SUPPLEMENTARY INFORMATION

A 150-year river water quality record shows reductions in phosphorus loads but not in algal growth potential.

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Supplementary Notes: The origins of the 150-year River Thames water quality dataset

Water-quality monitoring began in 1868, ten years after the "Great Stink" of 1858, when the City of London and the Houses of Parliament came to a standstill during the summer, as a result of the overwhelming stench from untreated sewage that was flowing unimpeded into the tidal reaches of the River Thames, from a rapidly growing urban population[1]. The widespread adoption of the water closet in the 1800s meant that human waste no longer collected in cesspools, but was transmitted from houses, via sewers, directly into the River Thames. Although this improved living conditions in homes, it led to heavy contamination of the tidal River Thames. Waterborne diseases, including cholera, were rife, because the tidal River Thames was the major source of London's domestic water supply[2]. By the 1850s, action had to be taken to address the pollution of the River Thames. In 1852, Parliament passed the Metropolis Water Act to develop a cleaner supply of drinking water to the population of London and, in 1855, the Metropolitan Board of Works was established, with a goal to develop a sewerage system to collect domestic wastewater before it entered the Thames, pioneered by chief engineer Joseph Bazalgette[1]. After 1855, it became unlawful for any water company to extract water for domestic use from the tidal reaches of the Thames. New water intakes and water treatment plants were developed upstream of the tidal limit (Teddington Lock) and, with these developments, there was a requirement to measure the water quality of the inflow river water[3]. Accordingly, river water-quality monitoring began on the River Thames at Teddington in 1868[4,5] (see "Methods"). Monitoring at this location has continued since 1868 to the present day, making it the longest continuous river water quality record in the world[4,5].

Supplementary Figures

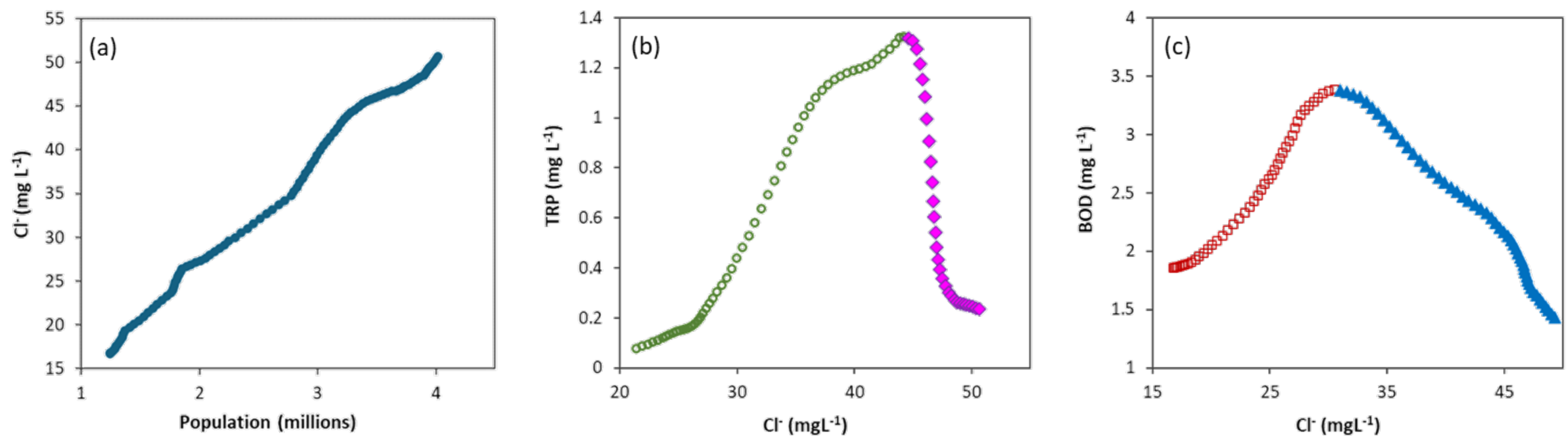

Figure S1: Scatterplots showing the relationships between: (a) chloride (Cl^-) Loess trend data (see manuscript Figure 1) and the population of the Thames catchment, from 1920 to 2020; (b) total reactive phosphorus (TRP) and Cl^- Loess trend data: from 1936 to 1990 (green open circles), and from 1991 to 2020 (closed pink diamonds); (c) biological oxygen demand (BOD) and Cl^- Loess trend data: from 1886 to 1963 (red open squares), and from 1964 to 2015 (blue closed triangles).

