Research papers

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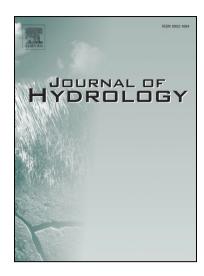
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Title: Impacts of droughts and heatwaves on river water quality worldwide

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Abstract

Droughts and heatwaves have a major impact on river water quality worldwide. However, previous studies of river water quality under these climate extremes are limited to a small number of river basins and regions, mainly located in North America, Europe or Australia. In this study, we estimate the large-scale effects of droughts, heatwaves and compound droughtheatwave events on river water quality for a total of 314,046 water quality monitoring stations worldwide over the period 1980-2021. We focus on 16 water quality constituents grouped into physical (e.g., temperature, salinity), chemical (e.g., pharmaceuticals, pesticides) and biological constituents (e.g., biochemical oxygen demand, faecal coliform). Further, we analyse the response of each constituent to droughts and heatwaves in relation to climate type, land use and level of wastewater treatment. We find a general deterioration in river water quality under droughts and heatwaves globally for most rivers and water quality constituents considered. For example, there is on average a 27% increase in river water temperature, 17% decrease in dissolved oxygen and 24% increase in salinity under droughts and heatwaves. In addition, we find that climate type, land use and level of wastewater treatment have a significant effect on the magnitude of response in each water quality constituent during these extreme events. The median increase in river water temperature under compound drought-heatwaves is strongly driven by climate zone with higher warming rates at the polar climate zone (+4.5°C) compared to

the tropical zone (+2.1°C). Increases in salinity under droughts are on average two times larger in irrigated regions compared to non-irrigated regions. The concentrations of nutrients (P and N) in rivers can either increase or decrease under droughts, depending on the nutrient form (dissolved vs. particulate) and land use (urban vs. rural). Higher levels of wastewater treatment contributed to a greater decrease in pathogenic concentrations under droughts and heatwaves (as indicated by faecal coliform). Pharmaceuticals show mixed responses mainly depending on the persistence of the constituent in surface waters, with for instance declines in diclofenac concentrations under droughts and heatwaves due to increased decay under higher water temperatures. The results of this study provide a broader understanding of how droughts and heatwaves affect river water quality compared to previous local and regional-scale analyses. In addition, this study could form the basis for large-scale modelling of river water quality under droughts and heatwaves.

1. Introduction

Droughts and heatwaves are increasing in frequency and severity in many regions of the world, likely due to climate change (Spinoni et al., 2019; Mukherjee and Mishra, 2021). Recent drought events in North America (Mankin et al., 2021), Europe (Rakovec et al., 2022), East Africa (Toreti et al., 2022) and China (Ma et al., 2022) were among the driest and hottest periods on record (Hari et al., 2020; Seager et al., 2022). The number of heatwave days has increased by, on average, two days per decade globally since 1950 (Perkins-Kirkpatrick and Lewis, 2020).

Water resources management is strongly affected by droughts and heatwaves, not only in terms of water quantity but also water quality (Whitehead et al., 2009; Hrdinka et al., 2012). For instance, decreases in river discharge during drought events can lead to increased concentrations of various pollutants (Macintosh et al., 2011; Burt et al., 2015). Furthermore, increased water temperatures under heatwaves can lead to faster rates of chemical processes and increased decay rates, while also affecting the solubility of water quality constituents (Tassone et al., 2022; Zhan et al., 2021). During compound drought-heatwave events, increases

in surface water temperatures can be especially severe, due to a reduced heat capacity (van Vliet et al., 2011). Some of the main challenges associated with water quality under droughts and heatwaves include algal blooms (e.g. Huang et al., 2021); increased salinity (e.g. Jones and van Vliet, 2018); and low levels of dissolved oxygen (e.g. Dai et al., 2006). Algal blooms can be caused by high concentrations of nutrients and increased water temperatures under droughts and heatwaves (Chen et al., 2021). They can produce hazardous toxins, damage ecosystems and raise water treatment costs (Paerl et al., 2016). Increased salinity under droughts and heatwaves is often caused by less dilution (Mosley, 2015). In regions where surface water is used for irrigation, high levels of salinity can adversely affect crop yields (Thorslund et al., 2022). Reduced levels of dissolved oxygen in surface waters under droughts and heatwaves can be directly caused by high water temperatures and can adversely impact the overall functioning of freshwater ecosystems (Arias Font et al., 2021; Sarkar et al., 2022).

Several studies have used in-situ data to analyse the effects of past droughts and heatwaves on river water quality (Zwolsman and van Bokhoven, 2007; Whitworth et al., 2012; Wolff and van Vliet, 2021). These studies typically use river discharge and air temperature time-series to identify historical droughts and heatwaves, respectively. Then, water quality data are analysed for statistically significant changes during these climate extremes compared to reference periods or long-term averages. These methods have been applied to a variety of river basins and regions, mainly in North America, Europe or Australia (Shehane et al., 2005; Ylla et al., 2010; Mosley et al., 2012). For instance, an extensive analysis of river salinity in the Southern United States showed statistically significant increases in electrical conductivity (EC) for ~90% of locations under drought (Jones and van Vliet, 2018). The median increase in EC was 21%, which was mainly attributed to the reduced dilution capacity of river discharge during drought conditions. Statistically significant increases in river water temperature have been observed under droughts and heatwaves in several river basins, such as the Rhine and Meuse in Europe (van Vliet and Zwolsman, 2008; Wolff and van Vliet, 2021). Measured concentrations of nutrients, dissolved oxygen and pathogens have shown highly varied responses under droughts and heatwaves between river basins (Mosley, 2015). Statistically significant increases in phosphorus and

nitrogen concentrations under droughts have been observed where point sources of pollution dominate (Macintosh et al., 2011; Hrdinka et al., 2012). Decreases in phosphorus and nitrogen concentrations under droughts have occurred in locations with mainly diffuse sources of pollution, mainly due to reduced runoff from agricultural land (Golladay and Battle, 2002; Baurès et al., 2013). Dissolved oxygen concentrations have been observed to both increase or decrease under droughts and heatwaves in different river basins, which has been attributed to either increased primary production or reduced oxygen solubilities, respectively (Sprague, 2005; Ylla et al., 2010). Pathogenic concentrations, measured using faecal coliform as a main indicator, have shown both increases and decreases under droughts, but the mechanisms of these diverse responses are poorly understood (Tunnicliff and Brickler, 1984; Caruso 2002). Increased concentrations of carbamazepine and metroprolol, two types of pharmaceuticals, were found in the Rhine and Meuse catchments in Europe, but these were statistically insignificant (Wolff and van Vliet, 2021).

