears that, in general, the major source of fluorine causing coal-combustion fluorosis is the clay used to make briquettes. This is the general phenomenon, but there are exceptions. One is bone coal (very high ash coals) in which fluorine is much higher than in most other types of coal.

Proving that the major source of fluorine causing indoor coal-combustion fluorosis is the clay binders used for making briquettes entails not only a great deal of analytical data, but also an explanation of the necessity of mixing clay with coal to form briquettes for burning. We need to know whether the fluorine concentration of all kinds of clay is high, whether fluorosis will be induced when high fluorine content clay is used, and whether there is a positive correlation between the severity of fluorosis and the concentration of fluorine in the clay.

Evidence of the clay binder hypothesis

During coal production, some coal powder will be generated and the price of coal powder is only one third that of the price of coal. Because of poverty in the countryside, local residents have to use coal powder instead of coal for indoor burning. When coal power is directly put into a stove the fire will be extinguished because of the absence of oxygen or the coal power will go directly to the bottom of the stove and fail to combust. Therefore, clay is necessary to mix with coal powder to form briquettes for effective burning. In cities, people are always using chunk coal and stoves with a chimney for indoor burning, so fluorosis rarely occurs.

The fluorine concentration in clay is higher than that in sandy soils and the percentage of clay in the soils of southwest China is higher than that of other parts of China (Zheng, Fu, & Zhang, 1982). The senior author tested fluorine concentrations in 102 soil samples in Zhijin County and found the average value to be 903 mg/kg, much higher than the average value of fluorine in the soil elsewhere in China and higher than the world average (Zheng, 1992). The average fluorine concentrations in clay from two fluorosis-affected villages were 6,100 and 2,600 mg/kg, including one sample whose value was as high as 16,000 mg/kg.

According to the geochemical characteristics of the fluorine, under the warm and wet climate conditions in south west China, fluorine coming from the weathering of rocks was extremely easily absorbed by clay (Liu et al., 1980).

Investigations by the senior author showed that clay was used to mix with coal for indoor combustion in almost all indoor coal-combustion fluorosis-affected areas, including Weijing, Bijie, Xingren, and Xingyi Counties in Guizhou Province; Zhenxiong, Fuyuan, Qujing, Zhaoyuan, Luliang, Jianjin, Daguan, and Weixin Counties in Yunnan Province; Xingwen, Xuyong, Gulin, Qianjiang, and Pengshui Counties in Sichuan Province; Baojing, Laiyang, and Xinhua counties in Hunan Province; Enshi, Jianshi, Balai, Lichuan, and Xianfeng in Hubei Province; Hedi in Guanxi Province; and some mining areas in Hebei and Beijing areas. Only one exception was found in Mufu Village, Enshi County, Hubei Province where local people were using bone (high ash) coal instead of mixing clay with coal powder to make briquettes for indoor combustion.

In the cooperative study on fluorosis in south west China, it was shown that fluorosis is compounded by the use of clay as a binder for making briquettes. The clay used is a high-fluorine (mean value 903 mg/kg) residue formed by intense leaching of a limestone substrate (Finkelman, Belkin, & Zheng, 1999).

In many previous research projects samples were not distinguished by pure coal samples and coal samples mixed with clay, and all of the samples were referred to as "coal samples." Therefore, much of the data on high fluorine concentrations in "coal samples" are actually data on coal briquettes (Zheng & Huang, 1987). Up to now, no true coal samples without clay were found to have a fluorine concentration higher than 500 mg/kg.

Moreover, there have been analytical problems with clay samples containing high aluminum. Aluminum is the main interference with fluorine determination based on the fluoride ion selection electrode method. Compounds of fluorine and aluminum are very stable in many solutions. In high aluminum-containing clays, EDTA and CDTA cannot completely separate the compounds of fluorine and aluminum except for the method of hot hydrolysis or distillation. In most previous research this problem was not taken into account.

