

# Speciation of Ions in Groundwater and its Applications

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## ABSTRACT

Speciation of ions in groundwater is very important to understand its hydrogeochemical evolutions from its origin to its present status. The speciation will help to understand the geochemical process which controls their evolution and their present day environmental conditions which will ultimately lead us to utilize them directly or after the required treatment process to make them safe and useable. Some of the ions and their speciation were discussed in this line in this chapter.

## INTRODUCTION

Water is the most powerful solvent of geochemical materials and plays the main role in their continuous redistribution in the environment, below, at and above the land surface. This capability of water is the result of a unique structure of the water molecule, which has an asymmetric distribution of the hydrogen nuclei with respect to the oxygen nucleus and the two pairs of unshared electrons. Water molecules are connected between themselves with strong hydrogen bonds: hydrogen atom (proton) of one molecule is bonded to the negatively charged side of another water molecule. Groundwater is an important part of earth's hydrologic cycle or movement of water between oceans, atmosphere and land. Groundwater is derived mostly from percolation of precipitation and to a lesser degree from surface water streams and lakes

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that lose water to underlying aquifers. Only minute quantities of groundwater have their origin from processes in the deeper crust, associated with magmatism (this water is often called juvenile water). Groundwater from aquifers and aquitards discharges to fresh surface water bodies on land and to oceans. This discharge is either concentrated via springs and seeps, or directly into surface water bodies, where it is normally not visible. The volume of groundwater stored and moving through aquifers and aquitards in the upper portion of earth's crust is much larger than any other form of mobile freshwater on earth, excluding glaciers and ice caps.

Groundwater contains a wide variety of dissolved inorganic species in various concentrations, as a result of chemical and biochemical interactions between groundwater and the geological materials through which it flows, and to a lesser extent because of contribution from the atmosphere and surface water bodies. The availability of various inorganic constituents in groundwater is controlled by the reaction mechanism such as dissolution-precipitation reactions and adsorption in addition to the rates (kinetics) of the geochemical process. Analytical techniques such as spectrometry and chromatography provide important information about the total metals concentration available in water, but ions in groundwater can form unlimited number of species due to the hydrolysis, complexation and redox reactions.

### **Major Cations**

Calcium and magnesium are predominantly sourced from dissolution of carbonate minerals, especially calcite ( $\text{CaCO}_3$ , which can also contain significant quantities of Mg) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), both of which are abundant in limestone terrains. Calcite is also a common cementing phase in many sandstones. In some sedimentary sequences, beds comprising the highly soluble minerals gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and anhydrite ( $\text{CaSO}_4$ ) can act as important source of dissolved Ca. In some cases, the dissolution of gypsum over geological time has led to the development of extensive cave systems (Klimchouk et al., 1996) of equal magnitude to the more common cave systems found in limestones.

Many silicate minerals are also important sources for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in groundwater for instance, in the so called ultrabasic and basic igneous rock (including basalt lavas), dissolved Ca and Mg are derived from the weathering of anorthitic plagioclase ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), diopsidic pyroxene ( $\text{CaMgSi}_2\text{O}_6$ ), and forsteritic olivine ( $\text{Mg}_2\text{SiO}_4$ ). In more acidic igneous rocks such as rhyolite tuffs and granites, and in the many sedimentary rocks derived from them, common sources for Ca and Mg include hornblende ( $\text{Ca}_2\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$ ) and Biotite mica ( $\text{K}(\text{Mg,Fe})_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ ). In contrast to the carbonate minerals which tend to dissolve completely in water without depositing any new solid phases

(so called congruent dissolution), these silicate minerals are all subject to incongruent dissolution, in which the release of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SiO}_2$  to solution is accompanied by simultaneous precipitation of clay minerals. The formation of clay minerals effectively traps nearly all of the aluminium (and much of the  $\text{SiO}_2$ ) in solid form.

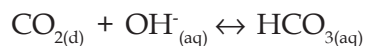
Silicate weathering is also a common source for dissolved  $\text{Na}^+$  and  $\text{K}^+$ . Most plagioclase feldspars contain at least some  $\text{Na}^+$ , and in many acidic igneous rocks and associated sediments, the Na rich plagioclase predominates, with a composition close to that of pure albite ( $\text{NaAlSi}_3\text{O}_8$ ). The same types of rock are similarly enriched in potassium feldspars ( $\text{KAlSi}_3\text{O}_8$ ) of various varieties, including sanidine (common in rhyolite tuffs and lavas), orthoclase (which forms the conspicuous pink mega crystals in many granites), and microcline (common in many coarse grained granites and hydrothermal veins). Because  $\text{Na}^+$  and  $\text{K}^+$  are both so soluble, neither of them forms carbonate minerals. However, they are abundantly present in the minerals halite ( $\text{NaCl}$ ) and sylvite ( $\text{KCl}$ ) which are both common constituents of ancient "evaporite" (i.e., salt lake) deposits, formed under hyper arid conditions. When such minerals gain access to modern groundwaters, they tend to dissolve so vigorously that they yield many thousands of mg/L of  $\text{Na}^+$  and  $\text{K}^+$  to solution.

