



Eutrophication mitigation in rivers

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Eutrophication mitigation in rivers: 30 years of trends and seasonality changes in biogeochemistry of the Loire River (1980–2012)

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Abstract

Trends and seasonality analysis since 1980 and longitudinal distribution from headwaters to estuary of algal pigment, nitrate and phosphate were investigated in the eutrophic Loire River. The continuous decline of phosphate concentrations recorded since 1991 both in the main river and in the tributaries led to a significant reduction in algal biomass across the whole river system. While eutrophication remained lower in the main tributaries than in the Loire itself, they were found to contribute up to 45 % to the total nutrient load of the main river. The seasonality analysis revealed that the river has always been under P limitation, explaining why reducing P inputs led to decreasing eutrophication in the whole Loire basin. The decline of seasonal amplitudes of algal pigments reduced the seasonal amplitude of phosphate and of daily variations of dissolved oxygen and pH but did not significantly affect the seasonal amplitude of nitrate. Thus, algal uptake responsibility on the summer nitrate loss seemed to be declining, questioning the exact role played by denitrification, terrestrial vegetation and fixed aquatic vegetation on the nitrogen cycle.

1 Introduction

For several decades, eutrophication has become a major issue affecting most surface waters (Smith et al., 1999; Hilton et al., 2006; Smith and Schindler, 2009; Grizzetti et al., 2012; Romero et al., 2012). The regulation of nutrient inputs in waters by the elimination of N and P during waste-water treatment, better agricultural practices and restriction of the use of phosphorus products (EEC, 1991a, b) led to a decrease in phosphate and/or nitrate content which is recorded in several European rivers presenting temperate and continental regimes since the mid-1990s, including the Elbe (Lehmann and Rode, 2001), the Seine (Billen et al., 2007), the Thames (Howden et al., 2010), the Danube (Istvánovics and Honti, 2012), the Rhine (Hartmann et al., 2007) as well as some Mediterranean rivers (Ludwig et al., 2009).

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Surface water quality is also affected by variations in hydro-climatic conditions (Durance and Ormerod, 2010). In Europe, both climatic models and observations show a general rise in air and water temperature since the 1970s (Moatar and Gailhard, 2006; Whitehead et al., 2009; Bustillo et al., 2013). Models predict lower water discharge and rising temperatures during summer, potentially intensifying the risk of eutrophication (Lecerf et al., 2007; Bärlocher et al., 2008). Besides, algal biomass remains at a high level in many water bodies, evidencing that leaching of long last stored nutrient in soils is still significant: if nutrient mobility should increase with global warming because of the acceleration of organic matter mineralization and of higher soil leaching (Bouraoui et al., 2002), the river system response time to a nitrogen input reduction is limited by the time required for nitrate to be released from soil to receiving waters (Jackson et al., 2008; Bouraoui and Grizzetti, 2011). Therefore we should expect that changes in current agricultural practices may improve water quality only after several decades (Behrendt et al., 2002; Howden et al., 2010).

The first regulatory studies of the largest French river eutrophication, i.e. the Loire River, were made in the 1980s in the Middle and Lower segments (Crouzet, 1983; Meybeck et al., 1988; Lair and Reyes-Marchant, 1997; Etcheber et al., 2007). The Middle reaches (Fig. 1) were recognized as being the most eutrophic sector (Lair and Reyes-Marchant, 1997) resulting from high P levels (Floury et al., 2012), low river velocity and shallow waters. In recent years, Loire eutrophication indicators and their trends recorded several variations: (i) decline of pigments in the Middle segment since the late 1990s (Floury et al., 2012), (ii) decline of phosphorus as well in the Middle Loire (Gosse et al., 1990; Moatar and Meybeck, 2005), (iii) development of *Corbicula fluminea* as an invasive species since the 1990s (Brancotte and Vincent, 2002) and (iv) dominance of small centric diatoms and green algae in phytoplankton population, for most of the year in the Middle and Lower river sectors (Abonyi et al., 2012, 2014; Descy et al., 2011).

