Science of the Total Environment 843 (2022) 157014

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Is water quality in British rivers "better than at any time since the end of the Industrial Revolution"?

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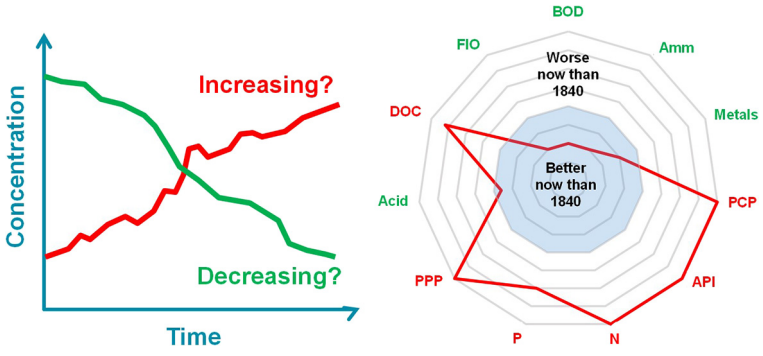
HIGHLIGHTS

- Water quality in British rivers has changed substantially since the industrial revolution.
- Between 1760 and 1940 point-source pressures are likely to have increased.
- From 1940 pressures from nutrients and pesticides have increased in many areas.
- The current picture is mixed: urban quality has improved, rural quality has declined.
- Diffuse-source pollution and novel pollutants remain as significant water quality threats.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: José Virgílio Cruz

Keywords:
Water quality
Trends
Sewage
BOD
Ammonia
Metals
Nutrients
Nitrogen
Phosphorus
Pesticides

ABSTRACT

We explore the oft-repeated claim that river water quality in Great Britain is "better now than at any time since the Industrial Revolution". We review available data and ancillary evidence for seven different categories of water pollutants: (i) biochemical oxygen demand (BOD) and ammonia; (ii) heavy metals; (iii) sewage-associated organic pollutants (including hormone-like substances, personal care product and pharmaceutical compounds); (iv) macronutrients (nitrogen and phosphorus); (v) pesticides; (vi) acid deposition and (vii) other variables, including natural organic matter and pathogenic micro-organisms. With a few exceptions, observed data are scarce before 1970. However, we can speculate about some of the major water quality pressures which have existed before that. Point-source pollutants are likely to have increased with population growth, increased connection rates to sewerage and industrialisation, although the increased provision of wastewater treatment during the 20th century will have mitigated this to some extent. From 1940 to the 1990s, pressures from nutrients and pesticides associated with agricultural intensification have increased in many areas. In parallel, there was an increase in synthetic organic compounds with a "down-the-drain" disposal

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http://dx.doi.org/10.1016/j.scitotenv.2022.157014
Received 20 February 2022; Received in revised form 15 June 2022; Accepted 23 June 2022
Available online 27 June 2022

Acidification
DOC
Faecal indicator organisms

pathway. The 1990s saw general reductions in mean concentrations of metals, BOD and ammonia (driven by the EU Urban Waste Water Treatment Directive), a levelling out of nitrate concentrations (driven by the EU Nitrate Directive), a decrease in phosphate loads from both point-and diffuse-sources and some recovery from catchment acidification. The current picture is mixed: water quality in many rivers downstream of urban centres has improved in sanitary terms but not with respect to emerging contaminants, while river quality in catchments with intensive agriculture is likely to remain worse now than before the 1960s. Water quality is still unacceptably poor in some water bodies. This is often a consequence of multiple stressors which need to be better-identified and prioritised to enable continued recovery.

Contents

1. Introduction

Water quality is a general term used to describe a wide range of physical, chemical and biological characteristics. These include its colour and taste as well as the concentration of suspended solids, temperature, pH, alkalinity, the concentrations of naturally occurring nutrients, organic matter and mineral ions, concentrations of potentially toxic metals and synthetic organic compounds, dissolved oxygen concentration and the presence of faecally-derived microbes, including human and animal pathogens. Water quality is often judged by reference to standards which are usually based on "fitness for purpose" criteria. Different standards may apply for water bodies used for drinking water supply, recreation, irrigation and industry. Similarly, different standards have been established as thresholds for ecological harm in different water body types, depending on the sensitivity of the natural system to the stressor of interest.

Water quality is controlled naturally by the amount and origin of precipitation and the contact between water and the vegetation, soil and rock through which it travels along hydrological pathways to aquifers, streams, rivers and lakes. It can also be affected by evapotranspiration, by temperature, by its contact with the stream bed and banks, by interactions in the hyporheic zone, by mixing with water from areas with different characteristics and by the actions of organisms such as microbes.

The quality of surface and groundwater bodies can be modified by a number of anthropogenic factors. These include the accidental and intentional emission of industrial and municipal waste and wastewater (which can contain a range of pollutants), diffuse-source transfers of pollutants from agricultural and urban areas and atmospheric deposition of airborne pollutants. These anthropogenic influences vary in space and time. In the short term, they vary with weather patterns, such as rainfall and evapotranspiration which control the seasonality of soil water deficit, runoff magnitude and pathways and river discharge (which provides dilution and influences water temperature). In the medium and long term, they vary with inter alia population size, the type and intensity of industrial activity, the provision and type of wastewater treatment, the nature and scale of urban development, sewer designs (e.g. combined versus separation of storm runoff from human sewage) and with prevailing agricultural or forestry practices. They may also be affected by engineered influences on hydrology such as river and groundwater abstractions, impoundments, irrigation and drainage.

Spatial and temporal information about the state of water quality and associated ecological condition is derived, principally, from monitoring. This can sometimes be achieved using high-frequency in situ sensors (e.g. for pH, turbidity, conductivity and dissolved oxygen concentrations). However, for most chemical and microbial water quality variables, water samples (or samples of aquatic indicator fauna such as macroinvertebrates) need to be collected and analysed in the laboratory. This is often expensive and time-consuming, which restricts the frequency at which samples are collected in most locations. Furthermore, although water quality is routinely monitored in many parts of the world, most records do not go back more than about 50 years and may be affected by changes in frequency, timings and (occasionally) analytical methods or analytical error (e.g. Guigues et al., 2016). There are some exceptions (e.g. Howden et al., 2010) but, for the most part, water quality data in Great Britain are limited prior to the 1970s. It should also be noted that samples are never analysed for all possible water quality characteristics and the frequency of data for some variables can be low or completely absent. These include "emerging" contaminants such as human or veterinary pharmaceuticals and microplastics (Windsor et al., 2019; Perkins et al., 2021). However improvements in analytical methods do now allow for more (qualitative) "non-target" detections and have lower quantitative limits of detections.

Prior to the Industrial Revolution, water quality in the Great Britain is likely to have varied relatively little over time except, perhaps, as a consequence of local mining activities, major episodes of deforestation and the growth of some cities, notably London. However, with the increase in urbanisation and associated population growth which occurred from approximately 1760 onwards, surface waters are likely to have become increasingly affected by industrial and municipal wastewater emissions. This resulted in a major documented deterioration of water quality within and downstream of cities and industrial centres (e.g. Ashton, 2017). Subsequent introduction of innovations such as wastewater treatment have undoubtedly made significant improvements to point-source pollution in the 20th century. However, these have been challenged by marked growth in population and by the introduction of a large range of novel organic compounds with "down-the-drain" disposal routes (e.g. the chemical ingredients in detergents and pharmaceutical products). The latter half of the 20th century also witnessed a major intensification of agriculture which resulted in increased losses of nutrients (Howden et al., 2010, 2011a, 2011b) and the transfer of novel organic toxicants used as pesticides to surface and ground waters.

In recent years, statements from ministers and senior government officials have repeatedly stated that water quality in England's rivers is now 'better than at any time since the start of the Industrial Revolution'. Variations of this claim (usually either referring to 'water quality' or 'cleanliness'), have been repeated by water companies, with respect to rivers as a whole, rivers within particular regions, or specific rivers. Such statements have attracted widespread media coverage and might have led to an impression that poor water quality was no longer a major challenge. Examples include:

- Water quality…now "better than at any time since the Industrial Revolution"[1] Environment Agency statement in 2019 BBC article
- '…our rivers and beaches are now cleaner than they have been at any time since the Industrial Revolution.' Prime Minister Theresa May's speech on the environment: 11 January 2018[2]
- Our water quality is better than at any time since the Industrial Revolution: 2019 letter to *The Financial Times* by Sir James Bevan, Chief Executive, Environment Agency[3]
- Rivers and estuaries in England and Wales are probably cleaner now than at any time since the dawn of the Industrial Revolution[4]: 2001 *Independent* article
- 'Environment Agency says [rivers] are now cleaner than at any time since before the Industrial Revolution': 2011 *Telegraph* opinion piece[5]
- 'Water quality in our rivers is now better than at any time since the start of the Industrial Revolution': 2019 letter to The Times from Emma Boyd, Chair of the Environment Agency[6]
- "Water UK, the trade association for the big water companies, said: 'Water quality in our rivers is now better than at any time since the start of the Industrial Revolution…'": 2019 *The Sunday Times*[7]

In this paper, we examine the degree to which these statements are supported by the available evidence. Specifically, we look at the key factors that govern spatial and temporal patterns in river water quality and review available data for a number of important water quality variables. Although it is not our principal focus, we also make some reference to the ecological impacts of water quality stressors, because the protection of aquatic wildlife is an important goal. Furthermore, healthy aquatic ecosystems deliver a range of important ecosystem services, including improved water quality (Brown et al., 2018), the maintenance of fisheries (Bergstrom and Loomis, 2017) and enhanced recreational value (Aberg and Tapsell, 2013). It is often difficult to link specific pollutant exposure to stress in individual organisms, particularly when pollutants are present as components of complex mixtures (Posthuma et al., 2019). However, the response of aquatic wildlife at the population level can be a useful indication of the integrated effects of exposure to multiple stressors including (but not restricted to) chemical toxicants, excess nutrients and depressed dissolved oxygen concentration. In fact, the attainment of "good" ecological status – incorporating water quality components – is a central goal of the European Water Framework Directive (WFD: Directive 2000/60/EC – now transposed via the Water Environment [England and Wales] Regulations 2017) that has underpinned water policy in the United Kingdom since 2000. That said, it should be noted that the WFD employs a "one out, all out" classification system which triggers overall failure for a water body if one of the many criteria used to characterise "good" ecological or chemical status is not met.

We concentrate here principally on the water quality of rivers upstream of the tidal limit in England and Wales (where water quality impacts have probably been greater than in other parts of the UK and where appropriate data are more readily available). However, we also make some limited reference to lakes and groundwater, where relevant (e.g. where there is a close connection between groundwater and surface water, such as in chalk streams) and, briefly, to coastal bathing waters in the context of microbiological parameters which are infrequently monitored in rivers. Over the study period, different rivers have been exposed to different pressures (used in the sense employed in the DPSIR framework: Drivers, Pressures, State, Impact and Response; EEA, 1998) reflecting the spatial and temporal patterns of industrial and agricultural development. We, therefore, expect to see variations in trends for different variables, with simultaneous improvement for some variables and deterioration for others. Where possible, we differentiate between trends in rivers affected by urban influences and those with predominantly rural land uses. However, it should be noted that, as a result of more frequent monitoring, our understanding of trends in water quality is often better for river reaches downstream of urban centres than it is elsewhere.

Our nominal starting point is 1760, the start of a decade in which steam power started to be used industrially and approximately the start of a marked acceleration in the rate of population increase in England (Fiaschi and Fioroni, 2019). However, we consider the end of the Industrial Revolution (ca. 1840, when adoption of early innovations slowed) as a key reference point for characterising the period – whilst recognising that water quality pressures on rivers undoubtedly worsened after this point in many catchments as population and industrial growth continued. We consider a wide range of variables in the context of defined water quality standards which are usually purpose-specific (i.e. they will vary for different uses such as swimming, fishing or drinking water supply, and for achieving "Good Ecological Status"). The overarching question we have tried to answer is whether water quality in the rivers of England and Wales is indeed better than it has been at any time since the end of the Industrial Revolution. Very little systematic monitoring of water quality was performed prior to the 1980s. However, monitoring records are available for more recent decades. As a supplementary question, we also examine these data to assess how current water quality compares to historical trends.

2. Approach

We group pollutants into seven broad categories, reflecting similarities in sources and ecotoxicological mode of action. Many pollutants have multiple sources, but these can be broadly split into point sources, associated with a single point of entry to a water body (such as a sewer or factory discharge), and diffuse sources, where pollutants originate from a multitude of

[1] https://www.bbc.co.uk/news/uk-england-49131405.
[2] https://www.gov.uk/government/speeches/prime-ministers-speech-on-the-environment-11-january-2017.
[3] https://www.ft.com/content/b35d35bc-8dd4-11e9-a1c1-51bf8f989972.
[4] https://www.independent.co.uk/environment/rivers-cleaner-than-they-have-been-for-200-years-9147298.html.
[5] https://www.telegraph.co.uk/comment/telegraph-view/8729334/The-flow-of-history.html.
[6] https://www.gov.uk/government/news/letter-to-the-times-from-emma-howard-boyd-chair-of-environment-agency.
[7] https://www.thetimes.co.uk/article/wild-swimmers-driven-from-rivers-by-sewage-spills-wmmd5bmz6.

locations across the landscape and travel to water bodies via runoff along a range of hydrological pathways. The seven categories considered are:

(1) "Sanitary" determinands (BOD and ammonia) which principally come from point sources (but can also arise from rural semi-diffuse sources such as septic tanks)
(2) Heavy metals which come from a mix of point and urban-diffuse sources, along with some natural background sources and mining operations
(3) Specific sewage-associated organic compounds (e.g. the ingredients of personal care and pharmaceutical products) which come from point sources but may also have some rural diffuse sources
(4) Macronutrients (nitrogen and phosphorus) which have a mix of point and diffuse sources
(5) Pesticides, which are commonly a diffuse-source pollution problem but can also have point sources of entry
(6) Acid deposition and catchment acidification which originates from atmospheric pollution
(7) Other water quality indicators (including indicators of faecal pollution, such as the bacterium *Escherichia coli* and natural organic matter) which have a variety of different origins

These categories of pollutant were selected following discussion between authors, based on our collective awareness of current water quality issues in Great Britain, our understanding of historical trends and drivers, and the availability of data. We acknowledge that there are other water quality issues which we have not captured here (e.g. the increased interest in microplastics: Eerkes-Medrano et al., 2015, and changes in fine sediment concentrations due to enhanced soil erosion: Collins and Walling, 2007 — which can often be associated with other contaminants). However, we posit that the seven categories presented are sufficiently comprehensive to allow the main question to be answered objectively. The first three categories are principally associated with point sources, whereas nutrients and pesticides are often considered to be diffuse-source in nature. However, many pollutants have multiple sources and the dominance of one source type or another will vary seasonally, between catchments and even within the same catchment depending on location.

