Report on the investigation of underground water contamination by discharged chromium contained waste water

JinZhou Antiepidemic Station
JinZhou alloy Plant

In 1964, some water wells were reported turning yellowish in the Nuer River village in JinZhou suburb.. An investigation revealed that the well water had been contaminated by chromium containing waste water discharged from JinZhou Alloy Plant.

In order to understand the contamination process and then find a proper treatment, we monitored the chromium contamination process in soil, water and the effect on human health. This is a report of the result of the monitoring over the past ten years.

Section One: Background Information

JinZhou Alloy Plant is located in the western suburb of JinZhou. The primary products are vanadium alloy and titanic alloy. The plant attempted to produce chromium alloy in 1959. At that time, the recovery rate of chromium was only 24.5%. This rate increased to 66.3% in 1963 and remained around 60% in the following ten years. A large amount of chromium containing waste water, waste ore residue and waste gas (The "Three Wastes") have been discharged in the process of smelting. Because of the low recovery rate and improper management, a large amount of chromium has been discharged into the surrounding environment via the route of the Three Wastes. The total amount of discharged chromium containing compound is estimated to be 930 tons. Large amounts of chromium discharged into environment would impact the surface soil and underground water.

Section II: Report of Investigation

(1) Underground water contamination:

Within six years after the plant's first attempt at smelting chromium, underground water in the Nuer River village was contaminated. Water wells turned yellowish and tasted bitter. Residents reported symptoms such as diarrhea, abdominal pain and developed oral ulcers. An investigation showed that Cr^{+6} concentration in underground water was 0.2-20.00 mg/L. Among 170 drinking water wells, 96% were contaminated. Nearly all of them exceeded the drinking water Cr^{+6} standard. The highest concentration level was 400 times more than the drinking water standard.

In order to approach the range of contamination, Cr^{+6} concentrations in underground water were measured in the villages located along the movement of underground water, which are JinChangBao, YangXing, Shilitai, WenJiaTun. In JinChangBao, 40.6% of 123 water wells have been contaminated; Cr^{+6} concentration varied between 0.002-0.4 mg/L; 12% of them exceed the drinking water standard; the highest concentrations were 8 times more than the drinking water standard. In the Nuer River Railway Station, Cr^{+6} concentrations varied between 0.09 -0.7mg/L. 26.3% of water wells were contaminated and all of them exceeded the drinking water Cr^{+6} concentration standard; the highest concentration was 15 times more than the drinking water standard. In Yangxing, 36 water wells among 66 drink water wells were contaminated; 20 contaminated water wells exceeded the drinking water Cr^{+6} concentration standard; the highest concentration was 96 times the drinking water standard. Shilitai, Wenjiatun and SandaoHao, which are located further, had a lower level of contamination. Although some water wells in these three villages were contaminated, they were all below the drinking water Cr^{+6} concentration standard. The overall pattern is that Cr^{+6} concentration in underground water deceases with the distance from the source of contamination.

Table 1.

Report on the concentration of Cr^{+6} in 473 water wells (1965)

Concentration of Cr^{+6}

Village	# of water wells	0	~0.05	~0.1	~0.5	~1.0	~5.0	5.0~
Control Group	5	5						
Nong Zhong	1	1						
Guo Lu Chang	6	2		2	2			

Jin Chang Bao	123	73	35	7	8			
Nuer River Village	170	7	1	5	27	17	76	37
Nuer River	19	14		1	3	1		
Yang Xing	50	14	16	5	12	2	1	
Shilitai	21	2	19					
Wei Jia Tun	33	27	6					
San Dao Hao	18	5	3					
Ba Jia Zi	22	20	2					
Nanshan Reservoir	5	2	3					

The total contaminated area was 20 Li^2, covering five villages. 515 water wells were contaminated. This contamination affected the drinking water and health of 3000 residents.

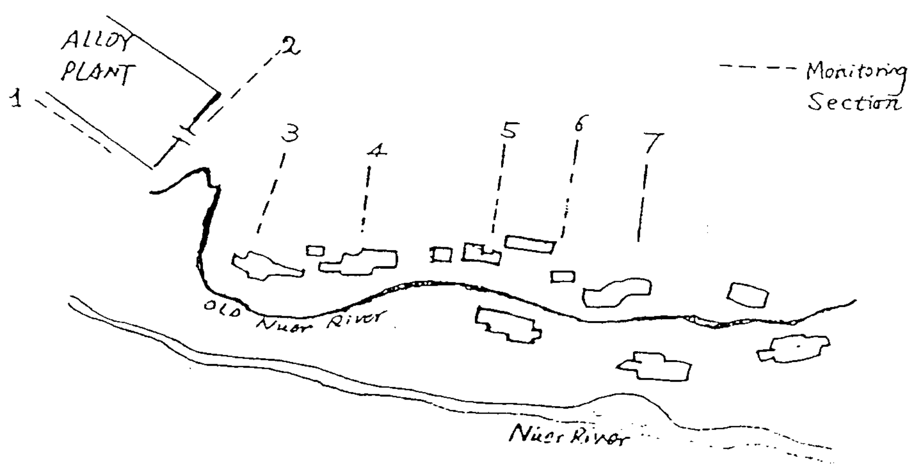


Figure 1 : Cr^{+6} contamination in 1965.

In order to understand the process of chromium contamination and the movement of the underground water, seven monitoring cross sections have been set-up in the contaminated area. Locations of the monitoring sections are presented in Figure 1. Monitoring results are presented in Table 2.

Table 2

Cr^{+6} concentration in monitoring wells of cross sections

Section Location	Well i.d.	Cr^{+6}	Section Location	Well i.d.	Cr^{+6}	Section Location	Well i.d.	Cr^{+6}
Dump Site	1	0.001	JinChang Bao	4	0.008	Railway Station	3	0
	2	0.17		5	0.08		4	0.056
	3	1.70		6	0.70		5	0.001
	4	8.00		7	1.50		6	0.1
	5	6.29		8	8.00	YangXing	1	0
	6	0.001		9	0.20		2	0.003
East Gate	1	0.01		10	0.008		3	0.054
	2	0.08	Nuer River	1	0.70		4	0
	3	0.40		2	6.0		5	0
	4	2.90		3	0.75		6	0
	5	5.10		4	3.50	Shilitai	1	0
	6	2.00		5	0.65		2	0.003
	7	1.05		6	0.70		3	0
	8	0.40		7	0.22		4	0

JinChang-Bao	1	0		8	0.003		5	0
	2	0	Nuer Railway Station	1	0		6	0
	3	0.028		2	0		7	0

Although the highest concentration is not shown in the Table 2, (for example the highest concentration at the east gate of the plant was 40mg/L), two patterns of the chromium movement in underground water in this region can be identified:

(1) Starting at the stack of ore residue and the east gate of the alloy plant, chromium contaminated waste water (from workshop and stack of ore residue) permeated into the underground, and then formed a contaminated area concordant to the movement of the underground water. Nuer River village is the first village that was contaminated by the flow. When underground water flowed further, chromium concentration became lower and the expanding tendency of the contaminated area became moderate.

(2) Discharged waste water permeated into the underground in the dried river bed of the old Nuer River course, and caused the contamination of the underground water. Because the Cr^{+6} concentration in waste water was lower, the villages located along the old Nuer River (Yangxing Shilitai) had a lower level of Cr^{+6} concentration than the Nuer River Village.

