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Distribution of groundwater arsenic and hydraulic gradient along the shallow groundwater flow-path in Hetao Plain, Northern China

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ABSTRACT

This paper investigates how spatial distributions of groundwater arsenic (As) concentration and speciation are related to and are dependent on regional hydraulic gradients in a shallow aquifer containing elevated groundwater As in the Hetao Plain of Northern China. Groundwater samples (n = 165) were collected along three representative transects in the western, central and eastern parts of the Hetao Plain, spanning a wide range of total As concentration (0.36–916.7 μg/l), arsenite concentration (0.2–719.4 μg/l) and hydraulic gradients (0.11–23.31‰). The hydrodynamic conditions of the aquifer generally fall into the following four categories from the north to the south: Piedmont and discharge areas with high hydraulic gradient, runoff areas with weak or strong hydraulic gradient, and areas influenced by recharge from the Yellow River. Along all three transects, high groundwater As usually corresponds to low hydraulic gradients except for the discharge areas. In the runoff area in central Hetao Plain and the recharge area in southern Hetao Plain, the concentration of arsenic is more than 10 μg/l when the hydraulic gradient is less than 0.8‰. An empirical relationship between groundwater As concentration and groundwater hydraulic gradient can be established for the runoff area. The systematic changes in As concentrations and speciation along the groundwater flow path in the shallow groundwater support the notion that low hydraulic gradient of the groundwater is important in promoting As enrichment in groundwater.

1. Introduction

Public concerns over arsenic(As) in groundwater have increased in recent years (e.g., Bangladesh; West Bengal, India; Vietnam; Taiwan; Agusa et al., 2006; Berg et al., 2001; Haquea and Johannesson, 2006; Nickson et al., 1998; Radloff et al., 2011; Smedley and Kinniburgh, 2002; van Geen et al., 2008; Welch et al., 2000). The Hetao Basin is a sediment-filled basin in Northern China, where high As groundwater was first reported in 1994 (Sun, 1994). Many studies have been done concerning geological, hydrological, geochemical, hydrogeological, hydrogeochemical, mineralogical and biogeochemical aspects of high As groundwater in the Hetao Plain (Deng et al., 2011; Guo et al., 2008a,b). Previous studies showed that As concentrations ranged between 1.1 and 969 μg/l in shallow groundwater, with a significant proportion (up to 90%) of the As occurring as As(III) (Tang et al., 1996). Li and Li (1994) and Tang et al. (1996) proposed that groundwater As occurred naturally under reducing conditions. However, Zhang et al. (2002) suggested that the As in groundwater of the Hetao Basin was released from higher elevations, where mining had been carried out for a long time, and was then transported from the mining district down gradient. High As groundwater generally (>50 μg/l) occurs in the shallow alluvial–lacustrine aquifers in reducing conditions and groundwater As is believed to originate from exchangeable As and Fe–Mn oxide-bound As in the aquifer sediments from the Hetao Basin (Guo et al., 2008a, b). However, to quantitatively understand the mechanisms that control As mobilization in groundwater systems, it is essential to determine its hydrogeological conditions in the aquifer system. van Geen et al. (2008) note that flushing history can serve as a hydrogeological control on the regional distribution of arsenic in shallow groundwater of the Bengal Basin. Deng et al. (2009a,b) and Guo et al. (2010) note that due to the gentle land surface in Hetao Plain of north China, groundwater flow conditions are generally sluggish, with a slow horizontal flow rate in comparison with the rate of vertical movement. However, the shallow groundwater flow system has locally been affected by irrigation channels and drainage channels in most of the study area (Deng et al. (2009a,b)). There are some relations between the concentration of arsenic and the hydraulic gradient along the shallow groundwater flow-path (Smedley et al., 2003). Moreover, previous researchers show clearly that low hydraulic gradient of the groundwater plays a great role in promoting arsenical enrichment (D. Kirk Nordstrom, 2003; Scott et al., 2010; Smedley et al., 2003). This work builds on previous studies that have sought to demonstrate the influence of hydraulic gradient on shallow groundwater arsenic

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heterogeneity in Northern China's Hetao Basin, but left open questions due to insufficient data coverage.

In this paper, three north-to-south transects of following the regional groundwater flow path in the Hetao Plain were used to examine the relationship between hydraulic gradient and arsenic enrichment in shallow groundwater (Fig. 1). Hydraulic gradient was calculated based on the groundwater level measurements. Groundwater samples were analyzed for arsenic concentrations and speciation. The linkage between groundwater flow and arsenic is discussed in order to utilize the hydraulic gradient to predict the distribution of high As groundwater.

2. Hydrogeological settings

The Hetao Basin is a Cenozoic rift basin, located in the western part of the Inner Mongolia Autonomous Region of China on the eastern fringe of the Wuranbuh Desert (Fig. 1). Kidney-shaped, it is bound by the Yellow River to the south and the Langshan Mountains to the north, with an area of about 10,000 km^2. The alluvial basin has a gentle southeastern slope with elevation between 1060 and 1007 m (Guo et al., 2008a,b). The Langshan Mountains are mainly composed of a metamorphic complex (slate, gneiss and marble), generally of Jurassic to Cretaceous age, which is folded and fractured (Li and Li, 1994). The basin is also fault-bound, with a sedimentary environment affected by both paleo-climatic and tectonic events over the past ~50 Ma, (i.e., Deng et al., 2011). In the Quaternary period, continuous subsidence has resulted in the accumulation of thick sedimentary sequences of fine grained lacustrine sediments during the Mid-Cenozoic era. The thickness of the sediment in the southeast of the basin ranges from 500 to 1500 m, and in the northwest of the basin from 7000 to 8000 m (Tang et al., 1996). The groundwater is recharged by the Yellow River, infiltration of precipitation and a lateral recharge from the Langshan Mountain in the north. Located in the piedmont depression of the northern Hetao Plain, a drainage channel (Fig. 1, thick purple line) is the most prominent drainage area where groundwater flows from the Piedmont area in the north and from the recharge area near the Yellow River in the south both discharge. This main drainage channel discharges water to the east close to Ulansuhai Nur in the eastern Hetao Plain, before it merges into the Yellow River (Guo et al., 2008a,b). The drainage channel is also the natural boundary between the two geomorphic units, the piedmont alluvial–proluvial plain in the north and the Yellow River alluvial lacustrine plain in the south.

In the piedmont alluvial–proluvial plain that is also an active recharge area, the shallow aquifer (<50 m) is mostly coarse sand and gravel. South of the main drainage channel (Fig. 1) is the groundwater runoff zone where the shallow aquifer (<50 m) is primarily composed of silt and fine sand. Usually, the area adjacent to the main drainage channel in the north is the "weak" runoff area, and the area near the Yellow River in south is the "strong" runoff area. The strong and weak runoff condition is a semi-quantitative description, and is considered "weak" when the hydraulic gradient is <0.8‰. There is a difference in clay particle content in the sediment from the "strong" and "weak" runoff areas, with higher clay particle content in the "weak" runoff area.

