

*Supplementary File*

# Evolution Mechanism of Arsenic Enrichment in Groundwater and Associated Health Risks in Southern Punjab, Pakistan

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**Table. S1. Saturation index values of various minerals phases in the study area.**

Mineral compositions	Vehari				Burewala				Mailsi			
	Mean	Minimum	Maximum	SD	Mean	Minimum	Maximum	SD	Mean	Minimum	Maximum	SD
Anhydrite (CaSO <sub>4</sub> )	0.71	0.05	1.30	0.26	0.68	-0.13	1.35	0.25	0.54	-0.53	1.48	0.33
Aragonite (CaCO <sub>3</sub> )	-2.01	-2.61	3.55	0.50	-2.04	-2.63	-1.45	0.18	-1.96	-2.82	-1.59	0.18
Calcite CaCO <sub>3</sub> )	-1.87	-2.47	3.6	0.50	-1.89	-2.49	-1.31	0.18	-1.82	-2.68	-1.44	0.18
Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]	-4.04	-5.16	7.24	0.98	-4.15	-5.33	-3.21	0.35	-3.80	-5.44	-3.12	0.33
Goethite (FeOOH)	0.160	-1.24	9.64	0.90	0.24	-0.96	1.80	0.52	0.39	-1.64	1.85	0.48
Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)	1.00	0.35	1.57	0.25	0.97	0.16	1.61	0.24	0.83	-0.23	1.76	0.33
Halite (NaCl)	-3.90	-5.67	-2.57	0.59	-4.18	-5.70	-2.61	0.56	-4.01	-5.07	-2.96	0.42
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	2.33	-0.45	21.30	1.81	2.50	0.09	5.62	1.04	2.80	-1.27	5.719	0.97

**Table. S2. Pearson's correlation matrix of physiochemical parameters in Vehari (*n* = 170).**

	EC	TDS	pH	Turbidity	Alkalinity	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Hardness	NO <sub>3</sub> <sup>-</sup>	Fe <sup>2+</sup>	F <sup>-</sup>	As
EC	1																
TDS	.952**	1															
pH	0.08	0.091	1														
Turbidity	-0.007	0.048	0.068	1													
Alkalinity	0.068	0.054	-0.022	-0.021	1												
HCO <sub>3</sub> <sup>-</sup>	.679**	.633**	-0.118	-0.013	.165*	1											
Cl <sup>-</sup>	.905**	.854**	0.148	-0.044	0.039	.462**	1										
SO <sub>4</sub> <sup>2-</sup>	.949**	.968**	0.123	0.041	0.071	.553**	.828**	1									
Ca <sup>2+</sup>	.222**	.464**	-0.029	.176*	-0.058	.223**	.173*	.312**	1								
Mg <sup>2+</sup>	.690**	.774**	0.043	-0.013	-0.032	.529**	.613**	.674**	.446**	1							
Na <sup>+</sup>	.934**	.841**	0.072	-0.025	0.126	.673**	.831**	.885**	-0.001	.485**	1						
K <sup>+</sup>	.253**	.249**	-0.03	0.014	-0.027	.266**	.228**	.197*	0.078	.348**	.165*	1					
Hardness	.485**	.687**	-0.001	0.105	-0.057	.409**	.415**	.536**	.877**	.793**	.236**	.222**	1				
NO <sub>3</sub> <sup>-</sup>	0.071	0.068	-0.046	-0.098	-0.033	0.069	0.119	0.022	-0.034	0.15	0.078	.224**	0.049	1			
Fe <sup>2+</sup>	0.111	0.126	-0.035	-0.055	-0.015	0.006	0.143	0.108	0.063	.191*	0.054	-0.004	0.137	-0.061	1		
F <sup>-</sup>	.524**	.388**	-0.01	-0.076	0.086	.323**	.446**	.468**	-.328**	.263**	.574**	0.103	-0.096	0.143	0.077	1	
As	-.180*	-.210**	0.026	-0.005	-0.051	-.191*	-0.136	-.155*	-.183*	-.347**	-0.084	-.259**	-.293**	-0.142	-.151*	-0.103	1

\*correlation is significant at p < 0.05, \*\*correlation is significant at p < 0.01, n means number of samples

