

Geochemical process of fluorine in soil

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Abstract Fluorine is in the dynamic balance of two geochemical processes, enrichment and leaching, reflecting the adsorption and desorption of fluoride by clay minerals, respectively. The two geochemical processes of fluorine in soil are influenced by factors including geochemical characteristics of soil and clay minerals, pH and salinity of soil solutions, climate, grazing and agriculture activities. Main factors controlling enrichment and leaching process of fluorine in soil can be found with interaction consideration.

Key words fluorine; soil; clay mineral; enrichment; leaching; adsorption; desorption

1 Introduction

Fluorine is an indispensable 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 fluorination (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 of 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 abundance 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-combustion 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 combustion 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 surface and ground water and induce drinking water type endemic fluorosis. Under certain

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 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).

In short, many factors influence the adsorption and desorption of fluorine by clay minerals, whereas main factors controlling enrichment and leaching process of fluorine in soil can be found with interaction consideration.

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References

- Alma Ruiz Payan, Ortiz M., and Maria Duarte Gardea (2005) Determination of fluorine in drinking water and in urine of adolescents living in three counties in Northern Chihuahua Mexico using a fluoride ion selective electrode [J]. *Microchemical Journal*. **81**, 19–22.
- Alvarez E., Perez A. and Calvo R. (1993) Aluminium speciation in surface water and soil solutions in areas of sulphide mineralization in Galicia (NW Spain) [J]. *Sciences of the Total Environment*. **133**, 17–37.
- American Dietetic Association (2005) Position of the American Dietetic Association: The impact of fluoride on health [J]. *Journal of the American Dietetic Association*. **105**, 1620–1628.
- Arnesen A.K.M., Abrahamsen G., Sandvik G., and Krogstad T. (1995) Aluminium-smelters and fluoride pollution of soil and soil solution in Norway [J]. *Science of the Total Environment*. **163**, 39–53.
- Bar-yosef B., Afik Isabel, and Rosenberg Rivka (1989) Fluoride sorption by montmorillonite and kaolinite [J]. *Soil Science*. **145**, 194–200.
- Colin Neal (1989) Fluorine variations in welsh streams and soil waters [J]. *Science of the Total Environment*. **80**, 213–223.
- Collins T.F.X., Sprando R.L., Black T.N., Shackelford M.E., Olejnik N., Ames M.J., Rorie J.I., and Ruggles D.I. (2001) Developmental toxicity of sodium fluoride measured during multiple generations [J]. *Food and Chemical Toxicology*. **39**, 867–876.
- Dai Shifeng, Li Weiwei, Tang Yuegang, Zhang Yong, and Feng Peng (2007) The sources, pathway, and preventive measures for fluorosis in Zhijin County, Guizhou, China [J]. *Applied Geochemistry*. **22**, 1017–1024.
- Dissanayake C.B. (1979) Geochemical provinces and the incidence of dental diseases in Sri Lanka [J]. *The Science of the Total Environment*. **13**, 47–53.
- Downey M. (2000) Muddying the waters: Fluoride in drinking water [J]. *The Lancet*. **355**, 1644–1645.
- Egli M., Durrenberger S., and Fitze P. (2004) Spatio-temporal behavior and mass balance of fluorine in forest soils near an aluminium smelting plant: Short-and long-term aspects [J]. *Environmental Pollution*. **129**, 195–207.
- Egli M., Mirabella A., and Fitze P. (2001) Clay mineral transformations in soils affected by fluorine and depletion of organic matter within a time span of 24 years [J]. *Geoderma*. **103**, 307–334.
- Fuge R. and Andrews M.J. (1988) Fluorine in the UK environment [J]. *Environmental Geochemistry and Health*. **10**, 96–104.
