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Hydrogeochemical Modeling of Groundwater in the Gadilam River Basin, South India

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Abstract: Hydrogeochemistry of a region is a reflection of hydrodynamic process, composition of lithology and physical constraints. The water chemistry is the resultant of all biogeochemical processes and reactions, which have acted on water from the moment it has condensed in atmosphere till the time it’s discharged. A case study has been carried out in a varied lithological terrain with Archaean, Alluvium and Tertiary rocks to unravel the hydrogeochemical process. The dominant facies in the entire litho units is sodium - chloride type indicating saline nature in the groundwater. The speciation of bicarbonate, sulphate and phosphate in the groundwater samples in different litho units was determined using the computer program WATQ4F. This study reveals that higher speciation with increasing concentration of bicarbonate in summer and south west monsoon indicates static environment, whereas lesser speciation in north east monsoon and post monsoon indicates flushing environment in the basin. Higher speciation with lesser contribution of sulphate in summer and south west monsoon and an increasing trend of speciation in north east monsoon and post monsoon was observed.

Keywords: Water chemistry, Speciation model, WATQ4F, Lithology.

I. INTRODUCTION

Surface water that percolates into the ground eventually becomes groundwater which further reacts with surface and subsurface soil/sediments or rock. The chemical composition of groundwater indicates its origin and history of underground materials that the water has been in contact. Referring to this evolutionary concept, geochemists and environmental chemists have often applied the word speciation to describe the transformations

taking place during cycling of the elements. An example is the changes that occur between the leaching of trace elements from soil or rock and their subsequent distribution in the aquatic environment. However, in order to avoid confusion, we recommend using the term “species transformation” to describe such processes. The term “speciation” has often been used to indicate the analytical activity of identifying chemical species and measuring their distribution. The term speciation is also used to indicate the distribution of species in a particular sample or matrix. The term species transformation is described in speciation analysis as the activity of identifying and measuring species, and restricted the use of the term speciation in chemistry to species distribution. Chemical compounds that differ in isotopic composition, conformation, oxidation or electronic state, or in the nature of their complexed or covalently bound substituents, can be regarded as distinct chemical species. The speciation analysis of a system yields a profile of sufficiently different and measurable species for the desired level of understanding the system’s behavior. The distribution of species in a system containing both metal and ligand will depend on factors such as concentrations, stoichiometry, pH and ionic strength (Ringbom, 1963). This means that such species cannot normally be separated from each other without changes in distribution. However, the lability of inorganic complexes varies within very wide limits from complexes that form and dissociate rapidly, to systems in slow exchange, to complexes that, for most practical analytical purposes, can be considered inert.

Gadilam River originates in the hard rock region and flows through the sedimentary terrain. The important large scale extraction sites in this basin are Neyveli Lignite Corporation (NLC) and the boreholes of New Veeranam Scheme (NVS). The open cast mining of Lignite requires heavy pumping at the rate of 9,000 – 10,000 m³hr⁻¹ as water table condition has to be brought down below the level of mining (Anandhan, 2005). Water from the Veeranam Lake is supplied through transmission line to Chennai city. To augment the supply during summer season, 48 deep bore wells were drilled and operations are done alternatively to pump the groundwater from deep aquifer and the pumped water is connected to the New Veeranam Scheme (NVS) pipelines. Apart from these large scale extraction features, an industrial estate SIPCOT (Small Industries Promotion Corporation of Tamilnadu) with groups of industries, which generate multi facet chemicals and raw materials are distributed along the downstream of the River Gadilam, near the coast at Cuddalore. The aim of this study is to characterize the bicarbonate, sulphate and phosphate concentrations in the groundwater, to model the speciation based on knowledge of potential complexing ligands present in the groundwater.

sandstone of the Tertiary age is the litho units of the area. The western part of the study area is composed of hard rock and the eastern part by sedimentary formation. It is inferred as a faulted contact between the hard rock and the sedimentary formation (Aravindan et al., 2004). The basin lies between the Ponnaiyar in the north and Vellar in the south. The open wells of the study area show a range of water levels from 3.10m BGL (meters in below ground level) to 48.85m BGL with an average of 15.25m BGL in sedimentary terrain and 5.23m BGL to 7.48m BGL with an average of 6.21m BGL in hard rock terrain.

