ARSENIC AND MANGANESE CONTAMINATION OF GROUNDWATER IN PUNJAB PLAIN, PAKISTAN – EFFECTS OF WATER-ROCK INTERACTION

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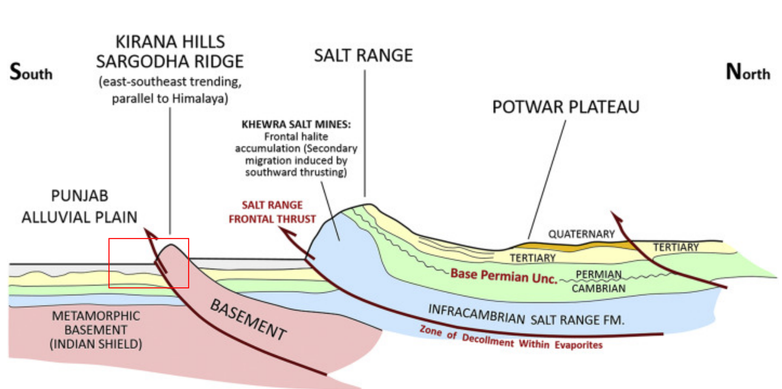
INTRODUCTION: Punjab plain is the most populous province in Pakistan, as its population reaches more than 100 million, where is characterized by a semi-arid climate, and in most area, drinking water and agricultural water are obtained from groundwater wells. Due to rapid population growth and expansion of agricultural fields, there has been a drastic increase in groundwater exploitation resulting in lowering of water tables and deterioration of water quality. District Chiniot, north central part of Punjab plain is one of the typical areas where such deterioration of water quality is significant. In the District, the Kirana Hills are located which exhibits a peculiar terrain of a series of Precambrian basement rock masses sporadically exposed on the Punjab plain.



Source: Petroleum systems and hydrocarbon potential of the North-West Himalaya of India and Pakistan. - Craig J. et al. (2018)

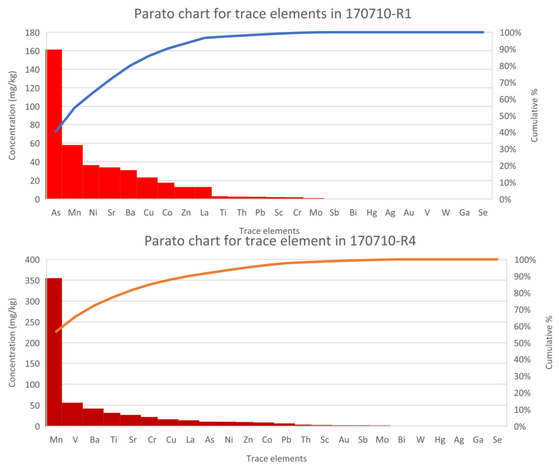
Figure1: Thematic geologic cross section of the study zone (red-colored box) and its surroundings, middle-northern Pakistan.

GROUNDWATER QUALITY: Previous study reported that groundwater distributed around the Kirana Hills showed high electric conductivity (averaged EC = 4,584 µS/cm), high total dissolved solid (averaged TDS = 2,505 mg/l), and high hardness (averaged Hardness = 827 mg/l), and high salinity (Cl = 1,241 mg/l). There is a subsurface barrier effect of the Kirana Hills that traps lateral migration of groundwater. Groundwater samples collected from school wells were analyzed using an ICP-MS. The concentration level of 5 elements, As, Mn, Cl, Br, and S, in groundwater samples exceeded the standards. In particular, the concentration of As (max. 25.1 µg/l) and Mn (max. 443 µg/l) showed high level, which may cause negative effects if the contaminated water is continuously consumed by pupils and local people.