In order to understand the relation of the Cr^{+6} concentration and the underground water level, a monitoring section was set 1000 meters form the pollution source. This monitoring section contained eight monitoring wells. Observation from the monitoring wells revealed that there existed a contrary trend of Cr^{+6} concentration in underground water and the level of underground water. On this section, the altitude of the underground water was higher on both sides (north and south) and lower in the middle. No.5 monitoring well is the lowest in altitude (4.87 meters), and had the highest chromium concentration among the eight monitoring wells in this section.

The altitude (gratitude) of underground water limits horizontal proliferation* of Cr^{+6}. This fact may be the reason that a long and narrow high density contaminated area was formed. Because of the location of Nuer River villages, it was under direct effect of the contamination. Contamination levels varied with different depths of wells in the Nuer River village.

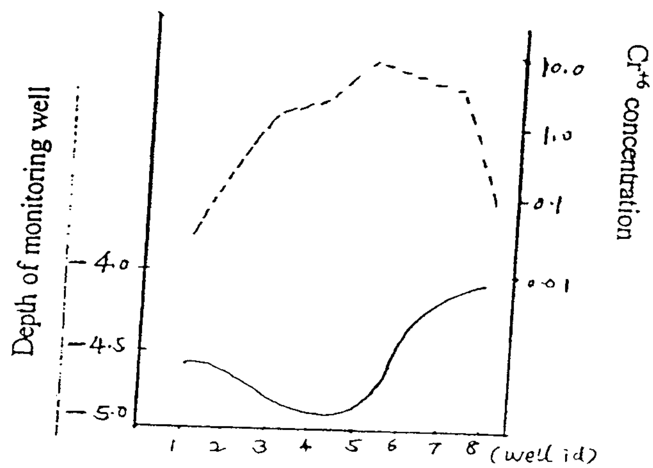


Figure 2: Relation between underground water altitude and Cr^{+6} concentration (monitoring section 2: east gate of the alloy plant)

Table 3: The relation between the depth of water wells and Cr^{+6} concentration

Depth of Water Wells (in meter)

	6	7	8	9	10
# wells	13	37	35	27	3
Cr^{+6} Concentration	0.12-5.0	0.05-12.0	0.25-10.0	0.5-10.0	2.0-10.0
Average concentration	2.23	2.53	2.95	4.11	4.85

The results in the table above revealed that there existed a positive correlation between the depth of wells and Cr^{+6} concentration.

There are two river courses located near to the alloy plant. One is the Nuer River, the other one is the old Nuer River. The old Nuer River is dried while the Nuer River is an all season river whose water comes from the upper reservoir. Because waste water was discharged into the old Nuer River, fluid in the old Nuer River contained Cr^{+6}. (concentration is between 5-20mg/L). Although waste water was not discharged into Nuer River, Cr^{+6} was detected in the river. The further the river from the alloy plant, the lower the concentration of Cr^{+6}. Cr^{+6} can be detected until the Nuer River merged into the Ling River.

Table 4: Cr^{+6} Concentration in Different Sections of The Nuer River (1966.3)

Location of Measure	# of Obs Taken	Average Cr^{+6} concentration
XiaoMaChang	4	0
JinChangBao	6	0
Nuer River Village	6	0
Nuer River Railway Station	4	0.018
YangXing	5	0.017
ShiLiTai	3	0.015
WenJiaTun	11	0.014
BaJiaZi	7	0.014
NanShanQiao	11	0.009
Ling River	3	0

According to the hydrogeological document, the old Nuer River is higher than the Nuer River in altitude, therefore the Old Nuer River supplies water to the Nuer River during the annual drought period. A clay layer in the old Nuer River course was heavily decayed. Waste water permeating into ground water may be the reason that the Nuer River after Nuer Railway station was contaminated by Cr^{+6}.

In order to assess the contamination from the ore residue to soil and to underground water, a study was conducted in 1966. Result are presented in the following table.

Table 5: Cr^{+6} Concentration in Soil under Stack of Ore Residue

Depth of swamp taken (cm)	Cr^{+6} concentration (mg/100g)	Cr^{+3} concentration (mg/100g)
-0.1	52.060	-
-0.2	18.2	20.26
-0.5	27.9	30.48
-1.0	18.3	22.7
-1.5	7.6	8.37
-2.0	0.037	0.031
-2.5	0.043	0.030
-3.0	0.017	0.021
-3.5	0.048	0.032

Soil samples were collected from the edge of the stack of ore residue, where Cr^{+6} can be detected at a depth of 3.5 meters below the earth surface. A study shows that the Cr^{+6} concentration in water well in a field, located 100-300 meters down the movement of underground water from the stack of ore residue, was 0.014-0.3 mg/L. This study was conducted 6 years after the establishment of the dump site. After that, the dump site continuously expanded, so did the contamination. The Cr^{+6} concentration in the underground water under the stack of ore residue was 7-8mg/L in 1972, and was 9-22 mg/l in 1974 (highest value was 130 m/L in fall). Total amount of ore residue was about 200,000 tons, occupying more than 30 mu. Dissolved with rain, a large amount of chromate was discharged. The intensity of the contamination expands if an effective clean up is not conducted immediately.

Section II: Effect of Environmental Contamination on Human Health:

To study the effect of underground water contamination on the residence health, a series of studies were conducted in the Nuer River, Yangxing and Shilitai. In a study conducted in the Nuer river village in 1965, most common symptoms included oral ulcer, diarrhea, abdominal pain and abnormalities of the digestive system. At the time of this study, the Cr^{+6} concentration in water wells in Nuer river Village was 0.1-20.0 mg/L. No such symptoms were found among the residents whose water wells were not contaminated. The study also indicated that the symptoms were acute. They disappeared when the human body accommodated to the condition of or improvement of drinking water.

Table 6: Statistics of 156 Residents in Nuer River Village

Symptoms	#cases	%cases
Oral Ulcer	51	33
Diarrhea	20	17
Abdominal Pain	48	31
Dyspepsia	26	17
Pain at pit of stomach	81	30
vomiting	20	17

In April 1971, similar symptoms were found in Shilitai Village. 58% (92 among 158 people in the study) shows some symptoms.

Table 7: Statistics of 158 Residents in ShiLiTai

Symptoms	# Cases	% Cases
Oral Ulcer	92	58
Diarrhea	48	30
Abdominal Pain	36	23
	16	10

In 1974, children in Wenjiatun and Sandaohao showed similar symptoms. In order to assess the effect of regularly drinking contaminated water on human blood, a study of blood sample was conducted in the Nuer River village in 1966. A higher white blood corpuscle count was found. The range of the count was 5100-163000 / cm3, and the average was 12116/cm3 which was 75% higher than normal. Other measures were in the normal range.(Table 8) Among 93 people in the blood study, a higher percentage of juvenile cells in neutrophilic granulocyte was found, and a trend of left shifting of cell nucleus was identified. The left shifting symptoms were more significant in the Nuer River village compared to Shilitai, which has less intense contamination. (table 9)

Table 8 Blood Test Results of 12 Individuals

	red hemopro -tein %	red blood cell	white blood cell	polymor phism nucleus cell%	lympho- cyte%	single nucleus cell %	eosino- phil
Range	64-90	350-430	5100- 16300	40-78	18-56	2-4	2-6
Average	77	441	12116	57	38	2	2.8

