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Study on correlation between humic acid and selenium in Kaschin-Beck disease areas

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Abstract — The relationship between humic acid and selenium content was studied in this research. The results of calculation showed that there is more humic acid and less selenium in Kaschin-Beck disease areas in China. Fulvic acid in soil could increase selenium level in plants. The chemical bonding between humic acid and selenium was observed with an I.R. spectroscope. It was remarkable for the changes of absorption peak and frequency in 1100–1000 cm^{-1}, 900–700 cm^{-1}.

Keywords: humic acid; selenium; Kaschin-Beck disease.

INTRODUCTION

The humic acid is a complex and macromolecular polymer. It has many functional groups that can complex with Fe, Mn, Cu and so on. And its influcence on the movements and transportations of inorganic elements in the environment is huge. Selenium is considered as an essential element to human life. Its biological effect is noticed because of its effect on Kaschin-Beck disease. In the late 1960s the relationship between humic acid and selenium has been suggested by Grosgova in U.S.S.R. (Grosgova, 1968). Peng An *et al.* indicated the antagonism between selenium and humic acid with experiment(Peng, 1987). Experiment on the absorption of selenium and molybdenum in soil by humic acid was done by us in 1990 (Ren, 1990), but the relationship between humic acid and selenium and its biological effect have not been studied in detail.

Selenium and humic acid in soil and drinking water in Kaschin-Beck disease areas have been determined in the past few years. Excessive humic acid and insufficient selenium in the environment of Kaschin-Beck disease areas have been found (Zhang, 1990). Therefore, the relationship between humic acid and selenium in environment was suggested.

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MATERIALS AND METHODS

Water and soil samples were collected from Kaschin-Beck disease areas in China, such as Heilongjiang, Jilin, Inner-Mongolia, Shaanxi, Gansu, Tibet provinces and autonomous regions in China.

Water samples were collected from the drinking water sources for the residents in Kaschin-Beck disease areas, including well water, river water, pond water, cellar water, spring water and so on. The collected samples were acidified by nitric acid to pH 1−2 on site for the determination.

Soil samples were collected from different kinds of soils in Kaschin-Beck disease areas, in which dark brown soil, meadow brown soil, meadow soil, brown soil, black soil, bog soil, and so on were put in plastic bags, respectively.

The influence of humic acid and selenium on plants in experiments have been simulated in laboratory in order to explain the relationship between humic acid and selenium in environment. The experiment methods were as follows:

100 ppm humic acid (HA) + 10 ppm Se^{4+} (SeO_2); 100 ppm fulvic acid (FA) + 10 ppm Se^{4+} (SeO_2); 100 ppm HA; 100 ppm FA; 10 ppm Se^{4+} (SeO_2) were added to soil for each pot, and then same corn seeds were grown in 6 pots which included control soil. After the corn in 6 pots have grown for 2 months, selenium contents in feet and leaves of corn in each pot were determined by fluorescence spectrophotometry.

Color spectrometry (Model-PG-5, Japan) was employed for analysis of humic acid and fulvic acid in water and soil samples.

Fluorescence spectrophotometry (Model-RF-510, Japan) was employed for analysis of selenium content in water and soil samples.

RESULTS AND DISCUSSIONS

The results of humic acid and selenium contents in water and soil samples in Kaschin-Beck disease areas in Heilongjiang, Jilin, Inner-Mongolia, Shaanxi, Gansu, Tibet provinces and autonomous regions are shown in Table 1 and 2. There is more humic acid and less selenium in drinking water and soil samples in Kaschin-Beck disease areas, compared with that of non-disease areas (Zhang, 1990). A negative correlation has been found in the relationship between humic acid and selenium in dirnking water samples through statistical calculation. But it was not clear for the correlation of humic acid and selenium in soil samples because of the influence of Se forms in soil on it.

In order to study the effect of humic acid on absorption of Se by plants, we have carried out the simulation experiments in laboratory. The results from simulation experiments are shown in Table 3.