Most previous studies focused on the Middle Loire, which represents only 25 % of the total drainage basin and excluded the main tributaries and their possible influences on

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the main river course. Besides, most studies on river eutrophication stayed at the inter-annual variations and did not investigate how long term trends might affect the river biogeochemistry at the seasonal or the daily scale, while seasonal and daily cycles are especially amplified in eutrophic rivers (Moatar et al., 2009). This paper examines longitudinal distributions and long-time trends of algal pigments and nutrients over three decades (1980–2012) and for the whole Loire basin. Thus, it includes the study of the main tributaries variations and their potential influences on the Loire main stem. It also focuses on how the noticeable long term changes affected the biogeochemical functioning of the river at the seasonal scale, exploring the seasonal variations of algal pigments and nutrients since 1980 and examining both seasonal and daily fluctuations of dissolved oxygen and pH since 1990.

2 Study area and data compilation

2.1 Geographical and physical characteristics

The Loire River basin (110 000 km²) covers 20 % of the French territory. Its hydrological regime is pluvial with some snow-melt influences because of high headwater elevation (6 % of the basin area is over 800 m a.s.l.). The main stem can be divided into three parts (Fig. 1, Table 1): (i) the Upper Loire (18 % of basin area; stations 1 to 9) extending from the headwaters to the confluence with the River Allier, (ii) the Middle Loire (24 %; stations 10 to 18) from the Loire–Allier confluence to the Loire–Cher confluence which receives only minor inputs from small tributaries, (iii) the Lower Loire (65 %; stations 19 to 21) which receives major tributaries (Cher, Indre, Vienne and Maine Rivers) doubling the river basin area and the average river water discharge.

As summer low flows can reach critically low levels in the Middle reaches where four nuclear power plants are located (Fig. 1), two dams were constructed on the Allier and Upper Loire (Naussac, 1981 and Villerest, 1984) to maintain low flows over a minimum of 60 m³ s⁻¹. Grangent dam was constructed in 1957 for electricity

production purposes. The median annual discharge over the last 30 years is $850 \text{ m}^3 \text{ s}^{-1}$ at the basin outlet (station 21) and the median in the driest period from July to September is only $250 \text{ m}^3 \text{ s}^{-1}$, corresponding to only $2 \text{ L s}^{-1} \text{ km}^{-2}$. The driest years were 1990, 1991, 2003 and 2011 with a daily discharge average at station 21 reaching sometimes $100 \text{ m}^3 \text{ s}^{-1}$.

The headwater catchment is a mountainous area and the Loire itself runs through narrow gorges and valleys (Latapie, 2011). After the confluence with the Allier, the geomorphology of the Middle Loire favors phytoplankton development, its multiple channels with numerous vegetated islands slowing down flow velocity and the valleys becoming wider (Latapie et al., 2014). As a consequence, average water depth can be low in the summer ($\approx 1 \text{ m}$), contributing to warming and lighting up the water column.

The temperature is always at least 2°C lower in the Upper part than in the lower reaches (annual medians are around 15°C in the Upper Loire during April–October vs. 19°C in the Middle and Lower segments) and is affected by global warming. Hence, Moatar and Gailhard (2006) showed that mean water temperature has increased by 2.4 to 3°C in spring and summer since 1975 due to rising air temperature (Gosse et al., 2008) without a significant impact on algal development (Floury et al., 2012). This general rise in water temperature during the warm period has been accompanied by a 40 % decrease in the May/June river discharge since 1977 (Moatar and Gailhard, 2006; Floury et al., 2012). The water returning to the Loire from the nuclear power plants only raises the temperature by a few tenths of a degree thanks to an atmospheric cooling system (Vicaud, 2008) and does not influence the thermal regime of the river studied here.

Urban pressure is significant with 8 million people living in the Loire Basin (2008 population census by INSEE), mainly concentrated near the main river course. It corresponds to an overall population density of $73 \text{ inhab. km}^{-2}$. The density is greater in the Upper Loire ($144 \text{ inhab. km}^{-2}$, Table 1) due to the city of Saint Etienne (180 000 inhab.). The Middle and Lower catchments contain some major riparian cities (Fig. 1) with a stable population density around $76 \text{ inhab. km}^{-2}$.

