EXPERIMENTAL STUDY OF F SORPTION BY HUMUS SOILS

Aksyuk A.M., Korzhinskaja V.S., Kotova N.P.Tkachenko H.A.
(Institute of Experimental Mineralogy RAS)
Anatoly.Aksyuk@iem.ac.ru

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Introduction. Experimental researches of fluorine behavior in an environment are an actual problem. F is the second after Hg on destructive action on an alive substance and the behavior of it remains poorly investigated in a quantitative sense. In drinking water physiologically safe concentration of fluorine is in a narrow interval 0.6-1.5 mg/L ($3.16*10^{-5}$ – $7.9*10^{-5}$ mol/L). Fluorine is widely widespread element in the nature. The average content of fluorine in soils is usually estimated in 200-350 ppm, and for humus is 450-1194 ppm. Locally, the fluorine content in soils is closely connected to it in environmental and spreading rocks. The fluorine content varies with composition of rocks and more often is in an interval 100-2000 ppm. In subsoil waters by S.R. Krainev, the concentration of fluorine changes in the range from the 0.0 mol/dm^3 up to the 0.5 mol/dm^3. For F-rich provinces of the Transbaikalia including in the Orlovka area, m_{HF} is more often in a range 0.7-1 mg/L.

General approach to the experimental study. Experimental study of fluorine sorption with natural soils has some advantage, despite of complexity of the subsequent experimental results interpretation. On the one hand, the complex chemical and mineralogical structure of natural soils allows receive only "average" parameters of the sorption process referred to the surfaces of the soil sample. On the other hand, in this case we receive direct characteristics of the sorption for the real soils including natural organic substance too.

The characteristic of soils. According to soil classification the soils of the East Transbaikalia, where the Orlovka tantalum deposit is located, concern to the type of dark grey or light brown wood soils which were formed in moderately cold climatic zone. The typical soil profile on the Orlovka area includes usual horizons: A_o is a vegetative layer with thickness up to 5-10 cm; A_1 is a humus horizon with thickness up to 15-20 cm; A_2 is an eluvial horizon with thickness some cm; B is illuvial horizon with thickness of the 50-70 cm. Sandy and sandy-loam varieties are prevail in the illuvial horizon of the soil. The soil samples have been taken for the experimental study from a humus horizon of the profile located in several hundreds meters from the Orlovka open pit. The horizon had brown color, thickness about 15 cm, and contained up to 40 % of debris rock and some % of organic substance. The initial contents of fluorine in soil samples were in an interval 600-730 ppm. The mineral structure included illite-smectite, quartz, feldspars, tremolite, and iron oxides.

Technique of the experiment. Experiments were carried out under room conditions. Duration of experiences was 1 day. Concentration of fluorine in initial and final solutions was measured by the ion - selective method (ISM) with TISAB. Measured by ISM the fluoride concentration of standard solutions with the humus water were in the 1.5 time less as real one in the HF range from $5*10^{-5}$ up to the $4*10^{-3}$ mol/L that was taken into account. The specific surface of initial soil powders has been determined by the BET method and has values 1.3-1.7 m^2/g. The soil/solution ratio was supported in runs as 1/5. Initial HF concentration varied from 10^{-4} up to the 0.5 mol/dm3. Initial three-distilled water with pH=5.75 changed the pH up to 6.45-6.74. Calculation of equilibrium concentration of fluoride species (F^-, HF^o, HF^{2-}) was carried out for final solution by the HCH program (by Shvarov J.V.) or using the experimental values pH.

