孟瑞芳，杨会峰，白华，等. 海河流域大清河平原区地下水化学特征及演化规律分析[J]. 岩矿测试，2023，42(2)：383–395. doi：10.15898/j.cnki.11–2131/td.202207010121.
MENG Ruifang，YANG Huifeng，BAI Hua，et al. Chemical Characteristics and Evolutionary Patterns of Groundwater in the Daqing River Plain Area of Haihe Basin[J]. Rock and Mineral Analysis，2023，42(2)：383–395. doi：10.15898/j.cnki.11–2131/td.202207010121.

海河流域大清河平原区地下水化学特征及演化规律分析

孟瑞芳[1,2]，杨会峰[1,2*]，白华[1,2]，徐步云[1]
（1. 中国地质科学院水文地质环境地质研究所，河北 石家庄 050061；
2. 河北沧州平原区地下水与地面沉降国家野外科学观测研究站，河北 石家庄 050061）

摘要： 地下水超采引发大清河流域范围内一系列生态环境负效应，地下水与地表水关系密切，厘清大清河流域平原区地下水化学特征及演化规律，对大清河流域水资源合理开发利用具有重要意义，然而目前尚缺乏对大清河流域地下水化学特征特别是其历史以来的演变规律作系统的分析。本文以海河流域大清河平原区地下含水系统为例，采集浅层含水层组 47 个水样和深层含水层组 32 个水样，测试了主要阴离子（Cl^-、SO_4^{2-}、NO_3^-）和阳离子（K^+、Na^+、Ca^{2+}、Mg^{2+}）等指标，利用水化学类型、吉布斯模型、离子比值关系等方法，研究其水化学特征及演化规律。测试结果显示：浅层含水层组受到气象和人为因素影响较大，浅层和深层含水层组 pH 值（7.35～8.92）差异不大，偏碱性；浅层含水层组由于农业活动等影响，造成局部地区的硝酸盐和硫酸盐污染。水岩相互作用分析显示：硅酸盐矿物风化是研究区主要的矿物来源，硅酸盐矿物溶解、阳离子交换为主要的水化学作用。研究区浅层地下水水化学特征总体上受地形和水文地质条件的影响，由山前平原–中部平原呈规律性分布。现状地下水化学类型为沿地下水径流方向由山前的 HCO_3–Ca·Mg(Ca) 型，经 HCO_3–Mg·Ca、HCO_3–Mg·Ca·Na、HCO_3–Na·Mg·Ca 向 HCO_3·Cl–Na·Ca、HCO_3·Cl·SO_4–Na 至平原中部冲湖积平原的 Cl(SO_4)–Na 转变。水化学演变分析显示中部平原地下水由以 Cl·HCO_3–Ca·Na、HCO_3·Cl–Ca·Na 型为主，转变为当前条件下以 Cl·HCO_3–Ca·Na、SO_4·Cl–Na·Mg 型为主。总体上，研究区现状水化学类型复杂多样，且分布上虽然仍受地形与地质条件的控制，但越来越多地受到以开采为主的人类活动的影响，应重视人类活动对该区域地下水的影响，合理布置开采方案。本文利用水化学方法研究了大清河流域平原区地下水化学特征及演化规律，厘清了大清河流域平原的水化学特征以及水化学类型演变规律，初步分析了演变趋势造成的原因，特别是指明地下水化学演变越来越受到人类活动的影响，后续将在水化学未来的演变预测上进行相关的研究。

关键词： 大清河流域平原区；地下水水化学全分析；水化学类型；水化学演变；人类活动

要点：

（1）浅层含水层组 TDS 变化幅度大，深层含水层组 TDS 变化幅度小，浅层含水层组受到气象和人为因素影响较大。

（2）硅酸盐矿物风化溶解、阳离子交换为主要的矿物来源和水化学作用。

（3）浅层地下水化学特征总体上受地形和水文地质条件的影响，由山前平原–中部平原呈规律性分布。

（4）研究区水化学类型复杂多样，且越来越多地受到以开采为主的人类活动的影响。

中图分类号： P641.12；P332.7 **文献标识码：** A

收稿日期： 2022–07–01；**修回日期：** 2022–08–16；**接受日期：** 2022–11–05
基金项目： 国家自然科学基金地质联合基金（U2244214）；中国地质调查局地质调查项目（DD20190336，DD2022175）；中国地质科学院基本科研业务费项目（SK202118，SK202216）；河北省创新能力提升计划高水平人才团队建设专项（225A4204D）

第一作者： 孟瑞芳，硕士，副研究员，主要从事水文地质与水循环研究工作。E–mail：631216332@163.com。
通信作者： 杨会峰，博士，研究员，主要从事水文地质与水循环研究工作。E–mail：yanghuifeng@mail.cgs.gov.cn。

地下水是水资源的重要组成部分，约占淡水总量的22.4%，人类可以开采利用以维持正常的生命和生产活动。除此之外，地下水对勘探、建设、水质监测、环境保护等方面也起到重要作用。但在人类活动的影响下，地下水已受到不同程度的污染，其化学组分不断地发生变化[1-2]。地下水污染导致城市供水困难，制约地区经济发展[3]，且严重危害人体健康。地下水化学特征演化受到自然和人为因素的共同影响[4]，通过地下水化学特征分析可以指示地下水径流过程中气象水文、水岩相互作用等，从而反映地下水循环路径、地下水系统特征及演化规律等[5]，也有助于对地下水动态的监测，预防地下水污染的发生。

水化学特征记录了地下水在流动中经历的水文地球化学过程及其补给、径流等特点，为分析地下水的流动过程及其演化特征提供了有力证据。利用多元统计法、图解法和水文地球化学模拟等方法分析水化学特征及演化规律已有大量成果。例如，Han等[6]利用主要离子比值指示了阳武河流域地下水盐分主要来自水-岩相互作用，并利用TDS、Cl、$r\text{SO}_4/r\text{Cl}$等识别了冲洪积扇局部水流系统与中间水流系统特征；Chen等[7]利用水化学方法分析了干旱区水文地球化学过程以及对湖泊补水过程的响应；Xiao等[8]利用图解法指出柴达木盆地地下水的化学演化受水流路径上不同过程的控制，从冲积扇至下游盆地，水岩相互作用控制程度减弱，蒸发浓缩控制程度增加。人类活动的加剧，对地下水天然条件下的水化学特征改变逐渐显现，如人类活动影响下华北平原从补给区到排泄区的水化学演化及其对地下水中氟富集的影响，结果表明过量开采地下水引起的地面沉降使得孔隙水中F^-释放是地下水中氟超标的主要原因[9]。刘君等[10]对中国北方区域大规模开采条件下的地下水化学变化特征进行分析，发现华北平原浅层地下水化学类型向重碳酸型水转变，地下水硬度增高，而深层地下水水化学类型由重碳酸型水向其他类型转变，地下水矿化度增大，水质变差。

大清河流域平原在气候调节和环境特征上均对冀中平原有着重要影响[11]。大清河流域是海河主要水系[12]及中国重要的粮食产区[13]，在大清河上修建的水库还对周边地区有防洪抗旱、灌溉、供水、养鱼、发电等综合效益，而地下水与地表水关系密切，地下水超采使得大清河流域范围内的地下水位下降，造成了地面塌陷、地裂缝、地表水枯竭等一系列生态环境负效应[14]。因此，本文厘清大清河流域平原区地下水化学特征及演化规律，对大清河流域水资源合理开发利用具有重要意义。

目前前人对大清河流域地下水进行补给状况和方式的研究[15]，对水源进行安全性评价[16]、地下水动态分析等[17]，尚缺乏对大清河流域地下水化学特征特别是其历史以来的演变规律开展系统的分析。本文以大清河流域平原区地下水为研究对象，采用水化学类型划分[18]、Gibbs模型[19]、离子比值等方法[20]，对其地下水的化学特征及其演化规律进行分析[21]，揭示水岩相互作用机理及人类活动对该区地下水的影响，为地下水资源的合理利用和污染防治提供理论依据。

1 研究区概况

本区包括河北省中部平原及北京房山区（图1），总面积$1.2\times10^4\text{km}^2$。本区位于太行山脉与河北平原的接壤地带，总体地势平坦，呈现西北高东南低[22]。西部为太行山区，中部、东南部为河北平原区。平原地势为北部拒马河冲洪积扇和南部唐河、大沙河冲洪积扇的扩展，地势低平。区内河流从西北流入平原后，因受新构造运动的影响，亦有向东、东北转折汇流的特点。大清河流域主要河流均源于太行山东麓，支流繁多，河短流急[23]。河网呈扇形以南、中、北三支水系汇入白洋淀。

