Nitrate and Fluoride Enriched Groundwater Purification in India

BY SAM MAROLT

NDSU GEOCHEMISTRY 2018


Himalaya Mountains
Haryana
Delhi
Nepal
Kathmandu
Thimphu
Uttar Pradesh
Rajasthan
Bihar
Bangladesh
Guna
Jharkhand
West Bengal
Madhya Pradesh
Gujarat
Chhattisgarh
Odisha
India
Maharashtra
Telangana
Andhra Pradesh
Goa
Karnataka
Bay of Bengal


Guna
Madhopura
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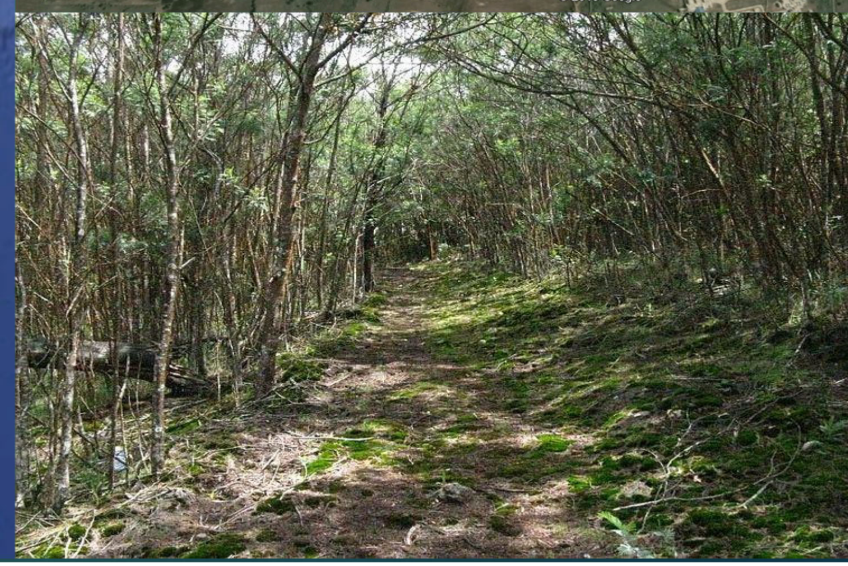


Photos found on www.alchetron.com/Guna, and Google Earth

Why This Topic?

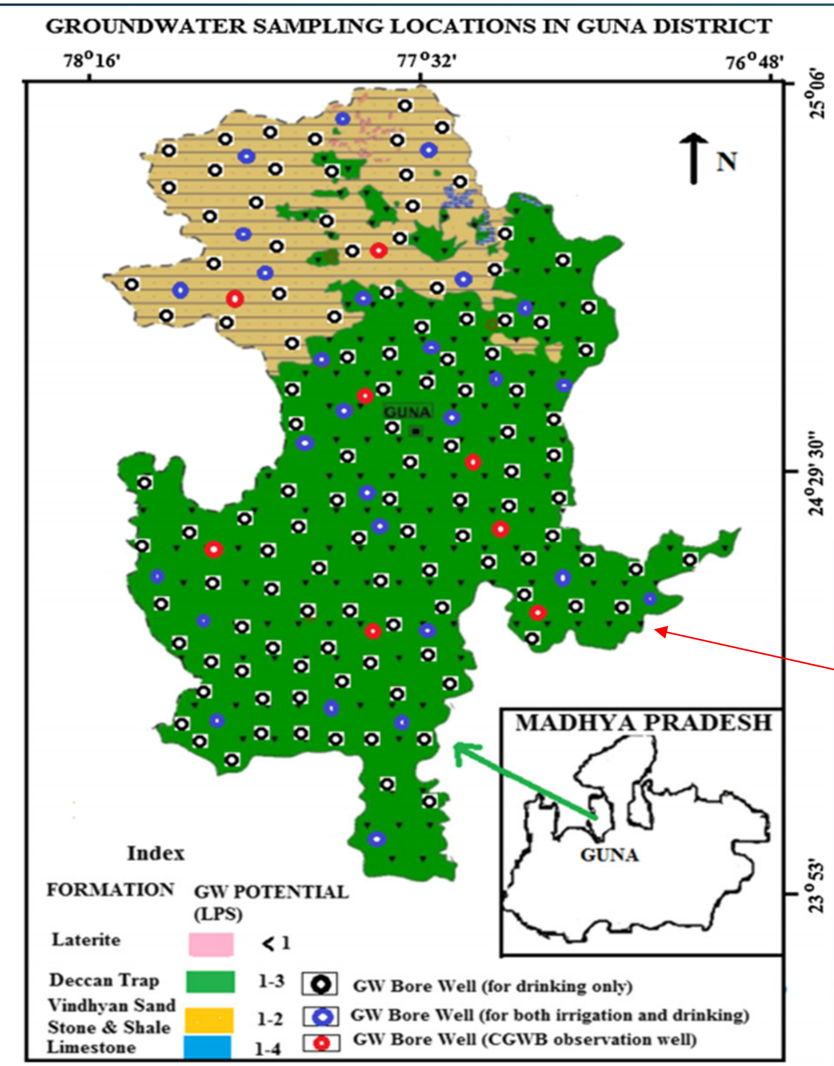
- Thought fluoride was a good thing, too much is bad
- Nitrate contamination is widespread worldwide
- Was interested in learning how to go about purifying water

