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River water quality shaped by land–river connectivity in a changing climate

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River water quality is crucial to ecosystem health and water security, 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 land–river connectivity and the quality of river waters. To advance 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 climate extremes, where the dynamics of water quality often challenge existing theories and models and call for shifts in conceptual paradigms.

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 km (refs. 2,3). The survival of humans, 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, however, is often considered as influenced more by human activities such as land use[5,6] and less by climate change, and is therefore often overlooked in climate risk assessments. As an example, the most recent IPCC report barely discusses the risks of a changing climate on inland water quality[4]. The effects of climate change on water quality have therefore remained 'invisible'[7].

These 'invisible' impacts of climate change on river water quality directly influence the estimation of water availability, scarcity and security[8,9], which quantifies and assesses risks associated with the amount of usable water, rather than simply considering the amount of available water. For 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 (ref. 10). Water availability is therefore inextricably linked to water 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[11]. Elevated sediment and nutrient concentrations have been estimated to increase the operation and maintenance costs of water treatment facilities by 53% (ref. 11). The United States, for example, has spent about US$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 US$400 per

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Table 1 | Common water quality variables and examples of their potential ecological, health and economic effects

Common water quality variables[a]	Ecological, health and economic effects
Water temperature	High water temperature can, for example, reduce concentrations of dissolved oxygen, change pH and threaten aquatic ecosystem health.
Dissolved oxygen	Low dissolved oxygen (hypoxia) can suffocate aquatic life and lead to fish kill. Low dissolved oxygen during algal blooms has caused dead zones worldwide. Low dissolved oxygen can also mobilize chemicals such as toxic metals and phosphorus.
pH	pH is a fundamental variable that drives chemical and biological processes. Most organisms survive in only a narrow pH range. Fluctuations in pH can significantly influence water quality. For example, low pH can facilitate the mobilization of toxic metals.
Nutrients, including dissolved and particulate forms of nitrogen and phosphorus	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 >US$2 billion annually in the United States[153].
Carbon: DOC, DIC and particulate organic carbon (POC)	High DOC concentrations cause brown colour 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 concentrations of cations such as calcium and magnesium (hardness). DOC, DIC and POC are sources of carbon dioxide to the atmosphere and are an important part of the global carbon cycle. DOC and POC are sometimes approximated as biochemical oxygen demand, and DIC can be approximated by alkalinity.
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, cations and 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 total dissolved solids 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 affects 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 (for example, 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[154]. They can be harmful in multiple ways. For example, some are endocrine system disruptors, impacting the reproductivity of humans and 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 faecal microbial contaminants such as *Cryptosporidium parvum* or *Salmonella*.

[a]Note that the list and examples are not exhaustive. Concentrations (mass per volume) and loads (rates of export, in mass per time) of solutes and sediments are two important measures of water quality. Loads are calculated as the products of concentrations and river discharge (water volume per time). The Clean Water Act, the water quality regulation in the United States, establishes total maximum daily loads and maximum concentration levels in drinking water standards for many variables discussed here. The water quality inventory in the United State Geological Survey 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. Based on refs. 155,156.

US citizen[12]. This makes clean water arguably one of the most expensive environmental investments in the United States—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 3 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. 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 wildfires[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[30–35], 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