We discuss the significance of the pollutants in each category for ecological and human health and present broad spatial and temporal trends using a combination of the available time series data and, where data are sparse or absent, other surrogate indicators of likely exposure and impact. Observed data for each water quality variable of interest were sourced from public domain data sets. Trend data on sanitary determinands, metals and phosphate were obtained from the Harmonised Monitoring Scheme (HMS: https://data.gov.uk/dataset/b17a2efa-bdd6-4740-8030-fb87f7f2bcff/historic-uk-water-quality-sampling-harmonised-monitoring-scheme-detailed-data). Data on pesticide usage were obtained from the Pesticide Usage Survey (https://secure.fera.defra.gov.uk/pusstats/index.cfm). Data on atmospheric sulphur dioxide emissions were obtained from the UK Department for Environment, Food and Rural Affairs: DEFRA (https://www.gov.uk/government/statistics/emissions-of-air-pollutants/emissions-of-air-pollutants-in-the-uk-sulphur-dioxide-so2). We also refer to (and occasionally reproduce) data from the published literature. The provenance of these published data are described in more detail in the cited references. With a few exceptions, widespread monitoring of water quality in surface waters was not conducted before the mid-20th century (and in many locations before the 1980's). However, despite the paucity of data, it is still possible to speculate on the likely water quality pressures prior to this using published and anecdotal information about human population size, industrial activity, sewerage construction, wastewater treatment provision and agricultural practices. That said, we try to make a clear distinction between statements which are speculative and those which are based on data and we put most emphasis on reporting observed trends. We also comment on some of the uncertainties which exist in the measured data (e.g. due to low spatial and temporal sampling frequencies).

3. Results and discussion

3.1. "Sanitary determinands": BOD and ammonia

Although poor water quality undoubtedly presented local issues throughout history, it became increasingly more acute around growing and industrialising cities during the Industrial Revolution — primarily as a consequence of the discharge of untreated domestic wastewater and emissions from industrial processing (Wheeler, 1979; Burton, 2003). Domestic sewage contains very high concentrations of degradable organic matter which can result in dissolved oxygen depletion of receiving waters, as micro-organisms in the water column and in the sediment break down the constituent organic compounds (e.g. Gray, 1999). It also contains high concentrations of ammoniacal nitrogen (ammonium and ammonia). Unionised ammonia is toxic to fish and other aquatic organisms (Alabaster and Lloyd, 1980). The increased emission of untreated sewage famously entered the public and political consciousness after the "Great Stink" of 1858 when warm summer weather exacerbated odours in the River Thames in central London (Halliday, 2004; Halliday, 2009; Ashton, 2017). This triggered a major refurbishment of the sewer system in London under the direction of Joseph Bazalgette (including the construction of large purpose-built brick-lined interceptor sewers to transport wastewater to the Thames estuary, downstream of the city, as well as culverting existing watercourses). This also occurred in other cities, such as Liverpool, where new sewer construction began in 1848, preceding developments in London (Halliday, 2004). However, accompanying wastewater treatment was not routinely employed until later, so untreated sewage was still primarily discharged into rivers or coastal waters. As urban populations grew, so did the discharge of wastewater, particularly after the introduction of the water closet in the late 18th century which became widely used by the mid- to late-19th century (Halliday, 2004; Naden et al., 2016).

Wastewater treatment plants (which substantially reduce both organic pollutant loads and ammonia in wastewater effluent) were first introduced in the latter part of the 19th century (Halliday, 2004) but did not become widespread until after 1912 when the eighth report of the Royal Commission on Sewage Disposal introduced standards for sewage discharges to rivers and tidal waters; specified concentrations of constituents that should not be exceeded in sewage discharges to rivers and tidal waters, and adopted the 5-day BOD test as the definitive measure of organic pollution. It is likely, therefore, that water quality downstream of major urban centres in the late 19th and early 20th centuries was very seriously impacted by wastewater, as their populations grew. To provide some perspective, the population of England and Wales was just 6.1 M in 1750 and grew to 17.9 M by 1851 (Anderson, 1988). By the 1901 census it was 32.5 M (National Archives, 2020), growing to 49.1 M by 1971 and to 59.1 M by 2018 (ONS, 2019). Typical water use per capita in Great Britain is currently approximately 150 L cap^{-1} d^{-1}, so 59.1 M people produce about 8856 ML wastewater d^{-1}.

In the latter half of the 20th century, wastewater treatment plants became much more widely introduced, serving small towns and villages as well as major urban centres. This is likely to have resulted in a gradual reduction of water quality issues related to untreated sewage (high BOD, low DO, high ammonia and faecal pollution, including potential pathogens), particularly as treatment efficiencies for the prevailing technologies also improved (e.g. as the slightly more effective activated sludge process started to replace trickling filters in larger plants). This was, in part, driven by better regulation for point source emissions (Johnstone and Horan, 1996). Of particular relevance is the implementation of the European Urban Waste Water Treatment Directive (UWWTD: 91/271/ED) which came into effect in 1991 (with compliance by 1998) which required (inter alia) secondary wastewater treatment for all settlements of >2000 population equivalents (p.e.) and more advanced treatment for towns

with >10,000 population equivalents in designated sensitive areas. The UWWTD resulted in a step change in wastewater treatment provision and an associated drop in point-source pollution. This is illustrated in Fig. 1 which shows BOD and total ammoniacal N concentrations at Moreden Bridge (downstream of Swindon on the River Ray) from 1976 to 2016, along with an index of ecological quality based on macroinvertebrate monitoring (the ASPT or Average Score Per Taxon is an index for which pollution-tolerant taxa have a low score and pollution-intolerant taxa a high score). There is a clear decrease in concentrations of both BOD and ammonia following upgrading of a failing trickling filter works with an activated sludge plant in 1991 (stimulated by a combination of the UWWTD and the privatisation of the water industry in England and Wales) which appears to be associated with an improvement in ASPT (Johnson et al., 2019).

This general positive trend in aquatic invertebrates following previous declines is evident in many locations (Vaughan and Ormerod, 2012). Fig. 2 presents a relative index of average annual occupancy for six invertebrate taxa with an aquatic life stage: Heteroptera, Trichoptera, Odonata, Emphemeropta, freshwater molluscs and Plecoptera, from 1970 to 2015 (from Outhwaite et al., 2020). The index was derived using recoded presence data (>24 M data points) from across the UK in records supplied by 29 national recording schemes or societies, which were processed using Bayesian occupancy modelling (Outhwaite et al., 2019). These data suggest that occupancy for five of the six taxa was higher in 2015 than in 1970. They also clearly show a trend reversal in the abundance of four invertebrate groups (Heteroptera, Trichoptera, Emphemeropta and Plecoptera) which is coincident with the implementation of the UWWTD. Data for Odonata also indicate a reversal of a downward trend but starting in the 1980s. For the other group, aquatic molluscs, the clear decline in occupancy levelled out between 1990 and 2008 but has subsequently continued. There are also ongoing problems with eel and migratory salmonid populations in many rivers. However, increasing recreational fish catches since the 1990s (Robinson et al., 2003) suggest that other fish species appear to be recovering, particularly compared to the 1950s and 60s when many river reaches in Britain were devoid of fish (Hynes, 1960). In parallel, many of the fish-eating bird populations closely associated with rivers, including heron, kingfisher and great crested grebe have expanded in recent decades (Massimino et al., 2019).

This pattern is illustrated more generally in mean annual data for the Harmonised Monitoring Scheme (HMS) sites across the whole of Great Britain. These sites are all located upstream of the tidal limit and close to gauging stations with a mean annual discharge of >2 m^3 s^{-1}, in order to estimate pollutant fluxes to the marine environment (Brown et al., 1982). The data, thus, represent an integrated water quality response to the many potential influences (i.e. diffuse- and point-sources) which exist in their contributing catchments. Fig. 3 shows a pronounced decrease in arithmetic mean ammoniacal nitrogen and BOD concentrations (and their variability) at these sites between 1980 and 2013 (the last year of the HMS). However, despite these clear improvements, treated and untreated sewage discharges still have substantial impacts on individual river reaches, at least periodically (e.g. Comber et al., 2019).

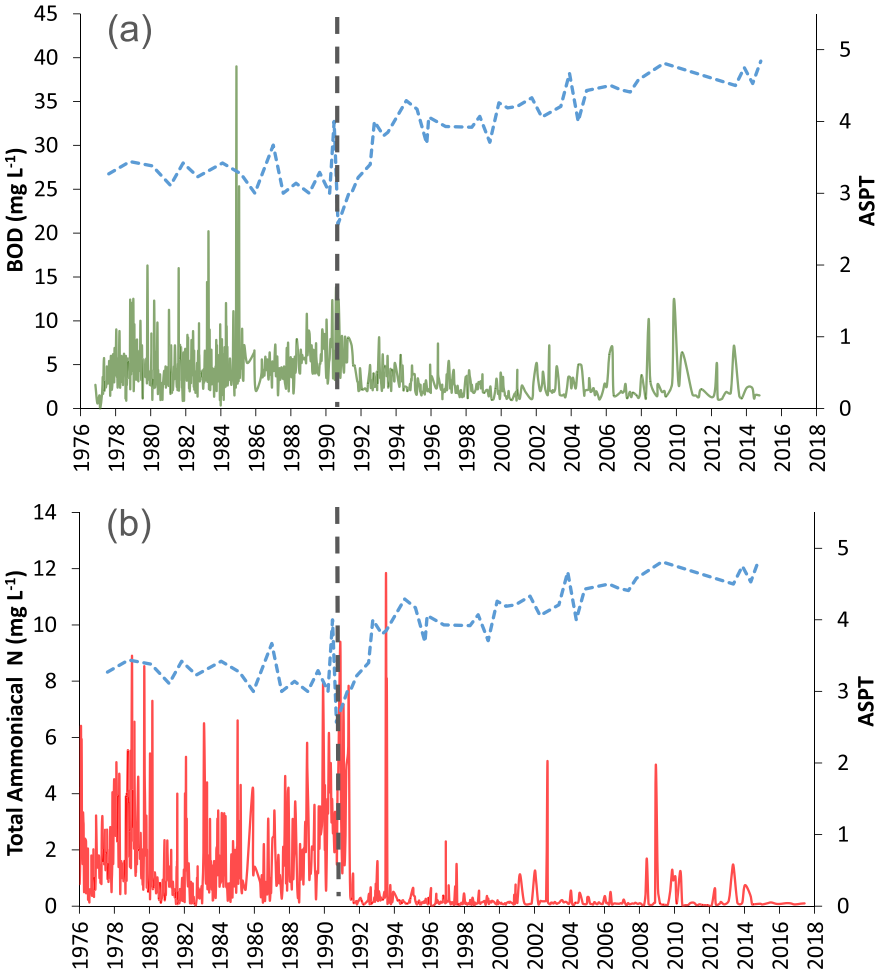

Fig. 1. (a) BOD and (b) total ammoniacal nitrogen (NH_4^+-N + NH_3-N) concentrations in the River Ray downstream of Moreden Bridge (Swindon) between 1976 and 2016. Change in the presence of pollution intolerant invertebrates as measured by ASPT (Average Score Per Taxon — see text) at the same site (blue dashed line, right vertical axis) is shown on each plot. Thick dashed vertical lines show approximate timing of WWTP upgrade (after Johnson et al., 2019).

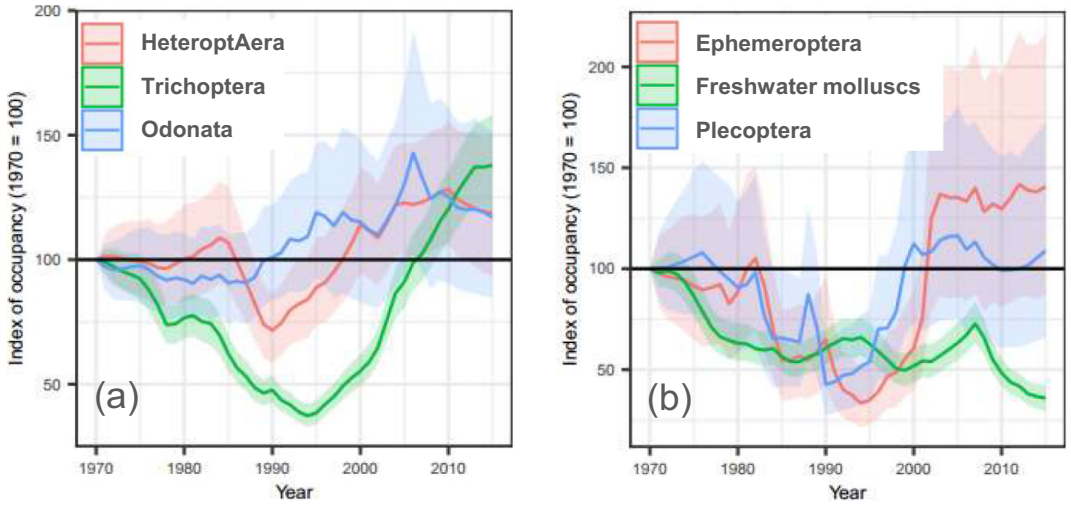

Fig. 2. Relative change in occupancy index for six invertebrate groups with an aquatic life stage between 1970 and 2015. Solid lines show the geometric mean occupancy. Shaded areas show the 95 % credible intervals of the posterior distribution of the geometric mean. The reversal in the downward trend for four groups coincides with the UWWTD implementation in 1991 with compliance required by 1998 (adapted from Outhwaite et al., 2020). The upward trend for Odonata (dragonflies) started earlier and the trend for freshwater molluscs shows no response to the UWWTD.

