Chemical speciation in semiarid environments – A review

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Received: 09 April, 2019. Accepted: 07 June, 2019
First published on the web September, 2019
DOI: 10.26545/ajpr.2019.b00038x

Abstract

In semiarid environments, the major cations in soil and surface waters are ionic calcium, magnesium, sodium and potassium (Ca²⁺, Mg²⁺, Na⁺, and K⁺), and the major anions are chloride, sulfate, bicarbonate, and carbonate (Cl⁻, SO₄²⁻, HCO₃⁻, and CO₃²⁻), respectively. However, watersheds impacted by fertilization, feedlots, or domestic waste water can also contain elevated levels of nitrate (NO₃⁻) and phosphate (PO₄³⁻), mainly in the form of HPO₄²⁻ and H₂PO₄⁻. The formation of complexes between all cations and anions entered needs to be evaluated and for that, Geochemical speciation programs allow being solved for all components present in the system. As an example, the composition of water in semiarid environments is strongly influenced by the dissolution and precipitation of minerals. Geochemical speciation programs such include a data base of reactions and equilibrium constants for minerals. Depending on the model application and knowledge of the environment being modeled, the user may make choices such as specifying that a specified amount of a given mineral is initially present, or the solution phase is always in equilibrium with a certain mineral. The user may also choose to allow or disallow certain minerals which may not be present initially to precipitate if super-saturation is reached. To start from chemical speciation and have it be meaningful and useful in today’s changing world of environmental health and the impact of water quality on all living organisms as well as the storage in our aquifers, learning the basics is truly just the beginning.

Key-words: Soil quality, Soil chemistry, Soil solution, Semiarid environments

Introduction

Chemical speciation is the distribution of an element among all chemical forms present. In semiarid climates, the major cations in soil and surface waters are ionic calcium, magnesium, sodium and potassium (Ca²⁺, Mg²⁺, Na⁺, and K⁺), respectively. The major anions are chloride, sulfate, bicarbonate, and carbonate (Cl⁻, SO₄²⁻, HCO₃⁻, and CO₃²⁻), respectively. Watersheds impacted by fertilization, feedlots, or domestic waste water can also contain elevated levels of nitrate (NO₃⁻) and phosphate (PO₄³⁻), mainly in the form of HPO₄²⁻ and H₂PO₄⁻. Although the monovalent alkaline earth cations tend to exist mainly in the free ionic form, the divalent cations can form complexes with the anions listed above to some degree. For example, calcium can form a soluble complex with sulfate as described by the following reaction (Stumm and Morgan, 1996):

\[ \text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4^{0} \quad \text{Eq. 1} \]

The corresponding equilibrium equation for this reaction is:

\[ K = \frac{[\text{CaSO}_4^{0}]}{[\text{Ca}^{2+}] \cdot [\text{SO}_4^{2-}]} \quad \text{Eq. 2} \]

Where K is the thermodynamic equilibrium constant and has a value of log K = 2.30 for this reaction.
In this equation, \{ i \} designates the activity of each chemical species. In order to incorporate equilibrium equations into chemical speciation models where mass balance equations are written in terms of concentrations, activities must be related to concentrations. Chemical activity is related to concentration as

\[
\{ i \} = f_i [ i ]
\]  \hspace{1cm} \text{Eq. 3}

Where \( f_i \) is the activity coefficient of the ion \([ i ]\) is the ion concentration in moles/L. Activity coefficients approach a value of 1.0 in dilute solutions. The activity coefficients for neutral complexes are set to 1.0. The activity coefficient may be calculated by use of the Davies equation (Stumm and Morgan, 1996), valid for Ionic strength up to 0.5 M.

\[
\log f_i = -AZ_i^2 ((I^{1/2}/1 + I^{1/2})^{.2I})
\]  \hspace{1cm} \text{Eq. 4}

In order to calculate activity coefficients, the ionic strength of the solution must be determined

\[
I = \frac{1}{2} \sum C_i Z_i^2
\]  \hspace{1cm} \text{Eq. 5}

In the calculation of ionic strength, all ions (including charged complexes) are included, each with charge \( Z \). Consequently, the concentration of the \( \text{CaSO}_4^0 \) complex may be calculated as a function of the concentrations of the free concentrations of the \( \text{Ca}^{2+} \) and \( \text{SO}_4^{2-} \) anions by

\[
[\text{CaSO}_4^0] = K [ \text{Ca}^{2+} ] [ \text{SO}_4^{2-} ] \times f_{\text{Ca}_2+} f_{\text{SO}_4^2-}
\]  \hspace{1cm} \text{Eq. 6}

