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Climate-influenced hydrobiogeochemistry and groundwater remedy design: A review

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Abstract

The process of designing a remedy for contaminated groundwater historically has not commonly included climate-future, hydrologic, and biogeochemical aquifer characteristics. From experience, the remedy design process also has not consistently nor directly integrated or projected future hydrologic and biogeochemical effects of the human-induced or developed environment—aka the anthropogenic influence—on potential remedy performance. The apparent practice of (1) not regularly assessing anthro-influenced hydrological (termed here as *anthrohydrology*) or biogeochemical characteristics (collectively *hydrobiogeochemistry*) of a site and (2) rarely accounting for future climatic shifts as design factors in remedy design may be due, in part, to the general practice-level view that groundwater remediation systems (whether in situ or ex situ) have seldom been anticipated to last more than a few years (or one or two decades at the most). Second, methods to reliably and quantitatively estimate site-specific, climate-future shifts in groundwater conditions using global and/or regional climate models and the resultant impacts on contaminant plume characteristics have not been readily available. The authors here suggest that while the concept of remedy design resilience and durability, within an envelope of climate change and anthropogenic influence, has been discussed in some technical circles as a component of "sustainable remediation," we have found that direct application of these technical concepts in quantifiable terms remains rare. By incorporating the potential influence of future hydrobiogeochemical scenarios into remedy design, however, the design process could account for reasonable climate-induced influence on the groundwater system for a given site. These scenarios could then be applied within the remedy selection process to assess performance durability under potentially changing hydrologic, biological, and chemical conditions.

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1 | INTRODUCTION: THE ANTHROHYDROLOGIC CYCLE, CLIMATE CHANGE, AND GROUNDWATER REMEDIATION

Designers of remediation systems for contaminated land and groundwater are tasked with integrating the hydrogeological, chemical, and biological characteristics of a site, with a contaminant management or mitigation approach that must perform to meet regulatory-defined human and/or ecological risk objectives. These objectives most commonly require the achievement of certain chemical concentration goals in the affected earth media (e.g., soil and/or groundwater) by a certain time and over a certain area or location to protect human and/or ecological receptors. The process to develop the appropriate remedy, whether that remedy involves the removal of a contaminant to treat above ground (the ex situ approach) or all mitigation occurs below ground (the in situ approach), requires attaining comprehensive knowledge of the site conditions, chemical source term, land use, and, sometimes, the projected future land use (if known), among other characteristics. This effort leads to a conceptual site model (CSM) that becomes the foundation for remedy development where the CSM is intended to include relevant site features and characteristics including elements of the physical, hydrological, chemical, and biological systems—the hydrobiogeochemistry—representing the past, present, and sometimes, future timescales for which the remedy is intended.

The CSM is not static, however. The derivation must remain open to the acquisition of new data or updated information and often adjusts. A question is how far into the future must the CSM be projected so that adequate projections of site characteristics could be integrated into remedy selection. Further, how much inclusion of future climate projections and the resultant influence on the hydrological, biological, and geochemical environment should be addressed. The initial construction of the CSM and the subsequent modifications rely on the integration of known hydrologic and chemical cycles and the dynamic and transient nature of environmental conditions. However, predictions of future conditions are uncertain; and uncertainty increases as the time into the future increases. Yet, the use of well-recognized and accepted relationships among and within the various physical environments, such as the hydrological environment, is arguably necessary for assuring that the CSM is as representative and valuable as it can be for assessing and mitigating the risk from a contaminated site.

That climate is changing is accepted science (Cook et al., 2016). Efforts by multinational groups such as the Intergovernmental Panel on Climate Change (IPCC, 2007, 2022) and individual national organizations from the United States Environmental Protection Agency (USEPA, 2022), the European Environment Agency (EEA, 2022), and the Commonwealth Science and Industrial Research Organization of Australia (CSIRO, 2022), among other global groups, have provided substantial information and projections regarding continuing changes in patterns of wind, rain, temperature, sea level rise, and severe events from drought to flood for the various regions of their respective geographies.

1.1 | Anthrohydrology

Some 90 years ago, the American civil engineer and scientist, Robert F. Horton wrote:

> …it is difficult to devise an investiture which will include all essential features of the subject and omit none. (Horton, 1931)

Here, Horton who arguably may be the "trail blazer" of American hydrology as a technical field (Bras, 1999) identified the challenge of fully describing the components that influence the "new science" of hydrology. Components that include the relationship of hydrology with other geosciences for characterizing the "natural occurrence, distribution, and circulation of water on, in, and over the surface of the earth." Nearly one century after Horton envisioned his *radical* new description of the hydrologic cycle (i.e., expanded to include surface water and atmospheric water in addition to "underground-water"), and more than 40 years since the enactment of the "Superfund Law" in the United States (i.e., the US Comprehensive Environmental Response, Compensation, and Liability Act of 1980 or CERCLA) formally acknowledged one type of human-created impact to the hydrologic environment, that is, contaminant impact (Dayley & Layton, 2004; Grad, 1982), the science of hydrology has evolved again to encompass the study of human-induced changes to global and regional climatic patterns (Cook et al., 2016; Owusu-Daaku, 2021). With studies reporting that pollution of air, water, and soil is responsible for millions of deaths each year globally (Münzel et al., 2022), attention to understanding the physical and human-driven stress on contaminant occurrence, distribution, and fate has never been greater. Therefore, acknowledging the influence that climate, with its variability and trends, imparts over the hydrologic cycle—including groundwater and surface water—becomes a more critical tenet in understanding the physics and biogeochemical behavior of contaminant plumes in a groundwater system as noted by numerous works over the past 25 years (Dragoni & Sukhija, 2008; Green et al., 2011; Kløve et al., 2013; Loaiciga et al., 1996; Moseki, 2018; O'Connell & Hou, 2015).

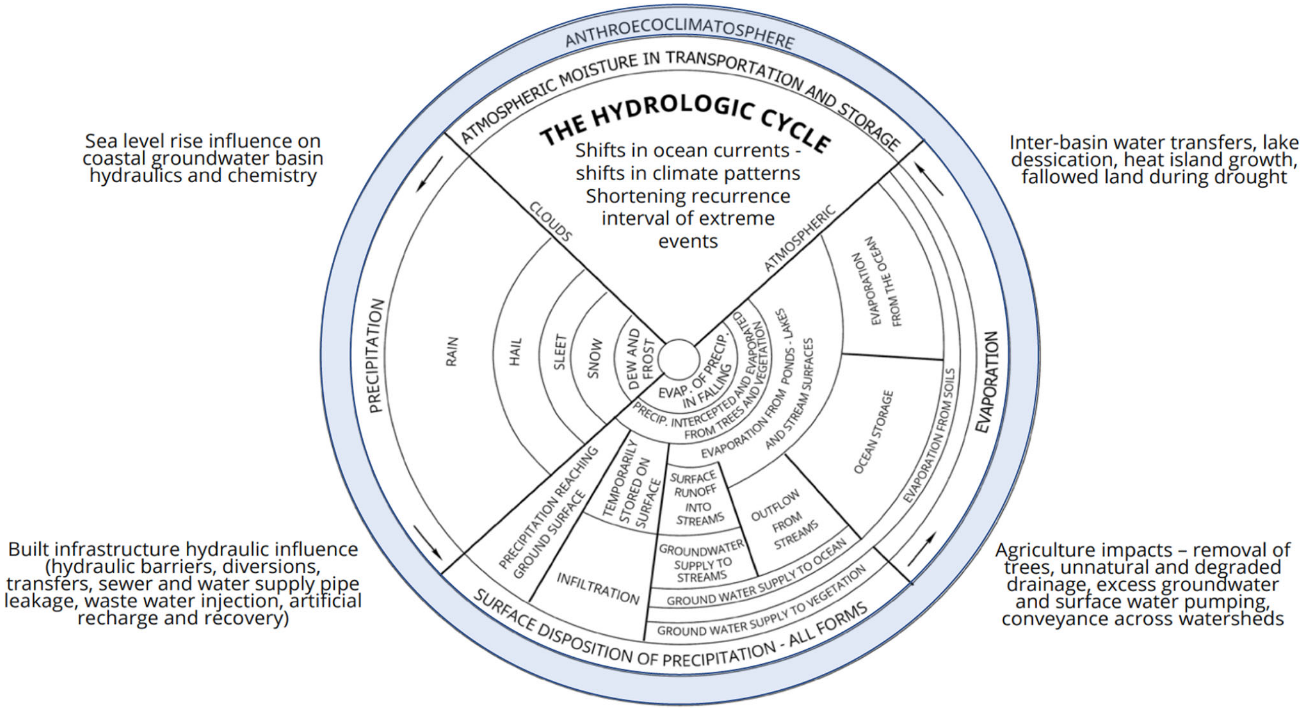
The acknowledgment by "20th (and 21st) Century science" that the hydrologic environment is completely integrated within the climatic biosphere is not to take away from the immense knowledge by indigenous and aboriginal communities who have long recognized the interplay of hydrologic conditions as a component of the complete environment and its coupling to the social-ecologic structure of a community (Wilson et al., 2015). But Horton's vision, modified to the present time, becomes valuable as a tool for evaluating the potential impact of *anthro*-influenced hydrologic changes, and the resultant biogeochemical effects, on contaminant mitigation measures for groundwater (Kumar & Reddy, 2020; Maco et al., 2018; O'Connell & Hou, 2015; Wick et al., 2018). Integrating the climate-driven effects as well as the hydrological disruptions created from human-induced changes to the landscape resulting from urban, agricultural, and other anthropogenic changes to the earth's environment (Attard et al., 2016) directs us toward modifying the conventional model of the hydrologic cycle as introduced by Horton (1931) to incorporate both climate and anthropogenic drivers.

