

Review

Groundwater chemistry and the Gibbs Diagram

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ABSTRACT

The ‘Gibbs Diagram’ represents some of the key processes controlling surface water chemistry. This review highlights that the processes listed on the Gibbs Diagram may not be applicable for assessing processes controlling groundwater chemistry. We discuss the importance of geochemical processes governing groundwater chemistry in the Gibbs Diagram framework. We show that the processes represented on the Gibbs Diagram—originally developed for surface waters—are unlikely to represent key processes controlling the chemistry of most groundwater systems.

1. Introduction

When J.R. Gibbs published *Mechanisms Controlling World Water Chemistry* in 1970, the author probably had no idea that Figure 3 (Gibbs, 1970) in the publication would take on a life of its own. As of June 2017, the paper has been cited 720 times (Web of Science, 2017) and there likely exist few hydrogeochemists who have not encountered the ‘Gibbs Diagram.’ However, some works misuse or misinterpret the original Gibbs figure by applying the diagram to invoke groundwater processes in a diagram originally developed for surface waters.

The objective of this manuscript is to emphasize that the processes listed on the original Gibbs Diagram are better suited for surface water chemistry and that their relevance to groundwater systems is at best untested.

2. The Gibbs Diagram

The original Gibbs (1970) article summarizes the evolution of surface water chemistry. Based on that study, the main governing processes include evaporation, precipitation, and water-rock interaction. The influence of these processes is clear on the scatter plot: where sodium/(calcium + sodium) ratios (x-axis) are plotted against total dissolved solids (salinity) on the y-axis (Fig. 1A). The pattern of world surface water bodies forms a boomerang-shaped cloud on the figure. Rivers and lakes are typically in a state of dynamic disequilibrium with basin sediments and bedrock geochemistry due to their amalgamation of waters with varying transit times, and often have higher Ca and HCO₃ concentrations compared to Na and Cl concentrations, respectively. Most rivers and lakes also have low or moderate salinities, and

thus plot in the middle part of the ‘boomerang.’ River and lake waters with chemistries that plot closer to the tips of a boomerang may arise either by evaporation (upper right of the plot) or because the water is less saline due to the high proportion of recent rainfall that has yet to have sufficient contact time with minerals for geochemical modifications (lower right of the plot). Both explanations can lead to high relative Na and Cl abundances, but evaporation salinizes (“evapo-concentrates”; i.e., shifts chemistry to upper right) whereas the presence of abundant recent-rain or -snowmelt tends to lower salinity (shifts chemistry to lower right in the diagram).

3. The use of the Gibbs Diagram in hydrogeology

The Gibbs Diagram depicting the boomerang contour has also been applied in groundwater hydrochemistry. Approximately half of all publications citing the Gibbs Diagram (382 out of 720) include the keyword “groundwater”. Based on a query from Web of Science database, 72% of these citations in 2017 (29 out of 40) focus on groundwater chemistry (Web of Science, 2017).

In principle, there is nothing incorrect about using the Gibbs Diagram in groundwater papers; on the contrary, plotting ion ratios and salinity can lead to improved understanding of key hydrochemical processes. Furthermore, possibly as much as two-thirds of global streamflow originates from delayed flows such as groundwaters (Jasechko et al., 2016); such strong ground-to-surface flows emphasize that even surface waters are in part ‘groundwater’ that has discharged to the stream (Alley et al., 1998). However, the use of conceptual process-based models developed specifically for surface waters and linked to the Gibbs Diagram to assess groundwater processes is likely