### Major Anions

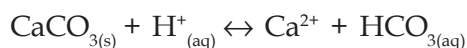
Anions which are present in the greatest concentrations (all > 1 mg/L) in most groundwaters are bicarbonate ( $\text{HCO}_3^-$ ), sulphate ( $\text{SO}_4^{2-}$ ) and chloride ( $\text{Cl}^-$ ). Although modest concentration of all three anions are introduced to aquifers in rainwater, even after evaporative concentration during the recharge process their rainwater derived concentrations seldom exceed about 20 mg/L.

Bicarbonate dissolved in groundwater is derived from two principal natural sources:

- **Biogenic:**  $\text{CO}_2$  is released into the soil atmosphere, and thus into waters draining through the soil, both directly from plant roots and (more importantly) by the microbial degradation of soil organic matter. A circum-neutral pH,  $\text{CO}_2$  dissolves in water to form bicarbonates as follows:



- **Minerals:** The dissolution of the same carbonate minerals which release  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to solution also yield abundant dissolved  $\text{HCO}_3^-$



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Sulphate dissolved in groundwaters has two principal natural sources:

- Weathering of sulphide minerals, most commonly pyrite  $\text{FeS}_{2(s)} + 3.5\text{O}_{2(g)} + \text{H}_2\text{O} \rightarrow \text{Fe}_{(aq)}^{2+} + 2\text{SO}_{4(aq)}^{2-} + 2\text{H}_{(aq)}^{+}$
- Weathering of gypsum and/or anhydrite, as already mentioned in relation to  $\text{Ca}^{2+}$  release.

Besides being a common source of dissolved  $\text{SO}_4^{2-}$ , gypsum also serves to impose an upper limit on sulphate concentration in most groundwater due to its maximum solubility limit of around 2500 mg/L, which is frequently reached in water which receives their  $\text{SO}_4^{2-}$  from pyrite oxidation (Younger et al. 2002a).

Chloride is one of the least reactive solutes found in groundwater, and as such it has very few natural mineral sources. Clearly where the evaporite minerals halite and sylvite are encountered by flowing groundwater, very high concentration of  $\text{Cl}^-$  can result. Beyond these evaporite minerals, few others dissolve to release  $\text{Cl}^-$ . One exception is sodalite ( $\text{Na}_4(\text{Si}_3\text{Al}_3)\text{O}_{12}\text{Cl}$ ), a minerals found in some (rather rare) alkaline igneous rocks. Given the sparsity of mineral sources for  $\text{Cl}^-$ , it can often be a very effective index of the degree of evaporation a given groundwater must have undergone after first arriving at the soil surface as rainwater. In many hydrogeological settings, concentration of  $\text{Cl}^-$  much greater than can be accounted for by evaporative concentration of rainwater can be taken to indicate that the groundwater in question actually represents a mixture of different water sources. Sea water is, of course very rich in chloride (averaging 18,980 mg/L), so that  $\text{Cl}^-$  concentrations can be a sensitive indicator of the intrusion of marine groundwater into terrestrial aquifers.

Many ancient groundwater trapped at depth in sedimentary aquifers are notably rich in  $\text{Cl}^-$ . In some cases, these ancient waters can be shown to be trapped sea waters which entered the aquifer during periods of the Quaternary when the relative positions of the land and sea were rather different than at present (Elliot et al., 2001). In other cases, the high  $\text{Cl}^-$  content of a deep-seated groundwater may reflect: (i) an ancient history of evaporation in the near-surface environment; (ii) dissolution of evaporite rocks at depth; or (iii) enrichment of solute concentration due to natural membrane filtration (Freeze and Cherry 1979). This is thought to occur at very great depths in some sedimentary basins, where the natural head gradient forces groundwater to flow through a mudstone bed which has pores so small that they even prevent the migration of solutes. The result is that hyperconcentrated brine accumulates on the upgradient side of the mudstone bed.

### Minor Ions

Having identified the major cations and anions present in most waters, it is important to note that there are a number of other ions which are usually present

at concentrations in the range 0.01–1 mg/L, but which are occasionally present at far higher concentrations, such that they can locally be regarded as major ions. Substances in this category include ferrous iron ( $\text{Fe}^{2+}$ ), manganese ( $\text{Mn}^{2+}$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), hydrogen sulphide ( $\text{HS}^-$ ), fluoride ( $\text{F}^-$ ), and boron ( $\text{B}^+$ ). Every one of these ions is problematical in relation to water use.