The reported case studies show quite some differences in methods used to analyse river water quality under droughts and heatwaves. Firstly, each case study analysed a different set of water quality constituents. As many as 24 water quality constituents have been analysed under droughts and heatwaves in a single case study (van Vliet and Zwolsman, 2008), whereas some studies focused on a single aspect of river water quality, such as salinity (Jones and van Vliet, 2018). Secondly, there are various ways that droughts and heatwaves can be identified from river discharge and air temperature time-series. For instance, some studies used a constant threshold of river discharge to identify drought events (Caruso, 2001; Zwolsman and van Bokhoven, 2007), and others used a variable threshold (Peña-Guerrero et al., 2020). Thirdly, the statistical methods used to quantify changes in river water quality under droughts and heatwaves varied greatly. Some studies used empirical relations between water quality constituents and river discharge/air temperature (Tunnicliff and Brickler, 1984; Zwolsman and van Bokhoven, 2007), whereas others used hypothesis testing, such as: Mann-Whitney U tests (van Vliet and Zwolsman, 2008), Wilcoxon Signed Rank tests (Jones and van Vliet, 2018) or Analysis of Variance (Shehane et al., 2005; Ylla et al., 2010). Fourthly, the temporal and spatial

resolutions and extents varied significantly between case studies. Water quality responses under droughts and heatwaves have been analysed at either daily, monthly or seasonal scales (Caruso, 2001; Macintosh et al., 2011; Baurès et al., 2013), and the spatial scale has ranged from a single river basin to the Southern United States (Zwolsman and van Bokhoven 2007; Jones and van Vliet, 2018). Lastly, several studies carried out risk assessments to analyse the effects of droughts and heatwaves on river water quality (Chadd et al., 2017; Kim et al., 2019; Ustaoğlu et al., 2020).

Because previous studies focused mainly on selected river basins and regions and differ greatly in methods used, it is difficult to extract general conclusions about the global response of river water quality to droughts and heatwaves. This requires large-scale (e.g., continental or global scale) analyses of river water quality under droughts and heatwaves. However, large-scale studies are lacking in the literature. The closest study that presents a large-scale analysis of river water quality under droughts and heatwaves is a review article by Mosley (2015), which summarises 43 local and regional scale analyses. However, as these local and regional scale analyses all used different methodologies, it is challenging to quantitatively compare water quality responses for different regions across the world in a consistent way. Also, local and regional-scale studies have a limited ability to assess the large-scale effects of droughts and heatwaves on river water quality. In addition, the influence of climate and human activity on water quality responses under droughts and heatwaves has not previously been quantified at the global scale.

With the recent development of online water quality databases (United Nations Environment Programme, 2018; European Environment Agency, 2022; Water Quality Portal, 2021), a large amount of river water quality data currently exists which is yet to be analysed under droughts and heatwaves. This data could be used to determine the large-scale effects of droughts and heatwaves on river water quality. In addition, this data could be used to improve our understanding of how climate, land use and level of wastewater treatment affect the magnitude of responses in river water quality under these climate extremes. In this study, we carry out the

first consistent large-scale analysis of river water quality under droughts and heatwaves, mainly focusing on the global level.

2. Materials and methods

2.1 River water quality data

The river water quality data are summarised in Table 1. A total of 8 water quality monitoring databases were processed into a single database. These included:

- Two global databases: GEMStat (United Nations Environment Programme, 2018) and
 GLORICH (Hartmann et al., 2014)
- One European database: Waterbase (European Environment Agency, 2022)
- Five national datasets:
 - Canada (Government of Canada, 2021)
 - United States (Water Quality Portal, 2021)
 - South Africa (Department of Water and Sanitation, 2022)
 - Australia (Government of Australia, 2022)
 - New Zealand (National Institute of Water and Atmospheric Research, 2022)

These data covered 16 water quality constituents (listed in Table 1) for a total of 314,046 monitoring stations over the period 1980-2021. Figure 1 shows the locations of the monitoring stations for each water quality constituent. This shows for most water quality constituents a high density of water quality monitoring stations in North/South America, Europe, South Africa, Australia/New Zealand and parts of Southeast Asia. However, there is a lower density of water quality monitoring stations for most parts of Africa and Asia. For the pharmaceuticals only water quality monitoring data were found for the US and Europe.

< Table 1 >

< Figure 1 >

Several steps were taken to ensure that each of the 8 water quality databases were processed in a consistent way. The type of water body was restricted to rivers for each database. Duplicate stations between multiple datasets were removed if they had the same original station IDs. For each water quality constituent, units were made to be consistent. Lastly, instantaneous measurements of river water quality were processed to the daily scale by taking the mean of water quality measurements that were taken on the same day at the same location.

2.2 Drought and heatwave identification

This study identifies hydrological droughts, heatwaves and compound drought-heatwaves globally over the period 1980-2021. Hydrological droughts are identified based on periods of extreme low river flow (discharge). A common procedure to evaluate hydrological droughts is the threshold level method (e.g., van Huijgevoort et al., 2012; van Loon, 2015; van Loon and Laaha, 2015). In this study, we apply the variable threshold level method to identify hydrological droughts worldwide, based on river discharge data from the Global Runoff Data Centre (for details see 2.2.1). We then identify heatwave events, based on periods when the maximum daily air temperature is above the 90th percentile for at least 3 consecutive days (section 2.2.2). Finally, we identify compound drought-heatwaves by combining the approaches to identify drought events and heatwave events (section 2.2.3).

Methods of drought identification that focus on precipitation, such as the Standardised Precipitation Index (SPI), are not considered in this study. The reason is there is only an indirect relationship between precipitation and river water quality, whereas there is a direct relationship between river discharge and river water quality (e.g., dilution capacity, heat capacity, mobilisation and transport capacity of pollutants). Furthermore, meteorological droughts (defined as a prolonged lack of precipitation) are often out of phase with hydrological droughts,

particularly at the daily scale, and this phase shift is dependent on river basin location and basin size. This means that one would need to work with varying integration intervals of SPI to capture this shift, while streamflow observations implicitly include this shift. These are the key reasons we do not consider precipitation (meteorological droughts) in this study, but focus on river discharge (hydrological droughts) for the drought identification.

2.2.1 Drought events

For the identification of droughts, we used the Global Runoff Data Centre (GRDC) (2022), which is an online database that provides daily discharge data for 10,027 stations worldwide. Gauging stations were selected with discharge data available over the period 1980-2021.

In this study, we identified drought periods for each of the GRDC stations over 1980-2021 using the variable threshold level method (e.g., van Huijgevoort et al., 2012; van Loon, 2015; van Loon and Laaha, 2015). This method involves defining a threshold of discharge for each day of the year (e.g., Jan 1), below which is considered a drought. This threshold was taken as the 10th percentile, which is consistent with previous literature (Prudhomme et al., 2014; Aryal and Zhu, 2020). The identified drought regions between 1980-2021 show consistent spatial patterns worldwide (Fig. S1). This indicates that the variable threshold level method is a suitable approach of drought identification for this study.

After the drought days were identified between 1980-2021, we then linked the GRDC stations to the water quality stations. This involved two main steps. Firstly, we delineated the sub-basins for each of the GRDC stations. This was done using the HydroSHEDs flow direction map (Lehner et al., 2008) and GRDC station locations as inputs to the 'Watershed' function in ArcGIS Pro.