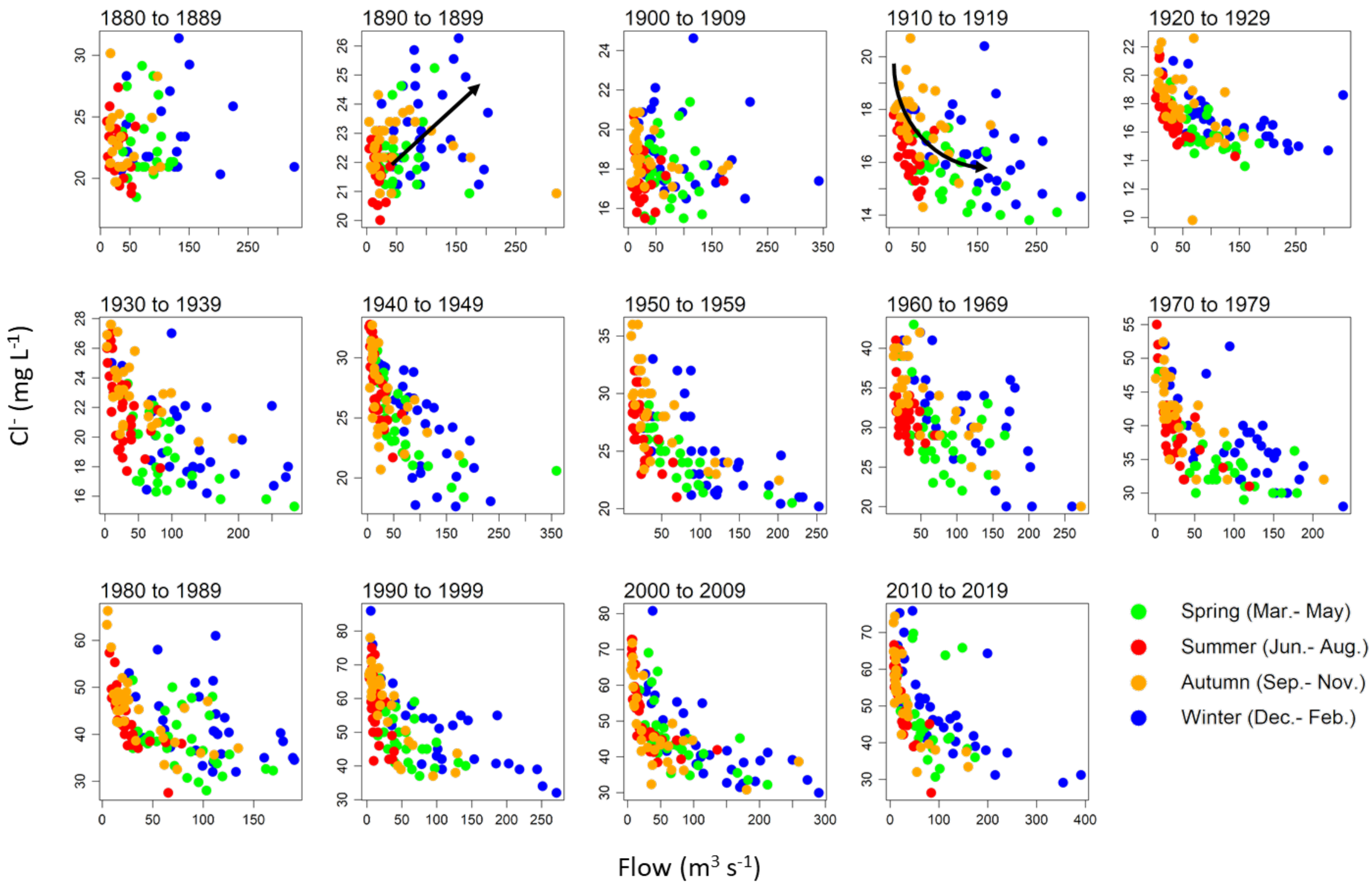

Figure S2a: Scatterplots showing the relationships between chloride (Cl^-; mgL^{-1}) concentration and flow ($m^3 s^{-1}$) in the River Thames, by decade, from the 1880s to the 2010s. Colours denote the season of sampling. The black arrows denote major patterns in flow dependency: from increases in concentration with increasing flow, to dilution with increasing flow