All sewer systems and wastewater treatment plants (WWTPs) have a limited carrying capacity. This can be overwhelmed if flow exceeds a certain level under intense rainfall, or if sewers are subject to groundwater ingress (which can cause problems when rainfall is unexceptional). This is common when wastewater is combined with stormwater (drainage from roads and buildings) in the same conduit (so-called combined sewers). In these systems, sewer discharge can exceed carrying capacity under wet weather conditions and cannot be fully treated by the WWTP, leading to the filling of storm tanks and the direct discharge of untreated wastewater to surface waters — known as a Combined Sewer Overflow (CSO). This practice was justified historically based on the assumption that they usually coincide with high discharge in the receiving water body and, hence, the impact of pollution is minimised by dilution. However, CSOs can have unacceptable impacts on water quality when the dilution in the receiving water is not concomitantly high. This could lead to dissolved oxygen depression and increased concentrations of ammonium, pharmaceutical compounds and illicit narcotics (Munro et al., 2019), which may have ecological impacts (Seager and Abrahams, 1990; Matthiessen and Law, 2002). It is also likely that CSOs will introduce elevated microbial pathogens into rivers, represented by Faecal Indicator Organisms (FIOs) (Ellis, 2004). This is likely to represent a risk to human health, especially given the recent increase in the use of rivers for recreation and particularly for "wild swimming" (Macfarlane, 2008). There has, therefore, been an effort in recent decades to reduce the frequency and volume of CSOs by building separate sewers, along with the introduction of sustainable urban drainage systems (e.g. Ellis, 2013) and by capturing untreated water in large storm tanks during high flows (e.g. the Thames Tideway Super Sewer Project: DEFRA, 2015). Notwithstanding these efforts, and despite design intentions to operate only in very wet weather, some CSOs still operate more than once per week (WWF-UK, 2017). Using machine learning techniques on two wastewater treatment plants as case studies, Hammond et al. (2021) estimated spills to have occurred on 926 out of 7160 days (13 %) reported as no-spill days by the operators. There are estimates that about half the national sewer network in England is currently at or close to capacity and that investment in sewerage asset maintenance in England and Wales is only one-sixth of the level required for functionality (Sayers et al., 2020). Thus, despite the substantial and well-documented overall improvements in the emission of sanitary determinands achieved since the 1980s, local issues remain — often associated with CSOs.

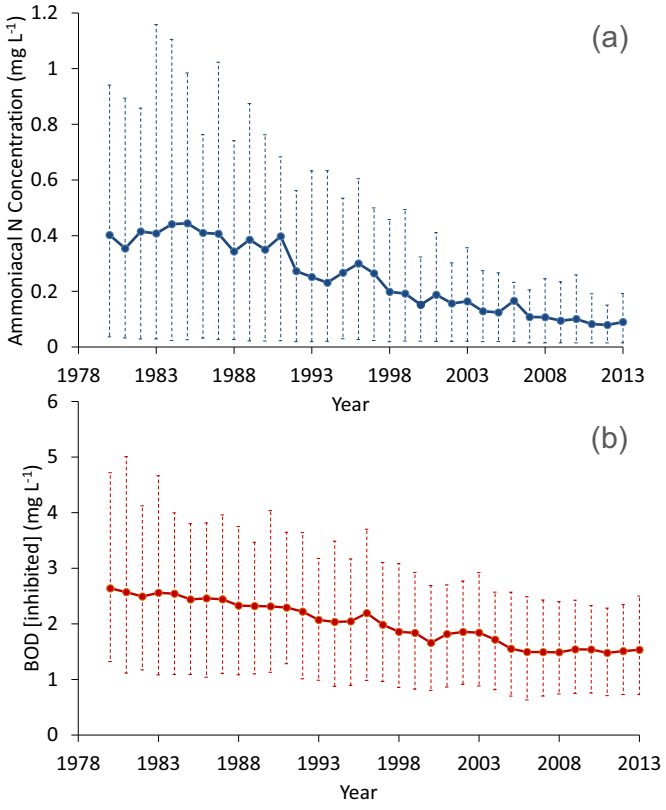

Fig. 3. Mean annual concentrations of (a) total ammoniacal N (NH_4^+-N and NH_3-N) and (b) BOD in data from the Harmonised Monitoring Scheme for Great Britain between 1980 and 2013. "Inhibited" BOD refers to the addition of a nitrification inhibitor to the BOD test to prevent oxygen consumption arising from the oxidation of ammonium. Symbols show the arithmetic mean concentrations of all sites for which data were available. Error bars show the range between the 10th and 90th percentile concentrations. Number of sites varied between 192 and 234 (average 220).

3.2. Metals

Heavy metals, such as mercury, lead, cadmium, nickel, zinc and copper can come from a range of sources, including atmospheric deposition, diffuse-source transfers from natural levels in soils and rocks in the

contributing catchment, sewage sludge (Kladivko and Nelson, 1979; Peyton et al., 2016) or metal-rich slurries applied to soils (Peyton et al., 2016), some agrochemicals, storm runoff from urban surfaces (Barco et al., 2008), leaking landfills, some industries and from active and abandoned mining operations (e.g. Clements et al., 2000; Coulthard and Macklin, 2003). Many metals have moderate to very high ecotoxicity, both on their own (Taylor et al., 2000) and when present as mixtures (Enserink et al., 1991). They are likely to be most problematic in or downstream of urban areas where (inter alia) vehicle corrosion and tyre wear (some tyres contain cadmium and zinc) can cause urban diffuse-source pollution of combined and separate sewer systems (e.g. Nawrot et al., 2020; Cowan et al., 2021). Concentrations are often especially high during the initial runoff following a dry period — the so-called "first flush" (e.g. Barco et al., 2008). Metals can also be emitted to sewers in wastewater: lead is still present in water supply pipes in older buildings (and, thus, may contaminate wastewater) and industries which use metals in their processes (e.g. chromium is traditionally used in leather tanning) can discharge wastewater directly or via municipal sewers. The history of emission will depend on the nature of the "sewershed" and the history of industrial activity. With the decline in heavy industry in Great Britain in the last two decades of the 20th century, a decrease in metal contamination of surface waters via the wastewater pathway might have been expected in recent years, but legacy effects from contaminated sediments stored within the fluvial system may contribute to elevated levels in some systems.

Observed metal concentrations (including copper, cadmium, lead, nickel and zinc) in British rivers are often close to (and sometimes exceed) ecotoxicological effect thresholds. This means that they are one of the most important ecological stressors (Johnson et al., 2017) and a common reason for poor WFD status (Environment Agency, 2015). The effect of metals at a given concentration varies spatially depending on the pH (which is affected by acid neutralising capacity: ANC) and organic carbon concentration (which can reduce bioavailability). Metals tend to have greater ecological impact in catchments with lower ANC and with lower concentrations of organic carbon (Tipping et al., 2016). In many upland catchments characterised by base-poor, acidic conditions and with a legacy of mining (e.g. many parts of Wales and the Pennine hills of northern England), metal concentrations are a more significant issue than in lowland catchments with higher pH (Campbell and Stokes, 1985).

Data on median annual concentrations of zinc, lead, copper and nickel from >200 river sites monitored at the tidal limit under the HMS between 1980 and 2013 are shown in Fig. 4. The data are highly variable. However, there is a clear decrease in both the median concentration (by approximately a factor of three or more in all cases) and the range over this period. In addition to the changes in the sources of metals described above, improvements in wastewater treatment provision will also have contributed to this decline. Metals are readily removed during wastewater treatment, principally via binding to organic matter which accumulates in sludge. However, this may create a diffuse-source pollution problem if sludge is applied to land and the sorbed metals are subsequently mobilised during runoff events (Kladivko and Nelson, 1979; Peyton et al., 2016). Similar declines in metal concentrations have also been reported in Europe, with maximal pollution observed in the 1960s to 1980s (Salomons et al., 1982). In Germany, which might be expected to have experienced similar trends to Great Britain, there has been a long-term decline of lead in river water, as a result of the gradual removal of lead in petrol from ca. 1990 (German Environmental Specimen Bank, 2022).

Historically, drainage waters from active and abandoned mines (for both coal and metals) have resulted in serious pollution of surface waters in mining areas. Mine drainage can be very acidic, particularly following groundwater rebound when active pumping ceases and iron pyrite (FeS_2) and other sulphidic minerals oxidise in the presence of both oxygen and water (Johnson and Hallberg, 2005). Mine drainage water can contain elevated concentrations of heavy metals such as iron, aluminium, manganese, cadmium, copper and zinc as well as metalloids like arsenic (Johnson and Hallberg, 2005; Beane et al., 2016). Erosion of particulate material from abandoned mine workings and spoil tips can also result in significant (and continued) metal transfers along with associated ecological impact in adjacent surface waters (Lord and Morgan, 2003; Beane et al., 2016). This kind of pollution is spatially restricted but continues to pose a potential threat to riverine ecology in affected areas. According to the Coal Authority (2016) metal pollution from mines affects around 1500 km of rivers in England. Until 2000, mine operators could abandon mines with little risk of being prosecuted. However, drainage at many seriously affected sites is

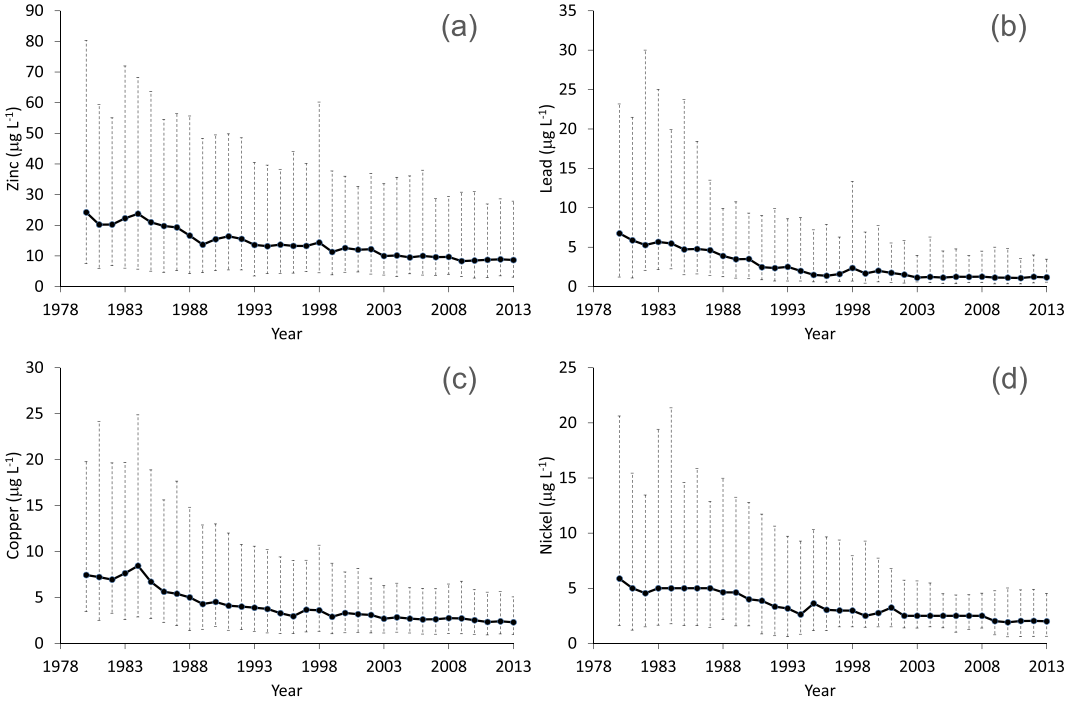

Fig. 4. Median (50th percentile) concentrations of selected metals in lowland GB rivers at the tidal limit from 1980 to 2013. (a) Zinc; (b) lead; (c) copper; (d) nickel. The error bars show the 10th–90th percentile range (HMS). Number of sites varied between 152 and 228 (mean 204).

now being treated or has been targeted for treatment under the Water and Abandoned Metal Mines programme, which was set up in 2011 by DEFRA, the Environment Agency and the Coal Authority (Jarvis et al., 2019; Mayes et al., 2021). This suggests that the problem may be reduced in the future.

3.3. Emerging organic contaminants in wastewater

Domestic wastewater contains a plethora of natural and synthetic organic compounds, which may pose ecotoxicological risks to wildlife in receiving waters. These compounds are sometimes referred to as micropollutants in recognition that they are often present at low but toxicologically-relevant concentrations. They are also known as emerging contaminants, in recognition of the fact that their presence has only recently been detected. They include chemicals used in human and veterinary pharmaceuticals (so called Active Pharmaceutical Ingredients or APIs: Boxall, 2004; Richardson and Ternes, 2014), illegal narcotics (e.g. Munro et al., 2019), the ingredients used in home and personal care products (e.g. detergents, fabric conditioners, cosmetics, sun screens and shampoos), synthetic hormones (such as ethinylestradiol (EE2) which is used in a number of medications including the contraceptive pill and menopausal hormone replacement therapy) along with naturally produced human hormones (e.g. estradiol [E2], progesterone and testosterone: Johnson and Williams, 2004). These compounds can be washed or excreted to wastewater during and after use and, hence, enter wastewater treatment (Watkinson et al., 2009). Their fate during treatment (i.e. the extent to which they are degraded, volatilised or sorbed to sewage sludge) will depend on their chemical characteristics and on the type of treatment technology employed and its operating parameters. Some compounds are removed efficiently (e.g. the typical removal rates for linear alkyl benzene sulphonate (LAS), a high tonnage surfactant used in laundry detergents is >90 % for trickling filter plants: Holt et al., 1998, and >99 % for activated sludge plants: McAvoy et al., 1998) but for others, removal rates are often lower. For example, Baronti et al. (2000) report mean removal rates for E2 and EE2 of 87 and 85 %, respectively, and a mean removal of estrone of only 61 % in activated sludge WWTPs. Removal rates can also vary widely (Wang et al., 2018). Even where removal efficiencies are high, compounds may still be present at toxicologically-relevant concentrations in receiving water bodies (Sumpter and Johnson, 2005). Furthermore, as for sanitary determinands and FIOs (see Section 3.7.2), untreated emissions from CSOs and poorly-performing septic tanks may contribute significantly to micropollutant loads (e.g. Phillips et al., 2012; Schaider et al., 2017).

APIs are designed to be biologically active, with specific modes of action, and hence may have effects on organisms in receiving ecosystems at low concentrations (Rand-Weaver et al., 2013). A wide range of effects have been reported for these molecules in the natural environment or in laboratory-based studies. For example, laboratory studies have demonstrated that antidepressants at close to environmentally-relevant concentrations can affect fish behaviour (Brodin et al., 2013). Toxicological studies on the veterinary anti-parasitic compound, ivermectin, have demonstrated effects on invertebrate growth and reproduction at a concentration of just 1 pg L^{-1} (Lopes et al., 2009) making it one of the most environmentally toxic molecules in existence. Model-based estimates suggest that aquatic life in up to 50 % and 4.5 % of river reaches are at risk from ibuprofen and diclofenac exposure, respectively (Boxall et al., 2014). There is also a growing evidence-base that the presence of antibiotics in the environment is contributing to the global antimicrobial resistance crisis (Wellington et al., 2013).