Secondly, we associated each of the water quality stations with a GRDC sub-basin. This enabled us to identify water quality measurements that were taken during a drought period, as identified from the GRDC stations.

2.2.2 Heatwave events

Global air temperature data were obtained from the ERA5-Land dataset (Muñoz Sabater, 2019). This dataset is a higher resolution version of land variables based on the ERA5 climate reanalysis. We use 2m air temperature data provided at 0.25x0.25 degree spatial resolution and hourly timestep over the period 1980-2021. To identify heatwave events between 1980-2021, we firstly converted the hourly air temperature data to daily maximum temperatures. Then, heatwave event was classified as when the daily maximum temperature is above the 90th percentile for at least three consecutive days, which is a common approach taken in the literature (Croitoru et al., 2016; Piticar, 2018).

2.2.3 Compound drought-heatwave events

Compound drought-heatwave events were identified between 1980-2021 by combining the approaches to identify drought events and heatwave events. Thus, a compound drought-heatwave event was classified as when the river discharge was below the 10th percentile and the daily maximum temperature is above the 90th percentile for at least three consecutive days.

2.3 Global analysis of water quality responses under droughts and heatwaves

We analysed the percentage change in each of the 16 water quality constituents (Table 1) under droughts, heatwaves and compound drought-heatwave events worldwide. This involved firstly applying the Mann-Whitney U test for statistically significant changes in water quality under these climate extremes (95% significance level). Following this, we computed the percentage change at each water quality monitoring station using Equation 1. The final reported values were the median percentage changes in each water quality constituent under droughts, heatwaves or drought-heatwaves. This study did not consider how the intensity and duration of droughts and heatwaves may affect the response in river water quality due to limited availability of river water quality measurements in some regions. Instead this analysis provides an overview of large-scale

river water quality responses under the occurrence of these hydroclimatic extremes compared to average (non-extreme) conditions.

$$\%\Delta = \frac{X_{extreme} - X_{non-extreme}}{X_{non-extreme}} \times 100 \tag{1}$$

Where $X_{extreme}$ is the median value in a water quality constituent under droughts, heatwaves or compound drought-heatwaves at a given monitoring station, $X_{non-extreme}$ is the median value in a water quality constituent under non-extreme conditions.

2.4 Hydro-climatic and environmental-geographic factors

We hypothesised that climate, land use and level of wastewater treatment affect the magnitude of responses in each water quality constituent under droughts and heatwaves. For example, we expected the type of climate to affect the magnitude of changes in river water temperature under droughts and heatwaves. Therefore, we quantified the median change in river temperature under these extreme events for each Köppen-Geiger climate zone (Geiger, 1961). In addition, we expected seasonality to also affect the responses in river water temperature under droughts and heatwaves. To test this, we analysed the seasonal correlations between river temperature and air temperature globally, using the Spearman's correlation (r_s). We expected the type of climate to also affect dissolved oxygen concentrations. Therefore, we quantified the median change in dissolved oxygen under droughts and heatwaves for each climate zone. In addition, we quantified the seasonal correlations between dissolved oxygen and air temperature. Overall, we expected dissolved oxygen concentrations to be more strongly linked to river water temperature than air temperature, and we quantified the median change in dissolved oxygen for each degree increase in river temperature globally.

Irrigation water use can be a main driver of increased salinity levels in rivers (Thorslund et al., 2022). Therefore, in this study, we hypothesised that irrigation water use could also affect the

magnitude of responses in electrical conductivity under drought events. To test this hypothesis, we compared the effects of droughts on electrical conductivity in regions without irrigation (irrigated crop area = 0) versus irrigated regions (irrigated crop area > 0) based on the MIRCA irrigated land dataset (Portmann et al., 2010). Additionally, we calculated the Spearman's correlation (r_s) between electrical conductivity and river discharge worldwide, to further understand the effects of dilution capacity on river salinity.

Nutrient pollution can be caused by point sources (e.g. wastewater treatment plants, more prevalent in urban areas) or diffuse sources (e.g. agricultural runoff, more prevalent in rural areas). We hypothesised that dissolved phosphorus (DP) and dissolved nitrogen (DN) would be prevalent in urban areas due to point source pollution and exhibit increased concentrations under drought from less dilution capacity. We tested this hypothesis by quantifying the changes in DP and DN under droughts in urban areas based on the Copernicus land use map (Buchhorn et al., 2020). In rural areas with mainly diffuse sources of pollution, we hypothesised that particulate phosphorus (PP) and particulate nitrogen (PN) would dominate and exhibit decreased concentrations under drought from less agricultural runoff. To test these hypotheses, we quantified the change in PP and PN under droughts in rural areas based on the Copernicus land use map (Buchhorn et al., 2020). In addition to analysing the dissolved and particulate forms of phosphorus and nitrogen, we also quantified the correlation between river discharge and total phosphorus (TP)/total nitrogen (TN). This provided further insight into the main sources of nutrient pollution worldwide.

The final groups of water quality constituents that were considered in this study were pathogens, pharmaceuticals and pesticides. We hypothesised that pathogen responses under droughts and heatwaves would be influenced by both land use and level of wastewater treatment. We therefore quantified the change in faecal coliform (a coarse indicator of pathogenic concentrations) under droughts and heatwaves in both urban and rural land, as well as for different levels of wastewater treatment. Faecal coliform data in urban and rural land were grouped based on the Copernicus land use map (Buchhorn et al., 2020). Level of

wastewater treatment was determined by the HydroWASTE dataset (Ehalt Macedo et al., 2022). This dataset provides the level of wastewater treatment for 58,502 treatment plants worldwide. We assigned each water quality station a level of wastewater treatment based on the most prevalent type in each sub-basin.

Pharmaceutical and pesticide concentrations were further analysed in terms of their relationships with river discharge and water temperature. We compared the responses of three pharmaceuticals (caffeine, sulfamethoxazole and diclofenac) and one pesticide (atrazine) under reduced river discharges and higher water temperatures using the Spearman's correlation, r_s .

3. Results

3.1 Responses in each water quality constituent under droughts and heatwaves

Diverse responses are shown in terms of percentage change in a wide range of water quality constituents under droughts and heatwaves (Fig. 2). The median increase in river water temperature under heatwaves is +27% compared to non-extreme conditions (for details see 3.2.1). Dissolved oxygen concentrations mainly decrease under heatwaves (median change: -17%). This is mainly due to the reduced solubility of oxygen at higher water temperatures (for details see 3.2.2). During drought events, salinity levels as indicated by electrical conductivity (EC) consistently increase (median change: +24%). This salinity increase is most likely caused by the reduced dilution capacity of rivers under droughts (3.2.3). Total suspended solids (TSS) show an overall decrease during drought conditions (median change: -52%), mainly due to less transport capacity for suspended solids during extreme low river flows. Total phosphorus (TP) shows mixed responses under droughts, with either increasing or decreasing concentrations, depending on the amount of dissolved and particulate phosphorus (for details see 3.2.4). Faecal coliform bacteria shows for most river monitoring stations a decrease in concentration resulting in a median change of -68% under droughts and heatwaves. This decrease in faecal coliform could be driven by less diffuse pollution from runoff and increased decay during extreme dry and

hot conditions (3.2.5). The concentration of caffeine in rivers increased in some locations under droughts, which could partially be explained by less dilution (for details see 3.2.6). The pesticide atrazine shows decreased concentrations under drought (median change: -56%), which is probably caused by less runoff and diffuse pollution from agricultural land.

