

Hydro-Geochemical Plots: An Efficient Tool for the Elucidation of Groundwater Chemistry

P. S. Ganvir

Assistant Professor, Department of Geology,
M. G. Arts, Science and Late N. P. Commerce College
Armori, Maharashtra (India).

Abstract:- The interpretation of the groundwater chemistry is an utmost vital procedure in any of the groundwater contamination study. The generation of the groundwater chemistry data inform of major ions and its interpretation are an utterly two diverse dealings. The generated groundwater chemistry data seems insignificant without the appropriate interpretation. To depict a comprehensive picture of the groundwater chemistry and to understand the liable dynamics, the hydro-geochemical plots are the usual tools to be engaged with. The Stiff's, Piper, Chadha's and Gibbs plots are the utmost encouraging tools for the hydro-geochemical interpretation; of them the Piper plot have versatile implications. Before subjecting the generated groundwater chemistry data to the interpretation procedures by the various plots, methodical operations over the data are required to be done. These operations includes ion balancing and conversions to mEq./l from mg/l. Only the furnished data are worthy enough to be subjected into different plots and to achieve the resourceful yields. In an entire investigation, the Piper plot was found to be most promising hydro-geochemical interpretation tool, generating an inclusive depiction of nearly all facets of the groundwater chemistry, along with the influence of the associated geology. However, the subsidiary part of other plots cannot be neglected in full and are of minor implication.

Keywords:- Stiff's diagram, Piper diagram, Chadha's diagram, Gibbs diagram, Hydro-geochemistry, Hydro-geochemical facies.

I. INTRODUCTION

The satisfactory, safe and accessible supply of the water must be available to all life form [1]. When the term safe comes into play, then the quality of water can be put on the priority. The groundwater is the undisputed key source of the freshwater but undoubtedly vulnerable to the acute contaminations in the regions of dynamics, say the coalfields [2]. The contaminated groundwater cannot be restored by informal means; hence, it's essential to monitor the quality of groundwater, before prevalence of the contamination [3]. Among the various facets of the groundwater monitoring, the chemical observation are the central ones. The natural chemistry of the groundwater is regulated by the geochemistry of the hosting rocks and the hydrochemistry of the aqueous portion of the earth [4]. Hence, a tool dealing with the interpretations related to the groundwater chemistry and associated influencer is much required by the young researchers. Accordingly the term hydro-geochemistry comes into play. The hydro-chemistry

reveals the water quality with reference to its suitability for drinking, agriculture and industrial purposes [5]; whereas, the hydro-geochemistry purely deals with the groundwater quality and its causal relationship with the associated geology [6].

The geochemical processes and the reactions with the associated minerals have a noteworthy influence over the groundwater chemistry [7]. A wide variety of the dissolved inorganic chemical constituents adds into the groundwater during the interactions with the host rock [8]. These inorganics basically constitutes major ions viz., anions: SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- and CO_3^{2-} ions; cations: Na^+ , K^+ , Ca^{2+} and Mg^{2+} . On the collective study of these dissolved inorganics in the groundwater, the respective geological cause can be asserted very efficiently [9]. The consideration of such collective groundwater chemistry is perfectly termed as hydro-geochemistry and is systematically executed by the various plots viz., Stiffs, Piper and Gibbs. The present article elaborates the groundwork on data preparation before hydro-geochemical interpretations and the orderly engagement of the various hydro-geochemical plots for prolific conclusions.

II. METHODOLOGY

To depict the substantial representation of the hydro-geochemical plots and to develop a convincing enough line of action for the budding hydro-geologists, an extensive literature survey has been taken through the most appreciated articles in the field of hydro-geochemistry. On deducing the essence from the literature survey, it is correlated with the contemporary developments in the field of hydro-geochemical interpretations. Lastly, all the observations were put together to develop a comprehensive depiction indicating the applicability, suitability, advantages and disadvantages of the various hydro-geochemical interpretations tools.

III. DATA PREPARATION

The moment after the outcomes of the groundwater samples analysis, the obtained data must be verified and validated on the scale of reliability. Simultaneously, the data has to be dressed according to the requirements of the tools designed for hydro-geochemical interpretations.