Table 9 Blood Test Result by Region

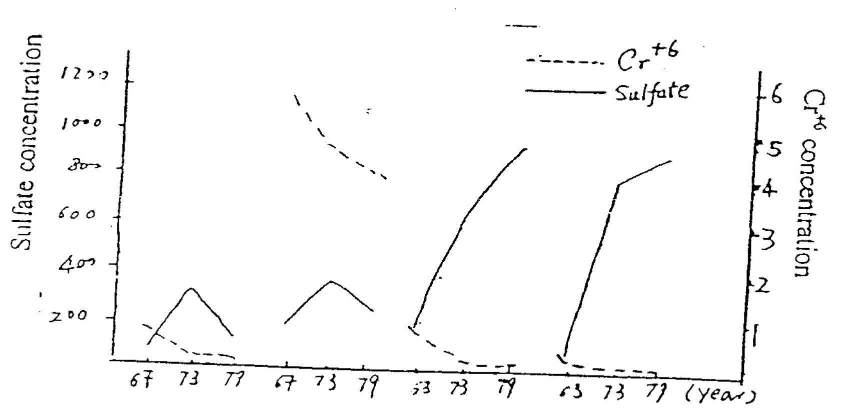
Region	#Sample	#Normal	#Nucleus Left Shifting	#Nucleus Right Shifting
Nuer River Village	61	26	46	28
Yang Xing	42	36	33	31

A study monitoring the urine of 12 individuals for 24 hours was conducted in order to observe the discharge of chromium after it was ingested. The age of the 12 individuals ranged between 2 to 46. Chromium was detected in urine of 8 persons (67% of 12 persons). Chromium concentration in urine was between 0.01mg/L-0.1mg/L, and the average was 0.024mg/L. One individual's urine contained a small amount of protein. The other 11 individuals had normal urine. It is estimated that each person ingested 10-60mg of chromium per day from drinking water based on the chromium concentration in this area. Another study indicates that a 0.008mg of chromium will discharged by urine if a person's intake was 0.08-0.1mg per day. (that is 8%). The rest of the chromium will be discharged by sweat glands and the intestinal canal. Considering that the residents also ingested chromium through food (0.8-6.0mg/kg in this area), there should be 0.8-6.0 mg chromium discharged in their urine. In this study, the average chromium in urine is less than 0.03mg/L. The difference between expectation from the previous study and the results of this study need more study.

The symptoms in the contaminated area were concordant to the progress of the contamination. The Nuer River Village is nearest to the alloy plant and the easiest one to find chromium contamination, therefore it is the earliest to show some health symptoms. In WenjiaTun and Sandaohao, which are located more remote, slight symptoms were not found until 1974.

When some symptoms were reported in the Nuer River Village, the Cr^{+6} concentration in drinking water was 0.1 -20.0mg/L, and sulfate concentration was 40-180mg/L. The Cr^{+6} concentration exceeded the drinking water standard 2-400 times while the sulfate concentration was below the drinking water standard. Former studies have shown that oral ingestion of chromium can cause chronic toxication. A study which involved feeding rabbits water containing 7.0 mg/L Cr^{+6} caused a higher rate of juvenile cells , which is nucleus left shifting. This may be because of the organ being irritated by Cr^{+6}. Another study showed that chromate can accumulate in some organs. 8 out of 16 guinea-pigs in the study, which were feed by 10 mg/L Cr^{+6} containing water, developed lung cancer. However, some studies do not support this conclusion. Our conclusion is that the symptoms in the Nuer Village and Yangxing may be due to regularly drinking Cr^{+6} contaminated water.

One may question the reason that WenJiaTun and Shilitai have similar symptoms in 1974 even when the Cr^{+6} concentration was only 0.003-0.05mg/L and 0.003-0.01mg/L, both under the drinking water standard. We may find the answer in the following figure.



Sulfate level was increasing after 1967 in these villages, while Cr^{+6} concentration was decreasing. In 1973, 55.7% of 43 water wells have sulfate levels higher than 300mg/L. It is possible that the cause of the symptoms in these villages is sulfate.

Because of improvements in smelting procedures, the discharge of Cr^{+6} was put under control. however, a large amount of sulfate was discharged daily, estimated to be 10 tons per day. Considering thousand of tons of sulfate have been discharged in the past ten years of treatment, sulfate pollution should be paid more attention.

Section Three: Treatment of the Contamination:

In order to solve the problem of contamination, a series of treatments have been used, including stopping production to treat. In the last few years, improvements in smelting procedures have been made, and drinking water has been provided to residents. The following are several improvements:

1) To prevent Cr^{+6} permeating into ground, 680 m^2 ground surface of workshop has been resurfaced. By integrating procedures, 40% of the valves were saved and the gap was filled.
2) Improved leaching procedures. Smelted residue is cooled before leaching. By doing so, the Cr^{+6} concentration in the air was reduced to 0.0084-0.0112mg /m^3 from 0.104-48.3mg/m^3. Two chemical procedures which produced high toxic ore reside were stopped.
3) Recycle the chromium contained sewage.
4)Waste water was treated with lime cream and ferrous sulfate before being discharged. Cr^{+6} concentration in discharged waste water reduced to 0.05mg/L.

Besides the above treatments, treatment wells were built in 1967 in serious contaminated areas. Each treatment well covered a range of 60-100 meters radius. Withdrawn underground water was treated with ferrous sulfate. After treatment, Cr^{+6} concentration reduced to 0.1-0.05 mg/L from 29.92-41.20mg/L. However, the sulfate concentration in treated water increased.

Table 10: Results of Sulfate Treatment

Cr^{+6} Concentration Before Treatment	After Treatment	
	Cr^{+6} Concentration	Sulfate Concentration
29.92	<0.05	338.2
40.39	<0.05	1900.0
39.10	<0.10	970

41.20	<0.10	600
40.80	<0.10	945
31.28	<0.10	280
31.28	<0.10	400
35.36	<0.10	376.3
35.36	<0.10	494.8
36.72	<0.10	359.5

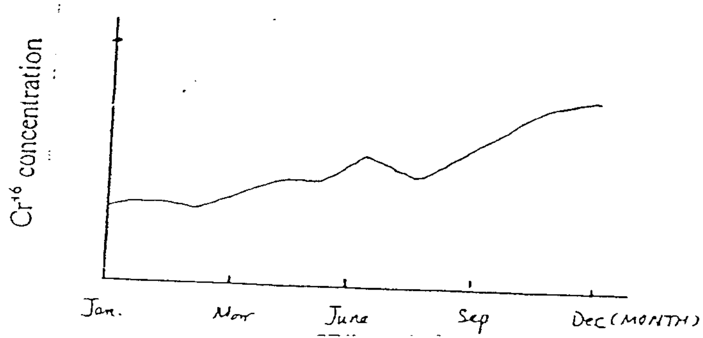


Figure 4: Cr^{+6} concentration of withdraw well No.4 by time. (1971)

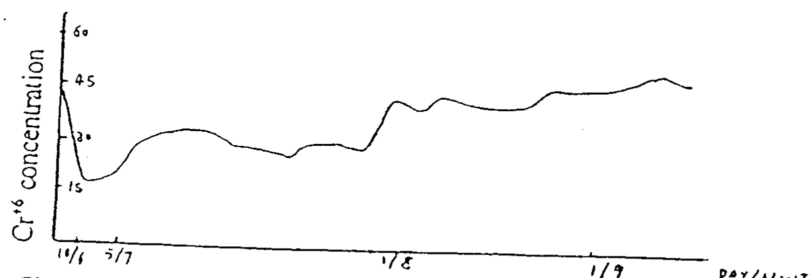


Figure 5: Effect of withdraw wells on Cr^{+6} concentration (1971)

Figure 4 which shows treatment well No.4 indicates that the Cr^{+6} concentration increased in a whole year with no seasonal pattern. When the withdrawing stopped, Cr^{+6} concentration in the treatment area dropped quickly and returned to a high level after resuming the withdrawing procedure. This fact indicates that continuous withdrawing treatment was necessary to clean up the underground water. After 8 years of withdrawing treatment, No.1 and No.6 water wells show a significant drop in Cr^{+6} concentration. However No .4 treatment well, which was located near the workshop, maintained a higher Cr^{+6} concentration. This may be because of the large amount of accumulation of Cr^{+6} in soil which cannot be cleared in a short time.

