The ferromanganese crusts in the sea coast soils and their activity in the processes of soil self-purification

The ferromanganese crusts in the sea coast soils and their activity in the processes of soil self-purification

Yana Timofeeva

The research worker, 690022, Vladivostok, ave. 100-years by Vladivostok, 159, the Institute of Biology and Soil Science FEB RAS, RUSSIA.

The peculiar characteristics of the sea coast soil cover consist in its economic and ecological significance. Economic significance is accounted for a big density of population and participation of coastal territories in the industrial and agricultural managements. The ecological importance is connected with a high man-made effect on soil ecosystems. So a question on soil resistance to redundant heavy metal enterings, the most popular pollutants, is in the area of the great importance. Heavy metals can be located long time in soil and cause numerous changes in the soil environment.

The soil is multifunctional, heterogeneous, thermodynamic and opened system. The soil has capability to retain heavy metals and protect the adjacent territories from pollution and contamination. That results in activization of protective soil mechanisms causing change of heavy metal forms and their toxicity. This soil function depends on many factors (such as the contents mineral particles, humus, pH, specific soil formations, etc.); so new soil formations as ferromanganese crusts are of especial interest to be studied. They are the integral components and important indicators of many processes occurring in soil. The ferromanganese crusts are unique formations of organic-mineral nature. Presence of active adsorption centers on their surface causing fixation of the elements migrating through soil profile is the essential mobilization factor. The crusts exert a direct influence on the profile and spatial allocation of chemical elements in soils.

Nowadays there is little information about the heavy metal contents in the crusts to make conclusions concerning influence of crusts on the processes of their migration. Accounting of that the aim of this work is to study an effect of ferromanganese crusts in the processes of accumulation and migration of heavy metals in the sea coast soils. To study the mechanisms of self-purification of the sea coast soils and find out their potential activity means to settle up the most actual problems of preservation environment and have ecology suitable for life.

The maritime soils (Sea of Japan Coast) have been studied and different degree of man-made activity and its influence has been established. That allowed to appreciate the intensity of the processes of adsorption occurring in the soils and soil's crusts. The contents of total and mobile forms of heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb) have been identified with the atomic absorption spectrophotometer method use. The average regional (klark) concentration has been used to identify degree of pollution by heavy metals of the researched samples. The coefficient of concentration has been computed by the results of definition total contents. It shows how many times an intensity of accumulation process of the elements in the crusts outstrips intensity of their accumulation in containing soil.

The ferromanganese crusts have been found in all samples of the studied maritime soils. They are dense contractions of dark-brown and dark grey color, the correct spherical form with rough and fine-pore character of their surface in most cases. The size of crusts varies within limits from 1 up to 10 mm. The maximum contents of crusts were determined in the upper part of the soil profile.

The results, obtained in studying of maritime soils, not affected by any direct man-made influence, testify to rather satisfactory soil condition concerning the content of heavy metals. But at studying of the store of the elements in the crusts the contents of heavy metals sharply increase, Zn and Cd excluding (Table 1). Their content is lower in the crusts, and in some cases is equal to the content in soil. An accumulation of heavy metals in the crusts is connected, by one hand, with the activity of special group of anaerobic microorganisms participating in the process of the ferromanganese crust formations. Under conditions of oxygen absence the microorganisms use the polyvalent chemical elements to support their activity. Such polyvalent elements, being able to lose electrons from an external orbit, can play role as an oxidizer instead of oxygen (Mn, Fe, Co, Mo, etc.). By another hand, this phenomenon may proceed because of the fact that pH of the crust is 3,8-4,5 in our case. The oxides of manganese prevailing in the structure of crusts are negatively charged and draw cations under such pH meaning.