A. Data Accuracy:

The reliability of the data is one of the most essential requisites before its interpretation. The elucidations done on behalf of the unreliable data can cause mega errors at the end of the endeavour [10]. Thus, a logical approach is

required to make sure the reliability of the data has been attained. The foremost criteria to verify the reliability of the hydro-geochemical data is to check the ion balance. In 1979, Freeze and Cherry [11] has proposed the charge balance error method. Where, the ratio of subtraction of summation of cations and anions by the sum of the same overall multiplied by 100 gives the percentage of error (equation 1).

$$\% \text{ Balance Error} = \frac{\Sigma \text{ cations} - \Sigma \text{ anions}}{\Sigma \text{ cations} + \Sigma \text{ anions}} * 100 \text{ (eq. 1)}$$

The percentage balance error is not applicable to the very dilute and high concentrated solutions. The acceptability of the data remains only when the percentage balance error stays below 5 %. If the error goes beyond the acceptable criteria, in that case the data needs to be regenerated in concern to the probable loophole. Once the data is affirmed to be reliable, it can be confidently forwarded for the various hydro-geochemical interpretation tools.

B. Unit Conversion:

A data generated from the analysis of major ions are usually measured in the milligram per litre and is expressed as mg/l. The hydro-geochemical plots may develop erroneous plots and subsequent interpretations on the input of data in the measured unit i.e. mg/l. Thus the conversion of the data into suitable unit i.e. milli-equivalence per litre abbreviated as mEq/l. suggested for hydro-geochemical interpretation is the pre-requisite [12]. The conversion is done by ratio of obtained value of the individual ion in mg/l multiplied with the valance and the atomic mass of the same and is mathematically expressed as (equation 2).

$$\text{mEq/l} = \frac{(\text{mg/l})(\text{valance})}{(\text{atomic mass})} \text{ (eq. 2)}$$

The data can also be directly subjected to the conversion by the ratio of obtained value of the ion in mg/l and the conversion factor of the same ion (Table 1).

Ions	Conversion factors
Ca ²⁺	20
Mg ²⁺	12.152
Na ⁺	23
K ⁺	39.1
CO ₃ ²⁻	30
HCO ₃ ⁻	61
Cl ⁻	35.45
SO ₄ ²⁻	48
NO ₃ ⁻	62.01

Table 1: Conversion factors of the ions to convert the unit from mg/l to mEq/l

IV. HYDRO-GEOCHEMICAL PLOTS

The graphical plots demonstrating the characterization of the groundwater and signifying the influence of associated geology are termed as hydro-geochemical plots. These plots are as essential as the analytical outcomes of the data. These plots not only narrow downs the dispersed hydro-chemical data but also provides countless clues regarding the origin of the existing groundwater chemistry through the geological conduit.

A. Stiff 's diagram:

In 1951, Stiff's [13] has proposed a plot signifying the groundwater chemistry, thereafter notably known as Stiff 's diagram. The Stiff's plot is kind of simple configure arranging cations concentration on the left side of the plot and anions on the right side as a points (Figure 1a). On joining these points, a polygonal shape develops elucidating multilevel interpretations of the groundwater chemistry including the change in chemistry at different point, flow path influence, etc. (Figure 1b).The diagram is friendly to geographical representations. The data required in Stiff's plot as an input must essentially be in unit of mEq/l.