The temporal pattern of micropollutant loads to rivers from wastewater is largely unknown prior to the mid-1990s, due to a combination of a lack of analytical methods with low detection limits and insufficient application of the prevailing methods available (e.g. Desbrow et al., 1998). Since many of these compounds are completely synthetic, their concentrations in surface waters will undoubtedly have increased since the Industrial Revolution. It was not until the early 1800s that the first synthetic pharmaceuticals, such as the anaesthetics chloroform and chloral hydrate, were developed (Jones, 2011). Classes of APIs which are now regularly detected in British rivers were not developed until later still. For example, penicillin was discovered in 1928 but not widely used until the 1940s (Ligon, 2004); the first contraceptive pill (containing norethynodrel and mestranol) was not approved until 1961 (Dhont, 2010); and fluoxetine, the first selective serotonin uptake inhibitor antidepressant, was developed in 1974. By 2008, there were 740 active ingredients authorised for veterinary use in Europe (Kools et al., 2008) and in 2018, there were 1912 APIs authorised for use in humans (Burns et al., 2018). It is estimated that between 20 and 30 new human-use APIs enter the European market every year. It is, therefore, likely that at least 2700 APIs are currently in use in Britain and many of these will be released to surface waters. In England, between 2006 and 2016, the total number of prescriptions increased by 47 %, with the number of prescriptions per person increasing by 35 % (Moody et al., 2016). In 2015/16 48 % of adults in England were taking at least one prescription medicine with 24 % of the population taking three or more (Moody et al., 2016). As the average age of the British population increases, it is anticipated that the use of APIs and subsequent emissions to the environment will continue to increase (Royal Commission on Environmental Pollution, 2011). Furthermore, changes in environmental conditions, arising from climate change, may affect the incidence and patterns of human disease which may change use patterns for some API classes (Redshaw et al., 2013).

The first APIs were not detected in British surface waters until the early 1980s, with the antibiotics, erythromycin and tetracycline, and the bronchodilator, theophylline, being identified, but not quantified, in river water samples (Crathorne et al., 1984). Since the late 1990s, over 30 monitoring studies have been reported on the occurrence of APIs in British surface waters. Combined, these studies have identified 154 active ingredients (Aus Der Beek et al., 2016) with the most commonly monitored classes being analgesics, antibiotics, antidepressants, antifungals, anti-inflammatories, β-blockers, estrogens, lipid regulators and morphine derivatives. With the exception of a handful of substances (e.g. cypermethrin, diazinon, copper and zinc, which are also emitted by other sectors) human and veterinary medicines have not been included in regulatory monitoring schemes in Great Britain. A number of APIs (17-β-estradiol, 17-α-ethinylestradiol, amoxicillin, azithromycin, ciprofloxacin, clarithromycin and erythromycin) have, however, been included in the WFD Watch List (European Commission, 2018). Even so, monitoring for APIs has not been systematic so it is difficult to determine whether trends exist.

Veterinary medicines pose similar ecotoxicological risks to human APIs. They can be emitted to the environment directly when used in aquaculture but more commonly they are excreted to soils and surface waters by grazing animals or emitted via the application of manures and slurry. These compounds can then be transferred to surface waters. There is also increasing recognition that given the large numbers of companion animals such as cats and dogs in the UK (*ca* 21 million), emissions of APIs from these sources could also be an important diffuse-source of water contamination (Little and Boxall, 2020). One study of 20 English rivers reported concentrations of ectoparasiticides which exceeded chronic toxicity thresholds, particularly downstream of WWTPs which collect urban runoff as well as sewage (Perkins et al., 2021).

In parallel with the development and uptake of new pharmaceuticals, there have been various introductions of other compounds used in industry and in home and personal care products over time (often unregulated prior to the late 1980s). These have created some local problems historically, such as “foam mountains” in rivers from poorly degrading synthetic surfactants (e.g. branched alkyl benzene sulphonates: ABS) which were introduced into laundry detergents from the 1930s (Snell and Snell, 1958). That said, many materials with very poor environmental profiles have now been replaced by more degradable alternatives which often have lower toxicity (e.g. LAS for ABS) or their uses have been effectively discontinued in domestic detergents (e.g. nonylphenol and nonylphenol ethoxylates). However, as for APIs, very little systematic monitoring of these compounds has taken place.

Hormones and hormone-like substances can be particularly problematic in surface water ecosystems, because they have endocrine disrupting effects

such as the manifestation of intersex phenomena in fish (Jobling et al., 1998, 2006) or developmental impairment in riverine birds (e.g. Morrissey et al., 2014). Intersex occurrence in fish is likely to be most acute in areas with high population density and low dilution potential — such as the southeast of England (Jobling et al., 1998; Williams et al., 2009). Modelling-based studies have indicated that up to 38 % of river reaches in England and Wales could be at risk from estrogen exposure (Williams et al., 2009, 2012). Increased wastewater discharge as a consequence of population growth will definitely have increased untreated hormone loads. As for other organic pollutants, this increase may have been offset, to some extent, by improvements to the wastewater treatment infrastructure described in Section 3.1.

Overall, the burden of hormones and micropollutants in many rivers is likely to have increased over the 20th century due to the introduction of new chemistries and to increases in population, despite improvements in wastewater treatment infrastructure. However, more systematic monitoring is required to assess current concentrations and potential effects. In future, decreases in dry weather flows in some catchments under climate change may reduce point-source dilution seasonally. This could exacerbate the threats posed by synthetic organic pollutants to British rivers in the future. Increased use of nature-based health interventions (so-called "green prescribing": Robinson et al., 2020) may offer some checks to this trend but the extent to which these measures will limit pollution is unknown.

3.4. Macronutrients

3.4.1. Nitrogen

Nitrogen (N) is an essential plant nutrient needed synthesise amino acids, proteins and other important structural and functional molecules. It can be assimilated by plants and algae, either as nitrate or as ammonium. However, if present in surface waters at high concentrations, these compounds can trigger eutrophication (characterised by algal blooms) if N is limiting (typically when the ratio of available N to available phosphorus is less than the Redfield ratio of 16:1 e.g. Turner et al., 2003). Eutrophication is often associated with dissolved oxygen depression, toxicity (especially for some cyanobacteria) and costly issues of taste and odour in drinking water reservoirs (Perkins et al., 2019). N is commonly limiting in marine systems (Howarth and Marino, 2006) which means that riverine N fluxes to the coastal zone may be the trigger for near-shore algal blooms (Whelan et al., 2009). Increased nitrogen has also been linked to ecological changes in the structure and biodiversity of lake macrophyte and phytoplankton communities (Bunting et al., 2007; Olsen et al., 2015).

Nitrate is regulated in the EU under the Nitrates Directive (91/676/EC; transposed via The Nitrate Pollution Prevention (Amendment) Regulations 2016). This directive was driven, in part, by (disputed) perceptions about the health effects of nitrate such as methaemoglobinaemia in infants and its association with cancer clusters (see Addiscott and Benjamin, 2004). Nitrate is often the main form of N which is present in ground and surface waters — partly because it is the "end-point" of the mineralisation process (in which organic N in soil or in water is converted by micro-organisms to ammonium which is then further oxidised to nitrite and nitrate by nitrifiers) but also because nitrate is an anion and is, therefore, mobile in soils where the solid phase often carries a net negative charge.

Concentrations of N (mainly as nitrate) increased markedly in many surface water catchments in Great Britain in the latter half of the 20th century (Howden et al., 2010; Burt et al., 2011). One of the longest directly measured water quality records in the world was collated by Howden et al. (2010) for nitrate in the Thames at Teddington (Fig. 5). This record shows a marked increase in the latter part of the 19th century, stable concentrations during the first part of the 20th century up to about 1940 and then two phases of increase: one during the 1940s and the second in the 1970s. Unfortunately, no other nitrate records of this length exist elsewhere but, given the ubiquity of agricultural developments in England, this trend is thought to broadly reflect the situation in many other lowland catchments (see Burt et al., 2011; Howden et al., 2011a). The increases seen in Fig. 5 were primarily a consequence of agricultural intensification, although increases in sewage effluent discharge due to population growth was also a minor contributor (Howden et al., 2010). Specifically, N losses from agricultural land to water were influenced by two main factors: (1) enhanced mineralisation in soils resulting from the widespread conversion of long-term pasture to arable land (Whitmore et al., 1992) and (2) the increased use of mineral fertilisers (primarily post 1945). The realisation that nitrate concentrations in many catchments were exceeding legislative limits (i.e. 11.3 mg N L^{-1} under the EU the Drinking Water Directive and, later the EU Nitrates Directive) occurred in the mid-1980s. It eventually resulted in restrictions of N fertiliser use in certain parts of Great Britain (initially via Nitrate Sensitive Areas and Nitrate Advisory Areas in 1990 and then, more widely, via Nitrate Vulnerable Zones [NVZs], which came into effect in 1999: Osborn and Cook, 1997). NVZs now cover approximately 55 % of land in England (DEFRA, 2018) and 2.4 % in Wales. However, an all-Wales NVZ has recently been proposed by the Welsh Government (Natural Resources Wales, 2022). There has also been a reversal in net conversion of long-term pasture to arable land in recent years (with farmers incentivised to take arable land out of production under the EU rules for "set aside"). Such conversion may be particularly effective in riparian buffer zones, where denitrification can reduce nitrate concentrations in shallow groundwater, as long as field drains do not "short circuit" the hydrological pathway between the hillslope and the river (e.g. Haycock and Burt, 1993). These land use changes have resulted in decreases in concentrations in some catchments (from the 1980s in the Thames but later elsewhere such as the Slapton catchments in South Devon: Burt et al., 2020). Improvements to wastewater treatment provision, despite increases in total population over this period may also have helped to keep the N flux from sewage at fairly constant levels since 1975 (Naden et al., 2016). That said,

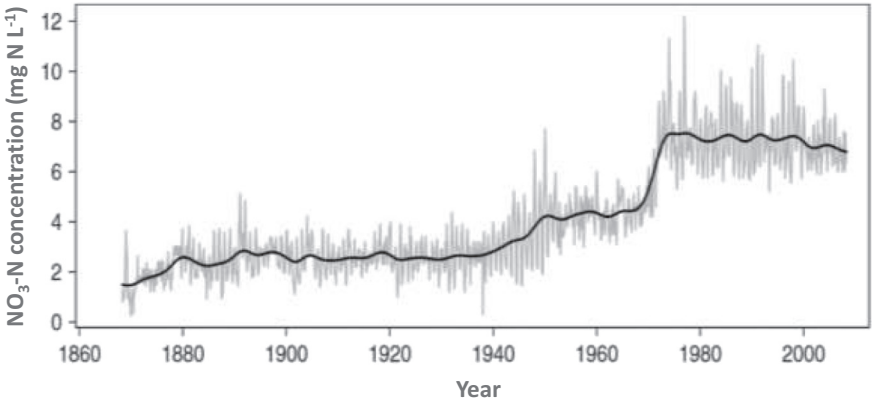

Fig. 5. Nitrate N concentrations in the river Thames at Teddington from 1868 to 2008 (adapted from Howden et al., 2010). The grey line shows the mean monthly concentration and the black line shows the one-year moving average concentration.

concentrations in many catchments remain stubbornly higher than they were in the 1960s and certainly higher than they were at the end of the Industrial Revolution (e.g. Howden et al., 2010; Bell et al., 2021).

Average nitrate N concentrations measured at the tidal limit in the HMS data set (data not shown) display a wide range of concentrations but, overall, no apparent trend from 1980 to 2012. This is consistent with the data from the Thames over the same period. It should be noted that concentrations at the tidal limit are also a reflection of transformation and losses (e.g. due to denitrification) of N in river water — particularly in lowland reaches (e.g. Mulholland et al., 2008).

Some catchments with large groundwater stores (e.g. in the chalk aquifer of southern England) have very long solute residence times. This is particularly the case where there is a deep unsaturated zone with few opportunities for solute to by-pass the rock matrix, which means that pulses of nitrate leached from the soil may not influence nitrate concentrations in the saturated zone or in spring-fed stream water for several years or decades. Howden et al. (2011a) illustrated the importance of delayed unsaturated zone nitrate transport in the Alton Pancras catchment in Dorset, where nitrate concentrations in a spring-fed stream were highly positively correlated with model estimates of the nitrate leached from the soil (derived from land use records) with a lag time of 37 years, corresponding with typical unsaturated zone travel times in the aquifer. Thus, even when nitrate leaching is controlled in these catchments (e.g. by better management of N inputs), concentrations in surface waters may continue to rise. Similar observations have been made elsewhere — for example in Chesapeake Bay (Sanford and Pope, 2013).

3.4.2. Phosphorus

Phosphorus (P) is also known to be an important control on eutrophication — particularly in freshwaters where N:P ratios are often >16:1 (e.g. Earl et al., 2014). Only ortho-phosphate (monophosphate) is available for plant uptake and algal growth (also known as reactive P because it reacts with ammonium molybdate in the main analytical method employed for phosphate). However, other P forms can be transformed into phosphate in the catchment. In most natural and uncontaminated water bodies P concentrations are low. However, concentrations can be increased by (1) the emission of wastewater and (2) by diffuse-source pollution (i.e. the transfer of P from agricultural soils). A mean reactive P concentration >50–100 μg P L^{-1} is often cited as the threshold above which there is potential for eutrophic conditions to occur (United Nations, 1992). However, this threshold is known to vary with alkalinity, with lower thresholds set in low alkalinity sites (UK TAG, 2013), although high alkalinity marl lakes, which have naturally low levels of P, have a specific and particularly low threshold (Wiik et al., 2014). According to Reynolds and Davies (2001) the OECD threshold for lake eutrophication (at which phytoplankton levels start to cause a nuisance) is 35 μg reactive P L^{-1}.