Background

- 62% of Guna's surface area is used for agriculture
- Fluoride is necessary in water for dental hygiene
- Higher amounts can cause Fluorosis
- EPA suggests no more than 4 mg/L
- World Health Organization has set its maximum contaminant level for fluoride at 1.5 mg/L
- Consuming more than 10mg of fluoride a day causes Fluorosis

www.epa.gov and www.indiawaterportal.org

Local Geology



ABUNDANCE OF FLUORINE IN ROCKS

Averages of the fluorine contents of various igneous rocks are as follows:

Rock type	Fluorine, in parts per million (number of samples in parentheses)	
	Fleischer and Robinson (1963, tables I, II)	This report[1]
Extrusive:		
Basalt	380 (268)	510 (187)
Andesite	220 (83)	630 (85)
Rhyolite	700 (145)	780 (261)
Phonolite	930 (14)	......
Intrusive:		
Gabbro	430 (47)	......
Granite,[2] granodiorite	840 (183)	......
Alkalic rocks	960 (71)	[3]2,640 (100)

Srivasta and Ramanathan, 2018 and Shawe et al. 1976

How was data collected

- 149 groundwater samples were taken in bore wells systematically spaced
- Digital electrodes were used to collect Temp., EC, DO, Redox Potential, and TDS.
- Data was then rechecked in a lab with 100ml water samples
- Sample ion activity was determined using electrodes, titrations, and a spectrophotometer
  - Spectrophotometer uses reflected light to determine concentrations of known chemical substances

Srivasta and Ramanathan, 2018

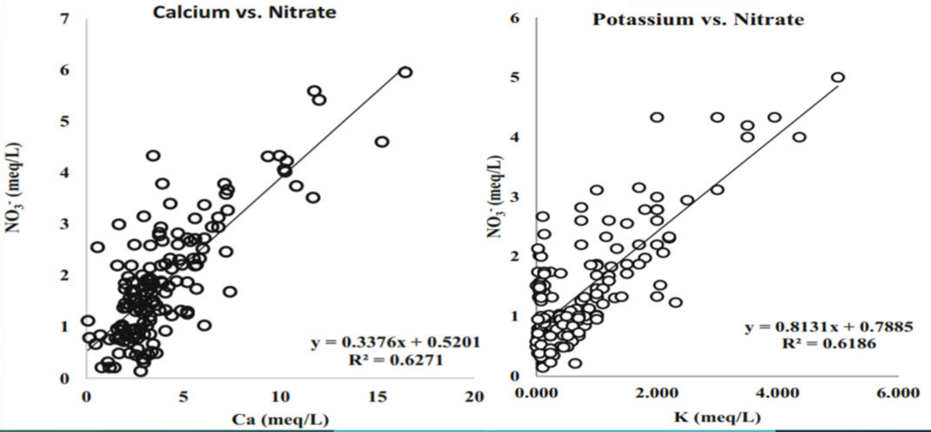
Table 1. *Summary of statistics of hydrogeochemical parameters.*