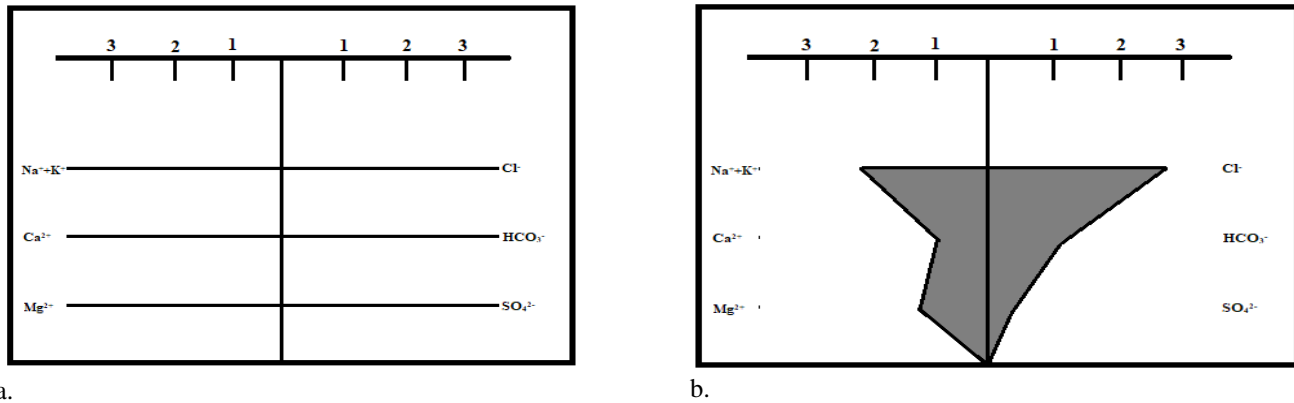


Fig. 1: (a) Stiff's Diagram Configuration and 1(b). Sample polygon in Stiff's diagram

B. Piper diagram:

In 1944, Arthur Piper [14] had proposed a graphical representation for the elucidation of the water chemistry and the accountable processes. The fundamental concept behind the Piper plot is the conjecture of electro-neutrality of the dissolved salts. The diagram is so designed that the cations and anions are designated with the separate ternary plots and a diamond shape plot projected by the linear transformation of the ternary plots (Figure 2). The tips of the ternary plots are assigned with Ca^{2+} , Mg^{2+} and $Na^{+} + K^{+}$ for cations and $HCO_3^{-} + CO_3^{2-}$, Cl^{-} and SO_4^{2-} . The Piper plots are extremely supportive in the classification and understanding of the hydro-chemical facies[5]. These facies explicates the set of chemical condition and the responsible process from the associated geology. The Piper diagram may not be supportive in spatial tools but is much efficient in hydro-geochemical interpretations. The data required in Piper diagram must essentially be in unit of mEq/l.

• **Detailed Portrayal of Piper diagram:** The various zones of the Piper diagram represent different facets of the groundwater chemistry. The groundwater can be classified either as the specific type in concern to the cations/anions or as the general type based on cumulative ionic

representation or as the hydro-chemical facies (Figure 2). The ternary plots of either cation or anions represents the dominance of respective ions and is represented as the zones with the denotation from A to G; whereas, the type on the projections of cumulative ionic constitution in the diamond shape is represented with the denoted from 1 to 6. The roman digits signifies the hydro-chemical facies, again on the projections of cumulative ionic constitution in the groundwater.

• **Significance of the Piper diagram:** The implications of the Piper diagram are versatile. The interpretation includes the general depiction of the groundwater chemistry, identification of the cation or anion specific type and general type of the groundwater. Apart from the individual zones, the combination of various zones (Figure 2) signifies for a certain set of condition, which can be observed as 1+4+5 implies Alkaline earth exceeds Alkalis; 2+3+6 implies Alkalis exceeds Alkaline earth; 1+3+6 implies Weak acids exceeds strong acids and 2+4+5 implies Strong acids exceeds weak acids. Along with this, the identification of the hydro-chemical facies aids in understanding the various processes responsible for the observed chemistry.