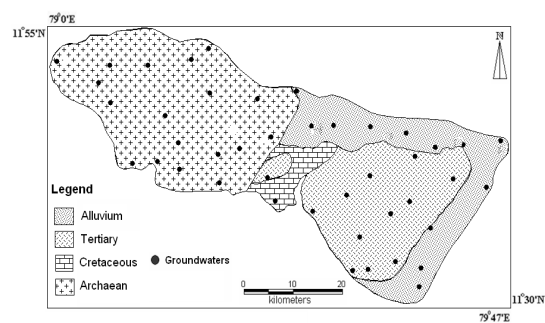


Figure 2. Geology and sampling location map

II. STUDY AREA

Area chosen for study is Gadilam River basin, which is located in Cuddalore and Villupuram district, Tamilnadu, India. The area is bounded between latitudes 11°30'N - 11°55'N and longitudes 79°0'E – 79°47'E. It covers a total area of about 1,394 sq.km (Fig. 1). Gadilam River basin covers different stratigraphic units viz. Archaean, Cretaceous, Tertiary to Recent alluvium (Fig. 2). Archaean complex consists of Garnetic gneiss,

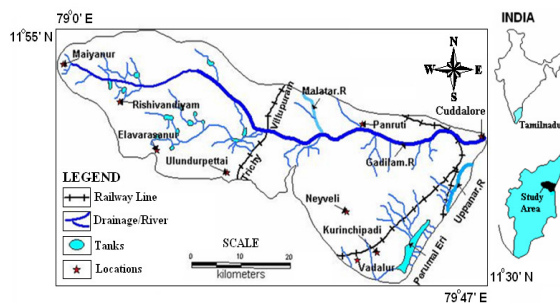


Figure 1. Location map of the study area

Charnockite, Leptinites and Schists. Limestone constitutes the cretaceous formation and Cuddalore

III. METHODOLOGY

The water samples were collected during March 2005, July 2005, November 2006, and January 2006 to broadly cover seasonal variation (Fig. 2). A total of 156 water samples were collected from bore wells in four different seasons (November 2006 represents NE monsoon; January 2006 represents Post monsoon; March 2005 represents summer; July 2005 represents SW monsoon). In summer (SUM) and south west monsoon (SWM), twelve groundwater samples was collected from Alluvium, ten groundwater samples from Tertiary, fourteen groundwater samples from Archaean and two surface water from tank. In north east monsoon (NEM) and post monsoon (POM), twelve groundwater samples was collected from Alluvium, twelve groundwater samples from Tertiary, seventeen groundwater samples from Archaean, one groundwater sample from Cretaceous, seven surface water from river and two surface water from tank. Cretaceous formation covers less than 5% of the study area. In certain location during summer and southwest monsoon periods the wells were dry. River Gadilam is an ephemeral river, the water flows only during NEM and POM periods.

The samples collected were analyzed for major cations like, Ca and Mg by Titrimetry, Na and K by Flame photometer (CL 378); anions, Cl and HCO₃ by Titrimetry, SO₄, PO₄, and H₂SiO₄ by Spectrophotometer (SL 171 minispec). EC and pH were determined in the field using electrode (Eutech). The analyses were done by adopting standard procedures (APHA, 1995). The geochemical reaction simulation model WATQ4F (Truesdell and Jones, 1973; Plummer et al. 1976) has been used to determine the solubility of equilibria for the groundwater of Gadilam River basin. The aqueous speciation is computed by an interactive process using equilibrium constant based on the Gibbs (1970) free energy of reaction.

IV. RESULT AND DISCUSSION

A. Hydrogeochemistry

Maximum, minimum and average values for groundwater samples are represented in Table 1. The total cations (TZ⁺) and total anion (TZ⁻) balance (Freeze and Cherry, 1979) is considered to show the charge balance error percentage. The error percentage in the samples of the present study ranges between ±1% to ±10%. Occurrence of errors in chemical analysis of groundwater is also due to the reagents employed, limitations of the methods and the instruments used presence of impurities in distilled water etc. The correlation coefficient between TZ⁺ and TZ⁻ is around 0.6 to 0.9. TDS / EC ratio was ranging from 0.5 to 0.9. The role played by other ions than those considered here for the cations and anions charge balance is less significant.