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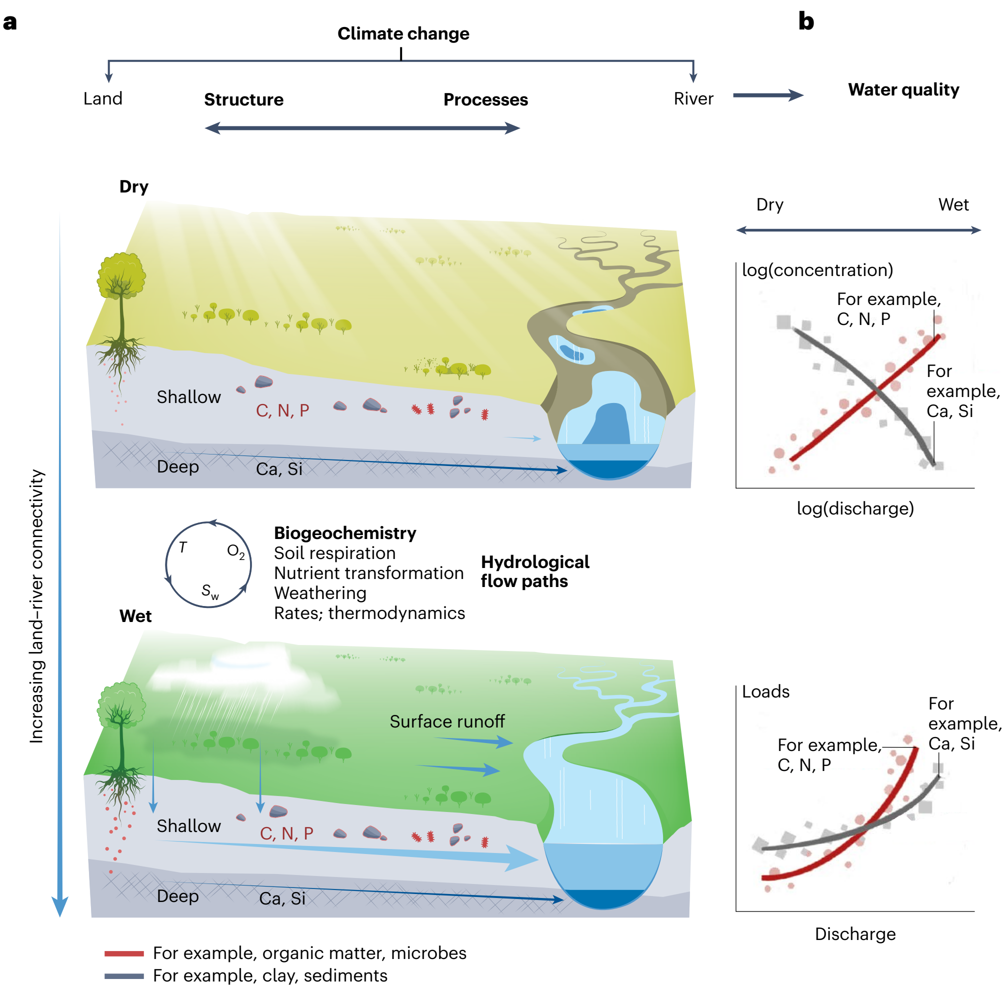

Fig. 1 | A conceptual diagram illustrating the propagating influence of climate change on water quality via land–river connectivity. a, Most precipitated water infiltrates and travels through shallow soils and deeper groundwater aquifers before ultimately emerging in rivers. The predominant flow paths differ under dry (for example, top hillslope) and wet (for example, 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 areas from shallow soil and deeper groundwater, respectively). Under wet conditions, rivers are fed more by surface runoff (sometimes carrying sediments) and shallow soil water enriched with biogenic carbon and nutrients (for example, C, N and P, from biogeochemical transformation of organic matter). **b**, Riverine concentrations of sediments and biogenic solutes (C, N and P) therefore increase with discharge, indicating that their concentrations are typically higher under wet conditions. The opposite is true for geogenic solutes such as Ca and Si. Their riverine concentrations often increase 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 on both land and in rivers. The rates and thermodynamics of these reactions are regulated by climate-driven temperature (T), water content (S_w) and oxygen (O_2) levels both on land and in rivers.

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[36–38] (Fig. 1). 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 conditions[39,40].

