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The distribution and influencing factors of chromium in regional groundwater at Sanmenxia Basin north-central China

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ABSTRACT

Hexavalent chromium (Cr^{6+}) is highly toxic and mobile in groundwater, and abundant in regions of high industrialization. To assess the status and migration influences of Cr^{6+} in groundwater, its distribution and influencing factors in a regional groundwater system of Sanmenxia Basin, north-central China, were investigated by monitoring changes in concentration along with hydrochemical characteristics in both shallow and deep aquifers. Groundwater samples were collected from 86 sites including 42 shallow wells (depth ≤ 100 m) and 44 deep wells (depth > 100 m) in several aquifer zones. Fifty-six samples (23 shallow and 33 deep wells) contained Cr^{6+}concentrations ranging from 0.004 to 0.192 mg/L, with many of the high chromium concentration points in the deep wells. There was a positive trend between groundwater depths with chromium concentration. The formation of high concentration of hexavalent chromium in deep well water is significantly affected by the hydrochemical characteristics (pH, Eh, etc.) and chemical composition of groundwater (coexistence of inorganic and organic substances). The accumulation of chromium has been favored by the alkaline environment in this study area, where a relatively high concentration of chromium (>0.05 mg/L) is associated with a relatively high pH value (>7.7). Moreover, F^-, Cl^-, K^+, Na^+, HCO_3^-, CO_3^{2}, SO_4^{2-}, Fe^{3+}, and TDS had positive trends with Cr^{6+}, while Ca^{2+}, Mg^{2+}, NO_3^- and total hardness had negative trends with Cr^{6+}. In addition, COD, dichloromethane, trichloromethane, and 1,2-dichlorobenzene detected in the groundwater negatively correlated with Cr^{6+} under current study conditions. These findings are crucial for hexavalent chromium accumulation and migration assessment in groundwater exploitation in this region.

Keywords: Groundwater; Hexavalent chromium; Distribution; Influencing factors

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1. Introduction

Groundwater is an essential resource and extensively used in the water supplies of municipal, domestic, and industrial activities [1,2]. Sanmenxia Basin is the main grain base, industrial, and mining enterprise region of the Henan Province, Central China. Due to the increasing pollution of the surface water, groundwater has become the main source of drinking water for local residents, and groundwater quality has a vital impact on the residents' daily life of this region [3–6]. Therefore, the study of regional groundwater quality is of particular importance.

The composition of regional groundwater is directly determined by its forming hydrogeological mediums. Loose

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Quaternary deposits are widespread in this region, although Cambrian system and Tertiary stratum have been found south of the WenTang village. According to the hydraulic characteristics and physical geological properties, groundwater in the study area is classified as either, carbonate rock fissure karst water, clastic rock cranny pore water, loess pore fissure water, or unconsolidated rock pore water [7,8]. The aquifer lithology of the carbonate rock fissure karst water mainly contains Cambrian middle dolomitic limestone, limestone, and brecciated limestone. The fracture development within the limestone causes a crushing area with a bandwidth up to 50 to 70 m thick, hundreds of meters below the surface, creating an adequate channel for an underground water cycle. Clastic rock cranny pore water is mainly distributed in the bottom of the loess tableland area, consisting of a Tertiary sandstone aquifer. It has a poor capacity for storing water. Loess pore fissure water is distributed in the loess tableland area, and its aquifer medium is the fissure within the loess, calcareous layers, and calcareous concretions of the Quaternary system and lower Pleistocene series. Both are poor in water content and thus the water depth is usually deep. Loose rocks pore water is the main type of regional groundwater in the area, distributed in the valleys, such as the Yellow River and its tributaries. The aquifer is mainly composed of pebble, coarse sand, and a silty sand layer caused by Quaternary alluvial, diluvial, and fluvial environments. This set of media is a multilayer structure and both the distribution and water content are vast vary across the layers. Moreover, the groundwater dynamically changes across the seasons, which results in a water table rise during the rainy season and decline during the dry season. Groundwater pollution typically originates from many natural (such as the rock weathering of chromite) and artificial sources, coupled with human activities, seasonal, and environmental changes.

Chromium is a common environmental contaminant not only in industrial wastewater, derived from electroplating, metal finishing, leather tanning, steel fabrication, and textile activities, but also can be naturally found in surface and groundwater originating from its native geological environment [9,10]. Chromium is ubiquitous normally with two stable oxidation states of hexavalent (Cr(VI)) and trivalent (Cr(III)) in natural conditions, and the former is known to be more toxic and mobile than the latter, although they can transform from one state to the other under certain conditions [11,12]. Hexavalent chromium (Cr(VI)) in the aquatic environment is a commonly identified proven carcinogenic heavy metal pollutant, whereas Cr(III) is nontoxic and considered to be an essential nutrient for living organisms [13,14]. Cr(VI) is closely related to human health and when its concentration exceeds 0.05 mg/L in drinking water, it is detrimental to human health. High chromium and chronic poisoning occurs because of long term and excessive intake of chromium [15,16].

Because of the toxicity, mobility, and transformation of hexavalent chromium, mapping of chromium distribution in groundwater is particularly important for the evaluation and prediction of Cr(VI) content in regional groundwater, which requires, in principle, an extensive knowledge of its distribution and controlling factors of migration, transformation, and fate of Cr(VI) ions [17]. Research on the cause of regional groundwater Cr(VI) abnormalities is relatively scarce and controversy exists on the controlling factors of Cr(VI) in regional groundwater. Therefore, this work presents a case study on the distribution and influencing factors of chromium in groundwater within the Sanmenxia Basin, north-central China. Multiple factors, including hydrochemical conditions, coexistence of groundwater, and human activities, are shown to be responsible for chromium content in the study area. The results provide not only technical support for groundwater exploitation, but also measures to control excessive chromium in groundwater.

2. Material and methods

2.1. Study area

The Sanmenxia Basin is located in the southeast edge of the Fenwei graben system and north limb of the Xiaoqinling anticline eastern sector, with east longitude between 110°21′ and 111°23′ and north latitude between 34°33′ and 34°40′ in the west of Henan province, north-central China. The basin adjoins the Xiaoqinling gold field and Yao Mountain in the south, the Shaoshan Mountain in the east, the Yellow River in the north, and the Shaanxi province in the west. It covers an area of 10,496 km^2, 116 km across east-west and 30 km north-south [18]. There are about 2.2 million people and many large cities such as Sanmenxia city and Lingbao city that are located within this region. The Sanmenxia Basin has a temperate to monsoonal climate, with four clearly distinct seasons.

