Distribution, Migration, and Conversion of Groundwater Manganese and Soil Manganese in a Chemical Cluster

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Abstract: Taking a chemical cluster as the study area, this paper investigated the spatial distribution of manganese in the groundwater and soil environments and analyzed the changes of manganese content in groundwater over time. The study results show that: the manganese content in groundwater of the cluster is relatively stable over time; however, it shows the characteristics of aggregation and concentration in scattered spots and local areas on a plane surface; the content of manganese in groundwater is highly correlated with that in the soil environment; in groundwater, manganese diffuses along water flows, resulting in a pollution plume, while in the soil environment, it migrates vertically from the shallow soil layer to the deep soil layer and then to the groundwater or directly goes to the groundwater due to the leaching of rainwater; at the same time, the humid environment of the cluster, a low pH value, intense reduction actions, and the increase of Mn$^{2+}$ content all make the manganese pollution worse.

1. Introduction
In nature, manganese mainly exists in the form of a compound. When participating in a chemical reaction, manganese would lose the outermost seven electrons and then exist in seven oxidation states from Mn$^0$ to Mn$^{7+}$, among which Mn$^{2+}$ and Mn$^{7+}$ are relatively stable; Mn$^{4+}$ has very a low solubility. Manganese in soils is present in five states: exchangeable state, carbonate-bound state, iron-manganese oxidation state, organic-bound state and residue state$^{[1-2]}$. The content of manganese in each state in soils is in a balanced state. If the total amount, external temperature, soil pH, and microbial activity are changed, the proportions of each state of manganese will be balanced again in soils$^{[3]}$. Manganese has a wide range of uses, which almost involves all aspects of human production activities and lives. Activities such as accumulation of manganese steel waste, improper handling of zinc-manganese batteries and old electrical appliances, weathering of natural rocks, and the use of manganese-containing fertilizers in agriculture all cause manganese to enrich in soils and then leach into groundwater through rainwater. Consequently, the pollution caused by manganese become increasingly prominent$^{[4-6]}$. Taking a chemical cluster as the research object, this paper studied the temporal and spatial distribution, migration, and conversion of manganese in the study area, which is not only of great significance to prevent groundwater pollution, but also has certain reference value for the treatment of manganese pollution in soils.

2. Study Area

2.1. Hydrogeology
The study area is located inside of the basin in the Yishu fault zone. The type of groundwater is pore
phreatic and confined water in the alluvium and diluvium layers. The terrain of the whole basin is relatively flat, with a slight inclination from the north to south, and the river flows in surrounding valleys all merge into the basin and are the main source of basin deposits. The thickness of the alluvial and diluvium layers of the basin is between 15m and 25m. The upper part of the layers is all made of clay sand, the lower part is mainly made of sand and gravel, and some part of the lower part is made of clay sand. In general, the thickness of the part made of clay sand is less than 2m. Affected by the fault, the thickness of the diluvium layer in local areas can reach 30m to 50m. The aquifer in the basin is dominated by medium-coarse sand and gravel. Horizontally, the burial depth of the roof gradually becomes deeper from the north to south. In the shallow area, the burial depth generally ranges from 3m to 4m; while in the deep area, it generally ranges from 8m to 10m. The burial depth is generally between 3.00m to 5.37m in the dry season, and between 1.68m to 3.18m in the wet season. The highest annual variation of groundwater level is 2.19m, the lowest is 0.63m, and the average is 1.39m. A map depicting the hydrogeological features is shown in Figure 1.

The Quaternary pore water mainly flows from north to south, which is basically consistent with the direction of the slope and surface water flows (see Figure 2). Due to the shallow burial of the aquifer, the coarse particles, the large hydraulic slope, and the fast runoff speed, most of the water is evaporated and discharged to the river. The groundwater type in the study area is of bicarbonate type.

Figure 1 Hydrogeological map of the study area
2.2. Detection of Manganese in the Study Area

Total 6 groundwater monitoring points were set up in and around the study area to conduct monitoring on a quarterly basis. At the same time, the manganese content in the groundwater around the study area was investigated, and a total of 9 groundwater samples were taken; 6 soil samples from the vadose zone were taken from groundwater monitoring points. The location of each monitoring point is shown in Figure 3, the monitoring results are shown in Table 1, the groundwater sample detection results are shown in Table 2, and the soil sample detection results are shown in Table 3.