Table 11: Result of Withdrawing Treatment

Time of Measure	No.4 Well (in workshop)	No.1 Well (East Gate)	No.2 Well (JinChangBao)
1966	90.00	39.90	17.00
1979	45-80.00	0.24-0.44	0.17-0.50

Withdrawing treatment is an effective method to prevent the proliferation of the Cr^{+6} contamination. After a few years of treatment, Cr^{+6} concentration in underground water decreased. JinChangBao, Nuer River Village, Yangxing and Shilitai are nearly reaching the same level of chromium concentration. Most of the water wells in those villages are under the drinking water standard. The Nuer River Village still has Cr^{+6} concentrations higher than the drinking water standard, while the variation of the concentration is large. In Nuer River Village, there are fewer water wells with high Cr^{+6} concentration and more low concentration water wells.

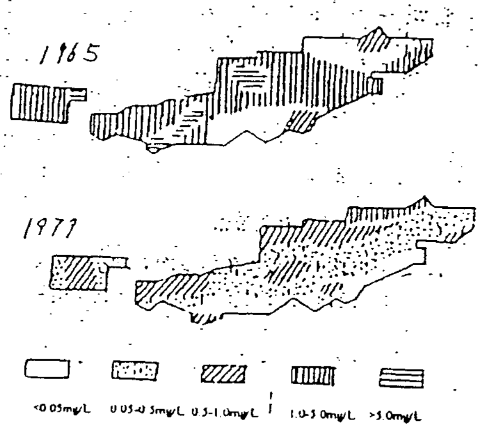


Figure 6: Cr^{+6} concentration in Nuer River Village in 1965 and 19

Because sulfate pollution was ignored, sulfate concentrations increased. Further treatment of sulfate in ShiLiTai and WenJiaTun is recommended.

Summary:

This paper summarized the chromium and sulfate contamination in the Nuer River region. After the treatments, Cr^{+6} concentrations in underground water in all villages are under the drinking water standard, except Nuer River village. However, since no treatment has been conducted for the stack of ore residue, the concentration of Cr^{+6} in underground water under the stack is 16 times higher than it was in 1966 (highest concentration is 130mg/L). A potential contamination can only be prevented by an immediate treatment of the stack of ore residue.

Residents living in Shilitai and Wenjiatun were exposed to high concentrations of sulfate. More attention should be paid to the sulfate contamination.

The symptoms in the contaminated areas (diarrhea, abdominal pain, oral ulcer) are associated with the chromium contamination.

The chromium contamination cannot be solved in a short time. Prevention will be the key solution in this type of contamination.

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锦州铁合金厂排出含铬废水对地下水污染的调查报告

锦州市卫生防疫站
锦州铁合金厂

1964年锦州西郊女儿河大队社员反映井水变黄。经调查证实，为锦州铁合金厂排…的含铬废水所污染。

为了解污染过程、掌握规律，以便为治理环境污染工作过程中提供依据。1964年…来，在综合防治的基础上，对六价铬对土壤、水体、农作物污染、铬离子对人体的一般影…响及其在环境污染过程中的动态变化进行了观察。现将十年来观测资料整理报告如下：

一、基本情况

锦州铁合金厂位于锦州西郊，以钒铁、钛铁等金属冶炼为主。1959年开始研究试炼金属铬，1961年小规模投入生产。当时的回收率只有21.5%，1963年提高到66.3%，此后十年间一直在60%左右。生产过程中的浸出、中合、浓缩、还原等工序排出大量含铬废水、废渣、废气。由于回收率低，生产管理不严，因而以"三废"形式向环境中排出了大量有毒的铬离子。估计十几年来通过上述形式，共损失铬盐 930 多吨。铬离子的大量流失，带来的必然后果就是对土壤地面水和地下水等环境的污染。

二、调查结果及分析

(一) 地下水污染

在锦州铁合金厂试制金属铬不到6年时间，其地下水下游的女儿河大队就发现了地下水污染现象。从感观上，井水出现黄色、味道变涩。污染区群众反映腹泻、腹痛、烂嘴角等。经分析井水六价铬浓度为0.02—20.00毫克/升。在170眼饮水井中有98%被污染，几乎全部超过饮水卫生标准，最高值超过饮水卫生标准400倍。

为了解地下水下游的污染范围，对金厂堡、杨兴屯、十里台、温家屯等地下水进行了调查，结果见表1。

其中金厂堡调查了123眼饮水井，井水六价铬浓度波动在0.002—0.1毫克/升，被污染的井水占调查的40.8%，超过饮水标准的有12%，最高值超过饮水标准8倍。女儿河…站地下水六价铬浓度波动在0.00…—0.7毫克/升，检出率为20.3%，全部超过饮水标…

准，最高值超过饮水标准15倍。杨兴屯50眼水井中有36眼（72%）被污染，被污染的水井中有20眼（55%）超过饮水卫生标准，最高值超过饮水标准的95倍。十里台、温家屯、三道壕等地，处于地下水下游的远端，虽然少数饮水井有六价铬检出，但都低于饮水卫生标准。总的趋势是，随着与污染源距离的增加，地下水六价铬浓度也相应的逐渐降低。

473眼井饮水六价铬分析（1966） 表1

地区	井数	井水六价铬浓度（毫克/升）						
		0	～0.05	～0.1	～0.5	～1.0	～5.0	5.0～
对照	5	5						
农中	1	1						
钢炉厂	6	2		2	2			
金厂堡	123	73	35	7	8			
女儿河	170	7	1	5	27	17	76	37
女儿河车站	19	14		1	3	1		
杨兴屯	50	14	16	5	12	2	1	
十里台	21	2	19					
温家屯	33	27	6					
三道壕	18	15	3					
八家子	22	20	2					
南山水源	5	2	3					

按表1污染区域面积达20平方里，波及5个大队，有515眼饮水井受到程度不同的污染（见图1），严重的威胁着3,000多人口的饮水安全和身体健康。

图1 1966年女儿河地区地下水污染范围示意图

为了进一步弄清六价铬对地下水污染的途径及在地下水中的运动规律，在污染区下游布置了7个观测断面，进行断面调查，断面布局见图1，调查结果见表2。

地下水断面调查　　表2

断面	井号	六价铬浓度毫克/升	断面	井号	六价铬浓度毫克/升	断面	井号	六价铬浓度毫克/升
渣场	1	0,001		4	0.008		3	0
	2	0.17		5	0.08		4	0.066
	3	1,70		6	0.70		5	0.001
	4	8,00		7	1.60		6	0.1
	5	6.29		8	8.00	杨兴屯	1	0
	6	0,001		9	0.20		2	0.003
广东门	1	0.01		10	0.06		3	0.064
	2	0,08	女儿河	1	0.75		4	0
	3	0.40		2	8.0		5	0
	4	2.90		3	0.75		6	0
	5	5.10		4	3.50	十里台	1	0
	6	2.60		5	0.65		2	0,003
	7	1,05		6	0.70		3	0
	8	0.40		7	0.22		4	0
金厂堡	1	0		8	0.0039		5	0
	2	0	车站	1	0		6	0
	3	0.028		2	0		7	0