In Alluvium formation, Cl is the dominant anion followed by HCO₃, SO₄ and PO₄ during SUM, NEM and POM seasons. But in SWM, HCO₃ is the dominant anion followed by Cl, SO₄ and PO₄. In POM, Na is the dominant cation followed by Ca, K and Mg. But in SUM, SWM and NEM, Na is the dominant cation followed by Ca, Mg and K.

In Tertiary Formation, Cl is the dominant anion followed by SO₄, HCO₃ and PO₄ during SUM. In POM, Cl is the dominant anion followed by HCO₃, SO₄ and PO₄. In SWM, HCO₃ is the dominant anion followed by SO₄, Cl and PO₄. In NEM, HCO₃ is the dominant anion followed by Cl, SO₄ and PO₄. In SUM, NEM and POM, Na is the dominant cation followed by Ca, K and Mg. But in SWM, Na is the dominant cation followed by Ca, Mg and K.

In Archaean formation, HCO₃ is the dominant anion followed by Cl, SO₄ and PO₄ during SUM, SWM and NEM seasons. But in POM, Cl is the dominant anion followed by HCO₃, SO₄ and PO₄. In SUM, SWM and POM, Na is the dominant cation followed by Ca, K and Mg. But in NEM, Na is the dominant cation followed by Ca, Mg and K.

B. Speciation Model

The results of speciation calculations for the groundwater samples are shown in Figure 3 to 5. The results for HCO₃, SO₄ and PO₄ species for different litho units present in the study area are considered. In general, the speciation calculations indicates that HCO₃, SO₄ and PO₄ occur in the groundwater chiefly in the form of CaHCO₃, MgHCO₃ and NaHCO₃ (Carbonate complexes), CaSO₄, MgSO₄ and NaSO₄ (Sulphate complexes) and HPO₄ and H₂PO₄ (phosphate complexes).

For carbonate complexes, HCO₃ in x-axis plotted against CaHCO₃, MgHCO₃ and NaHCO₃ in Y-axis (Fig. 3). In CaHCO₃ Vs HCO₃ plot, a linearity trend was observed in Archaean and Alluvium formations during SUM and SWM. This variant may be due to static environment leads to more speciation. In NEM, samples from Archaean and Alluvium fall within a range of 100 to 410 ppm of HCO₃ with lesser speciation was noticed. In POM, a steep increasing trend of speciation with lesser contribution of HCO₃ indicates flushing environment in the basin. Lesser speciation of HCO₃ in Tertiary formation was observed in all the seasons may be due to lesser concentration of HCO₃ in the system. It was observed that higher concentration of HCO₃ leads to higher speciation in SUM and SWM and lesser speciation in NEM and POM may be due to flushing environment. In MgHCO₃ Vs HCO₃ plot, a gentle slope increasing trend was noted in Archaean and Alluvium formation during SUM and SWM indicates the higher contribution HCO₃ to form higher speciation. In NEM and POM, samples from Archaean and Alluvium group as a cluster with less speciation. In Tertiary similar trend was followed as in CaHCO₃. In NaHCO₃ Vs HCO₃ plot, higher speciation was observed in Alluvium followed by Archaean and Tertiary irrespective of season. An increasing trend in SUM and NEM and lesser speciation in SWM and POM were noticed. This indicates the higher contribution of HCO₃ speciation was observed in SUM and NEM. The saturation index of Calcite (CaCO₃) and Dolomite (CaMgCO₃) is also substantiated the same factor.

In general, higher speciation with increasing concentration of HCO_3 in SUM and SWM indicates static environment, whereas lesser speciation in NEM and POM indicates flushing environment in the basin.