The anthropogenic influence is not just about the effect of a changing climate on the hydrologic environment. Direct examples of human-induced impact to the hydrological environment include the dewatering of earth materials for the construction of deep building foundations or below ground transportation systems as seen in major urban centers like San Francisco and New York City (McGrane, 2016) and the efforts to protect coastal resources from seawater incursion in areas of dense population and/or heavy agriculture (Jasechko et al., 2020) common from California to Israel (Luyun et al., 2011) to the Nile Delta of Egypt (Sherif & Singh, 2002). Other examples of projects that involve large-scale human-induced influences on the hydrologic environment, including resultant stress on biological and geochemical systems, include the complex and extensive interbasin water redistribution systems that supply large areas of the western United States including the Los Angeles megalopolis (Lehrman, 2018), the South-North Water Transfer Project in China (Ma et al., 2016), and the Tagus-Segura interbasin transfer in Spain (Rey et al., 2016). Although our research described herein does not directly assess the hydrologic (and associated biological, ecological, and geochemical) impacts of these anthrohydrology projects, we acknowledge that the human-hydrological nexus should be considered as one of the important puzzle pieces for designing effective water quality protection and restoration approaches in part to reconnect the broken bond between human and ecological receptors and the source of the water resources that these populations and communities rely on (D'Odorico et al., 2019).

Here, we refer to the anthrohydrologic cycle as an approach to include induced hydrological stresses within the Horton (1931) graphical representation (Figure 1). This construct is to support the derivation of the anthrohydrologic CSM for (1) describing and evaluating contaminant fate and transport in a present-day groundwater system; (2) estimating future conditions; and (3) designing contaminant mitigation measures that will adjust to predictions of future conditions that are directly related to climatic shifts or may be associated with the human response to climatic factors. Examples include but are not limited to (a) water resource redistribution and interbasin transfers; (b) extensive implementation of new hydraulic barrier or drainage infrastructure; (c) managed artificial recharge of aquifer systems; (d) excessive additional use of nutrients and fertilizers on agricultural fields; (e) release of industrial and municipal wastewater to the watershed and subsurface directly by intention or indirectly through leakage from infrastructure and utility corridors; and (f) drying of lakes, ponds, and fields due to precipitation and runoff changes. These concepts have been discussed and illustrated in recent years by the authors herein (Warner & Naidu, 2022) and are now being addressed by government research organizations as shown by the inclusion of some of these topics to an updated "water cycle" diagram created by the United States Geological Survey (USGS, 2022).

1.2 | Climate models and groundwater

Taking the hydrologic cycle a step further, we recognize that the climate–groundwater relationship exists in a dynamic equilibrium



Sea level rise influence on coastal groundwater basin hydraulics and chemistry

Inter-basin water transfers, lake dessication, heat island growth, fallowed land during drought

Built infrastructure hydraulic influence (hydraulic barriers, diversions, transfers, sewer and water supply pipe leakage, waste water injection, artificial recharge and recovery)

Agriculture impacts – removal of trees, unnatural and degraded drainage, excess groundwater and surface water pumping, conveyance across watersheds

FIGURE 1 Horton (1931) hydrologic cycle was modified to acknowledge climatic-human-induced or anthrohydrologic influence.

where the components of these physical systems reflect characteristics upon each other (Green, 2016; Maxwell & Kollet, 2008) as an integrated system of components within a common ecosphere (Hu et al., 2019; Kumar, 2012; Loaiciga et al., 1996; Stagl et al., 2014). The hydrologic interconnectedness illustrates the importance of groundwater to the overall ecosystem conceptual model (Fienen & Arshad, 2016; Tóth, 1999). The concept is that the integration of groundwater processes within the overall construct of a climatic system would allow effective analysis and projection using advanced climate models to help predict future groundwater conditions as influenced by climate stress and change.

The objective of our work, however, is not to review and critique climate models or provide other than a general opinion on which climate models, if any, may be useful for supporting the evaluation of future groundwater conditions or the design of groundwater contaminant remedies. We recognize that an active area of research is focused on the state of climate models and their utility for evaluating numerous physical and biogeochemical systems. A question is whether the state of such analysis and the tools available are sufficient for projecting future climate with enough certainty and at a scale useful for quantifying potential change to both regional and local groundwater conditions. More important and relevant to the topic of this paper is whether such climate models are useful for the selection, design, and monitoring of groundwater remediation systems.

Generally, we understand that climate models have continued to improve and are finding more value as multidimensional tools particularly for hydrologic impact studies. Giorgi (2019) noted that the year 2019 marked the 30th anniversary of the first regional climate model (RCM) and his article provides an overview of the continuing improvement in model development, resolution, and projections. However, work remains on how to the use these models effectively. Challenges in use stem from how data are represented within a model construct, and how to accomodate the inherent biases in data use and interpretation as discussed by Vrac et al. (2022) in their evaluation of temperature and precipitation correlations for Europe using modern model ensembles. We also recognize that many climate models and approaches have been developed to assess various aspects of surface water and groundwater hydrology including, for example, studies on groundwater recharge (e.g., Atawneh et al., 2021; Meixner et al., 2016), development of hydrologic impact studies (Teutschbein & Seibert, 2010), and studies on conjunctive groundwater and surface water management (e.g., Mani et al., 2016).

Our interest in using and recommending climate models for purposes other than (or in addition to) greenhouse gas (GHG) or hydrologic projections becomes greater as we assess the success of studies such as that of Bussi et al. (2018) who integrated water quality and climate models under GHG scenarios projected by the IPCC to simulate the response of aquatic organisms to climate stress and "anthropogenic pressures." The search for appropriate models to integrate climate and environmental/ecological systems for purposes other than projecting future climate, temperature, and precipitation conditions is a long-standing pursuit of the research community (e.g., Foley et al., 2000; Meyer et al., 1999; Smerdon, 2017). Smerdon (2017) went further and reviewed several studies that attempted to link hydrologic and groundwater models with climate models and noted that these studies were conducted, in part, due to this knowledge gap identified by the IPCC Fourth Assessment Report (IPCC, 2007).

The conclusion articulated by Smerdon (2017) that a large level of uncertainty remains with predicting site-specific groundwater recharge (and by default, other groundwater conditions) under climate change scenarios should not be discouraging but rather supports our view that groundwater and remediation scientists should not yet rely on climate models to design contaminant mitigation measures in most cases. Climate models may be informative for certain larger-scale purposes (and maybe even for some cases of predicting long-duration regional hydraulic capture schemes) but may still lack certainty for specific small-scale locations common to most sites in the remediation practice. For some unusual circumstances, involving exceptionally large (such as large agricultural areas or large regional industrial, mining, or watershed-size sites that are impacted by legacy contaminants) regional climate modeling may find value.