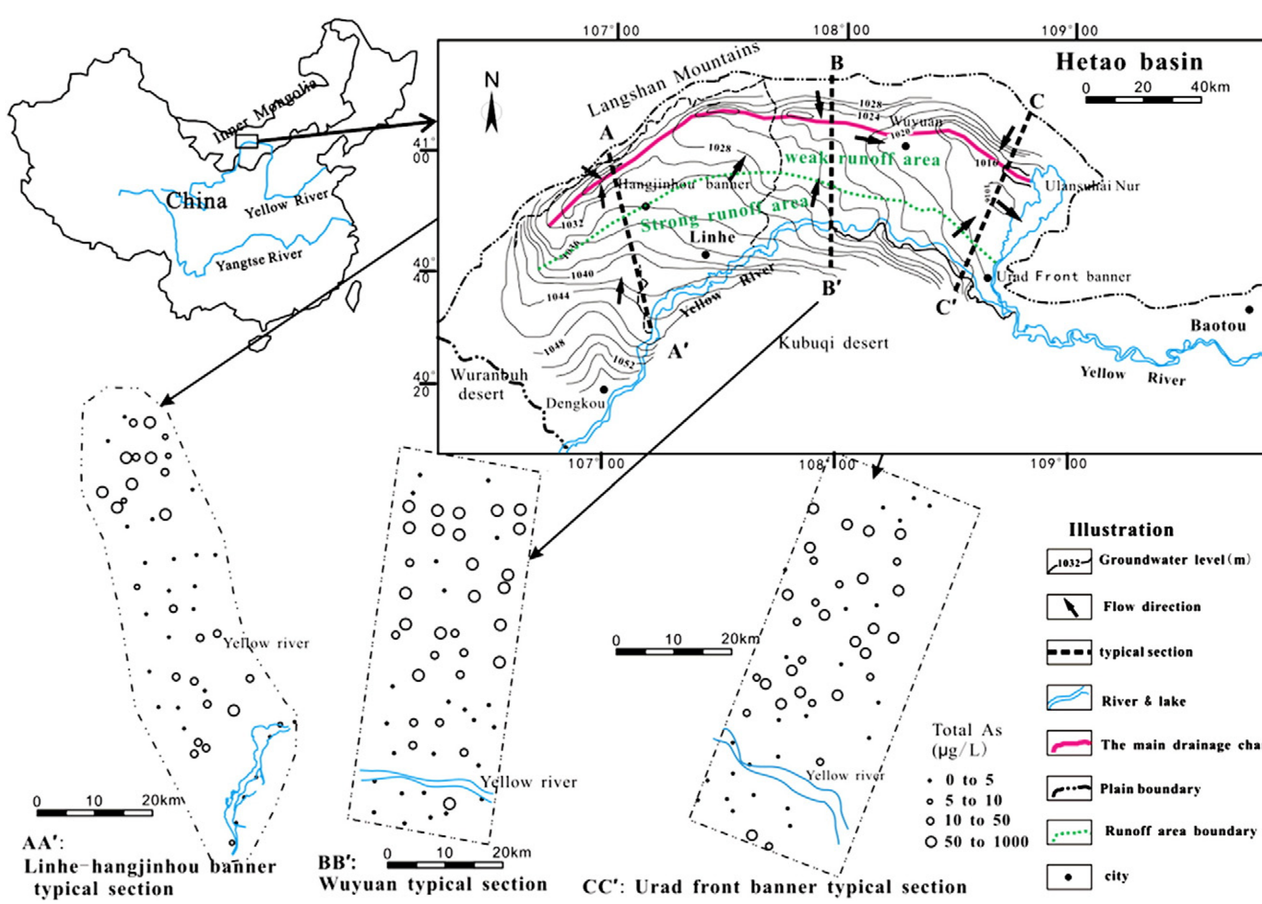

Fig. 1. Distribution of groundwater As along three transects representing the hydrogeological setting of the Hetao Plain.

Table 1
Concentration of total arsenic and arsenite along three north-to-south transects in Hetao Plain.