区内第四系各统均具有较明显的韵律旋回变化，除山前冲洪积扇中上部无稳定隔水层以外，其余广大地区各统地层中上部黏性土均较发育，厚6~25m，构成较稳定的相对隔水层，而中下部含水层富集且颗粒粗大，构成较独立的含水系统。根据含水层与相对隔水层的空间结构与分布，将第四系含水系统分为Ⅰ、Ⅱ、Ⅲ、Ⅳ含水组。由于第Ⅰ含水组厚度较小，多未单独开采，且第Ⅰ、Ⅱ含水组之间水力联系密切，可视为统一含水系统，即Ⅰ+Ⅱ含水层组，为“浅层含水层组”，是农业用水主要开采层。第Ⅲ、Ⅳ含水层组为“深层含水层组”，其中第Ⅲ含水组为研究区城镇生活和工业用水主要开采层。

本区第Ⅰ+Ⅱ含水层组与第Ⅲ含水层组地下水径流方向及径流特征基本一致，地下水径流方向均与地形倾向和地表水径流方向大致相同，即北部由北西向南东汇流，而南部则由南西向北东方向运动。近年来，随着气候偏干旱和对地下水的大量开采，在高阳-蠡县-清苑、雄县一带分别出现浅层地下水位降落漏斗，地下水流向则由漏斗周边指向漏斗中心。在本区中东部由于过量开采第Ⅲ含水层组地下水，致使其水位在保定市至高阳东部旧城一带形成向东

开口的簸箕形,使径流方向转为由西向东。冲洪积扇区地下水径流条件良好,水力坡度 0.85‰~1.18‰,导水系数均大于 $2000m^2/d$,扇顶多大于 1 $0000m^2/d$,为地下水强径流带。东部冲湖积平原区,随着地形变缓和含水层颗粒渐细及厚度减小,径流条件逐渐变差,水力坡度减缓,导水系数为 1000~$2000m^2/d$,扇间洼地带小于 $1000m^2/d$,地下水径流滞缓。

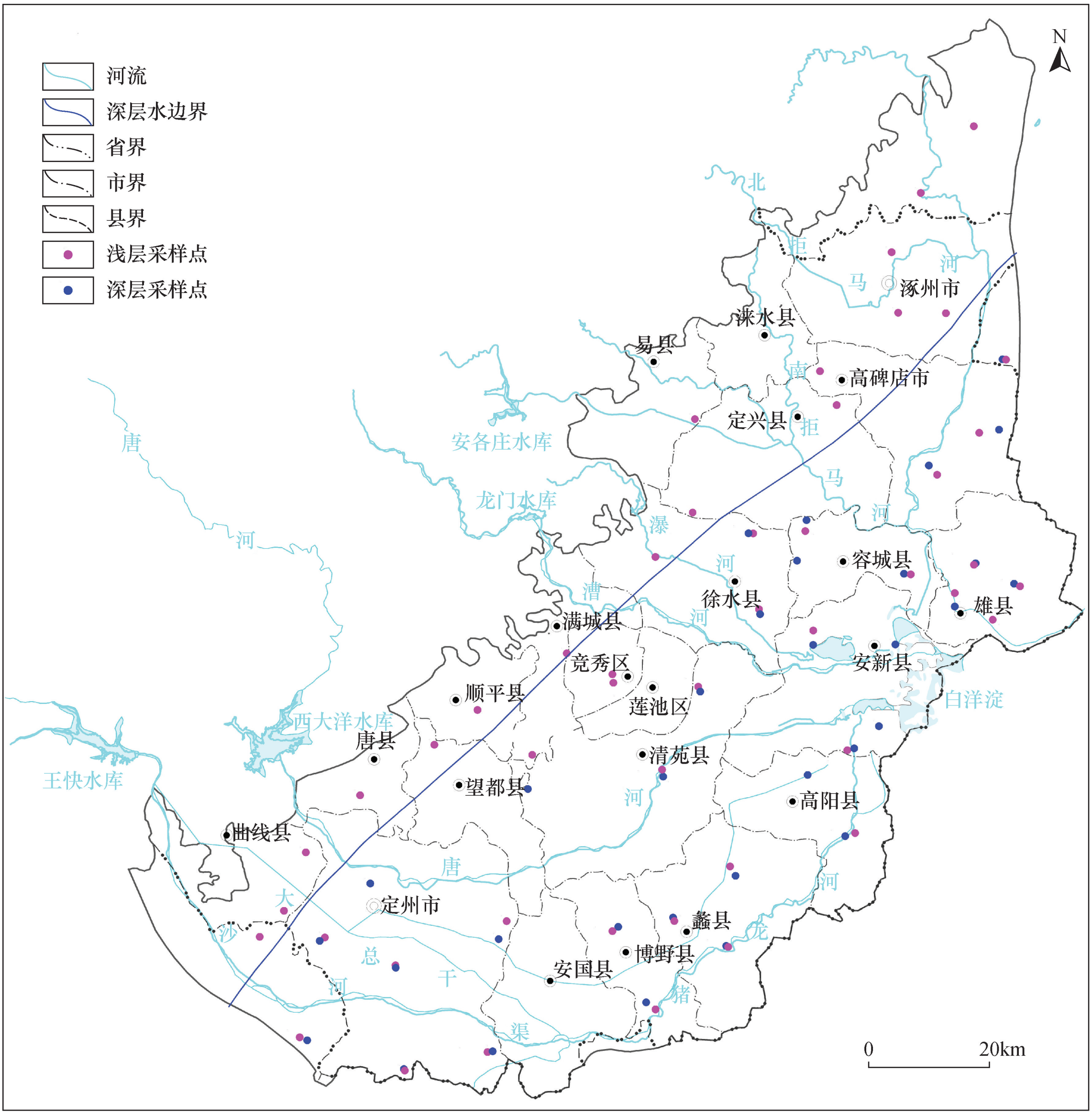


图 1　研究区水系分布及采样点分布

Fig. 1　Distribution of water systems and sampling points in the study area.

The red dots in the figure are shallow groundwater sampling points, blue dots are deep sampling points, and the solid blue line is the boundary between shallow water and deep water. According to the spatial structure and distribution of the aquifer and the relative water barrier, the Quaternary water-bearing system is divided into Ⅰ, Ⅱ, Ⅲ and Ⅳ water-bearing groups. As the thickness of the Ⅰ aquifer group is small, most of them are not exploited separately, and the hydraulic connection between the Ⅰ and Ⅱ aquifer groups is close, so it can be regarded as a unified aquifer system, i. e. Ⅰ+Ⅱ aquifer groups, which are "shallow aquifer groups" and are the main exploited layer section for agricultural water. The Ⅲ and Ⅳ aquifer groups are "deep aquifer groups", where the Ⅲ aquifer group is the main mining section for urban life and industrial water in the working area. The direction of groundwater runoff and runoff characteristics of the Ⅰ+Ⅱ aquifer groups and the Ⅲ aquifer group in this area are basically the same, and the direction of groundwater runoff is roughly the same as the topographic tendency and the direction of surface water runoff, i. e. the northern part flows from north west to south east, while the southern part moves from south west to north east.

2 实验部分

2.1 样品采集与测试方法

2020年5月在大清河流域平原地下水监测井采集了79个地下水样(图1),包括浅层含水层组47个,深层含水层组32个。参考《地下水水质分析方法》(DZ/T 0064—2021),采样前先把取样容器润洗3次,用0.45μm滤膜进行过滤,密封置于聚乙烯样品瓶中,阳离子分析水样采集后用硝酸酸化至pH<2后进行保存。

现场用便携式水质分析仪(哈希HACH-HQ40d)测试pH(精度0.01)、总溶解性固体(TDS,精度0.01)等参数,待各项指标稳定后采集地下水样品。所有样品低温送至实验室至于4℃冰箱冷藏保存,当天用滴定法测定地下水碱度。7天内送至中国地质科学院水文地质与环境地质研究所采用电感耦合等离子体发射光谱仪(iCAP6300)[24-25]测试主要阴离子(Cl^-、SO_4^{2-}、NO_3^-)和主要阳离子(K^+、Na^+、Ca^{2+}、Mg^{2+}),阴阳离子电荷平衡误差在5%以内,阴阳离子测试精度为0.01mg/L。

2.2 数据统计与分析

通过吉布斯图可以研究地下水的形成机理[19],根据$Na^+/(Na^++Ca^{2+})$质量浓度比以及$Cl^-/(Cl^-+HCO_3^-)$质量浓度比与TDS的关系绘制吉布斯图。蒸发盐、硅酸盐及碳酸盐矿物风化产生的Mg^{2+}/Na^+、HCO_3^-/Na^+和Ca^{2+}/Na^+摩尔浓度比常用来确定离子的来源,根据Ca^{2+}/Na^+与Mg^{2+}/Na^+以及Ca^{2+}/Na^+与HCO_3^-/Na^+绘制其摩尔浓度比之间的关系。利用PHREEQC软件计算方解石、白云石、石膏和岩盐等常见矿物的饱和指数(*SI*),以确定其在地下水中的溶解沉淀状态。当*SI*为正值时,矿物处于过饱和状态;当*SI*为负值时,矿物处于不饱和状态;当*SI*等于0时,矿物处于平衡状态。