1.3 | Integrating climate change with hydrobiogeochemistry

Numerous researchers have studied the impacts on hydrologic conditions from climate and some would claim that climate change is the most studied potential driver of hydrologic change in the past decade (Pumo et al., 2017). Under this consideration, climate projections for groundwater remediation involving long-duration hydraulic capture (and associated ex situ treatment) may be informative if reliable. And for in situ remedies, as this paper is primarily focused, the studies of the impact of climate change on a given hydrobiogeochemical system would assess how the ambient chemistry of natural waters in contact with earth materials, as comprehensively described by Hem (1985), would be affected by a shifting climate. Integrating climate projections with hydrobiogeochemistry would include an analysis of local and regional changes in rainfall and snow patterns (Barron et al., 2012; Cuthbert et al., 2019) and how such conditions might affect the characteristics of groundwater physically (e.g., changes to hydraulic gradient directions and contact with aquifer solids that may affect mineral dissolution, etc.), chemically (e.g., changes in aqueous dissolved oxygen [DO] content, effects on reduction−oxidation [redox] conditions that influence the solubility and fate of aqueous constituents, etc.), and biologically (e.g., changes to temperature, DO, redox, and mineralogical effects that affect microbiological communities).

Studies and articles that focus on the connection between temporal and spatial hydrologic influences due to climate change and anthropogenic environmental influences and the fate and transport of solutes within groundwater systems were relatively scarce before the 2000s. Since then, studies including Libera et al. (2019), Biswas et al. (2018), and Kløve et al. (2013) are examples of work that ponder and evaluate various aspects of subsurface chemical behavior in response to climatic-induced stress to hydrogeologic systems. The works of Ossai et al. (2020), Gmitrowicz-Iwan et al. (2020), Bondu et al. (2016), Caraballo et al. (2016), Manning et al. (2013), and Visser et al. (2012) have studied such processes as the transformation of inorganic and organic species to constituents with different physico-chemical makeup in response to changes to hydrologic conditions (e.g., potentiometric surface and vadose zone moisture saturation) and geochemical conditions (e.g., changes to pH, DO content, aquifer mineral solubility, and dissolved solids content). These observations point to a consideration of how the character of a contaminant plume may be affected under these (or future) circumstances, considering that such changes can lead to critical biogeochemical changes to a species as well as magnification and accumulation of target constituents (Schiedek et al., 2007) is a gap in the remedial design process.

As an example, Biswas et al. (2018) illustrate how adsorption and desorption of chemical pollutants chiefly metals and metalloids including arsenic, mercury, and hexavalent chromium are prone to relatively radical shifts with change to aqueous redox, pH, DO, and as changes in mineral solute content (consider dissolved carbon or organic matter, and salinity) shift with changes to hydrologic conditions. Examples of how climatic factors can negatively impact water quality parameters via changes to redox conditions often are focused on region- or country-wide disasters as exemplified by the case of arsenic occurrence and excess salinity of drinking water resources in deltaic environments such as Bangladesh and Cambodia—a matter of which the research community has been focused on for several decades (Huq et al., 2020; Khan et al., 2011; Mihajlov et al., 2020; Mitchell et al., 2011; Shahid, 2010).

As the technical practice of remediating contaminated land and water moves forward, considering the apparently increasing prevalence of extreme weather events over many areas of the globe (Ridder et al., 2022), the remedy designer will need to consider whether to include statistically low probability—high consequence events (such as intense storms, floods, tidal inundation) into remedial design or whether continuing with the common approach that designing for today remains sufficient because the rate of overall change in environmental systems remains low (e.g., considering the gradual increase in the sea level may be manageable by today's design standards, providing that the intervals between extreme events that compound rising sea conditions is not radically shortened). As an example, situation, *Los Angeles Times* reported that more than “400 toxic sites in California are at risk of flooding from sea level rise” (Xia, 2021). Similarly, research into the climate influence on nonocean shorelines, including that of Lake Michigan, USA, has been highlighting the potential impact to industrial facilities and contaminated land for inland hydrologic areas (Courtney et al., 2022). These situations alone bring us to the issue of how to adequately design remedies to perform during and through the inevitable changes to the hydrogeochemical environment that accompany this example of saline or freshwater intrusion into a chemical waste site.

The chronic case of the gradual influence of highly saline seawater still does not include the more dramatic case of extreme floods (that may also be a result of sea level rise) and other extreme hydrologic events. The consideration of whether to include disaster planning in environmental management or whether focusing on long-term chronic change is more appropriate from both a technical and economic perspective has been a debate ongoing for at least the past 40 years since the Superfund law was enacted (Gaddis et al., 2007; Santella et al., 2010; Summers et al., 2021; Zimmerman, 1985). Our work here does not focus on the protection of remediation sites from extreme events, which may be more a matter of geotechnical and engineering isolation measures or direct relocation of the waste material. However, where lingering effects from an extreme event create shifts (primarily long-term but shorter-term impacts also could be of interest), the efforts described herein are representative.

The 1994 installation of the world's first commercial permeable reactive barrier (PRB) composed of zero valent iron (ZVI) is a case in point where recognized future performance uncertainty was a key consideration for completing the design of this innovative in situ groundwater remediation technology (Warner, 2015; Warner et al., 1998). At the time, the quantifiable cost–benefit analysis focused chiefly on the value of replacing an operationally expensive ex situ approach consisting of a conventional “pump and treat” remedy with a novel passive in situ approach that required a substantial capital expenditure. Although the PRB design process involved numerical groundwater modeling and calculations of potential secondary geochemical mineralization as a function of reaction progress and aqueous geochemical aging of the inherent iron corrosion process, the consideration of climatic change as a functional design element was at least a decade premature. However, consideration for temporal changes in potentiometric surface and hydraulic gradient conditions was a concern because groundwater velocity through the passive treatment system is one of the key design components. Variable changes in both rate and gradient direction can affect the residence time criterion of the design calculations and were noted from historical records as a key parameter. To account for the potential shifts in future hydraulic head and orientation, lateral upgradient hydraulic guide walls were constructed from the ends of the treatment zone, and short lateral hydraulic guide walls were constructed upgradient from the treatment zone to prevent the potential for eddy-forced velocity changes within the ZVI core if shifts in the external hydraulic gradient direction forced a quickening of flow existing in the treatment zone (Warner et al., 2005). A further refinement that added a performance safety factor was to increase the flow through the length of the ZVI treatment zone and increase the percent of ZVI within the system. By all accounts, the safety factor was increased by several times, though only by semi-quantified analysis as much was at the decision-making of the site owner who wanted to secure the investment in the novel approach. The system remained in operation for over 20 years arguably becoming one of the first sustainable and durable in situ groundwater remediation systems (Warner, 2015).

If the early PRB example described herein were to be designed today, would it look different or would it consider different design algorithms? The answer may be yes to both. Although potential changes to the ambient subsurface hydraulic character were recognized, the tools used to perform the analysis were not overly sophisticated and relied on the surefooted early numerical modeling tools available at the time. Today's effort may investigate the future with greater sensitivity and evaluate different hydraulic scenarios while matching subtle engineering shifts in design to accommodate potential changes to groundwater velocity. Climate modeling may also be integrated to better understand future recharge scenarios and, finally, geochemical modeling would be integrated directly into the hydraulic model to best simulate geochemical changes that are influenced by the hydraulic patterns. While the general footprint of the early PRB may not in the end look radically different, we can be sure that a more precise geometric design that includes a lower volume (and thus cost) of the treatment material would be designed using the modern numerical tools of today.

2 | REMEDIATION-FOCUSED SUSTAINABILITY, RESILIENCY, AND DURABILITY AS A PROXY FOR CLIMATE CHANGE CONSIDERATIONS

As presented herein and from our experience, groundwater remedy designs have not consistently accounted for potential future climate-induced changes to hydrologic, geochemical, or biological conditions for a site. This is the case even though regulatory agencies including the USEPA recognize that climate-induced impacts that are both acute (such as exceptional precipitation from high-intensity storms) and chronic (such as sea level rise) have and will continue to negatively impact contaminant sites unless mitigation or protection is implemented (United States Government Accountability Office [USGAO], 2019; USEPA, 2023a). However, the remediation practice has increasingly been on a path that includes concepts of “sustainable remediation” and “resilient remediation” as a proxy for considering climate change in remedial design.