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Agricultural pressure is defined here with two indicators: the percentage of the basin occupied by arable land and the agricultural pressure indicator (API) represented as the quotient of (pasture + forest) over (pasture + forest + arable land). According to the Corine Land Cover database (2006), the headwater areas are mostly forested (75 %) or pastureland (24 %). Arable land accounts for only 6 % of the Upper catchment area (Table 1) but increases downstream to reach 30 % of the total basin area at station 21. API decreases continuously from 99 % at the headwaters (no arable land) to 70 % at station 21 (42 % pasture, 24 % forest, 30 % arable land). Land use distribution in the major tributaries differs widely (Table 2): the Allier (catchment at station A) is mostly composed of pasture (47 %), API = 87 %; the Cher at station B has similar amounts of pasture and arable land (respectively 39 and 36 %), most of the rest being forested (23 %); half of the Indre basin at station C is arable land, but this tributary drains only 3 % of the total basin; the Vienne and the Maine contribute very significantly to the total area of arable land in the Loire basin (arable land accounts for 25 % of the Vienne catchment, API = 74 and 49 % of the Maine catchment, API = 50 %). Urban pressure is also significant in the Maine catchment (82 inhab. km⁻²) due to the cities of Le Mans and Angers (Fig. 1).

2.2 River monitoring datasets

Water quality databases from regulatory surveys (AELB) used here (chlorophyll *a*, pheopigments, nitrate (NO₃⁻), orthophosphate (PO₄³⁻)) are available online on the OSUR website (<http://osur.eau-loire-bretagne.fr/exportosur/Accueil>). Sixty-nine monitoring stations were set up along an 895 km stretch. Stations sampled at least monthly between 1980 and 2012 (bi-monthly or weekly for some variables) were selected for analysis in this paper (17 stations, Fig. 1). To take into account the influence of major tributaries, five sampling sites at each of the major tributary outlets were also included (stations A to E).

The water quality of the Loire River has also been assessed during several other surveys, generally with high sampling frequency, but these data have seldom been used and/or compared in previous studies. They included:

1. Water quality surveys upstream and downstream of nuclear power plants carried out since the early 1980s by the French Electricity Company (EDF) (Moatar and Gailhard, 2006; Moatar and Meybeck, 2007); see stations 12, 14, 16 and 19 on Fig. 1. These datasets were used to improve the spatial analysis. These surveys included temperature, dissolved oxygen and pH recorded hourly at station 19 enabling us to analyze possible changes in day/night amplitude (variables hereafter named delta O₂ and delta pH).
2. The Orléans city experimental survey carried out by the Loire basin authority (AELB) at station 15 from 1981 to 1985, measuring nutrients and chlorophyll *a* every three days (Crouzet, 1983; Moatar and Meybeck, 2005).

River flow datasets on a daily basis were taken from the national “Banque Hydro” database (<http://www.hydro.eaufrance.fr/>). The local population census (INSEE, 2008) and the Corine Land Cover (2006) were also used to estimate the general characteristics at different water quality stations (Tables 1 and 2).

3 Methods

3.1 Data pre-processing

To validate the AELB datasets and eliminate remaining outliers, log–log relationships between concentration and discharge were analyzed and compared with previous research studies carried out during targeted periods (Grosbois et al., 2001; Moatar and Meybeck, 2005). The separation of living algal biomass (characterized by chlorophyll *a*) and algal detritus (characterized by pheopigments) depends on the protocol used and since this protocol may have changed over the last 30 years, we worked with



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total pigments (chlorophyll *a* + pheopigments), which increased the robustness of the data and corresponded better to algal biomass as an active biomass and organic detritus (Dessery et al., 1984; Meybeck et al., 1988). PO_4^{3-} time series included periods reaching the limit of quantification. When evidenced, such data were not taken into account to avoid mis-interpretation of such constant values. The datasets also included periods with missing values. In all cases, no infilling were realized. Sampling frequencies were most of the time monthly (only 10 % of datasets were sampled on average every two weeks or more often), but in order to homogenize the time series, the rest of the analysis was conducted on monthly medians.