Table 1: Results of ICP-MS trace element analysis for groundwater samples

Element	Ag	Al	As	B	Be	Cd	Cl	Cr	Cu	Fe	Hg	Mn	Pb	S	Sb	Se	Ti	U	Zn
Unit	PPB	PPB	PPB	PPB	PPB	PPB	PPM	PPB	PPB	PPB	PPB	PPB	PPB	PPM	PPB	PPB	PPB	PPB	PPB
LDL	0.05	1	0.5	5	0.05	0.05	1	0.5	0.1	10	0.1	0.05	0.2	1	0.05	0.5	10	0.02	0.5
170710-1	<100	<600	<3000	417	*	<700	*	<300	<80	<10000	*	121	<4000	333	<2000	*	<100	<3000	<300
170710-2	<100	<600	<3000	682	*	<700	*	<300	<80	<10000	*	86	<4000	321	<2000	*	<100	<3000	<300
170710-3	<100	<600	<3000	1269	*	<700	*	<300	<80	<10000	*	443	<4000	674	<2000	*	<100	<3000	<300
170711-1	<0.05	<1	4.9	86	<0.05	0.13	150	11.9	2.4	<10	<0.1	2.47	0.2	63	0.05	0.8	<10	7.48	1.9
170711-2	<0.05	<1	6.6	140	<0.05	<0.05	337	10.6	3.8	<10	<0.1	16.03	<0.2	108	<0.05	2.3	<10	7.21	4.1
170711-3	<100	<600	<3000	1339	*	<700	*	<300	<80	<10000	*	150	<4000	739	<2000	*	<100	<3000	<300
170711-4	0.1	<1	25.1	192	<0.05	<0.05	128	12.2	4.5	<10	<0.1	5.69	<0.2	110	0.06	3	<10	9.78	3.2
170711-5	<0.05	<1	5.7	114	<0.05	<0.05	59	17.3	7.5	<10	<0.1	73.64	<0.2	76	0.12	0.6	<10	2.19	86.8
170712-1	<100	<600	<3000	<400	*	<700	*	<300	<80	<10000	*	94	<4000	206	<2000	*	<100	<3000	<300
170712-2	<0.05	<1	18.3	113	<0.05	<0.05	495	9.8	7.8	<10	<0.1	85.54	<0.2	231	<0.05	2.6	<10	0.68	5.5
170712-3	<100	<600	<3000	689	*	<700	*	<300	<80	<10000	*	400	<4000	536	<2000	*	<100	<3000	<300
170712-4	<0.05	<1	4.8	95	<0.05	<0.05	386	8.2	3.5	<10	<0.1	130.39	<0.2	89	<0.05	1.6	<10	4.53	55.6
170713-1	<0.05	<1	3	41	<0.05	<0.05	16	8.9	2.6	<10	<0.1	4.35	<0.2	21	<0.05	<0.5	<10	5.57	1.3
170713-2	2.13	109	2.3	14	<0.05	0.19	4	2.7	24.7	47	<0.1	8.67	12.5	8	0.24	0.5	<10	0.69	21.2
MCL	100	50	10	2000	4	5	250	100	1000	300	2	50	0	250	6	50	2	30	5000

*: Not determined due to high TDS



ROCK CHEMISTRY: High concentration of As (max. 161 mg/kg) and Mn (max. 355 mg/kg) were detected in the Precambrian meta-volcano sedimentary rock samples from the Kirana Hills, using the aqua regia digestion whole rock ICP-ES/MS analysis. According to X-ray diffraction (XRD) and petrographic observations, arsenopyrite (FeAsS) and cryptomelane ($K(Mn^{4+},Mn^{2+})_8O_{16}$) were identified, and those minerals are considered to be the main sources of As and Mn contamination.

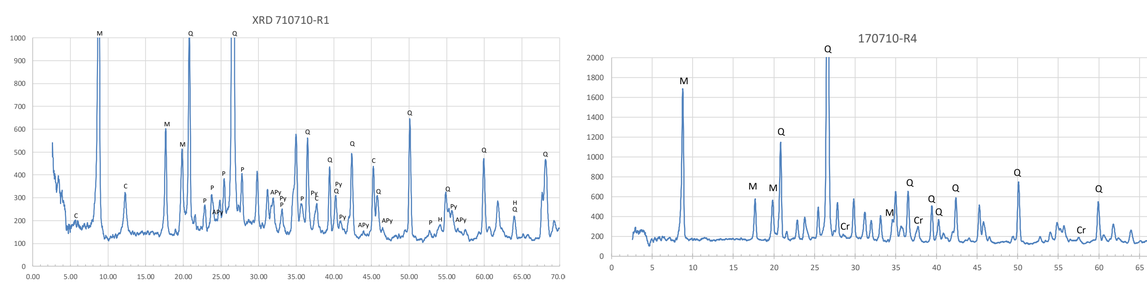


Figure2: XRD charts showing occurrences of arsenopyrite (Left) and cryptomelane (Right) in the Precambrian basement, Kirana Hills.

