Journal of Environmental Sciences (China) Vol. 3, No. 4, pp. 95–101, 1991 ISSN 1001-0742

Humic acid and free radical in environment of Kaschin-Beck disease areas

Ren Shufen[1], Zhang Xuelin[1], Li Wencheng[1], Wang Wensheng[1], Wang Jinda[1], Wang Wenjun[1] and Zhang Yuxia[1]

(Received July 11, 1991)

Abstract— The humic acid contents in drinking water and soil in Kaschin-Beck disease areas were found more than that of non-disease areas in this research. Changes of free radical concentration in drinking water were agreed with that of humic acid contents in drinking water of Kaschin-Beck disease areas. A positive correlation of free radical concentration and humic acid content in drinking water has been shown ($r=0.913$). The structure of I. R. spectra of humic acid under ultraviolet light has been changed. Thus it indicated that free radical was resulted from benzoqiunonyl groups of humic acid in environment.

Keywords: humic acid; free radical; Kaschin-Beck disease.

INTRODUCTION

Up to now, 3 etiologies have been formed to the cause of Kaschin-Beck disease in China. In general, low selenium in environment, toxicity of organic matter in drinking water, and organic compounds in grains from the Kaschin-Beck disease areas have been suggested, but not anyone was passed by all researchers. It was emphasized to need studying any more in the future. The materials in studying on the environmental cause of Kaschin-Beck disease have been shown that the cause of Kaschin-Beck disease was closely associated with high humic acid in environment of the disease areas. It was significant to study humic acid in drinking water to the cause and control of Kaschin-Beck disease. Less than 0.5 mg/L of humic acid in drinking water could be, in fact, made as a assessment standard to control Kaschin-Beck disease, which was resulted from our investigation of Kaschin-Beck disease areas in past few years (Zhang, 1982).

Some researchers of China have found that cartilage cell may be destroyed by humic acid and free radical in drinking water of Kaschin-Beck disease areas, and model of free radical to environmental cause of Kaschin-Beck disease has been supposed (Peng, 1990). This paper aimed at studying the relationship between humic acid and free radical, which was associated with Kaschin-Beck disease, and provide an information and basic data for the cause

[1] Changchun Institute of Geography, Chinese Academy of Sciences, Changchun, China.

and control of Kaschin-Beck disease.

MATERIAL AND METHODS

According to the geographical distribution, natural ecological environment, and epideological characteristics of Kaschin-Beck disease areas, the water and soil samples from the disease areas were collected, such as: Heilongjiang, Jilin, Inner-Mongolia, Shandong, Shaanxi, Sichuan and Tibet provinces or autonomous regions.

Then, it was as research system of experimental areas for studing the case of heavy disease areas-Tianshui disease area in Gansu Province.

Color spectrometry (model PG-5, Japan) was employed in the analysis of humic acid in drinking water and soil.

ESR spectrometry (ER200D, Germany) was employed in the analysis of free radical in drinking water.

GDX-102 resin without ESR signals which made in Tianjin was used in the richment of humic acid in drinking water, then, washed and purified, and then, was put in Quartz tubes for the determination with ESR spectrometry.

RESULTS AND DISCUSSION

Distribution characteristics of humic acid in Kaschin-Beck disease areas

Humic acid contents in drinking water and soil in Kaschin-Beck disease areas and non-disease areas have been shown in Table 1 and Table 2, respectively. Although the distribution of Kaschin-Beck disease areas was from northeast to southwest regions in China, over about 25°C latitude, the differences of natural landscapes and topography were very clear, humic acid contents in water and soil in Kaschin-Beck disease areas from north to south all were more than that in non-disease areas ($p < 0.01$).

Table 1 Humic acid contents in soil of Kaschin-Beck disease areas and non-disease areas (%)

Site	Disease	N	Range	$X \pm SD$	t	P
Heilongjiang	Yes	5	0.97 – 1.11	1.060 ± 0.066	31.01	$p < 0.0001$
	No	4	0.078 – 0.21	0.167 ± 0.061	31.01	$p < 0.0001$
Inner-Mongolia	Yes	9	0.391 – 1.21	0.756 ± 0.23	7.853	$p < 0.001$
	No	4	0.078 – 0.210	0.169 ± 0.061	7.853	$p < 0.001$
Jilin	Yes	22	0.092 – 1.920	0.647 ± 0.472	8.460	$p < 0.001$
	No	9	0.002 – 0.233	0.114 ± 0.089	8.460	$p < 0.001$
Shannxi	Yes	5	0.20 – 1.81	0.87 ± 0.648	4.295	$p < 0.001$
	No	5	0.02 – 0.21	0.086 ± 0.078	4.295	$p < 0.001$
Shichuan	Yes	7	0.21 – 0.62	0.466 ± 0.267	1.835	$0.1 < p < 0.2$
	No	4	0.11 – 0.40	0.288 ± 0.140	1.835	$0.1 < p < 0.2$
Shandong	Yes	8	0.154 – 1.12	0.719 ± 0.303	5.574	$p < 0.001$
	No	4	0.15 – 0.31	0.24 ± 0.063	5.574	$p < 0.001$
Tibet	Yes	14	0.061 – 0.933	0.285 ± 0.231	3.972	$p < 0.001$
	No	7	0.057 – 0.354	0.186 ± 0.113	3.972	$p < 0.001$

