Editor summary:

River water quality affects water availability and is expected to degrade under climate change —an issue that has garnered limited attention. Here, the authors review the impacts of climate change and climate extremes on water quality, highlighting the pivotal role of land-river connectivity.

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River Water Quality Shaped by Land-River Connectivity in a Changing Climate

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Abstract

River water quality is crucial to ecosystem health and water availability, yet its deterioration under climate change is often overlooked in climate risk assessments. Here we review how climate change influences river water quality via persistent, gradual shifts and episodic, intense extreme events. Although distinct in magnitude, intensity, and duration, these changes modulate the structure and hydro-biogeochemical processes on land and in rivers, hence reshaping the quality of river waters. To advance our understanding of and forecasting capabilities for water quality in future climates, it is essential to perceive land and rivers as interconnected systems. It is also vital to prioritize research under extreme conditions, where dynamics of water quality often challenge existing theories and models and call for shifts in conceptual paradigms.

Main text

Humans have settled along meandering rivers and streams since the dawn of hunting and gathering societies [1]. Today over 50% of the global population lives within 3 km of a surface freshwater body, and 90% within 10 kilometers [2, 3]. Human survival, along with the myriad forms of life sharing this Earth, hinges upon not only the rising and falling rhythm of inland flowing waters (quantity) but also the interwoven tapestry of their physical, chemical, and biological composition and conditions (quality).

Given the visible nature of water levels in events such as floods and droughts, river water quantity is known to change in a warming climate. These changes have been accounted for in the global calculation of climate risks [4]. River water quality, on the other hand, is often considered as influenced less by climate change and more by human activities such as land use [5, 6]. As an example, the most recent

Intergovernmental Panel on Climate Change (IPCC) report barely discusses the risks of a changing climate on inland water quality [4]. The effects of climate change on water composition and quality have therefore remained "invisible" [7].

This "invisible" impact of climate change on river water quality directly influence the estimation of water availability and scarcity [8], which quantifies the amount of usable water, rather than simply considering the amount of available water. As an example, when considering water quality variables such as water temperature and salinity, water scarcity levels can increase by a factor of 1.4 to 3 [9]. Water availability is therefore inextricably linked to water composition and quality. In fact, there is plenty of water on Earth: more than 70% of Earth's surface is covered by ocean seawater, yet seawater cannot be used because of its high salt content.

Water quality is essential for human consumption. In industrialized modern society, drinking water originates from inland rivers, lakes, and groundwater. These source waters often route through treatment facilities: sediments are filtered out; water hardness is reduced; and disease-causing microbes are removed. Water quality determines the costs of drinking water treatment [10]. Elevated sediment and nutrient concentrations have been estimated to increase operation and maintenance costs of water treatment facilities by 53% [11]. The United States, for example, has spent about $5 trillion to improve surface and drinking water quality since 1972, or approximately 0.8% of its gross domestic product and an annual spending of $400 per American[12]. This makes clean water arguably one of the most expensive environmental investments in the US, more than the cost of clean air. Such access to clean water, although often taken for granted, is a privilege that should be available to everyone. Globally, about 26% of the population does not have access to safely managed drinking water services; an estimated three billion people are at risk of disease because of unknown water quality due to the lack of monitoring data [13].

Water quality concerns not only domestic use but also ecosystem health, industry, and agriculture (Figure 1). Aquatic life depends on good water quality for survival (Table 1) [14, 15]. High water temperature can reduce electricity production in thermoelectric plants [16]. Saline irrigation waters degrade soil properties and reduce food production [17]. Deteriorating water quality also impacts global carbon-climate feedback: solutes such as dissolved carbon and nutrients drive the emission of greenhouse gases from inland waters, including methane [18], carbon dioxide [19], and nitrous oxide [20].

Climate change manifests itself in two distinct forms: persistent, gradual shifts and episodic, intense extreme events. Gradual warming elevates soil temperature and green water demand (by plants) and changes total precipitation, leading to longer durations and higher frequencies of zero-flow [21]. Climate change also modifies patterns of precipitation, leading to more frequent and intense events of climate extremes including floods [22], droughts [23], heatwaves [24], and wildfire [25, 26]. An extreme event can be defined broadly as "an episode or occurrence in which a statistically rare or unusual climatic period alters ecosystem structure and/or functions well outside the bounds of what is considered typical or normal variability"[27]. Extreme events often change water quality rapidly and substantially, thus exacerbating water treatment demands, threatening water supply and aquatic ecosystems [28, 29].

Existing literature has reviewed the direct impacts of gradual climate change and extreme events on river water quality [30, 31, 32, 33, 34, 35], with a primary focus on observed changes within rivers and streams. To forecast, manage, and adapt to changing water quality, it is essential to diagnose the processes and mechanisms that drive the degradation of river water quality; these processes and mechanisms often stretch beyond rivers. Here we aim to offer a mechanistic view, illustrating that river water quality is shaped not only by processes within rivers (the focus of most existing reviews), but also by their connection to the land. We highlight the changing structure and processes on the land and in rivers and the profound impacts of land-river connectivity on river water quality.

Land-river connectivity shapes river water quality

River water quality is shaped not only by the structure and processes in rivers but also by those on land. Understanding changing water quality necessitates the comprehension of the interconnected nature of land and rivers. The influence of processes within rivers (in-stream processes) tends to be more important under dry and warm conditions when land inputs are minimal. As conditions become wetter, the influence of source waters from the land gains prominence [36 37 38] (Figure 2). River water quality therefore depends on the extent of land-river connectivity and the input from different flow paths at different depths shaped by distinct biogeochemical reactions [39 40].

Decades of water tracer analysis and global surveys show that majority of the global river water derive from "old" water that has routed through and interacted with the land subsurface, instead of the relatively recent "new" rainfall and snowfall (within two to three months) [41 42, 43]. This contrasts with the common perception that most river water originates directly from recent precipitation via rapid surface runoff. In fact, after the arrival of precipitated water on land surface (global river and stream surface areas account for about 0.6% of Earth's non-glaciated land surface [44]), most of them then infiltrates into soils and rocks and travels along shallow and deep flow paths, often spending years to decades before entering rivers [45, 46, 47] (Figure 2). In some groundwater-fed rivers, precipitated water enters deeper paths, travelling for hundreds to thousands of years underground before reemerging in rivers [48].

The structure of and processes on land, from the top of the trees to the bottom of groundwater aquifers, the so-called Critical Zone [49], therefore can have tremendous impacts on river water quality in a changing climate. In particular, as water travels through the land, it interacts with materials along its flow paths and mobilizes solids and solutes, which changes its biogeochemistry before it enters rivers (Figure 2). The diversity and concentrations of mobilized solids and solutes depend on the chemical, physical, and biological structure along its shallow and deep flow paths. Weathered and highly permeable soils typically reside in the shallow subsurface, which also harbor leaf litter and roots and living things enriched with organic matter. The decomposition of organic matter via microbe-mediated biogeochemical reactions (e.g., soil respiration) generates biogenic solutes such as DOC and various forms of nitrogen, which are often enriched in the shallow subsurface and decline with depth [50, 51, 52]. Less permeable parent rocks typically reside in the deeper subsurface below soils, delivering slower, older waters enriched with geogenic solutes such as calcium (Ca) and silica (Si) derived from chemical weathering [53].