Technical discussions that integrate climate, sustainability, water quality and remediation are found within the recently published compendium by Hou (2020) and in work by others including Kumar and Reddy (2020), Favara et al. (2019), O'Connor et al. (2019), Lipczynska-Kochany (2018), Maco et al. (2018), Wick et al. (2018), Rowe et al. (2017), Ridsdale and Noble (2016), Rizzo et al. (2016), Smith and Nadebaum (2016), Harclerode et al. (2016), O'Connell and Hou (2015), and Ellis and Hadley (2009). These examples are included within an ever-increasing set of guidance and recommendation reports from governmental organizations and professional societies such as SuRF-UK (2020), the Washington State Department of Ecology (2017), the International Standards Organization (ISO) (2017), and New York State Department of Environmental Conservation (2011). The documents provide both general and specific risk management planning concepts relative to adaptation planning for groundwater and soil contaminant clean-up sites. The information is useful as a preliminary planning-level integration of potential risks to clean-up sites from climate-induced effects (such as intense precipitation, flooding, and wildfire) within the remedy selection process. However, likely due to the evolving nature of the practice, the level of engineering detail and the methodology to assess remedy performance under climatic impact is mostly qualitative in description with no substantial inclusion of the engineering-level design methodology. As Simon (2018) notes, the integration of climate change risks into remediation design and application also is a challenge because remediation professionals are not typically trained in evaluating climate risk and vulnerabilities to contaminated sites. Fortunately, the ability to project both the range of potential climatic influence and anthropogenic change likely to impact a clean-up site is improving. Methods that apply quantitative analysis for integrating future hydroclimatic conditions under a range of plausible scenarios are becoming more available and more credible (Alder & Hostetler, 2019; Chen et al., 2019).

Our proposed updated definition of sustainable, climate-durable remediation is:

A *viable remediation strategy for contaminated land and/or groundwater that*:

- Provides necessary (i.e., regulatory, and legally required) risk management including contaminant mitigation as appropriate.
- Balances the social, economic, and environmental demands of the remedy.
- Can be constructed and operated using materials and processes that conserve or limit the waste of resources (e.g., water, energy, land) to accomplish risk management objectives.
- Promotes—and prevents inhibition of—progress toward social and environmental sustainability goals that are consistent with local norms and conditions.

The admittedly broad definition is consistent with prior conceptions of “sustainable remediation” such as those applied by SuRF-UK (2020) involving limiting the environmental impacts of a remedy and Interstate Technology & Regulatory Council (ITRC, 2011a, 2011b), which furthers the concept of green and sustainable remediation (GSR) as:

> The site-specific employment of products, processes, technologies, and procedures that mitigate contaminant risk to receptors while balancing community goals, economic impacts, and environmental effects.

An apparent objective of the ITRC definition, which added discussion of “resiliency” in the 2021 guidance (ITRC, 2021) and similar to those promoted by SURF-UK (2020) and Hou (2020), was to promote a remedy selection process that applies an evidenced-based assessment of the sustainability tenets (i.e., environmental, social, and economic) considered by potential remedies so as to select a remedial approach (or technology) that is technically effective, economically reasonable, ecologically appropriate, and socially acceptable both locally and regionally. This is not to say that this apparently logical and inclusive approach was universally and unequivocally accepted by regulatory agencies, remediation managers, and design practitioners (Smith, 2019). However, the definition promoted herein is intended to add pragmatism by avoiding terminal words such as "maximum" and "minimum" for defining cost and impact endpoints and "optimal" as an attainable goal that identifies potential benefit or performance to focus on pragmatic and reasonable endpoints that are not distracted from the most important remedial goal of reducing, if not eliminating, actual and perceived risks from contaminated land and water.

Assuring that a contaminated land remedy will continue to perform through change if in fact the health and ecological risk of contamination is not quickly eliminated, then both "resilience" and "durability" become important design objectives for shrinking the vulnerability envelope and assuring a greater probability of consistent protection. Here, we define resiliency as the capacity to "recover intended performance from system shock or disruption" and durability as "the capacity to withstand shock or disruption and maintain intended performance." Although some, including (Holling, 1973), combined the two ideas of resiliency and durability—the ability to recover from the shock and the persistence to the shock—into the single idea of "resilience," we have chosen to separate the terms for both clarity and for considering how individual design components or parameters might be evaluated during the remedial design and selection exercise. For both constructions, that shock may be related to an acute or chronic disruption or change in the hydrologic system due to climatic impact. Of historical interest, the November 2015 US Presidential Memorandum that defines the term "durability" as it relates to the environmental benefit of impact mitigation as:

> …a state in which the measurable environmental benefits of mitigation will be sustained, at a minimum, for as long as the associated harmful impacts of the… activity continue. The "durability" of a mitigation measure is influenced by: (1) the level of protection or type of designation provided; and (2) financial and long-term management commitments. (United States Office of the Press Secretary, 2015).

The approach toward integrating "adaptive capacity" (again, as a proxy for climate change) into remediation design combines the concepts of sustainability (i.e., green materials and concepts), resiliency (i.e., the ability to rebound from the damage caused by systemic shock), and durability (i.e., a design that promotes longevity and ability to withstand systemic shock) into the CSM that provides the foundation for remedial system development. Discourse from Adger and Vincent (2005) and Engle (2011) help to define adaptive capacity as the vector of resources from which adaptation actions can be made or the ability of a system to a priori prepare for, adjust, and respond to predicted stresses and changes.

The terms *vulnerability, resilience, and remedial adaptive capacity* are not new even though the practice has recently appeared to embrace these notions. The USEPA (2014) defined these terms with respect to addressing climate change:

- *Vulnerability*: The degree to which a system is susceptible to adverse effects of climate change.
- *Resilience*: The capability to anticipate, prepare for, and recover from the threat of the impact of climate change.
- *Remedial Adaptive Capacity*: The capacity or ability of a system to adjust to climate variability and change or to cope with the consequences.

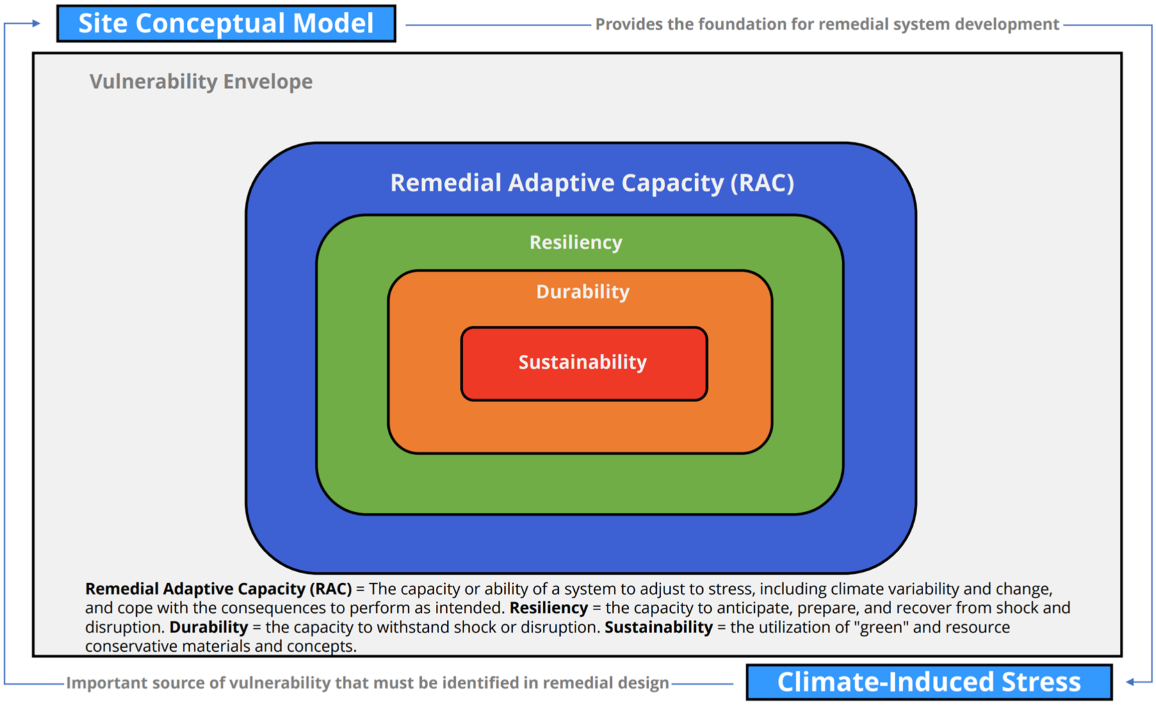
Here, we also add "durability" as the characteristic of performing at an acceptable level for an intended timespan regardless of environmental change or system shock. As illustrated by Figure 2, the remedial design components of sustainability, resiliency, and durability are built on a foundation set by the CSM but within the envelope of climate stress and vulnerability within the remedial design process.