< Figure 2 >

3.2 Influence of climate, land use and level of wastewater treatment

3.2.1 River water temperature

A strong correlation (r_s) is overall found between river water temperature and air temperature, although r_s also depends on latitude (Fig. 3a). The median correlation between river temperature and air temperature increases from 0.6 in the tropics to 0.9 in mid-to-high latitudes. This is likely due to increased seasonal variations in river temperature and air temperature at higher latitudes. The monthly anomalies in river temperature are on average greater during heatwaves compared to non-extreme conditions (Fig. 3b), and a further increase occurs during compound drought-heatwave events. The average monthly anomalies in river temperature during heatwaves and drought-heatwaves are +1.3°C and +1.6°C, respectively. The relative increase in river temperature under compound drought-heatwaves compared to heatwaves is probably due to a lower heat capacity i.e., less river discharge resulting in greater increases in water temperature under warm atmospheric conditions (van Vliet et al., 2011). The response in river temperature under compound drought-heatwaves strongly depends on climate (Fig. 3c). The median increases in river temperature under drought-heatwaves are +2.1°C (Tropical), +2.6°C (Dry), +2.2°C (Temperate), +3.7°C (Continental) and +4.5°C (Polar). Hence, climate regions with stronger seasonality seem to exhibit larger increases in river temperature under droughtheatwaves.

< Figure 3 >

3.2.2 Dissolved oxygen

Dissolved oxygen concentrations are significantly affected by river water temperature and biochemical oxygen demand (Fig. S2). The median correlation between dissolved oxygen and river water temperature worldwide is -0.6 (Fig. S2a). Increased river temperatures thus generally lead to decreased concentrations of dissolved oxygen. This relationship is further demonstrated in Fig. 4, which shows the change in dissolved oxygen concentrations for river water temperatures between 0-30°C, using a total of 622,820 measurements worldwide. The median change in dissolved oxygen for each 1°C increase in river temperature is -0.26mg/l. This is likely due to the reduced solubility of oxygen at higher river temperatures. The observed (median) dissolved oxygen concentrations are less compared to a theoretical model of dissolved oxygen saturation at sea level (Chapra et al., 2021). There are two likely reasons for this. Firstly, the model does not consider the effects of elevation on dissolved oxygen. Higher elevations cause reductions in dissolved oxygen due to the lower atmospheric pressure. Secondly, the model does not consider the biochemical oxygen demand (BOD). Higher BODs cause further reductions in dissolved oxygen due to the consumption of oxygen by microorganisms during the decomposition of organic matter. This can clearly be seen in Fig. 4 where the relationship between dissolved oxygen and river water temperature for observations with a lower BOD (i.e., < 2mg/l) is closer to the theoretical curve than with BODs above 2mg/l. The average monthly zscores in dissolved oxygen during heatwaves and compound drought-heatwaves are -0.34 and -0.37, respectively (Fig. S2b). Dissolved oxygen concentrations during heatwaves are generally lower in climate regions with higher average temperatures (Fig. S2c). For example, the average concentration of dissolved oxygen under heatwaves is 5.7mg/l in tropical regions and 9.7mg/l in polar regions.

< Figure 4 >

3.2.3 Electrical conductivity

A negative correlation is found between electrical conductivity (EC) and river discharge (Fig. 5a) in most regions (median r_s : -0.4). This is mainly due to the seasonal variations in EC and river discharge, combined with the effects of dilution. During drought events, there is a consistent increase in electrical conductivity compared to non-extreme conditions (Fig. 5b). The average monthly z-score in EC under droughts is 0.5. This is likely due to further reductions in the dilution capacity of rivers during extreme dry conditions. The response in EC under droughts is also affected by the amount of irrigation water use (Fig. 5c). In non-irrigated regions, the median EC increases from 246 μ S/cm to 283 μ S/cm under droughts (+15%). The median EC in irrigated regions under non-drought is 370 μ S/cm, which is greater than the median EC in non-irrigated regions under both non-drought and drought. This is likely due to both the accumulation of dissolved salts from irrigation return flows and increased evapoconcentration. During drought periods, the median EC in irrigated regions increases to 439 μ S/cm (+19%).

< Figure 5 >

3.2.4 Nutrients

There is an overall increase in dissolved phosphorus under droughts in urban areas, whereas the concentration of particulate phosphorus in rural areas generally decreases under droughts (Fig. 6a). The median concentration of dissolved phosphorus in urban areas is 0.043mg/l during non-drought and increases to 0.05mg/l under drought (+16%). This is possibly caused by the reduced dilution capacity of rivers during periods of extreme low flow. The median concentration of particulate phosphorus in rural areas during non-drought is 0.022mg/l and decreases to 0.016mg/l during drought events (-27%). This decrease in particulate phosphorus is likely due to reductions in agricultural runoff during extreme dry conditions. An equivalent analysis for nitrogen shows similar behaviour to phosphorus in rural areas but different responses in urban areas (Fig. S3a). The median concentration of particulate nitrogen decreases from 0.31mg/l to 0.25mg/l in rural areas under droughts (-19%). In addition, the median concentration of

dissolved nitrogen decreases from 0.36mg/l to 0.21mg/l in urban areas under droughts (-42%). Most likely, the effects of dilution capacity on dissolved nitrogen are not clearly seen in urban areas due to an overall reduction in the loads of dissolved nitrogen during periods of drought (e.g., due to less diffuse pollution from runoff).

Fig. 6b shows a histogram of the correlation, r_s , between total phosphorus and river discharge. For 60% of river basins we found a positive correlation between total phosphorus and river discharge. These are likely to be regions where there is greater particulate phosphorus than dissolved phosphorus. In contrast, a negative correlation between total phosphorus and river discharge is seen for 40% of river basins, which are likely to be regions with more dissolved phosphorus than particulate phosphorus. The relationship between total nitrogen and river discharge exhibits an overall similar behaviour compared to total phosphorus (Fig. S3b). However, there are 10% more river basins with a positive correlation between total nitrogen and river discharge compared to total phosphorus. This supports the findings in Fig. S3a, which indicated that sources of nitrogen were mainly diffuse rather than point sources in the river basins considered.