Demarcation of different types of indoor coal-combustion fluorosis

Based upon the source of the fluorine, indoor coal-combustion fluorosis can be divided into three categories: bone coal, clay coal, and pure coal fluorosis. Two mutual characteristics of the three types are: indoor combustion without a chimney, and contamination of indoor air and stored or dried foods. The characteristics that discriminate the three types of indoor coal-combustion fluorosis are as follows:

- Bone coal type: The concentration of fluorine in bone coal is very high, normally higher than 1,000 mg/kg. The amount of fluorine released from bone coal is high enough to induce fluorosis. The hardness of bone coal is high enough for combustion without mixing with clay so no clay is needed to mix with the bone coal. This type of fluorosis is prevalent in Mufu Village of Enshi County, Hubei Province, a mountainous areas in the southern part of Shaanxi Province and some bone coal mining areas in Hunan Province.
- Clay coal type: In this type of fluorosis the coal is moistened, ground to a paste, and mixed with clay to form briquettes for combustion. The average fluorine concentration of the clay is about 1,000 mg/kg and is lower than 200 mg/kg in the coal. Therefore, the primary source of this type of fluorosis is the clay. About 90% of all indoor combustion fluorosis is of this type.
- Pure coal type: The characteristic of this type of fluorosis is burning chunk coal instead of coal powder. This type of fluorosis can be divided into two sub-types: low fluorine type and high fluorine. In the low fluorine type of pure coal fluorosis, the fluorine content in coal is low (<200 μg/kg), but the humidity of indoor air is very high, wet corn and chili peppers very easily absorb the fluorine volatilized by the burning of the coal in the process of indoor drying and storing. In the high fluorine type of pure coal fluorosis residents neither use clay to mix with coal nor dry and store their foodstuff indoors, but fluorosis can still be prevalent.

These latter two types of fluorosis still require further research to confirm.

New focus on indoor coal-combustion fluorosis research

The following topics will be considered as the new focus on indoor coal-combustion fluorosis research.

- How prevalent is pure coal-type indoor combustion fluorosis?
- Is there a difference between fluorosis induced by the high fluorine content in drinking water, foods, and air? If there is no food and drinking water contaminated by fluorine, can fluorosis still be prevalent, caused only by gaseous fluorine from indoor air coming from indoor coal combustion?
- On the basis of distinguishing clay, clay coal, and coal, fluorine concentrations in coal in fluorosis-affected areas should be re-investigated. The control factor of fluorine concentration of coal should be re-evaluated.
- Research on the relationship between fluorosis and the percentage of clay in soil should be conducted.

Conclusions

The key factor inducing indoor coal-combustion fluorosis is the use of stoves without chimneys, which causes two geochemical processes inducing fluorosis: wet corn and chilies strongly absorb fluorine from indoor air; and semi-wet high aluminum- and iron-containing clay strongly absorb fluorine. Therefore, the prevalence of fluorosis will become severe with the increasing percentage of clay in soil, the percentage of corn in foodstuffs, and the coldness and humidity in indoor air. Except for bone coal, fluorine concentration in coal is not the controlling factor for fluorosis. For the time being, there are no efficient stoves with chimneys to prevent fluorine release into indoor air and at the same time meet the need for cooking, warming, and drying foodstuffs. More attention should be paid to the clay used to make briquettes in order to reduce indoor coal-combustion-type fluorosis.

References

Bragg, L. J., Oman, J. K., Tewalt, S. J., Oman, C. L., Rega, N. H., Washington, P. M., & Finkelman, R. B. (1998). U. S. Geological Survey Coal Quality (COALQUAL) Database: Version 2.0. U. S. Geological Survey Open-File Report 97–134.

Enshi Center for Disease Control in Hubei Province, Enshi People's Hospital (1980). Investigation on endemic dietary fluorosis. *Chinese Journal of Preventive Medicine, Beijing, 14*, 164–167.

Finkelman, R. B., Belkin, E., & Zheng, B.(1999). Health impacts of domestic coal use in China. Proceedings of the National Academy of Sciences, Colloquium Paper, 96, pp. 3427–3431.