To assess longitudinal distribution of nutrients and algal biomass, each year was divided into two seasons: “summer”, here considered as the phytoplankton growth period from April to October, when more than 90 % of algal bloom is observed (Leitão and Lepretre, 1998) and “winter”, here November to March when total pigments are usually under $20 \mu\text{g L}^{-1}$ (average winter pigments in the Middle Loire $\approx 20 \mu\text{g L}^{-1}$ for the considered period).

Uncertainties on estimates of concentration averages were assessed using Monte Carlo random draws (Moatar and Meybeck, 2005) on experimental high frequency data at Orléans city (station 15). Uncertainties on seasonal means varied between 10 % (NO_3^-) and 30 % (PO_4^{3-}) in summer and between 6 % (NO_3^-) and 10 % (PO_4^{3-}) in winter.

When both river discharge and nutrient concentration datasets were available during the period considered, average annual fluxes were calculated to assess the contribution of each major tributary to the Loire. This calculation was possible during 1980–1986 and 1994–2006 for the Allier input, 1985–1990 and 1999–2009 for the Cher, 2006–2011 for the Vienne and 1981–2012 for the Maine but not conducted at the Indre River confluence (not enough river discharge datasets).

3.2 Building up spatio-temporal diagrams

Time series were represented with a 2-D spatial *x* axis and seasonal *y* axis. This allowed the observation of both longitudinal and seasonal distribution during

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a certain period, between the river headwaters to the estuary and from January to December. When needed and possible, missing data were interpolated both spatially and temporally to represent a smoother diagram. Three periods were defined and separated the last three decades in three sub-periods on the basis of algal pigments:

5 1980–1989, 1990–2001 and 2002–2012.

3.3 Time series decomposition

Long-term trends and seasonal variations analysis were carried out using Dynamic Harmonic Regression (DHR) technique, extensively described in Taylor et al. (2007) (a brief outline of it is also explained in Halliday et al., 2012 and 2013). It decomposes

10 an observed time series into its component parts:

$$f(t) = T(t) + S(t) + C(t) + \text{Irr}(t) \quad (1)$$

where f is the observed time series, T is the identified trend, S the seasonal component, C the sustained cyclical component (e.g. diurnal cycle caused by biological activity) and Irr the “irregular” component defined as white noise, representing the

15 residuals. Because this method was used on monthly medians, the variable C was not assessed here.

The trend was defined using an Integrated Random Walk model. It is a special case of the Generalized Random Walk model (GRW) and has been shown to be useful for extracting smoothed trends (Pedregal et al., 2007). This provided the identified trend

20 and the slope of the trend.

The seasonal components were defined as follow:

$$S(t) = \sum_i^{N/2} [a_{i,t} \cos(\omega_i t) + b_{i,t} \sin(\omega_i t)] \quad \omega_i = \frac{2\pi \cdot i}{N} \quad i = 1, 2, \dots, \left[\frac{N}{2} \right] \quad (2)$$

where ω_i are the fundamental and harmonic frequencies associated with the periodicity in the observed time series chosen by reference to the spectral properties. For

25 instance, the period 12 was corresponding to a monthly sampling in an annual cycle.

The phase and amplitude parameters were modeled as GRW processes and estimated recursively using the Kalman Filter and the Fixed Interval Smoother. These parameters were defined as non-stationary stochastic variables to allow variation with time i.e. allow non-stationary seasonality and represent better the dynamic of the observed parameters.

Strength of the seasonality was based on the squared correlation coefficient between calculated seasonal component and detrended data. Similarly, strength of the trend was determined based on the squared correlation coefficient between calculated trend and deseasonalized data.

Stations 4 (Upper Loire), 18 (Middle) and 21 (Lower) presented a large amount of data and were selected here to present and discuss the DHR analysis.