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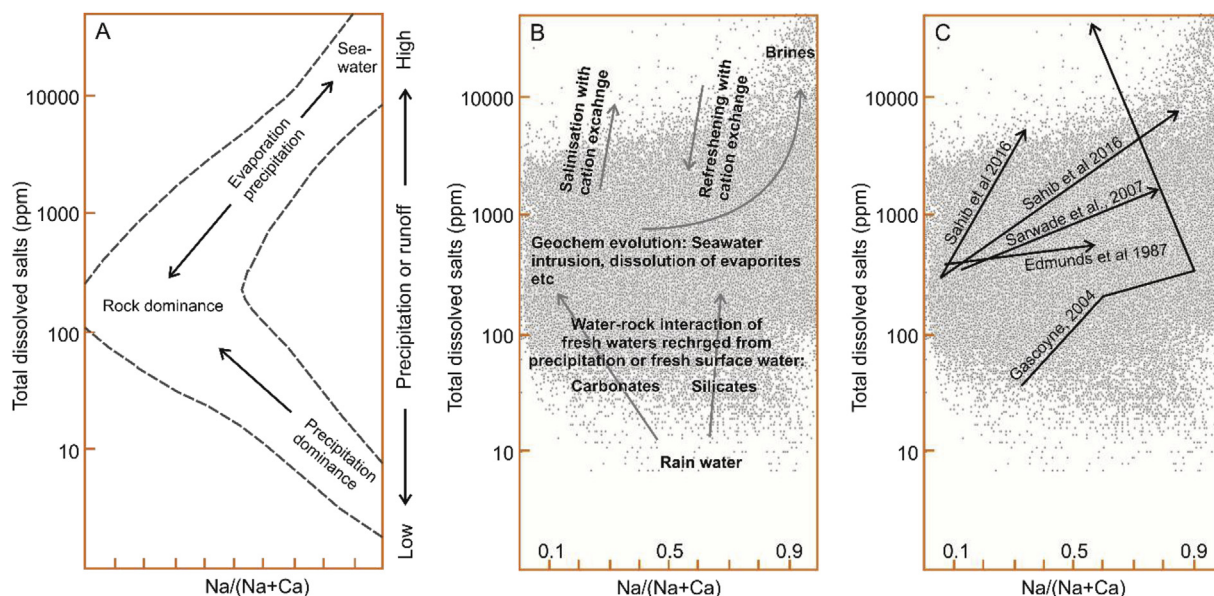


Fig. 1. Comparison of natural processes defining the water chemistry of surface water on Gibbs (1970) diagram (A) and in groundwater (B). The placement of example data reflecting the groundwater quality evolution on “Gibbs” diagram (C) along the groundwater flowline in crystalline rocks (Gascoyne, 2004), carbonate rocks (Edmunds et al., 1987), in case of seawater intrusion (Sarwade et al., 2007), and due to the dissolution of evaporate minerals (Sahib et al., 2016). The grey pattern cloud on B and C indicates the groundwater samples from USGS Brackish Groundwater Database (Qi and Harris, 2017).

inappropriate and may slow more sophisticated data interpretations.

Confusion may arise when works assess the importance of water-rock interaction and/or evaporation on groundwater quality based on the location of samples on Gibbs diagram (Adimalla and Venkatayogi, 2017; Barzegar et al., 2017; Chintalapudi et al., 2017; Hallouche et al., 2017; Haritash et al., 2017; Ibrahim Hussein et al., 2017; Latifa et al., 2017; Mahmoudi et al., 2017; Raj and Shaji, 2017; Singh et al., 2017). Some even suggest that Gibbs (1970) assessed the evolution of groundwater rather than surface water quality (Chintalapudi et al., 2017) (Song et al., 2017).

To understand potential imperfections that may arise when interpreting processes based on the Gibbs Diagram, one may recall that Gibbs (1970) studied how three processes alter surface water chemistry and expressed those processes on the plot. To apply a plot with same axes to describe groundwater processes, the conceptual processes driving the evolution of water quality may differ from those Gibbs (1970) originally developed for surface waters, even if the chemical composition of precipitation remains fixed. We propose, therefore, that plots involving groundwater systems should reconsider presenting the Gibbs ‘boomerang’ contour, because water-rock interactions potentially span most of the plot area (Fig. 1b), particularly for groundwaters with residence times far longer than those typical to surface waters. Indeed, many groundwaters have remained under the ground for more than 12,000 years; these fossil groundwaters likely comprise half of the total continental water storage (Jasechko et al., 2017) and, because of their old age, have provided ample time for substantial water-rock interactions.