Table 1 Humic acid and selenium contents in drinking water of Kaschin-Beck disease areas

Site	Sample	number	Range	$X \pm SD$	G	$C.V.\%$	r	p
Jilin	FA	16	0.219 – 1.377	0.778 ± 0.411	0.673	52.88	−0.638	< 0.01
	Se	16	0.06 – 0.270	0.115 ± 0.059	0.109	50.95	−0.689	< 0.01
Heilongjiang	FA	44	0.20 – 2.510	0.694 ± 0.443	0.488	74.71	−0.411	> 0.01
	Se	44	0.00 – 0.910	0.152 ± 0.164	0.129	107.98	−0.575	< 0.05
Inner-mongolia	FA	28	0.03 – 2.760	0.720 ± 0.605	0.526	84.07	−0.293	< 0.1
	Se	28	0.00 – 0.737	0.124 ± 0.146	0.084	118.27	−0.484	< 0.05
Shaanxi	FA	73	0.102 – 4.288	1.092 ± 0.981	0.878	89.84		
	Se	73	0.01 – 1.170	0.180 ± 0.160	0.162	88.89		
Gansu	FA	11	0.288 – 0.563	0.435 ± 0.101	0.419	23.22		
	Se	11	0.043 – 0.800	0.243 ± 0.240	0.132	99.12		
Tibet	FA	13	0.270 – 0.500	0.732 ± 0.381	0.676	52.07		
	Se	13	0.032 – 0.500	0.133 ± 0.123	0.105	93.09		

*FA-mg/L, Se-μg/L

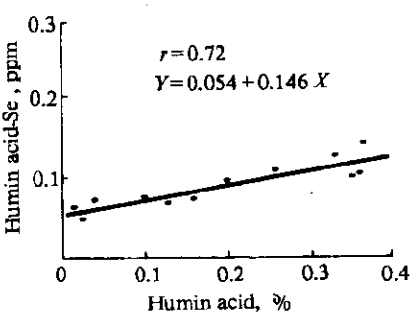

Fig. 1 The relationship between contents of HA and Se

Table 3 shows that Se level uptaken by feet of corn that grew in the pot with FA + Se^{4+} soil was highest among the 6 pots. Se level in feet was more than that in leaves in both experiment groups and control groups. This shows the fulvic acid in soil can increase Se level in plants. We then know that HA-Se level in soil of Kaschin-Beck disease areas was more than FA-Se level in soil of the same areas. HA-Se content accounted for 75% of total Se in soil. And a positive correlation has been found in the relationship between HA-Se and HA through calculation($r = 0.72$), which is shown in Fig.1.

I. R. spectra-analysis of humic acid showed that humic acid could complex with selenium chemically. The chemical bonding between humic acid and Se was clearly shown in the experi-

ment. It was remarkable for the changes of absorption peak and frequency in 1100−1000 cm^{-1}, 900−700 cm^{-1} in I.R. spectra. Se could be in the structure of humic acid, where it was as Se=0, Se-H to be bonded. Experimental results also indicated that the function of humic acid and selenium was affected by pH in environment. It was very clear for the changes of I. R. spectra of FA-Se if pH=2. I. R. spectra of FA-Se would be similar to I. R. spectra of FA if pH=6.0 (Fig. 2).

Therefore, the reason of selenium deficiency in environment of Kaschin-Beck disease areas was that selenium was bonded by humic acid under the reduction conditions except in the case of selenium deficiency in soil materials.

