

WINDLY WATER

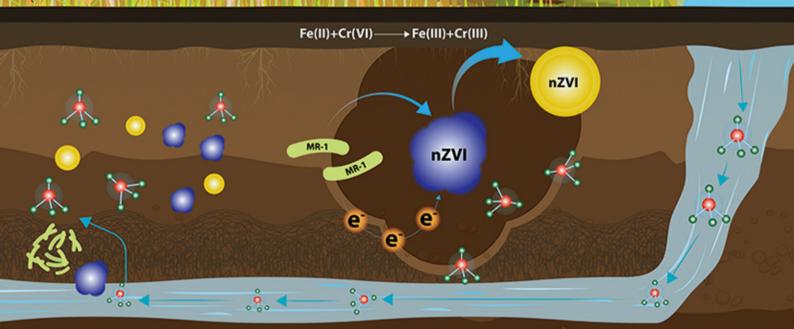
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ENVIRONMENTAL SCIENCE

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电活性微生物激活生物质炭/零价铁协同钝化Cr(VI)及机制

廖聪坚,赵晓蕾,刘凯,钟松雄,李芳柏,方利平,叶挺进,石虎砚



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# 永定河上游地表水-地下水水化学特征及其成因分析

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摘要: 永定河上游流域是冀西北重要的水源涵养区和生态屏障区,受气候变化和高强度人类活动影响,径流减少和水环境恶 化问题日益突出. 深入研究自然和人类活动共同影响下的地表水-地下水水化学特征及其成因,可为区域水资源可持续利用提 供科学参考. 本研究利用( $\delta^2$ H和  $\delta^{18}$ O)氢氧同位素关系明确地表水和地下水来源,并在此基础上结合数理统计和水文地球化 学方法,分析水化学特征及其成因.结果表明,地表水和地下水主要来源于降水.受自然因素及人类活动的共同影响,洋河和 桑干河流域水化学类型差异显著. 整体上,地表水离子浓度表现为:桑干河 > 洋河. 桑干河流域地表水主要阳离子为 Na<sup>+</sup>,主 要阴离子为 Cl-和 SO;-,且水化学类型多样;洋河流域地表水主要阴阳离子分别为 HCO;和 Ca<sup>2+</sup>,水化学类型分布相对集 中. 影响地表水水化学的自然因素主要为矿物溶解和蒸发,但人类活动却体现出流域差异,其中桑干河为支流的工业废水排 放,而洋河流域为农业生产和城市. 然而,由工业废水排放和酸雨输入导致的地表水 Cl<sup>-</sup>和 SO<sub>4</sub>-浓度持续增加,是地表水资源 可持续利用的限制因素. 因此,未来桑干河流域地表水资源利用要综合考虑总盐分和水化学组成的影响,而洋河流域主要考 虑总盐分的影响. 因地制宜地进行地表水资源利用,是永定河上游水资源可持续利用和恢复地下水位行之有效的措施.

关键词:半干旱区; 氢氧稳定同位素; 洋河; 桑干河; 水文地球化学过程

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# Hydrochemical Characteristics and Factors of Surface Water and Groundwater in the Upper Yongding River Basin

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Abstract: The Yongding River basin is an important water conservation and ecological barrier area in the Northwest of Hebei Province. Reduced runoff and deterioration of the water environment in this area have become increasingly prominent under the effects of climate change and intensive human activities. Clarifying the chemical characteristics and factors of surface water and groundwater in the upper Yongding River basin can provide data and support for the sustainable use of water resources. Stable isotopes of hydrogen and oxygen  $(\delta^2 H \text{ and } \delta^{18} O)$  were used to study the sources of surface water and groundwater. Mathematical statistics and hydrogeochemical methods were then used to analyze the regional hydrogeochemical processes and factors of surface water and groundwater. The results showed that precipitation was the main source of surface water and groundwater. Under the effects of natural factors and human activities, the Yang River and Sanggan River basins exhibited significant differences in surface water chemistry. The sub-basins were ranked by ion concentration as follows: Sanggan River > Yang River. The main cation and anions of the Sanggan River basin were Na<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2</sup>, while in the Yang River basin, Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> were the most common. The water chemistry of the Sanggan River exhibited greater variation than that of the Yang River. Surface water chemistry were mainly controlled by mineral dissolution and evaporation, but human activities were reflected in different sub-basins. Surface water in the Sanggan River basin was affected by industrial wastewater discharge, while that of the Yang River basin was affected by agricultural production and cities. However, the continuous increase of Cl<sup>-</sup> and SO<sub>4</sub><sup>-</sup> concentrations, caused by industrial wastewater discharge and acid rain, was the limiting factor for sustainable use of surface water resources. In future, surface water in Sanggan River basin should be used with consideration to the effects of both total salinity and chemical composition of the water, while in Yang River, a focus should be placed on total salinity. The use of surface water resources in accordance with local conditions is an effective measure for the sustainable use of water resources and the restoration of groundwater levels in this region.