Sample ID	Longitude	Latitude	Well depth	Water level (m)	Total arsenic (μg/l)	As(III) (μg/l)	%As(III) (%)	Sample ID	Longitude	Latitude	Well depth (m)	Water level (m)	Total arsenic (μg/l)	As(III) (μg/l)	%As(III) (%)
HL01	107.089	41.098	50	1053.57	0.62	0.32	51.6	WY29	108.144	41.018	14	1024.762	82.82	78.92	95.3
HL02	107.048	41.063	30	1038.95	4.59	2.88	62.7	WY30	108.066	40.996	10	1025.963	30.47	29.66	97.3
HL03	107.000	41.051	50	1031.71	1.49	0.78	52.3	WY31	107.988	40.993	13	1027.156	171.4	144.4	84.2
HL04	106.996	41.027	40	1035.02	89.48	79.18	88.5	WY32	107.942	40.976	15	1027.841	0.45	0.27	60
HL05	107.091	41.013	36	1033.51	148.8	136.2	91.5	WY33	108.127	40.956	12	1026.405	0.38	0.33	86.8
HL06	106.951	41.011	37	1034.45	37.2	32.39	87.1	WY34	108.047	40.955	12	1026.807	0.71	0.57	80.3
HL07	107.091	40.999	15	1034.33	176.6	149.1	84.4	WY35	108.084	40.946	13	1026.923	0.96	0.7	72.9
HL08	107.018	40.996	18	1034.56	8.76	7.06	80.6	WY36	108.098	40.928	12	1026.479	4.27	4.12	96.5
HL09	106.937	40.975	17	1032.23	6.45	6.19	96	WY37	108.134	40.927	14	1026.601	1.13	0.68	60.2
HL10	107.025	40.969	18	1032.23	6.8	3.79	55.7	WY38	108.029	40.924	12	1027.449	39.04	29.58	75.8
HL11	106.989	40.961	20	1034.36	54.6	50.74	92.9	WY39	107.981	40.923	12	1028.508	10.64	0.41	3.9
HL12	106.941	40.958	25	1033.5	193.7	178	91.9	WY40	107.930	40.922	13	1028.906	8.72	0.96	11
HL13	107.018	40.941	18	1035.88	16.32	12.53	76.8	WY41	107.980	40.890	14	1028.628	27.99	26.68	95.3
HL14	106.951	40.921	30	1034.73	745.7	719.4	96.5	WY42	108.078	40.884	11	1027.844	37.9	27.74	73.2
HL15	106.949	40.920	30	1034.8	3.3	3.03	91.8	WY43	108.022	40.882	10	1028.228	3.18	3.15	99.1
HL16	107.075	40.919	13	1034.57	1.08	0.8	74.1	WY44	107.949	40.881	15	1028.9	1.16	0.9	77.6
HL17	106.893	40.904	17	1034.44	57.12	49.35	86.4	WY45	108.108	40.866	12	1027.999	1.17	0.86	73.5
HL18	106.942	40.898	23	1034.44	7.02	6.99	99.6	WY46	107.912	40.837	7	1020.5	1.35	1	74.1
HL19	107.088	40.884	20	1035.02	6.23	2.35	37.7	WY47	107.966	40.821	5	1018.6	1.06	0.43	40.6
HL20	106.925	40.883	18	1035.09	81.51	68.95	84.6	WY48	108.006	40.821	8	1019.7	2.4	1.93	80.4
HL21	107.026	40.876	27	1035.24	135.3	127.2	94	WY49	108.120	40.818	9	1020.05	1.07	0.67	62.6
HL22	106.952	40.860	20	1035.98	0.92	0.78	84.8	WY50	108.056	40.813	9.5	1021.1	51	35.94	70.5
HL23	107.126	40.823	18	1037.25	0.47	0.38	80.9	WY51	108.049	40.793	12	1020.4	1.75	1.03	58.9
HL24	107.088	40.822	28	1036.32	0.93	0.62	66.7	WY52	107.915	40.792	8	1021.6	3.19	2.13	66.8
HL25	107.045	40.815	43	1036.84	0.73	0.64	87.7	WY53	108.019	40.790	8	1021.8	1.76	0.65	36.9
HL26	106.989	40.807	28	1036.91	0.83	0.8	96.4	WY54	107.972	40.780	12	1025.1	0.83	0.5	60.2
HL27	107.088	40.775	26	1038.09	1.38	1.13	81.9	WQ01	108.778	41.173	50	1027.22	1.18	0.82	69.5
HL28	106.975	40.773	16	1037.41	5.24	5.23	99.8	WQ02	108.853	41.170	45	1025.76	3.39	0.76	22.4
HL29	107.037	40.768	17	1038.46	0.55	0.3	54.5	WQ03	108.874	41.153	21	1016.93	3.24	2.08	64.2
HL30	107.088	40.741	17	1039.56	0.47	0.28	59.6	WQ04	108.803	41.146	30	1015	1.13	0.79	69.9
HL31	107.046	40.740	14	1039.25	21.72	19.84	91.3	WQ05	108.694	41.146	30	1017.52	53.03	38.01	71.7
HL32	106.996	40.730	12	1037.75	2.12	1.82	85.8	WQ06	108.636	41.145	30	1017.4	506	411.2	81.3
HL33	107.135	40.707	12	1040.55	13.26	12.94	97.6	WQ07	108.733	41.143	7	1016.86	80.05	67.08	83.8
HL34	107.042	40.699	15	1041.14	3.94	3.67	93.1	WQ08	108.605	41.142	12	1017.3	163.4	119.2	72.9
HL35	107.100	40.695	20	1041	13.79	12.76	92.5	WQ09	108.604	41.124	12	1018.48	34.09	34.25	100.5
HL36	107.008	40.646	17	1041.61	0.5	0.32	64	WQ10	108.796	41.123	12	1018.88	169.6	142.9	84.3
HL37	107.200	40.64	14	1042.88	22.12	19.66	88.9	WQ11	108.536	41.122	12	1018.61	0.89	0.37	41.6
HL38	107.058	40.637	60	1044.32	27.25	25.71	94.3	WQ12	108.773	41.082	12	1019.49	29.62	25.9	87.4
HL39	107.093	40.633	16	1043.44	23.03	21.66	94.1	WQ13	108.528	41.081	13	1020.57	162.8	157	96.4
HL40	107.119	40.618	12	1042.27	8.47	8.46	99.9	WQ14	108.641	41.074	15	1019.8	30.58	24.04	78.6
HL41	107.121	40.598	13	1044.1	10.41	9.79	94	WQ15	108.692	41.071	80	1020.1	56.8	55	96.8
HL42	107.066	40.595	10	1043.8	0.7	0.48	68.6	WQ16	108.584	41.059	90	1020.13	45.48	39.44	86.7
HL43	107.028	40.594	14	1044.36	2.53	1.89	74.7	WQ17	108.531	41.037	90	1019.45	18.65	17.02	91.3
HL44	107.172	40.590	14	1043.65	56.02	45.79	81.7	WQ18	108.758	41.037	80	1020.28	108.7	83.86	77.1
HL45	107.294	40.582	11	1041.94	1.23	0.84	68.3	WQ19	108.589	41.034	20	1020.3	108.4	72.17	66.6
HL46	107.260	40.572	8	1042.04	6.27	5.27	84.1	WQ20	108.639	41.032	30	1020.62	1.89	1.16	61.4
HL47	107.081	40.564	12	1045.02	1.28	0.76	59.4	WQ21	108.706	41.024	12	1019.61	4.47	0.79	17.7
HL48	107.246	40.557	9	1045.01	4.58	2.76	60.3	WQ22	108.683	40.990	12	1019.4	309.3	208.5	67.4
HL49	107.105	40.543	16	1044.07	24.34	22.86	93.9	WQ23	108.486	40.983	12	1020.14	0.36	0.2	55.6
HL50	107.122	40.535	18	1044.21	11.49	9.65	84	WQ24	108.517	40.977	13	1020.38	32.92	30.56	92.8
HL51	107.097	40.526	12	1044.42	21.21	19.91	93.9	WQ25	108.637	40.977	14	1020.31	218.7	159.7	73
HL52	107.225	40.496	8	1046.1	1.36	0.98	72.1	WQ26	108.416	40.969	15	1020.12	39	34.44	88.3
HL53	107.203	40.466	4.5	1046.74	2.63	1.74	66.2	WQ27	108.721	40.967	15	1019.87	57.98	40.54	69.9
HL54	107.190	40.427	4.5	1048.4	2.08	1.27	61.1	WQ28	108.491	40.965	15	1019.39	89.02	70.13	78.8
HL55	107.182	40.395	12	1049.63	4.59	3.14	68.4	WQ29	108.430	40.956	20	1017.64	146.4	117.7	80.4
WY01	107.977	41.284	40	1026.53	1.84	0.58	31.5	WQ30	108.650	40.956	22	1016.62	60.35	54.35	90.1
WY02	108.108	41.279	60	1023.779	0.47	0.39	83	WQ31	108.595	40.952	22	1017.74	1.19	1.11	93.3
WY03	107.965	41.259	30	1017.322	4.28	2.75	64.3	WQ32	108.493	40.927	70	1016.52	50.12	46.41	92.6
WY04	108.173	41.239	30	1022.829	146.6	144.7	98.7	WQ33	108.376	40.920	11	1017.13	32.14	27.18	84.6
WY05	107.960	41.238	20	1025.653	165.2	104.2	63.1	WQ34	108.644	40.917	12	1016.64	36.61	30.81	84.2
WY06	108.126	41.237	18	1023.497	58.09	52.68	90.7	WQ35	108.450	40.917	22	1016.68	89.43	68.89	77
WY07	108.055	41.231	14	1024.864	129	87.67	68	WQ36	108.515	40.906	10	1018.91	49.64	45.32	91.3
WY08	108.015	41.231	15	1025.056	382.7	364.1	95.1	WQ37	108.569	40.903	11	1019.15	58.61	53.7	91.6
WY09	108.172	41.209	24	1023.475	103.8	98.12	94.5	WQ38	108.432	40.891	11	1022.75	2.16	1.46	67.6
WY10	107.960	41.207	24	1025.714	76.75	67.28	87.7	WQ39	108.489	40.887	11	1022.15	0.6	0.4	66.7
WY11	108.016	41.206	15	1024.275	74.35	69.72	93.8	WQ40	108.326	40.878	10	1023.95	7.24	6.55	90.5
WY12	108.057	41.200	22	1024.16	916.7	692.1	75.5	WQ41	108.649	40.872	15	1022.14	0.73	0.43	58.9
WY13	108.130	41.198	12	1023.045	4.5	2.91	64.7	WQ42	108.353	40.837	11	1023.29	5.13	3.45	67.3
WY14	108.084	41.157	12	1024.184	89.22	76.32	85.5	WQ43	108.414	40.835	20	1023.43	8.79	8.13	92.5
WY15	107.961	41.155	30	1024.344	10.18	8.26	81.1	WQ44	108.250	40.832	9	1024.45	2.43	2.26	93
WY16	108.016	41.155	30	1024.34	0.42	0.23	54.8	WQ45	108.307	40.832	18	1024.34	1.86	1.45	78
WY17	108.151	41.144	30	1023.579	193	141.1	73.1	WQ46	108.605	40.824	11	1021.35	0.66	0.37	56.1
WY18	108.147	41.126	20	1024.207	112.5	106.3	94.5	WQ47	108.492	40.809	15	1020.78	42.5	34.49	81.2