At a specified ionic strength, the conditional equilibrium constant may be defined as

\[
K_{\text{cond}} = K (f_{\text{Ca}_2+} f_{\text{SO}_4^2-})
\]  \hspace{1cm} \text{Eq. 7}

This allows the equation to be written directly in terms of concentrations

\[
[\text{CaSO}_4^0] = K_{\text{cond}} [ \text{Ca}^{2+} ] [ \text{SO}_4^{2-} ];
\]  \hspace{1cm} \text{Eq. 8}

with the caveat that the conditional equilibrium constant is only valid at the specified ionic strength.

The remaining governing equations which allow the chemical speciation problem to be solved are the mass balance equations for each component in the system. In the current example, the mass balance equation for \( \text{Ca} \) is

\[
[\text{Ca}]_T = [\text{Ca}^{2+}] + [\text{CaSO}_4^0];
\]  \hspace{1cm} \text{Eq. 9}

Geochemical speciation programs such as MINTEQA2 (Allison et al., 1991) allow for the set of equations described above to be solved for all components present in the system. This program includes a database with equilibrium constants for many soluble complexes known to occur in natural waters. One application of the geochemical speciation model is to enter total concentrations for all elements measured in a water sample. The formation of complexes between all cations and anions entered is evaluated, and the output includes values for activities and concentrations of all chemical forms of each element.

**Mineral dissolution and precipitation**

The composition of water in semiarid environments is strongly influenced by the dissolution and precipitation of minerals. For example, the mineral gypsum dissolves according to the reaction (Stumm and Morgan, 1996):

\[
\text{CaSO}_4^0 \times 2\text{H}_2\text{O}_{(gypsum)} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}
\]

\[
\log K_{\text{gyps}} = -4.60
\]  \hspace{1cm} \text{Eq. 10}

The equilibrium equation for this reaction is expressed as:

\[
K_{\text{gyps}} = \{ \text{Ca}^{2+} \} \{ \text{SO}_4^{2-} \}
\]  \hspace{1cm} \text{Eq. 11}

where the activity of both the solid phase and water have been set to 1.0 by convention. As long as the solution phase is in equilibrium with the solid phase gypsum, this equation will be obeyed. The state of saturation of a solution with respect to a given mineral may be evaluated by the Ion Activity Product. For the current example, the Ion Activity Product is defined as:

\[
\text{IAP} = \{ \text{Ca}^{2+} \}_{\text{actual}} \{ \text{SO}_4^{2-} \}_{\text{actual}}
\]  \hspace{1cm} \text{Eq. 12}

where the actual activities are determined from measured (or modeled) data. Once the actual activities have been determined, comparison of the calculated IAP to the value of the equilibrium constant is interpreted. If the IAP is equal to the value of \( K \), then the solution is in equilibrium with that mineral. If IAP is less than \( K \), the solution is under-
saturated. If IAP is greater than K, then the solution is supersaturated with respect to that mineral, and the mineral may precipitate if kinetics are favorable. Geochemical speciation programs such as MINTEQA2 include a data base of reactions and equilibrium constants for minerals. IAP and degree of saturation with respect to minerals present in the database are also often included in the output for these models. Depending on the model application and knowledge of the environment being modeled, the user may make choices such as specifying that a specified amount of a given mineral is initially present, or the solution phase is always in equilibrium with a certain mineral. The user may also choose to allow or disallow certain minerals which may not be present initially to precipitate if super-saturation is reached.

**Salinity Background**

Within the United States Department of Interior, the Bureau of Land Management (BLM) administers about 53 million acres of public lands in the Colorado River Basin above Yuma, Arizona. Substantial portions of these public lands are ecologically classified as arid or semiarid rangelands. Point sources of salt on public lands include saline springs, seeps from marine sedimentary formations, abandoned flowing wells, discharge from abandoned mines, and discharge of waters from authorized activities such as oil and gas production or mining. Nonpoint sources of salt include surface runoff, soil erosion, stream sediments, and groundwater discharge to streams. Salts can be transported either in solution or with solids such as soils or coarse fragments. Past studies have indicated that salt loading in rangelands is closely associated with sediment loading.