Results of the experiments. Results of the experiments shown, that fluorine is actively sorbed by humus soils. The F sorption isotherms filling the first monolayer are well reproduced in various series of experiments (Fig. 1). The capacity of a monolayer is equal about 50 atoms of fluorine on 1 nm^2 of the BET soil surface determined before experience. This value appeared close to maximal calculated one if to accept the fluorine radius about 0,136 nanometers that is equal usual value. The monolayer of adsorbed fluorine is filled at the HF concentration about at the $2*10^{-3}$ mol/dm^3. It was reflected in reduction of the initial HF concentrations during experiment almost in 10 times. Adsorption occurs at pH=4.3-6.7, i.e. in solutions where a prevailing particle of the dissolved fluoride is F^-. The further "sorption" (F linkage) in soils has more complex character and experimental data have the much greater scatter. It is connected, apparently, to participation of an ion-exchange reactions or a new mineral formation. A kinetic of these processes is considerably slower and one-day duration of the run is insufficient for achievement of equilibrium. It is interesting, that «filling of the second layer» occurs at decrease of the equilibrium F^- and the “sorption” isotherm can get a "retrograde" kind, i.e. increase

of sorbed layers occurs at decrease of equilibrium concentration of fluoride in a solution. The further fluorine sorption continues to grow almost linearly up to equilibrium HF concentration in the solutions ~0.02 mol/dm^3. But saturation is not reached despite of increase fluorine sorption up to 1000 atoms on 1 nm^2 surface.

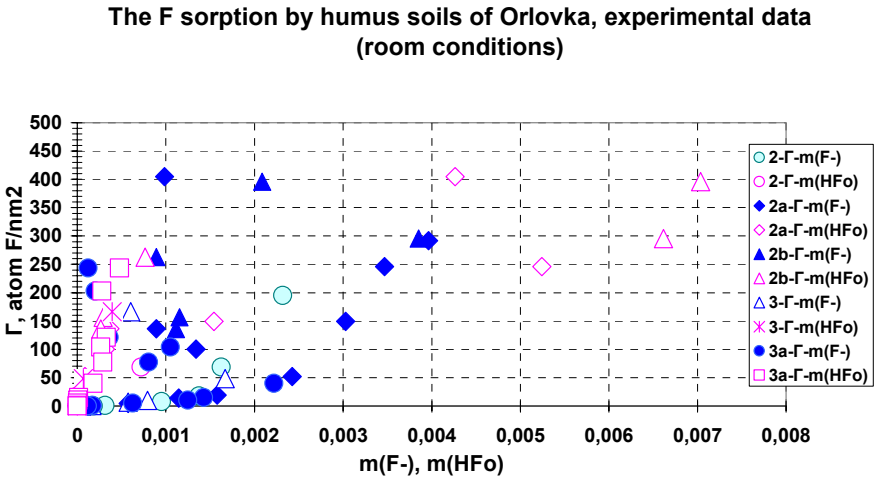

Fig. 1

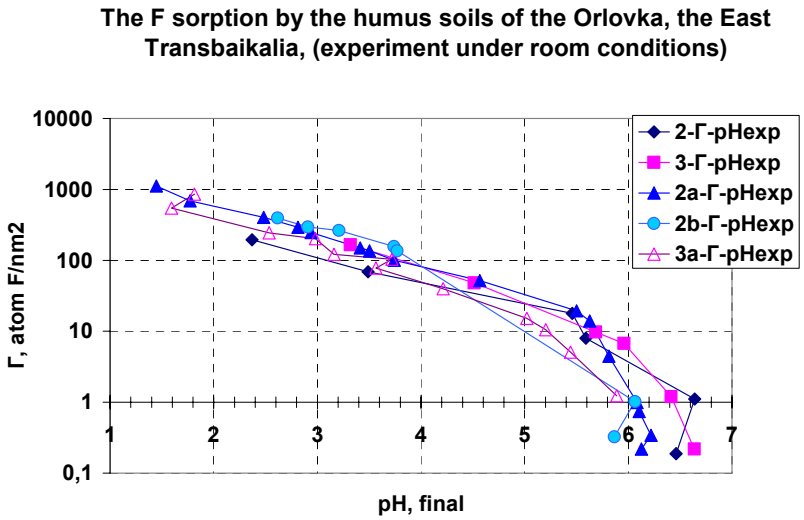

Fig. 2

If the first monolayer of fluorine is formed in the narrow range of pH, the further "sorption" of fluorine occurs in the wider interval pH from 4.5 up to 1.0 in which linear dependence lg Γ and pH (Fig. 2) is kept.

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