表2所列资料虽然没有反映出最高浓度，（广东门曾出现40毫克/升）但可以看出六价铬在这一地区地下水中运动的两个途径。

其一、以渣场和广东门两个断面为起点，含铬废水自污染源（铬生产车间、渣场）渗入地下后，形成与地下水流向相平行的高浓度污染带，向下流动。污染下游的地下水，首先受到影响的是女儿河大队，再往下流、六价铬浓度即逐渐降低。高浓度污染带两侧地下水由于地势、水位和稀释扩散等因素也有所降低。

其二、生产废水排入女儿河故河道后，渗入地下所造成的污染。由于废水中六价铬浓度较低，所以沿岸的杨兴屯、十里台一带地下水的污染程度一直低于女儿河大队。

为了证实地下水水位与六价铬浓度之间的关系，在厂内距污染源1,000米，设一个观测断面，断面由8个观测井组成。经地下水位及地下水六价铬分析，发现地下水位的高度与地下水中六价铬浓度之间呈相反趋势。在断面上，地下水位南北高而中间低，水位最低的是5号观测井（+4.80米），而8眼观测井中六价铬的峰值也出现在5号井（5,10毫克/升）。地下水位的梯度限制了六价铬在水体运动过程中的横向扩散（见表2，图2），这可能就是在地下水中形成的一条高浓度污染带的原因。由于地理环境关系，这条高浓度污染带直接影响着女儿河大队。在女儿河大队还可以看到不同取水深度对六价铬污染程度的影响。

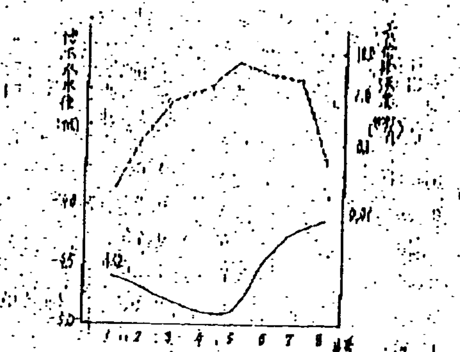

图2　地下水水位与六价铬浓度的关系（厂东门断面）

表3资料是女儿河大队116眼饮水井的调查结果。

井深与六价铬污染浓度关系（毫克/升）　　表3

	井深（米）				
	6	7	8	9	10
井数	13	37	35	27	3
六价铬浓度	0.12—5.0	0.06—12.0	0.26—10.0	0.5—10.0	2.0—10.0
平均浓度	2.23	2.53	2.95	4.11	1.85

调查结果反映了六价铬浓度与取水深度之间存在一定的正比关系。

锦州铁合金厂附近有两条河流通过。一为女儿河，一为女儿河故河道。女儿河故河道实际上是接纳铁合金厂生产废水的排污沟，基本上没有河水，而女儿河则常年有水，其流量受上游水库控制。由于故河道接纳含铬工业废水，所以全段都有六价铬检出，检出值一般在5.0—20.0毫克/升左右。而女儿河虽然没有生产废水排入，但是在女儿河东站以下河段却发现了污染，这段河水中六价铬浓度在整个流程中逐渐降低，直到在锦州市南郊汇入小凌河后才不再检出（见表4）。

女儿河六价铬分析结果（1986.8）　　表4

河水取样点	分析次数	六价铬平均浓度 毫克/升
小马厂	4	0
金厂桥	6	0
女儿河	6	0
女儿河东站	4	0.018
锦兴北	6	0.017
十里台	5	0.0105
杨家屯	3	0.014
八家子	11	0.014
南山桥	7	0.009
小凌河	11	0

据勘测水文地质资料，女儿河故河道的标高高于女儿河，而且在枯水季节故河道流域的地下水发出对女儿河补给，而故道河在女儿河车站以下河段的河床表面粘土层严重冲蚀，大批污水渗入地下，这可能是女儿河车站以下女儿河中检出六价铬的原因。

为了了解铬渣与土壤乃至地下水之间的污染关系，1966年对铬渣堆场土壤情况进行调查，调查结果见表6。

渣堆土壤中六价铬分析 表5

采样深度（厘米）	六价铬含量 毫克/100克	三价铬含量 毫克/100克
—0.1	52.060	—
—0.2	18.200	30.260
—0.5	27.900	30.430
—1.0	18.300	22.700
—1.5	7.600	8.370
—2.0	0.037	0.031
—2.5	0.043	0.030
—3.0	0.017	0.021
—3.5	0.048	0.032

土壤样品取至渣堆边缘，在这里，六价铬的污染在3.5米深仍能够见到。据当时在渣场下游100—300米处农田灌溉用井的水质分析，六价铬浓度为0.014—0.3毫克/升，此时渣场仅仅使用六年，而且范围较小。随着生产时间的延续，渣场使用面积不断扩大，地下水污染也随之日益严重，1972年渣场地下水六价铬浓度上升到7.0—8.0毫克/升，1974年又持续上升到9.0—22.0毫克/升（秋季最高为130.0毫克/升）。目前铬矿渣堆存量近20万吨，占地面积30余亩。由于露天堆放，风吹雨淋，铬盐流失十分严重，因此，如不采取有效措施，污染程度将进一步加剧。

（二）环境污染对人群健康的影响

为了研究地下水污染对当地居民健康影响，先后在女儿河、杨兴屯、十里台等地进行了调查。1965年对重点污染区——女儿河大队156名群众健康调查中，较为集中出现的症状有腹泻、腹痛、嘴角糜烂和消化机能紊乱等（见表6）

女儿河大队156人健康状况统计 表6

症状	例数	%
嘴角糜烂	51	33
腹泻	26	17
腹痛	48	31
消化不良	26	17
心口痛	31	30
呕吐	20	17

调查期间，女儿河大队饮水中六价铬浓度为0.1—20.0毫克/升之间，而在地下水未被污染的对照区人群中，则没有上述症状。调查还发现，上述反应是一过性发作，在机体对环境适应时或改善饮水条件之后，上述症状即告减轻甚至消失。

1971年4月，十里台大队也出现了上述反应，在158人调查中有阳性体征的92人，占调查总数的58%（见表7）

十里台大队158人健康状况统计　　表7

症　状	例　数	%
嘴角糜烂	92	58
腹　泻	48	30
腹　痛	36	23
消化不良	16	10

1974年春，温家屯和三道壕两地社员和儿童也出现了上述反应。为了了解污染区群众在长期饮用被污染的地下水，在血液学上的影响，1966年在杨兴屯、女儿河大队进行了末梢血液检验。发现污染区群众末梢血液的白细胞计数偏高，每立方毫米末梢血液中白细胞计数为5,100—16,300个，平均为12,116个/立方毫米，超过正常值者占调查人数的70%。其他指标基本上都在正常范围之内（见表8）。

5　高污染区12例末梢血液检验　　表8

	血红蛋白 %	红细胞 万/mm³	白细胞 个/mm³	多形核细胞 %	淋巴细胞 %	单核细胞 %	嗜酸细胞 %
范围	64—90	360—480	5,100—16,300	40—78	18—56	2—4	2—6
平均	77	441	12,116	57	38	2	2.8