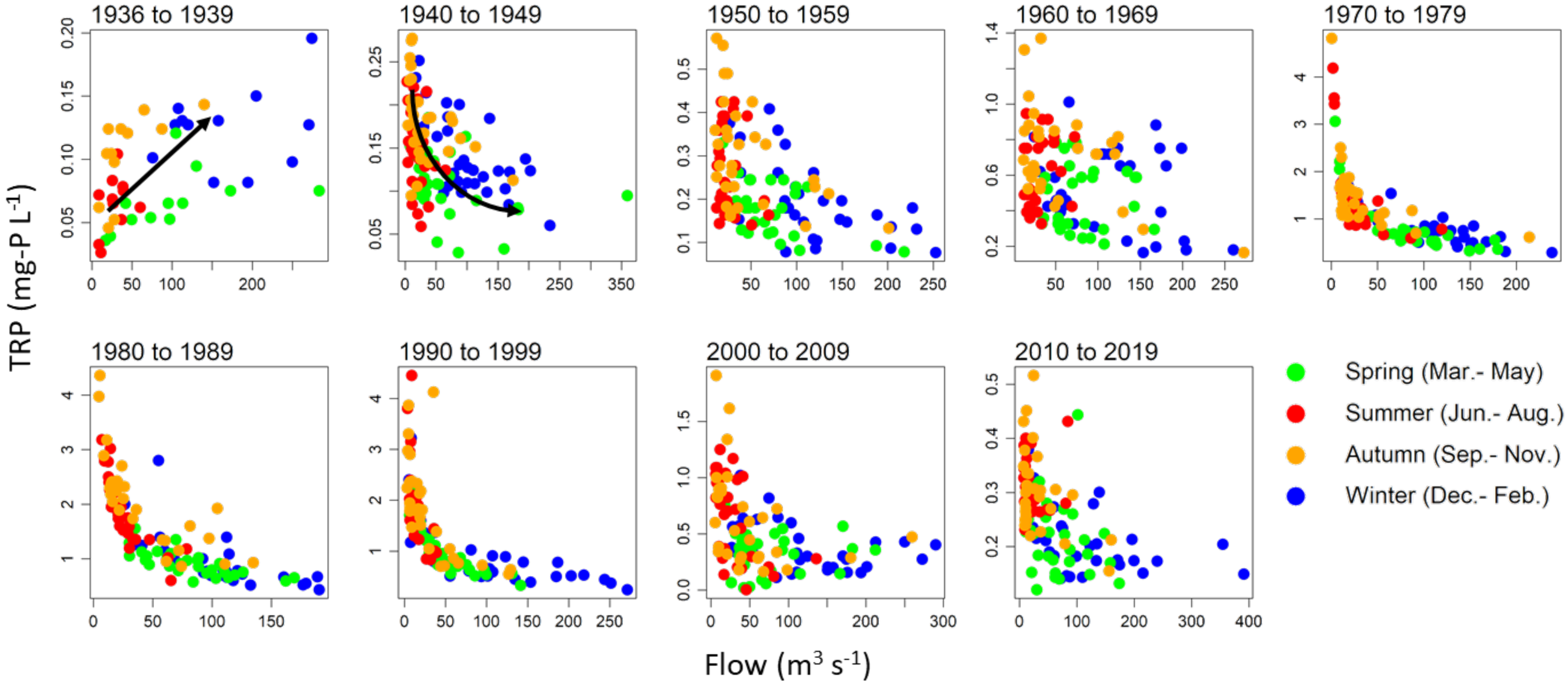

Figure S2b: Scatterplots showing the relationships between total reactive phosphorus (TRP; mg L^{-1}) concentration and flow ($m^3 s^{-1}$) in the River Thames, by decade, from the 1930s to the 2010s. Colours denote the season of sampling. The black arrows denote major patterns in flow dependency: from increases in concentration with increasing flow, to dilution with increasing flow