(continued on next page)

Table 1 (*continued*)

Sample ID	Longitude	Latitude	Well depth	Water level (m)	Total arsenic (μg/l)	As(III) (μg/l)	%As(III) (%)	Sample ID	Longitude	Latitude	Well depth (m)	Water level (m)	Total arsenic (μg/l)	As(III) (μg/l)	%As(III) (%)
WY19	108.030	41.115	10	1025.349	0.89	0.83	93.3	WQ48	108.223	40.808	7	1020.4	1.91	1.11	58.1
WY20	107.958	41.113	15	1025.527	54.42	48	88.2	WQ49	108.282	40.794	8	1020.8	2.26	1.84	81.4
WY21	108.085	41.111	15	1025.48	198.3	191.7	96.7	WQ50	108.338	40.789	8	1020	1.82	1.8	98.9
WY22	108.141	41.071	20	1024.255	79.79	63.59	79.7	WQ51	108.394	40.753	8	1015.4	3.31	1.64	49.5
WY23	107.963	41.067	10	1024.381	63.94	56.4	88.2	WQ52	101.118	40.727	8	1017.05	4.44	2.61	58.8
WY24	108.052	41.058	14	1024.843	21.49	15.83	73.7	WQ53	108.311	40.727	8	1018	53.42	34.65	64.9
WY25	108.028	41.055	17	1025.498	79.43	64.86	81.7	WQ54	108.390	40.727	12	1018.3	1.25	0.68	54.4
WY26	107.941	41.053	16	1026.083	44.79	40.51	90.4	WQ55	108.339	40.702	120	1019	22.05	20.45	92.7
WY27	108.073	41.029	15	1025.584	14.65	14.17	96.7	WQ56	108.339	40.702	120	1019.2	17.23	14.76	85.7
WY28	108.017	41.026	13	1026.651	46.51	44.57	95.8								

3. Sampling and analysis

3.1. Field sampling

Groundwater samples (n = 165, depths from 10 m to 50 m) were collected from the shallow aquifer which is composed of late Pleistocene and Holocene alluvial and lacustrine deposits. Of those, 140 wells are domestic water wells and the rest are the agricultural supply wells. The sampling campaign was undertaken during the period from September 9th to October 29th, 2009 along three north-to-south transects (Fig. 1, Table 1), all ending just south of the Yellow River but starting at the foot of Langshan Mountain. They are named after the towns close by: Hangjinhouqi (Fig. 1A–A′ n = 55; Table 1 HL01–H55), Wuyuan (Fig. 1B–B′ n = 54; Table 1 WY01–WY54), and Uradqianqi (Fig. 1C–C′ n = 56; Table 1 WQ01–WQ56). They generally follow the direction of groundwater flow (Fig. 1), and encompass two geomorphic units, namely the piedmont alluvial–proluvial plain and the Yellow River alluvial lacustrine plain.

3.2. Sampling and analysis for arsenic concentrations and speciation

The samples used for As speciation analysis were filtered through a 0.45 μm membrane filter and stored in new but pre-rinsed HDPE bottles (Nalgene) at a constant temperature of 4 °C. The filtered samples were then acidified to pH 1 by addition of ultra-pure HCl. All the samples were sent for laboratory analysis within 5 days. The As speciation was determined in the Laboratory of Hydrogeology and Environmental Geology Institute, Chinese Academy of Geological Sciences (CAGS), with high performance liquid chromatography (HPLC)–ICP-MS. An HPLC (1100 Series, Agilent) consisting of a system controller, a solvent delivery module, a column oven and a 6-port injection valve was used. A reversed-phase C18 column (Capcell, Pak, 250 mm × 4.6 mm, 5 μm particle size) was used for separation of As species. An ICP-MS (7500C, Agilent) was used as a detector, which was operated in the He mode for As determination in order to remove ArCl interference.

3.3. Calculation of hydraulic gradient

The groundwater depth was measured for each sampling well. High precision electronic leveling was performed to determine the height of each sampling site, so the elevation data is trustworthy (Table 1). The hydraulic gradient along the three north–south transects are calculated as follows (Devlin, 2003):

$$HG_1 = (h_1 - h_2)/L$$

where,

HG_1 is the hydraulic gradient designated as representing the location with high hydraulic head,

h_1 is the high hydraulic head at the well up gradient along the groundwater flow path,

h_2 is the low hydraulic head at the well down gradient along the groundwater flow path,

$(h_1–h_2)$ is the difference in head between the two neighboring wells along the groundwater flow path,

L is the vertical distance (north–south distance) of two neighboring wells along the groundwater flow path, calculated using latitudes.

Hydraulic gradient (*HG*) is dimensionless and is calculated here directly without interpolation.