Hydroclimatic conditions largely determine the depths of a river's source waters. Under dry conditions (e.g., with low precipitation and high evapotranspiration, Figure 2a, top hillslope), river waters are dominated by deeper groundwater enriched with geogenic solutes, reflecting chemical weathering of parent rocks in addition to in-stream processes [51, 53, 54]. Under wet conditions (e.g., with heavy rains or snowmelt, Figure 2a, bottom hillslope), river water mostly derives from source waters that move rapidly via shallow, permeable, moist soils across large, well-connected areas of watersheds, integrating soil biogeochemical signatures along its shallow flow paths with enriched carbon and nutrient content. Such distinct source water chemistry and dominant flow paths under different hydrological regimes lead to the commonly observed concentration-discharge relationships for sediments and solutes (Figure 2b). Specifically, sediments and biogenic C, N, and P-containing solutes often exhibit increasing concentrations with increasing discharge (flushing), whereas geogenic solutes such as Ca and Si exhibit the opposite dilution patterns [51, 55, 56, 57]. The loads however typically increase with discharge regardless of concentration-discharge relationships, because discharge often rises by orders of magnitude as the system transitions from dry to wet conditions, far exceeding the typical within-an-order change for solute concentrations.

Hydrological conditions are projected to change in the future with climate. In regions and times that become wetter, climate change likely results in increased flushing (or loading) of materials and nutrients from the shallow subsurface into rivers. Where climate change increases aridity, material loads may be lower but the concentrations of water quality variables may increase due to increasing mass accumulation and intensifying in-stream processing [58].

The characteristics of the hydrological and biogeochemical structure and processes in undeveloped land can differ substantially from urban and agriculture lands. Agricultural lands have abundant legacy store of nutrients in shallow soils and tile drainage that facilitate shallow flow [59, 60]. Urban watersheds are characterized by impervious surfaces that facilitate surface runoff and sewer and stormwater pipes that enhance rapid subsurface flow and elevate nutrients in groundwater [61, 62, 63]. These distinct structures in the subsurface could result in varying river water quality responses to a changing climate under diverse land uses.

Impacts of persistent and gradual climate change

Land-river connectivity implies that persistent, gradual climate change influences water quality primarily in two ways. In relatively short time scales from hours to years, it directly modifies conditions and processes in rivers and on land. Over the longer time scales of decades to centuries, persistent climate change additionally alters the physical, chemical, and ecological structure of rivers and land, exerting long-lasting impacts on the quality of river water.

Short-term alterations of conditions and processes

In the short term, climate change alters subsurface conditions on land and in rivers, including soil temperature (T), soil moisture (S_w), and O_2 levels, all of which are key drivers of reaction kinetics and thermodynamics that can change source water biogeochemistry [64] [65] (Figure 2). For example, warming often enhances microbiological activities and rates of reactions such as soil respiration, nutrient transformation, and chemical weathering [66]. Variations in soil moisture regulate rates of biogeochemical reactions. In very dry soils, limited water content often slows down microbial activities and reduce the rates of aerobic reactions that uses O_2 [67]. In very wet, O_2-limited soils, microbes rely on the generally slower anaerobic reactions including, for example, denitrification, iron reduction, sulfate reduction, and methanogenesis to obtain energy, similarly slows down overall reaction rates [64]. As a result, the rates of biogeochemical reactions often peak at intermediate soil moisture conditions where microbes can optimize the use of water and O_2 [65]. Different types of reactions also lead to different solutes and gas products, with anaerobic reactions generally diversifying reaction products in source waters. In aquifers, lowering of groundwater tables under drier and warmer conditions promotes deeper penetration of O_2. This enhances the oxidation of redox-sensitive bedrock such as those containing pyrite and other reduced metal-bearing minerals, which can mobilize toxic metals such as arsenic (As) [68].

Long-term alterations of land and river structure

At decadal to centennial time scales, the physical, chemical, and ecological structure of the land and rivers will evolve with climate change [69, 70, 71], further influencing water quality. For example, to adapt to warming, plants often modify their physiology and rooting architecture, growing roots deeper, shallower or more laterally to maximize water and nutrient acquisition [72, 73]. Soil microbes can adapt together with roots and alter the distribution and properties of organic matter [66] [74]. Alterations in root structure, soil aggregates, and macropores have been documented to modify soil properties over annual to decadal time scales—much shorter than the centennial timescale that is typically expected [75, 76, 77]. Dry river beds have been documented to function similarly to dry soil [78]. Globally, warming has been attributed to the encroachment of woody shrubs into drylands and grasslands that cover nearly 40% of the Earth's ice-free land surface [79] [80]. Woody shrubs modify not only water distribution and flow paths, but also biogeochemistry, possibly accelerating reactions such as rock weathering, soil respiration, and riverine solute export [81, 82]. Landscape units such as intermittent headwater streams and geographically isolated wetlands are essential for maintaining good water quality and can fluctuate rapidly between wet-dry and cold-hot transitions, making them particularly vulnerable to climate change [38]. The extent of such modification depends on the types and rates of reactions, and the shifting drivers in a changing climate. Gradual climate change therefore can impart a persistent, complex, interacting influence on ecosystems, roots, microbes, soils, and rocks, which modify flow paths and biogeochemical reactions and ultimately alter river water quality.

Deteriorating water quality during gradual climate change

While water quality changes often reflect the entangled effects of climate change and human activities, data from rivers with minimal anthropogenic activities can help differentiate the impacts of climate change. In remote Alpine lakes that integrate inputs from nearby mountain streams, decades of water chemistry data have shown concomitant increases in temperature, electrical conductivity, and solute concentrations [83]. In more than 500 US rivers with minimal human impacts, long-term mean concentrations of 16 commonly measured solutes universally increase with climate aridity (and decreasing mean river discharge) [58]. Such patterns of higher mean concentrations in more arid climates are similarly observed at regional [84] to global scales [85] [86], and have been attributed to lower water flushing capacity relative to the rates of solute production in arid climates [58]. This implies that in a warming climate, as streamflow dwindles in many places, water quality may generally decline due to lower flushing capacity, even without other direct human impacts.

The changing structure and processes on land and in rivers have led to widespread deterioration of river water quality. The concentrations of DOC (Table 1) and associated "water browning" have increased in Europe, North America, and Asia, often attributed to climate warming or recovery from acid rain [87] [88]. In the US, for example, salinity has increased significantly in 29-39% of the rivers; about 90% of the US rivers have seen increasing pH since the mid-20th century, and the degree of these effects are influenced by climate-driven variations in runoff [89]. Alkalinity, a measure of the water capacity to buffer pH changes (similar to DIC), has increased since the 1980s in the eastern US; and warming water may continue to exacerbate this trend [90]. Water quality in the Upper Colorado basins in the US shows strong dependence on lithology and climate (e.g., precipitation) [91]. In glaciated regions, warming-induced glacier retreat and melting of ice sheets have accelerated the export of solutes such as phosphorus and at least doubled the rates of chemical weathering compared to rates two decades ago [92, 93]. Gradual and abrupt permafrost thaws have become hot spots for carbon and nutrient export into rivers and greenhouse gas emission [94, 95].

The trends of changes across different regions of the world often vary, highlighting different drivers and conditions for water quality change. global literature survey shows that water quality has declined, improved, or has no significant trends in a gradually changing climate in 56%, 31%, and 13% of 956 case studies, respectively [32]. Water temperature and algae levels have generally increased. The concentrations of nutrients and pharmaceuticals mostly increased, whereas other variables including BOD, salinity, suspended sediment, metals, and microorganisms, have exhibited comparably increasing and decreasing trends [32].