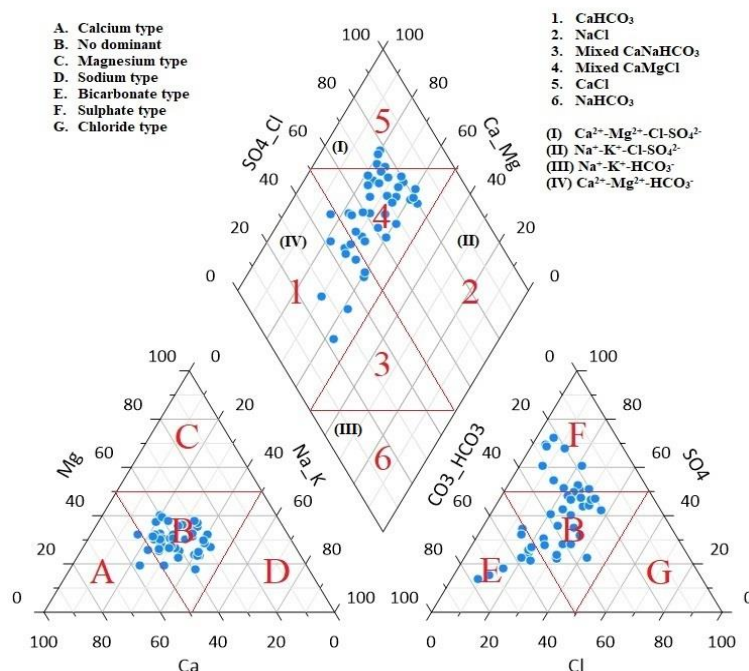


Fig. 2: A sample Piper diagram [9].

C. Chadha's diagram:

In 1999, D. K. Chadha[15] proposed a plot to classify the water geochemically. It is a bivariate plot of the major ions, where the various sub-plots signify a certain set of hydro-chemical condition. The Chadha's diagram is also well

known as modified Piper diagram, where the interpretations taken from the Piper diagram are used to achieve respective outcomes. The whole plot is divided into four distinctive plots viz., recharge type, reverse ion exchange type, sea water type and base exchange type (Figure 3).

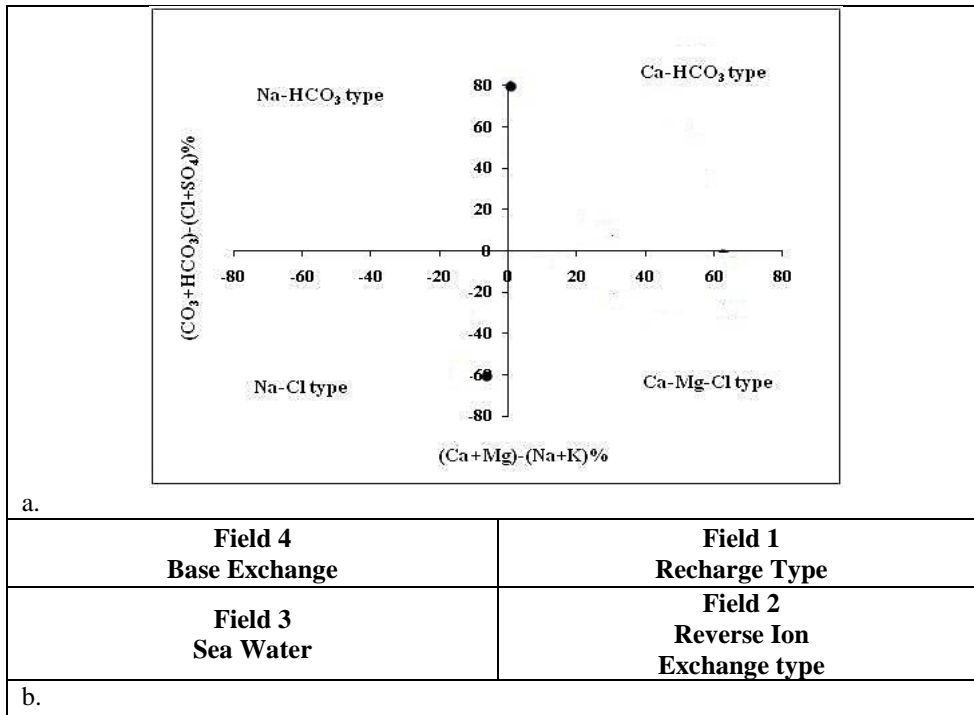
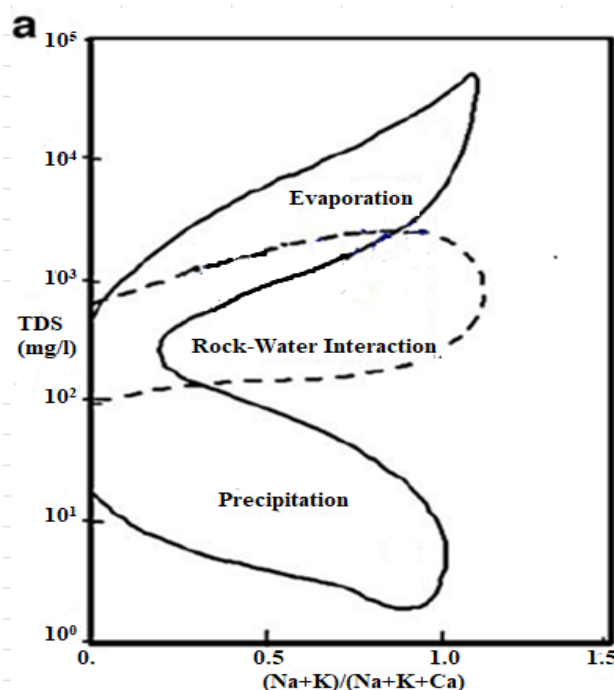