< Figure 6 >

3.2.5 Faecal coliform

The concentrations of faecal coliform in most rivers tend to decrease under droughts and heatwaves (Fig. 7), although the magnitude of the response depends on land use and level of wastewater treatment. In rural areas, the median faecal coliform concentration decreases from 130cfu/100ml to 100cfu/100ml (23% decline) under droughts and decreases to 96cfu/100ml (26% decline) under compound drought-heatwaves. This is likely due to a combination of less diffuse pollution from agricultural runoff and increased decay of faecal coliform under higher water temperatures. In urban areas, the median faecal coliform concentration under non-extreme conditions Is 260cfu/100ml, which is greater than the median faecal coliform

concentrations in rural areas under both non-extreme and extreme conditions. This is likely due to sources of faecal coliform associated with high rainfall events in urban areas, such as sewer overflows under non-extreme conditions. The median faecal coliform concentration in urban areas decreases to 190cfu/100ml (27% reduction) under droughts and 170cfu/100ml (34% reduction) under compound drought-heatwaves. Higher levels of wastewater treatment generally led to lower concentrations of faecal coliform under droughts and heatwaves. For instance, the median concentrations of faecal coliform under compound drought-heatwaves are 16% less for river basins with mainly advanced treatment compared to secondary treatment. This is likely due to a greater removal of faecal coliform from applying better treatment technologies during both non-extreme and extreme conditions.

< Figure 7 >

3.2.6 Emerging contaminants (pharmaceuticals and pesticides)

Pharmaceutical concentrations can either increase or decrease under droughts and heatwaves (Fig. 8), depending on the chemical properties of each compound. Decreases in river discharge overall lead to increased concentrations of the antibiotic sulfamethoxazole (median r_s : -0.8), as shown in Fig. 8a. This is likely due to the reduced dilution capacity of rivers under low flows and because sulfamethoxazole acts as a rather conservative (persistent) substance in surface waters. Caffeine concentrations also increase in some locations under reduced river discharges (median r_s : -0.4), as shown in Fig. 8b. This is probably because caffeine acts as a pseudo-persistent compound in the environment i.e., it degrades relatively easily but is consistently replenished (Bruton et al., 2010), and its concentrations may increase under drought due to less dilution. The painkiller diclofenac generally showed lower concentrations under higher water temperatures and air temperatures (Fig. S4), which is likely due to increased decay. Pesticide concentrations mainly show a positive correlation with river discharge (Fig. S5). The median correlation between atrazine and river discharge is 0.3. This implies that atrazine concentrations generally decrease

under periods of low river flow, which is probably due to less diffuse pollution from agricultural runoff.

< Figure 8 >

4. Discussion

This study carries out the first large-scale analysis of river water quality under droughts, heatwaves and compound events, based on analysing water quality monitoring data of 16 constituents. We find a general deterioration in river water quality under these extreme events for most rivers and water quality constituents considered. In addition, we find that climate, land use and level of wastewater treatment have a significant effect on the magnitude of responses in each water quality constituent under droughts and heatwaves. Increases in river water temperature and decreases in dissolved oxygen under droughts and heatwaves depend on the climate type, while increases in salinity (as indicated by EC) under droughts are largest in irrigated regions. Nutrient concentrations can either increase or decrease under droughts, depending on nutrient form (dissolved vs. particulate) and the dominant type of pollutant source (point vs. diffuse source). The concentrations of faecal coliform under droughts and heatwaves decrease the most in regions with higher levels of wastewater treatment. These results show that to understand the effects of droughts and heatwaves on river water quality, it is also critical to consider other factors such as climate type, land use and level of wastewater treatment.

Previous studies on river water quality under droughts and heatwaves were carried out at local or regional scales (Shehane et al., 2005; Ylla et al., 2010; Mosley et al., 2012). Our study extends the findings by analysing the large-scale effects of droughts and heatwaves on river water quality. In addition, we provide global and generic insights into the main processes which impact river water quality during droughts and heatwaves, which are otherwise more difficult to elucidate using limited data from local and regional scale analyses. Previous studies have shown increases in river water temperature under droughts and heatwaves for specific river basins,

such as the Rhine and Meuse in Europe (van Vliet and Zwolsman, 2008; Wolff and van Vliet, 2021). Our study finds statistically significant increases in river water temperature under these climate extremes for a total of 16,942 stations worldwide (p<0.05) (Table S1). Dissolved oxygen concentrations have showed varied responses under droughts and heatwaves when studied at local scales, either increasing or decreasing (Sprague, 2005; Ylla et al., 2010). Our study highlights that, at the global scale, dissolved oxygen mainly decreases under droughts and heatwaves. This is likely due to the reduced solubility of oxygen at higher water temperatures while that the level of decrease is also affected by the biochemical oxygen demand (BOD). The largest study of river salinity under droughts to date was carried out by Jones and van Vliet (2018), which found a median increase in electrical conductivity of 21% for 59 stations in the Southern United States. We find a similar magnitude in the response in electrical conductivity under droughts for 6,658 stations worldwide (with a median increase of 24%).

Local and regional-scale studies suggest that nutrient concentrations exhibit highly complex behavior under droughts (Macintosh et al., 2011; Hrdinka et al., 2012; Baurès et al., 2013).

However, in our study, we demonstrate that there are essentially two key processes affecting the response in nutrient concentrations under droughts. Either the particulate forms of nutrients decrease under droughts due to less diffuse pollution combined with lower suspended sediment or the dissolved forms of nutrients may increase due to less dilution. Some studies suggest that droughts could lead to increased concentrations of pathogens in surface waters (Levy et al., 2018; Wang et al., 2022). However, in our study, we show that faecal coliform concentrations (as coarse indicator for pathogen pollution) mainly decrease under droughts and heatwaves due to less diffuse pollution and likely combined with increased decay under higher water temperatures. A study by Wolff and van Vliet (2021) found increases in pharmaceutical concentrations for the Rhine and Meuse in Europe, but these were statistically insignificant. We find statistically significant (p<0.05) increases in caffeine concentrations under drought for 15 stations in the United States (Table S1).

Several studies discussed the potential effects of human activity and climate on water quality responses under droughts and heatwaves (Zwolsman and van Bokhoven, 2007; van Vliet and Zwolsman, 2008). In Mosley's (2015) review of 43 local and regional scale analyses, a main conclusion was that the impacts of droughts and heatwaves on water quality varied between river basins, largely due to human activity and climate. However, Mosley's (2015) review also highlighted the need for a consistent large-scale analysis to better understand the influence of other factors such as human activity and climate on water quality responses under droughts and heatwaves. Our study addresses this knowledge gap by quantifying the effects of climate, land use and level of wastewater treatment on water quality at large-scales. We find that there are strong similarities in the responses of water quality constituents between regions with the same climate, land use and level of wastewater treatment. For instance, during droughts and heatwaves, temperate climates generally exhibit larger ranges of water temperature compared to tropical regions, which is mainly due to larger ranges of air temperature. Further, increased concentrations of dissolved phosphorus under drought were more apparent in urban areas, which is likely due to the larger contribution of point sources of pollution. The response of faecal coliform to droughts and heatwaves was consistent for wastewater treatment levels, as areas with less treatment generally had greater faecal coliform concentrations. These examples provide a broader understanding of the effects of droughts and heatwaves on river water quality compared to studies carried out at local and regional scales.