Statistics	pH	Eh (mV)	EC (S/cm)	DO (mg/L)	TDS (mg/L)	Cl^- (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	F^- (mg/L)	PO_4^{3-} (mg/L)	$H_3SiO_4^-$ (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cu (mg/L)	Pb (mg/L)	Fe (mg/L)	Hg (mg/L)
Kumbharaj block, $N=12$																				
Min.	7.05	370	550	9.1	385	75.03	78.72	17.5	13	0.5	0.26	6.33	44	3	14	24	0.22	0.01	0.01	0.0006
Max.	7.89	410	2700	12.6	1890	455.6	510.45	107.1	108	8.46	0.44	36.67	154	133	126	204	1.33	0.875	1.03	0.0066
Mean	7.36	392.92	1075.8	11.28	753.08	177.06	350.97	49.46	43.92	2.25	0.3	23.82	79.04	20.91	54.46	88.43	0.975	0.33	0.249	0.004
Std.	0.31	12.5	632.65	0.96	442.85	124.36	142.47	26.59	22.95	2.35	0.05	8.79	35.81	37.62	31.12	62.72	0.37	0.22	0.29	0.0016
Raghogarh block, $N=59$																				
Min.	6.79	311	400	8.7	280	32.55	34.44	21	8.75	0.01	0.27	16.33	25	0.01	1.2	1.6	0.26	0.001	0.02	0.0001
Max.	7.81	415	4100	13.5	2865	1288.8	776.13	246.2	371.3	2.99	1.36	32.67	730	510	245.2	328.8	2.41	0.904	3.18	0.0097
Mean	7.21	367.93	1163.7	10.59	816.27	219.43	409.32	63.57	83.8	1.24	0.37	19.99	104.9	26.51	68.8	86.55	1.03	0.45	0.48	0.005
Std.	0.21	18.26	747.45	0.9	523.01	247.78	170.36	48.55	54.66	0.84	0.15	3.3	126.5	83.92	45.27	57.81	0.391	0.144	0.346	0.0065
Aron block, $N=22$																				
Min.	6.71	322	350	8.8	245	45.04	86.45	10.5	19.25	0.12	0.26	12.67	20	0.01	14	16	0.11	0.001	0.03	0.0003
Max.	7.24	395	1820	11.8	1274	465.23	543.66	88.1	123	1.87	0.38	31.33	112	29	103.6	206.4	1.93	0.863	1.98	0.0076
Mean	7.08	366.13	804.54	10.36	554	133.98	336.14	28.64	58.13	0.77	0.29	16.23	67.27	5.41	50.04	65.81	0.736	0.049	0.96	0.005
Std.	0.18	21.66	339.54	0.79	237.68	99.56	127.1	20.33	30.93	0.46	0.04	3.85	24.98	7.18	23.06	41.19	0.52	0.177	0.46	0.0018
Guna block, $N=17$																				
Min.	6.71	247	470	8.8	330	52.53	254.12	15.3	30.5	0.12	0.26	14.33	34	1	26.8	44.8	0.15	0.007	0.07	0.0003
Max.	7.27	388	1560	11.8	1090	300.32	536.28	78.2	136.3	1.87	0.52	22.67	91	170	84.4	144	2.33	0.016	3.73	0.0092
Mean	7.04	352.7	806.47	10.15	560	137.47	393.46	33.5	69.22	0.65	0.36	17.04	63.24	22.46	54.68	78.78	1.044	0.13	1.091	0.005
Std.	0.15	32.36	249.65	0.94	170	64.24	75.69	18.33	24.11	0.75	0.07	1.93	17.58	43	13.88	28.28	0.53	0.003	0.95	0.002
Bamori block, $N=29$																				
Min.	6.6	297	300	8.7	204	55.03	93.48	19	23.5	0.12	0.26	10.33	15	1	6	30.4	0.19	0.003	0.02	0.0001
Max.	7.32	425	1020	11.5	693.6	290.12	436.65	71.9	308.5	2.74	0.38	31.33	70	189	66.8	121.6	2.22	0.015	1.92	0.0074
Mean	6.96	380.86	549.31	9.81	373.53	107.46	244.99	29.8	75.44	0.73	0.33	18.53	39.48	23.48	37.13	57.23	1.078	0.012	0.601	0.004
Std.	0.18	23.96	167.95	0.71	114.2	53.12	91.28	13.35	54.65	0.72	0.06	4.67	13.92	43.87	17.5	19.89	0.46	0.003	0.51	0.0025
Chachoda block, $N=10$																				
Min.	6.91	305	520	10.4	525	105.4	27.06	23.9	13.25	0.25	0.28	14	55	1	23.6	3.2	0.37	0.01	0.07	0.0001
Max.	8.78	388	3300	12.2	2310	873.48	604.84	137.2	288	9.08	0.35	21	176	27	231.4	304.8	1.81	0.21	1.07	0.0097
Mean	7.39	355.5	1615	11.11	1130.5	363.03	335.49	74.2	106.6	2.74	0.31	16.97	109.6	5.5	84.99	133.8	0.94	0.055	0.25	0.004
Std.	0.66	24.06	962.06	0.51	673.82	290.01	212.33	33.98	77.44	3.1	0.03	2.26	41.59	7.56	74.08	98.18	0.49	0.057	0.3	0.0031
WHO*	6.5–8.5								50	1.5			200		50	200	1.5	0.01	0.3	0.006
BIS*	6.5–8.5				2000	1000	732	400	100	1.5			200		100	200	1	0.05	1	0.001