Salt concentrations on public lands tend to be highest in areas underlain by marine sedimentary rocks such as shales and mudstones that receive less than 20.3 cm of annual precipitation. Although salt concentrations can be very high in runoff from these lands, the frequency and volume of runoff is low because of the low precipitation and ephemeral nature of stream systems. Runoff from areas with highly saline soils in the upper basin is estimated to contribute about one-third of the annual salt load from BLM public lands.

The greatest volume of salt contributed from BLM-administered lands, however, is sourced from areas with moderate to low salt concentrations in soils that are relatively well-covered with perennial vegetation and receive more than 20.3 cm of annual precipitation. Although salt concentrations in runoff from these lands are low, total loading is relatively large because of higher water yields. These areas comprise about 67% of BLM-administered lands in the upper basin. Runoff from these areas is estimated to contribute more than half of the annual salt load from BLM-administered lands in the upper basin.

The BLM is committed to reducing salinity concentrations in the Colorado River sourced from its public lands as required by amendments to the Colorado River Basin Salinity Control Act of 1974 and mission mandates under the Federal Land Management Policy Act of 1976 (FLPMA). The BLM's primary strategy for reducing salt transport to the Colorado River is to minimize erosion from public lands through its existing land-management policies and practices. These policies and practices are intended to maintain or restore land-health as reflected by key ecological attributes such as soil and site stability, watershed function, and biotic integrity.

Fig. 1. Rangelands meeting all standards or making significant progress toward meeting the standards in the Colorado River Basin.
The BLM manages public lands according to a multiple-use mandate under the FLPMA. Many land-use activities such as livestock grazing, energy development, mining, recreation, timber production, utility transmission, and road management increase erosion and sediment transport. The BLM attempts to reduce these impacts to help maintain land-health standards by utilizing best-management practices; including terms, conditions, and stipulations in land-use authorizations; and requiring actions to restore lands upon completion of authorized activities. BLM also engages in many activities to restore degraded ecosystems that contribute excessive sediment and salts to Colorado River Basin watersheds. These activities include constructing and maintaining grade-control structures, spreader dikes, and retention structures; emergency stabilization and rehabilitation efforts following wildfires; removal of invasive plant species, channel stabilization and other riparian enhancements; maintaining road culverts; remediation of abandoned mine lands, and hire fuels reduction treatments. Salinity reductions for many of these activities continue to be difficult to quantify and report to the Forum because of factors such as the lack of adequate understanding about mobilization and transport of salts from rangelands and inability to conduct effectiveness monitoring for all projects. Reports from BLM State Offices reference many of these activities and the BLM is engaged in efforts with partner agencies to improve future ability to quantify salinity reductions from these efforts.

Currently, within the Colorado River Basin 472 rangeland allotments totaling more than 1210188.5 ha, already meet or are making significant progress toward the land health standards (Fig. 1).

Standards for Rangeland Health are ecologically-based goals that conform to the Fundamentals of Rangeland Health found in 43 Code of Federal Regulations Subpart 4180. Fundamentals of Rangeland Health are fundamental requirements for achieving functional healthy public lands. The Fundamentals, and the Standards for Rangeland Health that conform to the Fundamentals, address the necessary physical components of functional watersheds, ecological processes required for healthy biotic communities, water quality standards, and habitat for threatened and endangered species or other species of special interest.
In the future, one can employ an equation to identify the quantity of salinity eroded or deposited due to various funded BLM proposals by overlaying the funded proposal area with the correct bulk density (as found in the appropriate county’s soil survey) and the EC (Fig. 3).

Overall, the CRB has a gypsiferous (CaSO₄) surface layer, has a bulk density range of 1.1-1.6 g cm⁻³, pH 7.2-7.5, and average EC < 2 mmhos/cm; the soil is considered saline to highly saline. Therefore, the previous equation that has been used by the BLM for a minimum of the previous nine years requires adjustment and additional changes need to be made to the laboratory procedures that produce the mass of salt per mass of soil. While several uncertainties inherently exist with any measurement, our goal is to report BLM’s best measured data of erosion or deposition of salt/total dissolved solids. Additional uncertainty remains with the contract life of a dyke, the time it takes for it to be filled and maintained.

Other projects (i.e., gabions, fencing, headcuts) that need to be maintained and how often they need to be maintained also needs to be factored into the equation. In addition to using recent datasets (both chemical and physical for land and water), the Health Standards Index will be included and updated each year to provide a more thorough reporting of BLM activities effects on salinity control.