### **Trace Ions**

Virtually the entire periodic table can presently occur in groundwaters at low concentrations (typically  $< 0.01$  mg/L). Where the ions in quantification are toxic to humans (e.g.,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) and/or to wildlife (e.g.,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ) their importance in practical terms may far outweigh their contribution to the TDS of the water.

### **Inorganic Compounds and Complexes**

The distribution of an element among different inorganic compounds profoundly affects its transport and bioavailability by determining such properties as charge, solubility, and diffusion coefficient. Complexation reactions with inorganic ligands produce coordination complexes with varying stabilities. 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.

The interplay between kinetic and thermodynamic control of speciation can give rise to surprising effects. In the United Kingdom and Norway, it was found that the mixing of two waters, one acidic with high concentration of labile monomeric aluminum and the other with high pH, had serious effects on fish. In the actual mixing zone the water was considerably more toxic than any of the components on their own. The cause was found to be the formation of transient polymeric aluminium-hydroxo complexes with high toxicity and minutes later, the extreme toxicity was gone (Rosseland et al., 1992; Verbost et al., 1995).

A large variety of inorganic complexes can be found in the environment (Ure and Davidson, 1995; Tessier and Turner, 1995). Anions such as  $\text{SO}_4^{2-}$  and  $\text{Br}^-$  generally form weak complexes which are not very important in open fresh waters. However, in certain waters such as well water or soil solutions and in marine waters they may be important. Other anions such as  $\text{F}^-$  and  $\text{CO}_3^{2-}$  are important for specific elements.

### **Aqueous Complexes**

Ions in aqueous solution become attached to each other as ion pairs or aqueous

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complexes. Examples are major cation complexes like  $\text{CaSO}_4^0$ ,  $\text{CaF}^+$  or  $\text{CaOH}^+$ , but also heavy metals complexes exist like  $\text{CdCl}^+$ ,  $\text{HgCl}_3^-$  or  $\text{PbOH}^+$  and metal complexes with an organic ligand like oxalate, for example,  $\text{CuC}_2\text{O}_4$ . The complexes may be outer sphere, with water molecules present in between the constituent ions of the complex, or inner sphere when a covalent bond is formed and water molecules that surrounded the ions have been expelled. The inner/outer sphere state is gradual and fluctuates in time (Burgess 1988). Complexation will lower the activity of the “free” ion in water, thereby increasing the solubility of minerals and also the mobility of trace metals. Grassi and Netti (2002) found that the Hg concentration in groundwater in a coastal aquifer increased with the  $\text{Cl}^-$  concentration, apparently due to complexing of  $\text{Hg}^{2+}$  and  $\text{Cl}^-$  resulting in the solubilisation of Hg from the rock. Complexes may have detoxifying effects, and heavy metal poisoning can be abated by ingesting a strong complexer such as EDTA (ethylene-diamine-tetra-acetate). Complexation finds important application in analytical chemistry and separation technology and in the production of food and medicines.

The majority of complexes consist of a metal cation, surrounded by a number of ligands (Burgess, 1988; Stumm and Morgan, 1996). For examples,  $\text{Al}^{3+}$  in water is surrounded by 6 water molecules which together form the octahedrally shaped complex  $\text{Al}(\text{OH}_2)_6^{3+}$ . Depending on the pH, protons are released from the complex and its charge increases:



This complex is usually written simplified as  $\text{AlOH}^{2+}$ .

### Combined Complexes and Activity Corrections

Both aqueous complexing and activity coefficients will lower the activity of the free ions, and their combined effect must be calculated. The total amount of  $\text{Ca}^{2+}$  in solution is given by a mass balance equation comprising the various aqueous complexes of  $\text{Ca}^{2+}$ , given in molal units:

$$\Sigma \text{Ca} = m\text{Ca}^{2+} + m\text{CaF}^+ + m\text{CaSO}_4^0 + m\text{CaOH}^+$$

Similar mass balance equations can be written for all other substances in solution. In order to calculate the activities of, for example,  $[\text{Ca}^{2+}]$  and  $[\text{SO}_4^{2-}]$ , we have to solve simultaneously a set of mass balance equations, with concentrations in molal units, and a set of mass action equations with concentrations expressed as activities. The calculation proceeds through an iterative procedure. From the analytical data, first the activity coefficients and ion activities are calculated, which are used to calculate activities of complexes.



Then the molal concentrations of complexes are obtained which enables us to calculate improved mass balances and thereby a better estimate of the ionic strength. This procedure continues until no further significant improvement is obtained.

The importance of complexing and activity corrections, expressed as percentage of the total concentration, is illustrated for sea water in Fig. 1. For  $\text{Na}^+$  and  $\text{Cl}^-$  the effect of complexing is small which activity coefficients make the ultimate activity 30-40% lower than the total concentration. For the divalent ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , about 10% of the total concentration is complexes, which the activity of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , with the activity coefficient correction goes down to 20-30% of the total concentration. For  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  an aqueous complex constitutes 40-50% of the total concentration, and the activity of the free  $\text{SO}_4^{2-}$  ion is about 10% of the total concentration.