Key words: semi-arid area; stable isotopes of hydrogen and oxygen; Yanghe River; Sanggan River; hydrogeochemical process

干旱和半干旱地区地表水资源短缺是限制区域 社会经济发展的关键因素,地下水往往是工农业生

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产的主要水源<sup>[1]</sup>.人类活动对水资源的需求量远超出可利用量是水资源短缺的主要驱动因子,而气候变化更加剧了水资源短缺的态势<sup>[2,3]</sup>.受水资源短缺和高强度人类开发的影响,区域水文地球化学过程也发生了巨大变化.

永定河上游为农牧交错带,经济欠发达,贫困人 口相对较多,水资源需求大,供需矛盾突出.此外,上 游流域不仅是重要的水源地,更是遏制沙尘和涵养水 源的重要生态屏障及京津冀协同发展的生态大动脉. 过去几十年,受气候暖干化、土地利用剧烈变化及工 农业用水需求不断增加的影响,流域供需水矛盾突出 且水循环过程变得更加复杂,出现了水域面积明显缩 减、地下水位下降、径流量锐减乃至部分河道完全断 流的现象,且出现了水质恶化的现象[4~7].除少数监 测站点水生态状况为较清洁外,轻度污染和中度污染 站点占据了永定河流域的大部分[8],永定河河北段水 体总磷现状负荷已超过允许负荷[9],上游支流清水河 流域氨氮、总磷虽基本符合Ⅲ类水质标准,但水体中 总氮含量超标严重[10]. 此外,永定河不同支流的主要 污染物以及来源也存在较大的差异[11,12]. 虽然随着 国家水污染治理政策的实施和对点源污染的管理,洋 河和桑干河流域水质均有极显著改善,但部分河段仍 存在不同程度的污染[5].

综上,以往的研究主要集中在永定河地表水污染物种类、污染状况以及来源方面,然而针对自然和人为因素耦合作用下的地表水和地下水水化学特征及其影响因素的研究却相对缺乏.而在其它地区已经有学者通过地统计学的方法,研究自然和人为因素影响下的地下水的水化学特征及其形成机制,并人为农业灌溉和干旱是地下水盐化的关键驱动因素<sup>[13]</sup>.而过去,纵然有部分关于永定河地下水水文

地球化学过程的报道,也主要集中在永定河下游北京段的平原区<sup>[14]</sup>. 永定河上游肩负着上游经济发展和向下游持续供水的双重重任,明确上游地表水和地下水的来源、水化学类型及其影响因素,不仅可以为深入认识自然和人为耦合作用对地表水水化学特征的影响提供一些理论支持,同时也可以为区域水资源可持续利用提供科学参考. 因此,本文以永定河上游,桑干河和洋河两个支流地表水和地下水为研究对象,利用氢氧同位素关系明确地表水和地下水主要来源,并在此基础上结合数理统计和水文地球化学方法,分析水化学特征及其成因.

#### 1 材料与方法

#### 1.1 研究区概况

永定河流域是海河七大水系之一,河流全长 747 km, 发源于内蒙古高原南缘和山西高原的北部, 流经山西、内蒙、河北、北京、天津五省市(112°~ 117°45′E, 39°~41°20′N). 流域东邻潮白河、北运 河系,西临黄河流域,南为大清河系,北为内陆河.其 上游流域横跨燕山山脉、内蒙古高原和华北平原,以 山区为主(占80%),高程变化较大,总体上地势自 西北山区向东南倾斜,主要包括桑干河和洋河两大 支流. 洋河发源于内蒙古和山西省, 主要流经河北张 家口境内,总长度为 262 km,流域面积约15 078 km<sup>2</sup>: 桑干河主源发源于山西省宁武县,流经山西和 河北两省,长度为 241 km,流域面积约为16 748.7 km<sup>2[15,16]</sup>. 桑干河和洋河于河北省张家口怀来县朱 官屯汇合后称永定河,在官厅水库纳妫水河,经官厅 水库流入官厅山峡于三家店进入平原. 本研究区位 于三家店以上的山区,面积为45 254 km²,其分布范 围如图 1 所示,其中河流汇流区土地利用主要为草

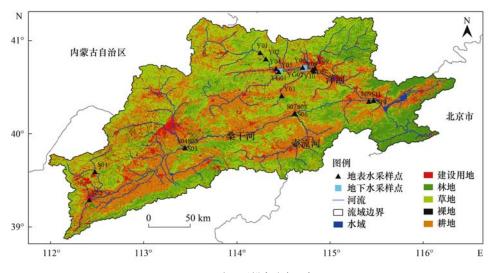


图 1 研究区采样点分布示意 Fig. 1 Location of water samples in the study area

地和林地,河谷地区主要为耕地和建设用地.