Fig. 3: a. A sample Chadha's diagram and b. Fields in Chadha's diagram

D. Gibbs diagram:

The Gibbs diagram [16] is actually a plot manifesting the exact process responsible for the existing water chemistry suggested in 1970. The ratio of Na+K to Na+K+Ca is plotted against respective TDS for classifying the sample points in the three different zones. The very first zone is

precipitation zone, where the water chemistry is completely controlled by the precipitation. The second zone above to it is of rock-water interaction, where the water chemistry is directly controlled by the geologic influence and the third one is the evaporation type, where the high TDS justifies the condition.



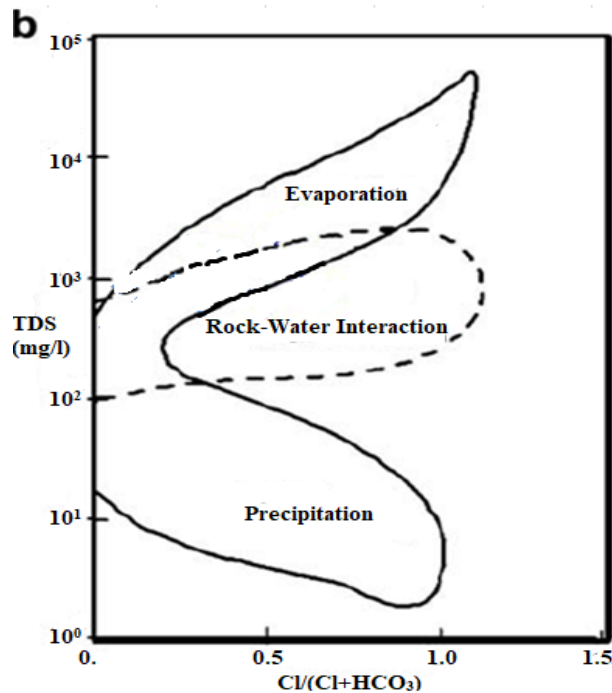


Fig. 4(a) and 4(b): A sample Gibbs diagram

V. CONCLUSION

The assurance of water quality is must and will become more vigorous with the encroachment of human settlements in natural environment. Hence, the hydro-geochemical studies will be the vital studies, the human kind would ever need. In such case the precision of interpretation is obligatory. The post analysis preparation of the data as a prerequisite for considering it as an input to the hydro-geochemical tools is the key step in entire interpretation process. The measurement of charge balance error, justifies the worthiness of the data for utilization. The conversion of the data from the measured unit to the hydro-geochemically suitable unit as mEq/l is the prerequisite. Among all of the plots viz., Stiff's, Piper, Chadha's and Gibbs, excluding the individual merits of the respective plots, the Piper diagram is very fruitful in hydro-geochemical interpretations and is advisable to execute with due obligation.