4 Results

4.1 Long term trends and longitudinal distributions of algal pigments and nutrients

Total pigments summer medians (used as the prime indicator of eutrophication) showed a very clear longitudinal increase from headwaters to river mouth (Fig. 2a). At the headwaters, total pigment concentrations remained below $30 \mu\text{g L}^{-1}$ between 1981 and 2012. In the lowest reaches of the Upper Loire (station 9), pigments were higher but showed a descending trend for the whole period. In the Middle segments, pigment levels increased between 1981 and 1990 by a factor of two (Table 3). The maximum ever measured occurred at station 18 in early October 1990 ($365 \mu\text{g L}^{-1}$). The next decade, the situation already started to decrease in the Middle Loire ($-5 \mu\text{g L}^{-1} \text{yr}^{-1}$) and even more in the Lower ($-9 \mu\text{g L}^{-1} \text{yr}^{-1}$). Finally, since 2002, the decline generalized to the whole river and trends slopes were $\approx -5 \mu\text{g L}^{-1} \text{yr}^{-1}$ in the Middle Loire and $-4 \mu\text{g L}^{-1} \text{yr}^{-1}$ in the Lower reach.



Winter medians of phosphate concentrations increased downstream of station 2 (Fig. 2b) and the maximum for the Upper segment was reached at station 4, where population density is $143 \text{ inhab. km}^{-2}$, a maximum for the whole basin. Population density decreased to $75 \text{ inhab. km}^{-2}$ between stations 4 and 9, with a corresponding reduction in the phosphate levels. PO_4^{3-} levels were stabilized in the Middle Loire (stations 10 to 18).

The general phosphorus decline during the last decade can be observed along the whole longitudinal profile. Phosphate was at its maximum in the 1980s (above $100 \mu\text{g PL}^{-1}$) for almost the whole main stem. It then decreased gradually to reach lower levels $< 70 \mu\text{g PL}^{-1}$. In the urbanized Upper part (stations 3 and 4), from a winter median of $190 \mu\text{g PL}^{-1}$ during 1980–1989, phosphate decreased to its current level ($60 \mu\text{g PL}^{-1}$). Average phosphate in the Middle and Lower reaches has reduced at least two-fold since 1980. At the Lower Loire outlet (station 21), phosphate contents increased during 1980–1989 and then decreased at the rate of $\approx -4 \mu\text{g PL}^{-1} \text{ yr}^{-1}$.

The winter nitrate longitudinal profile showed a regular increase from 1 mg NL^{-1} in the headwaters to 3.5 mg NL^{-1} at the river mouth (Fig. 2c). This longitudinal rise could be observed throughout the period of study. Annual median nitrate concentration remained stable in the Upper Loire, with no significant trends since 1980. In the Middle segment, it only presented an increasing trend during the 1990s ($+0.1 \text{ mg NL}^{-1} \text{ yr}^{-1}$) but the more significant variations were observed in the Lower reaches at station 21 where nitrate increased on average at $+0.3 \text{ mg NL}^{-1} \text{ yr}^{-1}$ during the 1980s, a bit less the next decade ($+0.1 \text{ mg NL}^{-1} \text{ yr}^{-1}$) and finally slightly decreased since 2002.

These trends provided by the DHR model were always significant and explained at least 50 % of the variations in the deseasonalized time series (Table 3). The most significant trends were observed in algal pigments and PO_4^{3-} . The long term variations in NO_3^- were less pronounced justifying a lower corresponding strength.

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4.2 Seasonal shifts across the longitudinal distribution of algal pigments and nutrients

Throughout the period of study, algal pigments reached their maximum in July or August for the whole Loire River. During the 1980s and 1990s, algal production usually started in early April, reached a peak in early May with a second peak in late August (Fig. 3a) suggesting different phytoplankton communities growth (Abonyi et al., 2012, 2014). After mid-November, pigment concentrations were very low. A slight change is nevertheless evidenced: between 1980 and 2000 in the Middle and Lower Loire, total pigments reached occasionally their maximum in October (it is the case of the years 1985, 1988, 1989, 1990, 1995); since 1996, it never happened again.