流域多年平均降水量不足 450 mm, 80% 径流量分布在雨季<sup>[4]</sup>,年平均蒸发量为1 182 mm<sup>[17]</sup>.地质资料显示,永定河大部分被第四系冲洪积层所覆盖,其上游土壤多为褐土和碳酸盐褐土,中游多为火山岩及碳酸岩的褐黄色的亚黏土,下游以盐潮土为主<sup>[18]</sup>.研究区北侧为内蒙古背斜,以风化剥蚀为主,第四系堆积厚度小,地貌为低缓的丘陵和波状高原;南侧为燕山沉降带,构造变动强烈,表现为沿盆地边缘断裂周边山区不断上升,遭受侵蚀切割,盆地相对沉降,接受堆积,形成了现代山间盆地的地貌景观.

#### 1.2 样品采集和分析

分别于 2016 年 9 月和 2019 年 9 月在永定河两个主要支流——桑干河和洋河进行了地表水和地下水取样,共取得 21 个地表水(河水)和 2 个浅层地下水水样.两个地下水采样点地下水埋深分别为 15 m和 23 m. 采用便携式参数仪现场测定 pH(pH/ORP/DO METER D-75, HORIBAR Scientific,日本)和电导率(EC, COND METER ES-71, HORIBAR Scientific,日本).地下水采样前先抽水 3 min 左右,然后用 100 mL 的塑料瓶采集水样装满并密封带回实验室,放于 4℃冰箱保存.

室内分析均在中国科学院农业水资源重点实验室,在采样一周之内完成. 水样  $K^+$ 、 $Ca^{2+}$ 、 $Na^+$ 、 $Mg^{2+}$ 、 $Cl^-$ 、 $SO_4^{2-}$  和  $NO_3^-$  采用离子色谱(ICS-600, Dionex,美国)分析,  $HCO_3^-$  和  $CO_3^{2-}$  采用双指示剂滴定法测定,所有水样进行阴阳离子平衡验证,保证可信的误差范围在  $\pm 5\%$  以内.  $\delta^2 H$  和  $\delta^{18}O$  采用液态

水稳定性同位素分析仪 (L2120-i Isotopic  $H_2O$ ; Picarro 美国) 进行测定,利用 VSMOW 标准, $\delta^2H$  和  $\delta^{18}O$  的分析精度分别为  $\pm 0.5$ ‰和  $\pm 0.2$ ‰.

#### 1.3 数据分析方法

水蒸发过程中<sup>2</sup>H 的动力分馏系数远大于<sup>18</sup>O,产生氘盈余. 氘盈余基于全球大气降水线(GMWL)进行计算[式(1)],当 d-excess < 10%e时代表水体存在二次蒸发<sup>[19]</sup>.

$$d\text{-excess} = \delta^{18}O - 8 \times \delta^2H \tag{1}$$

钠吸附比(SAR)常用于灌溉水质评价,确定钠引起的危害,其计算公式如下:

SAR = 
$$c(\text{Na}^+)/[c(\text{Ca}^{2+}) + c(\text{Mg}^{2+})]^{1/2}$$
 (2)

#### 2 结果与分析

#### 2.1 野外参数

地表水和地下水野外参数差异显著(表 1).整体上,地表水和地下水呈碱性,平均值分别为 8. 42和 8. 35;地表水 pH 变化幅度和标准差大于地下水.地表水和地下水 EC 平均值和变化幅度大于地下水,其中,EC 平均值分别为1 153  $\mu$ S·cm<sup>-1</sup>和671 $\mu$ S·cm<sup>-1</sup>,变化范围分别为 393~3 180  $\mu$ S·cm<sup>-1</sup>和458~885 $\mu$ S·cm<sup>-1</sup>.地表水 DO 平均值小于地下水,其中地表水和地下水 DO 值分别为 2. 46 mg·L<sup>-1</sup>和7. 44 mg·L<sup>-1</sup>;但地表水 DO 值变化范围大于地下水.地表水 ORP 平均值(96 mV)略大于地下水(82 mV),而地表水 ORP 的变化范围和标准差均大于地下水.地表水和地下水平均温度分别为 20. 59℃和23. 44℃.