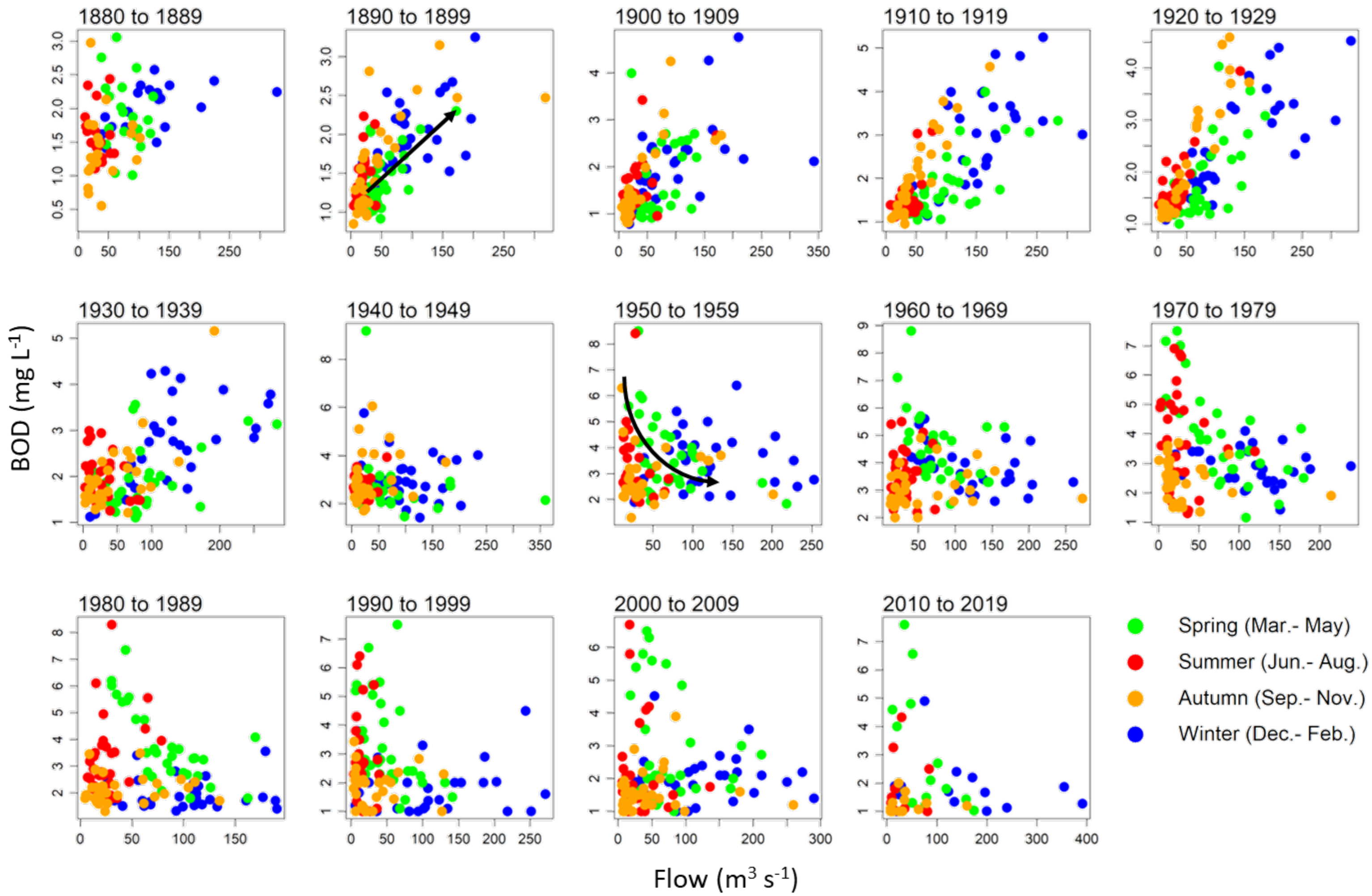

Figure S2c: Scatterplots showing the relationships between biological oxygen demand (BOD; mg L^{-1}) and flow ($m^3 s^{-1}$) in the River Thames, by decade, from the 1880s to the 2010s. Colours denote the season of sampling. The black arrows denote patterns in flow dependency: from increases in concentration with increasing flow, to dilution with increasing flow