The development of resilient and durable mitigation measures for contaminated groundwater will rely on the next generation of the CSM by incorporating future hydraulic predictions and associated geochemical and biochemical responses. Numerous guidance documents and standards have been developed to guide the development of the CSM based on academic and practical approaches including ASTM (2021), Suthersan et al. (2016), Rojas et al. (2008), Nathanail and Bardos (2004), and Pollard et al. (2004) and we anticipate that future scenarios will be more commonly added for use in remedial design to avoid the "surprise" factor that invalidates the conventional CSM due to the inclusion of new information (Bredehoeft, 2005). In this way, the CSM can be advanced by also considering the foundational work by Stumm and Morgan (1996), which classically detailed concepts on aquatic chemistry and chemical equilibria in natural waters (first published in 1970 with editions in 1996 and 2012) and should be considered a useful resource for considering the climate-induced impact on the hydrologic cycle and resultant effects on the aquifer and groundwater geochemical conditions.

3 | HYDROBIOGEOCHEMICAL SHIFTS AND CONTAMINANT BEHAVIOR

Resiliency and durability, as discussed in the prior paragraphs, are arguably the dominant characteristics for assuring the effective performance of a groundwater remedy as conditions change. Understanding the effects of change on the hydrobiogeochemical system and the resultant influence on contaminant behavior becomes a key analysis for designing a remedy to be resilient and durable.

Figure 3 is the schematic representation of the groundwater's hydrobiogeochemical system with the various components for



Remedial Adaptive Capacity (RAC) = The capacity or ability of a system to adjust to stress, including climate variability and change, and cope with the consequences to perform as intended. **Resiliency** = the capacity to anticipate, prepare, and recover from shock and disruption. **Durability** = the capacity to withstand shock or disruption. **Sustainability** = the utilization of "green" and resource conservative materials and concepts.

FIGURE 2 Conceptual framework for the site conceptual model that includes remedial adaptive capacity as related to the tenets of sustainability, resiliency, and durability within the context of climate-induced system vulnerability. Developed after the work of Cutter et al. (2008) and Engle (2011) by adding the concept of durability for remedial design and application.

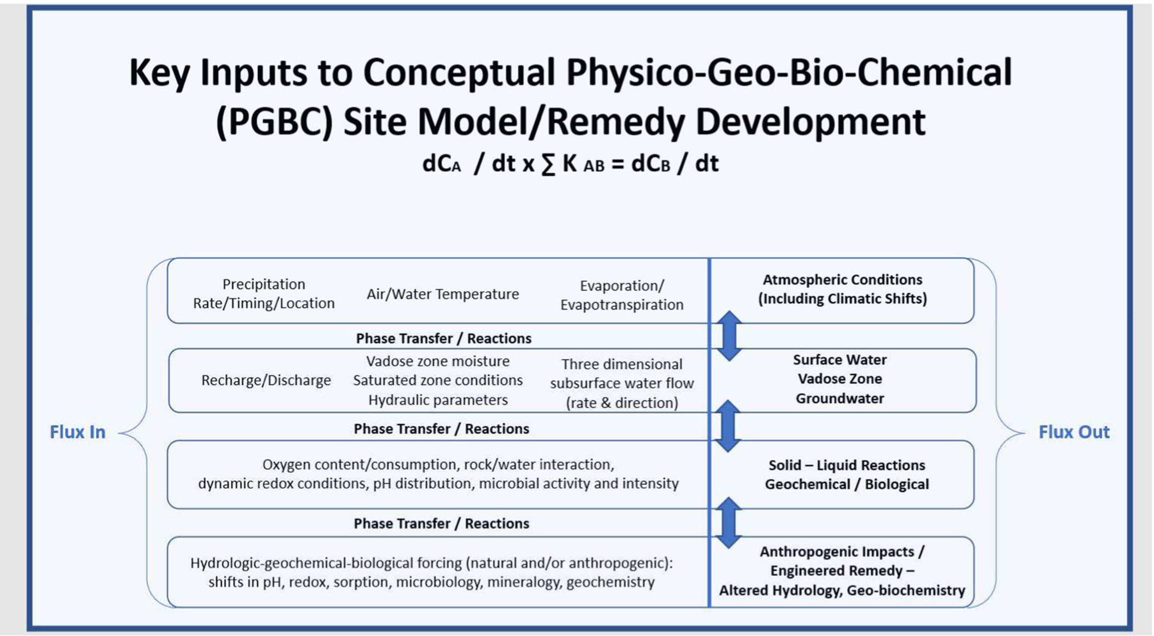


FIGURE 3 Representation of components involved in developing the PGBC site model that incorporates physical, chemical, and biological stress on phase transfers and reactions. CA and CB represent the chemical fate at the initial and next time steps, while ΣK_{AB} is the sum of climatic influence integrated over time.

which climatic- or anthro-induced stress and phase transfer processes would interact. Here, we represent the changes or fate in a chemical C_A over time to C_B as a function of the numerous stresses that could emerge from a changing climatic condition or ΣK_{AB} over time, t. Of course, the system is much more complex than is simplified here where each functional effect creates a multitude of reactions at both the micro- and macrolevels according to the mass transfer rate constants for each independent reaction. Even with the inherent complexity, this conceptual model becomes a framework for which remedial design measures can be initiated and future trends, for which design elements must address, can be anticipated.

Because the tendency in characterizing the aqueous system for which contaminants exist is to assume stability and equilibrium, constructing the CSM provides a framework for assessing current and future disruptions to the system. Examples of the system inputs include but are not limited to (1) rising and intruding seawater into a coastal fresh groundwater zone and (2) increasing vadose zone and atmospheric input in an area of decreasing groundwater level due to drought or extensive and sustained groundwater pumping. Examples like these can create systematic alterations to the biogeochemical environment that may have a substantial impact on contaminant fate, migration, and mitigation in the aqueous and vapor phases.

3.1 | Example disruptions to site conditions

3.1.1 | Groundwater elevation variability

Conditions of rising and falling groundwater levels can reflect both climatic and anthropogenic stress and can have major impacts on the vertical profile of chemical mass in the subsurface. Groundwater level changes in chemical source areas can result in so-called “smear-zones” of dissolved and nonaqueous phase liquid (NAPL) contaminants that affect both characterization and mitigation of the contamination (Van De Ven et al., 2021). The movement up and down of both groundwater and chemical mass will be reflected in changing geochemical and biochemical characteristics—changes in DO, redox chemistry, and microbial populations are to be anticipated as conditions can change from aerobic to anaerobic and back again (Borden et al., 1995). These changes may be advantageous for some contaminant distributions or may complicate matters by shifting chemical distribution and creating conditions that a given remedy may not have been intended to perform within. Rising and falling groundwater also can complicate ex situ strategies that rely on hydraulic capture from extraction wells. Adding and removing pumping wells or changing the pumping regime of an existing system to accommodate changes to a site's groundwater system is not necessarily an inexpensive nor simple administrative approach based on our experience with these situations.

What is perhaps less understood are the aqueous geochemical shifts in DO and redox conditions that would create disequilibrium and potential mobility among redox-sensitive species including reducible or oxidizable metals such as chromium and metalloids including arsenic. The occurrence of mercury in groundwater is another element that has been shown to be affected by an increase in atmospheric oxygen due to the extraction of groundwater for potable use. Spyropoulou et al. (2022) correlate an increase in mercury content with an increase in chloride concentration on the Greek island of Skiathos following an intensive period of groundwater extraction.

Geochemical shifts that accompany rising or falling groundwater can be profound. An informative example comes from the occurrence of high arsenic levels that were discovered in groundwater extracted from water supply wells drilled into the St. Peter Sandstone of northeast Wisconsin, USA (Burkel & Stoll, 2007). For this case, arsenic is believed to have been released into the well water from the oxidation of iron-sulfide minerals such as pyrite and marcasite (FeS_2) that created low pH conditions upon interaction with atmospheric oxygen during well drilling and dewatering of the aquifer. An analogous condition of arsenic release from natural sediment within an aquifer also has been observed from the injection of oxygen-rich surface water during the process of managed aquifer recharge (MAR), which is a program of greater interest for sustaining groundwater reserves in drought-stricken areas (Dillon et al., 2019). While not a direct climatic stress, this anthropogenic-derived approach to groundwater resource management involves the injection of surface water or treated water, which may be of a different hydrochemical type, into the underlying aquifer. The result of the interaction of the water mixing may create reactions of redox chemistry that alter the ambient hydrochemical nature of the natural groundwater. Fakhreddine et al. (2021) illustrate the changes in arsenic mobility, as an example, that could occur during MAR depending on whether the native sediment geochemistry is reduced or oxidized and whether the hydrochemical nature of the recharging water is reducing or oxidizing. The complex reactions from this hydrochemical mixing environment can create changes to pH and redox chemistry whereby numerous geogenic mechanisms within the aqueous environment can occur including combinations of dissolution, precipitation, and repartitioning involving numerous constituents and contaminants including complexes of oxyhydroxides, phosphorus, sulfate, and carbonates. As illustrated by the above examples, tools exist, including the use of geochemical modeling along with an analysis of analytical chemistry that can help evaluate the impacts of anthropogenic stress on the aqueous composition of both extracted and ambient groundwater.