Table 1 Mn content in each monitoring point

| No. | First Quarter (mg/L) | Second Quarter (mg/L) | Third Quarter (mg/L) | Fourth Quarter (mg/L) |
|-----|----------------------|-----------------------|----------------------|-----------------------|
| Zk1 | 1.4                  | 1.66                  | 1.772                | 1.55                  |
| ZK2 | 1.08                 | 1.13                  | 1.009                | 0.910                 |
| ZK3 | 0.43                 | 0.25                  | 0.304                | 0.313                 |
| ZK4 | 0.216                | 0.04                  | 0.087                | 0.317                 |
| ZK5 | 0.665                | 0.97                  | 0.84                 | 0.572                 |
| ZK6 | 0.084                | 0.07                  | 0.049                | 0.057                 |

Table 2 Total Mn content in groundwater monitoring points

| Point No. | D1 | D2 | D3 | D4 | D5 | D6 | D7 | D8 | D9 |
|-----------|----|----|----|----|----|----|----|----|----|
| Mn (mg/L) | 0.055 | 0.725 | 0.078 | 0.021 | 0.013 | 0.003 | 0.007 | 0.007 | 0.257 |

Table 3 Mn content in soil monitoring points

| Point No. | Z1 | Z2 | Z3 | Z4 | Z5 | Z6 |
|-----------|----|----|----|----|----|----|
| Mn (mg/Kg) | 1190 | 1125 | 890 | 675 | 998 | 640 |
Through the monitoring of groundwater manganese in 6 places in the chemical cluster, it is found that the manganese content in 4 out of 6 monitoring points exceeded the groundwater level III standards. Among the four monitoring points, Point zk1 had the highest concentration of manganese, which was about 17 times of the standards while Point zk6 had the lowest content, which was 0.049 mg/L. By detecting the manganese content in soils from the vadose zone around the monitoring points, we found that each point had a great difference in manganese content. Point z1 had the highest content in soils, reaching 1190 mg/Kg and far exceeding the background value of the cluster, while Point z6 had the lowest content, which was about 640m/Kg.

![Figure 3 Distribution of monitoring points](image)

### 3. Manganese Distribution Characteristics and Analysis

#### 3.1 Temporal and Spatial Distribution

According to the monitoring results of manganese content in four quarters at the monitoring points in Table 1, the content change curve is drawn and shown in Figure 4. The wet season started from the second quarter and ended in the third quarter. It can be seen from the figure that, as time went by, the manganese content at each monitoring point is relatively stable, and the content only showed an increasing trend at Point zk4; the manganese content at each point changed slightly during the transition between the dry and wet seasons. It can be seen from the figure that the manganese content of Point zk1, zk2 and zk5 was higher in the wet season that that in the dry season, while Point zk3 and zk4 showed the opposite characteristics, having a low content in the wet season and a high content in the dry season and the period in which water is at the normal level. The manganese content at Point zk2 and zk6 was basically unchanged over time.

After analysis, the reasons why the manganese content at each monitoring points was different are
as follows: In the wet season, the groundwater level increased and the topography of zk3 and zk4 causes the surrounding area to be seasonally water logged. The manganese in the surface soils was leached by the water and decreased with the water discharge. The surrounding terrain of Point zk2 and zk5 is relatively high, and leaching during the flood season caused the manganese in the surface soils to migrate to the groundwater.

Through the analysis of manganese content in groundwater and soils at the monitoring points, as shown in Figure 5, it can be seen that there is a high correlation between the manganese content in groundwater and that in soils. The manganese content in groundwater and soils in zone z1 was both the highest, then followed by z2 and z5, while the manganese content in soils at z4 and z6 was close to the background value;
The plane distribution of groundwater manganese is shown in Figure 6. From the figure, it can be seen that the manganese content in the central and southern parts of the study area was abnormal, exceeding 0.1 mg/l. In particular, the content in the southeastern part was highly abnormal. As for the northern part, the manganese content almost equaled the background value, showing no abnormality. The overall distribution of groundwater manganese presents the characteristics of aggregation and high concentration in scattered areas that look like dots on the plane and in a stripe-shaped area along the rivers in the eastern part.