**Table. S3. Pearson's correlation matrix of physiochemical parameters in Burewala (*n* = 170).**

	EC	TDS	pH	Turbidity	Alkalinity	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Hardness	NO <sub>3</sub> <sup>-</sup>	Fe <sup>2+</sup>	F <sup>-</sup>	As
EC	1																
TDS	.946**	1															
pH	-0.024	-0.013	1														
Turbidity	-0.064	-0.003	-0.022	1													
Alkalinity	.755**	.688**	-0.04	-0.09	1												
HCO <sub>3</sub> <sup>-</sup>	.740**	.667**	-0.049	-0.126	.972**	1											
Cl <sup>-</sup>	.864**	.805**	-0.021	-0.071	.655**	.646**	1										
SO <sub>4</sub> <sup>2-</sup>	.901**	.943**	-0.006	-0.009	.540**	.522**	.676**	1									
Ca <sup>2+</sup>	.458**	.645**	0.046	0.134	.382**	.346**	.429**	.461**	1								
Mg <sup>2+</sup>	.717**	.789**	-0.06	-0.012	.665**	.651**	.637**	.649**	.521**	1							
Na <sup>+</sup>	.936**	.850**	-0.038	-0.098	.717**	.711**	.805**	.869**	.210**	.562**	1						
K <sup>+</sup>	.226**	.213**	-0.038	-0.063	.285**	.273**	.219**	0.136	0.124	.311**	0.137	1					
Hardness	.648**	.807**	0.001	0.08	.574**	.544**	.591**	.618**	.910**	.828**	.410**	.233**	1				
NO <sub>3</sub> <sup>-</sup>	.249**	.235**	-0.039	-0.031	.287**	.293**	.217**	0.125	.269**	.301**	0.141	.163*	.323**	1			
Fe <sup>2+</sup>	0.108	0.117	-0.014	-0.068	.233**	.216**	0.066	0.093	0.083	0.061	.154*	-0.027	0.085	0.012	1		
F <sup>-</sup>	.531**	.445**	-0.055	-0.085	.430**	.430**	.364**	.485**	0.001	.362**	.546**	.198**	.175*	0.146	0.006	1	
As	-0.007	0.097	0.034	0.032	-0.126	-0.15	-0.029	0.089	.336**	-0.032	-0.083	-0.104	.206**	-.184*	-0.063	-.162*	1

\*correlation is significant at p < 0.05, \*\*correlation is significant at p < 0.01, n means number of samples

**Table. S4. Pearson's correlation matrix of physiochemical parameters in Mailsi (n = 170).**

	EC	TDS	pH	Turbidity	Alkalinity	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Hardness	NO <sub>3</sub> <sup>-</sup>	Fe <sup>2+</sup>	F <sup>-</sup>	As
EC	1																
TDS	.802**	1															
pH	-.26**	-.292**	1														
Turbidity	.233**	.162*	0.087	1													
Alkalinity	.670**	.702**	-.260**	.218**	1												
HCO <sub>3</sub> <sup>-</sup>	.679**	.713**	-.258**	.212**	.980**	1											
Cl <sup>-</sup>	.831**	.859**	-.338**	.152*	.571**	.571**	1										
SO <sub>4</sub> <sup>2-</sup>	.736**	.925**	-0.15	0.117	.538**	.546**	.759**	1									
Ca <sup>2+</sup>	.592**	.822**	-.350**	-0.001	.522**	.543**	.660**	.699**	1								
Mg <sup>2+</sup>	.411**	.611**	-.202**	.256**	.556**	.555**	.462**	.419**	.277**	1							
Na <sup>+</sup>	.811**	.750**	-0.143	.196*	.661**	.668**	.789**	.796**	.453**	.233**	1						
K <sup>+</sup>	.481**	.545**	-0.097	0.079	.383**	.396**	.416**	.569**	.412**	.257**	.424**	1					
Hardness	.635**	.906**	-.351**	0.149	.672**	.685**	.711**	.713**	.829**	.767**	.441**	.426**	1				
NO <sub>3</sub> <sup>-</sup>	.268**	.295**	-0.04	-.166*	.194*	.207**	.226**	.212**	.362**	.165*	0.119	.206**	.339**	1			
Fe <sup>2+</sup>	-0.038	-0.038	0.042	.189*	-0.006	-0.015	-0.063	-0.014	-0.061	0.001	-0.035	-0.007	-0.04	-0.076	1		
F <sup>-</sup>	.210**	.177*	0.006	.313**	0.132	0.149	.194*	0.14	0.124	0.118	.177*	0.101	.151*	0.108	-0.01	1	
As	0.07	-0.023	0.068	.403**	0.147	0.138	-0.018	-0.04	-0.189*	.160*	0.094	-0.06	-0.032	-.328**	0.1	0.118	1