This study highlights that, for some water quality constituents, there could be an increased risk of exceeding water quality standards during droughts and heatwaves. For instance, increases in river water temperature and nutrient concentrations and decreases in dissolved oxygen could lead to a greater ecological risk during these climate extremes (Chadd et al., 2017; Kim et al., 2019; Ustaoğlu et al., 2020; Jiang, 2021). In addition, increases in some pharmaceutical concentrations under drought could have negative impacts on both human and ecosystem health (Wolff and van Vliet, 2021). Increased water temperatures during droughts and heatwaves may lead to a lack of cooling water for energy production (Cook et al., 2015; Byers et

al., 2020). Increased salinity during droughts may also increase the chance of exceeding standards for irrigation water use and human/ecosystem health (Jones and van Vliet, 2018).

This study has several limitations, which are mainly associated with a lack of availability of water quality monitoring data in some regions. This is most clearly the case in central Africa and central Asia, where there is a notable lack of water quality data compared to other continents. For instance, when analysing the responses in river water temperature under drought-heatwaves for each climate type, there were 7 out of 30 climate types for which no data were available. Hence, the estimates in river water temperature responses under drought-heatwaves may be affected by this. Salinity (EC) responses were quantified for irrigated regions, however, some of the most intensely irrigated locations in the world (e.g., in India) were not included in the analysis, which affects the overall responses reported in our study. The analysis of nutrients is limited by a lack of data of dissolved and particulate phosphorus and nitrogen compared to the total forms of phosphorus and nitrogen. Faecal coliform concentrations were analysed for secondary and advanced treatment, but there was no data available for primary treatment. The sample sizes of pharmaceutical concentrations were much smaller compared to other water quality constituents, which introduces uncertainty into their response under droughts and particularly under short-term heatwave events. Although chlorophyll-a was not directly included in this study due to limited data availability, a correlation analysis shows an overall increase in chlorophyll-a concentration under higher water temperatures (median r_s: 0.5), indicating a potential risk of algal blooms during droughts and heatwaves. Finally, the response of pesticides were analysed just for one compound (atrazine) and only for the US.

Despite the lack of data in some regions, this study shows that large-scale analyses of water quality under droughts and heatwaves using in-situ monitoring data are feasible. In total, we analysed 314,046 monitoring stations and 39,033,384 daily measurements of water quality under droughts and heatwaves. This data volume suggests that methods such as machine learning could be highly beneficial to further understand the effects of droughts and heatwaves on river water quality (Desbureux et al., 2022). For instance, Long-Short Term Memory networks

(LSTMs) have already been used to study the main drivers of dissolved oxygen at local-to-continental scales (Zhi et al., 2021, Zhi et al., 2023a, Zhi et al., 2023b). In addition, random forests have been used to study the main drivers of salinisation in large rivers worldwide (Thorslund et al., 2021). Most of the existing process-based models of global surface water quality are evaluated at monthly or annual scales under average (non-extreme) conditions (e.g., Beusen et al., 2019; Jones et al., 2022). However, this study provides a strong basis for further developing and evaluating global water quality models specifically for drought and heatwave events. These models could be used to study the effects of climate change and future changes in droughts and heatwaves on global river water quality and the associated effects on ecosystems and human water uses which all strongly rely on water of suitable quality.

5. Conclusion

In this paper, we estimated the large-scale effects of droughts and heatwaves on river water quality based on analyses of 314,046 monitoring stations worldwide over the period 1980-2021. We focused on 16 water quality constituents covering a wide range of physical, chemical and biological characteristics of water quality. Further, we quantified the effects of climate, land use and level of wastewater treatment on the responses in each water quality constituent under droughts and heatwaves. We found a general deterioration in river water quality under droughts and heatwaves for most of the water quality constituents considered (e.g., river water temperature, salinity, dissolved oxygen). However, some water quality constituents showed a slight improvement with lower concentrations under these hydroclimatic extremes (e.g., faecal coliform, particulate nutrients). In addition, we found that climate type, land use and level of wastewater treatment have substantial effects on the magnitude of response in each water quality constituent under droughts and heatwaves. With climate change expected to increase the frequency and severity of droughts and heatwaves in many regions (Zscheischler et al., 2018; Mukherjee and Mishra, 2021), a greater deterioration in river water quality might occur in the future due to these climate extremes. In addition, the impact of socio-economic development on land use and level of wastewater treatment could be another driver affecting water quality

responses under future droughts and heatwaves. To ensure a sufficient water quality for human and ecosystem needs in the future, it might be critical to design water quality standards and provide permits for effluents that consider the effects of extreme droughts and heatwaves.

6. Code and data availability

The python scripts used to process each of the eight water quality databases are provided at https://doi.org/10.5281/zenodo.7558906. Here, we also provide the water quality datasets which can be distributed publicly.

7. Author contribution

The research was designed by DJG, MFPB and MTHvV. The data processing and analysis was performed by DJG. All authors contributed to and approved the manuscript.

8. Competing interests

The authors declare no conflict of interest.

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Figures and tables (below)

	GEMStat	GLORICH	GOC	WQP	Waterbase	DWS	GOA	NIWA	No. of	No. of
	(Global)	(Global)	(Canada)	(US)	(Europe)	(S.Africa)	(Australia)	(New	values	stations
								Zealand)		
Water temperature	*	√	✓	√	✓	*	✓	V	13,076,739	267,167
Dissolved oxygen	~	√	√	√	✓	*	-	*	4,034,640	184,917
Biochemical oxygen demand	/	-	✓	✓	✓	*	-	V	906,142	40,219
Electrical conductivity	~	~	~	~	~	*	~	1	11,159,003	227,858
Total suspended solids	~	✓	✓	✓	✓	✓	-		2,834,980	131,393
Total phosphorus	/	√	√	✓	*	~	-	~	3,233,541	121,037
Dissolved phosphorus	~	~	~	✓	-	-	4	-	590,984	24,649
Particulate phosphorus	~	✓	~	✓	-	-	·	-	51,367	1,362
Total nitrogen	~	✓	~	√	√	~	-	~	1,004,924	36,960
Dissolved nitrogen	~	√	~	~	-	-		-	170,058	6,180
Particulate nitrogen	~	√	~	~		-	-	-	46,602	1,386
Faecal coliform	*	-	✓	✓	: (~	-	-	1,474,786	63,950
Caffeine	-	-	-	*	1	-	-	-	20,892	2,999
Sulfamethoxazole	-	-	-	Y	~	-	-	-	4,718	1,048
Diclofenac	-	-	-	V	~	-	-	-	18,095	1,461
Atrazine	/	-	~	~	√	~	-	-	405,913	17,612
No. of values	2,366,838	2,376,407	191,542	20,542,115	1,865,428	1,014,126	10,521,196	155,732	39,033,384	-
No. of stations	6,964	15,705	223	270,716	15,235	3,697	1,429	77	-	314,046
										unique

Table 1. Number of daily observations and monitoring stations for each water quality constituent and database.