Corresponding author: timofeeva@biosoil.ru

The concentration some elements in the crusts exceeds regional klark one in several times, thus Mn, Ni, Cu is characterized by 3-5 time increase, Pb 4-6 time and Co is registered 10 time excesses. Mn, Co, Pb, and Ni are most inclined to be accumulated in the crusts. Their concentration coefficients are the highest among all investigated elements. Cu, Cr and Mo are rather less accumulated in crusts, Zn and Cd are not accumulated. The highest coefficients of concentration of heavy metals are noted in the crusts formed in the upper soil profile.

Table 1 The content of total and mobile forms of heavy metals in the soil and crusts of the Sea of Japan coast.

Element	Klark	Coefficient of concentration	Soil			Crusts		
			A_1	gB_1	GB_2	A_1	gB_1	GB_2
Mn	1510	4,2	701 300	1141 234	1508 537	4123 752	3014 925	6207 1137
Zn	70	0,9	336 100	232 97	148 76	238 143	185 95	174 134
Ni	46	3,8	27 4,5	44 5	41 5,7	100 11	220 28	119 12
Mo	1,6	1,5	1 0,7	1 0,8	1 0,6	1,5 0,6	2 0,8	1,1 0,4
Co	22	10,8	21 9	19 7	17 7	144 52	234 102	139 53
Pb	32	4,2	35 12	41 28	44 31	137 102	209 74	172 63
Cr	66	2,0	62 37	61 42	58 31	140 44	130 14	94 11
Cu	20	1,3	77 51	56 45	61 44	79 56	74 50	97 70
Cd	0,6	0,6	0,52 0,09	0,59 0,13	0,37 0,06	0,33 0,03	0,12 0,04	0,32 0,03

Element contents are given in ppm. In the numerator – total forms, in denominator – mobile forms.

The analysis carried out on the distribution of mobile forms of heavy metals in soil horizons and crusts has shown decrease potentially available to plants Mo, Co, Cr and Cd in crusts in 2,5 - 4 time within all soil profile. As for other elements, the most decrease of mobility is typical for the crusts formed in the upper organic horizons. While moving deeper into soil profile, less total heavy metals and more mobile form of heavy metals have been noted in the crusts.

The processes of accumulation of heavy metals in the crusts have proceeded more intensively in the soil where processes of acid hydrolysis occur and they are determined by degree of the soil moisture regime. It is the result of more contrast oxidation-reduction conditions which stimulate formation and growth of soil crusts.

The fixation of heavy metals by the ferromanganese crusts especially is very important for the soils formed in the areas with high industrial activity. The increased content of heavy metals has been detected in maritime soils formed near the railway. The intensity of the heavy metal entering causes a formation of positive geochemical anomaly that result in appearance of concentrations of the above considered elements unusual for nature environment. An enhancement of heavy metal contents in soils causes their active accumulation in the crusts. The crusts contain Mn, Cr, Ni in 5-6 times, Co at 8-10 times, Cu, Zn, Cd, Pb 20-40 times more than klark. A priority of heavy metal concentrations does not detect new regularities in the crusts. But the sizes of coefficient of concentration are much enlarged by that. The content of heavy metals is maximum in the soil tests collected at the distance 50 m from a polluter, while removing from a polluter the concentration of elements in soils is reduced. But the level of reduction of the heavy metal contents in the crusts occurs more slowly. Therefore the parameters on the heavy metal contents are more even at the considerable distance from the railway than those in klark. In the crust the content of mobile forms of elements is from 5 % (Cu, Cr, Mo) up to 25 % (Pb, Ni) of their total content. Consequently, the most part of heavy metals in crust is contained in the difficult of access or not exchange form and is temporarily excluded from a circulation of chemical elements.

Thus, soil ferromanganese crusts play a role of the biofilters. They enlarge intensity fixation and absorption of heavy metals alongside with increase of man-made influence on the top-soil in the crust that provides maintenance of soil system homeostasis. The process of accumulation of heavy metals by crust is accompanied by sharp decrease of mobility and their transition into the inert form. That advantages ecological soil enhancement resulting in temporary or possibly irreversible fixation of the considered elements.