For sulphate complexes, SO_4 in x-axis plotted against CaSO_4 , MgSO_4 and NaSO_4 in y-axis (Fig. 4). Higher speciation in Archæan followed by Alluvium and Tertiary was noted. In CaSO_4 Vs SO_4 plot, a steep linearity speciation of SO_4 was observed in SUM and SWM irrespective of terrains. In NEM and POM, a linearity speciation of SO_4 may be due to leaching of ions. In MgSO_4 Vs SO_4 , similar trend was followed as in CaSO_4 plot. But in SWM, samples form as a cluster within a range between 50 to 100 ppm of SO_4 respectively. In NaSO_4 Vs SO_4 plot, samples ranges between 0 to 5 ppm of NaSO_4 , indicates lesser speciation with low concentration of SO_4 in SUM. In SWM, samples form as a cluster with lesser contribution of SO_4 . In NEM and POM an increasing trend of linearity was observed indicating higher SO_4 concentration leading to higher speciation. In general higher speciation with lesser contribution of SO_4 in SUM and SWM and an increasing trend of speciation in NEM and POM was observed.

For phosphate complexes, pH in x-axis plotted against HPO_4 and H_2PO_4 in y-axis (Fig. 5). In HPO_4 Vs pH plot, samples in SUM fall within a range between 6.5 to 7.4 pH indicates higher speciation. In SWM, increasing trend of speciation with higher pH indicates higher speciation may be due to the variation of pH irrespective of terrain. This also indicates that static environment prevails in the basin will leads to higher speciation during SWM. In NEM and POM, lesser speciation indicates flushing environment due to monsoon. In H_2PO_4 Vs pH, samples irrespective of terrains form a negative relationship between pH and H_2PO_4 in SUM and SWM. Higher speciation with lesser pH in SUM and SWM indicates that the speciation was not affected by the pH. In NEM and POM, similar trend was followed as in HPO_4 Vs pH plot. In general, speciation of HPO_4 depends upon pH values and negative relationship exists between H_2PO_4 and pH in SUM and SWM. Lesser speciation during NEM and POM indicates flushing environment in the basin.

V. CONCLUSION

The geochemical study of the aquatic systems of the Gadialm River basin shows that the dominant hydrogeochemical facies of the groundwater is Na-Cl indicates alkali (Na) exceeds the alkaline earths (Ca and Mg) and strong acid exceeds (Cl) exceeds the week acids (HCO_3 and SO_4). In Speciation model, higher speciation with increasing concentration of HCO_3 in SUM and SWM indicates static environment, whereas lesser speciation in NEM and POM indicates flushing environment in the basin. Higher speciation with lesser contribution of SO_4 in SUM and SWM and an increasing trend of speciation in NEM and POM was observed. Speciation of HPO_4 depends upon pH values and negative relationship exists between H_2PO_4 and pH in SUM and SWM.

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TABLE I. MAXIMUM, MINIMUM, AVERAGE AND STANDARD DEVIATION FOR CHEMICAL COMPOSITION OF GROUNDWATER (IN MG/L) EXCEPT EC AND PH (EC IN $\mu\text{S}/\text{CM}$)