\*correlation is significant at p < 0.05, \*\*correlation is significant at p < 0.01, n means number of samples

**Table. S5. Physicochemical composition of six groundwater samples in mg/L, except As ( $\mu$ g/L) and pH used in the inverse modeling and results of mass transfer calculation along flow-path.**

Parameters	Path I			Path II			Mineral phases	Process	Path I		Path II	
	A	B	C	X	Y	Z			A → B	B → C	X → Y	Y → Z
pH	6.93	7.42	7.45	7.2	7.19	7.52	Anhydrite (CaSO <sub>4</sub> )	Mineral dissolution or precipitation	-0.0277	-6.539	-1.97	-
TDS	614	862	722	654	938	1274	Aragonite (CaCO <sub>3</sub> )		-0.01162	-0.3343	0.01496	0.02299
Na <sup>+</sup>	38	93	97	67	97	160	Calcite (CaCO <sub>3</sub> )		-0.01491	0.01113	0.00005814	-0.01724
Ca <sup>2+</sup>	80	100	88	92	110	152	Dolomite [CaMg(CO <sub>3</sub> ) <sub>2</sub> ]		-0.00204	0.006132	0.02315	0.005807
Mg <sup>2+</sup>	24	39	36	22	28	49	Goethite (FeOOH)		0.00003703	-0.00001053	0.000002681	0.00002438
HCO <sub>3</sub> <sup>-</sup>	225	350	360	270	250	400	Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)		-	1.517	-	0.0707
Cl <sup>-</sup>	34	48	84	53	62	182	Halite (NaCl)		0.008068	0.04089	0.05767	0.01149
K <sup>+</sup>	4.7	6.3	8	6.2	5.1	9	Hematite Fe <sub>2</sub> O <sub>3</sub>		0.00001851	-0.000005263	0.000001341	0.00001254
Fe <sup>2+</sup>	0.09	0.3	0.12	0.14	0.07	0.23	H <sub>2</sub> O(g)	Evaporation	-2.94	1.03	3.93	-1.5
NO <sub>3</sub> <sup>-</sup>	0.15	0.3	0.47	2.71	0.32	1.12	CO <sub>2</sub> (g)		-0.01689	0.07148	0.1465	-0.3339
SO <sub>4</sub> <sup>2-</sup>	146	185	100	115	270	210	CaX <sub>2</sub>	Cation Exchange	-0.01562	0.007318	0.01642	0.00596
As	14	27	50	11	21	30	NaX		0.03124	-0.01464	0.03283	-0.01192

Negative values mean phase removal from groundwater, while positive means phase dissolution. All mass transfers values in mmol/L.

**Table. S6. Chronic daily intake (CDI), Non carcinogenic risk hazard quotient (HQ), and carcinogenic risk (CR) of As exposure by adult and children in the study area.**

Maximum	$1.13 \times 10^{-3}$	$3.21 \times 10^{-4}$	3.75	1.07	$1.69 \times 10^{-3}$	$4.82 \times 10^{-4}$	$1.30 \times 10^{-3}$	$3.71 \times 10^{-4}$	4.33	1.24	$1.95 \times 10^{-3}$	$5.57 \times 10^{-4}$	$2.23 \times 10^{-3}$	$8.90 \times 10^{-4}$	7.42	2.97	$3.34 \times 10^{-3}$	$1.34 \times 10^{-3}$
S.D	$2.96 \times 10^{-4}$	$8.47 \times 10^{-5}$	$9.88 \times 10^{-1}$	$2.82 \times 10^{-1}$	$4.45 \times 10^{-4}$	$1.27 \times 10^{-4}$	$2.91 \times 10^{-4}$	$8.31 \times 10^{-5}$	$9.69 \times 10^{-1}$	$2.77 \times 10^{-1}$	$4.36 \times 10^{-4}$	$1.25 \times 10^{-4}$	$3.85 \times 10^{-4}$	$1.54 \times 10^{-4}$	1.28	0.51	$5.77 \times 10^{-4}$	$2.31 \times 10^{-4}$