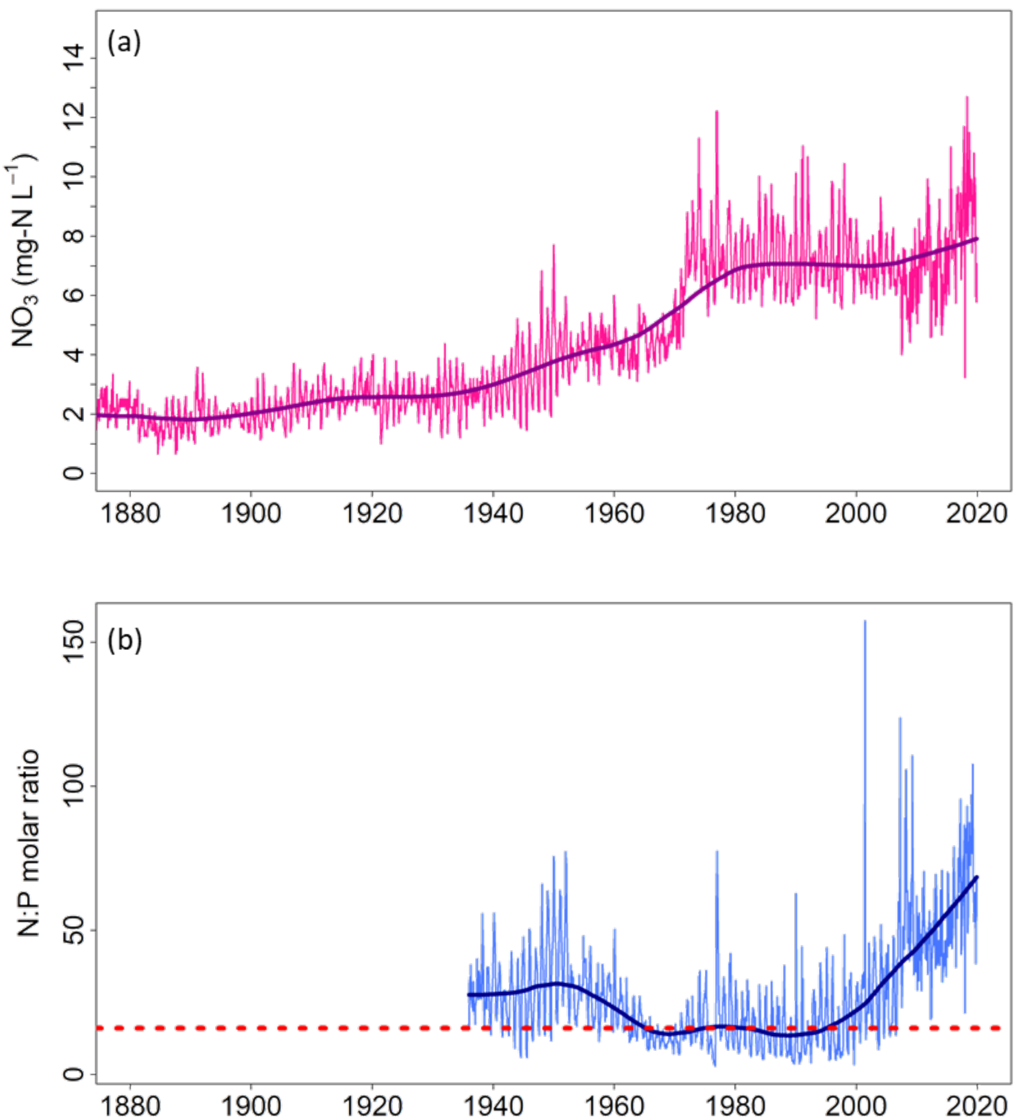

Figure S3: Time-series showing (a) nitrate; and (b) N:P molar ratios (NO_3-N:TRP) in the River Thames at Teddington (1868-2020). The dashed red line denotes the Redfield N:P molar ratio of 16:1 (see text). Loess trend lines are show for both timeseries. For a discussion of the nitrate timeseries, see Howden et al (2010)[4] and Worrall et al (2015)[5].