REFERENCES

- [1.] WHO, "Guidelines for drinking-water quality: fourth edition incorporating the first addendum" Geneva, 2017.
- [2.] P.S. Ganvir and R. Guhey, "Assessment of Some Heavy Metals Toxicity and Its Probable Remediation in Groundwater around Telwasa and Ghugus Area of Wardha Valley Coalfields, Maharashtra," *Journal of Indian Association of Sedimentologists*, v. 37(1), pp.33-43, 2020.
- [2.] P.S. Ganvir and R. Guhey, "Groundwater quality assessment with reference to some heavy metals toxicity and its probable remediation around Ballarpur area of Wardha valley coalfields, Maharashtra," *IOP Conference Series: Earth and Environmental Science*, 597:012001, 2020.
- [3.] Mufid al-hadithi "Application of water quality index to assess suitability of groundwater quality for drinking purposes in Ratmao –PathriRao watershed, Haridwar District," *India. Am. J. Sci. Ind. Res.*, v.3(6), pp.395-402, 2012.
- [4.] D.R. Satapathy, P.R. Salve and Y.B. Katpatal, "Spatial distribution of metals in ground/surface water in the Chandrapur district (Central India) and their plausible sources," *Environmental Geology*, v.56, pp.323-1352, 2009.
- [5.] C., Sadashivaiah, C. R. Ramakrishnaiah and G.Ranganna, "Hydrochemical Analysis and Evaluation of Groundwater Quality in Tumkur Taluk, Karnataka State," *India. Int. J. Environ. Res. Public Health*, v.5(3), pp.158-164, 2008.
- [6.] P.S. Ganvir and R.Guhey, "Geochemical Studies of some Heavy Metals' Toxicity in Groundwater with their Plausible Sources around Gondwana Supergroup, Wardha valley Coalfields, Maharashtra," *Journal Geological Society of India*, v. 97, pp.1415-1421, 2021.
- [7.] S. Singh, S. Tignath, D. K.Deolia, M.Jha and R.Dixit, "Geochemical Assessment of Groundwater Quality for its Suitability for Drinking and Irrigation Purpose in Jabalpur, Madhya Pradesh, India," *Int. J. Res. in Engineering, Science and Management*, v.3(08), pp.130-134, 2020.
- [8.] W. Kinzelbach, W.Schafer and J.Herzer, "Numerical modelling of nitrate transport in a natural aquifer," In: Kobus and Kinzelbach (Eds.), *Contaminant Transport in Groundwater*, Balkema, Rotterdam, pp.191-198, 1989.
- [9.] P.S. Ganvir and R. Guhey, "Hydro-geochemical elucidation and its implications in the Wardha valley coalfields of central India," *IOP Conference Series: Earth and Environmental Science*, 1032:012015, 2022.

- [9.] B.K. Handa, “Modified Hill-piper diagram for presentation of water analysis data,”*Current Science*, v.34, pp.131-314, 1965.
- [9.] J.D. Hem, “Study and interpretation of the chemical characteristics of natural water,”*USGS Water Supply Paper*, v.2254, pp.117-120, 1985.
- [10.] I.Rangeti, B.Dzwairo, G.J.Barratt and F.A.O. Otieno, “Validity and Errors in Water Quality Data — A Review,”*Research and Practices in Water Quality*, DOI: 10.5772/59059, 2015.
- [11.] R.A. Freeze and J.A. Cherry, “*Groundwater*,” Prentice-Hall, Inc. Englewood Cliffs, New Jersey,” 07632, 1979.
- [12.] U.Ewuzie, N.O.Aku and S.U. Nwankpa, “An appraisal of data collection, analysis, and reporting adopted for water quality assessment: A case of Nigeria water quality research,”*Heliyon*, 7(9):e07950, 2021.
- [13.] H.A.Jr. Stiff, “The interpretation of chemical water analysis by means of patterns,” *Journal Petroleum Technology* v.3(10), pp.15–17, 1951.
- [14.] A. Piper, “A graphic procedure in the geochemical interpretation of water-analyses,” *Transactions, American Geophysical Union*, v.25 (6), pp.914–928, 1944.
- [15.] D.K. Chadha, “A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data,” *Hydrogeology Journal*, v.7, pp.431-439, 1999.
- [16.] R.J. Gibbs, “Mechanisms Controlling World Water Chemistry,” *Science*, 170:1088-1090, 1970.