*Permissible limit.

Srivasta and Ramanathan, 2018

Previous studies



- Source of fluorine identified:
  - Aquifer is composed of fluorine rich basalts, this fluorine is then dissolved into the groundwater
- Source of nitrates identified:
  - Nitrates are being used for agricultural purposes and then running off into the groundwater
- Both nitrates and fluorine are above the permissible contamination level in the groundwater
- Proposed solution:
  - Reduce consumption of fertilizer to solve the nitrate issue
  - Drink water from lower fluorine rich wells

Srivasta and Ramanathan, 2018

Chachoda Block

Statistics	pH	Eh (mV)	EC (S/cm)	DO (mg/L)	TDS (mg/L)	Cl^- (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	F^- (mg/L)	PO_4^{3-} (mg/L)	$H_3SiO_4^-$ (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cu (mg/L)	Pb (mg/L)	Fe (mg/L)	Hg (mg/L)
Chachoda block, N=10																				
Min.	6.91	305	520	10.4	525	105.4	27.06	23.9	13.25	0.25	0.28	14	55	1	23.6	3.2	0.37	0.01	0.07	0.0001
Max.	8.78	388	3300	12.2	2310	873.48	604.84	137.2	288	9.08	0.35	21	176	27	231.4	304.8	1.81	0.21	1.07	0.0097
Mean	7.39	355.5	1615	11.11	1130.5	363.03	335.49	74.2	106.6	2.74	0.31	16.97	109.6	5.5	84.99	133.8	0.94	0.055	0.25	0.004
Std.	0.66	24.06	962.06	0.51	673.82	290.01	212.33	33.98	77.44	3.1	0.03	2.26	41.59	7.56	74.08	98.18	0.49	0.057	0.3	0.0031