在93例末梢血液检查中，中性粒细胞中幼稚型细胞数量偏高，有核左移的倾向，而且在污染较重的女儿河大队和较轻的杨兴屯两地相比较，前者 Schilling 指数测定，左移现象也更为明显（见表9）。

不同污染区人群末梢血 Schilling 指数测定　　表9

调查地区	调查人数	正常者（%）	核左移者（%）	核右移者（%）
女儿河大队	51 51	26 26	46	28
杨兴屯大队	42 42	36 36	33 33	31 31

为了观察铬离子在机体摄入后的排泄情况，在高污染区（饮水六价铬浓度为3.32—20.00毫克/升）对2—46岁的12名群众，进行了24小时全尿总铬分析。结果有8份尿标本检出了铬离子，占被检标本的67%，尿铬检出值波动在0.01—0.1毫克/升之间，平均浓度为0.024毫克/升，12份尿标本中除1例有微量蛋白（尿铬0.02毫克/升）外，其余

写此问题时未考虑到体内的蓄积容量问题。张洁 10-8

11例尿常规均属正常。根据当时饮水中六价铬浓度，估计每人每天从饮水中摄取铬离子量当在10—60毫克左右。据报导，在正常情况下，如果日摄取量为0.06—0.1毫克铬离子时，应有0.008毫克/日铬离子自尿道排除，尿道排泄率为8%，其余部份自汗腺、肠道排出。如果再考虑到从食物摄取的铬离子（如污染区自来食铬量为1.5毫克/公斤），每天至少应随尿排出0.8—6.0毫克铬离子，而实际随尿排出只有不足0.08毫克。我们所测定的排出量与报导的排出量相差悬殊的原因有待进一步探讨。

污染区域人群机体反应与地下水污染的发展顺序和污染程度是一致的。女儿河大队距污染源很近，发现污染最早，首先出现机体反应的也是女儿河大队，而且比其他地区也重。温家屯、三道壕位于污染源远端，直到1974年才出现轻微反应。

女儿河大队群众出现机体反应的当时，饮水中六价铬浓度为0.1—20.0毫克/升；硫酸盐浓度为40～180毫克/升。前者超过饮水卫生标准2—400倍，而硫酸盐浓度则低于饮水标准。据文献记载，铬酸盐经口摄入表现为慢性中毒，肠道炎症和溃疡，肝肾损害等，经口给予含7.0毫克/升六价铬的饮水，造成家兔幼稚型白细胞增高，即血象左移，此种征象可认为是造血器官受六价铬刺激的标志。有的报告指出饮用水中铬盐可在某些动物器官沉着，用含六价铬10毫克/升的水喂养16只实验动物，8个月后有8只实验动物患肺癌。但有的文献对此持否定的态度。所以可以认为女儿河、杨兴屯等地群众出现的消化系统症状、白细胞总数增高、嗜中性粒细胞核左移等反应可能与长期饮用被污染的井水有关。血液中嗜中性粒细胞出现核左移现象，反映造血系统受到侵害。

但是当经过“三废”治理，在铬污染受到控制的情况下，1972年十里台，1974年温家屯、三道壕等地地下水中六价铬浓度只有0.003—0.06毫克/升，和0.003—0.01毫克/升，基本都未超过饮水标准，为什么也出现了与女儿河、杨兴屯两地曾出现的相似症状？为此对地下水中六价铬及与该厂生产有关的盐类进行了分析，分析结果见图3。

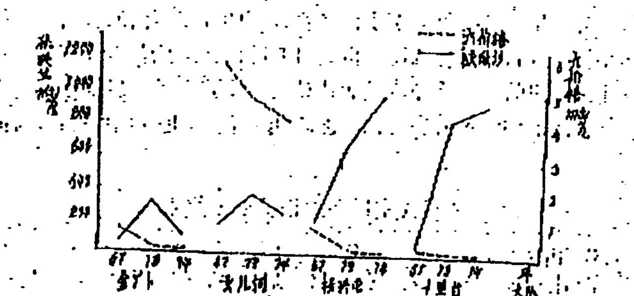

图3. 地下水硫酸盐与六价铬浓度变化（最高值）

1967年以来，地下水硫酸盐浓度不断上升，六价铬则持续下降。1973年十里台大队13眼饮水井的55.7%井水硫酸盐浓度大于300毫克/升，最高浓度达900毫克/升。因此这一地区群众所出现的消化系统症状也不能排除硫酸盐污染所引起的影响。

目前铁合金厂经过工艺改革，铬离子的流失已基本得到控制，但硫酸盐废水排放量较大，每天排出硫化物和硫代硫酸盐10余吨，加上十年来硫酸亚铁法处理含铬废水时排出的数千吨硫酸盐对环境的污染也应引起重视。

（三）综合治理和环境改善

由于人们对环境污染的规律及其后果的认识不断深入，推动着以"铬渣"为重点的治理工作广泛开展。

为了解决铬对环境的污染，根据调查提供的情况，采取了一系列的防治措施，直到停产治理。1972年以后，环境保护问题进一步引起了党委重视。

几年来，在及时解决污染区居民供水，保障饮水安全的前提下，对生产工艺进行不断改革，对已污染的地区进行了环境治理，取得了比较显著的成效。工艺改革和综合利用的开展，不仅充分利用了资源，减少了铬离子的流失，保护了环境而且也大大的改善了工人的劳动条件，推动了生产的发展。

下面是环境保护工作中的几项较大措施：

1．为了防止生产过程中高浓度的含铬废液渗入地下（这是过去造成环境污染的重要原因之一），将080平方米的车间地面，重新进行防水处理，从而杜绝了有害物质从车间及其生产装置渗入地下。

缩短工序、减少管道、砍掉40%阀门、填平了大部地沟、有效的控制了生产设备的跑、冒、滴、漏。

2．改进浸出工艺。焙烧的熟料经冷却浸出、杜绝了浸出槽的崩渣现象，使空气中铬离子浓度从每立方米0.104—48.3毫克降至0.0084—0.0112毫克。进而砍掉化工工段，不再产生两种毒性很大的含铬废渣。

3．回收含铬溶液，循环使用。

4．含铬废水采用硫酸亚铁——石灰乳法处理，使排出的废水含铬量控制在不高于0.05毫克/升。

除上述措施外，根据1966年地下水污染普查，1967年断面调查所提供的资料，在严重污染区和污染源附近钻井进行截流，由4口6吋深井组成截流井群，每口井的截水半径为60—100米。抽出的地下水经硫酸亚铁处理后排掉。处理后的地下水六价铬浓度从29.92—41.20毫克/升，降至0.1—0.05毫克/升，但是排水中的硫酸盐浓度增高（见表10）

4号井水硫酸亚铁法处理效果　　表10

原水六价铬浓度 毫克/升	处理后 六价铬 毫克/升	处理后 硫酸盐 毫克/升
29.92	<0.05	338.2
40.39	<0.05	1900.0
39.10	<0.10	970.0
41.20	<0.10	600.0
40.80	<0.10	945.0
31.28	<0.10	280.0
31.28	<0.10	400.0
36.36	<0.10	376.3
35.36	<0.10	494.8
36.72	<0.10	359.5