Additionally, the vertical movement of groundwater and thus subsurface contaminants can greatly affect vapor-phase distribution that may increase the potential for vapor intrusion to ground-based receptors creating additional challenges to the design and implementation of vapor mitigation approaches (Guo et al., 2019; Liu et al., 2021). Whether these example conditions are the result of natural environmental stress or are the manifestation of anthropogenic-induced processes is less important than recognizing or projecting that such conditions are either probable or are likely in each system.

3.1.2 | Sea water intrusion

Another example involves seawater incursion into a coastal zone and its influence on near-shore hydrology and freshwater geochemistry. As recognized for centuries by Du Commun (1828) and Bear et al. (1999), the physics and chemistry of seawater intrusion into coastal aquifers create conditions that can dramatically shift the hydrobiogeochemical conditions of the groundwater system. A long-observed coastal problem in areas of active groundwater abstraction for water resource development is the significant increase in groundwater salinity as on-shore pumping allows sea water to intrude far inland; a condition becoming critical in some Pacific Island environments where sea level rise is pronounced (Lal & Datta, 2018). In coastal areas not prone to groundwater pumping, rising seas may exacerbate the land-side mixing of saline water with fresh groundwater, creating hydrochemical stress from aqueous increases in alkalinity, sulfate, and ionic strength, on nontolerant vegetation forcing a landward migration of on-shore plant communities (Tully et al., 2019). Furthermore, the increase in the hydraulic head in adjacent shallow groundwater systems (Befus et al., 2020; Bosserelle et al., 2022) resulted in potential redistribution and influence on the fate and migration of soil and groundwater contaminants as well as conditions of emergent groundwater in low-lying areas within the coastal zones (Plane et al., 2019). Groundwater remedial actions in areas prone to these conditions may be faced with drastically different hydrologic, biological, and geochemical conditions from which they were intended.

Fortunately, numerical methods have existed for many years to help with assessing the aqueous reactions that theoretically take place as seawater mixes with freshwater. In an early example of an early modeling study, Appelo and Willemsen (1987) describe using geochemical speciation and reaction-path modeling to evaluate cation exchange and redox reactions as important to predicting aqueous composition shifts along mixing zones. More recently, Meyer et al. (2019) integrates numerical modeling with geochemical and geophysical data to show that progressive long-term saltwater intrusion can create noticeable cationic and redox shifts in groundwater geochemistry at substantial distances—laterally and vertically—inland from the coastal boundary.

Assessing the connection between seawater and terrestrial water (i.e., groundwater and surface water) under climatic impact should be a necessary component for the development of the CSM for coastal areas due to the overarching effects of seawater incursion. Costal et al. (2020), for example, report on a 30-year study of a shallow karstic coastal aquifer in Western Australia noting how saline ocean water can alter freshwater geochemistry while describing the negative effects on freshwater access both to crop irrigation (such as examined by Kotera et al. [2014] for rice field productivity in the Mekong River Delta) and potable groundwater (as evaluated by Jasechko et al. [2020] for thousands of coastal groundwater wells in the United States). Numerous researchers have evaluated the physical relationship between groundwater pumping, injection, and seawater intrusion (Sherif & Singh, 2002; Tsanis & Song, 2007; Van Camp et al., 2014) and studies have also been investigating the phenomenon of groundwater rise and impact from sea level rise and intrusion (Loáiciga et al., 2012; Plane et al., 2019). Regardless of the initiating process, the magnitude of seawater impact on coastal aquifers is a function of the hydrogeological parameters and heterogeneities that control hydrodynamics of the seawater/groundwater interface and the migration of the saltwater wedge landward thus making the point that detailed hydrogeological and land use characterization will remain a critical component for assessing impact and implementing mitigation schemes where appropriate (Carrera et al., 2010; Werner & Simmons, 2009).

Research into the geochemical impact of seawater influence on freshwater systems has become more prevalent in the past several decades but not necessarily because of the relatively recent integration with climate change research. Yet, these studies do provide an opening to evaluate longer-term trends that will be important to contaminant mitigation schemes in coastal areas. Andersen et al. (2005), for example, analyzed the groundwater hydrochemistry representing more than 100 piezometers along a coastal transect in northern Denmark. The study notes the changes in aqueous redox conditions, DO, and ferrous iron, among other parameters along the freshwater/seawater interface, and identifies a geochemical shift from methanogenesis to sulfate reduction coincident with pulses of dense sodium and magnesium-rich seawater sinking through calcium-rich groundwater. The generally well-observed hydrochemical trends along the seawater/freshwater interface involve the transition from calcium–magnesium bicarbonate (Ca, Mg-HCO_3^-) type facies through to sodium chloride (NaCl) facies with a range of composition along Na, Ca^- HCO_3^-, Cl mixing zones rather than along a bright hydrochemical facies boundary (Cooper, 1959; Giménez-Forcada, 2010; Hem, 1985). This transition influences the mineral saturation conditions that could lead to complex reactions that also will affect mineral solubility within the aquifer system.

4 | CLIMATE INDUCED INFLUENCE ON REMEDIATION APPROACHES

As the remediation design practice commenced in the late 1980s and continued through the early 1990s and took hold into the new century, practitioners took advantage of combinations of active "ex situ" measures to physically remove contaminated soil and groundwater where feasible, physical (or physicochemical) isolation to block the migration of contaminants from reaching receptors, or in place geochemical and biological processes to force certain "in situ" reactions that could destabilize, mineralize, retard, and detoxify contaminants through mostly passive (i.e., without the application of energy to create the reactions or route the contaminated groundwater through the remedy) physical, biological, and geochemical processes (Henry et al., 2003). The approaches applied relied on a systematic decision-making process that assessed site conditions, chemical occurrence and migration tendencies, risk management evaluations, land use (current and future), cost, and regulatory acceptability to choose an appropriate remedy. The remedy selection process is complicated and seldom straightforward; and due to the complex technical, regulatory, economic, and economic factors, few sites were subject to immediate restoration.

4.1 | Comparing ex situ with in situ remedial approaches

For physical and ex situ remedies, the approach taken relied on-site access, the ability to remove safely and reliably (or manipulate via mixing or injection using surface active agents but with large construction equipment) enough affected soil and groundwater to meet risk management and regulatory objectives, and the ability to treat and/or manage the off-site transfer of the material (if necessary) to an off-site acceptable treatment and/or management solution. These physical remedies relied on implementing excavation and/or isolation techniques or applying a controlling force (e.g., groundwater pumping) to control the migration and occurrence of contaminants that could be reached by the remedial technology. In this case, these "active" remedies overcame the ambient stress of the contaminant occurrence to reduce the potential impact of external forces in the open system such as ambient groundwater flow or site-typical groundwater recharge and discharge conditions. For example, and from experience, if a given extraction well network was seen as not providing sufficient hydraulic capture, the analysis could be performed to select alternative extraction well network designs (Russell & Rabideau, 2007), or a site could attempt to install new wells in different locations as an attempt to increase remedy performance.

In situ remedies, on the other hand, rely on the thermodynamics and sorption/desorption or degradation kinetic rate and functions of the introducing remedy materials that are emplaced via construction, injection, or mixing within the geochemically open soil and groundwater system. That is, the ambient environment controls both the background that the applied reactions are implemented within and the time-variant condition that continues to evolve during the life of the remedy. As the influence from the environment continues, the remedy ages through a similarly complex set of physical, biological, and geochemical reactions. Designers of the various remedies relied mostly on the condition of stationarity to engineered remedy for the site conditions seldom with an eye for either internal (system) or external (environmental) changes to the CSM. However, the rule of stationarity, which historically has defined the general environmental remediation approach, must be flawed if in fact, stress conditions, such as climate change-driven force to the hydrologic cycle, which is an open system, continue to evolve. By considering fundamental aqueous geochemical relationships (e.g., as comprehensively explained by Stumm & Morgan, 1996), future scenarios under which geochemical conditions may shift can be represented.