Dissolved oxygen exhibited a predominantly decreasing trend in a global survey [32], possibly attributed to the major influence of water temperature [96]. This is further corroborated by a recent study that used deep-learning-model-filled daily DO data to demonstrate widespread warming and DO decrease in > 87% and > 70%, respectively, of 800 rivers in the US and Central Europe [97]. The examination of global DO data in the 2,975 sites from the Global River Water Quality Archive (GRQA) database [98] however show somewhat different proportional changes in trends. Although long-term mean DO concentrations are generally higher in warmer rivers (Figure 3a and 3b) and that mean DO concentrations and solubility of O2 (DO_{sat}) correlate negatively with water temperature ($p<0.001$) (Figure 3c) [32], only about 50% of the sites exhibited increasing water temperature (Figure 3e) and decreasing DO (Figure 3d), lower than the reported >70% decreasing DO in US and Central Europe rivers [97] and predominantly decreasing DO in the global survey [32]. It is possible that rising WT may augment oxygen-producing photosynthesis, counteracting O2-consuming and solubility-related losses [99]. DO loss could also be exacerbated by land use and other watershed characteristics such that it does not directly scale with WT changes [100]. For example, deoxygenation has been shown to occur most rapidly in agricultural rivers with slowest warming rates [97]. Data inconsistencies across sites likely play a role in these observed discrepancies. Some sites only have a few or no data points in some years, such that a few abnormal values can skew temporal trends. This highlights the complex influence of climate change on water quality, calling for continued efforts to monitor rivers and to probe the role of entangled processes that drive global river water quality.

Impacts of episodic and intense climate extremes

In contrast to persistent and gradual climate change, climatic extremes such as droughts, heatwaves, wildfire, and storms and floods are episodic and intense [101]. They rapidly change land structure via processes such as landslides, soil erosion, and ecosystem destruction. Such alterations can quickly modify water flow paths, the extent of land-river connectivity, and biogeochemical reactions that mobilize solutes and sediments. Different extreme events can invoke similar reactions and exert long-lasting but distinct influence on river water quality [29, 102]. Here we focus on fire, droughts, and storms as examples, but it's important to note that other extremes, like heatwaves, have become increasingly consequential [32, 101, 103].

Fire

Wildfires have profound and lasting impacts on water quality via altering ecosystems and soil structures [104]. Wildfire burns plants, litter, and organic matter, produces ash, and changes microbial composition (Figure 4a) [105]. Lower post-fire water demand (transpiration) increases river discharge[106]. Burning also increases soil hydrophobicity, which can reduce water infiltration into soils [106] and generate more overland water flow in post-fire storms. Soil hydrophobicity additionally induces post-fire soil erosion and the transport of wildfire ash into rivers, often leading to orders-of-magnitude increases in concentrations and fluxes of sediments, nutrients, carbon, major ions, and metals, as documented in local [107, 108], regional [109], and continental analyses [110]. Concurrent with nutrient increases, altered C:N and C:P ratios have also been observed in many rivers, which can instigate enduring impacts on water quality and aquatic ecosystem health [109, 110].

Effects of wildfire often peak right after a fire and gradually diminish over time, with durations varying from years to decades. In some areas, solutes such as cations and metals decrease back to their original concentrations within five years after a fire, whereas concentrations of particulate matter continue to increase [109]. Elevated sediments and nutrients in rivers have been observed to persist for more than 10 to 15 years after burning [104]. Increasing frequency in wildfire are projected due to climate change and human activities [111], indicating growing and long-lasting impacts on water quality and water supply in the future [29].

Droughts

Droughts influence water quality directly via their impact on hydro-biogeochemical reactions in rivers [30, 32, 112]. Prolonged droughts induce dry riverbeds and generate fragmented pools of stagnant water or low-flow channels with minimal water input from the surrounding land [78] (Figure 4b). These low-flow conditions elevate temperature and prolong water residence times, which can intensify in-stream biogeochemical processing [113]. Prolonged stagnant and warm conditions also reduce air-water gas exchange and impede the replenishment of DO in rivers. In addition, low river flow is dominated by input from deeper groundwater with low DO [114]. All these conditions result in DO depletion, which has been observed to trigger greater occurrence of anoxic reactions that shift water quality away from non-drought conditions. Sustained stagnant water additionally can stimulate eutrophication and algal blooms, produce dangerous toxins that can sicken or kill people and animals, and create dead zones [15, 115]. A global survey indicates that concentrations of sediments, algae, and most solutes (including salinity, carbon, and nutrients) escalate during or after droughts [32] [115] (Figure 4).

In addition to direct impacts within rivers, droughts have wide-ranging impacts on soil and ecosystems [112, 116]. Droughts can induce ecosystem response (e.g., deepening roots and vegetation die off [72, 117]), destabilize soil and sediment structure by forming cracks [78, 112], and modify the properties of organic matter and the composition of microbial communities [74]. These changes often reduce rates of biogeochemical reactions. Flow paths often deepen during droughts as a result of low water content and deepening roots but can also become shallower post-drought due to the development of soil hydrophobicity. During post-drought storms and heavy precipitation, accumulated solutes and solids in dry riverbeds and land commonly flush out excessively, further deteriorating river water quality and exacerbate eutrophication [115].

Storms and Floods

Storms and floods influence water quality via modification of land structure and substantial export of solutes and sediments from land to rivers [118] [119]. Excessive water elevates water tables and surface water runoff, therefore promoting shallow flow paths [120]. Excessive surface flow can trigger landslides, collapse of riverbank, and soil erosion

[120]. These processes accelerate the mobilization of particulates and carbon- and nitrogen-containing solutes such as DOC and nitrate from topsoil. This is particularly noticeable in agricultural areas, where large hydrological events such as storms and rain-on-snow flush out nutrients in top soils, making water quality especially vulnerable to shifting hydroclimate patterns [121]. Extreme wet conditions connect rivers to uplands that are often disconnected under non-flooding conditions, leading to disproportionally large pulses of "stored" legacy solutes and nutrients entering rivers [122]. In urban areas, excessive surface runoff and flow paths connected with impervious surface and urban infrastructure (e.g., sewer pipes, wastewater treatment plants) not only flush out nutrients, carbon, and metals, but also emerging contaminants such as pharmaceuticals and microplastics.

Floods can additionally mobilize pathogens and microorganisms and spread waterborne disease [122, 123]. The occurrences of harmful algal blooms depend on the combination of nutrient levels, temperature, among other conditions, and often occur after storms (in addition to during droughts) [124]. Fish kills are common after flooding, often caused by the compound, abnormal conditions including high levels of organic materials, vegetation stress, low DO, and fish trapping in hypoxic floodwater [125]. In addition to the pulses of solutes and sediments, excessive water volumes during flooding often trigger hot moments of anoxic reactions, which can produce diverse solute and gas products that become rapidly mobilized under extreme wet conditions [126]. A global survey indicates that concentrations of sediments, algae, and almost all solutes increase during floods excepts DO and salinity [32] (Figure 4c).