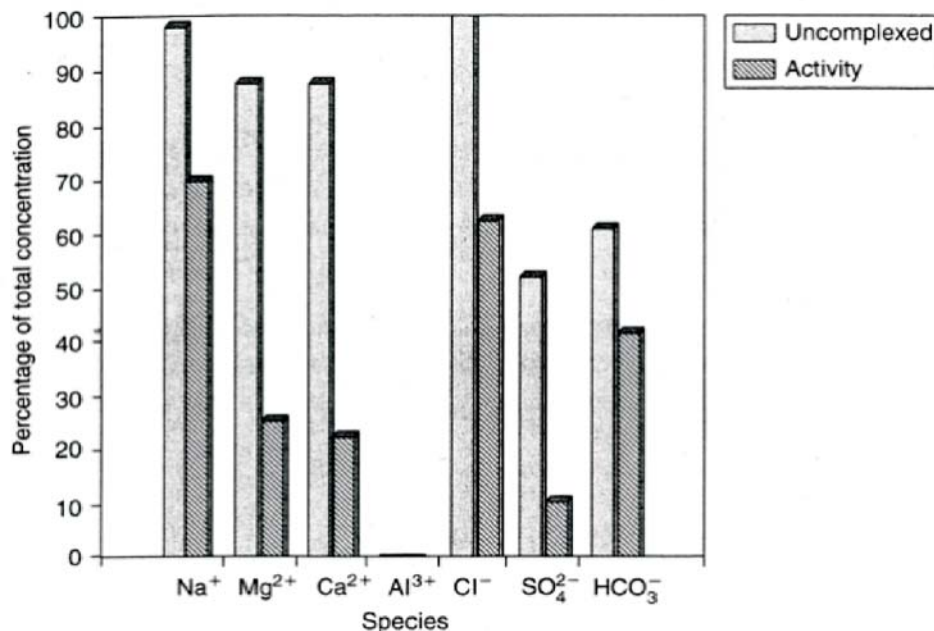


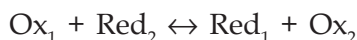
Fig. 1. The importance of complexing and activity corrections as percentage of total concentrations for 35‰ sea water with a pH of 8.22.

### Redox Reactions

Acid-base reactions play a very important role in weathering and other processes controlling the compositions of natural waters. There is an additional, analogous set of reactions that also play an important role in governing the compositions of natural waters, but that involve the transfer of electrons among species. These are reduction-oxidation (redox) reactions. Oxidation is where a species loses electrons, and reduction is where a species gains electrons.

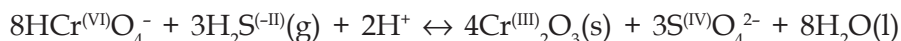
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Unlike protons, hydrated electrons do not exist in solution. Thus, electrons lost from one species must be immediately accepted by another species. In other words, oxidation-reduction processes are always paired, as shown in the schematic reaction,



In this reaction, the oxidized species  $\text{Ox}_1$  reacts with reduced species  $\text{Red}_2$  to form the reduced species  $\text{Red}_1$  and the oxidized species  $\text{Ox}_2$ . In the above,  $\text{Ox}_1$  is the oxidant and  $\text{Red}_2$  is the reductant, when the reaction runs from left to right.

Comprehending redox reactions is important to understanding the controls on the composition of natural waters. Many metals are far more mobile in one redox state than another.



In the above reaction, Cr(VI) is quite soluble as  $\text{HCrO}_4^-$ , but Cr(III) is essentially insoluble as  $\text{Cr}_2\text{O}_3(\text{s})$ . Here  $\text{H}_2\text{S}(\text{g})$  as the reductant, but others also might be important in nature, e.g.,  $\text{H}_2$ ,  $\text{FeS}_2$ ,  $\text{NH}_4^+$ , etc. When a metal is more soluble, it is more mobile (it can migrate longer distances) and more bioavailable (it can more readily cross cell membranes). Not only is Cr(VI) more soluble and mobile, it is also much more toxic than the less mobile Cr(III).

In the species  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ , we have Cr(VI), whereas in  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}_2\text{O}_3(\text{s})$  and  $\text{CrO}_2^-$  we have Cr(III). Among the oxidized species, the order of decreasing acidity is  $\text{HCrO}_4^- > \text{CrO}_4^{2-}$ , whereas among the reduced species, it is  $\text{Cr}(\text{OH})^{2+} > \text{Cr}_2\text{O}_3(\text{s}) > \text{CrO}_2^-$  (Fig. 2).

