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Processes occurring in the soil and fluorine

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ABSTRACT

Fluorine is in the dynamic balance of two geochemical processes, enrichment and leaching. These reflect the adsorption and desorption of fluoride by clay minerals, respectively. The two geochemical processes of fluorine in soil are influenced by interacting factors, including the geochemical characteristics of soil and clay minerals, pH and sanity of soil solutions, climate, grazing and agriculture activities.

Keywords**:** fluorine, soil, clay mineral, enrichment; leaching, adsorption, desorption

1. INTRODUCTION

Fluorine is an indispensible element in fluid and soft tissues of human body fluid, especially in the bones and teeth (Issa et al., 2003). Link between the lack of fluoride and the prevalence of dental caries has been researched for a long time (American Dietetic Association, 2005). Some countries conducted drinking water fluorindation (Collins et al., 2001; American Dietetic Association, 2005). Even necessary, the best concentration of fluorine for human health is only in a very narrow range (Ruiz et al., 2003; Ghorai and Pant, 2005). The harmful effect excessive fluoride intake have also been well documented (Hamilton, 1992; Downey, 2000; Collins et al., 2001; Alma Ruiz-Payan et al., 2005; Ghorai and Pant, 2005). A research in Sri Lanka shows that even if two areas are very close in geography, opposite endemic diseases can be prevalent due to their different environmental fluorine concentrations (Wu et al., 2004). The same situation can also be seen in China, a country with endemic diseases both fluorosis and dental caries.

2. ENRICHMENT AND LEACHING PROCESSES OF FLUORINE IN SOIL

Fluorine in the environment closely related to human beings has an important impact on health. The research on fluorine in soils has been a hot spot as the soil is critical resources for human survival. Typical concentrations of fluorine in soils are in the range of 20–500 mg/kg (Kabata-Pendias and Pendias, 1984), of course with over abound in some special territories (Fuge and Andrews, 1988). Fluorine in soil is in the dynamic balance of two geochemical processes, enrichment and leaching.

On the one hand, under the condition of enrichment of fluorine in the soil being dominant, surface soil forms weathering crust with humid climate, and furthermore this area may produce coal-conbustion type endemic fluorosis, an unique endemic fluorosis in China, combined with other conditions. High fluoride concentration in clay is an important factor causing coal combustion type fluorosis (Wu et al., 2004). Dai (2007) reported the average fluorine concentration in clay from Zhijin County, Guizhou Province, a coal conbusition type fluorosis area in China, as 2262×10^{-6}. He also found that fluorine is mainly in the compositions including hornblende, apatite, and layers with mixed clay minerals. At the same time, because of soil enrichment of fluorine, concentrations of fluorine in surface water is low, inducing drinking water of most cities in China has lower fluorine content than the recommended value by WHO, and resulting dental caries prevalence (Wang et al., 2004).

On the other hand, under the condition of leaching of fluorine in soil being the dominant process, specific areas with arid and semi-arid climate form high fluoride conditions, fluorine in soil can easily pass reach underlying soil through soil solution or ground water migration (Jacks and Sharma, 1995). With fluoride leaching, aluminum in clay minerals decreases, which may lead to the changes of clay minerals themselves (Egli et al., 2001). In soil solutions, ratio of aluminum fluoride is normally high and stable, with possibilities of forming complex, therefore, in water with high contents of aluminum, total fluorine may much higher than determined value of ion state fluorine (Colin, 1989; Alvarez et al., 1993). If these complexes are decomposed during certain process of metabolism, lots of fluoride and potential toxic aluminum will be released.

3. ADSORPTION AND DESORPTION OF FLUORINE BY CLAY MINERALS

In order to avoid harm caused by leaching or enrichment of fluorine in weathering crust or soil, main factors controlling these two processes must be found. Researches show that, in addition to the loess parent material with very fine soil particles, water soluble fluorine naturally presents in only a low percentage in soils, and largely in the form of different clay minerals in the soil (Lavado and Reinaudi, 1979; Ren and Jiao, 1988; Kafri et al., 1989; Pickering, 1985). Therefore, among the factors deciding dynamic equilibrium of fluorine in the weathering crust, clay mineral characteristics of absorption and desorption of fluorine are the most two critical factors. That is to say, the enrichment and leaching of fluorine in soil reflect the adsorption and desorption of fluoride by clay minerals, respectively.