Compound effects and extreme behaviors

Existing studies have primarily focused on the effects of individual events on water quality. Different types of extreme events, however, often occur simultaneously or consecutively with overlapping times. For example, droughts and heatwaves and wildfires often happen at similar times [127]. Post-fire and post-drought floods are common [104, 108, 115]. These simultaneously or consecutive-occurring events can cause compound, more severe impacts on water quality than individual events alone [128, 129]. Prolonged droughts during summer heat waves, followed by intense rainfall, have been observed to introduce large influxes of easily decomposable organic, leading to low DO conditions and fish kills [125]. Droughts, heatwaves, and fire all lead to high temperatures, low water content in soil, and low DO in rivers, conditions that induce algae bloom and toxin release.

Frequent extreme events additionally bring frequent in-between transitioning conditions [126]. Rapid dry-wet, hot-cold, and oxic-anoxic fluctuations between extreme events often create abnormal conditions that challenge existing theories. For example, thermodynamic theories prescribing redox ladders of biogeochemical reactions have been contradicted by observations under rapidly changing conditions [64]. Rates of soil respiration are expected to peak under oxic conditions. Periodic anoxic conditions however have been shown to sustain or even stimulate soil respiration during oxic-anoxic transitions, leading to unexpectedly high rates of soil carbon loss relative to static oxic conditions [130] and possible high production rates of solutes such as DOC.

Rewetting of dry soils leads to significant carbon and nutrient loss arising from sudden intensification of soil respiration [74, 131]. Methanogenesis, the process of methane production, is expected to occur under anoxic conditions. Yet it has been observed to occur faster and produce more methane in well-oxygenated dry soils than under anoxic conditions [132]. Soil respiration rates under wet, anoxic conditions have been observed to approximate those under oxic conditions, suggesting potentially widespread underestimation of solute production under wet conditions [133].

These studies suggest that extreme events, whether single or compound, can push land and river systems beyond typical conditions for which data and knowledge exist. For example, stream solute concentrations measured at high-frequency (every 5-30 minutes) suggest that solute concentrations respond to discharge variations in storm events differently compared to their responses during baseflow as identified using low frequency measurements [134]. Stream chemistry responses also vary by season, storm size, and solutes. In other words, responses of water quality during events may fall outside the expectations of existing theories and models, thus challenging the ability to understand, generalize, and predict water quality (Figure 5).

Advancing understanding and forecasting capabilities

Water quality management will become increasingly challenging in a changing climate [102]. This is especially true with shifts in extreme conditions, which have already been shown to deteriorate water quality to an extent that can threaten municipal water supplies [29]. Thus, hindcasting water quality and forecasting near-term responses to extreme conditions will be essential for designing robust water infrastructure, making real-time management decisions, and mitigating their impacts. Most existing theories and models of water quality have been developed for changes in climate that are more persistent and gradual. They provide a strong basis for assessing responses to gradual climate change but will likely need further refinement for new climate regimes. The effects of episodic, intense extreme events on water quality however have remained poorly understood such that we cannot rely on historical dynamics to predict future impacts of a changing climate [35, 135]. Data on river discharge and chemistry data under extreme conditions are generally limited, which stymies our capacity to develop new theories and models [136] [135]. It is therefore essential to direct future research efforts to 1) understand water quality response to climate extremes and 2) develop forecasting capabilities under extreme conditions.

Understanding water quality response to climate extremes

Given the poorly understood connections between extreme climate events and water quality, it is essential to explore how extreme events of different magnitude, durations, and intensities influence the concentration and export of solutes and sediments in rivers, including threshold conditions that trigger various responses. It is also important to understand which processes become dominant during different extreme events, and how these relationships may differ from those under typical conditions. The co-occurrence of distinct types of extreme events also necessitates the characterization of their combined effects on water quality. For instance, droughts and heatwaves can co-occur and both increase water temperatures and decrease dissolved oxygen levels, but it is not clear which has a more pronounced effect, whether their effects could compound nonlinearly, and whether compounds effects lead to thresholds or tipping point that trigger different types of responses under distinct extent of land-river connectivity.

Answering these questions will require collecting data before, during, and after extreme events. Data scarcity has been a long-standing challenge in the field of water quality [137]. This is particularly the case under extreme physical conditions. For example, floods and fires often prevent manual sample collection and damage automated sensors. The episodic and intense nature of extreme conditions additionally narrows the temporal windows for data collection. Advances in technology for sturdy and robust automated sensors are critical for monitoring in extreme conditions [138]. Understanding land-river connectivity also requires observations in the land subsurface, including physical and biogeochemical properties of soil and rocks and source water chemistries [139]. These data are harder and more expansive to obtain but are essential for illuminating land processes that shape river water quality [39, 51, 140].

Beyond direct field observations, uncovering causal relationships between water quality and extreme events calls for the integration of data with process-based models [141]. It is likely that dominant processes under extreme conditions differ from those under baseline, typical conditions. This would require paradigm shifts in process conceptualization to build new models that integrate emerging understandings about climate extreme impacts, and these models will need to undergo further testing with additional data collected under other extreme conditions. Such scientific iteration between observations, models, and hypothesis falsification can facilitate the growth of new knowledge and build better predictive models for extreme conditions [142].

Different land and river systems often respond to climate extremes distinctly. To generalize theories and models, it is also crucial to move beyond individual sites and explore patterns and drivers across gradients of climate, land use/cover, geology, and other characteristics. This would require juxtaposition of data from different places and events, and drawing interpretations through complementary deductive and inductive approaches [143, 144]. It is possible that some datasets, especially those from high-frequency sensors, have already encoded process-relevant information under extreme conditions [145]. Data-driven tools can be used to detect patterns and identify influential factors, while process-based models can be leveraged to reveal dominant processes that regulate water quality responses to extremes.

Developing forecasting capabilities

Processed-based models explicitly simulate underlying hydrological and biogeochemical dynamics from "first principles" but suffer from limitations in representing process complexity and high computational requirements, especially in real-time or for large-scale assessments. However, new advancements with these tools offer the greatest potential for forecasting future water quality under climate change, including those under extreme events that are challenging to characterize.

Machine learning models, in particular deep learning models with multiple hidden layers, have recently emerged as promising tools for river flow and water quality prediction [145] . For example, long-short-term memory (LSTM) neural network models have been shown to outperform traditional process-based hydrologic models, demonstrating versatility and accuracy in ungauged basins and flood forecasting. Although not as widely used in water quality prediction, LSTMs, among other approaches, have also shown promise in predicting WT and DO in rivers [96] and lakes [146] with no data and in future climate scenarios. Most of these models, however, are trained using data under typical conditions instead of climate extremes.

Forecasting water quality during climate extremes requires model generalizability, i.e., the capability to extrapolate beyond training data. Unlike process-based models, deep learning models usually rely solely on information encoded in training data; they must see sufficient input-to-output responses to extract trends and patterns. These limitations have triggered the recent development of theory- or process-guided deep learning (PGDL) that leverage the strengths of both types of models [147] [148]. Similarly, emerging differentiable modeling integrates process-based equations and machine learning and can support exploration of process representations [149]. PGDL has been shown to improve accuracy and reliability beyond training conditions and improve the physical realism of predictions with limited data [150]. When coupled with explainable artificial intelligence techniques, they also hold the potential to detect patterns and identify underlying processes that drive water quality. Although data availability will remain the bottleneck of forecasting under extreme conditions, deep learning models have been an underused tool in water quality prediction, and can be further explored for data filling, knowledge discovery, and computational power to enhance our forecasting capabilities.