2.2. Sample selection and sampling methods

The quality and degree of groundwater pollution directly represents its environmental quality. To reflect groundwater quality, 86 samples including regional control points and key control points were collected based on a comprehensive consideration of hydrogeological conditions of this region, which are shown in Fig. 1. Groundwater samples in the study area were collected from shallow (well depth ≤ 100 m) and deep (well depth > 100 m) wells. The shallow well was pore phreatic water, which was detected between 0.3 and 100 m, mostly from the upper Quaternary loose deposits. Deep well was pore-confined water, which was detected between 110 and 460 m, mostly from the middle and lower Quaternary loose deposits.

Depth to groundwater was measured at each well prior to sampling, using a portable reader. Groundwater samples were collected after being pumped continuously to remove stagnant well water. Water pH, electrical conductivity (EC), oxidation-reduction potential (Eh), dissolved oxygen (DO), and temperature (T) were measured on site immediately after sampling using a portable meter. Subsequently, samples were collected in polyethylene plastic bottles (50-mL) and brought to the laboratory for analysis of major cations, anions, and organics. For the cation test, subsample was taken from the bottle and pre-treated by acidification to pH lower than 2.0 with HCl, whereas there was no pretreatment for the anion test and the test was performed directly from the bottle. For the detection of metal contents in the water samples, ultrapure HNO_3 was used to adjust the solution pH to about 1.0 of a subsample, and then sealed in a polyethylene bottle. All water samples were returned to the laboratory within 2 h, maintained at 4°C, and tested within 48 h.

2.3. Sample testing

According to technical specifications for environmental monitoring of groundwater, a series of testing methods were applied to identify the chemical contents of groundwater within the Sanmenxia Basin [19]. Sample pH, EC, Eh, DO, and T were tested using a multi-parameter water quality analyzer (Multi 340i, WTW Corporation, Germany) according to the national standard methods (GB/T 5750–2006) (pH: 0.01, EC: 0.01 μS/cm, Eh: 0.01 mV, DO: 0.01 mg/L, T: 0.01 °C). Before the test, the instruments were calibrated according to the standard procedure including temperature and standard hydrogen electrode (SHE) calibration and compensation. Major ions of Cl^-, SO_4^{2-}, and NO_3^- were measured using ion chromatography (ICS2100, Dionex, USA). The ions of Na^+, K^+, Ca^{2+} and Mg^{2+} were tested with Shimadzu ICPS-7510 standard inductively coupled plasma atomic emission spectroscopy at the Ministry of Land and Resources of Groundwater, Mineral Water, and Environmental Monitoring Center, Chinese Academy of Geological Sciences. Bicarbonate concentration was measured by titration with normal diluted 0.01 N H_2SO_4 immediately after the sample was taken back to the laboratory. F^-content was determined using a Shanghai Rex PXSJ-226 ion meter electrode for fluoride ion selective electrode assay (0.001 mg/L). The analysis of Cr(VI) was carried out spectrophotometrically at 540 nm in a spectrophotometer (Shimadzu 2550, Japan), using diphenylcarbazide as the complexing agent (detection limit = 0.004 mg/L) [9]. A reasonable charge balance error limit for major ion analysis of 5% was adopted to select the valid values to analyze [20,21].

3. Results and discussion

3.1. Hydrochemical characteristics of groundwater

The chemical species and transformation of hexavalent chromium in an aqueous environment are closely related to groundwater hydrogeological conditions [22]. Accordingly, the chemical characteristics and its distribution principles of shallow and deep well water were investigated and analyzed, and the results are listed in Table 1. The pH of groundwater covers a large range, from an acidic (pH = 6.57) to alkaline (pH = 9.77) environment with a mean pH value of 7.78 in this area. Moreover, the EC values evidently change across the region, with a maximum value of 3,190.0 μS/cm and average of 803.79 μS/cm. The range of the Eh value in the study region is -894.20to541.0 mv, and the DO ranges from 5.61 to 9.77 mg/L. Groundwater temperature varied from 12.50°C to 24.0°C, which is a relatively narrow range of temperatures. The large range of pH values (variable coefficient 11.36%)

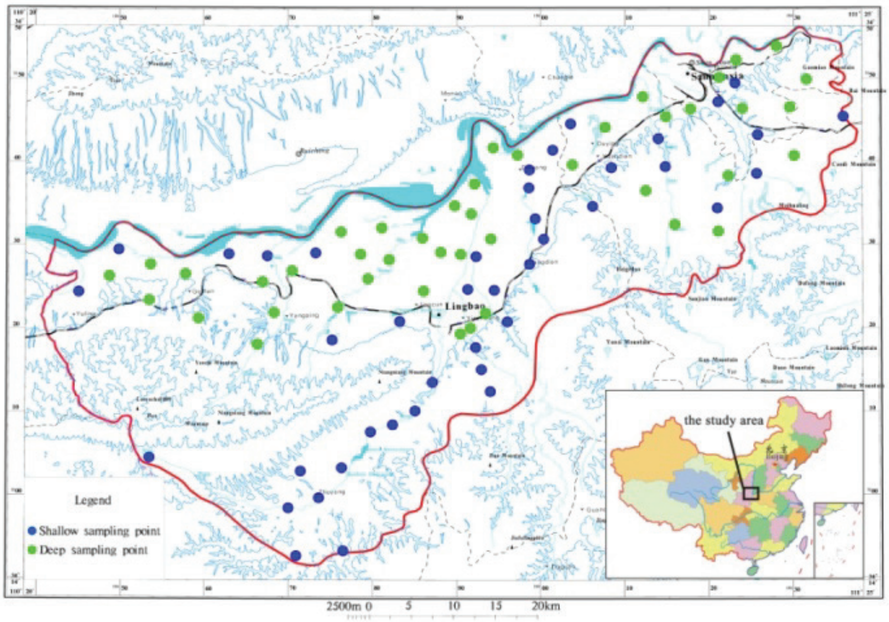

Fig. 1. Sampling sites in this study at Sanmenxia Basin, north-central China.

Table 1
Basic hydrochemical parameters of the Sanmenxia Basin groundwater

Item	Minimum	Maximum	Mean value	Standard deviation	Variable coefficient (%)
Temperature(°C)	12.50	24.40	17.69	2.37	7.49
pH	6.57	9.77	7.78	0.69	11.36
DO(mg/L)	5.61	9.77	7.93	0.63	12.61
EC(μS/cm)	264.00	3190.00	803.79	398.26	2.02
Eh(mV)	–894.20	541.00	176.19	99.29	1.77

in the groundwater greatly favors the transformation and migration of chromium ions, as chromium species are known to be closely related to the pH of groundwater[23,24].