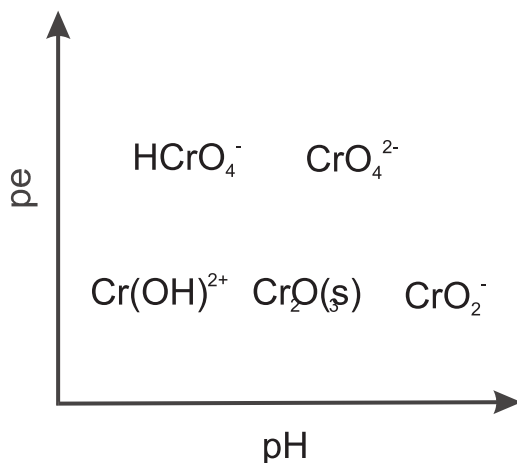
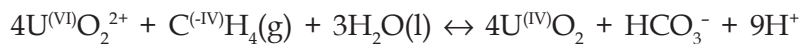


Fig. 2. Schematic diagram showing the approximate locations of Cr species and phases in pe-pH space.





In the above reaction, U(VI) is very mobile as  $\text{UO}_2^{2+}$  (uranyl ion), but when reduced by methane, it becomes insoluble as the mineral uraninite ( $\text{UO}_2$ ). A reaction such as that shown was probably responsible for depositing uraninite during the formation of many uranium deposits. The reaction also teaches us that, if we want to keep uranium from migrating away from a nuclear waste repository where spent nuclear fuel is stored, we must arrange to keep the repository reducing. This could be accomplished by incorporating graphite in the waste form, for example, U(IV) aqueous speciation in carbonate solution is pH depend (Fig. 3). If the  $\text{pH} < 5$ ,  $\text{UO}_2^{2+}$  is dominant, whereas  $\text{pH} > 8$ , gives carbonate species.

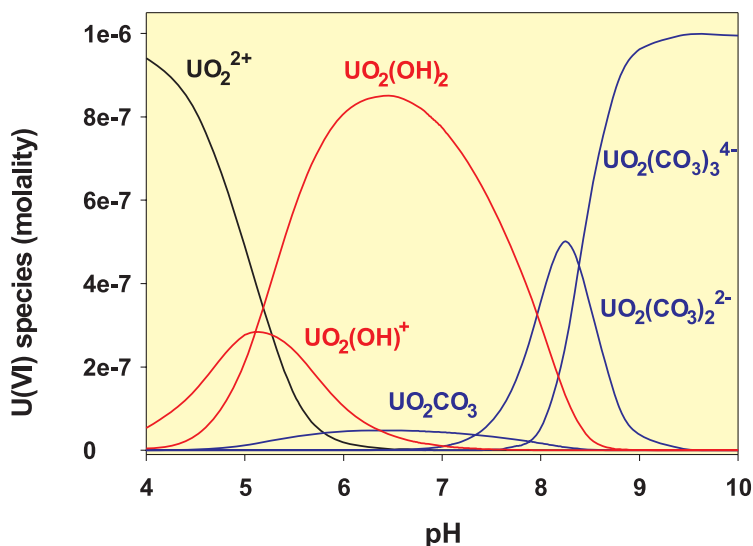


Fig. 3.  $\text{UO}_2^{2+}$  aqueous speciation in carbonate solutions.

### Case Study in South India

The speciation of bicarbonate ( $\text{HCO}_3$ ) and sulphate ( $\text{SO}_4$ ) in groundwater samples in different stratigraphic units of Gadilam river basin, Tamilnadu, South India was determined using the computer program WATQ4F (Trusdel and Jones, 1973). The aim of this study was to characterize the  $\text{HCO}_3$  and  $\text{SO}_4$  concentrations in the groundwater, to model the speciation based on knowledge of potential complexing ligands present in the groundwater. The speciation calculations indicates that  $\text{HCO}_3$  and  $\text{SO}_4$  occur in the groundwater chiefly in the form of  $\text{CaHCO}_3$ ,  $\text{MgHCO}_3$  and  $\text{NaHCO}_3$  (Carbonate complexes) and  $\text{CaSO}_4$ ,  $\text{MgSO}_4$  and  $\text{NaSO}_4$  (sulphate complexes). Previous work on such speciation of rare earth elements in groundwater was done by Shand et al. (1995).