In summary, water quality should be at the front and center of climate adaptation [151] but has been largely overlooked. Deteriorating river water quality threatens water availability not only for human consumption but also aquatic ecosystem health, food and energy production, among others. The quality of river water has already exhibited widespread and substantial alterations due to climate change through drivers and processes on land and in rivers. These changes need to be accounted for in future climate risk assessment in order to avoid underestimates in water scarcity and inadequate designs in mitigation and adaptation initiatives [152] [8]. This review particularly focuses on the influential role of land-river connectivity in regulating water quality amidst gradually changing climate and episodic climate extremes. Existing models and theories serve as strong foundations for gauging water quality responses to gradual climatic shifts and will nevertheless need further enhancements to adapt to unprecedented climate regimes. For climate extremes, forecasting water quality will necessitate fundamental paradigm shifts in process understanding and formulation of new theories and models that build upon innovative data collection technologies and strategies.

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Table 1: Common water quality variables and examples of their potential ecological, health, and economic effects [153, 154].

Common Water quality variables *	**Ecological / health/ economic effects**
Water Temperature (WT)	High water temperature can, for example, reduce concentrations of dissolved oxygen, change pH, and threaten aquatic ecosystems.
Dissolved Oxygen (DO)	Low DO (hypoxia) can suffocate aquatic life and lead to fish kill. Low DO during algal blooms has caused dead zones worldwide. Low DO can also mobilize chemicals such as toxic metals and phosphorus.
pH	pH is a fundamental variable that drives chemical and biological processes. Most organisms only survive in a narrow pH range. Fluctuations in pH can significantly influence water quality. For example, low pH helps mobilize toxic metals.

Nutrients: including dissolved & particulate forms of nitrogen (N) & phosphorus (P)	Nutrients are essential for growth, but can limit or boost aquatic productivity, cause hypoxia and harmful algal blooms. They are often excessive in human-impacted areas such as agriculture and urban land. Elevated nitrate in drinking water can cause health problems (especially in babies). Nutrient pollution treatments have been estimated to cost > $2 billion annually in the US [155].
Carbon: Dissolved organic & inorganic carbon (DOC & DIC)	High dissolved organic carbon (DOC) concentrations cause brown color in surface waters. DOC can also form carcinogenic disinfectant by-products during water treatment, and mobilize toxic metals. Inorganic carbon balances pH, and often affects Ca and Mg concentrations (hardness). Both DOC and DIC are sources of CO_2 to the atmosphere and are an important part of the global carbon cycle. DOC and DIC are sometimes approximated as Biochemical Oxygen Demand (BOD) and alkalinity, respectively.
Toxic metals	Metals such as arsenic, mercury and lead are toxic for aquatic and human life. They often transport together with organic matter, and bioaccumulate in the food chain.
Salinity, Total Dissolved Solids (TDS), cations & anions	Salinity quantifies the total concentrations of dissolved ions, often measured by electrical conductivity or specific conductance. Salinity can originate from human activities such as irrigation and road salt application for de-icing or natural geochemical processes such as rock weathering. High salinity waters with high dissolved ions can precipitate as solids in soils, water pipes and facilities. Highly saline water modifies soil properties and reduces food productivity when used for irrigation. Salinity impacts freshwater ecosystems and water availability for human consumption [89].
Turbidity	Turbidity measures the extent of light penetration in water. It reflects the concentrations of suspended particles (e.g., solids and microorganisms). High turbidity reduces light availability for photosynthesis and increases water treatment costs.
Emerging contaminants	Emerging contaminants include pharmaceuticals, pesticides and industrial chemicals such as per- and polyfluoroalkyl substances (PFAS) [156]. They can be harmful in multiple ways. For example, some are endocrine system disruptors impacting the reproductivity of aquatic life.
Microplastics	These include fragments of plastics less than 5 mm. They decay slowly and can enter organisms and biomagnify up the food chain.
Microbial contaminants	Pathogenic organisms cause disease in humans and animals. A common example is the pollution of waterways by fecal microbial contaminants such as Cryptosporidium parvum or Salmonella.

*Note that the list and examples are not exhaustive. Concentrations (mass/volume) and loads (rates of export, in mass/time) of solutes and sediments are two important measures of water quality. The Clean Water Act, the water quality regulation in the US, establishes total maximum daily loads and Maximum Concentration Levels (MCLs) in Drinking Water Standards for many variables discussed here. The water quality inventory in the United State Geological Survey (USGS) contains over 17 categories and hundreds of thousands of variables (https://help.waterdata.usgs.gov/codes-and-parameters/parameters), highlighting the complex nature of water quality.

Figure 1: **Water quality is at the center of water availability and water-food-energy (and broadly climate-earth-human) interactions**. Water quality influences the emission of greenhouse gases, ecosystem health, and food and energy production via a range of variables including water temperature (WT), Dissolved Oxygen (DO), pH, sediment levels, and salinity. Importantly, water quality also determines the cost and carbon footprint of water infrastructure and treatment facilities, and availability of clean and accessible water for all.