表 1 地表水和地下水野外参数、稳定同位素 ( $\delta^2$ H 和  $\delta^{18}$ O) 和氘盈余 (d-excess) 统计特征

Table 1 Statistical characteristics of field parameters, stable isotopes and deuterium excess in surface water and groundwater

水体类型	项目	рН	EC/ μS·cm <sup>-1</sup>	DO/mg·L <sup>-1</sup>	ORP/mV	T/°C	$\delta^2 H/\%$	$\delta^{18} O/\% o$	d-excess/%o
	最小值	6. 80	393	0. 17	20	16. 80	-110.0	- 14. 6	-0.9
地表水	最大值	9. 94	3 180	12. 10	175	27. 80	-53.9	-7.2	13. 7
(n = 21)	平均值	8.42	1 153	2. 46	96	20. 59	-66.7	-9.1	6. 2
	标准差	0.84	840	4. 02	38	2. 68	12.8	1.8	3.8
	最小值	8. 29	458	7. 28	71	17. 95	-68.9	-9.0	0. 5
地下水	最大值	8.40	885	7. 60	93	28. 93	-63.4	-8.0	3. 3
(n=2)	平均值	8.35	671	7. 44	82	23.44	-66.2	-8.5	1.9
	标准差	0.08	302	0. 23	16	7. 76	3.9	0.7	1.9

#### 2.2 地表水-地下水氢氧同位素关系

 $\delta^2$ H 和  $\delta^{18}$ O 稳定同位素是水分子的主要组成部分且受大气过程影响,是水分来源和运动过程的理想示踪剂 $[^{20]}$ . 永定河上游地表水和地下水 $\delta^2$ H 和  $\delta^{18}$ O 稳定同位素均值接近,但标准差和变化幅度差异明显(表 1). 其中,地表水  $\delta^2$ H 和  $\delta^{18}$ O 稳定同位素平均值分别为 -66.7‰和 -9.1‰,与之对应的地下水  $\delta^2$ H 和  $\delta^{18}$ O 稳定同位素平均值分别

为 - 66. 2‰和 - 8. 5‰. 但地表水  $\delta^2$ H 和  $\delta^{18}$ O 稳定同位素的标准差和变化幅度均大于地下水, 地表水  $\delta^2$ H 和  $\delta^{18}$ O 分布 范围分别为 - 110. 0‰ ~ -53. 9‰和 - 14. 6‰ ~ -7. 2‰, 而地下水  $\delta^2$ H 和  $\delta^{18}$ O 的分布范围则分别为 - 68. 9‰ ~ -63. 4‰和 -9. 0‰ ~ -8. 0‰. 此外, 地表水和地下水氘盈余的平均值均小于 10‰, 说明二次蒸发作用影响区域地表水和地下水. 地表水氘盈余结果远大于地

下水, 地表水和地下水氘盈余平均值分别为 6.2‰ 和 1.9‰.

统计特征仅代表整体状况,为更好地表征地表水和地下水  $\delta^2$ H 和  $\delta^{18}$ O 稳定同位素关系,分析了所有采样点的分布特征(图 2). 所有地表水和地下水均位于全球大气降水线[19]下方,说明降水是地表水和地下水的主要补给来源. 地表水蒸发线为:  $\delta^2$ H = 6. 781 1  $\delta^{18}$ O - 4. 919 5 ( $R^2$  = 0. 941 1),斜率为6. 781 1,略小于全球大气降水线斜率 8,说明区域地表水受蒸发作用的影响. 然而,虽然地表水和地下水  $\delta^2$ H 和  $\delta^{18}$ O 稳定同位素的分布范围接近,但地表水偏离降水线程度大于地下水.

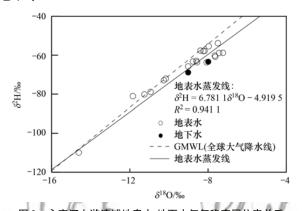


图 2 永定河上游流域地表水-地下水氢氧稳定同位素关系 Fig. 2 Relationship between  $\delta^2$ H and  $\delta^{18}$ O isotopes of surface water and groundwater in the upstream of the Yongding River

#### 2.3 地表水-地下水水化学组成

地表水和地下水流在运动过程中与周围环境相互作用,导致其水化学组成变化 $^{[21]}$ . 表 2 为地表水和地下水主要离子和总溶解性固体(TDS)统计特征. 地表水 TDS 变化范围和标准差均大于地下水,其中,地表水和地下水 TDS 平均值分别为 770 mg·L $^{-1}$ 和 445 mg·L $^{-1}$ ,变化范围分别为 239~2 386 mg·L $^{-1}$ 和 323~568 mg·L $^{-1}$ . 与 TDS 类似,地表水Na $^+$ 、K $^+$ 、Cl $^-$ 和 SO $^2$ -质量浓度平均值和标准差均大于地下水;NO $^-$ 。的变化特征则与 TDS 相反,其平均值和标准差均小于地下水;地表水 Mg $^{2+}$ 、Ca $^{2+}$ 和 HCO $^-$ 。质量浓度平均值大于地下水,而 Mg $^{2+}$ 标准差小于地下水.