Srivasta and Ramanathan, 2018

Phase	SI**	log IAP	log K(277 K, 1 atm)	
Aragonite	-0.10	-8.24	-8.14	CaCO3
Artinite	-7.35	3.85	11.20	MgCO3:Mg(OH)2:3I
Atacamite	-0.94	7.69	8.63	Cu2(OH)3Cl
Azurite	0.84	-14.80	-15.64	Cu3(OH)2(CO3)2
Brucite	-6.31	12.05	18.36	Mg(OH)2
Calcite	0.14	-8.24	-8.37	CaCO3
Calomel	-3.13	-22.27	-19.13	Hg2Cl2
Cerussite	0.21	-13.25	-13.46	PbCO3
CH4(g)	-66.92	-111.38	-44.46	CH4
CO2(g)	-2.05	-20.26	-18.20	CO2
Cotunnite	-6.76	-11.89	-5.13	PbCl2
Cu(OH)2	-0.85	8.57	9.42	Cu(OH)2
Cu2(OH)3NO3	-2.65	7.56	10.21	Cu2(OH)3NO3
CuCO3	-0.19	-11.69	-11.50	CuCO3
CuF	-6.45	-11.58	-5.13	CuF
CuF2	-16.15	-14.15	2.00	CuF2
CuF2:2H2O	-9.80	-14.15	-4.35	CuF2:2H2O
Cumetal	-1.90	-11.61	-9.71	Cu
Cupricferrite	8.99	17.77	8.78	CuFe2O4
Cuprite	-0.68	-0.44	0.24	Cu2O
Cuprousferrite	13.08	4.38	-8.71	CuFeO2
Dolomite(disordered)	-0.52	-16.44	-15.92	CaMg(CO3)2
Dolomite(ordered)	0.12	-16.44	-16.57	CaMg(CO3)2
Fe(OH)2	-6.76	6.81	13.56	Fe(OH)2
Fe(OH)2.7Cl.3	4.81	1.77	-3.04	Fe(OH)2.7Cl.3
Fe3(OH)8	-4.21	16.01	20.22	Fe3(OH)8
Ferrihydrite	0.43	4.60	4.16	Fe(OH)3
Fluorite	-0.09	-10.70	-10.61	CaF2
Goethite	3.30	4.60	1.30	FeOOH
Halite	-6.00	-4.44	1.55	NaCl
Hematite	8.91	9.20	0.29	Fe2O3
Hg(CH3)2(g)	-154.96	-235.06	-80.10	Hg(CH3)2
Hg(g)	-4.91	-13.08	-8.17	Hg
Hg(OH)2	-8.82	-12.31	-3.50	Hg(OH)2
Hg2(g)	-10.43	-26.16	-15.73	Hg2
Hg2(OH)2	-8.64	-3.38	5.26	Hg2(OH)2
Hg2CO3	-6.98	-23.63	-16.65	Hg2CO3
Hg2F2	-15.98	-26.09	-10.12	Hg2F2
Hg3O2CO3	-27.51	-57.19	-29.68	Hg3O2CO3
HgCl(g)	-32.78	-11.13	21.65	HgCl
HgCl2	-8.51	-31.20	-22.69	HgCl2
HgF(g)	-49.11	-13.05	36.06	HgF
HgF2(g)	-49.79	-35.03	14.76	HgF2
Hgmetal(l)	1.48	-13.08	-14.56	Hg
Huntite	-4.31	-32.85	-28.54	CaMg3(CO3)4
Hydrocerussite	-0.73	-19.50	-18.77	Pb3(OH)2(CO3)2
Hydromagnesite	-14.90	-20.77	-5.87	Mg5(CO3)4(OH)2:4H2O
Laurionite	-3.06	-2.44	0.62	PbOHCl
Lepidocrocite	3.23	4.60	1.37	FeOOH
Lime	-23.25	12.02	35.27	CaO
Litharge	-6.56	7.00	13.56	PbO
Maghemite	2.81	9.20	6.39	Fe2O3
Magnesioferrite	0.69	21.25	20.56	Fe2MgO4
Magnesite	-0.48	-8.20	-7.73	MgCO3
Magnetite	9.84	16.01	6.17	Fe3O4
Malachite	3.20	-3.12	-6.32	Cu2(OH)2CO3
Massicot	-6.78	7.00	13.78	PbO
Matlockite	-4.39	-13.80	-9.41	PbClF
Melanothallite	-17.42	-10.32	7.10	CuCl2
Mg(OH)2(active)	-6.74	12.05	18.79	Mg(OH)2
MgF2	-2.64	-10.67	-8.02	MgF2
Minium	-35.33	43.79	79.12	Pb3O4
Montroydite	-9.19	-12.31	-3.12	HgO
Nantokite	-2.37	-9.67	-7.30	CuCl
Natron	-8.07	-10.26	-2.19	Na2CO3:10H2O
Nesquehonite	-3.86	-8.21	-4.35	MgCO3:3H2O
O2(g)	-45.12	45.56	90.68	O2
Pb(OH)2	-1.92	7.00	8.93	Pb(OH)2
Pb10(OH)6O(CO3)6	-42.74	-51.50	-8.76	Pb10(OH)6O(CO3)6
Pb2(OH)3Cl	-4.23	4.56	8.79	Pb2(OH)3Cl
Pb2O(OH)2	-12.18	14.01	26.19	Pb2O(OH)2
Pb2O3	-24.25	36.79	61.04	Pb2O3
Pb2OCO3	-6.23	-6.25	-0.02	Pb2OCO3
Pb3O2CO3	-11.73	0.76	12.49	Pb3O2CO3
PbF2	-8.01	-15.71	-7.71	PbF2
Pbmetal	-20.01	-15.78	4.23	Pb
PbO:0.3H2O	-5.98	7.00	12.98	PbO:0.33H2O
Periclase	-11.54	12.05	23.59	MgO
Phosgenite	-5.33	-25.14	-19.81	PbCl2:PbCO3
Plattnerite	-23.75	29.78	53.53	PbO2
Portlandite	-12.49	12.02	24.51	Ca(OH)2
Siderite	-3.42	-13.45	-10.03	FeCO3