3.4.2.1. Point sources. Untreated wastewater often contains high P concentrations from human waste. The most widely accepted estimate of untreated per capita P generation from human wastes is 1.6 g P cap^{-1} day^{-1} (i.e. 0.58 kg P cap^{-1} $year^{-1}$: Morse et al., 1993). Assuming a (typical) water use rate of ca 150 L cap^{-1} d^{-1}, this gives an untreated wastewater concentration of 10.6 mg P L^{-1}. This will be enhanced by other emissions, such as from some home and personal care products and from intentional phosphate additions to domestic water supplies by water companies to reduce plumbosolvency (Hayes and Hydes, 2012). Furthermore, P removal in conventional secondary wastewater treatment can be as high as 80–90 % but is typically lower (Morse et al., 1998). Naden et al. (2016) estimated a range for effective P removal in secondary wastewater treatment of 53–63 %, based on measured P concentrations, although this may be higher with tertiary treatment, such as the addition of ferric chloride to precipitate P, or the use of natural or constructed wetlands. Historically (approximately in the period 1950–2010), many home care products such as laundry and machine dishwasher detergents employed sodium tripolyphosphate (STPP) as a "builder" to mop up base cations, which interfere with surfactancy. These products made substantial contributions to total P loads in wastewater and were blamed by many for causing eutrophication in inland waters. According to Naden et al. (2016) P emissions probably peaked in the late 1980s with STPP contributing approximately 50 % of the total wastewater load. However, after concerted campaigning, phosphate builders have now largely been replaced by other builder technologies (e.g. zeolites and polycarboxylates) in powdered laundry detergents (e.g. Morse et al., 1995). Furthermore, most modern liquid detergents are also phosphate-free. Even many machine dishwashing detergents (which for several years still contained P: e.g. Wind, 2006) are now also phosphate-free. Consequently, between 1985 and 2000, use of STPP in detergents in the UK reduced by approximately 40 % (Glennie et al., 2002). By 2009, detergents were estimated to contribute only 18 % of the P load to sewers (UKWIR, 2009). A comparable figure of 21 % was estimated by the International Association for Soaps, Detergents and Maintenance Products in 2004 (AISE: www.aise-net.org). Similarly, Comber et al. (2019) estimated that the combined contribution of laundry and dishwashing detergents to wastewater P was 23 %. The phase out of P in detergents was independently accompanied by enhanced wastewater treatment driven by the UWWTD in the 1990s which required tertiary treatment for all plants serving >10,000 population equivalents in "sensitive" areas.

3.4.2.2. Diffuse sources. P can be transferred from soils to surface waters either in dissolved form or as sediment-associated P in soil erosion. This transfer is referred to as diffuse- (or non-point) source P and depends on a range of factors including crop type, land use history (including previous fertiliser applications), livestock density, agricultural management (e.g. type of operations, presence of tile drains), soil type (e.g. texture, structure, mineralogy), underlying geology, climate, topography, proximity to water courses, and the characteristics of buffer zones, if present. In soils, most P is immobilised (fixed) by the soil solid phase (as part of the soil organic matter, as an integral part of the mineral composition of primary particles or as metal-P complexes). Consequently, significant amounts of fertiliser P applied in agriculture will usually not be lost through leaching of dissolved P. For the same reason, however, it may not reach the crop before being immobilised and so it has historically been applied as mineral fertiliser (e.g. Massey et al., 2016) and as organic amendments, such as manure (e.g. Bateman et al., 2011) in excess of agronomic requirements (often referred to as "surplus" P) to ensure crop demands are met. Continuous fertiliser P application can, thus, result in a build-up of total P levels in soils (since supply exceeds demand) leading to saturation (Withers et al., 2001) and an increased risk of leaching (Heckrath et al., 1995; Moss, 1998). High soil P levels resulting from surplus fertiliser applications in the past are sometimes referred to as "legacy P" (Kleinman et al., 2015; Powers et al., 2016). In many cases, the largest loss of P from arable land is as sediment-associated transport, caused by soil erosion (Ulén et al., 2007). This can be compounded by some modern agricultural practices such as the use of heavy machinery (if this results in compaction), by vehicle tramlines (especially if these are parallel with the slope: Withers et al., 2006) or by leaving soils bare over winter (especially where P has been recently added as a fertiliser). Recent trends for increased cultivation of maize (*Zea mays*) which is harvested in autumn, leaving soil bare over winter and, hence, more vulnerable to erosion, may also be locally problematic. In addition, where soil P levels are high, leaching losses can be significant (Heckrath et al., 1995). This may be one reason why P concentrations are elevated in some aquifers which is resulting in potentially high background P concentrations under baseflow conditions which can sometimes exceed eutrophication thresholds (Holman et al., 2008; Holman et al., 2010). It also means that some soils may be able to meet crop P requirements without additional fertiliser application (particularly if so-called P activators are employed to enhance legacy-P release: Zhu et al., 2018). In recent years, there has been an overall decrease in P application rates via, inter alia, targeting of P application to soils with low P status (Withers et al., 2017), although there are still examples of continued surplus P applications (e.g. McDonald et al., 2019 reporting for Ireland, where practices are similar to parts of Britain). More effort to target P applications has probably

been stimulated by recent increases in the global P price, driven by an increasing awareness of the finite nature of global P stocks (Zhu et al., 2018).

Notwithstanding the potential increase in baseflow P loads in some catchments (Holman et al., 2008), most significant transfers of P from land to water tend to occur during winter storm events when soil moisture content is relatively high and hydrological pathways are active. This means that most diffuse-source P losses are not coincident with the period of maximal biological activity in recipient rivers and lakes. In rivers, this implies that these transfers have minimal impact on eutrophication, although in lakes diffuse-source P inputs can be retained and recycled in subsequent seasons, also referred to as "legacy phosphorus" (Jarvie et al., 2013), which may result in eutrophic impacts even after P pollution has been curtailed (Reynolds and Davies, 2001).

P emissions from wastewater are approximately constant over the year so concentrations in catchments with substantial human populations tend to be higher in the summer months, when discharge in receiving waters is generally lower (i.e. dilution is lower). This is the period with highest biological activity and, hence, point-source P emissions may still make a disproportionately high contribution to riverine eutrophication, despite reductions in loads (Jarvie et al., 2006). The fact that solute rating curves for phosphate in many rivers continue to have a negative gradient (i.e. P concentration decreases with increasing river discharge, implying a dilution effect) also suggests that sewage remains a major contributor to elevated P concentrations (Jarvie et al., 2006; Bowes et al., 2009). Overall, the emission of P to surface waters via wastewater is likely to have been relatively high in densely populated areas with centralised sewage collection during the early part of the 20th century, before wastewater treatment plants became widespread. Wastewater treatment will have reduced emissions but the introduction of phosphate-based detergents in the 1950s is likely to have increased them again. Now that P use in detergents has decreased substantially and tertiary wastewater treatment has become more widespread, point source emissions are likely to have decreased (despite increases in population), although untreated sewage discharges (e.g. via CSOs) and effluent from smaller private systems such as septic tanks are likely to remain locally problematic for P, as well as for other pollutants. In parallel, application of fertiliser P has also decreased in recent years after awareness-raising about legacy P issues and an improvement in agricultural nutrient management in general. The combined effect of these developments has been an overall reduction in the mean annual measured orthophosphate concentrations in rivers at the tidal limit after about 1997 for the 225 HMS sites (Fig. 6). These data show a significant decrease in both the mean and range between 1980 (average 0.4 mg P L^{-1}) and 2013 (average 0.15 mg P L^{-1}) overall. However, the picture for individual catchments is mixed with most showing significant decreases but many showing significant increases, e.g. due to expansion of intensive agricultural activities producing high volumes of animal manure (e.g. Worrall et al., 2016).

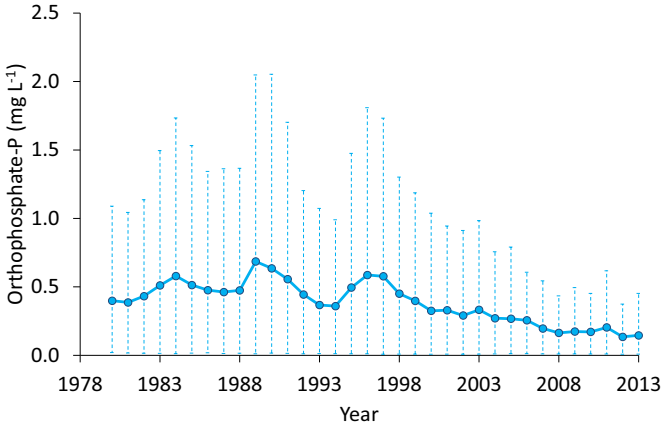

Fig. 6. Mean annual orthophosphate-P concentration measured in lowland rivers at the tidal limit between 1980 and 2013. The error bars show the 10th–90th percentile range (HMS; Civan et al., 2018). Number of sites varied between 200 and 238 (average 223).

Longer-term data on P concentrations and loads are available for the River Thames at Teddington, going back to the 1930s (Haygarth et al., 2014). These data suggest that total P loads started to increase in the 1950s, peaked in the late 1980s and have since declined to current levels which are similar to those observed in the 1930s and 1940s. This pattern is consistent with a decrease in both point and diffuse source loads since the 1990s. The trend in TP loads appears to be better correlated with the estimated P contribution from point sources and is consistent with the trends in STPP use described above. The input of P fertilisers to the catchment is estimated to have increased significantly in the 1940s in response to the need in World War II to become more self-sufficient in food production and stayed high until the late 1980s. Although the early increases in fertiliser applications do not seem to have resulted in major increases in observed loads, it is likely that they will have increased soil P stocks and may, therefore, have generated lagged "legacy" contributions to fluvial P losses in the 1950s, 1960s and 1970s.

3.5. Pesticides

Since the 1930s, a wide range of synthetic organic compounds has been developed for use as pesticides (e.g. herbicides, insecticides, fungicides and molluscicides). These compounds (also known as plant protection products: PPP) have helped to increase crop yield and quality. However, some of them have been associated with major environmental issues, including persistence, long-range transport, bioaccumulation and toxicity in wildlife. Many pesticides can also be leached to groundwater and transferred to surface waters via a number of routes. First, pesticides can be transported directly to surface water bodies by the wind during application (spray drift). The extent to which this occurs depends on factors such as the proximity of the sprayer to the water body in question, the height of the boom (higher booms tend to result in more drift), droplet characteristics (controlled by nozzle type and pressure), wind speed and sprayer forward velocity (Miller, 2003). Secondly, pesticides can be transported along hydrological pathways — e.g. via overland flow (sometimes associated with eroded soil particles), drain flow (a high fraction of arable land in Great Britain is under-drained and drains are known to be important conduits for pesticide transport to surface waters: e.g. Tediosi et al., 2012; Tediosi et al., 2013; Whelan et al., 2020a, b) and via throughflow. They can also be lost by overland flow from hard surfaces (e.g. farmyard hard standings but also herbicide applications to roads and railways). Typically, a relatively low fraction of the pesticide active ingredient (AI) applied is lost to surface water. For example, Brown and van Beinum (2009) reported that median and mean annual losses for 97 pesticide AI measured in 23 drainage experiments were 0.09 and 0.9 % of the amount applied, respectively, with a maximum of about 10 %. However, even these small fractions may be enough to generate local concentrations which are ecologically significant (e.g. Van Den Brink et al., 1996) and catchment-scale concentrations which can cause compliance challenges for water companies at abstraction points for water supply. British water companies are currently required to supply water to consumers with a maximum concentration of individual pesticides of 0.1 μg L^{-1} (the EU Maximum Admissible Concentration in drinking water). This is occasionally exceeded — particularly for compounds which are difficult to remove using conventional drinking water treatment trains (e.g. metaldehyde: Kay and Grayson, 2014; Ramos et al., 2019). Ecological and drinking water compliance failures can also be triggered by poorly managed sheep dip operations and by non-agricultural activities such as textile treatments, vegetable processing (e.g. Xie et al., 2021) and parasite treatments for domestic pets (e.g. Perkins et al., 2021).

The overall use of pesticides (and, by extension, associated exposure in surface waters) is likely to have increased up to the 1980s. However, the introduction of a more rigorous registration process in the EU in the early 1990s (EC 91/414 and subsequently EU Regulation 1107) has meant that many higher-risk substances have been replaced by alternatives with better

environmental profiles (e.g. lower potential for longevity, long-range transport, bioaccumulation and ecotoxicological effects).

As for many of the organic compounds used in "down-the-drain" products, there is a paucity of monitoring data for pesticides compared to other water quality variables with poor spatial and temporal cover in general. This is, in part, because quantitative analysis of pesticides in water samples is expensive and often specific for certain classes of compounds. Without continuous long-term data on measured concentrations, it is difficult to be conclusive about national trends. Moreover, what little monitoring there is has become more systematic over time to focus on sites which are most likely to have high concentrations (e.g. catchments with a high fraction of intensive arable land). This targeted shift will have introduced a systematic bias to sampling. In addition, the pesticide AI used have changed over time which further frustrates establishing a long-term picture. For example, in the 1980s and 1990s triazines (particularly atrazine and simazine) and urea herbicides (isoproturon, chlorotoluron and diuron) were commonly reported but many of these have since been removed from the market. Notable exceptions where catchments have been targeted for pesticide monitoring include some water supply catchments (where data are collected by water companies but may not be publicly available) and eight catchments which have been monitored for pesticides under the Catchment Sensitive Farming (CSF) initiative. CSF data are available for up to 14 pesticides in samples collected as frequently as twice per week over the period 2006 to 2018 (Environment Agency, 2019). According to the most recent CSF report (Environment Agency, 2019) there has been a decrease in several indicators in the last eight years of monitoring compared with the first three, including the frequency of detections at >0.1 $\mu g\ L^{-1}$ and average annual concentrations and loads. However, the detailed trend data are not convincing, with average annual concentrations for many AI increasing or remaining approximately stable over the whole monitored period. The data are also confounded by rainfall patterns in the monitored period which appear to be correlated with some of the indicators. In addition, the extent to which these data reflect overall trends remains uncertain because of the specific efforts to reduce diffuse-source pollution in these catchments. Even where regular pesticide monitoring has been conducted, the sampling frequency may still be too low to reveal the temporal details of exposure — which is often seasonal and very episodic. For example, twice weekly sampling will miss many storm events.

Data are available from the Environment Agency for pesticides in groundwater in England covering 113 pesticide AIs over the period from 2005 to 2017 for 3357 unique borehole locations. In total, there are >1.5 million observations. 98 out the 113 compounds were detected above 0.1 $\mu g\ L^{-1}$, with an average detection rate of 0.19 %. The detection rate has declined over the period. However, 38 of the 98 detected compounds were so-called legacy pesticides which were not on the market (and, thus, may never have been applied during the monitoring period). Furthermore, 11.4 % of all detections were legacy pesticides, with a constant detection rate over the study period, suggesting that these compounds are persistent in groundwater with long water residence times.