Due to the predominance of gypsum in CRB, the equation mentioned above also has to be adjusted to account for the dominant geologic surface layer (gypsum (CaSO₄) or halite (NaCl)) that is present to account for its chemical properties to calculate the most efficient % salt eroded or deposited.

Speciation of one averaged experimental solution for the 50-year storm event using the multiple equations listed above yields:

\[
\{\text{Ca}^{2+}\} = 2.10 \times 10^{-3} \text{ and } \{\text{SO}_4^{2-}\} = 3.13 \times 10^{-3}
\]

Eq. 13

These values yield an IAP = 6.57 x 10⁻⁶, and log IAP = -5.18. For this solution, IAP is less than K_{gypsum} which represents under-saturation with respect to gypsum.
Table 1. An example from a Gypsiferous site with a 50-year rainfall simulation on three plots with data averaged.

| Soil Measurements       | Mean (avg from triplicate plots) |
|-------------------------|----------------------------------|
| pH                      | 7.7                              |
| SAR                     | 0.5                              |
| CEC                     | 9.6                              |
| EC (mmhos/cm)           | 2.3                              |
| Clay/Silt/Sand (%)      | 13.3/68.9/17.8                   |

Table 2. Chemical species that impact Gypsum.

| Meq/L | Meq/L | Meq/L | Meq/L | Meq/L | Meq/L | Meq/L | Meq/L | Meq/L | Meq/L | Meq/L | Meq/L |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ca²⁺  | Mg²⁺  | Na⁺   | HCO₃⁻ | K⁺    | SO₄²⁻ | Cl⁻   | Ca²⁺  | Mg²⁺  | Na⁺   | HCO₃⁻ | K⁺    |
| 108.4 | 13.7  | 14.5  | 451.6 | 9.8   | 0.95  |

Fig. 6. Illustrations of low flow versus high flow rainfall simulations where the low flow event can lead to more ions staying on the premises while the greater intensity storm can lead to ions reaching the stream depending on their solubility and reach to stream.

Fig. 7. Illustrates that by using the Photogrammetry method (Nouwapko) demonstrating spatial erosion and deposition assessment along one of the rainfall simulation plots that the above data are taken from.

Influence of vegetation on rangeland hydrology and erosion processes

A governing principle of land management is that changes in land cover result in changes in watershed condition and response. Land management practices influence runoff, soil erosion, and transport of salt and other contaminants on rangelands because they affect plant distribution, biological diversity, canopy and ground cover, and soil properties. Vegetation is the primary factor controllable by human activity that influences the spatial and temporal variability of surface runoff and water quality on rangelands. As a consequence, when rangeland landscapes are denuded by human activities such as grazing, road building, mining, construction, vegetation rehabilitation programs are often required to achieve specific post-disturbance outcomes in water quality (Audet et al., 2013).

It is recognized that when rangeland landscapes undergo vegetation-reducing disturbances water quality is often impaired. Pierson et al. (2009) found for example that immediately following prescribed-
fire, loss of vegetation and soil property changes lead to increased erosion, especially to that caused by concentrated flow. This finding was further supported by Al-Hamd an et al. (2012) who reported post-disturbance increase in concentrated flow erodibility as high as 500-fold on burnt rangeland sites. Areas disturbed for construction activity have soil erosion rates from 2 to 40,000 times greater than pre-construction conditions and runoff from these activities significantly degrades surface water quality (Harbor, 1999).

Carroll et al. (2000) evaluated slope, type of vegetation, and native bare soil versus mine spoils to determine soil erosion and water quality impacts with various mine reclamation techniques. They reported that the greatest risk of soil erosion and salt transport was before vegetation was fully established. If rainfall occurs during this stage then it was likely rills would form and concentrated flow induced soil erosion and salt transport would be greatly accelerated. If vegetation is not eventually established in these rills then soil erosion and salt transport will continue to accelerate as the rills become persistent and increase in depth and width and eventually become gullies. Most rangeland management actions aimed at improving water quality on rangeland are based on the premise that increase in exposed bare ground is directly linked to a decrease in water quality.