地表水和地下水主要阴离子均为 HCO<sub>3</sub><sup>-</sup>,地表水主要阳离子为 Na<sup>+</sup>,地下水主要阳离子为 Ca<sup>2+</sup>和 Na<sup>+</sup>(表2). Piper 图显示(图3),地表水分布在图的右上侧,表明地表水 Cl<sup>-</sup>和 SO<sub>4</sub><sup>-</sup>的百分比大于地下水. 地表水主要水化学类型为 Na·Ca-HCO<sub>3</sub>、Ca-HCO<sub>3</sub>、Na·Mg-Cl·SO<sub>4</sub>和 Mg·Ca·Na-HCO<sub>3</sub>; 地下水主要化学类型为 Mg·Ca·Na-HCO<sub>3</sub>和 Ca·Mg-HCO<sub>3</sub>. 此外,两条支流的水化学类型也呈现出较大的差异. 整体来看,洋河水化学类型集中分布于图 3 的 a 区域,而桑干河水分布在除 a 外的其它区域,且两条河流的水化学类型从上游到下游体现出较大的空间差异性,具体原因将在下面结合离子分布特征进行讨论.

表 2 地表水和地下水主要离子和 TDS 统计特征/ $mg \cdot L^{-1}$ 

Table 2 Statistical characteristics of major ions and TDS in surface water and groundwater/mg*	Table 2	tatistical characteristics of major ions and TDS in surface water and groundwater/mg·L	- 1
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水体类型	项目	Na +	K +	$\mathrm{Mg}^{2}$ +	Ca <sup>2+</sup>	Cl -	SO <sub>4</sub> -	NO <sub>3</sub>	HCO <sub>3</sub>	$TDS^{1)}$
	最小值	25	2	15	30	21	60	0	120	239
地表水	最大值	553	39	86	170	508	819	35	664	2 386
(n = 21)	平均值	139	12	39	72	121	209	10	332	770
	标准差	165	11	19	42	147	218	9	153	644
	最小值	32	3	23	54	16	38	9	256	323
地下水	最大值	66	6	53	76	52	91	28	403	568
(n=2)	平均值	49	5	38	65	34	64	19	329	445
	标准差	24	2	21	15	26	37	14	104	173

1) TDS 为 Na  $^+$  、K  $^+$  、Mg  $^2$  + 、Ca  $^2$  + 、Cl  $^-$  、SO  $_4^2$  、NO  $_3^-$  与(1/2) HCO  $_3^-$  的和

#### 3 讨论

#### 3.1 地表水和地下水主控因素识别

Gibbs 图是区分地表水和地下水水化学影响因素的重要手段,一般可分为:降水控制型、风化控制型和蒸发/结晶控制型等<sup>[22]</sup>. 永定河上游地表水和地下水点大部分分布在岩石风化控制区,部分分布在蒸发控制区,说明地表水和地下水水化学的主控制因素为矿物溶解和蒸发,其中矿物溶解占主导地位(图4). 阳离子变化幅度较大,部分采样点落在

 $Na^+/(Na^+ + Ca^{2^+})$  比值大于 0. 5 的范围内, 阳离子以  $Na^+$ 为主, 部分采样点分布在  $Na^+/(Na^+ + Ca^{2^+})$  比值小于 0. 5 的范围内[图 4(a)]; 大部分阴离子分布在  $Cl^-/(Cl^- + HCO_3^-)$  比值小于 0. 5 的范围内, 阴离子以  $HCO_3^-$  为主[图 4(b)]. 阴阳离子之间比例的不一致性, 反映了阳离子交换吸附作用. 氯碱指数 CAI- I 和 CAI- I 为负值时[图 5(a)和 5(b)]可以说明阳离子交换作用的存在, 即含水层中 $Na^+$ 交换了地下水中  $Ca^{2^+}$  和  $Mg^{2^+}$ , 使得含水层中 $Na^+$ 进入水体, 水体中  $Na^+$ 比例增加. 反应过程

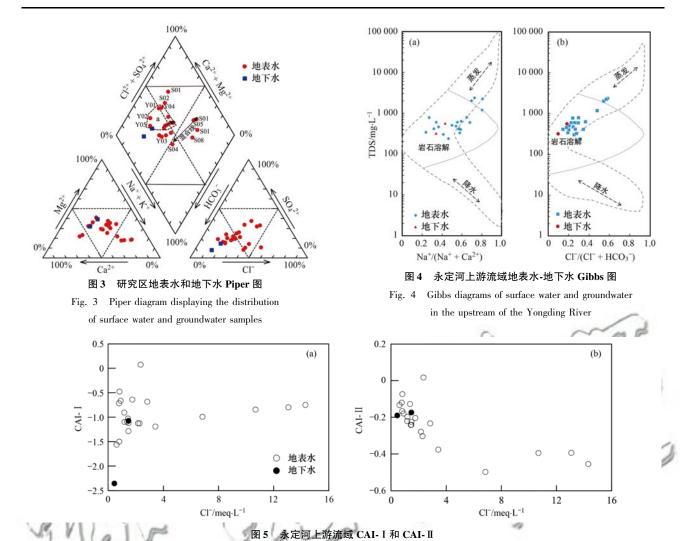


Fig. 5 CAI- I and CAI-II for surface water and groundwater in the upstream of the Yongding River

如下:

 $4\text{Na-X}_2 + \text{Ca}^{2+} + \text{Mg}^{2+} \longrightarrow 4\text{Na}^+ + \text{Ca-X}_2 + \text{Mg-X}_2$ 式中 X 为黏土矿物[23].