3.2. Distributions of Cr^{6+} in regional groundwater

The chromium concentration of the groundwater sample was tested, and the detectable chromium sampling points are shown in Fig. 2(a) and Table 2. There were 44 sample points which had detectable levels of chromium, ranging from ≤0.005 to > 0.1 mg/L, among which included 33 sample points whose chromium concentration ≤0.005 mg/L, 2 points ≤0.01 mg/L, 5 points ≤0.05 mg/L, 2 points ≤0.1 mg/L, and 2 points >0.1 mg/L. About 50% of the samples had detectable levels of chromium.

Higher chromium concentrations were typically found along the banks of the Yellow River, with decreasing levels further from the river banks. This phenomenon is most likely due to the amount of water storage within the Sanmenxia Reservoir, as during the time of sampling, the reservoir was actively storing water and recharging the groundwater in the area. Chromium pollution sources also tend to exist near the river, and the pollutants migrate along with the groundwater flow [5,25], resulting in high concentrations of chromium along the river banks.

In particular, from Fig. 2(b), it appears that high chromium concentrations (>0.05 mg/L) were detected in the deep well water (well depth >100 m), while the concentration of chromium in shallow well water (well depth ≤100 m) were relatively low (≤0.05 mg/L). The relationship of groundwater depth with chromium concentration is shown in Fig. 2(b). There is a general positive trend between groundwater depths with chromium concentration ($R^2 = 0.0412$). This indicates that the groundwater of this area may perhaps be affected by the native local aquifer medium or the source of surface pollution [26–28].

3.3. Potential factors affecting Cr^{6+} accumulation in groundwater

3.3.1. Eh and pH

Hexavalent chromium exists in the environment primarily as chromic acid (H_2CrO_4) and its salts, such as hydrogenchromate ion ($HCrO_4^-$) and chromate ion (CrO_4^{2-}), depending on the pH and Eh of the groundwater environment. H_2CrO_4 predominates at pHs less than about 1.0, $HCrO_4^-$ at pHs between 1.0 and 6.0, and CrO_4^{2-} at pHs above about 6.0 [29,30]. The dichromate ion ($Cr_2O_7^{2-}$) is a dimer of $HCrO_4^-$, less a water molecule, which forms when the concentration of chromium exceeds approximately 1 g/L [31].

The connection of Eh and pH values with Cr^{6+} concentration is shown in Fig. 3. Groundwater Eh when Cr(VI) is detectable ranges from 100 to 300 mv, and Eh values are mostly concentrated around approximately 200 mv. High Cr(VI) concentrations (>0.05 mg/L) are accompanied by relatively low Eh values (<200 mv). As shown in Fig. 3(b), the pH range of groundwater with detected Cr(VI) is from 7.2 to 8.2 with a median value of 7.7. Moreover, a relatively high concentration of chromium (>0.05 mg/L) is associated with a relatively high pH value (>7.7) in the present study. The accumulation of chromium appears to be connected with low Eh and high pH conditions of groundwater; although, the chemical species of chromium are affected by pH and Eh conditions [31,32], which affects the mobility and transformation of chromium in groundwater.

3.3.2. Chemical composition of groundwater in the Sanmenxia Basin

Water-rock interaction of groundwater and its surrounding media occurs during groundwater flow, causing the chemical composition of groundwater to continually change with time and distance [33,34]. Therefore, through the water chemistry data, we can obtain store environment, runoff, substance exchange, and other important information of Cr^{6+} in the groundwater, which can reveal the characteristics of mobility and transformation of Cr^{6+}. In order to better analyze these aspects, the hydrochemical characteristics of both shallow (depth ≤100 m) and deep (depth >100 m) well water were investigated.

Table 2
The detectable chromium of sample points

Cr(VI) concentration (mg/L)	≤0.005	≤0.01	≤0.05	≤0.1	>0.1
Number of wells	33	2	5	2	2

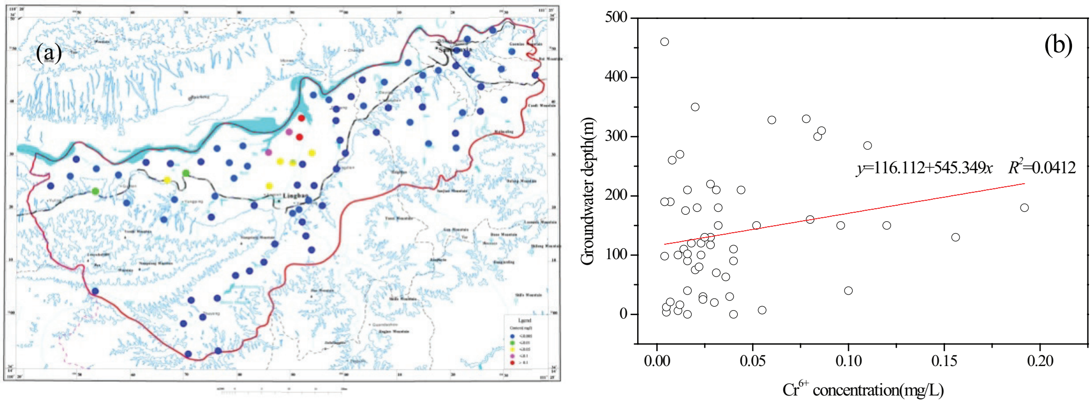

Fig. 2. Distribution of Cr^{6+} (a) and relationship between well depths with Cr^{6+} concentration (b) in the Sanmenxia Basin.

As seen from Table 3, the water chemical characteristics are vastly different for the shallow and deep wells. The anion concentrations of Cl^-, SO_4^{2-}, and NO_3^- in the shallow well water are slightly higher than that in deep well water, while HCO_3^- in shallow well water is lower than deep groundwater. As for cations, the average contents of Mg^{2+}, K^+, and Ca^{2+} in shallow well water are higher than that of deep well water. The proportion of Na^+ and Ca^{2+} is the largest in shallow well water while Na^+ proportion is the largest in deep well water. Although the specific ion concentrations vary between the two groundwater systems, the average of TDS in the shallow well water and deep well water are relatively similar, which is consistent with the distribution of EC values.

Overall, the hydrochemical composition of groundwater in the Sanmenxia Basin mainly includes the anions of $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$ and the cations of $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ with an average TDS value of 433.90 mg/L. The variable coefficients of ions in the shallow groundwater is higher than that of deep well water, of which the greatest change is the K^+ ion, and indicating that hydrology chemical properties of the shallow well water has a greater variability than that of the deep groundwater. This in turn indicates that the shallow well water is more easily influenced by external factors, such as aquifer medium, landform, hydrology, and meteorology conditions, and human activity, while deep groundwater is less influenced by these external factors [33,35,36].