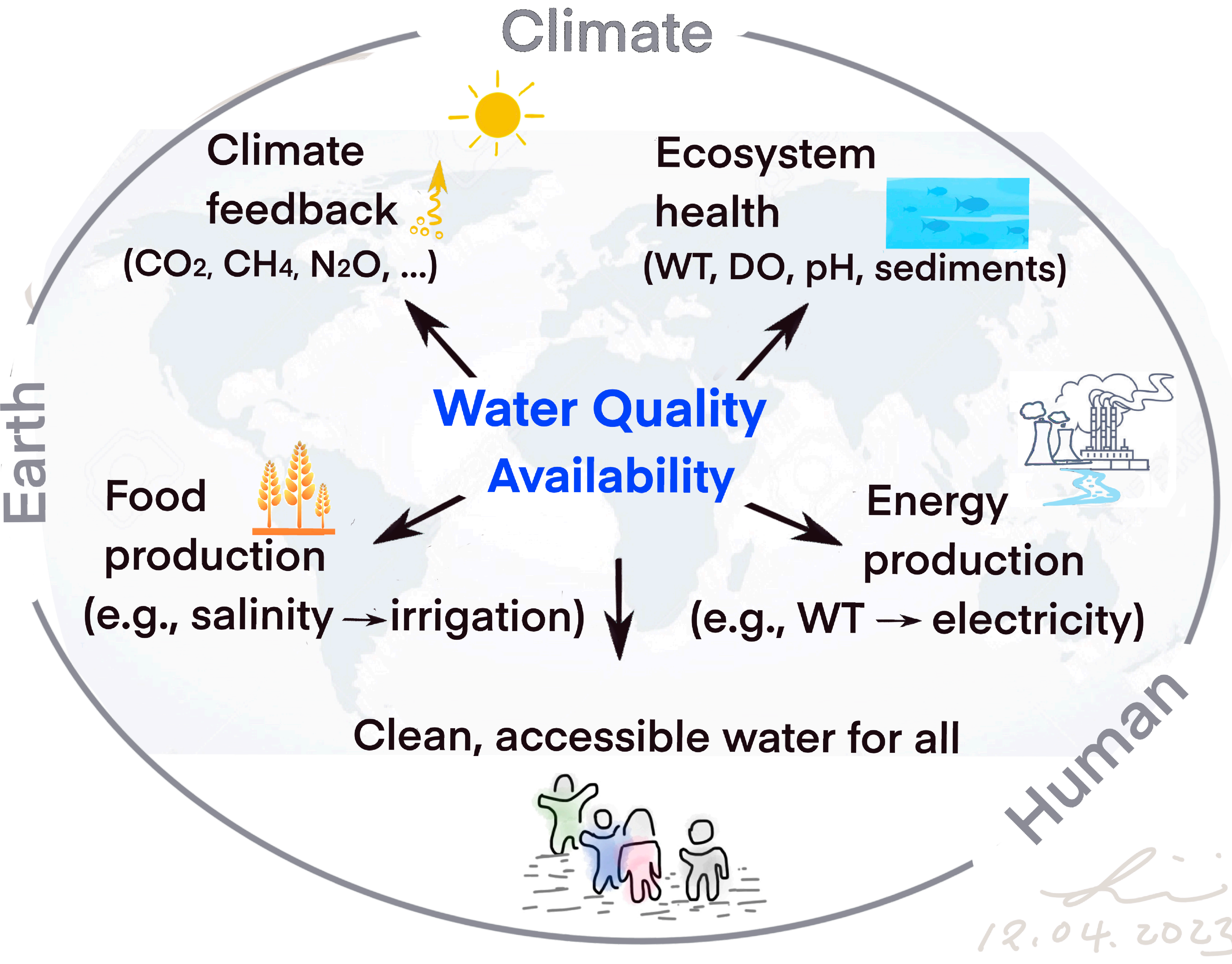
Figure 2: A conceptual diagram illustrating the propagating influence of climate change on water quality via land-river connectivity. a) Most precipitated water infiltrates and travels through shallow soils and deeper groundwater aquifers before ultimately emerging in rivers. The predominant flow paths differ under dry (e.g., top hillslope) and wet (e.g., bottom hillslope) conditions. Under dry conditions, low flow from deeper groundwater enriched in geogenic solutes such as Ca and Si (from soil and rock weathering) predominantly feeds the river, often with low water inputs leading to potentially disconnected water puddles (light and dark blue circles from shallow soil and deeper groundwater). Under wet conditions, rivers are fed more by surface runoff (sometimes carrying sediments) and shallow soil water enriched with biogenic carbon and nutrients (e.g., C, N, P, from biogeochemical transformation of organic matter). b) Riverine concentrations of sediments and biogenic solutes (C, N, and P) therefore increase with discharge, indicating their concentrations are typically higher under wet conditions. The opposite is true for geogenic solutes such as Ca and Si. Their riverine concentrations often escalate under drier conditions when river water is dominated by deeper groundwater [51]. The loads of sediments and solutes generally increase with river discharge when the climate becomes wetter. Sediments and solutes are generated by soil erosion and biogeochemical reactions such as soil respiration, nutrient transformation, and chemical weathering in both land and rivers. The rates and thermodynamics of these reactions are regulated by climate-driven temperature (T), water content (S_w), and O2 levels both on land and in rivers.

Figure 3. Dissolved oxygen and water temperature across the globe. (a and b) Global maps of long-term mean DO and water temperature (WT) in 2,975 sites from the Global River Water Quality Archive (GRQA) database [98]; each site has at least 40 data points over a minimum of five years; (c) mean DO-WT and DO_{sat}-WT correlations (2,975 sites); DO_{sat} is the solubility of O2 (the capacity of water for dissolved O2); (d) statistical distribution of long-term DO changing rates in 395 data-rich sites with DO and WT data for at least 25 years The figures generally show lower DO in places with higher WT. Rates of change for DO and WT were quantified using Thiel-Sen slopes from the R package *openair*; the "deseason" option was used to account for potentially important seasonal influences. DO_{sat} was estimated using the *calc_DO_sat* function from the stream Metabolizer R package [157]. Positive and negative rates indicate increasing and decreasing trends, respectively.

Figure 4: A conceptual diagram illustrating the impacts of climate extremes on land and river structure, processes, and ultimately water quality: (a) fire, (b) drought, and (c) storms and floods. These events cause structural and process changes on land and in rivers, which further influence river water quality. The upward and downward arrows indicate increasing and decreasing trends, respectively; the presence and thickness of the arrows indicate the

proportional occurrence of each trend. For fire impacts on water quality, the proportional trends are based on a meta-analysis in the US [110] and may not have global representation. For droughts and storms / floods, proportional trends are based on a global literature survey [32].

Figure 5. **The distinct impacts of gradual change and climate extremes on river water quality**. a) Climate change manifests itself via gradual change (grey solid lines) and climate extremes (red dashed lines). Air temperature generally increases with time. Gradually changing precipitation leads to drier or wetter conditions, whereas climate extremes such as droughts, storms and floods cause disruption. b) Changing climate alters structure of land and rivers, and processes therein, including flow partitioning and biogeochemical reactions. It regulates temperature (T), water content (S_w), and O2 levels, key drivers of reaction rates and flow paths. Extreme events (dashed red arrows) may lead to rapid structure changes (e.g., landslides, soil erosion, ecosystem destruction) that deviate from typical patterns under gradual changes (grey area). c) Concentrations and loads of representative water quality variables that generally increase (e.g., C, N, P) or decrease (e.g., Ca, Si) with increasing discharge. Climate extremes can lead to a much larger uncertainty range (light red shade) than those under typical range (grey shade), potentially deviating from patterns predicted by existing theories and models.



Climate

Earth

Human

Climate feedback (CO_2, CH_4, N_2O, ...)

Ecosystem health (WT, DO, pH, sediments)

Water Quality Availability

Food production (e.g., salinity → irrigation)

Energy production (e.g., WT → electricity)