It is possible to get a crude idea about possible trends by looking at pesticide usage data – with the important caveats that exposure in surface waters will also be strongly controlled by both meteorological factors, such as rainfall, and pesticide properties, such as their half-lives in soil and their propensity to sorb to the soil solid phase. Longer half-lives mean that pesticides will be present at high concentrations in the soil for longer and, thus, be available for leaching. Stronger sorption means that pesticides will be present in the soil pore water at lower concentrations and will be less likely to be displaced. Fig. 7 shows data on the total area treated with six different pesticide classes between 1990 and 2016. For some pesticide classes there has been a notable decrease in usage (e.g. benzimidazole fungicides, triazine herbicides and organophosphate insecticides). However, this has been accompanied by concurrent increases in other (e.g. triazole fungicides, sulfonourea herbicides and pyrethroid insecticides). The mass of each pesticide class used is often well correlated with the area treated for an individual AI, although the total mass of pesticides applied has probably decreased due to the fact that many modern compounds are more bioactive and hence have lower application rates. For example, sulfonylureas are typically effective at 10s of g of AI ha^{-1} whereas many older herbicides had application rates in the range 1–2 kg AI ha^{-1}. Unfortunately, some of these more active substances are also more toxic to aquatic plants, with ecotoxicological thresholds of only a few $\mu g\ L^{-1}$. Such marked differences in effect thresholds mean that overall changes in concentrations have little ecological significance if the profile of chemistries used has changed. Whilst we can be confident that any ecological impacts of pesticides in surface waters are clearly worse now than in the pre-pesticide era, it is more difficult to say how this effect has changed in recent decades. Moreover, <400,000 ha of land is farmed organically in England and Wales (ca 3.3 % in England and 4.9 % in Wales) which has changed little over the last 20 years (DEFRA, 2021a). Thus, organic growers are not likely to have made any substantial impact on riverine pesticide pollution.

3.6. Acidification

The acidification of surface waters in the UK has reflected a contrast between local and geographically extensive processes. In local areas affected by mining, acidification can result from groundwater rebound into abandoned mine workings, which often leads to the discharge of acidic groundwater and associated heavy metals (see Section 3.2). Acidification can also result from the emission of ammonia (NH_3), predominantly from agriculture (e.g. animal housing units, containment facilities for slurry and anaerobic digestate, manure spreading and associated volatilisation following the application of some types of inorganic fertilisers such as ammonium nitrate and urea: Skinner et al., 1997). However, this is often seen as a local effect resulting from the deposition of ammonium and subsequent nitrification in soil, which generates excess protons and a pH depression if ANC is insufficient.

More geographically extensive acidification arose post-industrially as a consequence of the combustion of fossil fuels that emitted gases, such as sulphur dioxide (SO_2) and nitrogen oxides (e.g. NO_2) into the atmosphere. The dissolution of these gases reduces the pH of precipitation, in turn linked to the acidification of soils and surface waters, where large rainfall volumes fall over base-poor regions. Subsequent changes in stream chemistry include reduced pH, the mobilisation of metals such as aluminium and depletion of base-cations particularly in upland areas underlain by rocks which weather slowly (Gray et al., 2016, and references therein). Many such environments also have peaty or naturally acidic soils with low base cation content and limited agricultural utility other than for sheep or plantation forestry. Afforestation can exacerbate the problem – particularly with conifers (Ormerod et al., 1989), although deciduous woodland can also lead to acidification and elevated aluminium concentrations (e.g. Gagkas et al., 2008). In Britain, acidification hotspots were located in the north of England (e.g. Cumbria and the Pennine hills), in mid and north Wales, and parts of Scotland, notably Galloway. At its worst in the 1970s and 1980s, acidification in these same areas was linked to impacts on a range of organisms including invertebrates, fish and birds (Ormerod and Durance, 2009) as a result of lowered pH and associated ecotoxic effects of various aluminium species around pH 5 (e.g. Baker and Schofield, 1982).

Acidification through acid deposition is different to most other impacts on water quality discussed in this paper in affecting remote, upland catchments most. Once this was recognised as a major environmental issue during the 1970s and 80s, laws were passed in the EU that limited SO_2 and NOx emissions from industry and vehicles (e.g. European directives 70/220/EEC and 72/306/EEC on transport, and 84/360/EEC and 88/609/EEC on industry). This has resulted in a marked reduction in emissions (Fig. 8a) and acid deposition which has been accompanied by increases in mean pH in many catchments (e.g. Ormerod and Durance, 2009; Broadmeadow et al., 2019; Fig. 8b) and decreases in mean aluminium concentrations (Fig. 8c). These effects are evidenced, for example, by trends at the 26 lake and river sites in UK Uplands Water Monitoring Network (UWMN; monitored since 1988), and at the 14 streams in the Llyn Brianne Stream Observatory in Wales (www.cardiff.ac.uk/llyn-brianne-observatory) monitored from 1981.

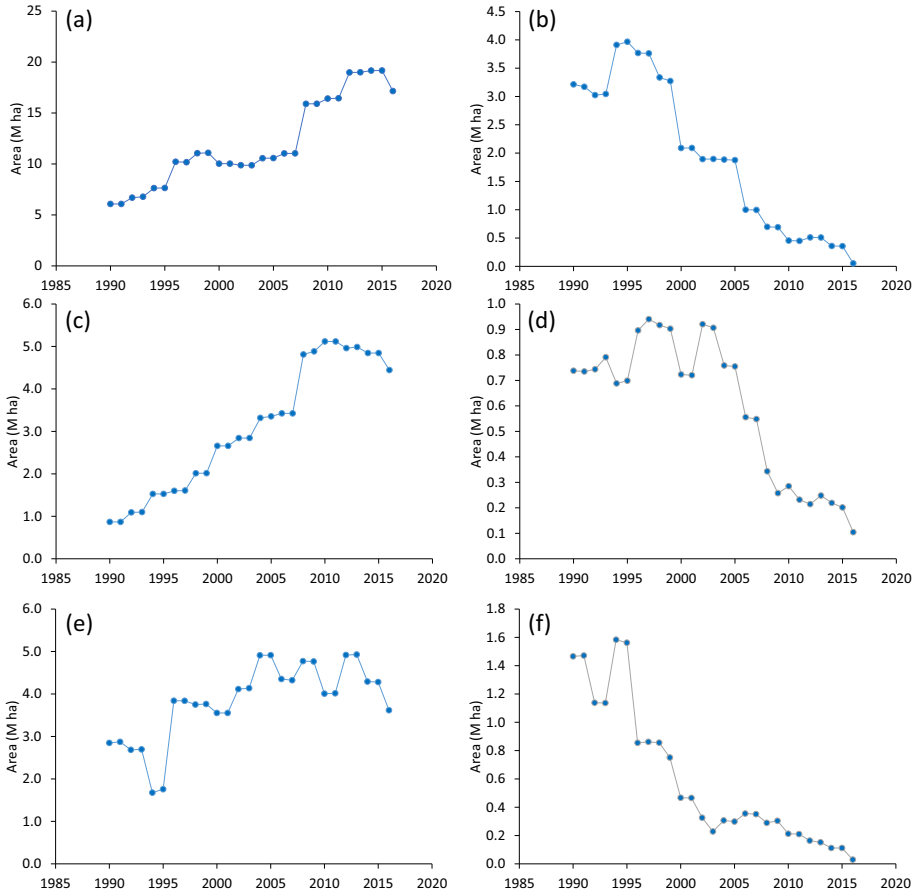

Fig. 7. Treated area (million hectares) in Great Britain from 1990 to 2009 and for the United Kingdom from 2010 onwards for six example pesticide classes: (a) triazole fungicides; (b) benzimidazole fungicides; (c) sulfonylurea herbicides; (d) triazine herbicides; (e) pyrethroid insecticides; (f) OP insecticides. Data from the Pesticide Usage Survey.

There have been questions about the extent to which recovering chemical conditions in acidified streams have been reflected in ecological recovery (Monteith et al., 2005). This has been judged as delayed or partial, most likely because continued episodes of low pH during rainstorms or snowmelt still exceeded the survival thresholds of sensitive taxa into the 2000s. This prevented the re-establishment of acid-sensitive communities (Kowalik et al., 2007; Ormerod and Durance, 2009; Gray et al., 2016). Ormerod and Durance, 2009). Additional constraints might also arise through climate warming, dispersal limitations or the resistance of biological communities to invasion where established communities outcompete recolonising circumneutral species (Frame et al., 2016). The most recent evidence suggests that episodic pH is now increasing in upland streams to the point where fuller recovery might be enabled.

Since acidification is primarily caused by fossil-fuel combustion, over timescales longer than can be assessed from available data, it is plausible to infer that conditions gradually worsened as the UK industrialised. The best assessments of these longer-term trends come from lake cores and palaeolimnological data (e.g. Battarbee and Charles, 1987) that reveal ecological status before, during and after acidification. Many microscopic algal taxa, such as diatoms, respond rapidly and sensitively to pH changes (Battarbee et al., 2008). They are deposited in lake sediment and indicate changes in water quality over time. Unfortunately, equivalent long-term records for rivers do not exist due to the more dynamic nature of sediment deposition and resuspension. The extent to which standing waters have recovered from reduced emissions will depend on the fall in total emissions (i.e. the extent to which reductions in power station emissions have been offset by increased emissions from vehicles or from ammonia volatilisation from agriculture) and the nature of any lags between emission and ecological response (e.g. due to releases of low-pH water and or aluminium from soil after atmospheric deposition has ceased). For example, a study of a Yorkshire moorland pool showed exceptionally low pH in its most recent history, attributed to the release of centuries-long accumulation of acidity in the peat (Battarbee et al., 2015). This acidity may also influence the streams and rivers in the catchment. Similar conclusions can be drawn from studies combining paleolimnological data with long-term monitoring. In an analysis of 11 AWMN lakes, Battarbee et al. (2014) found limited microfloristic recovery from acidification when comparing fossil assemblages to the pre-industrial baseline, reflecting incomplete recovery.

In summary, whilst acidified water courses are clearly not yet pristine, existing evidence does support the conclusion that they are probably now of higher water quality than they were over much of the 20th century.

3.7. Other water quality variables

3.7.1. Natural organic matter

Natural organic matter (NOM) includes both particulate organic matter (POM) and dissolved organic matter (DOM), originating from both natural sources, such as soils and plant litter, and from wastewater emissions and industrial effluents. Fluvial NOM processing (e.g. in-stream degradation of NOM) and NOM transfers to the ocean are important components of the global carbon cycle. Changes in NOM concentrations and fluxes can arise from perturbations to the terrestrial ecosystem resulting from land use and other changes. DOM (expressed as Dissolved Organic Carbon: DOC) concentration data from 118 catchments in England (1974–2017) are shown in Fig. 9 (Worrall et al., 2018). Concentrations remained approximately constant in the period up to the mid-1990s and then decreased to the early 2000s. This downward trend has been partly driven by reductions in wastewater emissions in response to the UWWTD. Longer term DOC

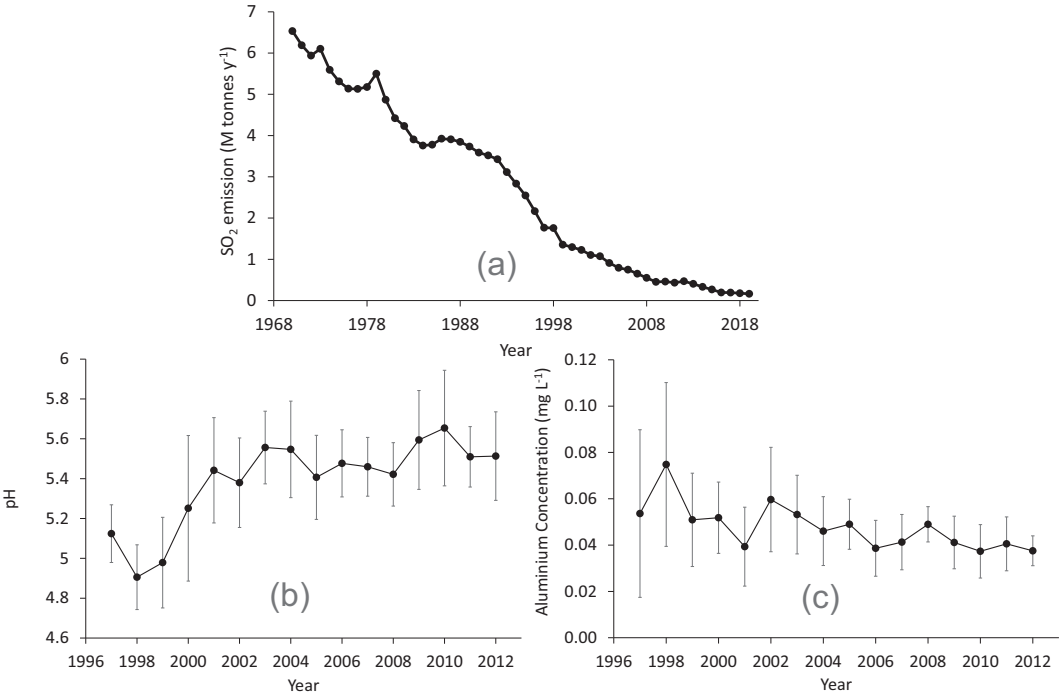

Fig. 8. (a) Changes in estimated annual SO_2 emissions in the UK 1970–2019 (https://www.gov.uk/government/statistics/emissions-of-air-pollutants/emissions-of-air-pollutants-in-the-uk-sulphur-dioxide-so2). Lower panels show changes in (b) mean annual pH and (c) mean annual Aluminium concentrations measured between 1997 and 2012 in the Nant Teyrn stream, Snowdon, north Wales (based on approximately weekly samples collected for the UK Environmental Change Network: Rennie et al., 2017). Error bars show standard deviations. Note different time frames for (a) versus (b) and (c).

records (in part, reconstructed from water colour) are available for the lower River Thames going back to the 1880s (Noacco et al., 2017). These data (Fig. 10) suggest that over this time period there was a long-term increase in DOC up to the 1990s. Peaks can be seen in the 1940s (possibly as a consequence of the conversion of long-term pasture to arable land in World War II) and in the late 1990s (possibly due to changes in land management practices such as the move away from overwinter bare soils and an increased use of minimum tillage: Brown et al., 2021). Since the 1990s concentrations have been declining, but current levels are still higher than those in the late 19th century. In addition to changes in wastewater effluent discharge and quality, NOM transfers are likely to have been affected by land use and climate change. The picture also varies spatially. For example, high DOC fluxes are often associated with upland catchments containing organic soils. In these catchments, DOC concentrations have been increasing in recent years at least to 2008 (e.g. Monteith et al., 2014). Several explanations have been proposed for these trends including a decrease in acid deposition following the adoption of flue gas desulphurisation at UK power plants (Monteith et al., 2007), increased summer drying of peaty soils (due to a tendency for drier summers) which can make DOC more available for mobilisation in subsequent re-wetting events (Mitchell and McDonald, 1992) and burning of moorland to improve game bird habitat (e.g. Yallop and Clutterbuck, 2009). Whatever the reason, increased DOC concentrations in reservoirs used for drinking water supply are a problem for water companies because they are associated with discoloration (and, hence, consumer complaints) and because they can result in the formation of chlorination by-products such as trihalomethanes (THMs) which are known to be carcinogenic (Richardson et al., 2007). Long term trends in POM concentrations at the tidal limit follow a similar pattern to those for DOM with a peak