In the investigation area, the aquifer medium is mainly composed of Quaternary and Neogene sediments, and thus the groundwater type is dominated by loose rocks pore water. According to Schukalev hydrochemical classification method, the pattern structures of the Sanmenxia Basin groundwater can be divided into 36 types, of which Na-Mg-HCO_3 type groundwater is the most vastly distributed across the basin, followed by Mg-Na-Ca-HCO_3, Na-Mg-Ca-HCO_3, Ca-Mg-HCO_3-SO_4, etc. However, although there are so many different groundwater chemical types, Ca-Mg-HCO_3-SO_4 groundwater is mostly distributed within the shallow wells while Na-Mg-HCO_3 type in typically in the deep well water system. The reason for this particular phenomenon may be that shallow well water has been affected by other factors, such as human activities. The differences of species and concentration of anions as well as cations in groundwater have a diverse binding capacity with Cr^{6+} which has significant impact on the mobility and accumulation of Cr^{6+} in groundwater.

For a better analysis of the chemical characteristics and evolution of groundwater in the Sanmenxia Basin, Piper diagram and hydrochemical facies evolution diagram (HFE-D) [37–39] were used to visualize the monitoring data, as shown in Figs. (4) and(5). From Fig. 4, there was no significant difference in the distribution of the Piper triangular diagrams between the shallow and deep well water. Ca^{2+} is the major cation both in deep well water and shallow well water, and

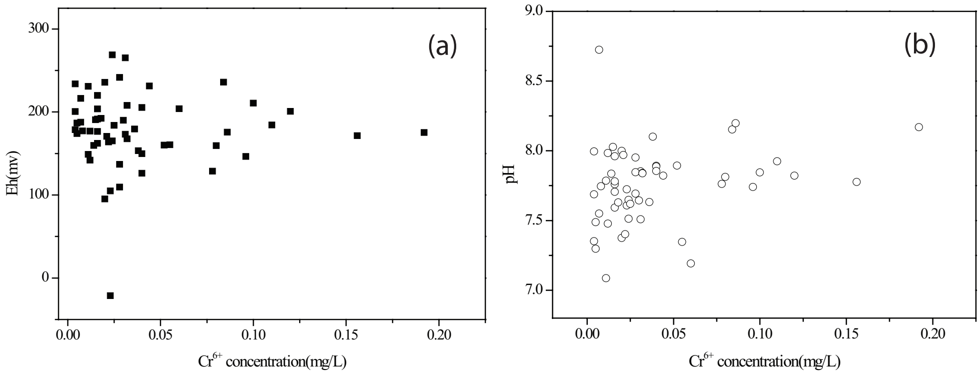

Fig. 3. Comparisons of (a) Eh and (b) pH values with Cr^{6+} concentrations.

Table 3
Hydrochemical characteristics of shallow and deep well water in the Sanmenxia Basin

Item	Shallow well (≤100m)					Deep well (>100m)				
	Maximum (mg/L)	Minimum (mg/L)	Mean value (mg/L)	Standard deviation (mg/L)	Variable coefficient (%)	Maximum (mg/L)	Minimum (mg/L)	Mean value (mg/L)	Standard deviation (mg/L)	Variable coefficient (%)
Na^+	223.00	4.47	50.62	51.10	1.01	202.40	6.32	78.47	50.11	0.64
K^+	133.40	0.36	5.78	20.47	3.54	5.38	0.62	1.88	0.90	0.48
Ca^{2+}	139.00	19.81	50.06	27.54	0.55	120.00	7.67	34.73	24.32	0.70
Mg^{2+}	135.60	9.84	35.51	23.25	0.65	72.42	7.45	27.31	13.29	0.49
Cl^-	294.70	1.07	33.07	51.20	1.55	123.20	2.50	30.97	31.51	1.02
SO_4^{2-}	585.70	3.96	96.07	107.59	1.12	491.60	4.57	81.28	96.15	1.18
HCO_3^-	373.00	125.30	233.41	59.03	0.25	354.60	113.10	238.32	65.36	0.27
NO_3^-	204.50	3.24	32.42	38.87	1.20	89.40	1.08	20.79	18.43	0.89
TDS	1444.00	188.40	443.60	266.72	0.60	1014.00	199.50	424.65	175.96	0.41

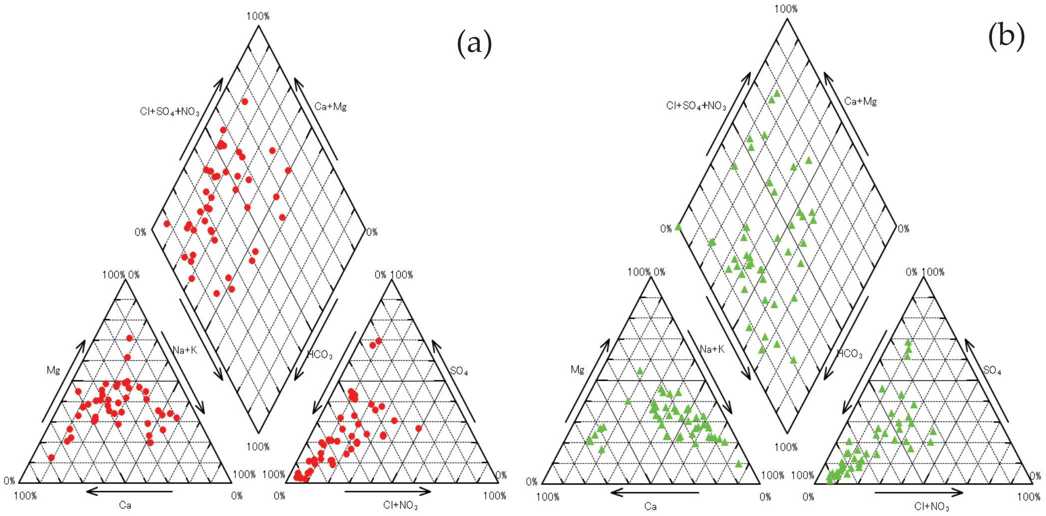

Fig. 4. Piper diagrams showing the characteristics of major water ions in the Sanmenxia Basin groundwater (a) shallow well water (b) deep well water.

the milligram equivalent of Mg^{2+} and $Na^+ + K^+$ are relatively low. However, $Na^+ + K^+$ are the dominate cations, and the cations of milligram equivalent of Mg^{2+} and Ca^{2+} have a tendency to increase. $Cl^- + NO_3^-$ show the same features, as they are affected by human activities in shallow well water. HCO_3^- is the main anion in the deep well water and SO_4^{2-} milligram equivalent are relatively low compared with the shallow well water. HCO_3^- and SO_4^{2-} are the main anions of deep well water while their milligram equivalents are low in deep well water [37–39]. Furthermore, $Cl^- + NO_3^-$ milligram equivalent proportions also have a tendency to increase when affected by human activities, such as mining industry and agricultural production. According to the HFE-D (Fig. 5), although the HCO_3^- and SO_4^{2-} are the main anions, their preponderance is not obvious. The shallow and deep aquifers in the Sanmenxia basin have a significant tendency of salinization.