地下水在水岩相互作用下产生的各个新离子组分比值被广泛地应用于很多水文地球化学问题的研究,可利用的离子毫克当量浓度绘制其$(Na^++K^+)/Cl^-$、$(Cl^-+SO_4^{2-})/(HCO_3^-)$、$(HCO_3^-)/(Ca^{2+}+Mg^{2+})$、$(Ca^{2+}+Mg^{2+})/(HCO_3^-+SO_4^{2-})$的比值关系。$NO_3^-/Ca^{2+}$与$SO_4^{2-}/Ca^{2+}$的毫摩尔浓度比值可以揭示人类活动对地下水组分的影响程度,因此,利用离子的毫摩尔浓度绘制了NO_3^-/Ca^{2+}与SO_4^{2-}/Ca^{2+}比值关系图。用MAPGIS绘制水化学类型分布图,所有数据处理图都在Origin软件中完成。

3 结果与讨论

3.1 水化学指标统计分析

测试结果显示偏差最大的为河北省保定市安新县刘李庄镇韩堡村水样,为浅层含水层组,TDS最大达6015.00mg/L。浅层含水层组TDS为254.10

表1 研究区地下水水化学参数统计

Table 1 Statistical results of groundwater hydrochemical parameters in the study area

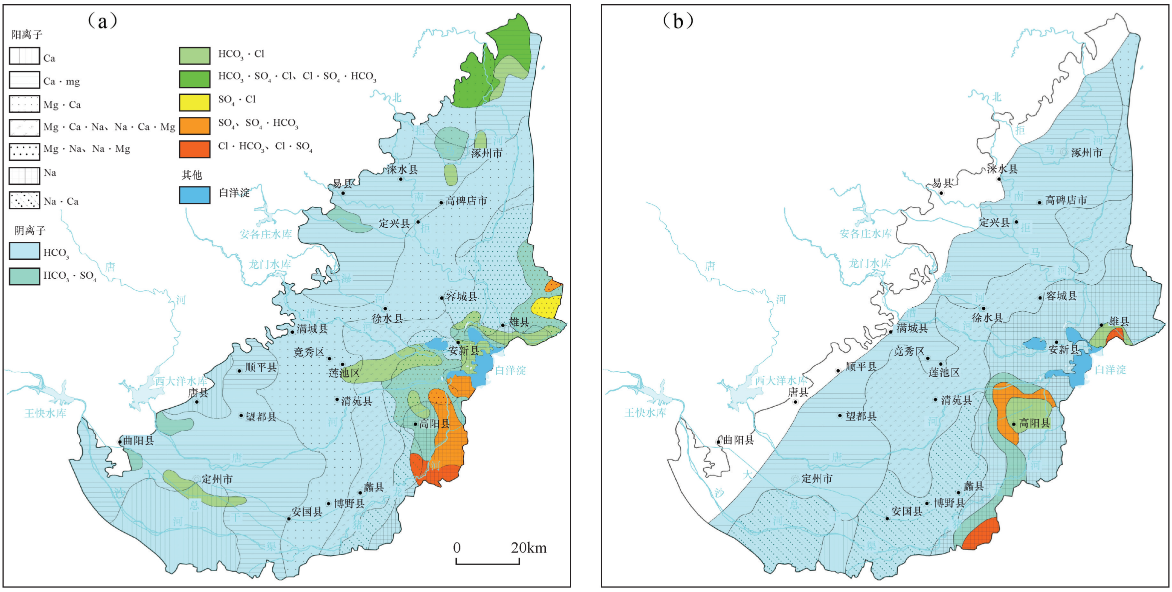
地下水类型	特征值	pH	TDS (mg/L)	K^+ (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	NO_3^- (mg/L)
浅层含水层组	最小值	7.35	254.10	0.26	7.61	12.88	14.44	5.26	6.48	177.30	0.20
	最大值	8.92	6015.00	2.69	1393.00	194.00	341.40	693.30	3091.00	558.30	298.40
	平均值	7.90	664.14	1.14	87.49	76.15	47.60	70.66	162.27	333.28	28.78
	标准偏差	0.35	907.40	0.66	218.22	39.03	51.66	120.67	483.46	90.21	48.99
	变异系数	0.04	1.37	0.58	2.49	0.51	1.09	1.71	2.98	0.27	1.70
深层含水层组	最小值	7.40	197.10	0.30	8.26	4.43	1.12	1.75	4.99	155.60	0.71
	最大值	8.80	691.40	2.61	189.80	58.29	20.82	86.22	255.70	305.10	17.46
	平均值	8.03	278.58	1.46	56.52	28.98	10.60	15.37	27.41	221.23	4.55
	标准偏差	0.38	88.95	0.65	37.97	14.91	5.54	19.14	43.89	39.67	4.05
	变异系数	0.05	0.32	0.45	0.67	0.51	0.52	1.25	1.60	0.18	0.89

Note: The test results showed that the largest deviation was in the water sample from Hanbao Village, Liu Lizhuang Town, Anxin County, Baoding City, Hebei Province, which was from the shallow aquifer groups, and the maximum TDS reached 6015.00mg/L. The TDS of the shallow aquifer groups ranged from 254.10 to 6015.00mg/L, with an average of 664.14mg/L, with a large coefficient of variation and a large variation in TDS, indicating that the shallow aquifer groups were affected by meteorological and human factors. The TDS of the deep aquifer group ranged from 197.10 to 691.40mg/L, with an average of 278.58mg/L, and the coefficient of variation was small, indicating that the groundwater of the deep aquifer groups was less affected by meteorological and human activities than that of the shallow aquifer groups. The pH values of the shallow and deep aquifer groups in the study area were not significantly different (7.35-8.92) and were alkaline. The NO_3^- maximum value of 298.40mg/L and the SO_4^{2-} maximum value of 3091.00mg/L in the shallow aquifer groups, but the average value is not significant, indicating that the shallow aquifer groups have caused local nitrate and sulfate pollution due to agricultural activities and other influences.

~6015.00mg/L(表 1),平均 664.14mg/L,变异系数较大,TDS 变化幅度大,说明浅层含水层组受到气象和人为因素影响较大。深层含水层组 TDS 为 197.10~691.40mg/L,平均 278.58mg/L,变异系数较小,深层含水层组地下水相对浅层含水层组受到气象和人类活动的影响较小。该区东部浅层含水层组少部分采样点为微咸水、咸水,深层含水层组 TDS 普遍小于 1000mg/L。研究区浅层和深层含水层组 pH 值差异不大(7.35~8.92),偏碱性。浅层含水层组 NO_3^- 最大值 298.40mg/L,SO_4^{2-} 最大值达到 3091.00mg/L,但是平均值不大,说明浅层含水层组由于农业活动等影响,造成局部地区的硝酸盐和硫酸盐污染。

3.2　水化学空间分布特征分析

研究区山前为单一结构潜水区域,含水层颗粒较粗,地下水补给充沛,循环交替强烈,水化学类型较简单,主要为重碳酸钙镁型(HCO_3-Ca·Mg)水(图 2),矿化度较低。沿地下水径流方向,水化学类型由山前的 HCO_3-Ca·Mg(Ca)型,经 HCO_3-Mg·Ca、HCO_3-Mg·Ca·Na、HCO_3-Na·Mg·Ca 型向 HCO_3·Cl-Na·Ca、HCO_3·Cl·SO_4-Na 型至平原中部冲湖积平原的 Cl(SO_4)-Na 型转变。研究区浅层地下水水化学特征总体上受地形和水文地质条件的影响,由山前平原-中部平原呈规律性分布。除北部山前平原水力条件的差异出现片状或点状 HCO_3·Cl·SO_4、HCO_3·Cl 型水,山前大部分地区阴离子主要为 HCO_3



a—浅层含水层;b—深层含水层。

图 2　研究区现状地下水化学类型分布图

Fig. 2　Distribution of current groundwater chemical types (a. shallow aquifer, b. deep aquifer).