4. Groundwater chemistry on the Gibbs Diagram

The concentration of chemical components in natural groundwater depends on numerous processes and conditions, including the availability and solubility of minerals (Freeze and Cherry, 1979), geochemical environment (e.g. pH and Eh) and exchange processes, which may be different to those important to surface environments. A typical sequence of groundwater evolution for anions was established by Chebotarev (1955) more than half a century ago. It stated that along the long flow path with increasing time, the groundwater chemistry tends to change from HCO_3 -type to Cl-type water with increasing salinity.

This is often accompanied by a change in the dominant cation from Ca to Na.

The evolution series starts from the HCO_3 series because most of the aquifer forming minerals and also many soils contain carbonate minerals, typically calcite. Due to the relatively high solubility and widespread occurrence of calcite, carbonate mineral dissolution often dominates the chemical evolution of natural waters, even if these minerals are present in only small amounts (Appelo and Postma, 1993). Therefore, the evolution of rain water (low TDS and usually a Na–Cl water type) to a Ca– HCO_3 water type upon interaction with sediments and bedrock usually occurs relatively rapidly. The majority of fresh groundwater occurs in the middle part of the boomerang (water-rock interaction) on Gibbs Diagram, but groundwaters—unlike most surface waters—can span the entire range of $\text{Na}/(\text{Na} + \text{Ca})$ values (i.e., from < 0.1 to > 0.9) at mid-range TDS levels. We evidence the wide range of groundwater chemistry in Gibbs Diagram space by plotting USGS Brackish Groundwater Database (Qi and Harris, 2017) chemistry in Fig. 1B and C.

The positioning of groundwater either on the left or right side of diagram depends on soil and aquifer properties. If carbonate minerals dominate, groundwater chemistry will likely be driven to lower $\text{Na}/(\text{Na} + \text{Ca})$ ratios. In other areas dominated by silicates (Banks and Frengstad, 2006) $\text{Na}/(\text{Na} + \text{Ca})$ ratios can be higher. Gascoyne (2004) express groundwater quality evolution of a granitic batholith in Manitoba, Canada along the flowline from surface sediments to approximately 1000 m underground in crystalline rocks, evidencing a wide-ranging and nonlinear trajectory of groundwater chemistry on the Gibbs Diagram (Fig. 1C).

In addition to other shortcomings, the Gibbs Diagram does not provide information about processes impacting groundwater SO_4 concentrations such as pyrite oxidation (Shand et al., 2016) or gypsum dissolution (Woldemariam and Ayenew, 2016), which can be critically important to groundwater major element compositions. The evolution of groundwater quality in carbonate aquifers is presented in Hanshaw and Back (1979), where the processes were described by using a Piper (1944) diagram. One common evolution of groundwater in carbonate aquifers trends from Ca– HCO_3 type waters to Ca–Mg HCO_3 – SO_4 type waters. Such evolution—which occurs on the left sides of Piper diagram triangles and in the upper part of diamond (Hanshaw and Back,

1979)—cannot be observed on Gibbs Diagram because the change is caused by Ca–Mg ratio and $\text{HCO}_3\text{--SO}_4$ ratios while the Ca–Na and Cl– HCO_3 ratios remain unchanged. In summary, by plotting only sodium and calcium ion relationships in Gibbs Diagram space, it is possible that other key processes such as those captured by SO_4 concentrations may be overlooked.