3.3.3. Correlation of coexisting inorganic and organic substances with Cr^{6+}

The chemical compositions of groundwater may have an appreciable impact on chromium accumulation, mobility, and transformation [26,34,40]. Correlation analysis can determine similar or heterogeneity of groundwater hydrochemistry parameters as well as their consistency and differences of source. Thus, the correlations of inorganic and organic ions that coexist with chromium were analyzed and the results are shown in Figs. 6 and 7.

Fig. 6 presents the correction of F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, TDS, and total hardness with chromium. Under the conditions of this study, the ions of F^-, Cl^-, K^+, Na^+, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Fe^{3+}, and TDS show a positive trend with Cr^{6+}. And more notably, the positive correlation of Na^+, Fe^{3+}, CO_3^{2-}, and HCO_3^- with Cr^{6+} is distinct, better than that of F^-, Cl^-, K^+, and SO_4^{2-} with Cr^{6+}. This indicates that a high concentration of Cr^{6+} is often associated with high concentrations of Na^+, Fe^{3+}, CO_3^{2-}, and HCO_3^-. When Na^+, Fe^{3+}, CO_3^{2-}, and HCO_3^- ion are dominate in groundwater, the mobility, transformation, and accumulation of Cr^{6+} are affected by the contents of Na^+, Fe^{3+}, CO_3^{2-}, and HCO_3^- through formation binding state chromium compounds, and thus a high Cr^{6+} environment is formed accordingly [39].

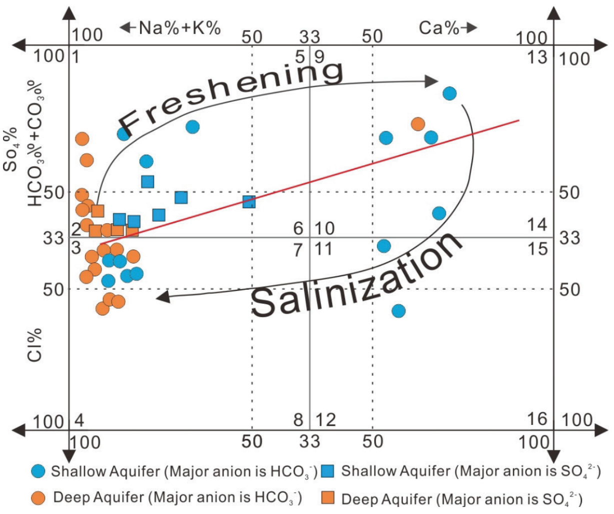

Fig. 5. Application of HFE-D to the aquifer of Sanmenxia Basin.

However, Ca^{2+}, Mg^{2+}, and NO_3^- ions and total hardness show a negative trend with Cr^{6+}, and the negative trend of Ca^{2+} and total hardness with Cr^{6+} is more significance than that of Mg^{2+} and NO_3^- with Cr^{6+}. The existence of Ca^{2+}, Mg^{2+}, and NO_3^- ions tend to form an environment conducive to low chromium contents, indicating that these coexisting ions will inhibit the mobility of Cr^{6+} in groundwater. Generally, different species of ions have different effects on Cr^{6+}, and even the same valence ions can have different effects.

Groundwater is a complex environmental system, and the behaviors of Cr^{6+} and its interactions with other pollutants may be influenced by various factors [35,41]. In addition to inorganic substances, organic matter may also have influence on the occurrence of Cr^{6+} [27,42,43]. Therefore, organic matter detected in groundwater, mainly the volatile organic compounds (VOCs), halogenated hydrocarbons and