	Alluvium																
	Summer				South West Monsoon				North East Monsoon				Post Monsoon				
	Max	Min	Avg	Std	Max	Min	Avg	Std	Max	Min	Avg	Std	Max	Min	Avg	Std	F.Avg
pH	7.30	6.60	6.99	0.21	8.65	6.40	7.29	0.65	7.83	6.01	7.17	0.61	9.20	6.83	8.15	0.91	7.40
EC	6337.31	420.18	1424.31	1605.68	6278.93	387.00	1543.82	1538.59	6728.00	468.00	1829.58	1645.38	6005.00	345.00	1652.59	1621.56	1612.58
Cl	2394.01	62.03	347.77	646.29	1994.06	26.59	357.67	526.91	2782.82	96.42	498.17	734.87	2375.15	51.00	393.60	639.42	399.30
HCO ₃	677.10	48.79	289.84	241.36	1293.20	91.50	397.77	334.67	634.39	54.30	270.75	151.37	1500.59	12.20	271.44	399.28	307.45
SO ₄	341.00	23.00	96.28	84.30	189.00	27.00	90.23	39.78	368.00	1.00	69.82	106.03	312.20	5.00	107.21	85.42	90.83
PO ₄	10.10	0.25	6.08	3.76	6.80	0.10	4.20	2.55	6.60	0.01	1.25	1.92	6.80	0.00	0.90	1.97	3.11
H ₂ SiO ₄	34.00	8.10	19.02	9.15	50.00	1.60	30.06	14.15	147.50	8.80	58.60	36.30	160.00	27.00	73.92	40.62	45.40
Ca	261.33	11.00	64.11	69.41	264.00	16.00	103.14	76.12	352.00	6.00	64.33	93.63	168.00	10.00	50.16	41.09	70.44
Mg	91.20	1.00	14.47	25.00	62.39	0.00	17.09	17.51	134.40	1.00	27.51	35.31	124.80	4.79	19.50	33.78	19.64
Na	1210.03	81.00	279.94	310.56	1400.20	49.30	267.35	365.38	1091.95	74.71	317.34	274.98	1149.43	52.00	293.71	307.29	289.59
K	42.00	3.00	11.71	11.11	48.71	3.00	13.61	12.21	36.40	1.00	15.14	10.46	108.40	1.00	25.21	32.74	16.42
TDS	4436.44	267.81	994.45	1122.35	4395.25	271.00	1080.07	1077.38	4710.00	328.00	1291.44	1149.91	4204.08	242.00	1157.33	1134.97	1130.82
	Tertiary																
	Summer				South West Monsoon				North East Monsoon				Post Monsoon				
	Max	Min	Avg	Std	Max	Min	Avg	Std	Max	Min	Avg	Std	Max	Min	Avg	Std	F.Avg
pH	7.30	6.10	6.69	0.35	8.52	6.00	7.36	0.87	7.50	5.56	6.68	0.57	8.60	6.21	7.76	0.72	7.12
EC	867.00	250.00	492.93	214.50	1280.00	197.00	543.72	330.01	822.00	165.00	448.75	220.10	981.00	286.21	476.58	198.16	490.49
Cl	241.05	26.59	84.19	64.26	239.29	8.86	89.69	73.97	194.97	8.00	81.67	52.13	255.23	44.00	95.32	61.99	87.71
HCO ₃	274.50	18.30	72.51	74.60	323.30	36.60	100.65	81.60	195.19	12.20	84.36	55.25	195.10	24.40	72.52	46.72	82.51
SO ₄	171.00	0.07	3.92	4.69	247.00	18.00	98.60	66.33	196.00	0.01	50.29	63.45	141.00	7.00	46.89	38.38	71.22