从4号截流井在一年间运转情况来看，随着时间的延长，排出水的六价铬含量保持持续上升的趋势，但看不出明显的季节对截流效果的影响（见图4）。

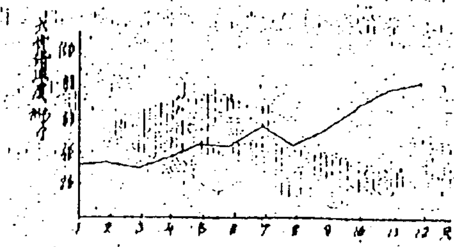

图4．4号截流井排出水六价铬月平均浓度动态（1971）

当截流排水停止后，截流区地下水中六价铬浓度立即下降，恢复排水时又逐渐升高（见图5）。因此为了保持较高的截流效果，和改善已被污染的地下水体状况，截流排水工作不应间断。

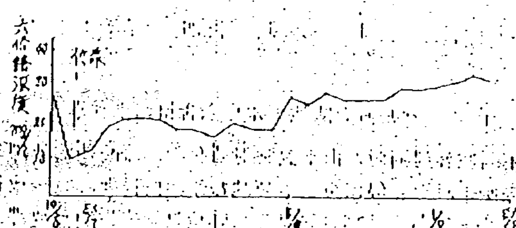

图6．截流井停泵对排水中六价铬浓度的影响（1971）

地下水经8年长期排水截流，除铬生产车间附近的4号井由于远处污染中心，土壤及底下水污染较为严重，土壤中吸附的六价铬很难在短时间内消除，因而截流效果较差外，下游的1号、3号截流井效果都十分显著，两井六价铬浓度都降低百倍左右（见表11）

截流井截流效果　　表11

观测时间	4号井（三车间）	1号井（厂东门）	3号井（金厂堡）
1966年	90.00	39.90	17.00
1979年	45.0—80.0	0.24—0.44	0.17—0.50

上述资料说明，采用排水截流的方法，能够在污染源附近将已被污染的地下水抽出，控制其向下游稀释扩散，并且能够有效的改善地下水的环境状况。

几年来，通过综合治理，原来污染较重的女儿河一带，地下水的污染水平不断降低，金厂堡、杨兴屯、十里台等地地下水六价铬浓度已基本上接近、达到或低于饮水

标准。女儿河大队地下水中六价铬浓度大部分仍然高于饮水标准，但其变化幅度也较大（见图6），而且在不同年度的动态变化中，低浓度的井数不断增加，高浓度的井数相应的逐年减少。沿古道河一带的变化则反映生产废水净化处理的效果（见图8）

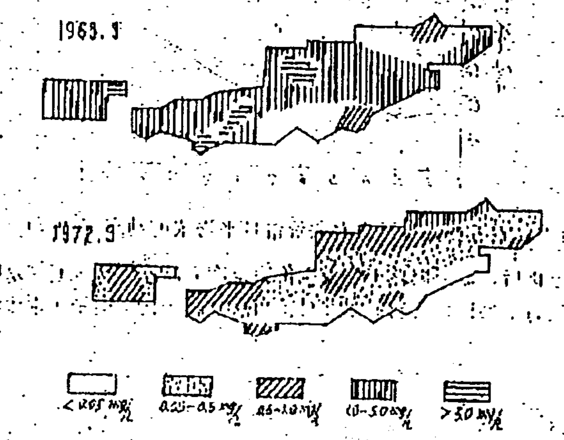

图6　女儿河大队地下水中六价铬污染动态

在地下水污染不断减轻的同时，由于忽视对硝化物、硫酸盐的处理致使硫酸盐的污染不断加重，因而控制十里台、温家屯一带硫酸盐的污染程度，减少或杜绝污染物质的生产废水排出，进一步保护和改善环境将是今后环境保护工作的重要课之一。

三、总　　结

1．本文对女儿河地区地下水被六价铬、硫酸盐污染及综合治理情况进行了讨论，对地下水受工业废水污染及其变化规律有了初步认识，肯定了针对铬污染所采取的综合治理所取得的成果。目前除女儿河大队外，地下水中六价铬浓度已接近或低于饮水标准，但是由于对铬渣至今仍未处理，渣场一带地下水中六价铬浓度较1966年增高了16倍多，最高浓度达130.0毫克/升。如不尽快处理，则可能使十年来取得的治理成果遭到破坏。

2．十里台、温家屯一带地下水中硫酸盐浓度不断增高，居民健康及农副业生产都受到一定影响，极应引起严重注意。

3．污染区人群中出现的腹痛、腹泻、咽炎、口角糜烂、白细胞计数增高、嗜中性粒细胞中幼稚型细胞增多等现象与六价铬污染有关，至于硫酸盐所引起的影响尚有待进一步观察。

4．实践证明地下水一但被工业废物污染，很难在几年、十几年内消除，所以只有在发展生产的同时认真贯彻"预防为主"的环境保护方针，合理利用资源，严格管理，防止跑、冒、滴、漏，最大限度的控制有害物质向环境排放，才是环境保护的积极有效措施（全文完）

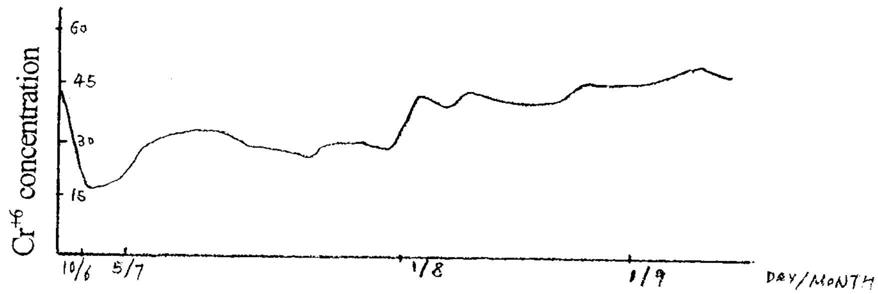

Figure 5: Effect of withdraw wells on Cr^{+6} concentration (1971)

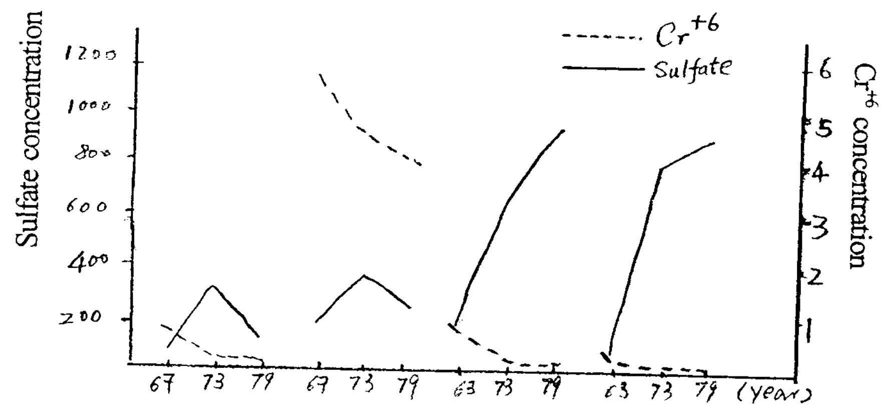

Figure 3: Comparison of Cr^{+6} concentration and sulfate concentration (maximum value)