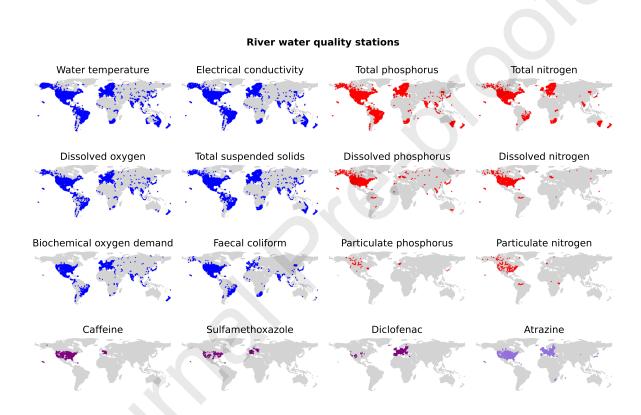


Figure 1. Locations of monitoring stations per water quality constituent. Blue: general constituents. Red: nutrients. Dark purple: pharmaceuticals. Light purple: pesticides.

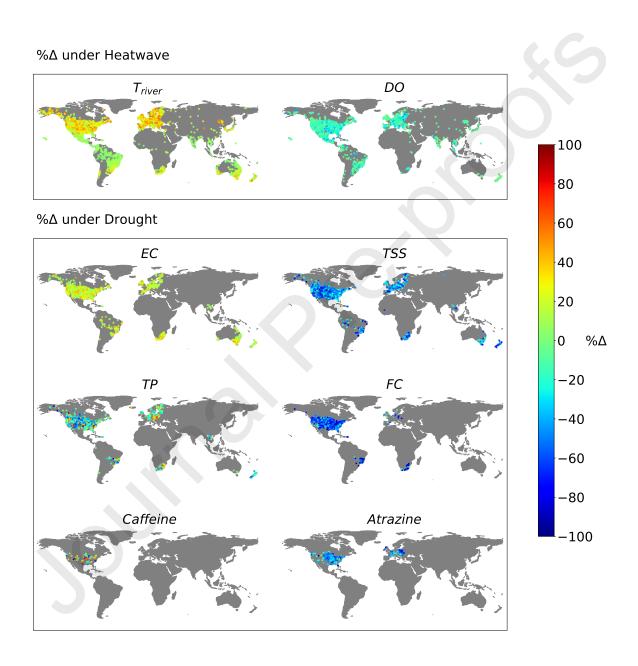


Figure 2. Percentage change (% Δ) under droughts and heatwaves: River water temperature (T_{river}); Dissolved oxygen (DO); Electrical conductivity (EC); Total suspended solids (TSS); Total phosphorus (TP); Faecal coliform (FC); Caffeine; Atrazine.

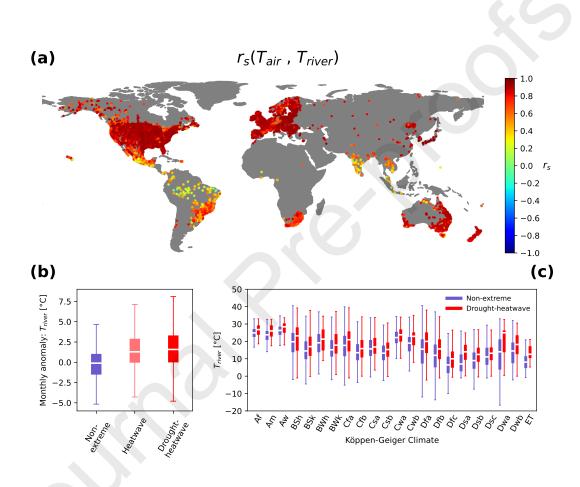
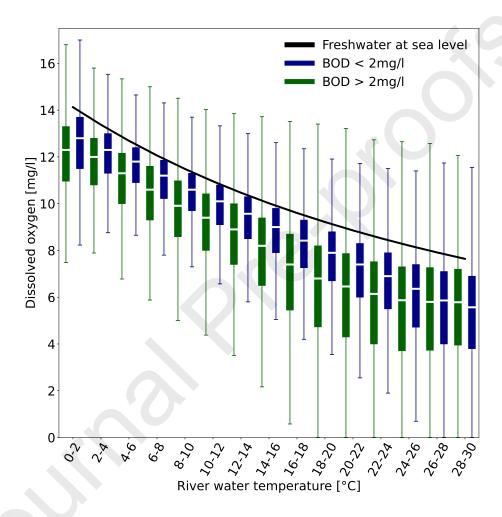


Figure 3. (a) Spearman's correlation (r_s) between river water temperature and air temperature (b) Monthly anomalies of river water temperature for non-extreme, heatwave and drought-heatwave conditions (c) Response in river water temperature under drought-heatwaves for each Köppen-Geiger climate zone.



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Figure 4. Dissolved oxygen concentrations versus river water temperature for BOD < 2mg/l (blue) and BOD > 2mg/l (green) compared against theoretical relationship for freshwater at sea level (Chapra et al., 2021).

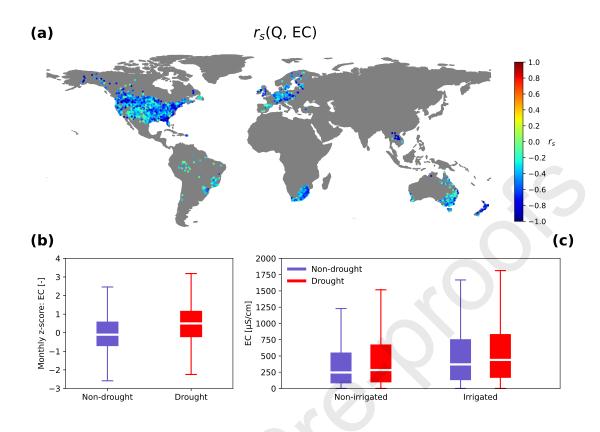


Figure 5. (a) Spearman's correlation (r_s) between electrical conductivity and river discharge (b) Monthly z-scores of electrical conductivity for non-drought and drought (c) Response in electrical conductivity under drought for non-irrigated and irrigated land.

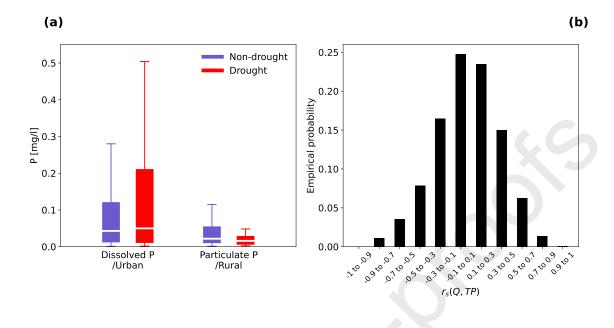


Figure 6. (a) Response in dissolved phosphorus under drought in urban areas and response in particulate phosphorus under drought in rural areas (b) Histogram of the correlation between total phosphorus and river discharge.

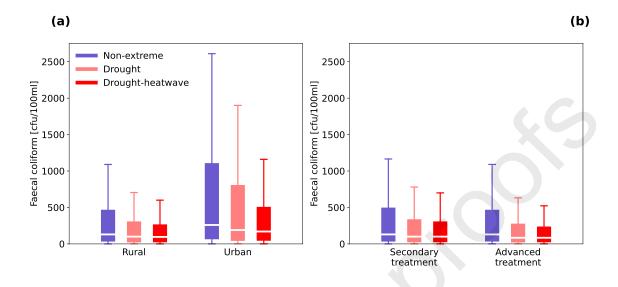


Figure 7. Response in faecal coliform under drought and compound drought-heatwave for different types of (a) land use and (b) wastewater treatment.