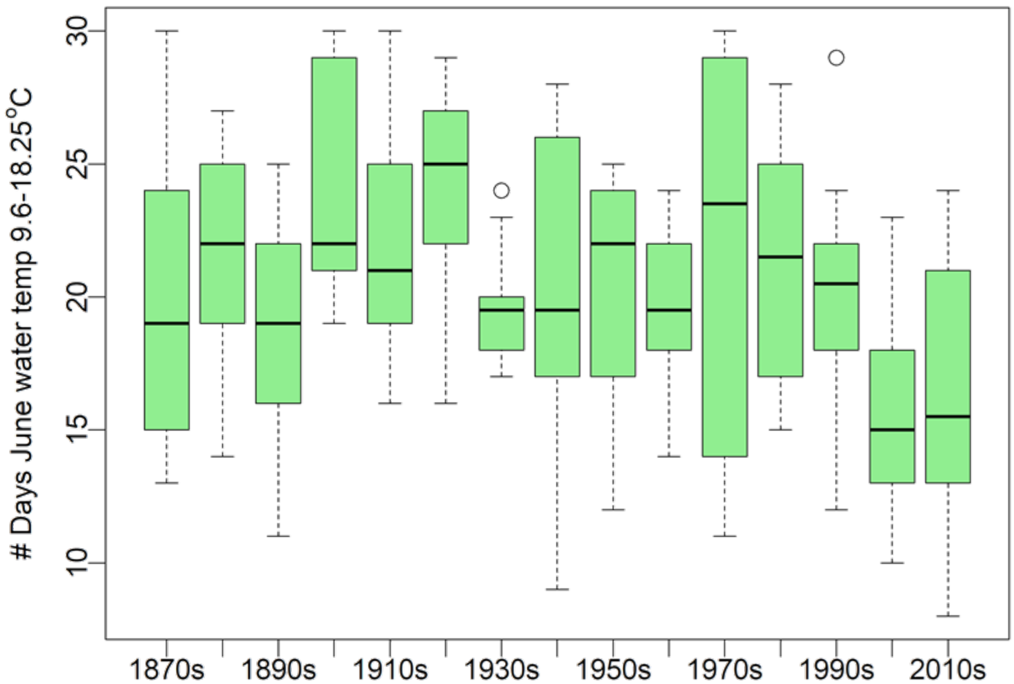

Figure S4: Boxplot showing the number of days from June 1st through June 30th, when water temperatures were within the ecological range favourable for diatom blooms (9.6-18.25°C; see text for details), for each decade from the 1870s to the 2010s. Boxplot elements: centre line, median; box limits, upper and lower quartiles; whiskers, 1.5 x interquartile range; points, outliers.

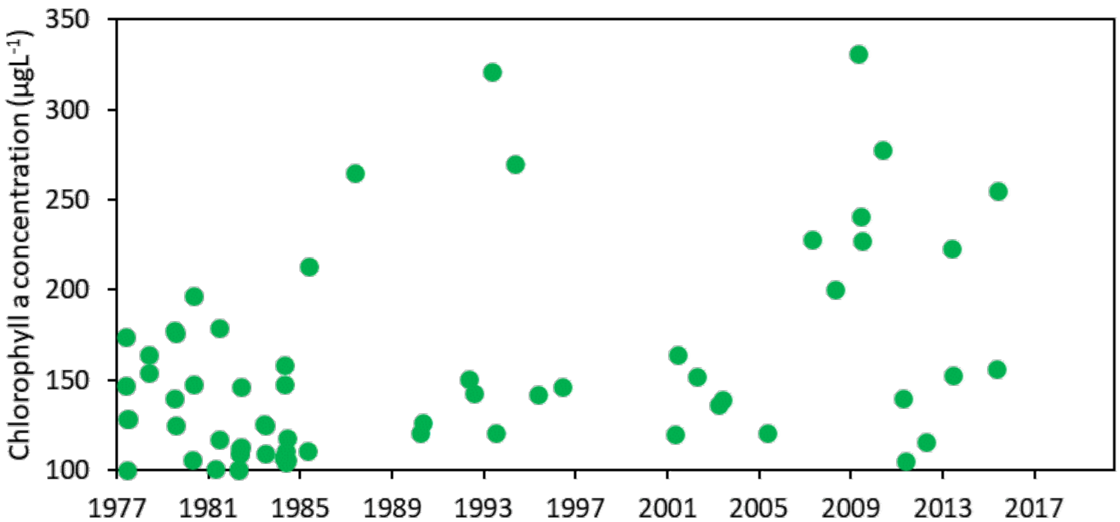

Figure S5: Chlorophyll-a concentrations exceeding the 100 μg L^{-1} threshold for the onset of algal blooms[6] in the lower River Thames from 1977 to 2019. Note: only concentrations above 100 μg L^{-1} are presented here, and care must be taken in use and interpretation of these data, because sampling frequency varied (and was more frequent than monthly in the late 1970s and early 1980s) with a gap in data collection from 1987 to 1990. This figure is provided as supporting evidence: demonstrating that algal blooms of >100 μg L^{-1} occurred across the entire timeseries of chlorophyll-a measurements, and that some of the highest chlorophyll-a concentrations occurred after 2005, when P loads were ~80% lower than in the 1980s. The SiO_2 timeseries (Figure 5b) also showed silica depletion indicative of intense diatom blooms after 2005 and, taken together, the SiO_2 and chlorophyll-a data indicate that the reductions in P loads and concentrations, to date, have not yet been sufficient to limit algal blooms in the lower River Thames at Teddington.