The study area is a single-structure diving area in front of the mountain, with coarse aquifer particles, abundant groundwater recharge, strong alternating circulation, and simple water chemistry type, mainly bicarbonate calcium-magnesium (HCO_3-Ca-Mg) type water with low mineralization. Along the direction of groundwater runoff, the water chemistry type changes from HCO_3-Ca-Mg (Ca) type in piedmont plain, through HCO_3-Mg-Ca, HCO_3-Mg-Ca-Na, HCO_3-Na-Mg-Ca to HCO_3-Cl-Na-Ca, HCO_3-Cl-SO_4-Na to Cl(SO_4)-Na in the central alluvial plain. The distribution of chemical characteristics of deep groundwater is generally controlled by hydrogeological conditions, and is regularly distributed from the piedmont plain to the central plain; compared with shallow groundwater, the chemical type of deep groundwater is relatively simple, from the top of the piedmont plainalluvial floodplain fan to the bottom of the alluvial floodplain fan, and the main anion in most parts of the plain is HCO_3 type; the cations of deep groundwater are relatively complex, and the zonation is more obvious: from the piedmont plain to the bottom of the alluvial floodplain fan, the cations change to HCO_3-Cl-Na and HCO_3-Cl-SO_4-Na. The deep groundwater cations are relatively more complex and more obvious: from the piedmont plain to the bottom of the alluvial fan, the cations transition from Ca, Ca-Mg, Mg-Ca, Na-Mg-Ca (Mg-Ca-Na) type to Na-Ca, Na type water.

型,阳离子主要为 Ca 及 Ca·Mg、Mg·Ca,地下水沿山前向冲洪积扇口排泄过程中,阳离子由 Ca·Mg 型依次经 Ca·Mg·Na、Na·Ca·Mg、Na·Mg·Ca、Na·Ca 向 Na 型转变,阴离子由 HCO_3 型依次经 HCO_3·SO_4、HCO_3·SO_4·Cl、HCO_3·Cl·SO_4、SO_4·Cl 向 SO_4 型和 Cl 型转变(图 2)。

深层地下水化学分布特征总体上受水文地质条件的控制,由山前平原至中部平原呈规律性分布;相对于浅层地下水,深层地下水水化学类型相对较简单,由山前冲洪积扇顶至冲洪积扇底,平原大部分地区主体阴离子为 HCO_3 型,仅在平原东部的雄县、高阳县附近出现 HCO_3·Cl、HCO_3·SO_4、SO_4·Cl 及 Cl·HCO_3 型水;深层地下水阳离子相对较复杂,且分带性较明显:由山前向冲洪积扇扇底,阳离子由 Ca、Ca·Mg、Mg·Ca、Na·Mg·Ca(Mg·Ca·Na)型向 Na·Ca、Na 型水过渡(图 2)。

3.3　水化学揭示矿物来源及水岩相互作用规律

吉布斯图(图 3)显示,TDS 与 $Na^+/(Na^++Ca^{2+})$ 关系图中大部分水样点位于图中部,少部分分布在框外,TDS 与 $Cl^-/(Cl^-+HCO_3^-)$ 关系图中水样点都分布在框内。浅层含水层组基本都位于水岩相互作用区域内,个别点显示出蒸发浓缩的一定影响。深层含水层组都受到水岩相互作用,受到蒸发和大气降水影响较小。分析结果显示 $(Ca^{2+}+Mg^{2+})+(HCO_3^-+SO_4^{2-})$ 与 $Na^++K^+-Cl^-$ 的毫克当量浓度比值接近−1,表明阳离子交换作用较为显著。研究区地下水样多分布在靠近硅酸盐矿物的端元(图 3),表明硅酸盐矿物(如长石等)风化是研究区主要的水文地球化学控制因素,符合大清河

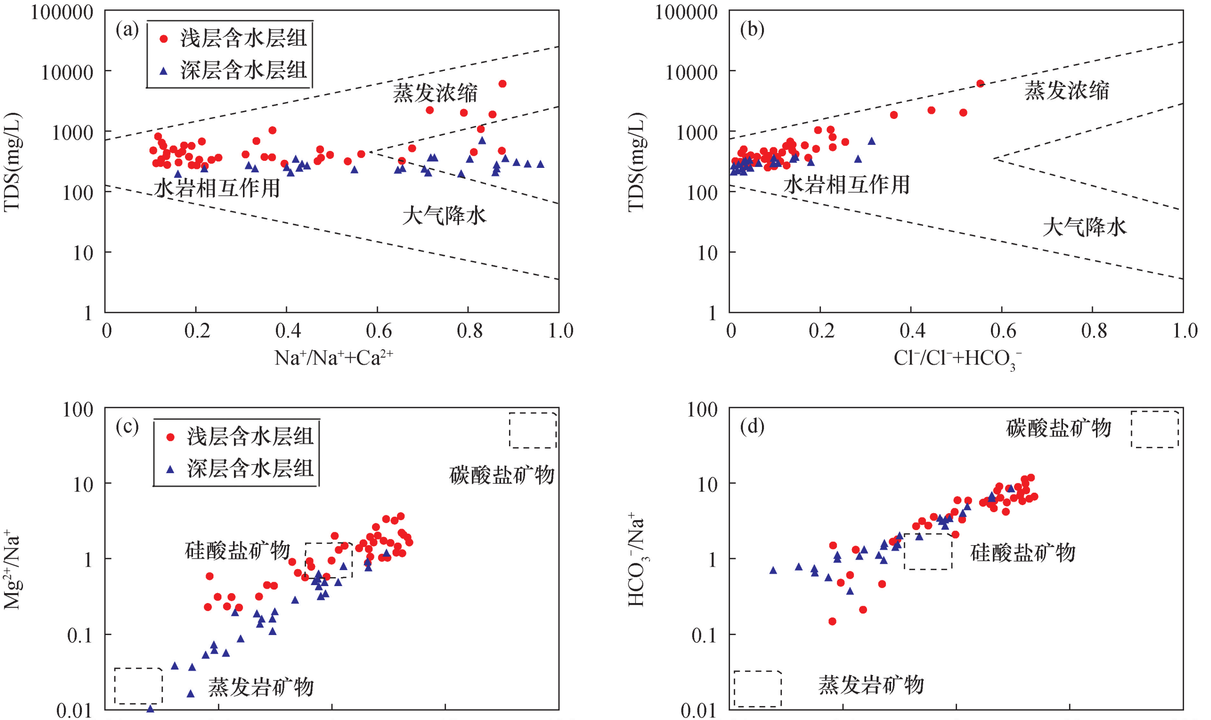


图 3　地下水样品(a,b)吉布斯图;(c) Mg^{2+}/Na^+ 与 Ca^{2+}/Na^+ 比值关系图;(d) HCO_3^-/Na^+ 与 Ca^{2+}/Na^+ 比值关系图

Fig. 3　(a, b) Gibbs diagrams of groundwater samples; (c) Ratio relationship chart of Mg^{2+}/Na^+ and Ca^{2+}/Na^+; (d) Ratio relationship charts of HCO_3^-/Na^+ and Ca^{2+}/Na^+.

Most of the water sample points in the TDS *vs.* $Na^+/(Na^++Ca^{2+})$ diagram are located in the middle of the diagram, and a few are distributed outside the box, and the points in the TDS *vs.* $Cl^-/(Cl^-+HCO_3^-)$ diagram are all distributed inside the box. The shallow aquifer groups are basically located within the water-rock interaction area, and individual points show some influence of evaporation concentration. The deep aquifer groups are all subject to water-rock interaction and is less affected by evaporation and atmospheric precipitation. The analysis results show that the milligram equivalent concentration ratio of $(Ca^{2+}+Mg^{2+})+(HCO_3^-+SO_4^{2-})$ to $Na^++K^+-Cl^-$ is close to −1, indicating that the cation exchange is more significant. Groundwater samples in the study area are mostly distributed near the end elements of silicate minerals, indicating that weathering of silicate minerals is the main hydrogeochemical control factor in the study area.