![Contour map of regional manganese distribution](image)

**Figure 6** Contour map of regional manganese distribution

### 3.2. Analysis of manganese distribution characteristics

The groundwater manganese at each monitoring point was basically the same, there was no significant increase or decrease, and the changes over time were relatively stable. It is concluded after analysis that the process of getting polluted was slow and continuous or a stable source of pollution exists. However, according to Figure 6, the spatial distribution of groundwater and the water flow direction do not show obvious rules, and no manganese-related enterprises have been found through the investigation of enterprises in the cluster. Therefore, the pollution must be caused by a single source and polluted areas were distributed like dots on the plane. Currently, the dot-shaped pollution has not expanded to make a large part of area get polluted.

The soil in the cluster is rich in organic matter, which makes it easy to bring the manganese in the surface soil into the groundwater through leaching. The groundwater level in the shallow layer around the study area is not buried deeply, the topography is less undulating and low-lying, and the vadose...
zone is mainly made of silt. The surface soil around point zk1 where the groundwater manganese exceeds the standard had a high manganese content (as high as 1190mg/kg). The reason is that the point is located in an environment that is conducive to converting the valence electrons of the manganese element. The Mn$^{4+}$ in the soil and vadose zone is reduced to Mn$^{2+}$ and enters the groundwater through leaching, causing the manganese content to exceed the standard. In the traceability analysis of manganese pollution in the cluster, a source of manganese pollution in the groundwater or in the vadose zone causes the groundwater manganese to exceed the standard.

4. Analysis of manganese migration and conversion

In order to further analyze the migration and conversion of manganese in soil and groundwater, we obtained samples of groundwater at 50m, 100m, and 200m away from Point zk1 in the downstream. Taking Point zk1 as an example, the content of manganese at Point zk1 is 1.55mg/l, and that for the samples is 0.66mg/l, 0.24mg/l, and 0.09mg/L, respectively, as shown in Figure 7. The concentration of manganese gradually decreases, creating a plume of groundwater pollution.

![Figure 7 Manganese content change in groundwater](image)

The migration and conversion process of manganese in the soil is as follows: the surface soil is contaminated by manganese and the element vertically leaches from the shallow soil to the deep soil or directly goes to the groundwater together with rainwater. At the same time, the soil environment affects the conversion of manganese in the soil; taking the soil at Point z1 for a 24h-leaching experiment, the total manganese content in the sample is 1,190mg/kg, and the calculated content of manganese that is leached is about 11.2mg/kg, indicating that manganese migrates from soil to groundwater in the rainy season. The conversion of manganese in the soil is affected by the pH value, Eh, humidity, organic matter and soil aeration status; in a low-pH and humid environment, the reducibility of the soil is enhanced, the manganese is converted to Mn$^{2+}$, and the effective amount of manganese increases; at the same time, the chelates formed by the combination of manganese in the soil with various organic matters will be released into the soil again when the soil potential changes or the environment is changed to an oxidizing environment.

5. Conclusions

Through the study of the temporal and spatial distribution and conversion of manganese in the environment of a certain chemical cluster, we can understand the change of manganese content in different periods and regions, which can provide guidance and reference for the protection, development and utilization of groundwater resources.

(1) In the cluster, the content of groundwater manganese is relatively stable over time, showing the
characteristics of aggregation and high concentration in scattered spots and local area on the plane; and the manganese content in the groundwater is highly correlated with that in the soil. After analysis, we concluded that there is a single and continuous source of pollution in the cluster;

(2) Groundwater manganese diffuses along with the water flows; therefore, the content decreases gradually, creating a pollution plume. The migration and conversion process of manganese in the soil is as follows: the surface soil is contaminated by manganese and the chemical element vertically leaches from the shallow soil to the deep soil or directly goes to the groundwater together the rainwater.

(3) The pH value, Eh, humidity, and organic matters in the soils all affect the conversion of manganese in the soil. In a low-pH and humid environment, the reducibility of the soil is enhanced and the manganese is converted to Mn$^{2+}$, resulting in serious manganese pollution.

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