Decades of water tracer analysis and global surveys has shown that the majority of the global river water derives 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)[41–43]. This contrasts the common perception that most river water originates directly from recent precipitation. In fact, after the arrival of precipitated water on the land surface (global river and stream surface areas account for about 0.6% of Earth's non-glaciated land surface[44]), most of it then infiltrates into soils and rocks and travels along shallow and deep flow paths, often spending years to decades before entering rivers[45–47] (Fig. 1). In some groundwater-fed rivers, precipitated water enters deeper paths, travelling for hundreds to thousands of years underground before re-emerging 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 (Fig. 1). 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 harbour leaf litter and roots and living things enriched with organic matter. The decomposition of organic matter via microbe-mediated biogeochemical reactions (for example, soil respiration) generates biogenic solutes such as dissolved organic carbon (DOC) and various forms of nitrogen, which are often enriched in the shallow subsurface and decline with depth[50–52]. 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 (for example, with low precipitation and high evapotranspiration; Fig. 1a, 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 (for example, with heavy rain or snowmelt; Fig. 1a, 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 (Fig. 1b). Specifically, sediments and biogenic carbon (C)-, nitrogen (N)- and phosphorus (P)-containing solutes often show increasing concentrations with increasing discharge (flushing), whereas geogenic solutes such as Ca and Si show the opposite dilution patterns[51,55–57]. The loads, often quantified as products of concentrations and river discharge, 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 probably 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 agricultural and urban lands. Agricultural lands have abundant legacy stores of nutrients in shallow soils and tile drainage that facilitates 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[61–63]. These distinct structures in the subsurface could result in different hydrological flow paths and biogeochemical reactions, and therefore varying river water quality responses to a changing climate under diverse land-use conditions.

Impacts of persistent and gradual climate change

Land–river connectivity implies that persistent, gradual climate change influences water quality primarily in two ways. On relatively short timescales from hours to years, it directly modifies conditions and processes in rivers and on land. Over the longer timescales 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 oxygen (O_2) levels, all of which are key drivers of hydrological flow paths and reaction kinetics and thermodynamics that can change source water biogeochemistry[64,65] (Fig. 1). 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 reduces the rates of aerobic reactions that use O_2 (ref. 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, which similarly slows down overall reactions[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 (ref. 65). Different types of reaction 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[68].

Long-term alterations of land and river structure

At decadal to centennial timescales, the physical, chemical and ecological structure of the land and rivers will evolve with climate change[69–71], 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 timescales—much shorter than the centennial timescale that is typically expected[75–77]. 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 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[85,86] scales, 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 United States, for example,

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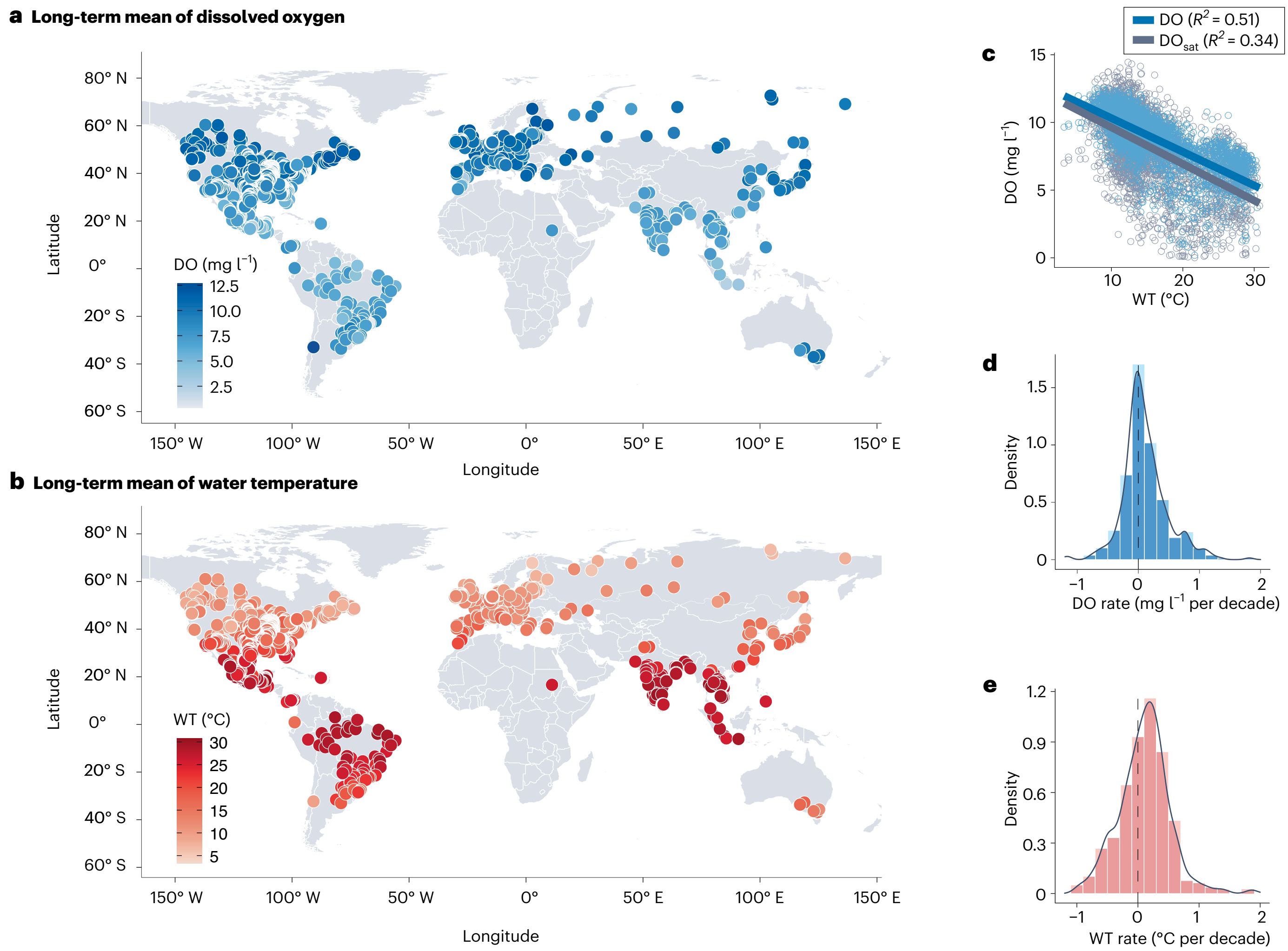