Modern ecological theory has changed from a concept of climax-based linear succession and retrogression to Ecological Site Descriptions (ESDs) that incorporates concepts of State and Transition (S&T) models, thresholds, resilience, and multiple stable plant communities. The concept of Ecological Site (ES) is now the principal method of organizing and describing rangeland plant communities in the United States. The shift to ES theory has contributed to the development of concepts to address resilience-based management, and has provided land managers a standardized method of managing rangelands and evaluating ecosystem health. Rangelands typically exist as heterogeneous or sparsely vegetated landscapes in which the vegetation structure strongly influences infiltration and soil retention. Infiltration and soil retention further influence soil water recharge, nutrient availability, and overall plant productivity. These key ecohydrologic relationships govern the ecologic resilience of the various states and community phases on many rangeland ESs and are strongly affected by management practices, land use, and disturbances. In a recent review of ESs and S&T models, it was concluded that S&T models are mostly conceptual, built on expert opinion, have not been uniformly developed, and have not been scientifically evaluated to determine if the proposed cause and effect changes in plant communities provided in the S&T models are accurate and achievable.

**Erosion and runoff redistribution as adaptation drivers in open shrub rangeland communities**

Landscape evolution studies in arid climatic regimes have determined that accelerated soil erosion has resulted from changing from a wet, moist climate to drier, warmer climate across the intermountain western U.S. These observations led to the development of a process-response model to explain the relationship between decreasing precipitation and increased soil erosion at the hillslope scale (Bull and Schick, 1979; Wells et al., 1987; Miller et al., 2001). Bull and Schick (1979) hypothesized that changes in climate altered the effective precipitation which resulted in a corresponding change in vegetation with a reduction in grass and forb understory and an open shrub community. This open shrub community had decreased vegetative cover and a corresponding increase in bare ground. Schlesinger et al. (1990) proposed that sparse rangeland ecosystems such as shrubland exploit effectively an unpredictable and episodic source of water and nutrient supply to ensure higher production than allowable by average annual inputs. These researchers also noted that shrubs were more productive along intermittent streambeds and in local areas of water accumulation. Resource redistribution interconnectivity across the landscape seems to be an essential component of ecosystem dynamic in sparsely vegetated rangelands.

Numerous authors have discussed the importance of hydrologic connectivity in controlling runoff and sediment movement at the hillslope scale (Reid et al., 1999; Cammeraat 2002, 2004; Bracken and Croke, 2007; Mueller et al., 2007; Reaney et al., 2007). These authors and numerous others proposed that vegetation patterns and connectivity of bare interspaces are significant controlling factors of hillslope erosion and contaminant transport on rangelands (Tongway and Ludwig, 1997; Valentín et al., 1999; Imeson and Prinsen, 2004). Dominant
hydrologic processes vary with rangeland conditions, the type of plants present, gap between plant basal areas, and the spatial distribution and connectivity of the bare interspaces (Okin et al., 2009). Plant basal areas, rocks, litter, woody debris, and biological soil crusts prevent soil loss from occurring from raindrop splash by protecting the soil surface from impact (Belnap, 2006). These obstructions will cause water to flow around them resulting in concentrated soil erosion in the interspace areas (Puigdefabregas, 2005). This process results in an island affect where excessive soil erosion occurs in the interspace area where runoff is concentrated (Ravi et al., 2010). The erosion and contaminate transport process can be accelerated in these situations and result in loss of biotic integrity, desertification, and sustainability of the site (Schlesinger et al., 1996; Chartier and Rostagno, 2006; Ridolfi et al., 2008). Examples of this is often seen in shrub dominated landscapes which have formed coppice dunes [e.g., sagebrush (Artemisa spp.), creosotebush (Larre spp.), and mesquite (Porsopis spp.) ] and in woodlands where Juniper (Juniperus spp.and Pinyon Pine (Pinus spp.) have expanded into sagebrush steppe communities in arid and semi-arid rangelands (Pierson et al. 1994; Spaeth et al., 1994; Davenport, 1998).

**Proposed framework for salinity reduction**

The Colorado Plateau and Great Basin regions have prevailing climatological and geological conditions that limit development of soil and plant communities. In these landscapes abiotic processes dominate and soil loss is inherently high (e.g., Mancos-shale region of the Colorado Plateau). Simanton et al. (1991) evaluated soil loss on a Mancos shale rangeland site near Meeker, CO and reported that soil loss rates were twice as high as other western rangelands sites evaluated. They ascribed the high soil loss rates to rill processes on these fragile soils which were unnoticeable on other rangeland sites. This region has an arid to semi-arid climate and much of the exposed geological parent material is weakly cemented; high in dispersible salts; soils are shallow, poorly developed and highly erodible; and the region is prone to high intensity convective precipitation events. As a result of these constraints these regions has minimal vegetation and the vegetation tends to be clumped and scattered across the landscape making the region vulnerable to rilling and high soil loss rates. As soil loss is related to rainfall intensity, most of the soil loss occurs during rare storm events. Consequently, rill and arroyo formation is pronounced and average sediment yield frequently exceeds 3 ton ha-1 year-1 on the Colorado Plateau (Langbein and Schumm, 1958; West, 1983).