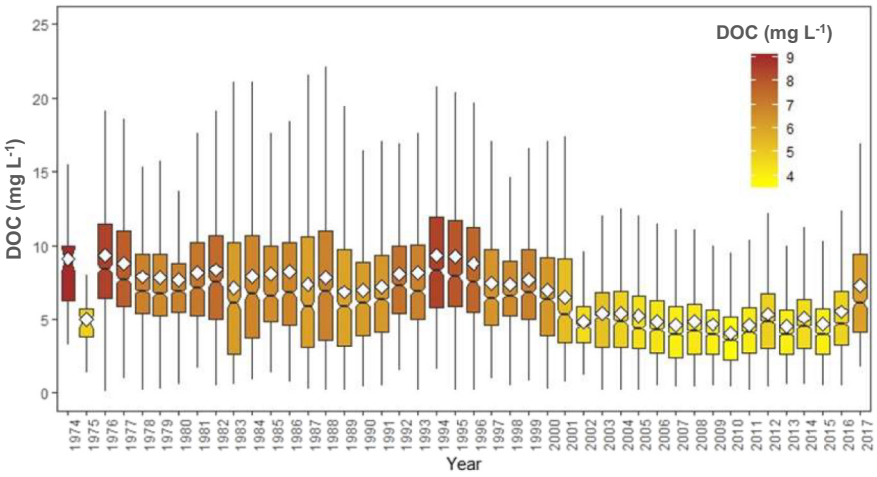

Fig. 9. Dissolved organic carbon (DOC) concentrations for 118 catchments in England as reported in Worrall et al. (2018). Boxes depict the inter-quartile range with the notch showing the median concentrations. The whiskers show the range. White diamonds show arithmetic mean concentrations.

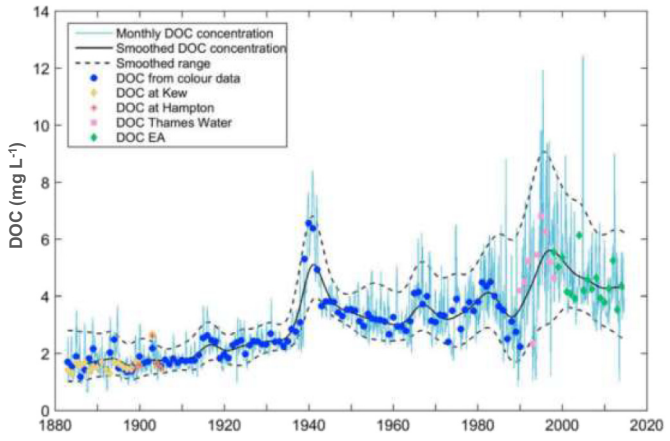

Fig. 10. Changes in DOC concentrations in the River Thames from the late 19th century to the early 21st century, as reconstructed by Noacco et al. (2017) from various datasets. The points show annual means and the continuous pale blue line shows monthly means. The solid black line shows the smoothed trend and the dashed lines show the smoothed range.

and decline in POM flux coincident with the development and implementation of the UWWTD (Worrall et al., 2014).

3.7.2. Microbial compliance parameters

Perhaps the most important aspect of water quality in terms of health risks to humans (potability and bathing) is its microbiological composition and, in particular, the presence of microbial pathogens. The detection of microbial pollution is generally inferred through the use of FIOs, such as *E. coli* and intestinal enterococci. Higher levels of faecal pollution are associated with increased FIO concentrations, so the presence of FIOs in a sample signals a connection to a faecal source. Although the presence of FIOs in surface waters does not confirm the presence of human pathogens, it does suggest that other faecal microorganisms of concern may be present. FIOs are, therefore, used as microbial compliance parameters. Unfortunately, routine regulatory monitoring of microbial pollution is very limited in British rivers. Instead, regulatory monitoring for microbial pollution focuses on designated bathing waters. In Great Britain, these are typically located on the coast, although a small number of inland bathing waters (river, lakes and lochs) are also monitored.

The European Bathing Water Directive (BWD: introduced 76/160/EEC; revised 2006/7/EC) allows for rivers to be classed as an inland water for bathing. However, until recently at least, the popularity of river swimming in the UK has been judged to be insufficient to warrant designation of any river bathing waters. In late 2020, following a DEFRA consultation, the first UK river to be given designated bathing water status was announced and in 2021 a stretch of the River Wharfe in England was monitored for FIOs during the summer bathing water season (May to September). This stretch of river will now be sampled each year to record FIO concentrations (DEFRA, 2020). The designation of the UK's first river bathing water followed months of campaigning by local groups and it is hoped that bathing water status will deliver improvements upstream (e.g. upgrades to wastewater treatment, reduced CSO discharges and better management of diffuse agricultural contributions of FIOs). It is likely that further river sites will be considered for bathing water status as catchment stakeholders prepare applications as part of river clean-up campaigns. However, the lack of any co-ordinated national-scale riverine monitoring for microbial compliance equates to a scarcity of spatially-distributed FIO data compared to many other traditional water quality parameters (Kay et al., 2007; Oliver et al., 2016). This presents a challenge for understanding the factors which control microbial quality of British rivers and for deciphering both long-term trends and shorter temporal patterns in FIOs.

British coastal waters were widely recognised to be of poor microbial quality in the 1970s but steadily improved over subsequent decades, with significant reductions in FIO flux from point sources (Quilliam et al., 2019). This was largely attributed to a combination of the 1976 BWD (along with more stringent revisions in 2006) and improvements as a result of the UWWTD. Although coastal water quality is influenced to some extent by freshwater transfers, trends at designated bathing waters tell us little about concentrations of microbial pollutants in rivers because (i) there is a seasonal monitoring focus for bathing water quality between May and September; and (ii) microbial survival at monitoring points is affected by environmental variables such as dilution and salinity.

Within river catchments, human faecal sources, such as sewage and urban storm water runoff, can introduce microbes of human health significance (e.g. Norovirus) in addition to FIOs. There are also rural diffuse source contributions of FIOs and zoonotic pathogens (e.g. *E. coli* O157 and *Cryptosporidium* spp.) from agricultural land (particularly from grazed pasture). The point-source contribution of human-derived microbial pollution is generally recognised as being easier to manage than the diffuse source contribution. Secondary and tertiary wastewater treatment has continued to provide opportunities for reduced microbial export from outflows, although effectiveness of treatment is reduced in high flows (Kay et al., 2008). However, CSO contributions of FIOs and other microbes of concern remain an issue (see Section 3.1). Increasing storminess, predicted as a result of climate change (e.g. Catto et al., 2019), may lead to more frequent CSO spills, to the detriment of microbial (and other) water quality.

Some catchment-wide data on FIOs are available as a result of targeted monitoring; for example, when a designated bathing water is at risk of not meeting regulatory standards, resulting in the contributing catchment being identified as a 'priority' for understanding FIO sources. In such cases, recent initiatives such as the CSF programme have facilitated more detailed fluvial monitoring to characterise FIO contributions. However, data are not long-term or nationally available. Furthermore, it is important to recognise that these datasets focus on microbial compliance parameters relevant to the BWD (i.e. FIOs) and not on specific pathogens of human health concern. Datasets on specific pathogen concentration in British rivers over time are even scarcer. Microbial quality of raw water at the intake of drinking water treatment plants will also be determined but in general the long-term evidence base of microbial water quality of British rivers is very limited.

4. Summary and perspectives

4.1. Summary

The spatial and temporal patterns of surface water pollution in Great Britain have changed markedly since the start of the Industrial Revolution (ca. 1760). These changes have been influenced by several major socio-economic and demographic developments, which can be seen as "drivers" for changes in pollutant emissions ("pressures"), resulting water quality ("states") and associated "impacts" on human and ecosystem health under the well-known DPSIR framework (Drivers, Pressures, State, Impact and Response: EEA, 1998).

Important drivers which have resulted in the deterioration of water quality over time include substantial population growth and urbanisation (leading to an increase in domestic wastewater emissions); increased wealth and consumer demand leading to industrial development (e.g. the construction of factories employing processes and manufacturing products which could potentially influence water quality, during and after use, and via associated direct wastewater emissions); the expansion of electrical power and an increase in energy demand, fuelled initially by coal, combined with coal- and petroleum-powered transport, which increased atmospheric acid deposition; an increased demand for agricultural products and need for food security which drove agricultural innovations and practices (e.g. mechanisation, new crop varieties, the conversion of significant areas of long-term pasture to arable land during World War II, the introduction of synthetic nitrogen fertilisers and organic pesticides in the post-war era, accompanied by an increased use of mineral fertiliser P, which probably all peaked in the 1980s).

Responses to water quality issues over the period of interest include the development of interceptor sewers in the mid-19th century (which concentrated sewage emissions in certain locations and which may have accentuated local water quality problems initially); the development of wastewater treatment in major cities in the early 20th century followed by major upgrades of wastewater treatment in the 1990s after the implementation of the EU UWWTD (resulting in a greater fraction of wastewater receiving secondary and tertiary treatment); legislation to limit SO_2 and NO_X emissions from power stations and vehicles causing acidification (e.g. EU directives 70/220/EEC and 72/306/EEC on transport, and 84/360/EEC and 88/609/EEC on industry); the EU Nitrates Directive which led to the establishment of NVZs and restrictions on the use of N fertiliser applications; phased removal of sodium tripolyphosphate as a builder in detergents from the mid-1990s, which reduced point-source phosphate loads; the introduction of more rigorous legislation on the authorisation of plant protection products (e.g. EU Directive 91/414 during the 1990s and, subsequently, Regulation 1107/2009); and the introduction of the WFD (EU Directive 2000/60/EC) which drove the adoption of a more holistic perspective of water quality in an ecological context. Current drivers influencing water quality include climate change which is influencing patterns of rainfall and runoff which, in turn, potentially affect wastewater discharge in relation to the capacity of sewerage infrastructure (and the frequency of CSO activation), diffuse-source transfers of N, P, pesticides, NOM and FIOs and the capacity of rivers to assimilate pollution.

Key features of spatio-temporal patterns in water quality in Great Britain (and in England and Wales, specifically) include:

- A decrease in the concentrations of sanitary determinands (BOD and ammonia) over the last 30 years in many locations, despite an increase in population. Concentrations are likely to have been highest in the early 20th century and to have decreased after the introduction and subsequent improvement of wastewater treatment. That said, over a third (36 %) of all failures to meet WFD Good Ecological Status in English rivers in 2019 cite wastewater pollution as a contributing factor (DEFRA, 2021b). Furthermore, while there have been improvements since the 1980s, the recovery of English rivers now appears to have plateaued, with local issues connected to sanitary determinands (e.g. due to CSO discharges) often reported in the media. Downstream of major cities, concentrations are probably lower now than at any time since the mid-19th century.
- A decrease in the concentrations of many metals since the 1980s. In general, concentrations are likely to be lower now than in the mid-20th century, although they locally still exceed effect thresholds. Furthermore, metal removal during wastewater treatment may result in high concentrations in sewage sludge — much of which is applied to land where metals can potentially cause issues of toxicity in soil and be lost to surface waters in runoff. In general, concentrations of metals are probably lower now than at any time since the early-20th century, but may not be lower than they were during much of the 19th century (with the exception of specific industrial sites) due to the increase in urban diffuse sources (e.g. associated with transport).
- Variable emissions of novel synthetic organic chemicals (including APIs) into surface waters (e.g. via treated wastewater, industrial effluents and CSOs). Most of these compounds did not exist before the late 20th century. In addition, the composition of the chemical mix in wastewater will be different now compared to the past, with different ecotoxicological effects. The incidence of these effects is likely to be local in both space and time — mostly under low flow conditions. It is not possible to compare current concentrations with any period before the late-20th century and, in any case, data for most of these substances, either individually or collectively are scarce. Overall, the concentrations and ecotoxicological effects of organic chemicals used in home and personal care products are probably lower now than they were in the 1970s and 1980s (due to a phase out of chemicals with poor environmental profiles). However, concentrations of many emerging pollutants (e.g. plastics, pharmaceuticals) may be rising due to increases in population, changing age profile and pharmaceutical consumption. In general, they are almost certainly higher now than they will have been during much of the early part of the period of interest.
- A decrease in the emission of biologically-available phosphate concentrations from urban point sources compared with the period 1960–2005, primarily due to the replacement of phosphate builders in detergents with alternatives (e.g. zeolite and polycarboxylates) and improvements in wastewater treatment (including the introduction of tertiary treatment) partly driven by responses to the UWWTD. Comparison with earlier periods is challenging but, given the increases in population over the period of interest, they are probably still worse now than they are likely to have been in the first half of the 19th century. High phosphate concentrations are still an issue for WFD compliance in many rivers. Some rural populations still rely on on-site treatment which may not be particularly effective for phosphate removal (Weiskel and Howes, 1992).
- A decrease in diffuse-source transfers of phosphate from a peak in the 1990s. This is, in part, a consequence of a realisation that legacy soil P stocks are able to meet some crop needs and also due to an increase in the cost of P-based fertiliser. The impact of these emission shifts on the quality of receiving water bodies depends on the relative contributions of point and diffuse sources. Legacy P levels are still high in many soils which could potentially maintain elevated diffuse-source P losses for several decades. In addition, P concentrations in some groundwater bodies are high which may elevate baseflow P concentrations in groundwater-dependent ecosystems. This suggests that concentrations in some rural catchments are still likely to be higher now than they were in the first half of the 20th century. Furthermore, high P concentrations in some lake sediments are likely to pose additional legacy issues in the near future, even where emissions have been reduced.
- A decrease in nitrate concentrations in many catchments compared to 20 years ago. However, in some catchments (e.g. those with long unsaturated zone residence times) peak concentrations may still occur in the future. For nitrate, water quality in most catchments with moderate-to-high agricultural activity is probably still worse now than at any time before the 1960s. The rate of improvement is likely to be hindered by an approximate steady-state in N management in intensive agriculture.
- An increase in synthetic pesticides now compared with the period before the 1950s. Since most synthetic pesticides were only developed in the latter half of the 20th century, it is reasonable to assume that pesticide pollution is a relatively modern phenomenon. Few data on measured pesticide concentrations are available before the 1980s. However, we do have some information on pesticide registrations and usage since the introduction of EU regulations. We can, therefore, speculate about associated transfers to surface waters. Like other synthetic organic pollutants, the palette of available chemistries has changed over the last few decades which makes interpretation of trends difficult. Lower concentrations do not necessarily mean lower ecotoxicological risk if the chemicals concerned have been replaced with ones which are more potent. In principle, the risk assessments employed in the pesticide registration process should prevent the use of pesticides with the potential to cause severe ecological damage in receiving environments. However, the extent to which this process is effective is uncertain because current monitoring efforts are limited. In the few catchments where monitoring is conducted, trends over recent years have been inconclusive and the situation across the country is uncertain. For pesticides, water quality now is definitely not better than at any time since the Industrial Revolution.
- A decrease in acid deposition since the early 1990s and an improvement in affected ecosystems (principally those with low acid-neutralising capacity) due to the introduction of flue gas desulphurisation at power stations, a phase-out of coal and the diffusion of catalytic converters on vehicles. That said, recovery may be undermined, to some extent, by increases in stream temperature and increased winter rainfall driven by global warming. Since acidification was driven by burning fossil fuels (mainly coal) it is likely to have had an increasingly important influence on water quality and ecosystem health since the start of the Industrial Revolution. The extent to which recent recovery compares with the mid

to late 19th century is still uncertain.