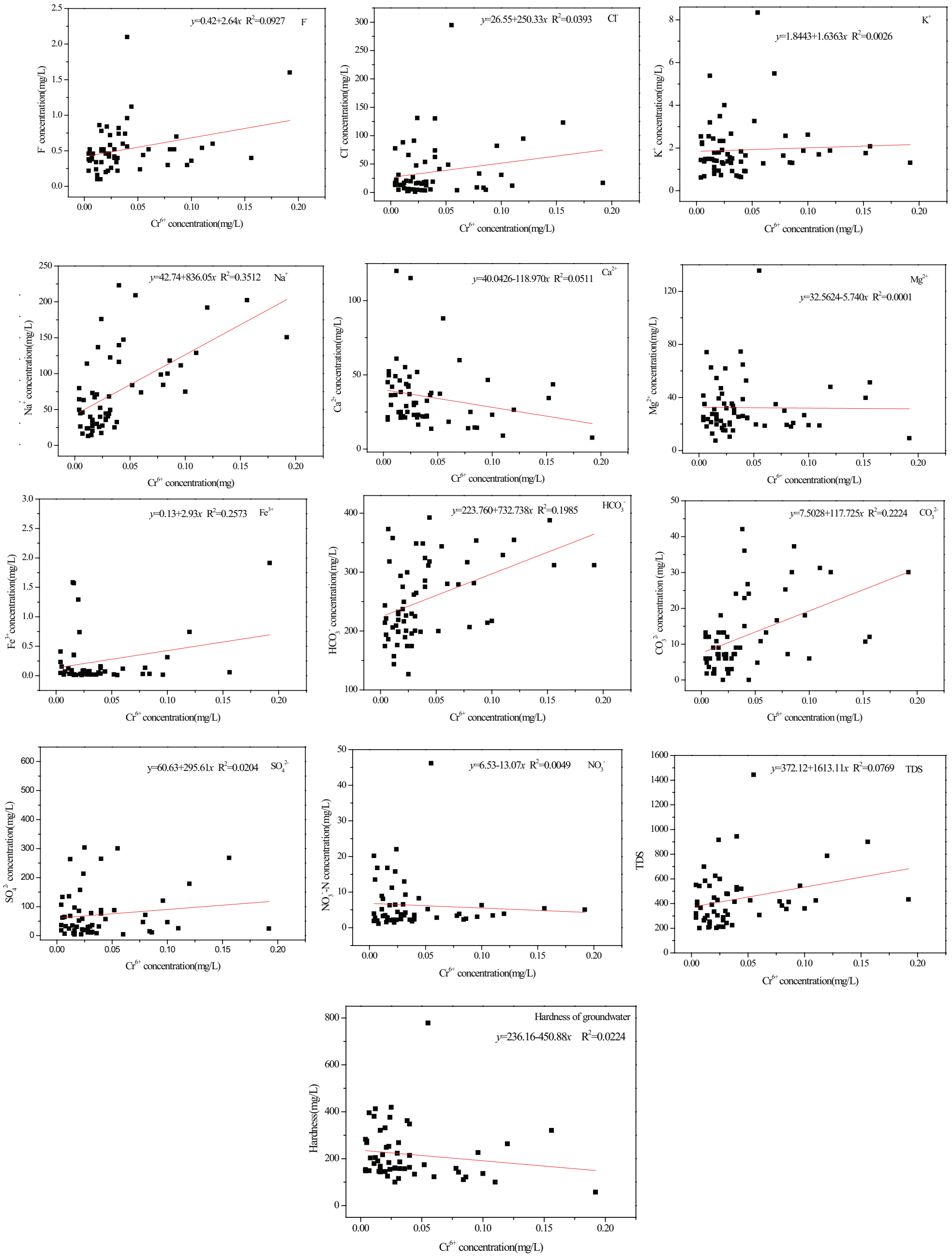

Fig. 6. Correlation of typical inorganic ions (F^-, Cl^-, K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, HCO_3^-, CO_3^{2-}, SO_4^{2-}, NO_3^-), TDS and hardness with Cr^{6+} in the Sanmenxia Basin groundwater.

chlorobenzene, such as methylene chloride, chloroform, and 1, 2-dichlorobenzene, were also analyzed, and the results of the correlation between Cr^{6+} and chemical oxygen demand (COD), dichloromethane, trichloromethane, 1,2-dichlorobenzene are shown in Fig. 7.

COD, dichloromethane, trichloromethane, 1,2-dichlorobenzene negatively correlate with Cr^{6+} under the current study conditions. This shows that high concentrations of organics are usually associated with a low level of Cr^{6+}, and such organics have an inhibiting effect on the mobility of Cr^{6+}. Moreover, in the investigation conditions, inhibitions are distinctly different in the presence of dichloromethane, trichloromethane, and 1,2-dichlorobenzene. This phenomenon implies that the mobility, transformation, and accumulation of Cr^{6+} are greatly influenced by the nature of organics, not solely the presence of organics, which is closely connected to the structures and properties of each organic species.

From the earlier analysis, coexisting inorganic and organic substances in groundwater can have a significant effect on the mobility, transformation, and accumulation of Cr^{6+}, which formed a high or low Cr^{6+} groundwater environment. Therefore, groundwater chemical type is an important factor that influences chromium content in the groundwater in certain areas.

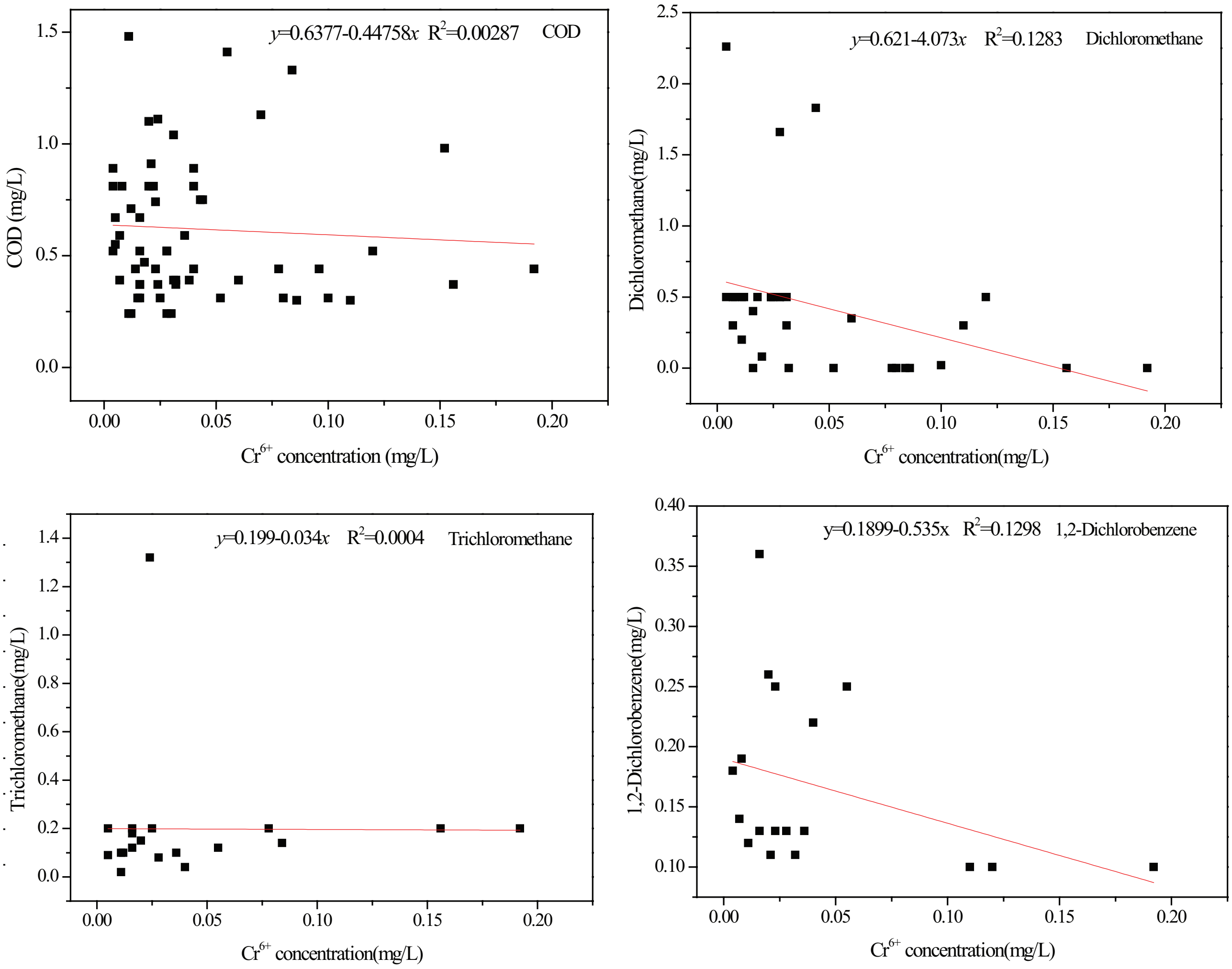

Fig. 7. Correlation between COD, dichloromethane, trichloromethane, 1,2-dichlorobenzene with Cr^{6+} in the Sanmenxia Basin groundwater.