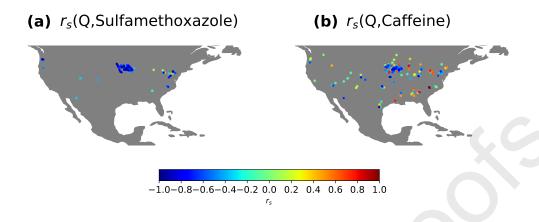


Figure 8. Spearman's correlation (r_s) between (a) sulfamethoxazole and river discharge (b) caffeine and river discharge.

SUPPLEMENTARY DATA

Figure S1 shows the identified regions of hydrological drought at the beginning of each year (Jan 1) over the research period (1980-2021). In this study, drought regions were identified for each day of the year and produced consistent spatial patterns over the period 1980-2021.

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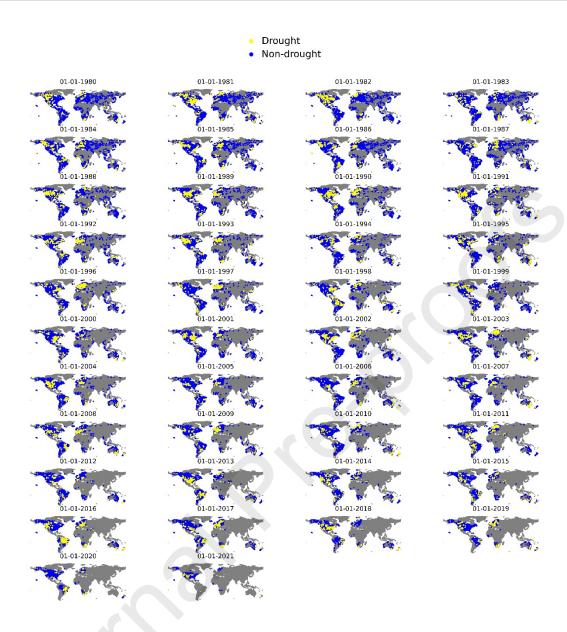


Figure S1. Identified regions of hydrological drought at the beginning of each year over the research period (1980-2021).

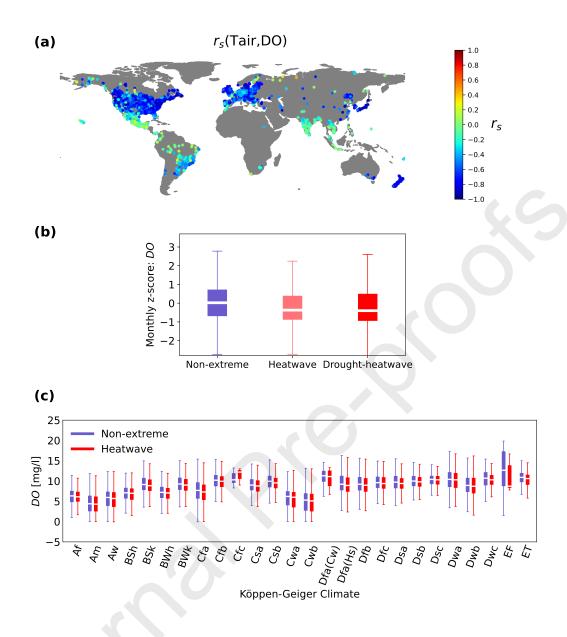


Figure S2. (a) Spearman's correlation (r_s) between dissolved oxygen and air temperature (b) Monthly anomalies of dissolved oxygen for non-extreme, heatwave and drought-heatwave conditions (c) Response in dissolved oxygen under heatwaves for each Köppen-Geiger climate zone.

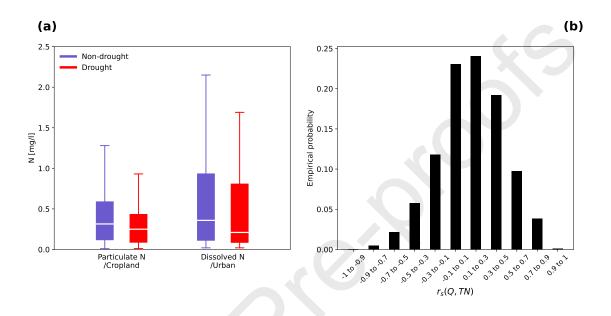


Figure S3. (a) Response in particulate nitrogen under drought in rural areas and response in dissolved nitrogen under drought in urban areas (b) Histogram of the correlation between total nitrogen and river discharge.

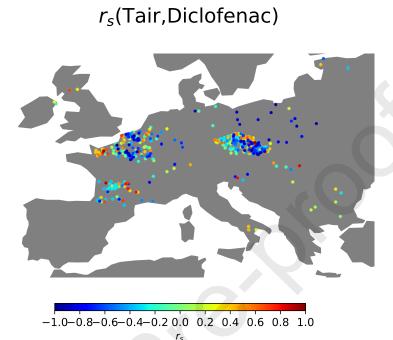


Figure S4. Spearman's correlation (r_s) between diclofenac and air temperature.

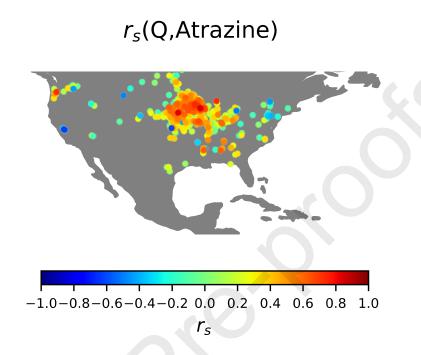


Figure S5. Spearman's correlation (r_s) between atrazine and river discharge.

	Number of stations:	Number of stations:
	n_{extreme} >5 and % Δ (p<0.05)	n _{extreme} >5 and %Δ (p>0.05)
River water temperature	16,942	27,900
Dissolved oxygen	4,798	22,756
Electrical conductivity	6,658	8,449
Total suspended solids	2,070	4,945
Total phosphorus	1,895	5,584
Faecal coliform	1,225	3,756
Atrazine	201	720
	Number of stations:	Number of stations:
	%Δ (p<0.05)	%Δ (p>0.05)
Caffeine	15	236

Table S1. Number of stations with statistically significant (p<0.05) changes in water quality under droughts and heatwaves per constituent based on the Mann-Whitney U test.

Credit author statement

The research was designed by DJG, MFPB and MTHvV. The data processing and analysis was performed by DJG. All authors contributed to and approved the manuscript.

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Highlights (Revision 2)

- River water quality tends to deteriorate during droughts and heatwaves
- Water quality data from 314,046 monitoring stations are analysed
- Climate type, land use and wastewater treatment affect water quality responses under extremes