Phosphate spatio-temporal variations showed inverted seasonal patterns between the Upper and Middle–Lower Loire (Fig. 3b). Maximum phosphorus levels were observed in the middle part of the Upper section (stations 3 to 5) as a result of urban pressure, previously mentioned in the longitudinal profile description. In this upstream reach where algal development is limited, the seasonal maximum level was observed in summer when low flows cannot dilute urban phosphorus inputs; during the period 2002–2012, PO_4^{3-} medians reached $140 \mu\text{g PL}^{-1}$ at station 4 in June. This was probably partly due to P retention in the Villerest reservoir between stations 4 and 5 (Fig. 1), which has always been hypertrophic since it was first put into operation in 1984 (Aleya et al., 1994; Jugnia et al., 2004). In the lower reaches of the Upper Loire, the Middle and the Lower reaches (stations 8 to 21), the seasonality of phosphate was inverted compared to the Upper Loire and clearly controlled by eutrophication with a minimum ($< 30 \mu\text{g PL}^{-1}$) occurring during summer due to algal uptake.

Nitrate concentrations had a very clear seasonality (Fig. 3c) with maximum levels during winter (leaching) along the whole Loire River. In summer, nitrate was very low with concentrations around 1 to 2.5 mg NL^{-1} along the whole river profile and the lowest concentrations were recorded in August in the Middle Loire. The summer nitrate minimums have increased since 1980: around 0.4 mg NL^{-1} in the Middle Loire between

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1980 and 1999, the average summer 10 % percentile increased to 1 mgNL^{-1} this last decade.

The Dynamic Harmonic Regression model represented well the time series, depending on the river reach and the type of variable (Table 4). Seasonal components were stronger in Middle and Lower Loire than in Upper, with better correlations between detrended time series and calculated seasonal component (45–85 % variance explained by the seasonal component in the Middle and Lower against 15–45 % in the Upper). Algal pigments series were well represented by the seasonal component, whereas PO_4^{3-} was sometime poorly explained, illustrating the high variability of this parameter. Nitrate time series presented the best fits, with around 80 % of the variance explained by the seasonal component in the Middle and Lower reaches.

4.3 Analysis of the main tributaries variations and their impacts on the Loire long-term trends

Trends in the main tributaries of the Loire River (stations A to E) mimicked the Loire River variations with high signs of eutrophication during the 1980s and 1990s followed by a general decline (Table 5).

Algal pigments in the tributaries remained under the Loire main stem levels in each of the major tributaries except for the Cher River (station B): its highest pigments concentrations during the 1990s were very close to the extreme values reached at the same time in the Middle Loire (average seasonal amplitude $\approx 190 \mu\text{g L}^{-1}$ during the 1990s). Nonetheless, trends in total pigments were everywhere following the same pattern, with high seasonal variations and high annual medians between 1980 and 2001, and then clearly declined the last decade.

Phosphate concentrations decreased everywhere continuously from high values in the 1980s ($\approx 200 \mu\text{g PL}^{-1}$) down to $\approx 50 \mu\text{g PL}^{-1}$ except at station E (Maine River) where PO_4^{3-} first increased during the 1980s from $200 \mu\text{g PL}^{-1}$ to peak in 1992 at $300 \mu\text{g PL}^{-1}$ and finally declined towards $50 \mu\text{g PL}^{-1}$.

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Like in the Loire River, nitrate concentrations in the main tributaries increased slightly since 1980, but levels and seasonal amplitudes progressed differently: quite low in the Upper tributary (station A, annual medians $\approx 1.5 \text{ mg NL}^{-1}$), NO_3^- reached higher concentrations in the other tributaries and extreme values in the Maine River with winter maximums over 10 mg NL^{-1} during the 1990s. At each station but station A, NO_3^- seasonal amplitudes slightly started to decrease since 2002 i.e. the summer minimum slightly increased.

At each major tributary confluence, the tributaries inputs could contribute on average to 35 % of the main river nutrient fluxes. The more significant inputs were coming from the Allier River (station A) discharging almost the same amount of NO_3^- and PO_4^{3-} as the Upper Loire River. Because of the lack of data allowing nutrient fluxes calculations on a fine temporal scale, these results are to be considered with caution. But they are certainly giving good approximations of how much these tributaries can influence the Loire main stem eutrophication trajectory.