Fig. 2 | Dissolved oxygen and water temperature across the globe. a,**b**, Global maps of long-term mean dissolved oxygen (DO; **a**) and water temperature (WT; **b**) in 2,975 sites from the GRQA database[98]; each site has at least 40 data points over a minimum of five years. **c**, Mean dissolved oxygen–water temperature and DO_{sat}–water temperature correlations (2,975 sites); DO_{sat} is the solubility of O_2 (the capacity of water for dissolved O_2). **d**,**e**, Statistical distribution of long-term change rates in 395 data-rich sites with dissolved oxygen and water temperature data for at least 25 years. The figures generally show lower dissolved oxygen in places with higher water temperature. Rates of change for dissolved oxygen (**d**) and water temperature (**e**) were quantified using Theil–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. Only about 50% of the sites showed increasing water temperature (**e**) and decreasing dissolved oxygen (**d**), lower than the reported >70% in the United States and Central Europe rivers[97] and predominantly decreasing dissolved oxygen in the global survey[32]. These contrasting results highlight the complexity of climate change on water quality and data scarcity challenges in water quality.

salinity has increased substantially in 29–39% of the rivers; about 90% of US rivers have seen increasing pH since the mid-twentieth 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 dissolved inorganic carbon (DIC)), has increased since the 1980s in the eastern United States; and warming water may continue to exacerbate this trend[90]. Water quality in the Upper Colorado basins in the United States shows strong dependence on lithology and climate (for example, 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 with rates two decades ago[92,93]. Gradual and abrupt permafrost thaws have become hotspots 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. A global literature survey showed 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 have mostly increased, whereas other variables, including biochemical oxygen demand, salinity, suspended sediment, metals and microorganisms, have shown comparably increasing and decreasing trends[32].