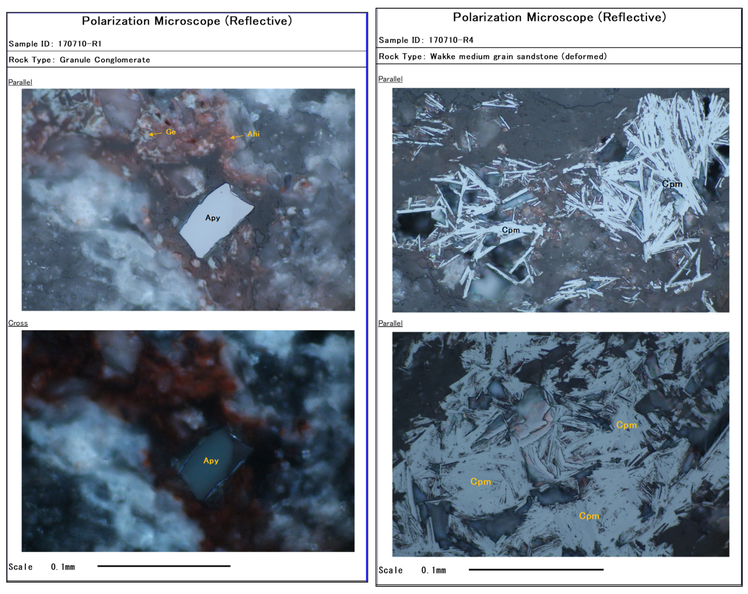


Figure 3: Microscopic thin-section images of arsenopyrite (Apy) observed in the As-rich rock (Left) and of cryptomelane (Cpm) in the Mn-rich rock (Right) collected from the Precambrian basement, Kirana Hills.

CONCLUSIONS: Groundwater chemistry is largely related to chemical composition of the aquifers as well as mineral composition of surrounding hydrological basement. Evaporation and concentration, dilution due to an infiltration of rainwater also change the chemical composition of groundwater but water-rock interaction is considered to be the major process because solid phases are the primary sources and sinks of dissolved constituents in groundwater. The groundwater contamination by As and Mn is probably caused by a water-rock interaction with basement rocks of Kirana Hills. The composition of groundwater in the area is not only controlled by a physical barrier effect, it is largely controlled by the chemical reaction of water and rocks, a water-rock interaction.

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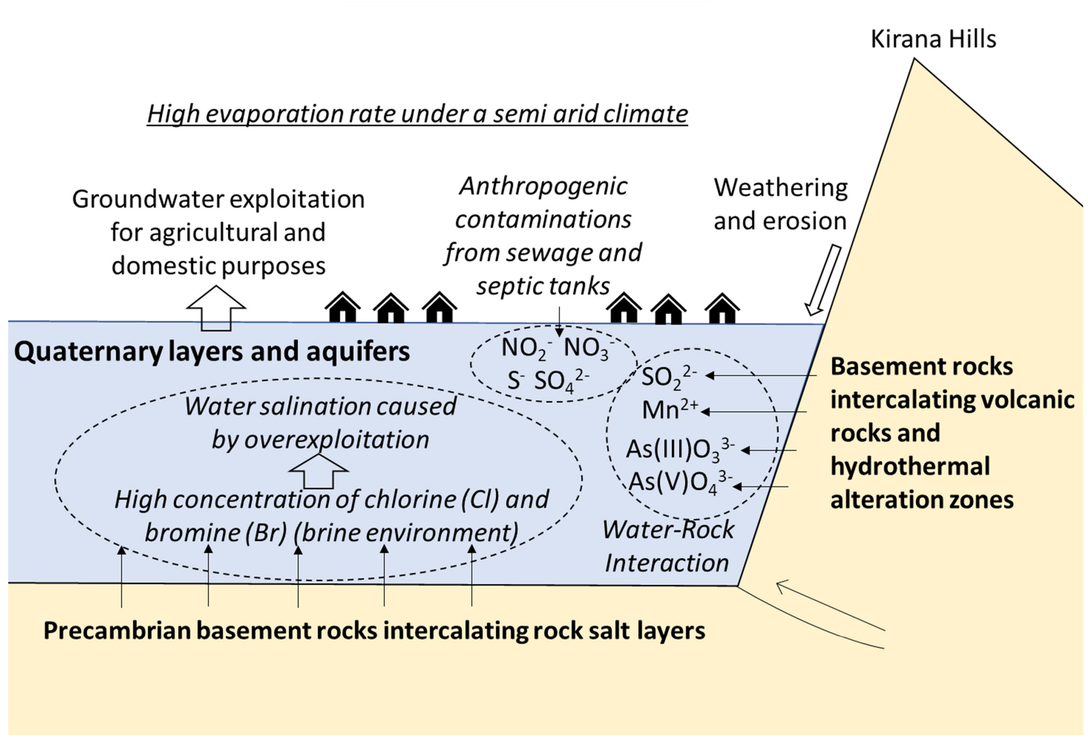

Figure 4: A model of groundwater contamination around Kirana Hills, Chiniot area, Punjab, Pakistan, and the water-rock interaction.