Finkelman, R. B., Orem, W., & Castranova, V., et al. (2002). Health impacts of coal and coal use: possible solutions. *International Journal of Coal Geology, 50*, 425–443.

Group of Environmental Hygiene, Guiyang Medical College, Institute of Geochemistry (1981). Investigation on endemic dietary fluorosis in Zhijin county, Guizhou province, New Chinese Medicine, Zhongshan University Press, Guangzhou, 12, 343.

Guiyang Center for Disease Control, Guiyang Yunyan People's Hospital (1981). Investigation on endemic dietary fluorosis causing by indoor combustion. *Chinese Journal of Preventive Medicine, Beijing, 15*, 281–283.

Guiyang Medical College et al. (1979). Endemic dietary fluorosis in Guizhou province. *Chinese Journal of Preventive Medicine, Beijing, 13*, 148–151.

Li, H., Xu, S., & Wang, M. (1995). Researches on fluorine concentration in clay mixing coal in different layers. *Chinese Journal of Endemiology, 14*, 290–291.

Li, J., Wen, S., & Lu, S. (1992). Endemic fluorosis causing from burning high fluorine clay mixed with coal. *Journal of Hunan University of Medicine, 17*, 290–291.

Li, Y., Wang, W., & Yang, L. (2002). Researches on the characters of indoor coal combustion fluorosis and the safe range for fluorine intake. *Chinese Journal of Endemiology, 21*, 41–43.

Liu, D., Chen, Q., & Yu, Z. (1980). Geochemical problems on endemic fluorosis in China. *Geochemistry, Guangzhou, 1*, 13–22.

Lyth, O. (1946). *Endemic Fluorosis in Kweichow*. China: The Lancet, pp. 233–235.

NSB (National Statistical Bureau of the People Republic of China) (2000) Public report on fifth investigation on the national population in 2000.

Swaine, D. (1990). *Trace elements in cool*. London: Butterworths, 278pp.

Zheng, B.. (1992). *Researches on endemic fluorosis and industrial pollutions*. Beijing: Chinese Environmental Sciences Press, pp. 151–194.

Zheng, B., & Hong, Y. (1988). *Geochemical environment related to human endemic fluorosis in China*. Northwood, UK: Geochemistry and Health, Science Reviews, pp. 93–96.

Zheng, B., Huang, R. (1984). *Analysis on pathogeny of fluorosis in some areas in China*. Environmental Problems and Technology III. Ocean Press, pp. 170–173.

Zheng, B., & Huang, R. (1985). Fluorosis caused from indoor coal combustion. *Agricultural Sciences, 2*, 24–25.

Zheng, B.., & Huang, R. (1986). Researches and preventions on indoor coal combustion fluorosis. *Journal of Applied Endemic Diseases, 1*, 11–13.

Zheng, B., & Huang, R. (1987). Researches on concentration of fluorine in Chinese coal. *Chinese Journal of Endemiology, 3*, 70–72.

Zheng, B., & Huang, R. (1989). Human fluorosis and environmental geochemistry in southwest of China. Developments in Geoscience. Contribution to 28th International Geological Congress, Washington DC, USA. Beijing: Sciences Press.

Zheng, B., Wang, A. (1994). Absorption rate of fluorine in the air by maize. Proceedings of the 20th Conference of the International Society for Fluorine Research, Beijing, P.R. China, pp. 5–9.

Zheng, B., Fu, Y., & Zhang, W. (1982). Background value of fluorine in Baotou area. *China Environmental Sciences, 2*, 9–15.

Zheng, B., Huang, R., & Wang, A. (1984). Environmental geochemical researches on indoor coal combustion fluorosis in southwest areas. *Communication on Endemic Diseases, 3*, 49–51.

Zheng, B., Zhang, J., & Ding, Z. (1999). Issues of health and disease relating to coal use in southwestern China. *International Journal of Coal Geology, 40*, 119–132.

Zhou, D., Fu, Q., & Wang, Z (1991). Investigations on relation between fluorine concentration in clay mixing with coal and fluorosis. *Chinese Journal of Endemiology, 6*, 243–245.