Dissolved oxygen showed 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 dissolved oxygen data to demonstrate widespread warming and dissolved oxygen decrease in >87% and >70% of 800 rivers in the United States and Central Europe, respectively[97]. Examination of global dissolved oxygen data in the 2,975 sites from the Global River Water Quality Archive (GRQA) database[98], however, showed somewhat different proportional changes in trends. Although long-term mean dissolved oxygen concentrations are generally higher in warmer

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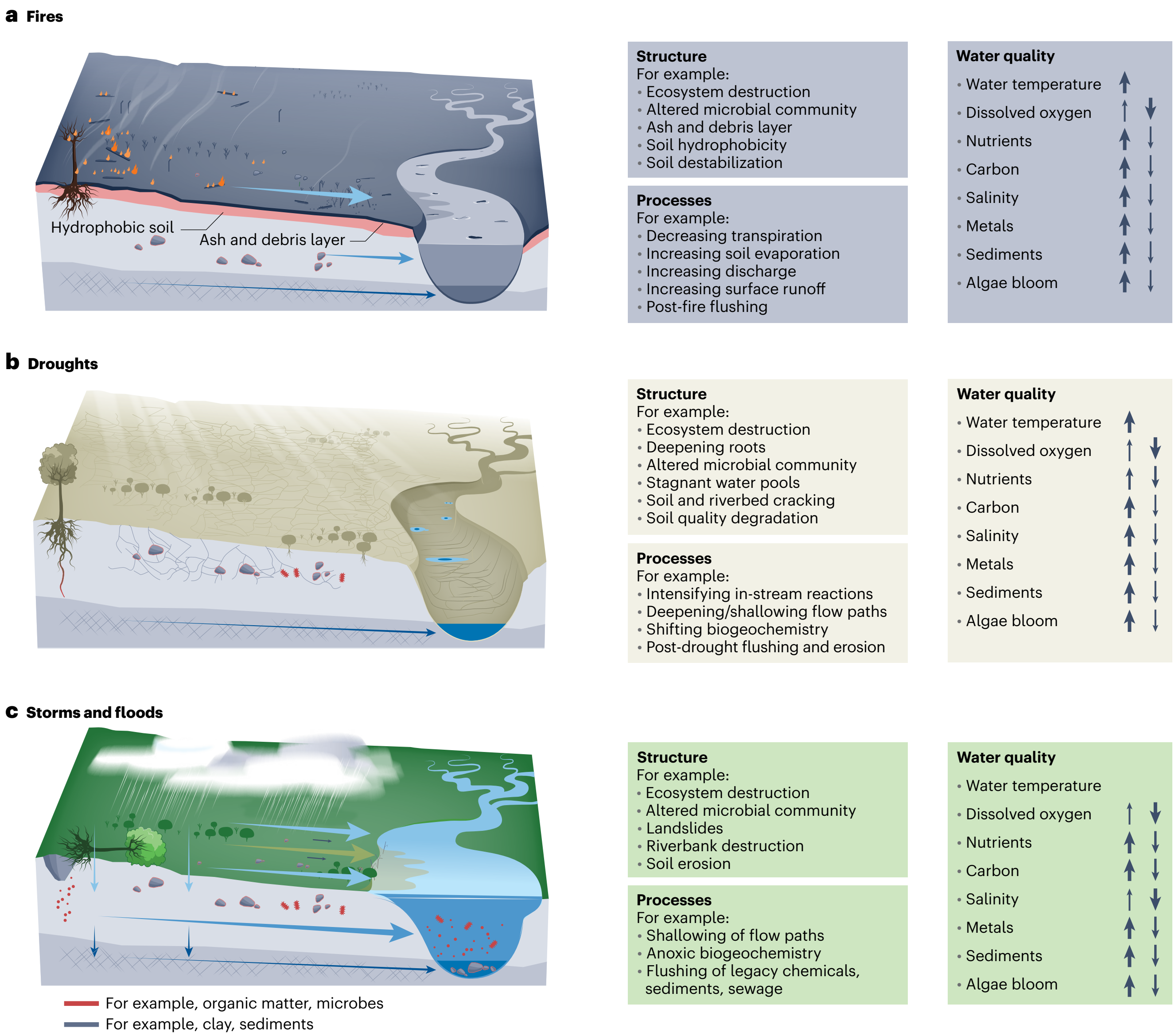