PO ₄	10.10	0.00	3.40	3.13	33.60	1.00	8.48	10.03	14.40	0.00	6.51	4.35	14.40	1.00	6.40	4.20	6.20
H ₂ SiO ₄	69.00	18.10	31.62	17.51	54.00	7.30	27.16	15.29	72.40	8.00	39.37	18.93	120.00	18.00	68.38	27.02	41.63
Ca	55.99	8.00	24.90	14.18	88.00	10.00	36.00	27.36	40.00	6.00	23.16	11.83	34.00	10.00	22.08	7.78	26.54
Mg	9.00	0.00	3.40	3.13	33.60	1.00	8.48	10.03	14.40	0.00	6.51	4.35	14.40	1.00	6.40	4.20	6.20
Na	195.40	45.98	91.53	51.13	272.00	1.80	82.49	83.15	191.00	6.00	69.56	61.11	183.91	22.99	72.30	45.89	78.92
K	14.00	0.00	4.60	4.70	21.90	1.00	7.01	6.71	14.60	1.00	7.68	3.89	23.90	1.00	7.41	5.71	6.68
TDS	646.27	175.00	349.06	158.05	897.22	138.76	380.88	231.05	633.30	122.60	319.83	162.71	687.00	200.35	329.56	140.48	344.83
	Archaeal																
	Summer				South West Monsoon				North East Monsoon				Post Monsoon				
	Max	Min	Avg	Std	Max	Min	Avg	Std	Max	Min	Avg	Std	Max	Min	Avg	Std	F.Avg
pH	8.10	6.73	7.14	0.33	8.00	6.80	7.14	0.32	8.60	6.78	7.46	0.41	9.20	8.10	8.52	0.32	7.56
EC	2610.32	657.13	1500.32	580.51	2725.89	618.29	1498.53	642.83	2810.00	617.00	1364.24	591.00	2574.00	490.37	1129.36	583.25	1373.11
Cl	771.03	59.03	342.01	225.96	771.03	53.17	361.46	248.08	638.10	35.44	233.55	152.64	620.37	35.45	229.38	168.76	291.60
HCO ₃	524.60	284.50	425.76	90.61	579.50	274.50	416.11	92.70	414.79	183.00	278.44	84.44	268.39	109.80	185.15	48.27	326.36
SO ₄	124.60	43.00	70.97	21.56	158.20	53.40	87.03	28.66	336.22	1.50	67.27	98.55	288.18	4.00	116.98	82.67	85.56
PO ₄	15.00	4.80	8.76	2.75	6.40	3.80	5.36	0.81	3.60	0.20	0.75	1.01	1.60	0.00	0.18	0.40	3.76
H ₂ SiO ₄	63.00	5.80	27.10	21.81	53.00	21.20	39.63	10.19	94.00	6.60	50.08	28.69	120.00	22.00	72.82	28.03	47.41
Ca	225.99	35.99	108.14	50.11	240.00	55.99	143.00	61.72	111.99	23.99	56.47	27.78	96.00	18.00	49.05	24.64	89.16
Mg	40.80	4.79	20.50	13.82	52.80	4.79	24.25	18.19	33.59	4.80	16.35	7.99	24.00	0.00	12.98	6.95	18.52
Na	405.00	55.20	231.60	90.11	491.00	50.30	188.58	122.44	581.20	69.80	192.60	129.67	551.72	54.90	188.04	128.68	200.21
K	208.00	1.00	56.11	66.48	115.30	3.30	31.24	34.95	17.40	9.40	10.12	1.93	78.00	6.60	14.95	17.78	28.11
TDS	1827.23	459.99	1050.22	406.35	1908.12	432.80	1048.97	449.98	1967.00	436.00	972.94	403.76	1802.47	343.26	795.56	409.11	983.92