流域平原地下水的含水层岩性特征，测试结果也显示 HCO_3^- 为浅层和深层含水层组的优势离子。

研究区浅层含水层组中方解石 *SI* 值为-0.46～1.35，白云石 *SI* 值为-0.88～3.02，石膏 *SI* 值为-3.1～-0.68，岩盐 *SI* 值为-8.53～-4.75，说明方解石和白云石部分饱和部分不饱和，石膏和岩盐都为不饱和状态。$Cl^-/(Na^++K^+)$ 可以判定地下水是否受到硅酸盐岩溶解的影响。研究区地下水样大部分表现为 $Cl^-/(Na^++K^+)<1$（图 4），说明除了处于溶解状态的岩盐，硅酸盐矿物溶解（如钾长石和钠长石）是过量的 Na^+ 和 K^+ 的主要来源。Na^+ 含量可能还源自阳离子交换作用，部分样品的 Cl^- 浓度较高则可能是外来污染的输入。浅层含水层组样品 $HCO_3^-/(Ca^{2+}+Mg^{2+})$ 基本小于 1，显示出过量的 Ca^{2+} 和 Mg^{2+}，表明 Ca^{2+} 或 Mg^{2+} 有其他来源，而浅层含水层组的 $(HCO_3^-+SO_4^{2-})/(Ca^{2+}+Mg^{2+})$ 分布在 1∶1 线上下两侧，说明蒸发岩矿物（如石膏）也可能是浅层含水层组 Ca^{2+} 的重要来源，石膏在地下水中的未饱和状态证明了这一点，此外人类活动会导致 SO_4^{2-} 增加。深层含水层组 $HCO_3^-/(Ca^{2+}+Mg^{2+})$ 和 $(HCO_3^-+SO_4^{2-})/(Ca^{2+}+Mg^{2+})$ 都位于 1∶1 线的上方，过量的 HCO_3^- 意味着硅酸盐溶解作用的主导地位，或存在阳离子交换作用，导致 Ca^{2+} 含量降低。$(Cl^-+SO_4^{2-})/(HCO_3^-)$ 可以指示蒸发岩和碳酸盐岩的溶解状况，浅层和深层含水层组水样主要分布在 $(Cl^-+SO_4^{2-})/$

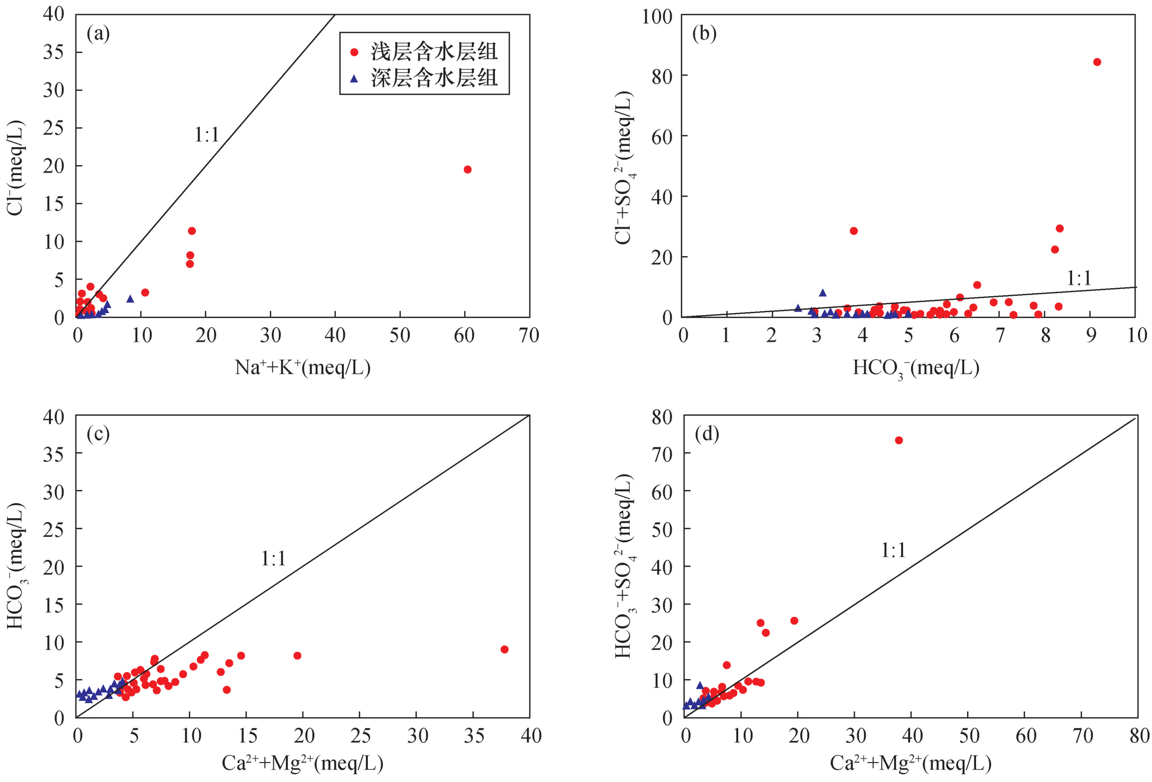


图 4　研究区地下水样品主要离子比值图

Fig. 4　Major ion ratios of groundwater samples.

Most of the groundwater samples exhibit $Cl^-/(Na^++K^+)<1$, indicating that silicate mineral dissolution (such as potassium feldspar and sodium feldspar) is the main source of excess Na^+ and K^+, except for rock salt in dissolved state. The $HCO_3^-/(Ca^{2+}+Mg^{2+})$ of the shallow aquifer groups samples is basically<1, showing excess Ca^{2+} and Mg^{2+}, indicating other sources of Ca^{2+} or Mg^{2+}, while the $(HCO_3^-+SO_4^{2-})/(Ca^{2+}+Mg^{2+})$ of the shallow aquifer groups is distributed above and below the 1∶1 line on both sides, suggesting that evaporite minerals (e.g. gypsum) may also be an important source of Ca^{2+} for the shallow aquifer groups. Both $HCO_3^-/(Ca^{2+}+Mg^{2+})$ and $(HCO_3^-+SO_4^{2-})/(Ca^{2+}+Mg^{2+})$ of the deep aquifer groups are located above the 1∶1 line, with excess HCO_3^- implying silicate dissolution dominance, or the presence of cation exchange, leading to lower Ca^{2+} content. The water samples of the shallow and deep aquifer groups are mainly distributed below the $(Cl^-+SO_4^{2-})/(HCO_3^-)=1∶1$ line, indicating that their chemical components are subject to great dissolution by carbonate rocks

(HCO_3^-)=1∶1 线下方，说明其化学组分受碳酸盐岩溶解作用较大。

3.4 水化学特征演化规律分析

与历史资料[19,26]对比，研究区浅层地下水水化学的分带性并没有改变，但各分带的水化学类型却存在不同程度的变化，各主要水化学类型的分布范围也发生了变化。总体上，研究区现状水化学类型更为复杂多样，且分布上虽然仍受地形与地质条件的控制，但越来越多地受到以开采为主的人类活动的影响。

太行山山前平原地下水化学类型总体演变不明显，但局部水化学类型有所变化。保定平原山前冲洪积平原的水化学类型变得复杂多样。变化较为明显的区域主要为：满城区北部漕河河道影响带，水化学类型由 HCO_3-Ca · Mg 型水，转变为 Cl · HCO_3-Ca · Na 型水；顺平县的界河冲洪积扇缘处、涿州市的拒马河冲洪积扇缘处，地下水 Na 含量占比逐渐超过 Mg 成为仅次于 Ca 的阳离子含量，水化学类型由 HCO_3-Ca · Mg 型水转变为 HCO_3-Ca · Na · Mg 型水。

由于中部及东部平原河道纵横，水文地质条件相对复杂，因此其浅层地下水化学特征受河道、河间带的密集分布和复杂沉积环境的影响而较为复杂，其演变也比较复杂。总体而言，中部平原地下水由以 Cl · HCO_3-Ca · Na、HCO_3 · Cl-Ca · Na 型水为主，并呈岛状、带状分布有 SO_4 · HCO_3-Na · Mg、SO_4 · HCO_3-Na、SO_4-Na · Mg、HCO_3-Na · Mg 等型水，转变为当前条件下以 Cl · HCO_3-Ca · Na、SO_4 · Cl-Na · Mg 型水为主，并杂布着 HCO_3 · Cl-Ca · Mg、Cl · SO_4-Na · Mg、HCO_3 · Cl · SO_4-Na、HCO_3 · SO_4-Na、HCO_3 · SO_4-Na · Mg、Cl · SO_4-Na · Mg 等型水。由于区域上水位的快速下降，浅层地下水受到垂向补给的路径增大，地下水在运移过程中受到水岩交换作用增强，间接地增大了阳离子交替吸附作用，从而更多的 Na 从岩土颗粒上迁移至地下水中，而 Ca、Mg 被交替吸附至岩土颗粒，造成地下水 Na 含量普遍增大，Na 型水逐渐成为平原中部的主要阳离子水化学类型。

3.5 人类活动对水化学特征的影响分析

浅层含水层 NO_3^- 含量平均值为 28.78mg/L，深层含水层 NO_3^- 含量平均值为 4.55mg/L，说明研究区浅层地下水局部地区硝酸盐污染严重。参照《地下水质量标准》(GB/T 14848—2017)三类水标准，浅层含水层组有 17 个采样点 NO_3^- 含量超过 20mg/L，有 5 个采样点 SO_4^{2-} 含量大于 250mg/L，说明这几个采样点受到人为活动的影响，造成硝酸盐和硫酸盐污染。研究区 SO_4^{2-}/Ca^{2+} 与 NO_3^-/Ca^{2+} 的比值可以揭示人类活动对地下水组分的影响程度。一般而言，SO_4^{2-}/Ca^{2+} 与 NO_3^-/Ca^{2+} 的比值大于 1 时，意味着工矿活动对地下水的影响较大，比值小于 1 则受到农业活动和居民生活污水的干扰较大。