Figure 4 depicts a range of common remediation approaches along a continuum of active to passive methods with the added consideration of sustainability and resilience to climate-driven impact and trends. Each of these remedies, including combinations thereof, also would have an impact on the hydrogeochemical makeup of the target contaminated media. Although not explicitly shown by Figure 4, any intrusive remedy, whether active or passive, will introduce nonnatural geochemical conditions to the subsurface environment as discussed previously. Even soil excavation will allow atmospheric conditions, such as increased oxygen, to interact with once-buried geologic material and contaminants and extend to a depth that may have been beyond reach or at least not to the point of substantially influencing contaminant occurrence or migration. While perhaps only a temporary effect, oxidation of iron species under a now "open" atmospheric environment could create conditions that allow certain reactions to occur that would not otherwise be observed.

Regarding climatic stress, those examples most prone include the in situ passive and biological approaches. These technologies are intended to create subsurface conditions that destroy, destabilize,

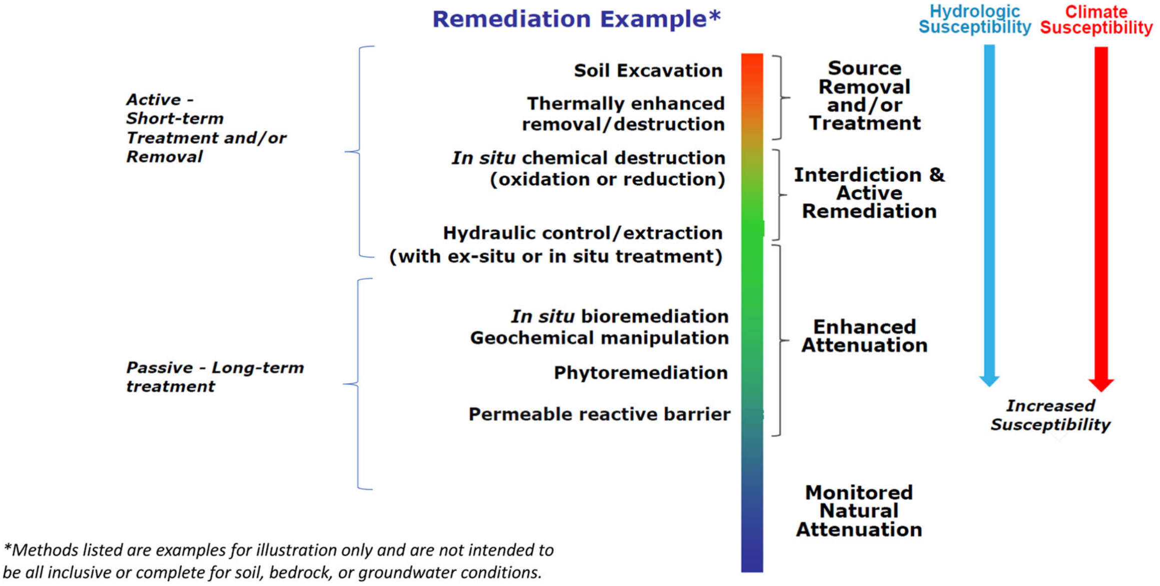


FIGURE 4 General categories of remediation methods showing qualitative vulnerability to hydrologic and climatic stress. Examples are not intended to be a complete list and several approaches, such as hydraulic control, may exist over a range of conditions. Generally, the least active (hydraulic or otherwise) remedies may be more susceptible to hydrologic and climatic stress. (Figure modified after ITRC, 2008, figures 1–4).

immobilize, or otherwise isolate contaminants passively. Except for so-called in situ "energetic" treatments (e.g., direct chemical oxidation or reduction of a target contaminant), these methods are based on the application or enhancement of "natural" processes and in many ways would be consistent with the core ideas intended by the concept of "green and sustainable remediation" (Bardos, 2014). A group of four basic so-called sustainable and passive remediation concepts—bioremediation, phytoremediation, redox reactions, and monitored natural attenuation (MNA). These remediation approaches were initially contrived to utilize natural chemical, biological, and physical processes to degrade, immobilize, or reduce the toxicity of dissolved contaminants in groundwater without actively manipulating groundwater flow or by applying a constant supply of energy.

These remedies arguably are the more developed sustainable remediation techniques having been applied and implemented at hundreds if not thousands of sites before the relatively recent concept of sustainable remediation became part of the restoration lexicon in many countries and jurisdictions. Under the context of sustainable remediation where the intent is to consider all likely environmental effects (positive and negative) of remedy implementation including the net environmental benefit of the clean-up action, the in situ methods that rely on hydrologically passive operation promote sustainability. However, the reliance on ambient subsurface conditions, including advective-only processes, to remain within a future design regime so that performance can be maintained until the project is completed creates a potentially risky future if the anticipated or predicted design conditions change. This acknowledgment increases the need to prepare for changes that may occur and how the selected remedy approach will be affected. Table 1 provides a summary of some of the characteristics and parameters potentially affected by climate-induced changes to hydrologic, geochemical, and biological systems that remedial methods are designed to perform within. Although the research literature contains numerous examples of system impacts on specific geochemical and biochemical conditions, little information on the potential impact of future climate or hydrologic conditions on remedy resilience exists. The information in Table 1 explores some of the anticipated concerns.

4.2 | Climate induced shifts to perfluoroalkyl/polyfluoroalkyl substances (PFAS) and persistent organic pollutants (POPs)

Finally, for completeness, we provide a brief discussion on the matter of potential climate-induced hydrological and biogeochemical changes that affect the distribution, fate, and transport of perfluoroalkyl and PFAS. A full treatise on the chemistry and fate of PFAS within the groundwater environment is beyond the intent of the discussion herein; however, an acknowledgment of the hydrochemical complexities within this family for which the USEPA now contains nearly 15,000 unique entries on PFAS structures as of August 2022 (USEPA, 2023) cannot be understated. The recognized wide-ranging hydrophobic (hydro-repelling) and hydrophilic (hydro-affinity) characteristics of PFAS (Li et al., 2018) as influenced by the organic carbon, iron oxide, and aluminum oxide composition of soil and aquifer media particles (Higgins & Luthy, 2006) demonstrate a necessity to evaluate not just current conditions, but also the potential future climatic conditions that affect the ambient geochemical characteristics as reasonably as possible due to the recognized persistence of these constituents in the environment.

Generally, the research and analysis of how climate-induced shifts to hydrobiogeochemistry may affect this suite of chemicals appear to be at an early stage. A review of the available literature shows that, over the past decade, studies exist that attempt to review the potential influence of climatic factors (and climate change) on this suite of high-interest chemicals (e.g., Gander, 2022; Kallenborn et al., 2012; Ma & Cao, 2010; Wang et al., 2016). The studies somewhat are consistent in that they note that, whether due to chronic shifts or extreme events, changes to temperature, wind and climate patterns, rainfall and recharge, or erosion and flooding should have some influence on the environmental cycling and fate of these constituents, but that quantification of the impact still remains unclear. Other studies look at specific influences including, although not limited to, the investigation of (a) seasonal concentrations in PFAS as influenced by biogeochemical condition-related surface-water/groundwater mixing (Tokranov et al., 2021); (b) changes in the global cycling of PFAS in response to climate-induced permafrost degradation (Mahmoudnia et al., 2022); and, (c) mobility of PFAS and related constituents under different hydroclimatic conditions including semi-arid (Wallis et al., 2022) and humid, subtropical environments (Cui et al., 2020).

The work assessing PFAS degradation under various biological and redox regimes also has a climatic component because of their general stability and long-term persistence in the environment. This is an important topic not just because of the potential degradation of PFAS directly or indirectly from current or future biological processes (Berhanu et al., 2022; Zhang et al., 2021), but also because some PFAS and PFAS precursors (i.e., compounds that have the ability to form PFAS) have potential to transform to constituents that may have different and more challenging toxicological, mobility, and fate profiles (Liu & Mejia Avendaño, 2013; Shahsavari et al., 2021). Finally, an important consideration that exists regarding PFAS is whether the global distribution and occurrence of these chemicals in the environment will continue to be exacerbated by shifting climatic (e.g., wind patterns and extreme events) conditions because of their relative stability and very slow (if not negligible) degradation under ambient environmental conditions (Newell et al., 2022).

The brief discussion of PFAS in the context of climate-induced stress is not intended to diminish the potential climate impact on other constituents including POPs as defined by the United Nations Stockholm Convention (United Nations Environment Programme, 2020) and other government agencies. These compounds, so designated as POPs due to their general persistence to environmental degradation, include polychlorinated biphenyls, numerous pesticides and herbicides, dioxins, furans, and some PFAS. These chemicals have their own unique characteristics, which may be

TABLE 1 List of typical, but not all, in situ groundwater remedy types and potential impact from climate-induced changes to the conceptual site model (CSM).