4. Results

4.1. Arsenic and hydraulic gradient along the Hangjinhouqi transect

From south to north there are the main irrigation canal, the Yangjia River and the main drain channel crisscrossing each other (Fig. 1). The density of irrigation channels is high, at 0.48 km/km^2. The hydrodynamic conditions of groundwater are complicated, with greatly fluctuating hydraulic gradient of the groundwater.

In the Piedmont recharge area of alluvial–proluvial fan located in the front of Langshan Mountain, the groundwater level ranges from 1031.71 m to 1053 m, the median hydraulic gradient is 4.68‰, the highest in the transect. The concentration of the total As is the lowest with a median concentration of only 2.23 μg/l (Table 2).

For the discharge area (Fig. 2), the water level was the lowest of the entire transect, ranging from 1033.5 m to 1035 m. The hydraulic gradient ranges from 0.71‰ to 2.54‰. The total As concentration of the discharge area ranges from 37.2 μg/l to 176.6 μg/l with all samples exceeding the Type-III (> 10 μg/l) drinking water quality standard of China, and also the World Health Organization's guideline value for drinking water. The majority of arsenic is As^{3+} (Table 2).

For the runoff area that is part of the alluvial lacustrine plain of the Yellow River (Fig. 2), the terrain in the south is higher than that in the north. Here, the groundwater is recharged by the Yellow River, and also through infiltration of precipitation. The lateral groundwater flows from the south to the north, but the movement of groundwater is slow. Along the S–N groundwater flow path, the groundwater level decreases gradually from the south to the north (Fig. 2). Based on the hydraulic gradient, the runoff area can be divided into two areas: (1) The weak runoff area belongs to the alluvial plain of the Yellow River, and most of the area is located in proximity to the discharge area. The hydraulic gradient ranges from 0.003‰ to 1.3‰. The total As concentration of the discharge area ranges from 3.3 μg/l to 745.7 μg/l with 89% of samples exceeding the Type-III (> 10 μg/l) drinking water quality standard of China, and also the World Health Organization's guideline value for drinking water. The 97% of arsenic is As^{3+} (Table 2). (2) The strong runoff area is located closer to the recharge

Table 2
Hangjinhouqi transect based on 2009 data.

Classify	Sample size	Total As (μg/l)			As^{3+} (μg/l)			As^{5+} (μg/l)			Hydraulic gradient (‰)			Water level (m)		
		min	max	median.	min	max	median.	min	max	median.	min	max	median.	min	max	median.
Piedmont recharge area	3	0.62	4.69	1.49	0.32	2.88	0.78	0.3	1.71	0.71	3.79	5.56	3.79	1038.9	1053.5	1038.9
Discharge area	4	37.2	176.6	119.14	32.4	149.1	107.7	4.81	27.5	11.45	0.71	2.54	0.84	1033.5	1035	1034.2
Weak runoff area	11	3.3	745.7	54.6	3.03	719.4	49.35	0.03	26.3	3.88	0.003	1.3	0.42	1033.5	1035.8	1034.7
Strong runoff area	33	0.47	56.0	5.24	0.28	45.8	3.79	0.01	10.2	0.39	0.11	3.47	1.07	1036.0	1045.0	1041.6
Recharge area of Yellow River	4	1.39	4.59	2.35	0.98	3.14	1.50	0.38	1.45	0.85	0.19	0.39	0.34	1046.1	1049.6	1047.6

zone of the Yellow River. The hydraulic gradient ranges from 0.11‰ to 3.47‰. The total As concentration of the discharge area ranges from 0.47 μg/l to 56.0 μg/l with 16% samples with As concentrations exceeding > 10 μg/l (Table 2).

4.2. Arsenic and hydraulic gradient along the Wuyuan transect

Wuyuan transect lies to the west of Wuyuan County, with only the southern part extending into the Xixiaozhao town near the Urad Front Banner. Most of Wuyuan City is located on the alluvial–lacustrine plain of the Yellow River. With all of the farmland irrigated by water diverted from the Yellow River, the groundwater level is thus high. Soils suffer from serious salinization. Residents suffer from the bitter and salty waters in the past.

Along the Wuyuan transect from south to north, there are also the main irrigation canal, the main drainage channel, crisscrossing each other and the network of canals for irrigation. There are also a large and a small lake in the Taerhu town and Yindingtu in the middle section of the transect.

The Piedmont recharge area in the front of Langshan Mountain of the Wuyuan transect is smaller than that of the Hangjinhouqi transect. Along the N–S groundwater flow path, the groundwater level decreases from 1026.5 m to 1023.8 m (Fig. 3). The median hydraulic gradient is 3.42‰. This gradient is the highest along the transect, but