Fig. 3 | A conceptual diagram illustrating the impacts of climate extremes on land and river structure, processes and, ultimately, water quality. **a**, Fires. **b**, Droughts. **c**, Storms and floods. The lightest, light and dark blue arrows represent water flow paths via ground surface, shallow soils and deeper subsurface, respectively. The upwards and downwards arrows in the right-most column indicate increasing and decreasing trends, respectively; the presence and thickness of the arrows approximate the proportional occurrence of each trend. For fire impacts on water quality, the proportional trends are based on a meta-analysis in the United States[111] and may not have global representation. For droughts, and storms and floods, proportional trends are based on a global literature survey[32].

rivers (Fig. 2a,b) and mean dissolved oxygen concentrations and solubility of oxygen correlate negatively with water temperature ($P < 0.001$; Fig. 2c)[32], only about 50% of the sites showed increasing water temperature (Fig. 2e) and decreasing dissolved oxygen (Fig. 2d), lower than the reported >70% in the US and Central Europe rivers[97] and predominantly decreasing dissolved oxygen in the global survey[32]. It is possible that increasing water temperature may augment oxygen-producing photosynthesis, counteracting oxygen-consuming and solubility-related losses[99]. Dissolved oxygen loss could also be exacerbated by land use and other watershed characteristics such that it does not directly scale with water temperature changes[100]. For example, deoxygenation has been shown to occur most rapidly in agricultural rivers with the slowest warming rates[97]. Data inconsistencies across sites probably play a role in these observed discrepancies. Some sites have only 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, wildfires, 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 a long-lasting but distinct influence on river water quality[29,102]. Here we focus on fires, droughts and storms as examples, but it is important to note that other extremes, such as heatwaves, have become increasingly consequential[32,101,103].

Fires

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 the composition of microbial communities[105] (Fig. 3a). Lower post-fire water demand (transpiration) and nutrient demand also increases river discharge[106] and nutrient concentrations[107], respectively. 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[108,109], regional[110] and continental[111] analyses. 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[110,111].

The effects of wildfire often peak immediately 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[110]. Elevated sediments and nutrients in rivers have been observed to persist for more than 10 to 15 years after burning[104]. An increasing frequency of wildfires is projected due to climate change and human activities[112], 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 biogeochemical reactions in rivers[30,32,113]. 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] (Fig. 3b). These low-flow conditions elevate temperature and prolong water residence times, which can intensify in-stream biogeochemical processing[114]. Prolonged stagnant and warm conditions also reduce air–water gas exchange and impede the replenishment of dissolved oxygen in rivers. In addition, low river flow is dominated by input from deeper groundwater with low dissolved oxygen[115]. All these conditions result in dissolved oxygen 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[15,116]. A global survey indicated that concentrations of sediments, algae and most solutes (including salinity, carbon and nutrients) escalate during or after droughts[32,116] (Fig. 3).

In addition to direct impacts within rivers, droughts have wide-ranging impacts on soil and ecosystems[113,117]. Droughts can induce ecosystem response (for example, deepening roots and vegetation die off[72,118]), destabilize soil and sediment structure by forming cracks[78,113], 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 exacerbating eutrophication[116].

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[119,120]. Excessive water elevates water tables and surface water runoff, therefore promoting shallow flow paths[121]. Excessive surface flow can trigger landslides, collapse of riverbank and soil erosion[121]. 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[122]. 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[123]. In urban areas, excessive surface runoff and flow paths connected with impervious surface and urban infrastructure (for example, sewer pipes, wastewater treatment plants) flush out not only nutrients, carbon and metals but also emerging contaminants such as pharmaceuticals and microplastics.

Floods can additionally mobilize pathogens and microorganisms and spread waterborne disease[123,124]. The occurrences of harmful algal blooms depend on the combination of nutrient levels and temperature, among other conditions, and often occur after storms (in addition to during droughts)[125]. Fish kills are common after flooding, often caused by the compound, abnormal conditions, including high levels of organic materials, vegetation stress, low dissolved oxygen and fish trapping in hypoxic floodwater[126]. 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[127]. A global survey indicated that concentrations of sediments, algae and almost all solutes increase during floods except dissolved oxygen and salinity[32] (Fig. 3c).