4. Conclusions

Groundwater samples were collected from 86 sites, including 42 shallow well samples (well depth ≤ 100 m) and 44 deep well samples (well depth > 100 m) in groundwater typical zones of the Sanmenxia Basin. The results show that 56 samples (23 shallow and 33 deep well samples) contained hexavalent chromium, with concentrations ranging from 0.004 to 0.192 mg/L. The high chromium concentrations were typically in the deep well water, showing a positive correlation between chromium concentration and increased depth. The formation of high concentration of hexavalent chromium in deep well water is significantly affected by the hydrochemical characteristics (pH, Eh etc.) and chemical composition of the groundwater (coexisting inorganic and organic substances). The accumulation of chromium has been favored by the alkaline environment in this study area. Moreover, F^-, Cl^-, K^+, Na^+, HCO_3^-, CO_3^{2-}, SO_4^{2-}, Fe^{3+}, and TDS showed positive trends with Cr^{6+}, while Ca^{2+}, Mg^{2+}, NO_3^- and total hardness had negative trends with Cr^{6+}. In addition, COD, dichloromethane, trichloromethane, and 1,2-dichlorobenzene detected in groundwater negatively correlated with Cr^{6+} under current study conditions. These findings are crucial for assessment of hexavalent chromium accumulation and migration in groundwater, and are beneficial to groundwater usage in this region.

Acknowledgments

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References

[1] S. Foster, H.Garduño, Groundwater-resource governance: are governments and stakeholders responding to the challenge?, Hydrogeol. J., 21 (2013) 317–320.
[2] S. Hu, Y. Wu, Y. Zhang, B. Zhou, X. Xu, Nitrate removal from groundwater by heterotrophic/autotrophic denitrification using easily degradable organics and nano-zero valent iron as co-electron donors, Water Air Soil Poll., 229 (2018) 56.