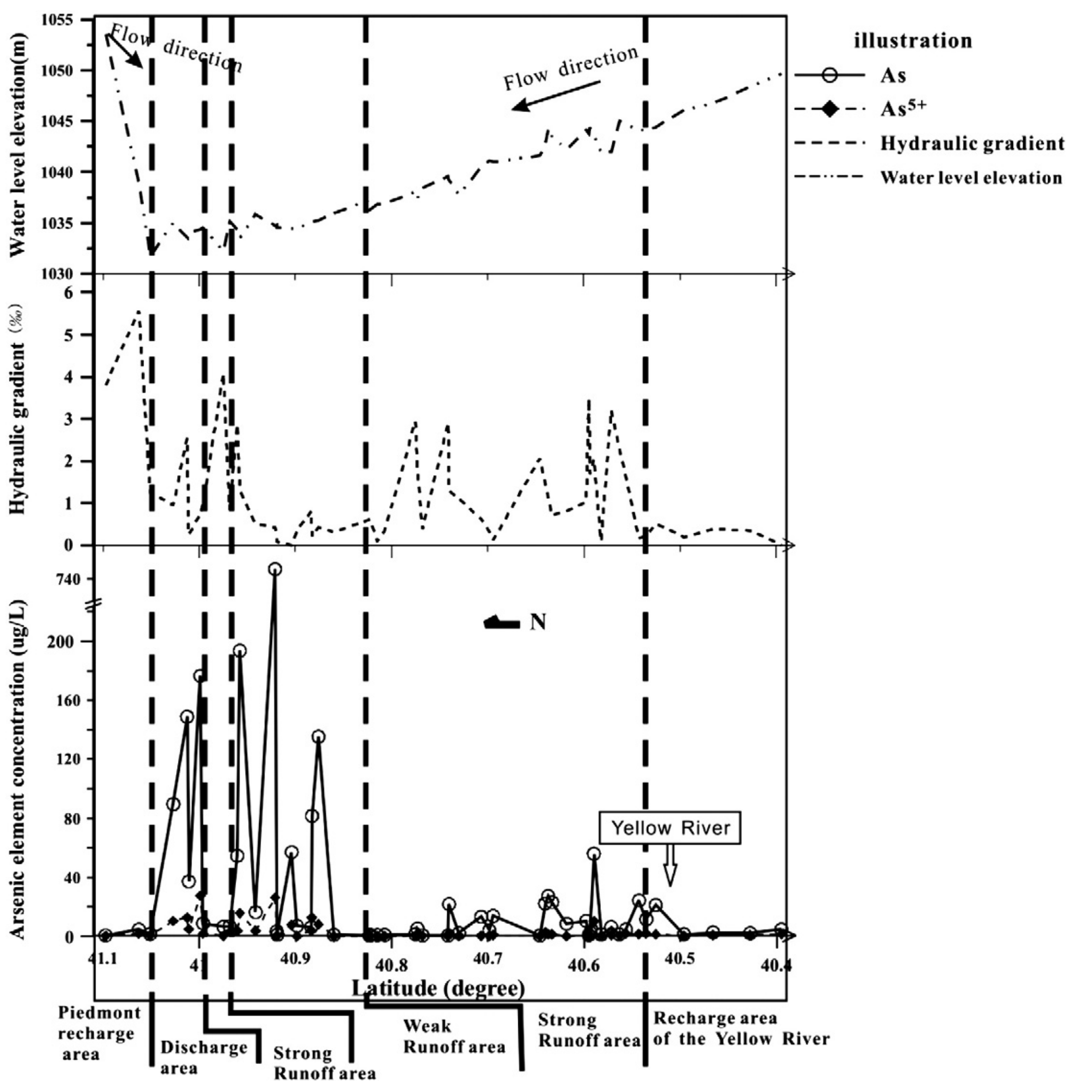

Fig. 2. Water level, hydraulic gradient and As concentration curve along the Hangjinhouqi (western) transect based on data collected in 2009.

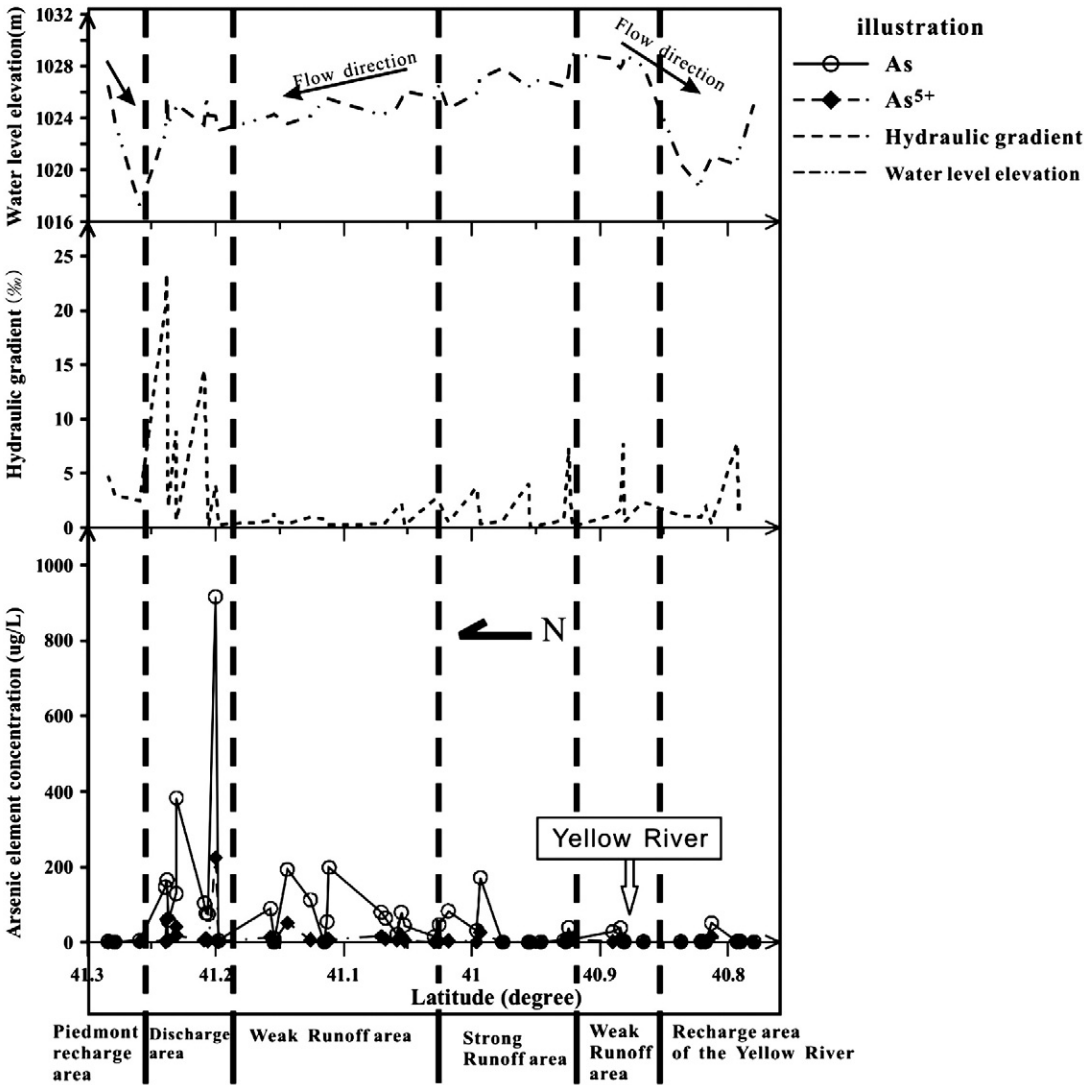

Fig. 3. Water level, hydraulic gradient and As concentration curve along the Wuyuan (central) transect based on data collected in 2009.

corresponds to lowest concentration of the total As with the median value of 2 μg/l (Table 3).

The discharge area along the main drainage channel is located in the depression in the front of alluvial fan. Both the elevation and the groundwater level are the lowest for the entire transect (Fig. 3). Lateral flows from the Langshan Mountains and the Yellow River converge here and discharge. The total As concentration ranges from 58.09 μg/l to 916.7 μg/l with a median value of 116.4 μg/l and 93% of samples containing > 10 μg/l As. The majority of arsenic is As^{3+} (Table 3).

The runoff area is located between the main drainage channel and the Yellow River where the lateral movement of groundwater is slow but is more complex than the other transects (Fig. 3). Based on the hydraulic gradient and the groundwater level, the runoff area can be divided into two areas: (1) The weak runoff area belongs to the alluvial plain of the Yellow River, and most of the area is located in proximity to the discharge area between the latitude of 41.02 to 41.19° and only a small part next to the Yellow River (Fig. 3). Here, the median hydraulic gradient is 0.92‰, the lowest of the transect. But, the total As concentration ranges from 0.42 μg/l to 198.3 μg/l

Table 3
Wuyuan transect based on 2009 data.