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For carbonate complex studies in groundwaters of Gadilam river basin (Prasanna 2008),  $\text{HCO}_3^-$  was taken as x-axis plotted against  $\text{CaHCO}_3$ ,  $\text{MgHCO}_3$  and  $\text{NaHCO}_3$  in y-axis (Fig. 4, 5 and 6). In  $\text{CaHCO}_3$  vs  $\text{HCO}_3^-$  plot, a linearity

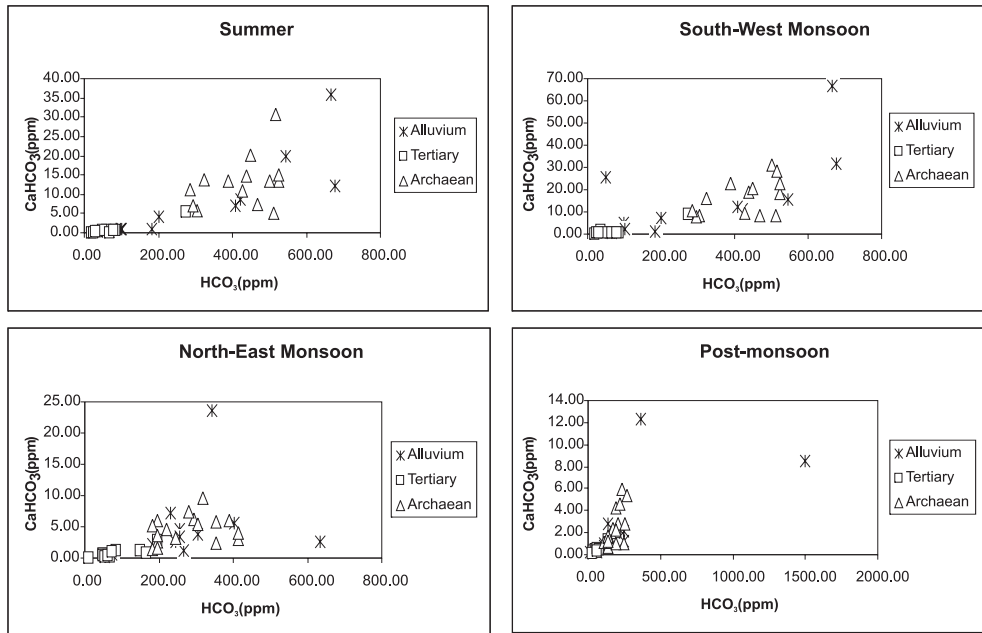


Fig. 4. Speciation of carbonate complexes ( $\text{CaHCO}_3$ ) in groundwater.

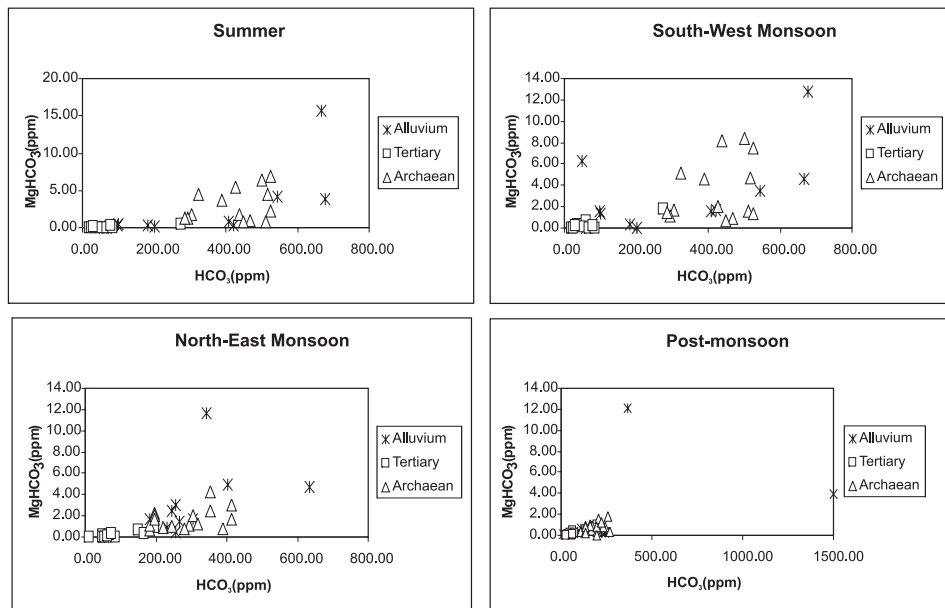


Fig. 5. Speciation of carbonate complexes ( $\text{MgHCO}_3$ ) in groundwater.