Compound effects and extreme behaviours

Existing studies have primarily focused on the effects of individual events on water quality. Different types of extreme event, however, often occur simultaneously or consecutively with overlapping times. For example, droughts and heatwaves and wildfires often happen at similar times[128]. Post-fire and post-drought floods are common[104,109,116]. These simultaneously or consecutively occurring events can cause compound, more severe impacts on water quality than individual events alone[129,130]. Prolonged droughts during summer heatwaves, followed by intense rainfall, have been observed to introduce large influxes of easily decomposable organic, leading to low dissolved oxygen conditions and fish kills[126]. Droughts, heatwaves and fire all lead to high temperatures, low water content in soil and low dissolved oxygen in rivers—conditions that induce algae bloom and toxin release.

Frequent extreme events also bring frequent in-between transitioning conditions[127]. 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[131] 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[74,132]. 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[133]. 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[134].

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

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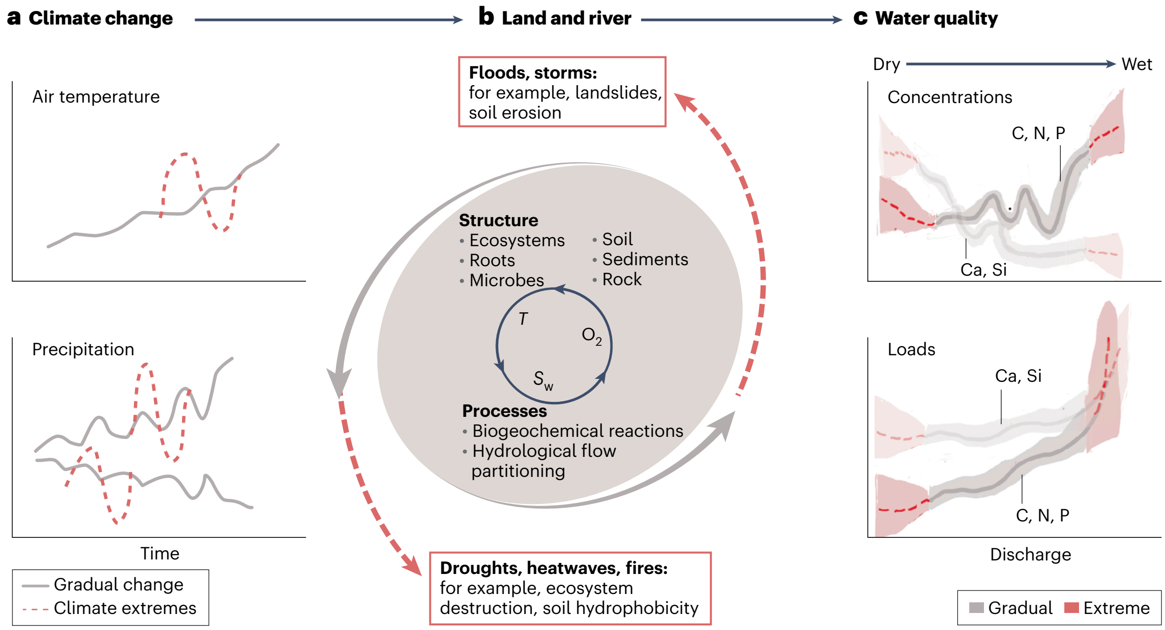

Fig. 4 | The distinct impacts of gradual change and climate extremes on river water quality. a, Climate change manifests itself via gradual change (grey solid lines) and climate extremes (red dashed lines). Air temperature generally increases with time. Gradually changing precipitation leads to drier or wetter conditions, whereas climate extremes such as droughts, storms and floods cause disruption. **b**, Changing climate alters the structure of land and rivers, and the processes therein, including flow partitioning and biogeochemical reactions. It regulates temperature (T), water content (S_w) and O_2 levels, key drivers of reaction rates and flow paths. Extreme events (dashed red arrows) may lead to rapid structure changes (for example, 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 (for example, C, N and P) or decrease (for example, Ca and Si) with increasing discharge. Climate extremes can lead to much larger uncertainty levels (light red shading) than those under typical range (grey shading), potentially deviating from patterns predicted by existing theories and models.

events differently compared with their responses during baseflow as identified using low-frequency measurements[135]. 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 (Fig. 4).