[3] J. He, L. Charlet, A review of arsenic presence in China drinking water, Hydrogeol. J., 492 (2013) 79–88.
[4] B. Hu, Y. Teng, Y. Zhai, R. Zuo, J. Li, H. Chen, Riverbank filtration in China: a review and perspective, Hydrogeol. J., 541 (2016) 914–927.
[5] D. Han, M.J. Currell, G. Cao, Deep challenges for China's war on water pollution, Environ. Pollut., 218 (2016) 1222–1233.
[6] Z. Han, H. Ma, G. Shi, L. He, L. Wei, Q. Shi, A review of groundwater contamination near municipal solid waste landfill sites in China, Sci. Total Environ., 569–570 (2016) 1255–1264.
[7] Y. Li, T. Zhang, Y. Zhang, Q. Xu, Geometrical appearance and spatial arrangement of structural blocks of the Malan loess in NW China: implications for the formation of loess columns, J. Asian Earth Sci., 158 (2018) 18–28.
[8] J. Shen, H. Wu, Y. Zhang, Subsidence estimation of breakwater built on loosely deposited sandy seabed foundation: elastic model or elasto-plastic model, Int. J. Nav. Arch. Ocean, 9 (2017) 418–428.
[9] Y. Wu, Y. Zhang, J. Qian, X. Xin, S. Hu, S. Zhang, J. Wei, An exploratory study on low-concentration hexavalent chromium adsorption by Fe(III)-cross-linked chitosan beads, Roy. Soc. Open Sci., 4 (2017) 170905.
[10] J.P. Beukes, S.P. du Preez, P.G. van Zyl, D. Paktunc, T. Fabritius, M. Päätalo, M. Cramer, Review of Cr(VI) environmental practices in the chromite mining and smelting industry - Relevance to development of the Ring of Fire, Canada, J. Clean. Prod., 165 (2017) 874–889.
[11] J.M. Heikoop, T.M. Johnson, K.H. Birdsell, P. Longmire, D.D. Hickmott, E.P. Jacobs, D.E. Broxton, D. Katzman, V.V. Vesselinov, M. Ding, D.T. Vaniman, S.L. Reneau, T.J. Goering, J. Glessner, A. Basu, Isotopic evidence for reduction of anthropogenic hexavalent chromium in Los Alamos National Laboratory groundwater, Chem. Geol., 373 (2014) 1–9.
[12] J. Zhao, T. Al, S.W. Chapman, B.L. Parker, K.R. Mishkin, D. Cutt, R.T. Wilkin, Determination of Cr(III) solids formed by reduction of Cr(VI) in a contaminated fractured bedrock aquifer: evidence for natural attenuation of Cr(VI), Chem. Geol., 474 (2017) 1–8.
[13] J.A. Izbicki, J.W. Ball, T.D. Bullen, S.J. Sutley, Chromium, chromium isotopes and selected trace elements, western Mojave Desert, USA, Appl. Geochem., 23 (2008) 1325–1352.
[14] P. Kar, T.K. Maji, P.K. Sarkar, P. Lemmens, S. K Pal, Development of a photo-catalytic converter for potential use in the detoxification of Cr(VI) metal in water from natural resources, J. Mater. Chem. A, 6 (2018) 3674–3683.
[15] D. Fantoni, G. Brozzo, M. Canepa, F. Cipolli, L. Marini, G. Ottonello, M. Zuccolini, Natural hexavalent chromium in groundwaters interacting with ophiolitic rocks, Environ. Geol., 42 (2002) 871–882.
[16] D. Dermatas, T. Mpouras, M. Chrysochoou, I. Panagiotakis, C. Vatseris, N. Linardos, E. Theologou, N. Boboti, A. Xenidis, N. Papassiopi, L. Sakellariou, Origin and concentration profile of chromium in a Greek aquifer, J. Hazard. Mater., 281 (2015) 35–46.
[17] N.S. Magesh, N. Chandrasekar, L. Elango, Trace element concentrations in the groundwater of the Tamiraparani river basin, South India: insights from human health risk and multivariate statistical techniques, Chemosphere, 185 (2017) 468–479.
[18] J. Peng, S. Chen, P. Dong, Temporal variation of sediment load in the Yellow River basin, China, and its impacts on the lower reaches and the river delta, Catena, 83 (2010) 135–147.
[19] Ministry of Environmental Protection of the People's Republic of China, General Administration of Quality Supervision (EPA) Technical specifications for environmental monitoring of groundwater, (HJ/T 1642004) (2004).
[20] S. Wang, W. Zheng, M. Currell, Y. Yang, H. Zhao, M. Lv, Relationship between land-use and sources and fate of nitrate in groundwater in a typical recharge area of the North China Plain, Sci. Total Environ., 609 (2017) 607–620.
[21] J. Qian, M. Zhang, Y. Wu, J. Niu, X. Chang, H. Yao, S. Hu, X. Pei, A feasibility study on biological nitrogen removal (bnr) via integrated thiosulfate-driven denitratation with anammox, Chemosphere, 208 (2018) 793–799.
[22] M. Lelli, S. Grassi, M. Amadori, F. Franceschini, Natural Cr(VI) contamination of groundwater in the Cecina coastal area and its inner sectors (Tuscany, Italy), Environ. Earth Sci., 71 (2014) 3907–3019.
[23] A. Stefánsson, I. Gunnarsson, H. Kaasalainen, S. Arnórsson, Chromium geochemistry and speciation in natural waters, Iceland, Appl. Geochem., 62 (2015) 200–206.
[24] K.P. Sedlazeck, D. Höllen, P. Müller, R. Mischitz, R. Gieré, Mineralogical and geochemical characterization of a chromium contamination in an aquifer - A combined analytical and modeling approach, Appl. Geochem., 87 (2017) 44–56.
[25] J. Li, F. Li, Q. Liu, Y. Zhang, Trace metal in surface water and groundwater and its transfer in a Yellow River alluvial fan: evidence from isotopes and hydrochemistry, Sci. Total Environ., 472 (2014) 979–988.
[26] J.A. Izbicki, M.T. Wright, W.A. Seymour, R.B. McCleskey, M.S. Fram, K. Belitz, B.K. Esser, Cr(VI) occurrence and geochemistry in water from public-supply wells in California, Appl. Geochem., 63 (2015) 203–217.
[27] N. Kazakis, N. Kantiranis, K. Kalaitzidou, E. Kaprara, M. Mitrakas, R. Frei, G. Vargemezis, P. Tsourlos, A. Zouboulis, A. Filippidis, Origin of hexavalent chromium in groundwater: the example of Sarigkiol Basin, Northern Greece, Sci. Total Environ., 593–594 (2017) 552–566.
[28] F. Li, Z. Qiu, J. Zhang, W. Liu, C. Liu, G. Zeng, Investigation, pollution mapping and simulative leakage health risk assessment for heavy metals and metalloids in groundwater from a typical brownfield, middle China, Inter. J. Env. Res. Pub. Heal., 14 (2017) 768.
[29] Dionex, Determination of Cr(VI) in water, wastewater and solid waste extracts, Technical Note 26 LPN 34398–011M7/96, Dionex Corporation, 1996 http://www1.dionex.com /en-us/webdocs/4428 tn26.pdf.
[30] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review, J. Hazard. Mater., 180 (2010) 1–19.
[31] D. Mohan, C.U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater., 137 (2006) 762–811.
[32] M. Novak, E. Martinkova, V. Chrastny, M. Stepanova, O. Sebek, A. Andronikov, J. Curik, F. Veselovsky, E. Prechova, M. Houskova, F. Buzek, J. Farkas, A. Komarek, The fate of Cr(VI) in contaminated aquifers 65years after the first spillage of plating solutions: a ?53Cr study at four Central European sites, Catena, 158 (2017) 371–380.
[33] H. Wang, X. Jiang, L. Wan, G. Han, H. Guo, Hydrogeochemical characterization of groundwater flow systems in the discharge area of a river basin, Hydrogeol. J., 527 (2015) 433–441.
[34] X. Shi, Y. Wang, J.J. Jiao, J. Zhong, H. Wen, R. Dong, X. Shi, Y. Wang, J.J. Jiao, J. Zhong, Assessing major factors affecting shallow groundwater geochemical evolution in a highly urbanized coastal area of Shenzhen City, China, J. Geochem. Explor., 184 (2018) 17–27.
[35] N. Kazakis, N. Kantiranis, K.S. Voudouris, M. Mitrakas, E. Kaprara, A. Pavlou, Geogenic Cr oxidation on the surface of mafic minerals and the hydrogeological conditions influencing hexavalent chromium concentrations in groundwater, Sci. Total Environ., 514 (2015) 224–238.
[36] Z. Li, G. Wang, X.Wang, L. Wan, Z. Shi, H. Wanke, S. Uugulu, C.I. Uahengo, Groundwater quality and associated hydrogeochemical processes in Northwest Namibia, J. Geochem. Explor., 186 (2018) 202–214.
[37] E. Giménez-Forcada, Dynamic of sea water interface using hydrochemical facies evolution diagram, Ground Water, 48 (2010) 212–216.
[38] E. Giménez-Forcada, Space/time development of seawater intrusion: a study casein Vinaroz coastal plain (Eastern Spain) using HFE-diagram, and spatial distribution of hydrochemical facies, J. Hydrol., 517 (2014) 617–627.
[39] E. Giménez-Forcada, M. Vega-Alegre, S. Timón-Sánchez, Characterization of regional cold-hydrothermal inflows enriched in arsenic and associated trace-elements in the southern part of the Duero Basin (Spain), by multivariate statistical analysis, Sci. Total Environ., 593–594 (2017) 211–226.

[40] M. Economou-Eliopoulos, R. Frei, C. Atsarou, Application of chromium stable isotopes to the evaluation of Cr(VI) contamination in groundwater and rock leachates from central Euboea and the Assopos basin (Greece), Catena, 122 (2014) 216–228.

[41] S. Hu, Y. Wu, N. Yi, S. Zhang, Y. Zhang, X. Xin, Chemical properties of dissolved organic matter derived from sugarcane rind and the impacts on copper adsorption onto red soil, Environ. Sci. Pollut. R., 24 (2017) 21750–21760.

[42] S. Hu, C. Lu, C. Zhang, Y. Zhang, H. Yao, Wu Y., Effects of fresh and degraded dissolved organic matter derived from maize straw on copper sorption onto farmland loess, J. Soil. Sediment., 16 (2016) 327–338.

[43] Y. Wang, J.J. Jiao, K. Zhang, Y. Zhou, Enrichment and mechanisms of heavy metal mobility in a coastal quaternary groundwater system of the Pearl River Delta, China, Sci. Total Environ., 545–546 (2016) 493–502.