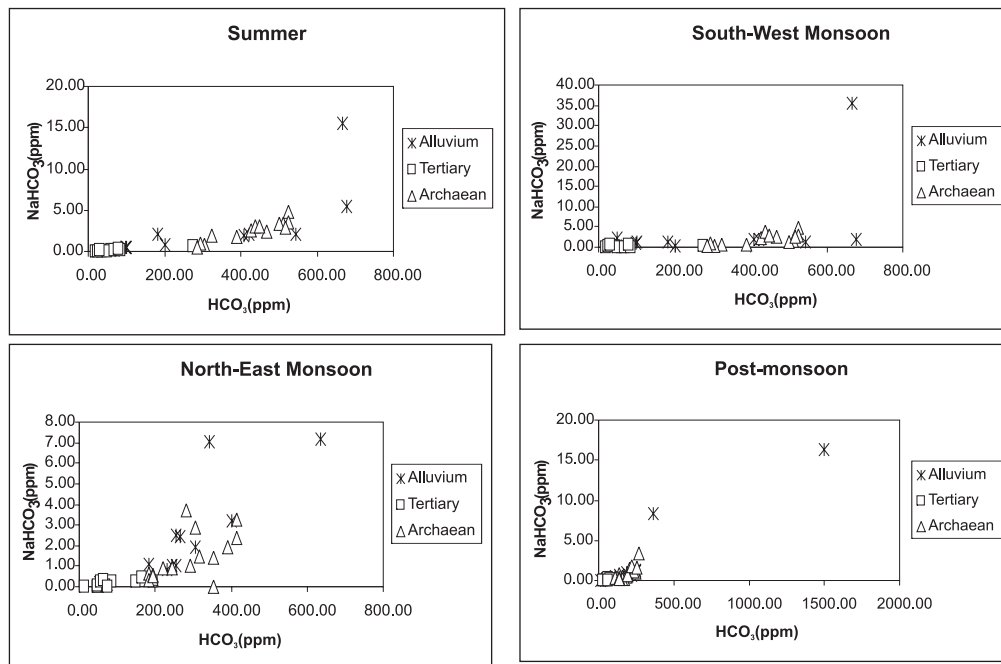


Fig. 6. Speciation of carbonate complexes ( $\text{NaHCO}_3$ ) in groundwater.

trend was observed in Archaean and Alluvium formations during summer (SUM) and south-west monsoon (SWM). This variant may be due to static environment leads to more speciation. In north-east monsoon (NEM), samples from Archaean and Alluvium fall within a range of 100 to 410 ppm of  $\text{HCO}_3$  with lesser speciation was noticed. In post-monsoon (POM), a steep increasing trend of speciation with lesser contribution of  $\text{HCO}_3$  indicates flushing environment in the basin. Lesser speciation of  $\text{HCO}_3$  in tertiary formation was observed in all the seasons may be due to lesser concentration of  $\text{HCO}_3$  in the system. It was observed that higher concentration of  $\text{HCO}_3$  leads to higher speciation in SUM and SWM and lesser speciation in NEM and POM may be due to flushing environment. In  $\text{MgHCO}_3$  vs  $\text{HCO}_3$  plot, a gentle slope increasing trend was noted in Archaean and Alluvium formation during SUM and SWM indicates the higher contribution  $\text{HCO}_3$  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  $\text{CaHCO}_3$ . In  $\text{NaHCO}_3$  vs  $\text{HCO}_3$  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  $\text{HCO}_3$  speciation was observed in SUM and NEM. In general, higher speciation with increasing concentration of  $\text{HCO}_3$  in SUM and SWM

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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. 7, 8 and 9). Higher speciation in Archaean followed by

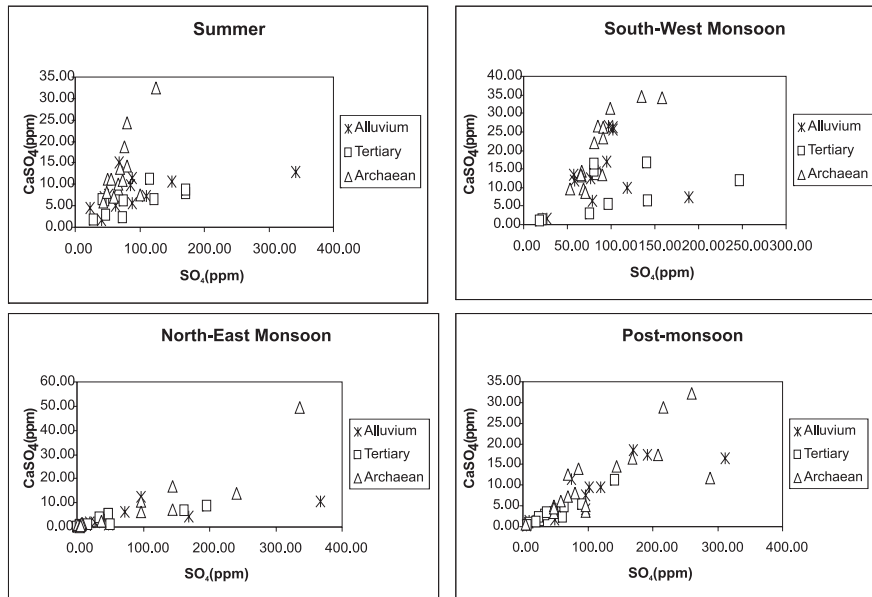


Fig. 7. Speciation of sulphate complexes ( $CaSO_4$ ) in groundwater.