离子关系是认识水文地球化学过程的依据,图 6 为永定河上游地表水和地下水不同离子之间关 系. Cl-和 TDS 关系可以很好地指示蒸发作用,但 Cl<sup>-</sup>和 TDS 之间无明显的线性相关关系 [图 6(a)], 说明地表水和地下水除蒸发作用外,还受矿物溶解 的影响. 理论上,岩盐溶解会释放出等量 Na + 和 Cl -进入水体中,但大部分采样点 Na \* 浓度大于 Cl - 且 位于 Na+: Cl-的1:1线左上方[图 6(b)],大多数比 值在1~2.5之间[图6(c)],说明除岩盐溶解外,还 受含钠矿物溶解的影响.其中,含钠硅酸盐矿物溶解 会导致  $Na^+$ 和  $SO_4^{2-}$  以 2:1的比例释放进入水体,然 而 Na + 和 SO<sub>4</sub> - 之间的离子关系表明二者比例小于 2:1[图 6(d)],说明 SO<sub>4</sub><sup>2-</sup> 存在其它溶解来源,如石 膏  $CaSO_4 \cdot 2H_2O$ . 大部分采样点分布在  $\gamma(Ca)$  $\gamma(SO_4)$ 1:1线左上侧 [图 6(e)],说明研究区  $Ca^{2+}$ 不 止有石膏溶解还有碳酸盐矿物(方解石和白云石)

溶解. 大部分采样点位于  $Ca^{2+} + Mg^{2+}$ :  $HCO_3^-$  左上侧[图 6(f)],说明碳酸盐和方解石溶解作用是  $Ca^{2+}$ 和  $Mg^{2+}$ 主要来源. 除了方解石  $Calcite(CaCO_3)$ 溶解外[图 6(g)],当  $Ca^{2+}$ / $Mg^{2+}$ 等于 1 时,主要溶解矿物为白云石[ $CaMg(CO_3)_2$ ],而图 6(h)显示,地表水和地下水  $Ca^{2+}$ 部分分布在 1:1和 2:1线之间,表明了方解石溶解作用;部分采样点位于 2:1线的左上侧,说明了硅酸盐溶解作用;部分位于 1:1线下侧,说明主要受到方解石和石膏等贫镁矿物影响,或是阳离子交换作用导致钙减少[图 6(h)]. 同时,大部分采样点都位于  $Ca^{2+} + Mg^{2+}$ 和  $HCO_3^- + SO_4^2$ 为 1:1平衡线上方及附近,表明碳酸盐和硅酸盐矿物溶解作用的共同影响[图 6(i)].

3.2 不同支流上下游主控因素及其水化学特征差异为明晰地表水和地下水水化学空间分布特征及其主控因素的差异性,本研究从桑干河和洋河两个流域进行讨论. 然而由于地下水数量的限制,以下部分的讨论以地表水为主. 整体上来看,桑干河流域地表水各大离子均大于洋河流域(图7),且两流域地

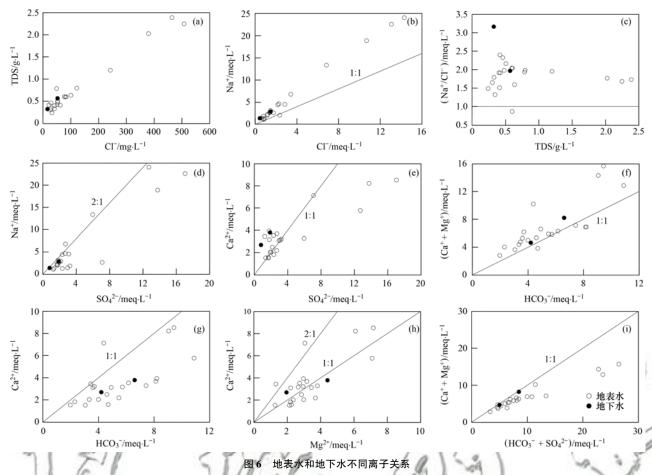
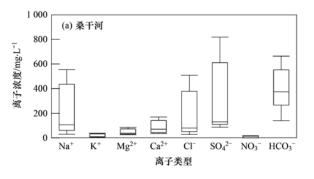


Fig. 6 Relationship between different ions in surface water and groundwater

表水水化学特征存在较大差异. 桑干河流域地表水主要阴离子为  $C1^-$ 和  $SO_4^{2^-}$ 、主要阳离子为  $Na^+$ [图 7 (a)]; 而洋河流域主要阴阳离子分别为  $HCO_3^-$  和  $Ca^{2^+}$ [图 7 (b)].