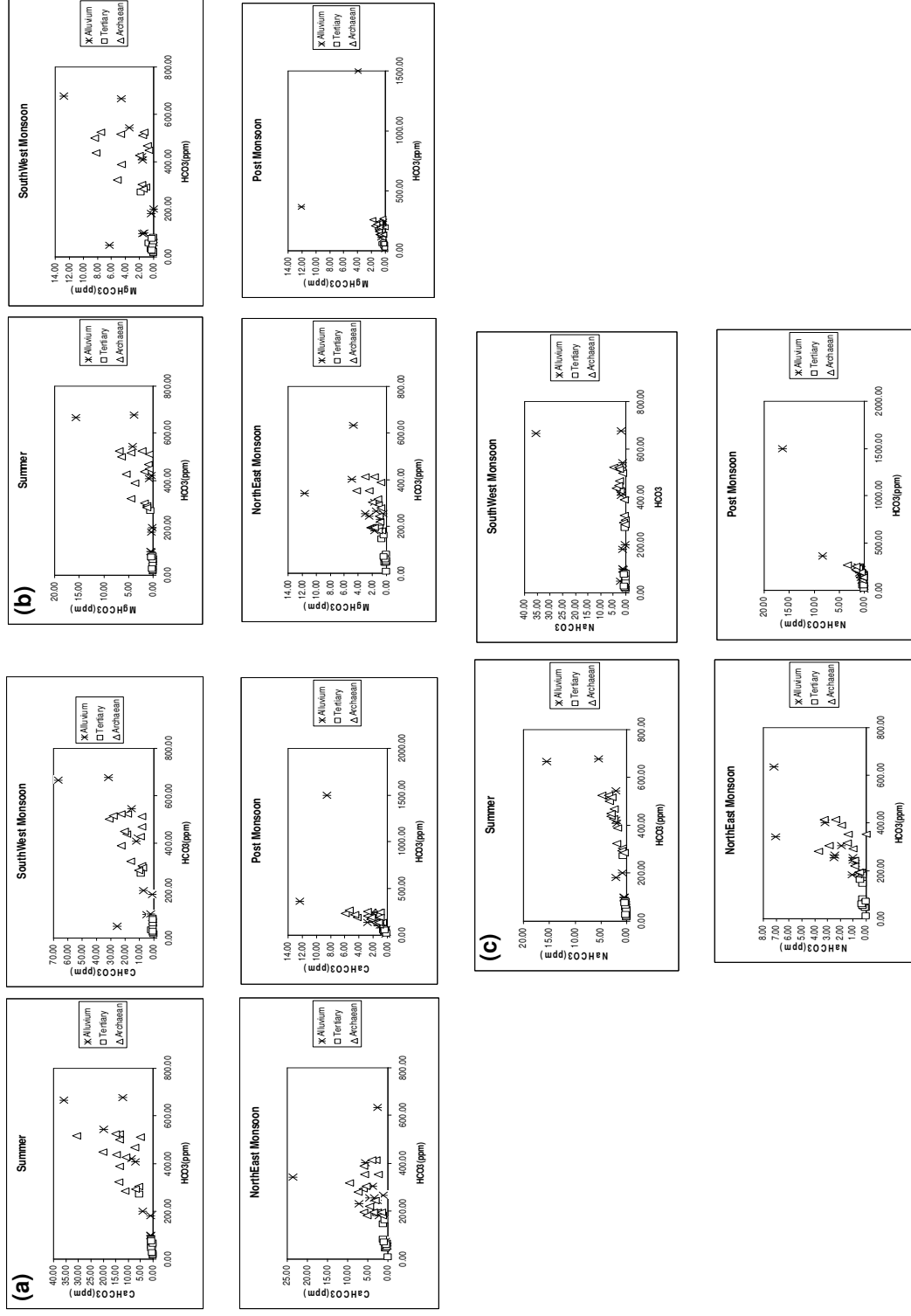


Figure 3. Speciation of Carbonate complexes in groundwater (a) CaHCO₃ (b) MgHCO₃ (c) NaHCO₃