The key to minimizing soil erosion and salt transport in revegetation projects is to have adequate spatial distribution of vegetation and litter to reduce rainfall splash erosion and to prevent concentration of overland flow that is required for rill initiation and eventually gullies formation if the soil erosion process is unchecked. The revegetation plan should address more than the average vegetative and ground cover, it must address the spatial distribution of the vegetation distribution down slope to prevent concentrated flow from accumulating. It is the spatial distribution of cover, plant density, and basal gaps between plants that needs to be addressed to prevent concentration flow accumulation, rill formation, accelerated soil erosion and salt transport.

Currently there is no historical data for use in developing prediction models to estimate salt mobility and transport for the 11 western states. No single Federal agency has the expertise and funding to develop a salt mobility and transport prediction system by themselves. A new multi-agency effort is required to collect data from across the intermountain west and develop science-based methods to accurately predict salt mobility and transport on Federal rangelands similar to the multi-agency Water Erosion Prediction Project (WEPP) effort (Simanton et al., 1991; and Pierson et al., 2002). To address this void, we propose a framework for developing resilience-based hydrologic interpretations of ES state dynamics and for integration of those interpretations with plant community dynamics within the existing structure of an ESD using the Rangeland Hydrology and Erosion Model (RHEM) and the Agricultural Policy Environmental/eXtender (APEX) model. The development of this structure is supported by a recent synthesis of key ecohydrologic relationships for assessment and management of rangelands (Pierson et al., 2011).

Research is needed to improve our understanding of the linkage and potential coupling between spatial distribution of vegetation, plant density, vegetative and ground cover and sediment transport and salt transport processes. Recent preliminary data from Price, Utah collected in 2014...
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indicate that salt load expressed as the sum of ions in runoff was significantly correlated \((r^2 = 0.5)\) with soil loss (Fig. 7). This is consistent with earlier findings (Hawkins et al., 1977) from experimental research conducted in the same area demonstrating a consistent relationship between concentrated flow erosion processes and salt load. A good prediction of salt transport in runoff requires therefore a robust soil erosion prediction tool in saline environments and a full understanding of how the spatial distribution of vegetation alters these processes. In the saline semiarid rangeland, low vegetation cover combined with the physiochemical effect of salts on clay dispersion and aggregate slacking enhance the erosive power of raindrop impact compared to non-saline rangelands (Fig. 7).

Fig. 8. Water Salinity (mg/L) as a function of sediment concentration (g/L).

\[ y = 6.8592x + 140.35 \]
\[ R^2 = 0.4925 \]

Below is another figure that shows new results from additional analyzed samples new results on relationship of salinity and sediment concentration that the forum might be interested in we could present next week. We have analyzed the two sites and found that the combined dataset has a \(r^2 > 0.8\) for relating sediment concentration to salinity in the runoff water. The relationship has the same surface response that was found with the previous samples relationship and are from two distinct (vegetation and slope) sample sites in Utah.

Fig. 9. Salinity (sum of concentration of \(\text{Ca}^{2+}, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{Na}^+, \text{Cl}^{-}\) ions in surface runoff) as a function of sediment concentration from the two distinct (vegetation and slope) sample sites in Utah.

**Conclusion**

In conclusion, to start from chemical speciation and have it be meaningful and useful in today’s changing world of environmental health and the impact of water quality on all living organisms as well as the storage in our aquifers, learning the basics is truly just the beginning. This chapter has presented a few field examples that are being conducted by field crews and professional research scientists. Together we are all trying to fix problems and answered continued questions in an evolving world. With climate change altering crops and water that was once more available now shifting over land and altering where it can be accessed, greater attention is now being placed on the soil chemistry. Most environmental projects take teams because to have a successful project takes input from several disciplines from sociology to statistics to soil chemists. This chapter took a hard look at chemical activities, which we could have spent a lot of time on, to modeling and building a photogrammetry rainfall simulator. This has all taken a lot of time and publications are in the works. The approach then to best share was an overall glance at how important it is to demonstrate where chemical speciation can take us to gain an insight into the broad world of environmental sustainability and problem solving.