Remedy type	Description	Climate change impact on the CSM
Bioremediation (carbon/nutrient addition, biowalls and biozones, compost systems, bioaugmentation, landfarming, bioventing–bioslurping–oxygen enrichment)	The use of microorganisms to transform, degrade, or immobilize contaminants to remedial objectives. May include bioaugmentation (adding bacteria) and biostimulation (adjusting the subsurface environment through nutrient addition and/or geochemical manipulation of the subsurface environment)	Hydrologic impacts from severe drought: • Reduction in soil moisture • Temperature increases outside of the effective bioactive range. • Drying of organic matter • Increased salt content negatively impacts biological activity. Hydrologic impacts from excessive recharge: • Increase in dissolved oxygen (DO) may reduce anaerobic microbial activity. • Mobilization outside of the bioactive zone • Excess moisture • Increase in groundwater velocity may decrease contaminant residence time in the bioactive zone. • Dilution of bioactive agents and microbial population
Phytoremediation	The use of vegetation (including trees, shrubs, and flowering plants) to remove contaminants through groundwater uptake or reduce/degrade contaminants through root zone processes	Impacts from long-term drought: • Excessive stress on vegetation creates weak growth and insufficient hydraulic capture. • Concentration of salt content in soil • Potential increase in both air and groundwater temperatures creating stress on vegetation health. Impacts from rising seas or lowering groundwater. • Reduced availability of fresh water (for most species) • Increased salt content in groundwater and soil • Inability to capture mobile contaminants. • Increased stress in bioactive root zone limiting microbial-enhanced contaminant mitigation
Permeable reactive barrier	An engineered in situ remedy whereby the contaminant treatment material is placed in a defined geometry within the subsurface—often across and perpendicular to a groundwater plume to mitigate the occurrence or migration of chemical contaminants through a combination of physical, chemical, and/or biological processes.	Impacts from changing hydrologic conditions. • Changed groundwater gradient creates a potential loss of capture. • Changes in groundwater velocity outside of design residence time promote incomplete contaminant mitigation (destruction or immobilization) • Both increased and decreased recharge may cause an increase or a decrease in ambient dissolved inorganic loading of groundwater, a change in dissolved oxygen content, and a change in pH conditions—all of which may not be consistent with design aspects of the PRB treatment media.
Monitored natural attenuation	The use of unenhanced natural (including physical, chemical, and biological) processes and reactions to mitigate chemical contaminants as part of a site remediation strategy.	Impacts from changing hydrologic conditions. • Changed groundwater gradient creates a potential loss of plume control and expansion of contaminant plume toward receptors. • Changed plume dimensions may evade the existing monitoring network. • Changes in groundwater velocity outside of the plume stability regime reduced the ability of natural processes to promote complete contaminant mitigation (destruction or immobilization) • Changed recharge conditions could cause systematic or acute changes to geochemical conditions (e.g., DO, pH, redox) by which MNA

(Continues)

TABLE 1 (Continued)

Remedy type	Description	Climate change impact on the CSM
		processes have stabilized contaminant migration and reduction—these changes may create a need for active remedies to be implemented to control the expanding plume.
In situ chemical oxidation	A remedial process by which chemical oxidants are injected or placed within the subsurface to oxidize chemical contaminants to less toxic and/or less mobile constituents.	Exceptional precipitation events may: • Create excessive dilution of the oxidant or change plume geometry away from the remedy implementation area • Results may substantially increase oxidant demand and reduce the effectiveness
In situ chemical reduction	A remedial process by which chemical reductants are injected or placed within the subsurface to chemically reduce chemical contaminants to less toxic and/or less mobile constituents.	Exceptional precipitation events may: • Create excessive dilution of the reductant or change plume geometry away from the remedy implementation area • Add excessive oxygen to the system increasing reductant loss and reducing the effectiveness of the contaminant reduction process.

Note: Although only in situ remedy types are listed, there is no intent to minimize the potential influence and disruption to conventional ex situ remedies that may be substantially affected by climate-induced stress.

strongly affected by climatic stress and conditional change in the ecosystem in which they occur. Work to characterize and predict the environmental behavior of POPs also is at a relatively early stage although the work of numerous researchers, including Najam and Alam (2023), de Wit et al. (2022), Kallenborn et al. (2012), and Teran et al. (2012), provides insight into the immense challenge of understanding the long-term behavior of these chemicals as the environment around them continues to change. Consistent with the discussion on PFAS, earth matrix and aqueous geochemical properties will have a strong influence on the fate and migration potential of POPs.

For both the PFAS and POP suites of chemicals, understanding the current physical, chemical, and biological environments in which these constituents exist is critical to risk management decision making under today's conditions. Importantly, the inherent stability and persistence of PFAS and POPs also provide an incentive to test their presence under potential future scenarios where the hydrobiogeochemical environment differs from that of today. Although it may be easy to presume that changes from today's conditions may exacerbate the present occurrence of these chemicals, there may be future conditions that also reduce risk through ambient environmental change. For example, as discussed by Newell et al. (2021), there may be future (and, of course, current) “physiochemical factors” that allow risk management strategies to take advantage of natural attenuation processes (e.g., via sorption, matrix diffusion, geochemical and biochemical reactions, hydrologic shifts, etc.) that reduce the movement, increase the isolation of, and thus, decrease the risk of these chemicals to human and ecological receptors. As more data that accurately describe the properties of both the specific chemical and its environment become available for analysis, the reliability of management strategies will undoubtedly increase and provide a basis for designing appropriate and durable mitigation approaches for today and in the future.

5 | CONCLUSIONS

The approach to developing in situ remedies for mitigating groundwater contamination has progressed from the intensive methods employing high environmental impact, high energy consumption, and inefficient and seldom sufficient physical removal of contaminated groundwater to the concepts of sustainable and “nature-based” concepts. While meeting many of the intended elements of sustainability—that is, hydraulically passive, low energy needs, and relying primarily on natural hydraulic, geochemical, and biochemical methods—the potential ability of these methods to withstand either acute or chronic changes to the design environment due to anthropogenic or natural causes for which a remedy was applied is uncertain. Qualitative assessments for improving remedy design with sustainability principles exist and make the development of a complete hydrobiogeochemical CSM critical for improving reliability and long-term success. Nevertheless, remedy performance, which includes the ability to both be resilient and durable under the stress of acute and chronic climate change, should be a condition that receives attention during the design phase and postinstallation monitoring. Recommendations for considering hydraulic, biological, and geochemical elements—the hydrobiogeochemical characteristics—toward resilient and durable groundwater remedy design under changing conditions include the following:

1. Consider whether potential future shifts to the hydrobiogeochemistry of a site's subsurface earth and groundwater system will influence the fate and transport of inorganic and organic contaminants, including PFAS and other POPs. If so, consider remedial design scenarios that account for the potential shifts to allow for the development of a design that maintains performance and risk management durability over time.

2. Broaden the concepts of sustainable and nature-based remediation to account for resiliency and successful performance if environmental conditions change, particularly in climate-vulnerable locations.
3. Continue to rely on established or project-developed groundwater and geochemical models for evaluating scenarios that assess the potential impact of climate-induced stress on the hydrobiogeochemical environment to assure the development of resilient and durable contaminant mitigation and risk management approaches. Our conclusion is that climate-specific models, global and regional, are not yet seen as a necessary element for most conventional project needs (although they will continue to develop) except for informational purposes or for exceptional cases.

From our review and experience, there is a paucity of publicly available detailed assessments of remedies that may have failed or underperformed due to climatic shifts or anthropogenic stress. Does this mean that a majority, a large number, or even a few remedies have been compromised because of such change? We cannot conclusively answer this question but the fact that USEPA has developed a guidance document for "Superfund Climate Resilience" (USEPA, 2023) is evidence that government agencies are aware of the potential impact of climatic forces on the performance of remediation programs.

As presented herein, the geochemical and hydraulic effects of a changing climate on contaminant occurrence and distribution are well documented. Consequently, we recommend that the gap between contaminant behavior and remediation performance under climate and anthropogenic influence should be addressed to deliver greater confidence that remedies will provide durable improvement in groundwater quality under a wide variety of environmental and climatic conditions. Reassessing the CSM by more completely acknowledging the influence of anthropogenic behavior and processes on the hydrologic and biogeochemical environment will undoubtedly lead to more questions but will also promote a more complete understanding of the total environment for which contaminant remedies are intended to successfully perform until contaminant risk has been mitigated.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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