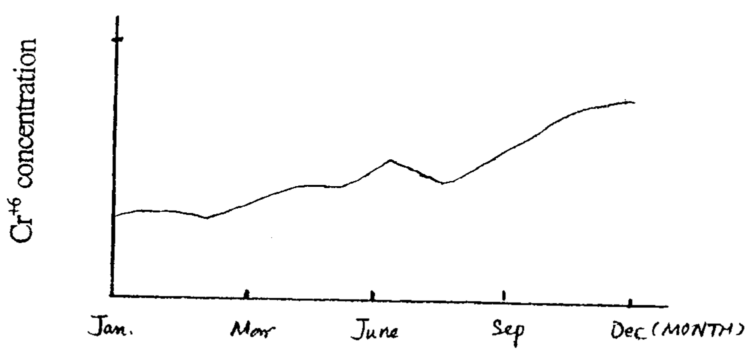

Figure 4: Cr^{+6} concentration of withdraw well No.4 by time. (1971)

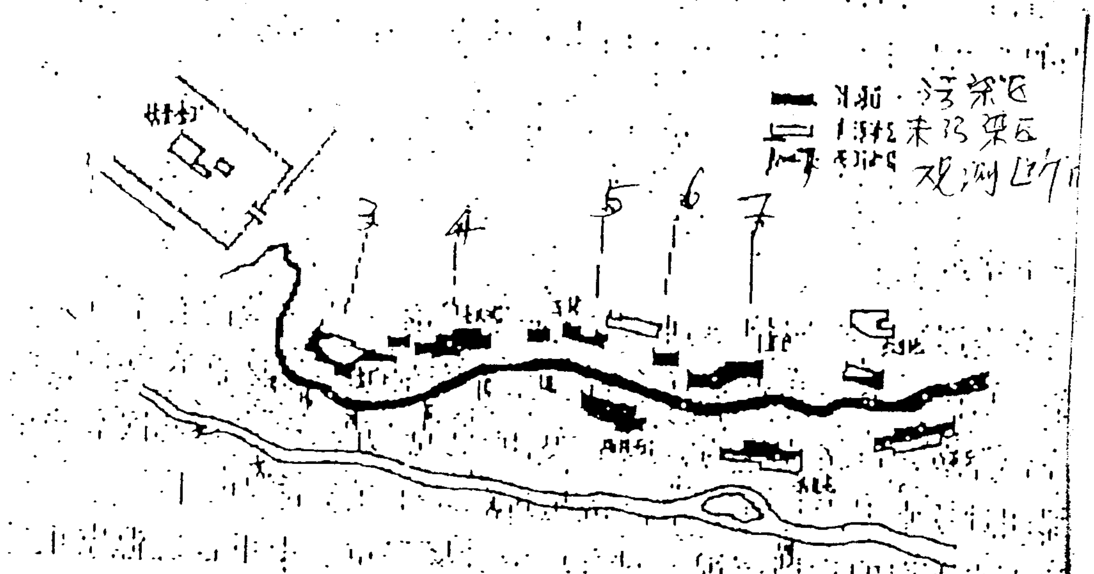

图1　1966年女儿河地区地下水污染范围示意图

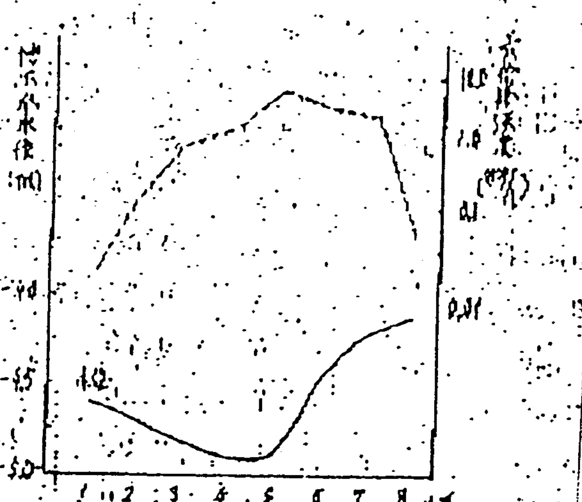

图2　地下水水位与六价铬浓度的关系（广东门断面）

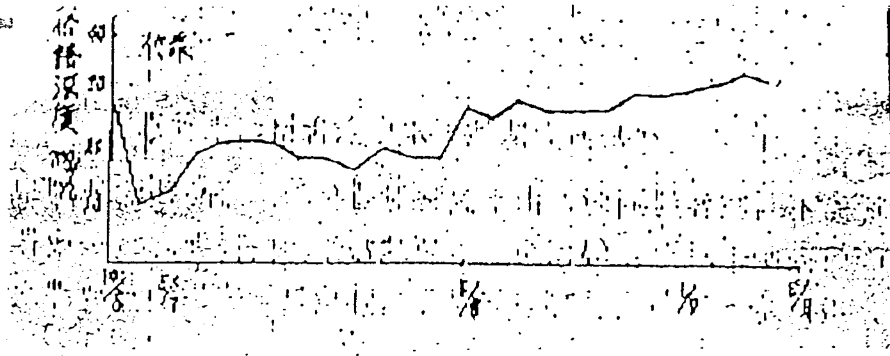

图6．截流井停泵对排水中六价铬浓度的影响（1971）

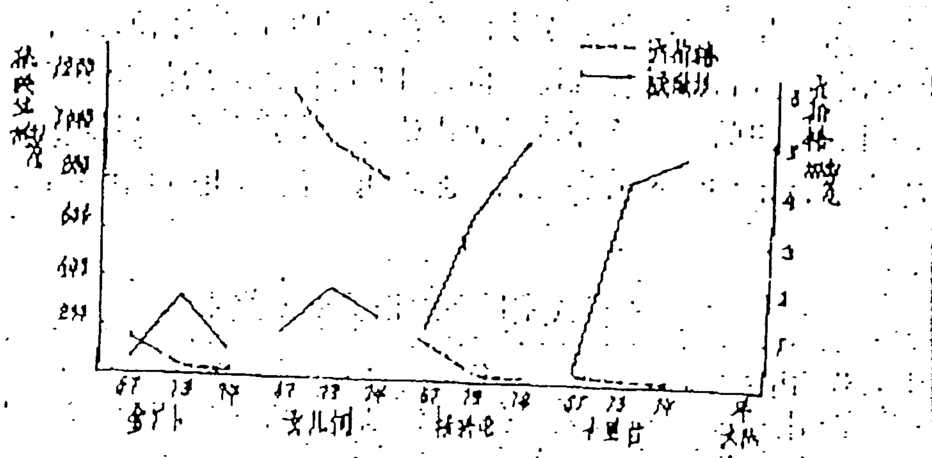

图3．地下水硫酸盐与六价铬浓度变化（最高值）

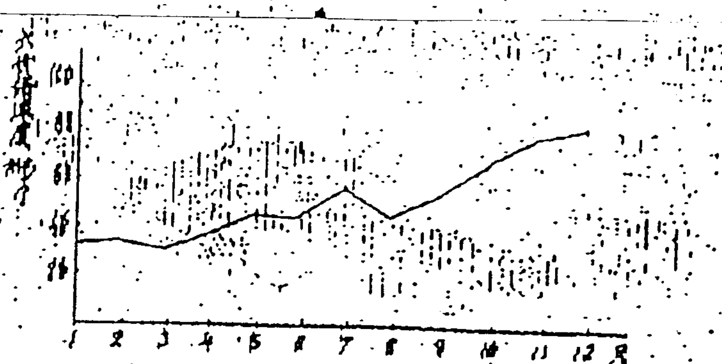

图4．4号截流井排出水六价铬月平均浓度动态（1971）