**Acknowledgments:** We would like to acknowledge the support of the Colorado River Basin Advisory Council and funding from the United States Bureau
of Reclamation, Bureau of Land Management, and United States Department of Agriculture-Agricultural Research Service, the University of Reno, Nevada and the Desert Research Institute for all that they have contributed. *All data are preliminary and should not be used for any other purpose. The Federal Government does not endorse any products contained within.

Conflict of interest: All authors declare no conflict of interest.

References

Allison, J.D., Brown D.S., and K.J. Novo-Gradac. 1991. MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 User’s manual. EPA/600/3-91/021. Environmental research Laboratory Office of research and Development U.S. Environmental Protection Agency Athens, GA

Al-Hamdan, O.Z., F.B. Pierson, M.A. Nearing, C.J. Williams, J.J. Stone, P.R. Kormos, et al. 2012. Concentrated flow erodibility for physically based erosion models: Temporal variability in disturbed and undisturbed rangelands. Water Resources Research 48. https://doi.org/10.1029/2011WR011464

Audet, P., S. Arnold, A.M. Lechner and T. Baumgartl. 2013. Site-specific climate analysis elucidates revegetation challenges for post-mining landscapes in eastern Australia. Biogeosciences 10: 6545-6557. https://doi.org/10.5194/bg-10-6545-2013

Belnap, J. 2006. The potential roles of biological soil crusts in dryland hydrologic cycles. Hydrologic Processes. 29: 3159-3179

Bracken L.J, and J. Croke. 2007. The concept of hydrological connectivity and its contribution to understanding runoff-dominated geomorphic systems. Hydrol. Process. 21:1749-1763

Bull, W.B., Schick, A.P., 1979. Impact of climatic change on an arid watershed, Nahal Yael, southern Israel. Quat. Res. 11, 153–171.

Cammeraat E.L.H. 2002. A review of two strongly contrasting geomorphological systems within the context of scale. Earth Surf. Process. 27:1201–1222.

Cammeraat E.L.H. 2004. Scale dependent thresholds in hydrological and erosion response of a semi-arid catchment in southeast Spain. Agr. Ecosyst. Environ. 104:317–332.

Carroll, C., L. Merton, and P. Burger. 2002. Impacts of vegetative cover and slope on runoff, erosion, and water quality for field plots on a range of soil and spoil materials on central Queenslands coal mines. Australian Journal of Soil Research. 38: 313-327

Chartier, M.P. and C.M. Rostagno. 2006. Soil erosion thresholds and alternative states in northeastern Patagonia rangelands. Range. Ecol. Manage. 59: 616 – 624

Davenport, D. W., D.D. Breshears, B.P. Wilcox, and C.D. Allen. 1998. Viewpoint: sustainability of piñon-juniper ecosystems – a unifying perspective of soil erosion thresholds. J. Range Manage. 51:231-240

Harbor, J. 1999. Engineering geomorphology at the cutting edge of land distributance: erosion and sediment control on construction sites. Geomorphology. 31: 247-263

Hawkins, R.H., G.F. Gifford and J.J. Jurinak. 1977. Effects of land processes on the salinity of the upper Colorado River Basin: Final project report. Utah State University, Logan, Utah. p. 196

Imeson AC, and H.A.M. Prinsen. 2004. Vegetation patterns as biological indicators for identifying 478 runoff and sediment source and sink areas for semi-arid landscapes in Spain. Agr. Ecosyst. Environ. 104: 333–342

Langbein, W.B. and S.A. Schumm. 1958. Yield of sediment in relation to mean annual precipitation. Amer. Geo. Union Trans. 39: 1076-1084

Miller, J., D. Germananoski, K. Waltman, R. Tausch, and J. Chambers. 2001. Influence of late Holocene hillslope processes and landforms on modern channel dynamics in upland watersheds of central Nevada. Geomorphology. 38: 373-391

Mueller E.N., J. Wainwright, and A.J. Parsons. 2007. Impact of connectivity on the modeling of overland flow within semiarid shrubland environments. Water Resour. Res. 43. https://doi.org/10.1029/2006WR005006

Okin, G.s., A.J. Parsons, J. Wainwright, J.E. Herrick, B.T Bestelmeyer, D.C. Peters, and E.L. Fredrickson. 2009. Do changes in connectivity explain desertification? Bioscience. 59:237-244

Pierson, F.B., C.J. Williams, S.P. Hardegree, M.A. Weltz, J.J. Stone, and P.E. Clark. 2011. Fire, plant invasions, and erosion events on western rangelands. Range. Ecol. Manage. 64:439-449

Pierson, F.B., W.H. Blackburn, S.S. Van Vactor, and J.C. Wood. 1994. Partitioning small scale spatial variability of runoff and erosion on sagebrush rangeland. Water Resour. Bull. 30:1081-1089.