Classify	Samples size	Total As (μg/l)			As^{3+} (μg/l)			As^{5+} (μg/l)			Hydraulic gradient (‰)			Water level (m)		
		Min	Max	Median.	Min	Max	Median	Min	Max	Median	Min	Max	Median	Min	Max	Median
Piedmont recharge area	3	0.47	4.28	2.19	0.39	2.75	1.24	0.08	1.53	0.96	2.47	4.80	3.42	1023.8	1026.5	1025.2
Discharge area	9	58.09	916.7	116.4	52.68	692.1	92.9	1.9	224.6	14.04	0.19	23.31	2.62	1022.8	1025.7	1024.6
Weak runoff area	17	0.42	198.3	54.42	0.23	191.7	48.0	0.06	51.9	5.66	0.19	2.56	0.58	1023.0	1026.6	1024.8
Strong runoff area	16	0.38	171.4	3.72	0.27	144.4	21.07	0.05	27.0	4.83	0.12	7.31	1.18	1026.0	1028.5	1027.6
Recharge area of Yellow River	9	0.83	51.0	1.75	0.43	35.94	1.0	0.33	15.06	0.63	0.32	7.77	1.72	1018.6	1025.1	1020.5

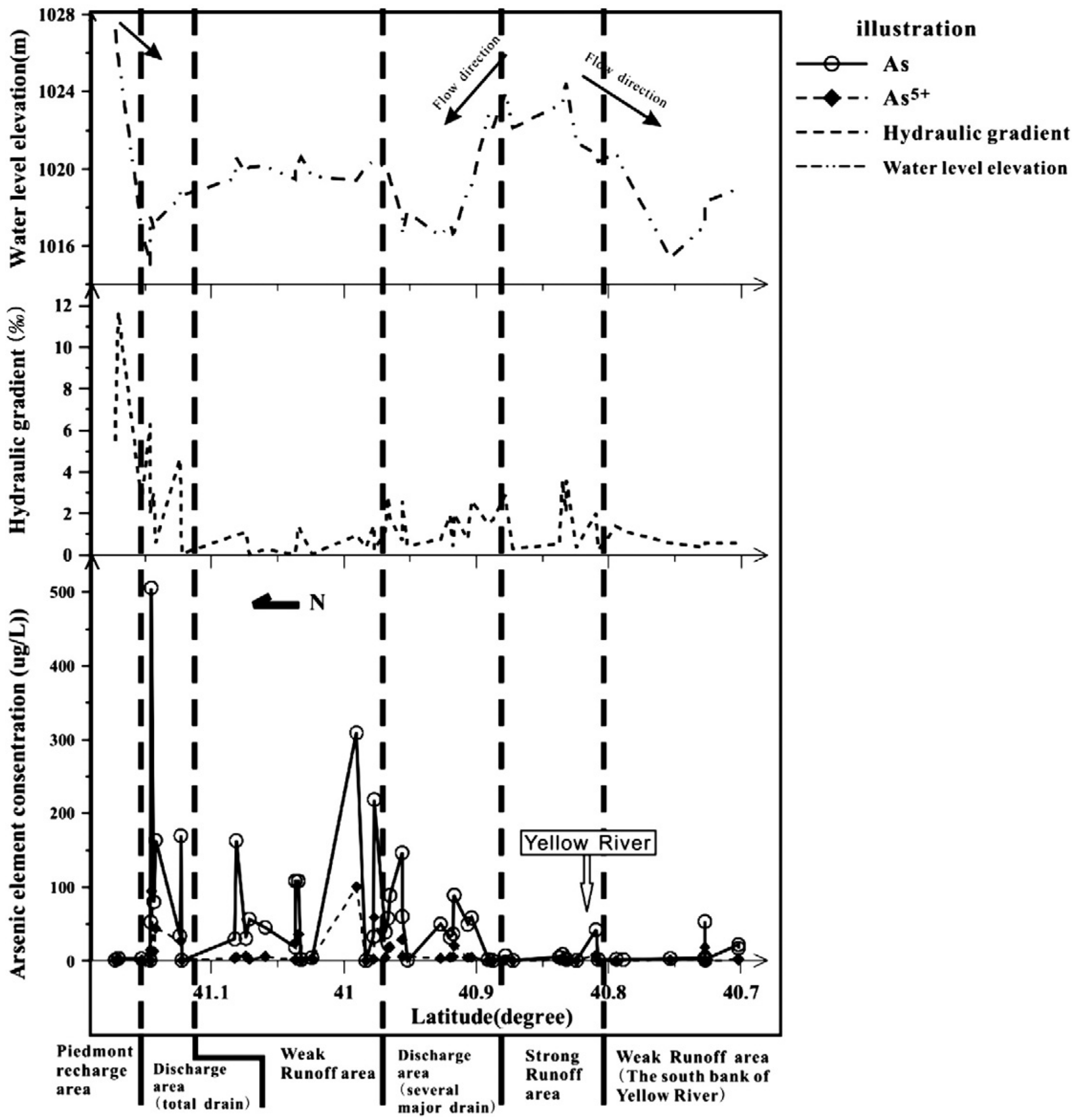

Fig. 4. 2009 data, water level, hydraulic gradient and arsenic element concentration curve in Urad Front Banner typical section.

with 82% of samples with As concentrations exceeding > 10 μg/l and a median value of 54.42 μg/l. (2) The strong runoff area is located closer to the recharge zone between the latitude of 40.92 to 40.99° in the middle of the alluvial plain of the Yellow River. Here, the median hydraulic gradient is 1.18‰ but the total As concentration ranges from 0.38 μg/l to 171.4 μg/l with a median value of 3.72 μg/l and 42% samples with As concentrations exceeding > 10 μg/l.

The recharge area of Yellow River is located in the southern part of the transect (Fig. 3). The hydrodynamic conditions of groundwater are poor in the south bank of Yellow River. Here, the median hydraulic gradient is 2.26‰. The total As concentration ranges from 0.83 μg/l to 51.0 μg/l with a median value is 1.75 μg/l and 21.1% of samples with As concentrations exceeding > 10 μg/l.

4.3. Arsenic and hydraulic gradient along the Urad Front Banner transect

The Urad Front Banner transect lies in the eastern part of the Hetao Plain and is mostly consisted of the alluvial lacustrine plain of the

Table 4
Uradqianqi transect based on 2009 data.