Clean, accessible water for all

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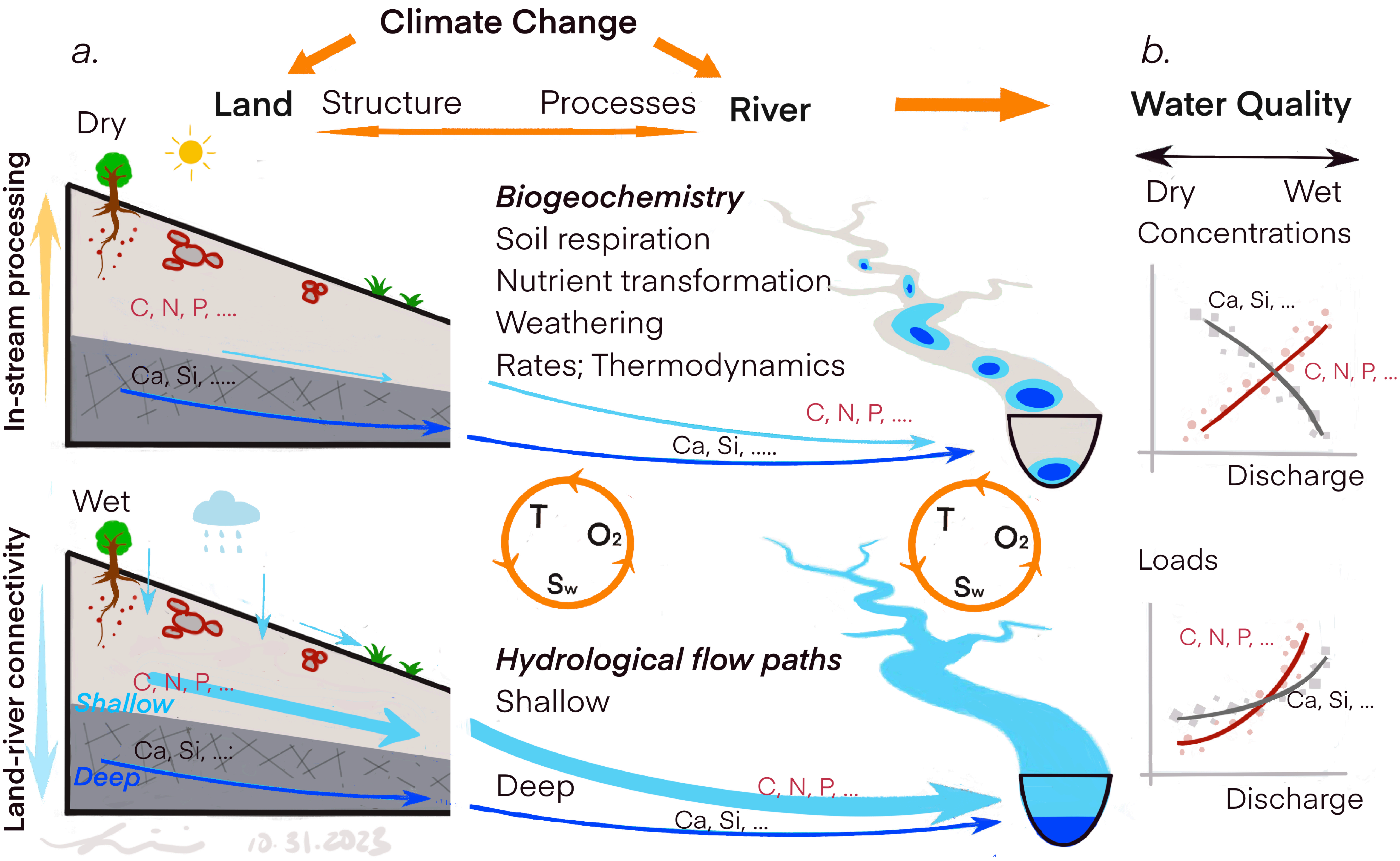
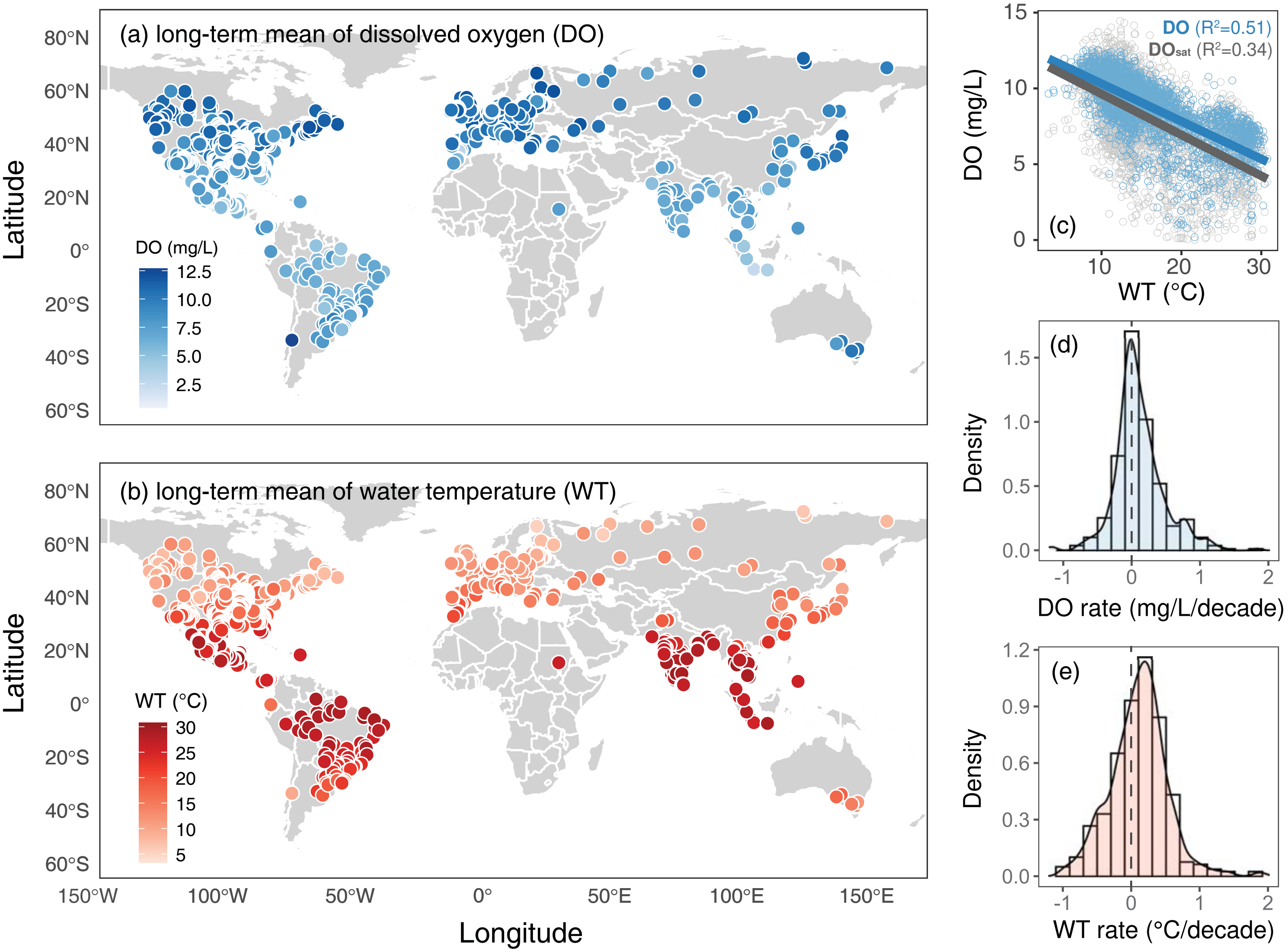
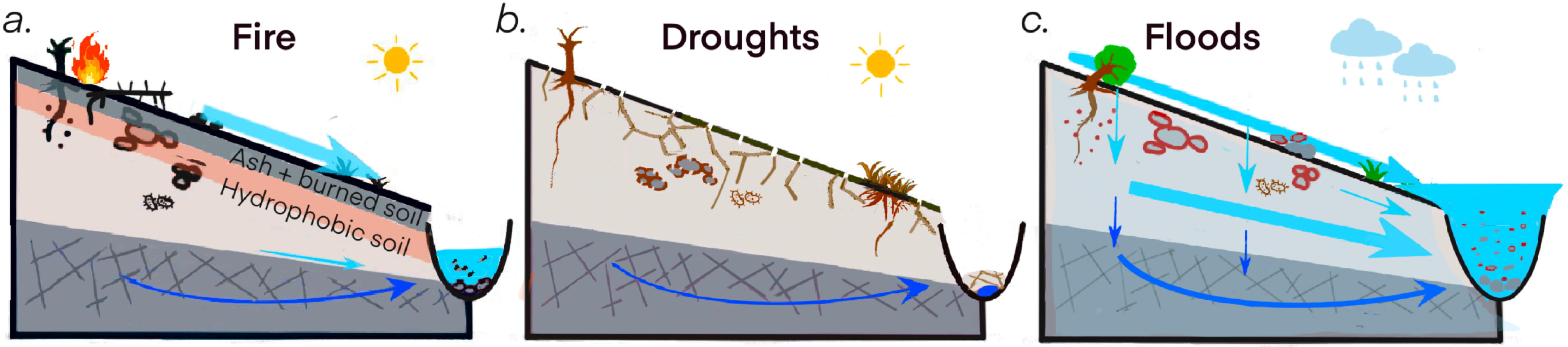
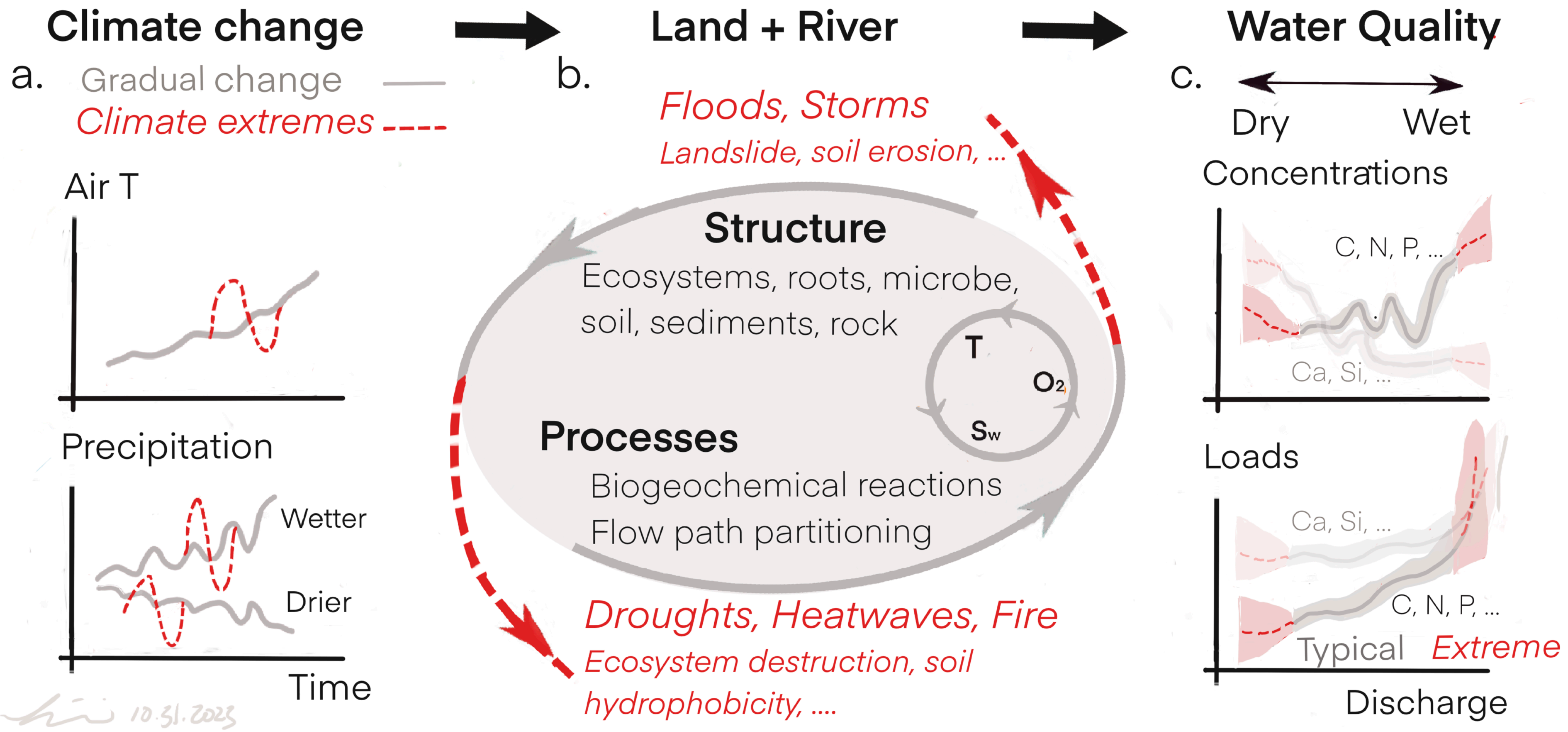