图 5 显示，深层含水层组的比值都大于 1，只有保定定州市叮咛店镇二郎庙村北 240m 水井小于 1，说明深层含水层组基本上都受到工矿活动的影响，未受到农业活动和居民生活污水的影响。浅层含水层组，有 27 个水样的 SO_4^{2-}/Ca^{2+} 与 NO_3^-/Ca^{2+} 比值大于 1，有 20 个水样的 SO_4^{2-}/Ca^{2+} 与 NO_3^-/Ca^{2+} 比值小于 1，说明浅层含水层组部分受到工矿活动的影响，部分受到农业活动和居民生活污水的影响。浅层含水层数据绘制的工矿活动影响、农业活动和居民生活污水影响分区显示，沿定州市、清苑县、徐水县、涿州市以北基本都属于农业和居民活动影响区，以南基本为工况活动影响区，说明此线以南的工矿活动较为强烈，以北则农业活动较为强烈。

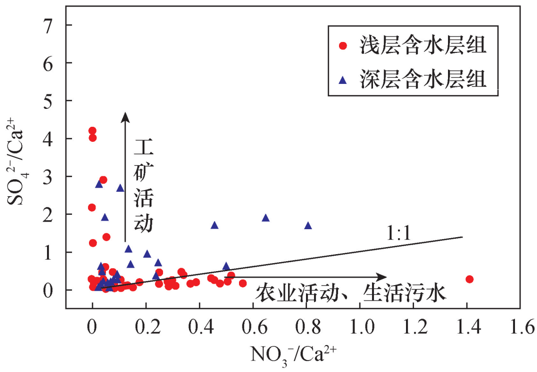


图 5 地下水样 SO_4^{2-}/Ca^{2+} 与 NO_3^-/Ca^{2+} 的比值关系图

Fig. 5 Relationship between SO_4^{2-}/Ca^{2+} and NO_3^-/Ca^{2+} in groundwater samples.

The SO_4^{2-}/Ca^{2+} to NO_3^-/Ca^{2+} ratios of the deep aquifer groups were all greater than 1, except for the 240m water well in the north of Erlangmiao Village, Dingzhou City, Hebei Province, which was less than 1. This indicates that the deep aquifer groups are basically affected by industrial and mining activities, but not by agricultural activities and residential sewage. In the shallow aquifer groups, the SO_4^{2-}/Ca^{2+} to NO_3^-/Ca^{2+} ratio of 27 water samples is greater than 1, and the SO_4^{2-}/Ca^{2+} to NO_3^-/Ca^{2+} ratio of 20 water samples is less than 1, which means that the shallow aquifer groups are partly influenced by industrial and mining activities, and partly influenced by agricultural activities and domestic sewage of residents

4　结论

调查结果显示,浅层含水层组受到气象和人为因素影响较大,浅层和深层含水层组 pH 值(7.35~8.92)差异不大,偏碱性;浅层含水层组由于农业活动等影响,造成局部地区的硝酸盐和硫酸盐污染。水岩相互作用分析显示,硅酸盐矿物风化是研究区主要的矿物来源,硅酸盐矿物溶解、阳离子交换为主要水化学作用。现状水化学类型分析显示,沿地下水径流方向,水化学类型现状由山前的 HCO_3-Ca · Mg(Ca)型,经 HCO_3-Mg · Ca、HCO_3-Mg · Ca · Na、HCO_3-Na · Mg · Ca 向 HCO_3 · Cl-Na · Ca、HCO_3 · Cl · SO_4-Na 至平原中部冲湖积平原的 Cl(SO_4)-Na 转变。水化学演变分析显示中部平原地下水由以 Cl · HCO_3-Ca · Na、HCO_3 · Cl-Ca · Na 型水为主,转变为当前条件下以 Cl · HCO_3-Ca · Na、SO_4 · Cl-Na · Mg 型水为主。

本文利用水化学方法研究了大清河流域平原区地下水化学特征及演化规律,厘清了大清河流域平原的水化学特征以及水化学类型演变规律,初步分析了演变趋势造成的原因,特别是指明地下水化学演变越来越受到人类活动的影响,但没有对该区未来的地下水水化学演变进行预测,后续将在水化学未来的演变预测上进行相关的研究。

Chemical Characteristics and Evolutionary Patterns of Groundwater in the Daqing River Plain Area of Haihe Basin

MENG Ruifang[1,2], *YANG Huifeng*[1,2*], *BAI Hua*[1,2], *XU Buyun*[1]

(1. Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang 050061, China;
2. National Field Scientific Observation and Research Station on Groundwater and Ground Subsidence in the Plain Area of Cangzhou, Shijiazhuang 050061, China)

HIGHLIGHTS

(1) The TDS of the shallow aquifer groups varies greatly, while the TDS of the deep aquifer groups has a small variation. The shallow aquifer groups are more influenced by meteorological and anthropogenic factors.

(2) Weathering dissolution of silicate minerals and cation exchange are the main mineral sources and water chemistry.

(3) The chemical characteristics of shallow groundwater are generally influenced by the topography and hydrogeological conditions and are regularly distributed from the piedmont plain to the central plain.

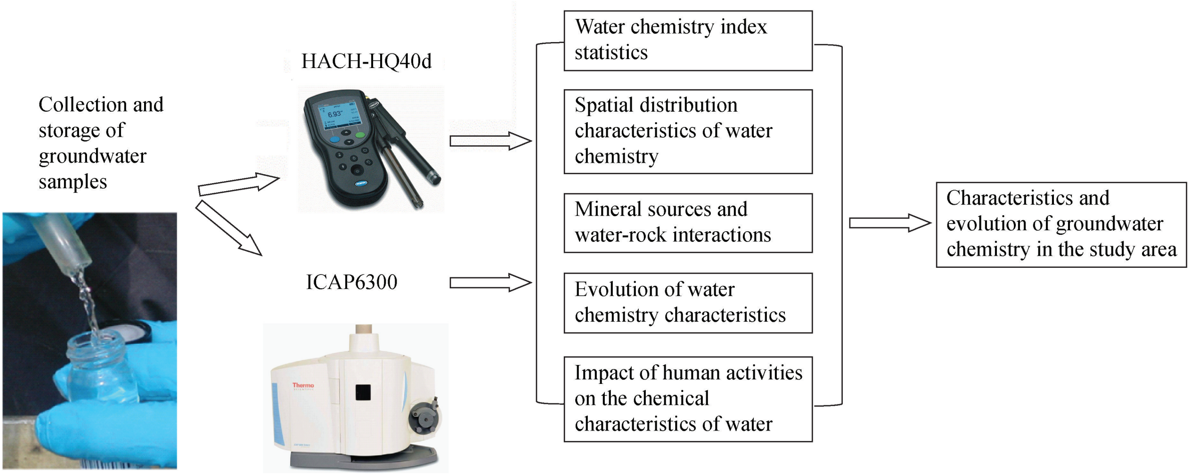
(4) The current water chemistry types are complex and diverse and are increasingly influenced by human activities such as mining.

ABSTRACT

BACKGROUND: Groundwater is closely related to surface water. Groundwater over-extraction has triggered a series of negative ecological effects in the Daqing River basin. The evolution of groundwater chemical characteristics is influenced by both natural and anthropogenic factors. The analysis of groundwater chemical characteristics can indicate the meteorological-hydrological and water-rock interaction during groundwater runoff, thus reflecting the groundwater circulation path, groundwater system characteristics and evolution laws, etc. It also helps to monitor groundwater dynamics and prevent the occurrence of groundwater pollution.

OBJECTIVES: To clarify the chemical characteristics and evolution of groundwater in the plain area of the Daqing River basin, which will be important for the rational development and utilization of water resources in the basin.

METHODS: 47 water samples from the shallow aquifer groups and 32 water samples from the deep aquifer groups were collected to analyze the main anions (Cl^-, SO_4^{2-}, NO_3^-) and cations (K^+, Na^+, Ca^{2+}, Mg^{2+}). The water



chemistry characteristics and evolution laws were studied by using the water chemistry type, Gibbs model and ion ratio relationship. *On-site* portable water quality analyzer (HACH-HQ40d) was used to test pH (accuracy 0.01), total dissolved solids (TDS, accuracy 0.01) and other parameters, and groundwater samples were collected after the indicators were stabilized. All samples were sent to the laboratory at low temperature and stored in a refrigerator at 4℃, and groundwater alkalinity was determined by titration on the same day. Seven days later, the samples were sent to the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences for testing of major anions (Cl^-, SO_4^{2-}, NO_3^-) and major cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) using inductively coupled plasma-optical emission spectrometry (iCAP6300). The anion and cation charge balance error was less than 5%, and the anion and cation test accuracy was 0.01mg/L.