Classify	Sample size	Total As (μg/l)			As^{3+} (μg/l)			As^{5+} (μg/l)			Hydraulic gradient (‰)			Water level (m)		
		Min	Max	Median	Min	Max	Median	Min	Max	Median.	Min	Max	Median.	Min	Max	Median.
Piedmont recharge area	4	1.13	3.39	2.1	0.76	2.08	0.8	0.34	2.63	0.76	2.63	11.68	5.45	1016.9	1027	1021.3
Discharge area	18	1.19	506	58.3	1.11	411.2	50.06	3.71	94.8	14.0	0.40	4.62	1.94	1015	1020.1	1018
Weak runoff area	15	0.36	309.3	32.92	0.2	208.5	30.56	0.16	100.8	3.72	0.02	1.44	0.36	1018.6	1020.6	1020.0
Strong runoff area	6	0.6	8.79	3.64	0.4	8.13	2.45	0.2	1.68	0.67	0.30	3.60	1.68	1022.1	1023.9	1022.9
Recharge area of Yellow River	9	0.66	42.5	8.6	0.37	34.49	6.92	0.17	8.01	1.68	0.26	3.57	1.60	1022.4	1024.4	1023.0
Weak runoff area	4	1.25	53.42	4.44	0.68	34.65	2.6	0.02	18.77	1.75	0.36	1.17	0.58	1015.4	1020	1018.0

Yellow River (Fig. 1). The irrigation canals along this transect are one of the most dense in the Hetao Basin, with a density of 0.48 km/km^2.

The Piedmont recharge area featured high groundwater level, high hydraulic gradient and low arsenic concentration (Fig. 4). Along the groundwater flow path, the groundwater level decreases from 1027.5 m to 1016.9 m, The median hydraulic gradient is 5.45‰, the highest level of the transect. Again, the concentration of the total As is the lowest with a median value only of 2.24 μg/l (Table 4).

Based on the water level, there are two discharge areas along the Urad Front Banner transect (Fig. 4). One area along the main drainage channel is located in the depression in front of the alluvial fan of this transect, the other is located in the alluvial–proluvial plain of the Yellow River (Fig. 4). The hydraulic gradient of both ranges from 0.4‰ to 4.62‰ with a median value of 2.75‰. The median total As is 167.7 μg/l and 95% of samples containing > 10 μg/l As. The majority of arsenic is As^{3+} (Table 4).

Runoff area belonging to the alluvial–proluvial plain of the Yellow River, mainly accepts the lateral recharge of the Yellow River. Based on the hydraulic gradient, runoff area can be divided into two areas:(1) The weak runoff area is situated next to the discharge area between the latitude of 40.97 to 41.12°. Here, the median hydraulic gradient is 0.36‰. The total As concentration ranges from 0.36 μg/l to 309.3 μg/l with a median value of 32.92 μg/l and 73% of samples with As concentrations exceeding > 10 μg/l (Table 4). (2) The strong runoff area is located in proximity to the main drainage channel between the latitude of 40.83 to 40.89°. Here, the median hydraulic gradient is 1.68‰. The total As concentration ranges from 0.6 μg/l to 8.79 μg/l with a median value of 3.64 μg/l and just 20% of samples with As concentrations exceeding > 10 μg/l (Table 4).

The recharge area of Yellow River in the southern end of the transect featured low arsenic concentration and high hydraulic gradient. The groundwater level ranges from 1022.4 m to 1024.4 m. The median hydraulic gradient is 1.6‰. The total As ranges from 0.66 μg/l to 42.5 μg/l with a median value of 8.6 μg/l and 16.7% of samples with As concentrations exceeding > 10 μg/l (Table 4).

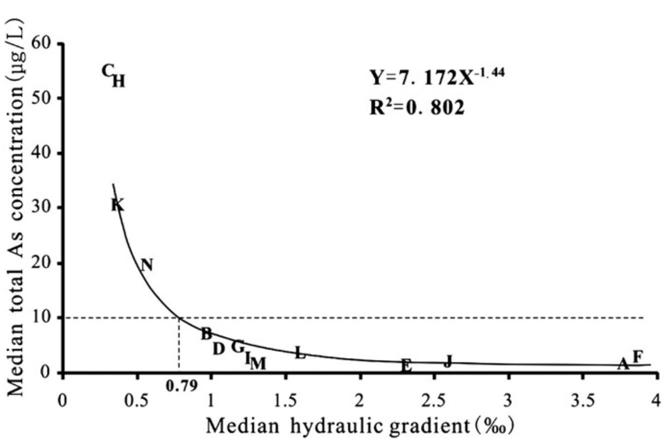

Fig. 5. The median groundwater [As] plotted against the median hydraulic gradient along the groundwater flow path in Hetao Plain, with each letter representing an area along the transects (see Tables 2, 3, and 4 for legends). A: Piedmont recharge area, Hangjinhouqi transect. B: Strong runoff area, Hangjinhouqi transect. C: Weak runoff area, Hangjinhouqi transect. D: Strong runoff area adjacent to the Yellow River Hangjinhouqi transect. E: Recharge area of Yellow River, Hangjinhouqi transect. F: Piedmont recharge area, Wuyuan transect. G: Strong runoff area, Wuyuan transect. H: Weak runoff area, Wuyuan transect. I: Recharge area of Yellow River, Wuyuan transect. J: Piedmont recharge area, Urad Front Banner transect. K: Strong Runoff area, Urad Front Banner transect. L: Weak Runoff area, Urad Front Banner transect. M: Recharge area of Yellow River, Urad Front Banner transect. N: Weak Runoff area, on the south bank of the Potomac river, Urad Front Banner transect.

5. Discussion: hydraulic gradient control of As concentration in groundwater

When the median total arsenic concentrations were plotted against the median hydraulic gradients for the runoff areas and the recharge areas of all three transects (Tables 2, 3, and 4) in the Hetao Plain, it is evident that the total As concentration is inversely related to the hydraulic gradient. A power function can be used to describe the relationship between the two (Fig. 5), with a correlation coefficient (R^2) of 0.802.

$$y = 7.172x^{-1.14}\left(R^2 = 0.802\right)$$

where:

y the median value of total arsenic concentration (μg/l),
x the median hydraulic gradient along the groundwater flow path (‰),

In addition, the median total As concentration value of 10 μg/l corresponds to the median value of hydraulic gradient of < 0.79‰ should this power relationship hold up.

A limitation of this relationship is that it does not apply to the discharge area and the reason for this is not clear. The discharge area located in the low-lying area in front of the alluvial fan has high-As groundwater area. It is narrow and is distributed in the east–west direction along the main drainage channel. Here, the median of total As concentration is among the highest in the Hetao Plain with 80 to 100% of sample exceeding > 10 μg/l but the hydraulic gradient tends to be high for each transect (Tables 2, 3, and 4). Future studies will explore why this is the case, with possible explanations including lack of mechanisms to remove or retard As transport in organic rich, reducing aquifers with limited surface areas to effectively sorb As.

6. Conclusion

An empirical power function can be established between hydraulic gradient and groundwater arsenic along the groundwater flow path in Hetao Plain but only for the recharge and runoff flow regimes. When the hydraulic gradient of groundwater is less than 0.79‰, the concentrations of arsenic are usually more than 10 μg/l. However, this empirical correlation breaks down in the discharge area where hydraulic gradient and arsenic concentrations of shallow groundwater are completely unrelated. The implications for this relationship and the lack thereof in the discharge zone require further investigation.

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