上游 S01 和 S02 分布在左上方,体现了较大的  $Ca^{2+}$ 和  $Mg^{2+}$ 百分比的特征(图 3).整体上来看 S03 ~ S06 段,八大离子之和较高,除 S04 以外均在2 000  $mg \cdot L^{-1}$ 以上,该段体现了支流污水对洋河的影响. S03 为污水河御河的采样点,其八大离子之和为 2 670  $mg \cdot L^{-1}$ [图 8(a)],水化学类型为 Na-SO<sub>4</sub>-Cl; S04 为桑干河与御河汇流前的采样点,其八大离子之和为1 042  $mg \cdot L^{-1}$ ,水化学类型为 Na-Ca-HCO<sub>3</sub>;

S05 为桑干河与御河汇流后的采样点,混合后的桑干河水八大离子之和为2 297 mg·L<sup>-1</sup>,水化学类型为 Na-SO<sub>4</sub>-Cl-HCO<sub>3</sub>,位于图 3 的混合线上.桑干河的污染在此段持续增加,直至册田水库上游 S06,八大离子之和仍然达到2 575 mg·L<sup>-1</sup>,水化学类型为 Na-Cl-SO<sub>4</sub>-HCO<sub>3</sub>.在壶流河入口(S08)八大离子之和仍然大于1 000 mg·L<sup>-1</sup>,其余采样点均小于1 000 mg·L<sup>-1</sup>[图 8(a)].除了受御河影响的河段外,其余桑干河采样点从河流上游到下游,地表水 TDS 变化不大,但主要阳离子却发生了很大变化,上游和下游主要阳离子分为 Ca<sup>2+</sup>和 Na<sup>+</sup>,体现了上游产流区矿物溶解特征和下游汇流区流速慢的高矿化度水特



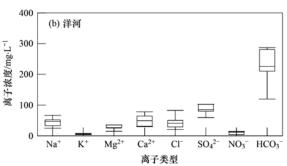


图 7 桑干河和洋河地表水主要离子统计特征

Fig. 7 Statistical characteristics map of main ions in surface water of the Sanggan River and Yanghe River

征,其主要水化学类型分别为 Ca-SO<sub>4</sub>-HCO<sub>3</sub> 和 Na-Mg-Ca-HCO<sub>3</sub>-SO<sub>4</sub>.

洋河流域从上游到下游,TDS 呈现先增加后减小,Na<sup>+</sup>和 Cl<sup>-</sup>的百分比有增加的变化趋势[图 8(b)],其中,上游水化学类型为 Ca-HCO<sub>3</sub>和 Ca-Mg-HCO<sub>3</sub>-SO<sub>4</sub>,中游为 Mg-Na-Ca-HCO<sub>3</sub>-SO<sub>4</sub>,下游为 Ca-Na-Mg-HCO<sub>3</sub>-SO<sub>4</sub>. 对洋河而言,Y03 支流和 Y01 支流的 Y01~Y05 河段,八大离子之和在 448~850 mg·L<sup>-1</sup>之间波动[图 8(b)],但水化学类型差异较大. Y03 水化学类型为 Na-Mg-Ca-HCO<sub>3</sub>,Y01~Y05 河段水化学类型由 Ca-Mg-HCO<sub>3</sub>-SO<sub>4</sub> 过渡为 Ca-HCO<sub>3</sub>和 Ca-Mg-HCO<sub>3</sub>(图 3).而 Y06~Y10 河段,虽然八大离子之和体现出了较大的差异在 299~785 mg·L<sup>-1</sup>之间波动,但主要离子却体现出了阳离子百分比变化不大,而阴离子中的 Cl<sup>-</sup>和 SO<sub>4</sub><sup>2-</sup>百分比增加的趋势(图 3 中的箭头所示).

两支流水化学特征的差异也体现了人类活 动的差异,20世纪80年代后,高覆盖草地向旱 地转化、城乡居民建设用地规模不断扩大[4],桑 干河流域承载着重要的煤炭等能源化工基地,如 大同和朔州等,虽然煤炭开采矿山已经关停,但 是大部分尾矿堆积[24];而洋河流域主要为农业 生产和城市. 研究认为该区域地表水质恶化的主 要原因与工业废水的排放和集约化的农业生产 活动有关,且有证据认为 Cl 和 SO<sub>4</sub> 的增加导致 地表水水质恶化,并且桑干河的 Cl-和 SO2-的含 量已经超过了国家饮用水质量标准(GB 5749-2006) 和灌溉水质量标准(GB 5084-2005) 中规 定的限值[6]. 自然条件下, 地表水的 Cl 和 SO4-与岩石风化有关,然而该过程却比较缓慢,且影 响有限;而工业废水中的 Cl-以及酸雨中包含的  $SO_4^{2-}$  是人为因素影响下,地表水中  $Cl^-$ 和  $SO_4^{2-}$ 增加的主要原因[25