RESULTS: The test results showed that the largest deviation was in the water sample from Hanbao Village, Liu Lizhuang Town, Anxin County, Baoding City, Hebei Province, which was from the shallow aquifer groups, and the maximum TDS reached 6015.00mg/L. The TDS of the shallow aquifer groups ranged from 254.10 to 6015.00 mg/L, with an average of 664.14mg/L, a large coefficient of variation and a large variation in TDS, indicating that the shallow aquifer groups were affected by meteorological and human factors. The TDS of the deep aquifer groups ranged from 197.10 to 691.40mg/L, with an average of 278.58mg/L, and the coefficient of variation was small, indicating that the groundwater of the deep aquifer groups was less affected by meteorological and human activities than that of the shallow aquifer groups. A small portion of the sampling points of the shallow aquifer groups in the area were brackish water and salt water. The TDS of the deep aquifer groups was generally less than 1000mg/L, which was suitable for use as a mining layer. The pH values of the shallow and deep aquifer groupss in the study area were not very different (7.35-8.92) and were alkaline. The NO_3^- maximum value of 298.40mg/L and SO_4^{2-} maximum value of 3091.00mg/L in the shallow aquifer groups, but the average value was not significant, indicating that the shallow aquifer groups have caused nitrate and sulfate pollution in local areas due to agricultural activities and other effects.

In the shallow layer of the study area, except for the difference in hydraulic conditions in the northern piedmont plain where flaky or spotty HCO_3-Cl-SO_4 and HCO_3-Cl type water occurred, the anions in most of the piedmont plain were mainly HCO_3 type, and the cations were mainly Ca and Ca-Mg and Mg-Ca. During the discharge of groundwater along the piedmont plain to the mouth of the alluvial fan, the cations changed from Ca-Mg type to Na type in order through Ca-Mg-Na, Na -Ca-Mg, Na-Mg-Ca, Na-Ca to Na type, and anions from HCO_3 type to SO_4 and Cl type via HCO_3-SO_4, HCO_3-SO_4-Cl, HCO_3-Cl-SO_4, SO_4-Cl. The deep groundwater cations were relatively more complex, and the zonation was more obvious: from the piedmont plain to the bottom of the alluvial fan, the cations transition from Ca, Ca-Mg, Mg-Ca, Na-Mg-Ca (Mg-Ca-Na) type to Na-Ca and

Na type water.

The shallow aquifer groups were basically located in the area of water-rock interaction, and individual points showed some influence of evaporation concentration. The deep aquifer groups were subjected to water-rock interaction and less affected by evaporation and atmospheric precipitation. The analysis results showed that the milligram equivalent concentration ratio of ($Ca^{2+}+Mg^{2+}$) + ($HCO_3^-+SO_4^{2-}$) to $Na^++K^+-Cl^-$ was close to -1, indicating a more significant cation exchange effect. The groundwater samples in this study area were mostly distributed near the end elements of silicate minerals, indicating that weathering of silicate minerals (such as feldspar) was the main hydrogeochemical control factor in the study area, which was consistent with the lithological characteristics of aquifers in the groundwater of the Daqing River basin plain, and the test results also showed that HCO_3^- was the dominant ion in both shallow and deep aquifer groups.

The SI values of calcite in the shallow aquifer groups in this study area ranged from −0.46 to 1.35, dolomite SI values from −0.88 to 3.02, gypsum SI values from −3.1 to −0.68, and rock salt SI values from −8.53 to −4.75, indicating that calcite and dolomite were partially saturated and partially unsaturated, and both gypsum and rock salt were unsaturated. $Cl^-/(Na^++K^+)$ could determine whether the groundwater was influenced by the dissolution of silicate rock. Most of the groundwater samples in this study area exhibited $Cl^-/(Na^++K^+)<1$, indicating that, in addition to rock salt in dissolved state, silicate mineral dissolution (e.g., potassium feldspar and sodium feldspar) was the main source of excess Na^+ and K^+. The Na^+ content may also originate from cation exchange, and the high Cl^-, the higher concentration may be the input of foreign contamination. The $HCO_3^-/(Ca^{2+}+Mg^{2+})$ of the samples from the shallow aquifer groups was basically less than 1, showing excess Ca^{2+} and Mg^{2+}, suggesting other sources of Ca^{2+} or Mg^{2+}, while the $(HCO_3^-+SO_4^{2-})/(Ca^{2+}+Mg^{2+})$ of the shallow aquifer groups was distributed above and below the 1∶1 line on both sides, suggesting that evaporite minerals (e.g. gypsum) may also be an important source of Ca^{2+} for the shallow aquifer groups, as evidenced by the unsaturated state of gypsum in groundwater, in addition to the increase in SO_4^{2-} due to human activities. Both $HCO_3^-/(Ca^{2+}+Mg^{2+})$ and $(HCO_3^-+SO_4^{2-})/(Ca^{2+}+Mg^{2+})$ of the deep aquifer groups lay above the 1∶1 line, and the excess HCO_3^- implied silicate dissolution dominance, or the presence of cation exchange, leading to a lower Ca^{2+} content. $(Cl^-+SO_4^{2-})/(HCO_3^-)$ could indicate the dissolution status of evaporites and carbonates, and water samples from shallow and deep aquifer groups were mainly distributed in the $(Cl^-+SO_4^{2-})/(HCO_3^-)=1∶1$ line below, which indicated that its chemical components were more dissolved by carbonate rocks.

In the influence zone of the Caohe River in the northern part of Mancheng District, the water chemistry changed from HCO_3-Ca-Mg water to Cl-HCO_3-Ca-Na water; at the alluvial fan margin of Jiehe River in Shunping County and at the alluvial fan margin of Rejected Horse River in Zhuozhou City, the proportion of Na content in groundwater gradually exceeded that of Mg as the cation content second only to Ca, and the water chemistry changed from HCO_3-Ca-Mg water to HCO_3-Ca-Na-Mg type water. The groundwater in the central plain changed from Cl-HCO_3-Ca-Na and HCO_3-Cl-Ca-Na type water with island and strip distribution of SO_4-HCO_3-Na-Mg, SO_4-HCO_3-Na, SO_4-Na-Mg and HCO_3-Na-Mg type water to Cl-HCO_3-Ca-Na, SO_4-Cl-Na-Mg type water dominated and mingled with HCO_3-Cl-Ca-Mg, Cl-SO_4-Na-Mg, HCO_3-Cl-SO_4-Na, HCO_3-SO_4-Na, HCO_3-SO_4-Na, HCO_3-SO_4-Na-Mg, and Cl-SO_4-Na-Mg type water.

The average NO_3^- content of the shallow aquifer was 28.78mg/L, and the average NO_3^- content of the deep aquifer was 4.55mg/L, indicating that nitrate pollution was serious in the shallow groundwater local area of the study area. Referring to the groundwater quality standard (GB/T 14848—2017) for Class Ⅲ water, there were 17 sampling points in the shallow aquifer groups with NO_3^- content over 20mg/L and 5 sampling points in the shallow aquifer groups with SO_4^{2-} greater than 250g/L, indicating that these sampling sites were affected by anthropogenic activities, resulting in nitrate and sulfate pollution. A ratio of SO_4^{2-}/Ca^{2+} to NO_3^-/Ca^{2+} greater than 1 indicated that

industrial and mining activities had a greater impact on groundwater, and a ratio less than 1 was more disturbed by agricultural activities and residential sewage. The results showed that the ratio of the deep aquifer groups was greater than 1, and only the 240m well in the north of Erlangmiao Village, Dingzhou City, Baoding City, Hebei Province, was less than 1. This indicated that the deep aquifer groups were basically affected by industrial and mining activities, but not by agricultural activities and residential sewage. In the shallow aquifer groups, there were 27 water samples with $SO_4^{2-}-Ca^{2+}$ to NO_3-Ca^{2+} ratio greater than 1, and 20 water samples with $SO_4^{2-}-Ca^{2+}$ to $NO_3^{-}-Ca^{2+}$ ratio less than 1, indicating that the shallow aquifer groups were partly influenced by industrial and mining activities, and partly influenced by agricultural activities and domestic sewage of residents.