Advancing understanding and forecasting capabilities

Water quality management will become increasingly challenging in a changing climate[102]. This is especially true with shifting extreme conditions, which have already been shown to deteriorate water quality to an extent that can threaten municipal water supplies[29]. Forecasting water quality and 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 persistent and gradual climate change. They provide a strong basis for assessing responses to gradual climate change but will probably need further refinement for new climate regimes (Fig. 4). The effects of episodic, intense extreme events on water quality, however, have remained poorly understood such that historical dynamics cannot be relied on to predict future impacts of a changing climate[35,136]. Data on river discharge and chemistry under extreme conditions are generally limited, which stymies capacity to develop new theories and models[136,137]. It is therefore vital 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, duration and intensity influence the concentrations and loads of solutes and sediments in rivers, including thresholds that trigger changing patterns in 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, non-extreme conditions. The co-occurrence of distinct types of extreme event 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 reduce dissolved oxygen levels, but it is not clear which has more pronounced effects, whether their effects could compound nonlinearly, and whether compounds effects lead to thresholds or tipping points that trigger different types of response under distinct extents 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[138]. This is particularly the case under extreme 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[139]. Understanding land–river connectivity also requires observations in the land subsurface, including physical and biogeochemical properties of soil and rocks and source water chemistries[140]. These data are harder and more expensive to obtain but are essential for illuminating land processes that shape river water quality[39,51,141].

Beyond direct field observations, uncovering causal relationships between water quality and extreme events calls for the integration of data with process-based models[142]. 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, and these models will need to undergo further testing with additional data collected under extreme conditions. Such scientific iteration between observations, models and hypothesis falsification is crucial for discovering new knowledge and building better predictive models under climate extremes[143].

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 and 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[144,145]. It is possible that some datasets, especially those from high-frequency sensors, have already encoded process-relevant information under extreme conditions[146]. Data-driven tools can be used to fill data gaps, detect patterns and identify influential factors, whereas 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 based on existing knowledge but suffer from limitations in representing process complexity and high computational requirements, especially in real time or for large-scale assessments. However, new advancements in modelling tools offer potentials for forecasting the future of water quality under climate change.

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[146]. 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 yet widely used in water quality prediction, these approaches have shown promise in predicting water temperature and dissolved oxygen in rivers[96] and lakes[147] with no data. 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, that is, the capability to extrapolate beyond training data. Unlike process-based models, deep-learning models rely almost solely on information encoded in training data; they must see sufficient input-to-output patterns to extract trends and patterns. These limitations have inspired the development of theory- or process-guided deep learning (PGDL) that leverages the strengths of both types of model[148,149]. In addition, emerging differentiable modelling integrates process-based equations and machine learning and can potentially support the exploration of process representations[150]. PGDL has been shown to improve accuracy and reliability beyond training conditions and the physical realism of predictions with limited data[151]. In particular, when coupled with explainable artificial intelligence techniques, it also holds the potential to detect patterns and identify influential factors that drive water quality. In general, deep-learning models have been underused in water quality prediction and can be further explored for data filling, knowledge discovery and computational power to enhance forecasting capabilities. Data availability, however, will remain the bottleneck of forecasting under extreme conditions.

In summary, although water quality should be at the front and centre of climate adaptation[152], it has been largely overlooked. Deteriorating river water quality threatens water availability and security not only for human consumption but also for aquatic ecosystem health, food and energy production, among others. The quality of river water has already shown 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 assessments to avoid underestimates in water scarcity and inadequate designs in mitigation and adaptation initiatives[8,9]. This Review particularly focuses on the influential role of land–river connectivity in regulating water quality amid gradually changing climate and episodic climate extremes. Existing models and theories serve as strong foundations for gauging water quality responses to gradual climatic shifts but will nevertheless need further enhancements under 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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