Table 2 Humic acid contents in drinking water of Kaschin-Beck disease areas and non-disease areas, μg/L

Site	Disease	N	Range	$X \pm SD$	P
Heilongjiang	Yes	18	0.26 −2.51	0.844 ±0.537	$p<0.001$
	No	22	0.13 −1.38	0.357 ±0.266	$p<0.001$
Inner-Mongolia	Yes	71	0.19 −2.76	0.672 ±0.472	$p<0.001$
	No	24	0.03 1.52	0.463 ±0.405	$p<0.001$
Jilin	Yes	18	0.563 −1.61	0.962 ±0.387	$p<0.001$
	No	6	0.219 −0.87	0.474 ±0.537	$p<0.001$
Shannxi	Yes	95	0.49 −2.80	1.15 ±1.07	$p<0.01$
	No	5	0.232 −0.564	0.36 ±0.08	$p<0.01$
Shichuan	Yes	6	0.30 −1.09	0.82 ±0.173	$p<0.01$
	No	5	0.32 −0.59	0.45 ±0.107	$p<0.01$
Shandong	Yes	5	0.25 −8.34	3.67 ±3.90	$p<0.001$
	No	25	0.10 −0.69	0.279 ±0.151	$p<0.001$
Tibet	Yes	3	0.30 −1.06	0.787 ±0.423	$p<0.3$
	No	3	0.300 −0.75	0.510 ±0.227	$p<0.3$

The distribution of humic acid from the different kinds of water sources

We can see that there were different types of water sources in Fig. 1, where there was the big difference in humic acid contents in several kinds of water sources. The order of humic acid contents in the different types of water sources are as follows:

Celler water > river water and stream > well > crevice water > spring water. Humic acid contents in cellar water, river and stream water or well water were high, as they are the disease areas of Shannxi, Shandong, Heilongjiang and Jilin provinces, respectively (Table 3).

If humic acid contents in water were changed from high to low, the incidence of disease would be from high to low, or disappear, for example, the morbidity of Kaschin-Beck disease in Fusong County of Jinlin Province was 92.7% in 1950, humic acid contents in drinking water were 1.14% mg/L. If humic acid content has been declined to 0.36 mg/L in 35 years, the morbidity of the disease would be 1.3% by examinating the residents in the disease areas. No new one has been happened here up to now.

The distribution of humic acid in drinking water in typical heavy disease areas

Tianshui region in Gansu Province was more heavy disease area. It was chosen as an important object of the research and investigation. From Fig. 2 we can see that a positive correlation has been shown in the relation of humic acid in drinking water to incidence of Kaschin-Beck disease, $r=0.785$ ($p<0.01$), logarithmic correlation $r=0.796$ ($p<0.01$). Logarithmic correlation equation $Y=1.149+0.586\ \ln X$, here $Y=X$-ray%, $X=$humic acid content. This result was agreed with others (Proceedings, 1984).

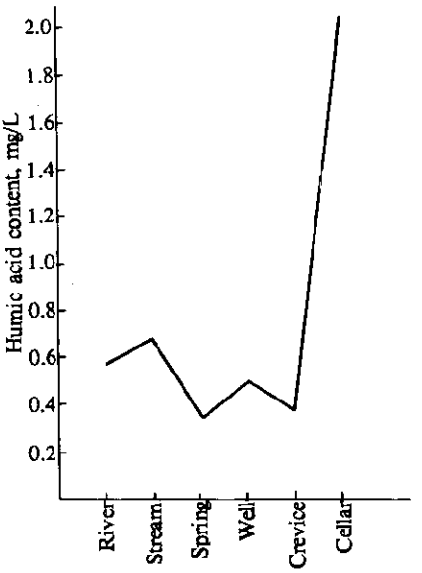

Fig 1 Relationship between different types of water sources and humic acid content

Table 3 Situation of the changes of disease (X-ray%) in the in and out of improving water source

Site	Water type	FA, mg/L	Disease degree, X-ray%
Fusong County (Jilin Province)	Well	1.14	Heavy disease in history
	Crevice	0.36	Stable slight disease situation
Qianan County (Jilin Province)	Well	0.72	Disease village in history
	Crevice	0.26	Non-new one
Shangzhi County (Heilongjiang Province)	Well	1.20	Heavy disease in history
	Crevice	0.37	Stable situation
Qingzhou County (Shandong Province)	Cellar	1.14	Disease village
	Crevice	0.18 −0.37	No-new one

Distribution of free radical in humic acid in Kaschin-Beck disease areas

From Fig. 3 we can see that distribution of free radical is corresponding with that of humic acid in drinking water. The free radical concentration in drinking water of Kaschin-Beck disease areas was more than that of non-disease areas. It was very clear for a positive correlation of free radical and humic acid contents, $r = 0.913$, regression equation $Y=0.1721+5.114X$, here Y is free radical concentration, X is humic acid ($p<0.01$).