- An increase in DOC concentrations in some catchments over much of the 20th century, based on evidence from the long record for the Thames (Noacco et al., 2017). However, DOC concentrations appear to have been declining in general over the last 20 years (as evidenced in the average HMS data). Concentrations are still likely to be higher than at the end of the 19th century in many catchments. In upland catchments with organic soils, increases in DOC concentrations (with associated discolouration of stream water) have been observed in recent decades. These increases have been attributed variously to reduced acid deposition, moorland burning, artificial drainage and to more pronounced summer drying and winter re-wetting. In general, DOC concentrations are probably higher now than they were in the 19th century.
- A probable decrease in microbial pathogen levels in urban-affected rivers compared to much of the 19th century when rivers routinely received untreated wastewater. Data on microbial contamination (e.g. FIOs) in rivers are scarce. Diffuse-source transfers of FIOs to rivers can result from poor agricultural management. However, riverine contamination with raw sewage is now restricted to CSOs which should, in theory, be infrequent, although recent reports in the media suggest that emissions remain unacceptably high in some locations. On balance, microbial contamination overall is probably better now than it has been since the mid-19th century when interceptor sewers were built in many cities. In some locations, concentrations may be better now than at any time since the start of the Industrial Revolution.

We should note that our analysis of concentration data, where available, did not formally attempt to quantify trends in a statistical sense. This would require accounting for inter-annual variability in discharge (wet years and dry years) using flow-normalised concentrations (e.g. Hirsch et al., 2010) but is beyond the scope of the qualitative review presented here. That said, the geographical scale and record length of the HMS data, used to support many of the points we make, is such that these effects should not influence our overall conclusions.

4.2. Future perspectives

There are already indications that our climate is changing as a consequence of the increased concentrations of greenhouse gases in the atmosphere (e.g. Royal Society and US National Academy of Sciences, 2020; IPCC, 2021). Outputs from global and regional climate models suggest that this will result in a broadening of the frequency distribution of weather events and associated hydrological responses (i.e. an increase in extreme conditions — both wet and dry) in Great Britain (e.g. Reynard et al., 2017; Kay et al., 2021). This implies an increase in the expected frequency of high flow (flood) events which may increase diffuse-source pollutant loads and the frequency of CSOs, but which may otherwise decrease point-source concentrations at high flows due to dilution. Model predictions also suggest that the frequency of extreme low flows is likely to increase. This is likely to result in an increase in peak concentrations in rivers for pollutants that derive from wastewater and may drive increased fluxes for some urban diffuse-source pollutants as a consequence of the often-observed post-drought "flush" (e.g. Woodward et al., 2016). In addition to hydrologically-driven changes in pollutant exposure, increases in stream temperature may have impacts on species survival (local extinctions from climate change have already been reported – e.g. Durance and Ormerod, 2010), population viability (e.g. there is a current decline in salmonids – Clews et al., 2010) and the sustainability of ensuing ecosystem services such as angling (e.g. Worthington et al., 2020). Some of these effects may be interactive. A major challenge in the near future is to reduce reliance on CSOs which continue to create local water quality problems which may pose human and ecosystem health risks. This will require water company investment but could also be helped by changes to local planning rules and by reducing the sources of sewer blockage (e.g. the use of wet wipes and the emission of fat, oil and grease to the sewer system) which will need behavioural change or new regulations. Reductions in domestic water use may also contribute to lower wastewater discharge to both treatment plants and CSOs.

4.3. Monitoring

Historically, Great Britain has been relatively well served by a network of hydrometric and water quality sampling stations. Much of the data collected are publicly available via the National River Flow Archive (https://nrfa.ceh.ac.uk/) for discharge and (in England) the Environment Agency's Water Information Management System (https://environment.data.gov.uk/water-quality/) for water quality. However, in recent years, monitoring at many stations has been discontinued. Since the detection of change is usually only possible using long-term data (Burt et al., 2008; Howden et al., 2011b), these closures represent a major erosion of the national capacity to understand the controls on water quality and the direction and magnitude of any changes occurring. There is, therefore, a clear need to halt and reverse station closure and/or to invest additional resources in a modern and extensive monitoring network. Where resources are constrained, there is also a need to deploy available resources more effectively, although overall sampling density should be maintained at a level that provides a comprehensive understanding of status and trends. Moreover, there are increasing opportunities to harness: (i) the cheap capability of Earth Observation to monitor determinands with strong spectral signals, such as chlorophyll and DOC, particularly for large water bodies; (ii) digital innovations such as the Internet of Things to relay near real-time data from distributed sensors; (iii) advances in big data and computing power that may allow data gaps to be bridged and sampling efficiency to be optimised; (iv) improved analytical methods including in-situ sensors and high-throughput laboratory instruments; (v) novel next-generation molecular advances that could allow simultaneous detection of both biological and chemical states of surface waters; and (vi) the mobilisation of appropriately designed citizen science. Similarly, for water quality monitoring, there are existing monitoring sites that are not sited optimally for providing good information, so there is scope for rationalising the monitoring network. In general, the total number of monitoring sites is insufficient and in decline. The introduction of new sampling and analytical methods also requires inter-calibration periods to ensure that long term trends can be detected reliably. In summary, with proportionate investment, there is a need and an opportunity for investment to ensure that water quality monitoring in British rivers transitions from an approach developed primarily in the 20th century, to one that is fit for the strategic challenges of the 21st century.

5. Conclusions: are rivers in Great Britain cleaner now than at any time since the Industrial Revolution?

So, is it right to assert that British, English or Welsh rivers are now "cleaner" than *at any time since the Industrial Revolution*? In this paper, we have looked across a wide range of pollutants including sanitary determinands, heavy metals, synthetic organic contaminants (pharmaceutical and personal care product ingredients and pesticides), macronutrients (N and P), natural organic matter and faecal indicator organisms. These pollutants, individually and collectively, affect river condition, ecosystem status and function. Most water quality monitoring records do not go back more than about 40 years. Comparison between current water quality and that before the implementation of widespread monitoring is, therefore, challenging. This in itself means that such a definitive statement about rivers being cleaner than the start (or end) of the Industrial Revolution is difficult to defend.

Nevertheless, we have used expert judgement of the historical variations in the *drivers* of water pollution to infer speculatively about general patterns, corroborated by the small number of longer-term records (e.g. for the River Thames). We assigned a score between 0 and 2 to two questions for each pollutant considered in the paper: are concentrations of the pollutant likely to be higher now than (i) at the end of the Industrial Revolution (nominally 1840) and (ii) peak monitored concentrations (typically

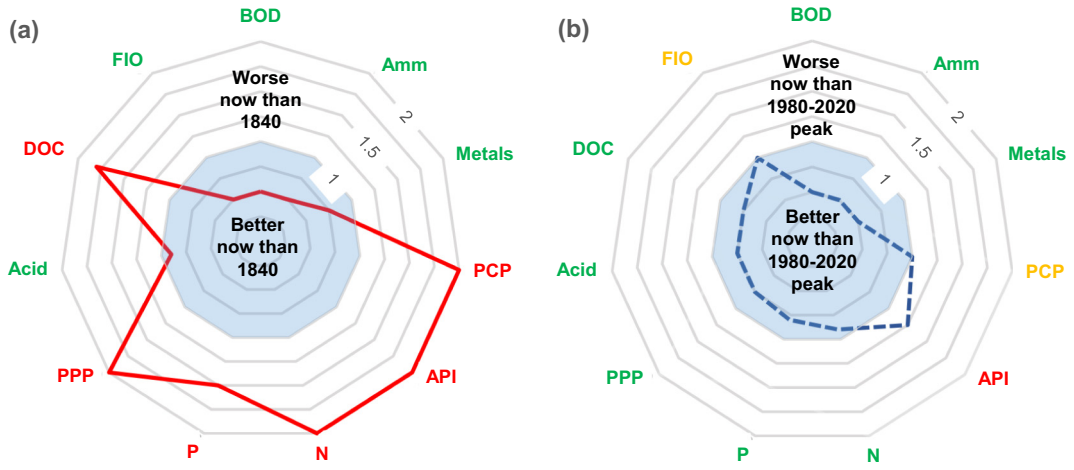

Fig. 11. A schematic illustration of whether, based on the available evidence, current concentrations of the pollution categories considered in this review are higher (worse — red text), lower (better — green text) or about the same (amber text) compared with two benchmarks: (a) any time since 1840 (nominally the end of the Industrial Revolution — red solid line) and (b) the highest levels indicated by recent monitoring (dashed blue line). The solid blue area indicates the benchmark of ≤1 (either the estimated maximum industrial revolution levels or maximum annual average data derived from recent monitoring). Vertices lying within the blue area indicate improved water quality compared to the benchmark (values <1), whilst those outside indicate poorer water quality (values >1). PCP is personal care products; API is active pharmaceutical ingredients; PPP is plant protection products; FIO is faecal indicator organisms; DOC is dissolved organic carbon; Amm is ammonia; BOD is biochemical oxygen demand; Acid is catchment acidification.

after 1980, where measured)? A score of 1 implies that concentrations are similar now, compared to the reference point. Scores <1 and >1 imply that concentrations are, respectively, lower and higher now compared to the reference point. These inferences are summarised in Fig. 11. They suggest that some river reaches (e.g. downstream of major urban areas) have concentrations of some pollutants (e.g. sanitary determinands and FIOs) which are lower now than at any time since the mid-19th century (vertices on the red line in Fig. 11a are within the blue area suggesting that the nominal score is <1). However, diffuse pollution in urban areas (e.g. from the prolific increase in motor vehicle use and the expansion of impermeable surfaces) is likely to be higher now than in the pre-monitoring era (nominal score > 1 with vertex outside the blue area). Diffuse-source pollution of macronutrients for many rivers with catchments dominated by intensive agriculture is also likely to be higher now than it has been historically. Nevertheless, we acknowledge that concentrations of some of these pollutants are probably lower now, in general, than at the highest point in the monitored record, largely as a result of legislation, such as the EU Urban Waste Water Treatment Directive, the Nitrates Directive and the Water Framework Directive. On the other hand, for some variables, typical current concentrations often still exceed their historical monitored lows (vertices on the dashed blue line in Fig. 11b are outside the blue area) and, for others, progress appears to have levelled off.

Importantly, many rivers currently fail to achieve Good Ecological Status under the WFD due to poor water quality. Furthermore, British rivers are now exposed to a number of novel (emerging) contaminants (including pesticides, pharmaceuticals and industrial chemicals) which were simply not present for most of the period since the Industrial Revolution. Many of these novel pollutants have not been monitored comprehensively. However, the limited data that are available suggest some may be present periodically in some places at or near concentrations that are likely to have ecological impacts. In light of this overall assessment, our conclusion is that, while good progress has been made in reducing some pollutants over the past three decades, the picture is mixed and the scientific evidence does not comprehensively support claims that British rivers are "cleaner now than at any time since the Industrial Revolution".

Framing current water quality in a historical context is useful as a measure of the extent to which the general situation has improved or deteriorated. However, it is, perhaps, more helpful for ministers and government officials to, instead, be asking whether rivers are currently fit for purpose and whether we can make them more resilient to future pressures (e.g. from climate change, new types of pollution, physical modification and increased abstraction pressures). Although populations of many taxa have improved in recent decades, according to the Environment Agency and Natural England (2021), only 14 % of rivers in England and Wales currently reach Good Ecological Status overall (although this partly reflects the "one out, all out" nature of the WFD classification system). Only 45 % of rivers in England currently meet Good status for phosphorus and none meet the criteria for Good Chemical Status (although 93 % are good if ubiquitous, persistent, bio-accumulative and toxic substances are excluded). Further improvements in water quality are urgently required in many rivers and streams and targeted enhancements in water quality monitoring are needed (e.g. increased frequency and geographical cover of sampling and the range of pollutants monitored) in order to understand the drivers and potential impacts of pollution with confidence and to implement effective interventions. The additional costs incurred from such enhancements should be justified in terms of the ecosystem services which clean rivers deliver. River ecosystems are typically affected by multiple stressors which include artificial influences on flow regime, the introduction of invasive species and habitat modification as well as impaired water quality. In order to understand and effectively manage ecosystems we need to understand trends in individual pollutants in the context of all potential stressors. Future monitoring regimes and policy positions need to respond to emerging science on this issue.

CRediT authorship contribution statement

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Howden: Writing – original draft, Writing – review & editing, Investigation, Data curation. **T.P. Burt:** Writing – original draft, Writing – review & editing, Investigation, Data curation. **A. Boxall:** Writing – original draft, Writing – review & editing, Investigation, Data curation. **C.D. Brown:** Writing – original draft, Writing – review & editing, Investigation, Data curation. **D.M. Oliver:** Conceptualization, Writing – original draft, Writing – review & editing, Investigation, Data curation. **D. Tickner:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing, Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was initiated and facilitated by WWF via two workshops held in London. Andrew Johnson is grateful to funding from NERC grant NE/S000100/1 for the ChemPop project which has supported his contribution. We are grateful to Monika Juergens from CEH for supplying the data for Fig. 1. We also thank three anonymous reviewers for making constructive suggestions on the paper.

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