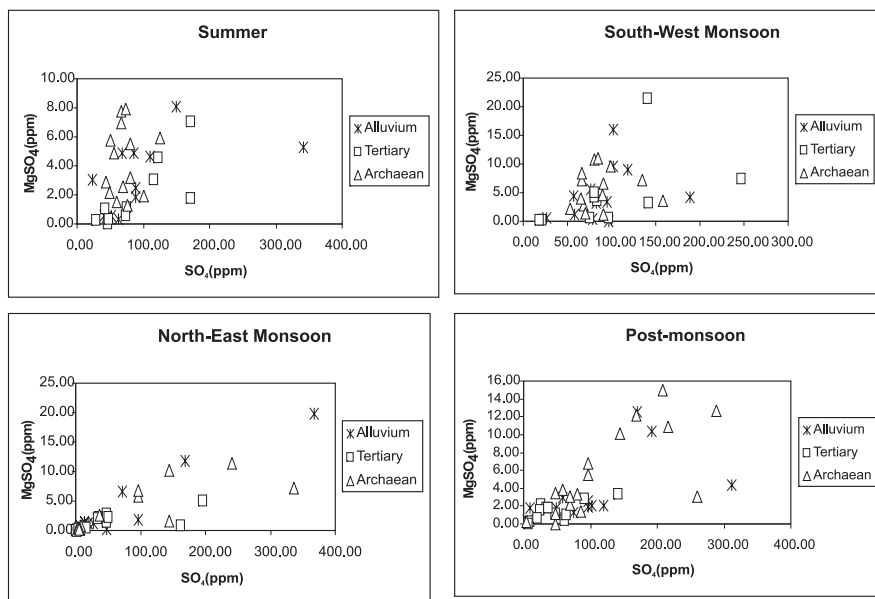


Fig. 8. Speciation of sulphate complexes ( $MgSO_4$ ) in groundwater.

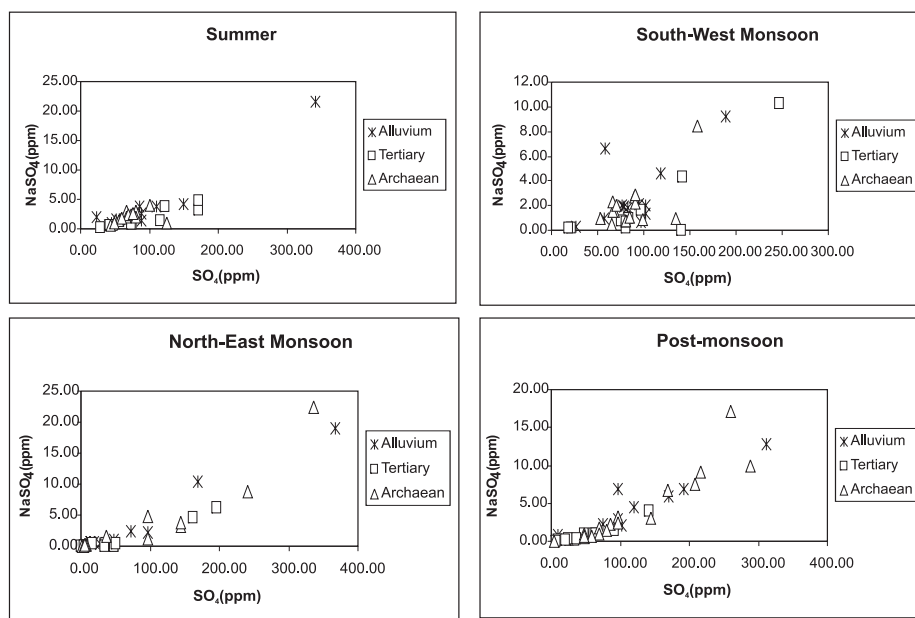


Fig. 9. Speciation of sulphate complexes ( $\text{NaSO}_4$ ) in groundwater.

Alluvium and Tertiary was noted. In  $\text{CaSO}_4$  vs  $\text{SO}_4$  plot, a steep linearity speciation of  $\text{SO}_4$  was observed in SUM and SWM irrespective of terrains. In NEM and POM, a linearity speciation of  $\text{SO}_4$  may be due to leaching of ions. In  $\text{MgSO}_4$  vs  $\text{SO}_4$ , similar trend was followed as in  $\text{CaSO}_4$  plot. But in SWM, samples form as a cluster within a range between 50 and 100 ppm of  $\text{SO}_4$  respectively. In  $\text{NaSO}_4$  vs  $\text{SO}_4$  plot, samples ranges between 0 and 5 ppm of  $\text{NaSO}_4$ , indicates lesser speciation with low concentration of  $\text{SO}_4$  in SUM. In SWM, samples form as a cluster with lesser contribution of  $\text{SO}_4$ . In NEM and POM an increasing trend of linearity was observed indicating higher  $\text{SO}_4$  concentration leading to higher speciation. In general, higher speciation with lesser contribution of  $\text{SO}_4$  in SUM and SWM and an increasing trend of speciation in NEM and POM was observed.

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