a.
Climate Change
Land
Structure
Processes
River
b.
Water Quality
Dry
Wet
Dry
Wet
Concentrations
In-stream processing
C, N, P, ...
Ca, Si, ...
Biogeochemistry
Soil respiration
Nutrient transformation
Weathering
Rates; Thermodynamics
C, N, P, ...
Ca, Si, ...
Ca, Si, ...
C, N, P, ...
Discharge
T
O2
Sw
T
O2
Sw
Loads
Land-river connectivity
Wet
C, N, P, ...
Shallow
Ca, Si, ...:
Deep
Hydrological flow paths
Shallow
Deep
C, N, P, ...
Ca, Si, ...
C, N, P, ...
Ca, Si, ...
Discharge
10.31.2023


(a) long-term mean of dissolved oxygen (DO)
DO (mg/L)
12.5
10.0
7.5
5.0
2.5
(b) long-term mean of water temperature (WT)
WT (°C)
30
25
20
15
10
5
80°N
60°N
40°N
20°N
0°
20°S
40°S
60°S
Latitude
150°W
100°W
50°W
0°
50°E
100°E
150°E
Longitude
(c)
DO (R^2=0.51)
DO_{sat} (R^2=0.34)
DO (mg/L)
WT (°C)
15
10
5
0
10
20
30
(d)
Density
DO rate (mg/L/decade)
1.5
1.0
0.5
0.0
-1
0
1
2
(e)
Density
WT rate (°C/decade)
1.2
0.9
0.6
0.3
0.0
-1
0
1
2



	Fire	Droughts	Floods
Structure	Ecosystem destruction Ash + debris layer Soil hydrophobicity Soil destablization	Stagnant river water pools Ecosystem destruction Deeping roots Alterred microbial community Soil + riverbed cracking Soil quality degradation, ...	Land slides River bank destruction Soil erosion ......
Processes	Lower transpiration Higher soil evaporation Higher discharge Higher surface runoff Flushing sediments + ash + solutes	Intensifying in-stream reactions Deepening / shallowing flow paths Shifting biogeochemistry Post-drought flushing + erosion	Shallowing of flow paths Anoxic biogeochemistry Flushing of legacy chemicals .....
Water Quality	Water T ↑ DO ↑↓ Nutrients ↑↓ Carbon ↑↓ Salinity ↑↓ Metals ↑↓ Sediments ↑↓ Algae bloom ↑↓	Water T ↑ DO ↑↓ Nutrients ↑↓ Carbon ↑↓ Salinity ↑↓ Metals ↑↓ Sediments ↑↓ Algae bloom ↑↓	Water T DO ↑↓ Nutrients ↑↓ Carbon ↑↓ Salinity ↑↓ Metals ↑↓ Sediments ↑↓ Algae bloom ↑↓

11.04.2023


Climate change
Land + River
Water Quality
a.
Gradual change
Climate extremes
Air T
Precipitation
Wetter
Drier
Time
10.31.2023
b.
Floods, Storms
Landslide, soil erosion, ...
Structure
Ecosystems, roots, microbe, soil, sediments, rock
T
O2
Sw
Processes
Biogeochemical reactions
Flow path partitioning
Droughts, Heatwaves, Fire
Ecosystem destruction, soil hydrophobicity, ...
c.
Dry
Wet
Concentrations
C, N, P, ...
Ca, Si, ...
Loads
Ca, Si, ...
C, N, P, ...
Typical
Extreme
Discharge

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