CONCLUSIONS: The characteristics and evolution of groundwater chemistry in the plain area of the Daqing River basin was investigated by using the water chemistry method, clarifying the characteristics of the water chemistry and the evolution of water chemistry types in the plain area of the Daqing River Basin. Reasons for the evolution trend were also investigated, indicating that the evolution of groundwater chemistry is increasingly influenced by human activities. Relevant research will be conducted on the prediction of the future evolution of water chemistry.

KEY WORDS: plain area of Daqing River Basin; full analysis of groundwater water chemistry; water chemistry type; water chemistry evolution; human activity

参考文献

[1] 何宝南,何江涛,孙继朝,等.区域地下水污染综合评价研究现状与建议[J].地学前缘,2022,29(3):51-63.
He B N,He J T,Sun J C,et al. Comprehensive evaluation of regional groundwater pollution: Research status and suggestions[J]. Earth Science Frontiers,2022,29(3):51-63.

[2] 陈典,张照荷,赵微,等.北京市再生水灌区地下水中典型全氟化合物的分布现状及生态风险[J].岩矿测试,2022,41(3):499-510.
Chen D, Zhang Z H, Zhao W, et al. The occurrence, distribution and risk assessment of typical perfluorinated compounds in groundwater from a reclaimed wastewater irrigation area in Bejing[J]. Rock and Mineral Analysis, 2022,41(3):499-510.

[3] 胡宗义,何冰洋,李毅.中国流域水污染协同治理研究[J].中国软科学,2022(5):66-75.
Hu Z Y,He B Y,Li Y,et al. Research on collaborative governance of water pollution in river basin[J]. China Soft Science,2022(5):66-57.

[4] Said I, Merz C, Salman E R, et al. Identification of hydrochemical processes using multivariate statistics in a complex aquifer system of Sohag region, Egypt[J]. Environmental Earth Sciences,2020,79(8):1-14.

[5] Ahmed A,Clark I. Groundwater flow and geochemical evolution in the central Flinders Ranges,South Australia[J]. Science of the Total Environment,2016,572(1):837-851.

[6] Han D M,Liang X,Jin M G,et al. Hydrogeochemical indicators of groundwater flow systems in the Yangwu River Alluvial Fan,Xinzhou Basin,Shanxi,China[J]. Environmental Management,2009,44(2):243-255.

[7] Chen J,Qian H,Gao Y Y,et al. Insights into hydrological and hydrochemical processes in response to water replenishment for lakes in arid regions[J]. Journal of Hydrology,2020,581,124386.

[8] Xiao Y,Shao J L,Cui Y L,et al. Groundwater circulation and hydrogeochemical evolution in Nomhon of Qaidam Basin, northwest China[J]. Journal of Earth System Science,2017,126(2):1-16.

[9] Jla B,Ywa B,Cza B,et al. Hydrogeochemical processes controlling the mobilization and enrichment of fluoride in groundwater of the North China Plain[J]. Science of the Total Environment,2020,730:1-11.

[10] 刘君,陈宗宇,王莹,等.大规模开采条件下我国北方区域地下水水化学变化特征[J].地球与环境,2017,45(4):408-414.
Liu J, Chen Z Y, Wang Y, et al. Evaluation of hydrochemical characteristics of regional groundwater systems in northern China under the conditions of large-scale exploitation[J]. Earth and Environment,2017,45(4):408-414.

[11] 赵奕博,尹钊,史常青,等.大清河流域河岸植被带污染物净化能力研究[J].水土保持学报,2022,36(5):1-6.
Zhao Y B, Yin Z, Shi C Q, et al. Study on pollutant purification capacity of riparian vegetation zonein daqing river basin[J]. Journal of Soiland Water Conservation,2022,36(5):1-6.

[12] 杨忠俭,董思远. BIM 技术在京杭运河大清河航道工程中的应用[J]. 山东交通科技,2022(2):151-153.
Yang Z J, Dong S Y. Application of BIM technology in the Daqing River waterway project of the Beijing—Hangzhou Canal [J]. Shandong Communications Technology,2022(2):151-153.

[13] 姜鲁光,杨成,封志明,等. 面向多目标情景的大清河流域水资源利用权衡[J]. 资源科学,2021,43(8):1649-1661.
Jiang L G, Yang C, Feng Z M, et al. Multi-scenario trade-off on water resources utilization in Daqing River Basin [J]. Resources Science,2021,43(8):1649-1661.

[14] 王钰升. 大清河流域平原区地下水人工补给方式研究[D]. 长春:吉林大学,2021.
Wang Y S. Study of groundwater artificial recharge modes in plain area of Daqing River Basin[D]. Changchun: Jilin University,2021.

[15] 赵婧彤. 地下水人工补给过程中的促渗技术研究——以大清河流域典型区为例[D]. 长春: 吉林大学,2021.
Zhao J T. Study on infiltration promotion techniques during artificial recharge of groundwater——A case study of Daqing River Basin [D]. Changchun: Jilin University,2021.

[16] 庄玉峰. 大清河中下游地下水水源评价区水量安全性评价[J]. 水利规划与设计,2017(5):24-25,83.
Zhuang Y F. Water safety assessment of groundwater source assessment area in the middle and lower reaches of Daqing River [J]. Water Resources Planning and Design,2017(5):24-25,83.

[17] 董冬,边静. 趋势面分析法在地下水动态预测中的应用[J]. 吉林地质,2020,39(2):96-99.
Dong D, Bian J. Application of trend surface analysis method in groundwater dynamic prediction [J]. Jilin Geology,2020,39(2):96-99.

[18] 刘旭东,张瑞,万宝. 基于 Piper-PCA-MLP 神经网络的矿井涌水水源识别方法研究[J]. 中国煤炭地质,2022,34(7):50-55.
Liu X D, Zhang R, Wan B. Study on mine water inrush source discrimination method based on Piper - PCA - MLP neural network[J]. Coal Geology of China,2022,34(7):50-55.

[19] Ma B, Jin M G, Liang X, et al. Groundwater mixing and mineralization processes in a mountain - oasis - desert basin, northwest China: Hydrogeochemistry and environmental tracer indicators[J]. Hydrogelogy Journal,2018,26:233-250.

[20] 陈毅. 白洋淀流域平原区地下水-孔隙水的水化学特征和水文地球化学过程[D]. 北京:中国地质大学(北京),2018.
Chen Y. Pore - water and groundwater hydrochemical characteristics and hydrogeochemical processes in Baiyangdian Lake Basin[D]. Beijing: China University of Geosciences (Beijing),2018.

[21] 秦怡,唐小惠,李艳龙,等. 枣庄市南部地下水水化学特征及其主要控制因素[J]. 安全与环境工程,2022,29(6):132-138,155.
Qin Y, Tang X H, Li Y L, et al. Hydrochemical characteristics and main controlling factor of the ground water in southern Zaozhuang [J]. Safety and Environmental Engineering, 2022, 29 (6): 132 - 138, 155.

[22] 李锴雯. 河北省自然地理环境对植物的影响[J]. 现代农村科技,2016(6):73.
Li K W. Influence of natural geographical environment on plants in Hebei Province[J]. Modern Rural Science and Technology,2016(6):73.

[23] 侯思琰,徐鹤,刘德文,等. 大清河流域主要河流与湿地生态水量计算与保障分析[J]. 吉林水利,2021(8):1-4.
Hou S Y, Xu H, Liu D W, et al. Calculation and guarantee analysis of ecological water volume of main rivers and wetlands in Daqing River Basin[J]. Jilin Water Conservancy,2021(8):1-4.

[24] 任宇,曹文庚,潘登,等. 2010—2020 年黄河下游河南典型灌区浅层地下水中砷和氟的演化特征及变化机制[J]. 岩矿测试,2021,40(6):846-859.
Ren Y, Cao W G, Pan D, et al. Evolution characteristics and change mechanism of arsenic and fluorine in shallow groundwater from a typical irrigation area in the lower reaches of the Yellow River (Henan) in 2010—2020 [J]. Rock and Mineral Analysis,2021,40(6):846-859.

[25] 李谨丞,曹文庚,潘登,等. 黄河冲积扇平原浅层地下水中氮循环对砷迁移富集的影响[J]. 岩矿测试,2022,41(1):120-132.
Li J C, Cao W G, Pan D, et al. Influences of nitrogen cycle on arsenic enrichment in shallow groundwater from the Yellow River Alluvial Fan Plain [J]. Rock and Mineral Analysis,2022,41(1):120-132.

[26] 曹文庚,杨会峰,高媛媛,等. 南水北调中线受水区保定平原地下水质量演变预测研究[J]. 水利学报,2020,51(8):12.
Cao W G, Yang H G, Gao Y Y, et al. Prediction of groundwater quality evolution in the Baoding Plain of the SNWDP benefited regions [J]. Journal of Hydraulic Engineering,2020,51(8):12.