Pierson, F.B., C.A. Moffet, C.J. Williams, S.P. Hardegree and P.E. Clark. 2009. Prescribed-fire effects on rill and interrill runoff and erosion in a mountainous sagebrush landscape. Earth Surface Processes and Landforms 34: 193-203. https://doi.org/10.1002/esp.1703
Pierson, F.B., K.E. Spaeth, M.A. Weltz, and D.H. Carlson. 2002. Hydrologic response of diverse western rangelands. J. Range Mgmt. 55: 558-570
Puigdefabregas, J. 2005. The role of vegetation patterns in structuring runoff and sediment fluxes in drylands. Earth Surf. Processes 30:133-147
Ravi, S., P. D’Odorico, T. E. Huxman, and S. L. Collins. 2010. Interactions between soil erosion processes and fires: Implications for the dynamics of fertility islands. Range. Ecol. Manage. 63:267-274
Reaney S.M., L.K. Bracken, and M.J. Kirkby. 2007. Use of the Connectivity of Runoff Model (CRUM) to investigate the influence of storm characteristics on runoff generation and connectivity in semi-arid areas. Hydrol. Process. 21:894–906
Reid, K.D., B.P. Wilcox, D.D. Breshears, and L. MacDonald. 1999. Runoff and erosion in a pinyon-Juniper woodland: Influences of vegetation patches. Soil Sci. Soc. of Amer 63: 1869-1879
Ridolfi, L., F. Laio, and P. D’Odorico. 2008. Fertility islands formation and evolution in dryland ecosystems. Ecol. Soc.13:5
Rominger, J.T. and H.M. Nepf. 2011. Flow adjustment and interior flow associated with a rectangular porous obstruction. J. Fluid Mech. 680: 636-659. https://doi:10.1017/jfm.2011.199
Schlesinger, W.H., J.F. Reynolds, G.L. Cunningham, L.F. Huenneke, W.M. Jarrell, R.A. Virginia, et al. 1990. Biological feedbacks in global desertification. Science(Washington) 247: 1043-1048
Schlesinger, W. H., J. A. Raikes, A. E. Hartley, and A. F. Cross. 1996. On the spatial pattern of soil nutrients in desert ecosystems. Ecology 77:364–374
Simanton, J.R., M.A. Weltz, H.D. Larsen. 1991. Rangeland experiments to parameterize the water erosion prediction project model: vegetation canopy cover effects. Journal of Range Management 44:276-282
Spaeth, K.E., M.A. Weltz, F.B. Pierson, and H.D. Fox. 1994. Spatial pattern analysis of sagebrush vegetation and potential influences on hydrology and erosion, p. 35-50. In: Variability of Rangeland Water Erosion Processes. W.H. Blackburn, F.B. Pierson, G.E. Schuman, and R.E Zartman , ed. Madison, Wisconsin, Soil Science Society of America. Special Publication 38
Stumm, W., and J.J. Morgan. 1996. Aquatic Chemistry Chemical Equilibria and Rates in Natural Waters. 3rd edition. Wiley-Interscience, New York
Tongway, D.J., and J.A. Ludwig. 1997. The nature of landscape dysfunction in rangelands. In: Landscape Ecology: Function and Management, 49-61. J.Ludwig, D. Tongway, D. Freundenberger, J. Noble, and K. Hodgkinson, eds. Collingwood, Victoria, Australia: Commonworth Scientific and Industrial Research Organization
Wells, S.G., McFadden, L.D., Dohrenwend, J.C., 1987. Influence of late Quaternary climatic changes on geomorphic and pedogenic processes on a desert piedmont, eastern Mojave Desert, California. Quat. Res. 27, 130–146
West, N.E. 1983. Great Basin-Colorado Plateau sagebrush semi-desert, p. 331-350 In: Temperate deserts and semi deserts, Vol. 5, Ecosystems of the World, N.E. West, ed., Elsevier, Amsterdam

Cite this article as:
Rossi, C.G.; Heil, D.; Weltz, M.; Nouwakpo, S.K. 2019. Chemical speciation in semiarid environments – A review. Amaz. Jour. of Plant Resear 3(2): 305-315.
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