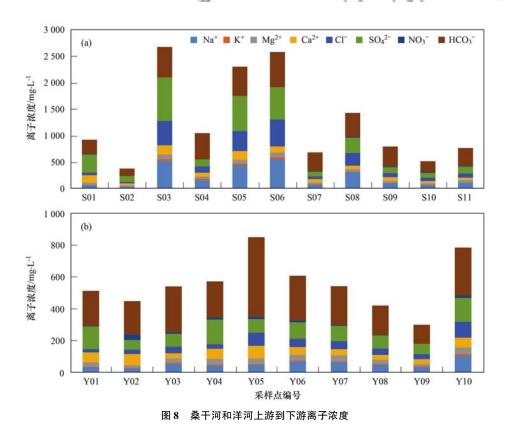
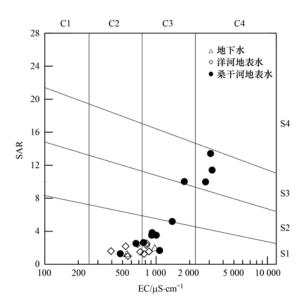


Fig. 8 Ion content from upstream to downstream of the Sanggan River and Yanghe River

区域农业发展主要依赖地表水和地下水. 本研究采用钠吸附比(SAR)和 EC 之间的关系对灌溉水进行分级,来评估钠离子毒害<sup>[28]</sup>. 图 9 为地表水和地下水灌溉水水质分类,整体来说,洋河流域地表水 EC 值和 SAR 均较小,是盐渍化风险较小的优质水源,在排水条件良好时、适合耐盐度较好的作物土壤灌溉利用,不会引起钠离子毒害效应. 洋河上游地表

水主要分布在 C2-S1 区域,下游地表水主要分布在 C3-S1,虽然从上游到下游地表水 EC 值增加,但是 Na<sup>+</sup>的风险没有明显地上升,均处于低风险范围内. 桑干河流域,地表水主要分布在 C3-S3 区和 C4-S3 区,盐分和钠离子毒害风险较高,在经过化学改良和 淋滤条件很好的土壤中,可直接灌溉利用. EC 值相 差不大的地下水与地表水相比, SAR 值较低,说明



C1、C2、C3 和 C4 区域分别对应低、中、高和很高的盐渍化风险; S1、S2、S3 和 S4 分别对应低、中、高和很高的钠离子毒害风险

#### 图 9 地表水和地下水灌溉水水质分类

Fig. 9 Irrigation waters classification of surface water and groundwater

总盐分含量接近的情况下,用地表水灌溉的钠离子 毒害风险大于地下水.

#### 4 结论

- (1) 永定河流域地表水和地下水主要来源于大气降水. 大部分地表水和地下水均为淡水, 其 TDS变化范围分别为 239~2 386 mg·L<sup>-1</sup>和 323~568 mg·L<sup>-1</sup>. 地表水和地下水主要阴离子均为  $HCO_3^-$ , 地表水主要阳离子为  $Na^+$ , 地下水主要阳离子为  $Ca^{2+}$ 和  $Na^+$ . 不同支流离子含量也体现出较大差异,整体上桑干河流域大于洋河流域,桑干河流域地表水主要阴离子为  $Cl^-$ 和  $SO_4^{2-}$ 、主要阳离子为  $Na^+$ ;而洋河流域主要阴阳离子分别为  $HCO_3^-$ 和  $Ca^{2+}$ .
- (2)地表水的水化学特征受自然因素和人为因素的共同影响,其中自然因素包括岩石风化,碳酸盐、硅酸盐和岩盐等矿物溶解以及离子交换作用.而人为因素如工业废水和酸雨等导致该区域地表水中Cl<sup>-</sup>和SO<sub>4</sub><sup>-</sup>持续增加.
- (3)洋河和桑干河两个支流,主要离子组成特征及其主要影响因素存在显著差异.桑干河流域上游 S01 和 S02 处受自然因素影响, S03 至 S06 段体现了污水排放的影响, S08 以下的河段受自然因素和污水的共同影响.而洋河流域,受主要受农业耕作和城市的影响,并未体现出工业污染的特征.
- (4)虽然地表水和地下水仍然是良好的灌溉水源,灌溉不存在盐分和钠离子毒害风险,但 Cl<sup>-</sup>和 SO<sub>4</sub><sup>2</sup> 的过高含量可能引起的离子毒害,需要引起足

够的重视. 同时,对桑干河河水的利用还要注意工业 废水排放的影响,从而实现流域地表水资源的可持 续利用.

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