Further evolution of groundwater chemistry—changes to the type and salinity of the groundwater—may occur through the further water-rock and redox-controlled reactions, mixing of different groundwaters along flow paths, exchange with aquitards, cross-formational flows or by inputs of surface waters with higher salinities and different water types. In general, these processes often result in high salinity groundwater having a Na–Cl water type. An example of groundwater evolution along the flow path is given by Edmunds et al. (1987) in the Chalk aquifer in Berkshire, U.K, where the groundwater type evolves from a Ca– HCO_3 water to a Ca–Mg– HCO_3 type, to a Na– HCO_3 type, and ultimately to a Na–Cl type during the prolonged travel time of groundwater in the aquifer system. Such evolution would cause the shift of fresh groundwater towards the upper right corner of Gibbs Diagram (Fig. 1B). The same shift, however, can also be caused by dissolution of evaporite minerals in the aquifer matrix or by mixing with saline surface waters (seawater, coastal rivers, evaporative lakes etc.). The evolution of Na– HCO_3 type waters by ion-exchange, seawater intrusion (freshening) or silicate hydrolysis (Banks and Frengstad, 2006) (Sarwade et al., 2007) along with a wide range of other processes can lead to substantially greater scatter on the Gibbs Diagram relative to surface waters and loss of the classic boomerang shape.

Perhaps the clearest oversimplification of the Gibbs Diagram occurs when the evaporation is discussed. Some waters that plot in the upper right part of Gibbs Diagram are used to explain that evaporation is the main process driving groundwater chemistry (Gowrisankar et al., 2017; Kozłowski et al., 2017). Evaporation from groundwater is often negligible when the groundwater table exists deeper than a few meters, as shown by Barica (1972). Further, global groundwater isotope compositions often show little evidence of evaporation prior to or during recharge, usually plotting close to local meteoric water lines in $\delta^2\text{H}\text{--}\delta^{18}\text{O}$ space (e.g., Jasechko et al., 2014). It is possible that, in some cases, evaporation may occur directly from groundwater, particularly where the water table rests within ~1 m of the land surface or where groundwater discharges to the surface. The influence of evapoconcentration is likely of secondary importance to groundwater quality relative to water-rock interactions in the great majority of groundwater flow systems. In such cases, the dissolution of evaporite minerals (Sahib et al., 2016) is responsible for the changes in groundwater salinity and chemistry instead of evaporation in some cases. In some arid and semi-arid regions of the world (e.g. North Africa, Australia), transpiration (which does not significantly alter stable O and H isotope ratios in water) alongside evaporation may lead to the development of saline Na–Cl type groundwaters (Herczeg et al., 2001). The nature of such processes is complex and different from the evaporation of surface water, therefore, a simple interpretation of the Gibbs Diagram would be inappropriate.

Interpretations of groundwater chemistry logically begin with an assessment of the origin and the chemistry of the source water, as the recharge source defines initial conditions of the system. We emphasize that the initial conditions of groundwater chemistries shown in Fig. 1B are not fixed. The arrows on that figure express an increasing influence of modifying processes in several case studies. Surface water can supply groundwater recharge in many areas, supplementing direct precipitation inputs. It remains possible that recharging waters cross the water table with a chemical composition plotting in the upper right corner of the Gibbs Diagram, perhaps particularly in regions where land uses have caused salinization of soils or other artificial impacts to near-surface mineralogy.

5. Conclusions

Major ion concentrations in many groundwater samples can be explained in large part by mixing and water-rock interactions. Key processes that increase groundwater salinity depend on reactions with host rocks controlled by the network of flow paths, and the time each path spends in contact with various minerals and mixing with older waters at depth. Therefore on the Gibbs Diagram, where only ratios of Na/(Na + Ca) (or Cl/(Cl + HCO_3)) are expressed, the patterns of several different processes may coincide. Thus, the use of Gibbs (1970) graphs, especially the boomerang shape and the placement of main processes, for the identification of governing processes may yield limited information. The application of the diagram, for example, to groundwaters should be considered in the broader context of processes and hydrogeochemistry which differ significantly from surface water chemistry and processes, due to longer residence times and more variable geochemical environments (e.g., redox conditions) of many groundwater systems. Overall, the use of interpretations linked to the original Gibbs (1970) diagram for defining groundwater geochemical processes may oversimplify the interpretation of aquifer systems and overlook important processes. Instead, other more sophisticated diagrams (e.g. Piper plot) and analytes (e.g., isotope geochemistry) will lead to improved understanding of hydrogeochemical processes.

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