Supplementary Tables

Table S1: Biological Oxygen Demand (BOD)		
Method	Reference	Monitoring organisation
(i) 'Oxygen absorbed' method (potassium permanganate test)	Thresh (1904)[7]; Thresh et al. (1943, 1949)[8,9]; Hamlin (1990)[10]	Grand Junction Water Company (1868–1901); London Metropolitan Water Board (1902– 1950)
(ii) Biochemical oxygen demand (BOD)	Royal Commission on Sewage Disposal (1908)[11]; Methods for the Examination of Waters and Associated Materials (1981, 1988)[12,13]; Jouanneau et al (2014).[14]	London Metropolitan Water Board (1908– 1977); Thames Water Authority (1978–1988); National Rivers Authority (1989–1996); Environment Agency of England & Wales (1996-2020).

Table S1: Methods used for analysis of biological oxygen demand (BOD) in the River Thames (1868-2020).

Table S2: Chloride (Cl^-)		
Method	Reference	Monitoring organisation
(i) Silver nitrate titration with potassium chromate indicator; Potentiometric titration with silver nitrate.	Thresh (1904)[7], Thresh et al. (1943, 1949).[8,9]	Grand Junction Water Company (1868–1901); London Metropolitan Water Board (1902– 1950)
(ii) Automated segmented mercuric-ferric thiocyanate colorimetry (using air-segmented continuous flow autoanalyzers).	Methods for the Examination of Waters and Associated Materials (1981)[15].	London Metropolitan Water Board (1950– 1977); Thames Water Authority (1978–1988); National Rivers Authority (1989–1996); Environment Agency of England & Wales (1996-2020).
(iii) Ion chromatography	Methods for the Examination of Waters and Associated Materials (1981)[15].	Thames Water Authority (1978–1988); National Rivers Authority (1989–1996); Environment Agency of England & Wales (1996-2020).

Table S2: Methods used for analysis of chloride (Cl^-) concentrations in the River Thames (1868-2020).

Table S3: Total Reactive Phosphorus (TRP)		
Method	Reference	Monitoring organisation
(i) Colorimetric determination of phosphate, by formation of a reduced phosphomolybdenum blue complex, based on the Tschopp and Denigés methods. Colour match using standard colour solutions.	Denigés (1920)[16]; Tschopp and Tschopp (1932)[17]; Thresh et al (1943, 1949)[8,9].	London Metropolitan Water Board (1936–1950)
(ii) Reaction with acidic molybdate reagents to form a reduced phosphomolybdenum blue complex whose concentration is measured spectrophotometrically. Later using the same colorimetric method, but automated using air-segmented continuous flow autoanalyzers.	Methods for the Examination of Waters and Associated Materials (1980)[18]; Murphy and Riley (1962)[19]; Popovsky (1970)[20].	London Metropolitan Water Board (1950–1977); Thames Water Authority (1978–1988); National Rivers Authority (1989–1996); Environment Agency of England & Wales (1996-2020).

Table S3: Methods used for analysis of total reactive phosphorus (TRP) concentrations in the River Thames (1936-2020).

Table S4: Silica (SiO_2)		
Method	Reference	Monitoring organisation
(i) Gravimetric determination following dehydration with concentrated HCl, followed by filtering, washing the residue with hot water acidulated with HCl, and finally igniting and then weighing the silica residue.	Thresh (1904)[7]	London Metropolitan Water Board (1936–1950).
(ii) Colorimetric determination, based on the formation of a silicomolybdenum blue complex, whose concentration is measured spectrophotometrically, later using automated air-segmented continuous flow autoanalyzers.	Thresh et al. (1949)[9]; Diénart and Wandenbulke (1923)[21]; Methods for the Examination of Waters and Associated Materials (1992)[22]	London Metropolitan Water Board (1950–1977); Thames Water Authority (1978–1988); National Rivers Authority (1989–1996); Environment Agency of England & Wales (1996-2020).

Table S4: Methods used for analysis of silica (SiO_2) concentrations in the River Thames (1936-2020).

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