- Fung K.F., Zhang Z.Q., Wong J.W.C., and Wong M.H., (1999) Fluoride contents in tea and soil from tea plantations and the release of fluoride into tea liquor during infusion [J]. *Environmental Pollution*. **104**, 197–205.
- Ghorai Subhashini and Pant K.K. (2005) Equilibrium, kinetics and breakthrough studies for adsorption of fluorine on activated alumina [J]. *Separation and Purification Technology*. **42**, 265–271.
- Hamilton M. (1992) Water fluoridation: A risk assessment perspective [J]. *Journal of Environment and Health*. **54**, 27–32.
- Issa A.I., Preston K.P., Preston A.J., Toumba K.J., and Duggal M.S. (2003) A study investigating the formation of artificial sub-surface enamel caries-like lesions in deciduous and permanent teeth in the presence and absence of fluoride [J]. *Archives of Oral Biology*. **48**, 567–571.
- Jacks G. and Sharma V.P. (1995) Geochemistry of calcic horizons in relation to hillslope processes, southern India [J]. *Geoderma*. **67**, 203–214.
- Kabata-Pendias A. and Pendias H. (1984) *Trace Elements Soils Plants* [M]. CRC Press, Boca Raton, FL.
- Kafri U., Arad A., Halicz L., and Ganor E. (1989) Fluorine enrichment in groundwater recharged through loess and dust deposits, southern israel [J]. *Journal of Hydrology*. **110**, 373–376.
- Lavado R.S. and Reinaudi N. (1979) Fluoride in salt affected soils of La Pampa (Republica Argentina) [J]. *Fluoride*. **12**, 28–32.
- Meenakshi S., Sairam Sundaram C., and Rugmini Sukumar (2008) Enhanced fluoride sorption by mechanochemically activated kaolinites [J]. *Journal of Hazardous Materials*. **153**, 164–172.
- Noureddine Hamdi and Ezzeddine Srasra (2006) Removal of fluoride from acidic wastewater by clay mineral: Effect of solid liquid ratios [J]. *Desalination*. **1**, 238–244.
- Pickering W.F. (1985) The mobility of soluble fluoride in soils [J]. *Environmental Pollution (Ser. B)*. **9**, 281–308.
- Reid R.L. and Horvath D.J. (1980) Soil chemistry and mineral problems in farm livestock, a review [J]. *Animal Feed Science and Technology*. **5**, 95–167.
- Ren Fuhong and Jiao Shuquin (1988) Distribution and formation of high-fluorine groundwater in China [J]. *Environmental Geology and Water Science*. **12**, 3–10.
- Ruiz T., Persin F., Hichour M., and Sandeaux J. (2003) Modelisation of fluoride removal in Donnan dialysis [J]. *Journal of Membrane Science*. **212**, 113–121.
- Sergio Bellomo, Alessandro Aiuppa, Walter D. Alessandro, and Francesco Parello (2007) Environmental impact of magmatic fluorine emission in the Mt. Etna area [J]. *Journal of Volcanology and Geothermal Research*. **165**, 87–101.
- Wang Binbin, Zheng Baoshan, Zhai Cheng, Liu Xiaojing, and Yu Guangqian (2004) Relationship between fluorine in drinking water and dental health of residents in some large cities in China [J]. *Environment International*. **30**, 1067–1073.
- Wang Wuyi, Li Ribang, Tan Jian'an, Luo Kunli, Yang Lisheng, Li Hairong, and Li Yonghua (2002) Adsorption and leaching of fluoride in soils of China [J]. *Fluoride*. **35**, 122–129.
- Wu Daishe, Zheng Baoshan, Wang Aimin, and Yu Guangqian (2004) Fluoride exposure from burning coal-clay in Guizhou Province, China [J]. *Fluoride*. **37**, 20–27.
- Xu Liying and Xing Huangxi (1995) Fluorine in the soil [J]. *Soil*. **27**, 191–194 (in Chinese with English abstract).
- Yu Ping, Alasdair P., Brian Lee, Phillips L. and William H. Casey (2003) Potentiometric and ¹⁹F nuclear magnetic resonance spectroscopic study of fluoride substitution in the GaAl12 polyoxocation: Implications for aluminum (hydroxide) mineral surfaces, [J]. *Geochimica et Cosmochimica Acta*. **67**, 1065–1080.
- Zhang Hongmei, Su Baoyu, Liu Penghua, and Zhang Wei (2007) Experimental study of fluorine transport rules in unsaturated stratified soil [J]. *Journal of China University of Mining and Technology*. **17**, 382–386.
- Zhuang Jie and Yu Guirui (2002) Effects of surface coatings on electrochemical properties and contaminant sorption of clay minerals [J]. *Chemosphere*. **49**, 619–628.