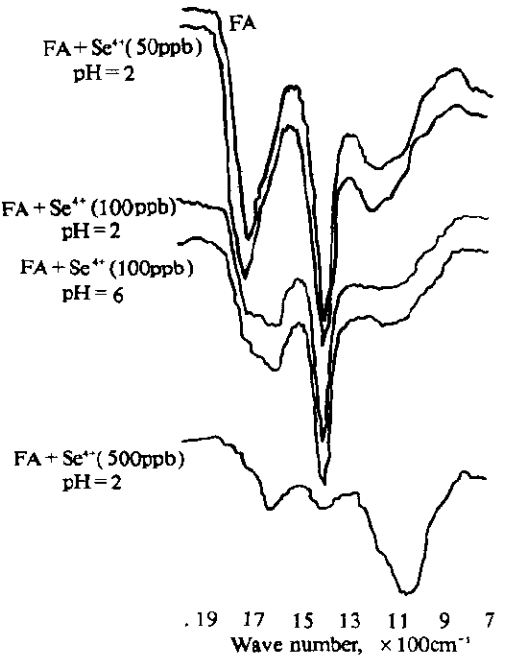

Fig. 2 I. R. spectra of FA-Se

as Se=0, Se-H to be bonded. Experimental results also indicated that the function of humic acid and selenium was affected by pH in environment. It was very clear for the changes of I.R. spectra of FA-Se if pH=2. I.R. spectra of FA-Se would be similar to I.R. spectra of FA if pH=6.0 (Fig.2).

Therefore, the reason of selenium deficiency in environment of Kaschin-Beck disease areas was that selenium was bonded by humic acid under the reduction conditions except in the case of selenium deficiency in soil materials.

Table 2 Humic acid and selenium contents in soil of Kaschin-Beck disease areas

Site	Sample	number	Range	$X \pm SD$	C.V.%	r	p
Jilin	FA	19	0.230—1.920	0.856±0.375	43.81	−0.435	< 0.05
	Se	19	0.073—0.280	0.169±0.075	44.27		
Heilong-	FA	9	0.078—1.130	0.664±0.473	71.23	+0.743	< 0.01
jiang	Se	9	0.070—0.260	0.158±0.08	50.71		
Inner-	FA	9	0.576—1.190	0.785±0.199	25.39	−0.602	< 0.01
Mongolia	Se	9	0.090—0.190	0.133±0.034	50.22		
Shananxi	FA	10	0.000—0.381	0.134±0.125	93.14	−0.123	> 0.2
	Se	10	0.060—0.110	0.088±0.015	16.77		
Tibet	FA	16	0.003—0.279	0.164±0.113	68.95	+0.0780	
	Se	16	0.064—0.180	0.104±0.036	34.44		

*FA —%, Se —μg/g.

Table 3 Selenium level in feet and leaves of corn in experimental groups and control groups, 3 times

	HA + Se^{4+}		FA + Se^{4+}		HA	
	feet	leaves	feet	leaves	feet	leaves
Se, μg / g	7.213	5.68	16.19	7.533	7.64	4.990
	FA		Se^{4+}		Control	
	feet	leaves	feet	leaves	feet	leaves
Se, μg / g	14.21	4.951	7.92	3.412	4.286	2.332

CONCLUSION

As mentioned above, the results from the study and experiment point out that a negative correlation existed in the relationship between humic acid and selenium in drinking water of Kaschin-Beck disease areas. Correlation coefficient of humic acid and selenium was −0.638, −0.689, −0.411, −0.575, −0.484, respectively ($p < 0.05$).

Fulvic acid in soil can increase selenium level in plants, but humic acid was not as good as FA. HA-Se level was more than FA level in soil of the same areas. A positive correlation has been found in the relationship between HA-Se and HA through calculation ($r = 0.72$). I. R. spectra of humic acid showed that there are the chemical bonding between humic acid

and Se.

REFERENCES

Grosgova, T.B, J. of Pedology, 1968, 1 : 60

Peng An and Xu Langqiu, Scientia Sinica(Series B), 1987, 30(1) : 66

Ren Shufen and Zhang Xuelin, Proceedings of International Symposium on Peat and Peatland Character and Uses, USA, 1990 : 292

Zhang Xuelin and Ren Shufen, Chinese J. of Contr. End. Dis, 1990, 5 (2) : 65