Firstly, a large body of research shows that, under certain conditions clay minerals have very strong adsorption potential of fluoride. This is a natural barrier to protect groundwater from fluoride pollution in some area (Sergio et al., 2007). Clay minerals in soil is an effective adsorbent for fluoride (Wang et al., 2002), and the adsorption capacity of fluoride by clay minerals is higher than by soil organic matter (Arnesen et al., 1995).

Meenakshi et al. (2008) found that kaolinite adsorbs fluorine more easily than other clay minerals with internal diffusion as the controlling rate of the first-order reaction. Fluoride can quickly replace OH- in clay minerals thus improves pH of the soil solution (Zhang et al., 2007; Yu, 2003). So in the soil with low content of clay minerals, fluorine concentration is low. 50% of surface and ground water and induce drinking water type endemic fluorosis. Under certain fluorine in water can penetrate the soil profile with the main content of sand and low clay minerals, iron or aluminum (Pickering, 1985). Noureddine and Ezzeddine (2006) found in the kinetic experiments on clay mineral adsorption of fluoride that 10% kaolinite can reach the maximum value in 48 hours in adsorption of fluoride from high fluoride solution and maintain this equilibrium.

Secondly, clay minerals also have certain capacity of desorption of fluoride. In this process, fluorine can fast be leached and the capture aluminium in clay minerals. Eventually all other clay minerals will be changed in the direction of being montmorillonite (Egli et al., 2001, 2004). But compared with clay mineral adsorption of fluorine, desorption process requires longer time (Zhang et al., 2007).

4. CONTROL FACTORS FOR GEOCHEMICAL PROCESS OF FLUORINE IN SOIL

Factors for clay mineral adsorption and desorption of fluoride include concentration of fluoride in clay minerals, soil pH, salinity, and their fluoride contains (Fung et al., 1999; Ren and Jiao, 1988; Lavado and Reinaudi, 1979). According to above literatures, the order of adsorption capacity of different clay minerals can be summarized as: fluorine containing $Al(OH)_3$ bentonite, $Al(OH)_3$ > halloysite > gibbsite, kaolinite >> soapalkaline soil, vermiculite, goethite; layered silicate mineral > various oxide. New precipitation of $Fe(OH)_3$ or $Al(OH)_3$ are very beneficial to adsorption.

In addition, slightly acidic soil is easy to adsorb fluoride with adsorption capacity 10 times higher than alkaline soil (Xu and Xing, 1995). Fluoride adsorption by smectitic and kaolinite can be described well by the Langmuir formula in fluorine concentration of 0-180 μm and pH range between 4 and 9 (Baryoseg et al., 1989; Noureddine and Ezzeddine, 2006). At the same time, free iron and aluminum in the soil solution (Fung et al., 1999), amorphous iron, and aluminum oxide (Zhuang and Yu, 2002) can affect the adsorption capacity of fluoride by changing electrochemical properties of clay minerals. In addition, the rainfall (Dissanayake, 1979), agricultural use intensity, natural vegetation and even grazing (Reid and Horvath, 1980) will also affect the adsorption and desorption of fluorine by clay minerals. In addition, soil with fine grain is easier to retain fluorine than sandy soil (Pickering, 1985).

5. CONCLUSION

The presence of fluoride in exceeding limits and its related problems of drinking water prevailing in many parts of India is well documented. Fluoride in drinking water is known for both beneficial and detrimental effects on health. Many solutions to these problems were also suggested. Fluoride from water or wastewater can be removed by an ion exchange/adsorption process or by a coagulation, precipitation process. The ion exchange/adsorption can be applied to either concentrated or diluted solutions and they are capable of achieving complete removal under proper conditions. The method suitable for a given situation needs to be judiciously selected considering the various aspects. The paper presents the current information on fluoride in environment and its effects on human health and available methods of defluoridation in detail.

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