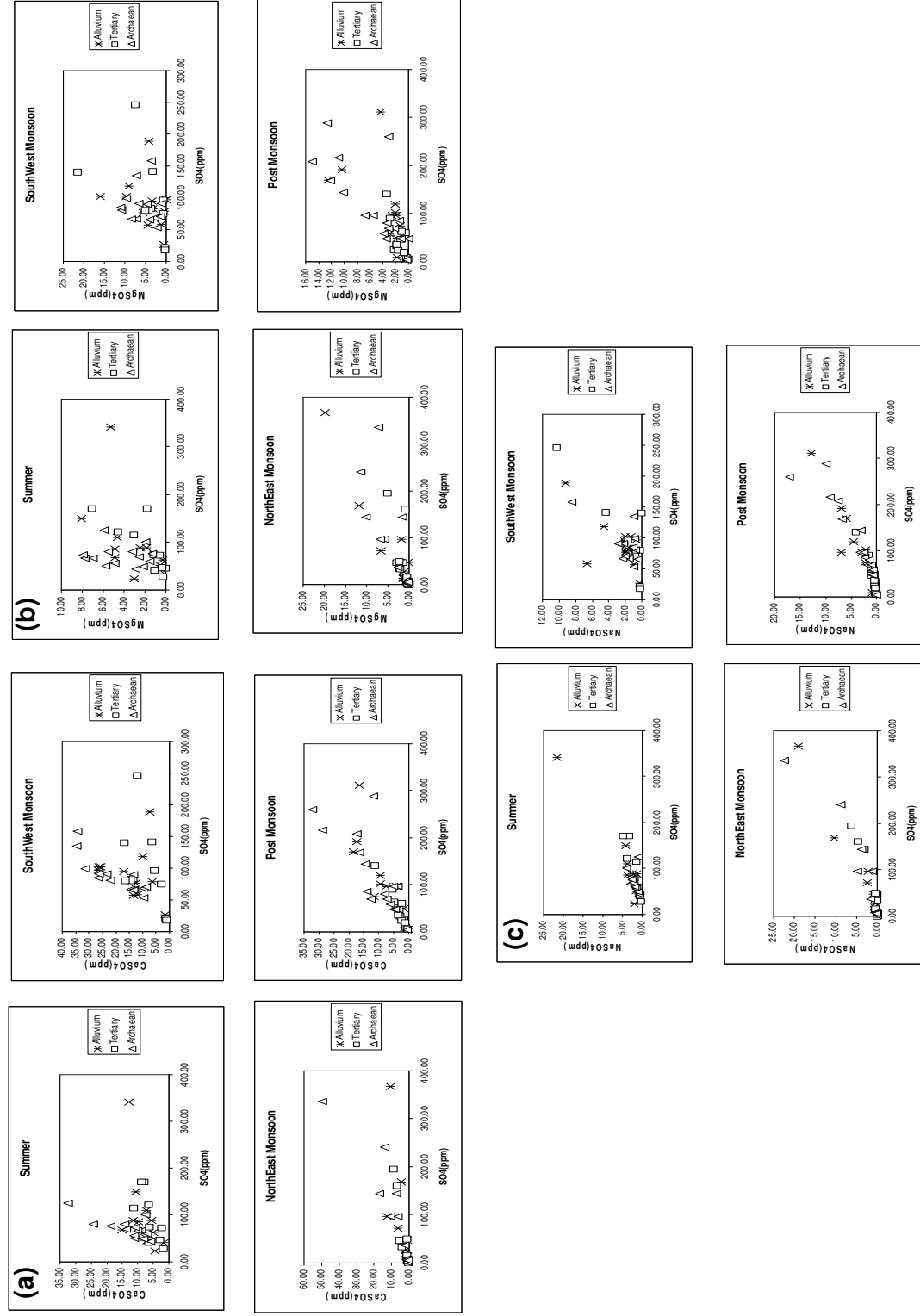


Figure 4. Speciation of Sulphate complexes in groundwater (a) CaSO₄, (b) MgSO₄, (c) Na₂SO₄

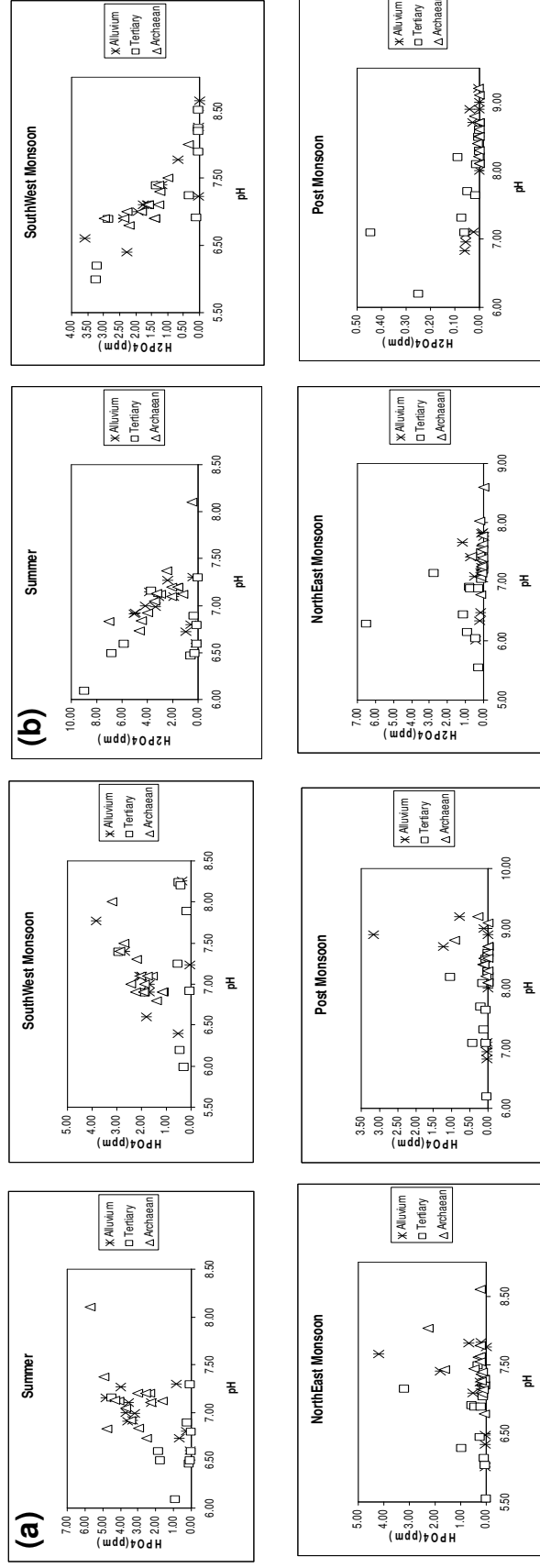


Figure 5. Speciation of Phosphate complexes in groundwater (a) HPO₄ (b) H₂PO₄