And the same time, we have carried out the study on the degradation of humic acid in drinking water under the condition what ultraviolet-ray lighted on, and supposed the changes from macromolecular to small molecular in the structure of humic acid of drinking water in Kaschin-Beck disease areas. By examination of I. R. spectroscope (Fig. 4), I. R. spectra of humic acid in drinking water showed that it was clear for the changes in the peak of 1600 – 1700 cm^{-1} and 1000 – 1200cm^{-1}. There is small peak in this areas, and the peak to be enlarged with increasing of time. The peak of 1655 cm^{-1} is quite in the position of more cycle-benzoquinonyl groups. But it could not be in new group with oxygen because of reaction process was so slow other than fast. Thus, 1655cm^{-1} peak in I. R. spectra of humic acid has been meaned as benzoquinonyl groups. It was agreed with the signal of ESR that was determined by ESR spectrometry ($g=2.0040$). The enlarge of the peak 3400cm^{-1} and the appear of

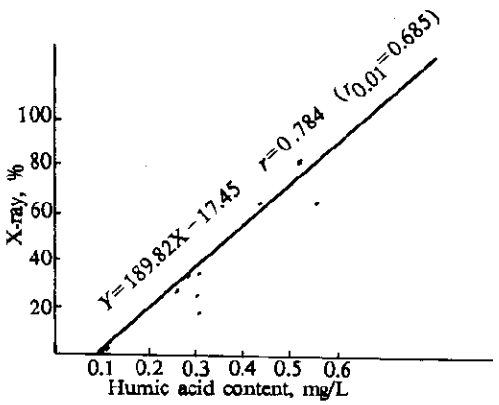

Fig. 2 Relationship between humic acid and X-ray% of Kaschin-Beck disease

1100—1200 cm^{-1} peak were then associated with phenol and hydroxyl groups. More stable free radical could be total free radicals in the different kinds of side chains, and was from humic acid in drinking water. On the other hand, it could be increased in the production of free radical with active oxygen, where free radical could affect on plants, animals and human health (Vagghan, 1982).

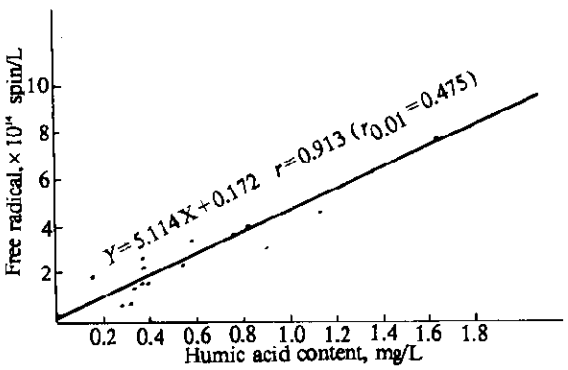

Fig. 3 Relationship between humic acid and free radical in drinking water

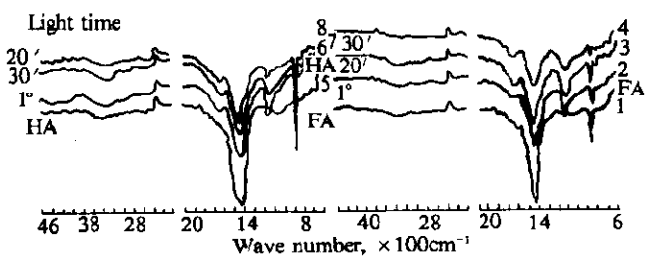

Fig. 4 I. R. spectra of FA and HA under ultraviolet light

SUMMARY

As mentioned above, we have known that humic acid contents in drinking water and soil in Kaschin-Beck disease areas were more than that of non-disease areas. A positive correlation between humic acid and incidence of Kaschin-Beck disease has been shown by calculation (r=0.78).

Changes of free radical concentration in drinking water were agreed with that of humic acid contents in drinking water of Kaschin-Beck disease areas. Correlation coefficient of free radical concentration and humic acid content in drinking water was 0.913.

The structure change of I. R. spectra of humic acid under ultraviolet light has been presented in this paper. Thus, it indicated that the free radical was resulted from benzoquinonyl

group in humic acid in environment.

REFERENCES

Peng An and Yang Chunlin, Chinese J. Contr. Ende. Dis., 1990, 5 : 29

Vagghan, D. Plant and Soil. 1982, 66 : 113

Wang Zhongyi and Lin Nianfang, Proceedings of Scientific Investigation of Kaschin-Beck Disease in Yongshou County, People's Health Press, 1984 : 81

Zhang Xuelin, Wang Zhongyi, Li Shulan, Ren Shufen, Wang Wensheng, Proceedings of the Second Songhua River Symposium on Environmental Science, Jilin People's Press, 1982 : 71