Decreasing Free Fluorine

4ppm = 2.105E-4 M, and 1.5ppm = 7.895E-5 M

	CaF2 SI Values	MgF2 SI Values	F- activity based on percent	F- activty
Raw Data	-0.09	-2.64	0.869	0.00013
1st solution	-0.59	-2.97	0.578	4.2E-05
2nd solution	-1.03	-3.39	0.137	9.9E-06
3rd solution	-8.44	-6.08	0.00000014	9.8E-12

- 1st solution= 1,000ppm of Ca^{2+} and Mg^{2+}
- 2nd Solution= 10,000ppm of Ca^{2+} and Mg^{2+}
- 3rd Solution= 100,000ppm of Ca^{2+} and Mg^{2+}

To Reduce Nitrate

50ppm of Nitrate is the maximum contaminant concentration, or 8.06E-4 M (WHO)

Initial Activities

N(5)	3.809e-03
NO3-	3.794e-03
CaNO3+	1.481e-05
CuNO3+	7.761e-09
PbNO3+	7.492e-10
Pb(NO3)2	4.897e-12
Cu(NO3)2	2.551e-12
FeNO3+2	3.237e-19
HgNO3+	1.959e-20
Hg(NO3)2	2.409e-23

After mixing with a 48,700ppm Ca^{2+} solution

N(5)	3.809e-03
CaNO3+	3.003e-03
NO3-	8.057e-04
CuNO3+	2.618e-08
PbNO3+	1.222e-09
Cu(NO3)2	5.480e-13
Pb(NO3)2	5.088e-13
FeNO3+2	1.666e-16
HgNO3+	1.308e-20
Hg(NO3)2	1.024e-24

My Work Summary

- Ran data as a solution in PHREEQC
  - Found high iron oxides, explains yellow/red tinge
- Made a mixture of the water sample data and another liquid that could be added to purify the water of fluorine and nitrate.
  - High Ca^{2+} and Mg^{2+} to bond with fluorine
- Attempted to get nitrates to precipitate out
  - Mixture had high Ca^{2+}

Conclusion

- To purify the drinking water 48,700 ppm (48.7g/L) solution of Ca^{2+} would need to be added to lower the nitrate
- 1,000 ppm (1g/L) of Ca^{2+} and Mg^{2+} needs to be added to lower the fluoride
- That's a lot of calcium!
- Agree with Dr. Srivastava and Dr. Ramanathan
  - Drink from cleaner wells
  - Reduce fertilizer use

Sources

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