4.4 Seasonal amplitudes of algal pigments, nutrients, O_2 and pH in the Middle Loire

As described above, algal pigments, nitrate and phosphate concentrations presented different patterns of seasonality depending on the location. This paragraph focuses on seasonality of nutrients and pigments at station 18 and on dissolved oxygen, pH and temperature at station 19. Both of these stations are representative of the Middle Loire reach where the highest signs of eutrophication occurred in the early 1990s.

Algal pigments seasonal amplitude at station 18 increased during the 1980s (Fig. 4a) from 150 to $240 \mu\text{g L}^{-1}$ (1990) and then presented a spectacular decline in two steps: first, it went down to $150 \mu\text{g L}^{-1}$ in 1992 and remained at the same level the next 8 years; then, it kept on decreasing since 2000 to finally reach levels of amplitude around $50 \mu\text{g L}^{-1}$. Phosphate seasonal amplitude decreased continuously from $150 \mu\text{g PL}^{-1}$ in 1980 to $30 \mu\text{g L}^{-1}$ in 2012 (Fig. 4b), at the rate of $-6 \mu\text{g PL}^{-1} \text{ yr}^{-1}$ in the 1980s, $-4 \mu\text{g PL}^{-1} \text{ yr}^{-1}$ in the 1990s and finally reached a stable variation since 2008 (Table 4).

The seasonal amplitude of NO_3^- presented another pattern through the last 30 years (Fig. 4c): it increased from 2.2 mgNL^{-1} in 1980 to 2.8 mgNL^{-1} in 1991, then remained stable around 2.9 mgNL^{-1} the next 7 years to finally decrease slightly down to 2 mgNL^{-1} .

Interannual dissolved oxygen concentration and pH at station 19 did not present any significant trend (Fig. 4d and e): since 1990, annual average $\text{O}_2 = 10.8 \text{ mgL}^{-1}$ and $\text{pH} = 8.3$. At the daily scale, the variations of O_2 were synchronous with water temperature: the typical O_2 daily cycle corresponded to a minimum at sunrise, followed by a rapid increase and a maximum observed two hours after solar mid-day; the amplitude could reach 10 mgL^{-1} , with oxygen saturation ranging from 60 to 200 %. These daily variations greatly challenge the validity of O_2 measurements as a water quality indicator within the regulatory monthly survey of such eutrophic river. Alongside daily oxygen cycles, significant daily pH cycles were observed (see also Moatar et al., 2009). Dissolved CO_2 and/or bicarbonate uptake by primary producers during the solar day led to increasing pH. By contrast, night-time bacterial respiration was reducing pH. In the Loire, daily pH cycles were pronounced with the same phase as the O_2 cycle. The common daily pH amplitude in summer was 0.8 unit and could reach 1 pH unit. Because these variations are linked to the in-stream biological activities, daily O_2 and daily pH amplitudes presented a well-defined seasonality, with maximum reached in summer.

Summer q_{90} % temperature and summer q_{10} % discharge anti-covariated (Fig. 4f): cold temperatures in summer were matching high summer flows. Besides, there were no obvious relationships between extreme algal pigments concentration and high summer temperature. This observation supports a recent study describing the effects of global warming on the River Loire, seen from station 15 in the Middle Loire (Floury et al., 2012): according to these authors, climatic variability explains only 20 % of the long-term variations in major water quality variables, and the notable decline of chlorophyll pigments since 1991 contradicts the expected trends (Bouraoui et al., 2002) as a result of global warming.

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5 Discussion

5.1 Role of agricultural and urban pressures on the Loire long-term variations

The population density profile (Fig. 2) illustrates well the fact that phosphate concentrations are linked with urban P inputs. Thus, most changes in phosphate levels are connected to more efficient sewage treatment plants (de-phosphatation steps were set up) and the use of phosphate-free detergents. De-phosphatation technologies were not implemented at the same time across the basin, explaining different trends for different catchments. These observations support previous studies highlighting the need for phosphorus control (Gosse et al., 1990; Oudin, 1990). This control has considerably reduced phosphate concentration in the surface waters of the Loire basin (Bouraoui and Grizzetti, 2011). Nevertheless, Descy et al. (2011) assessed the biogeochemical processes using numerical models of the Middle reaches during the year 2005 and the phosphorus reduction could not totally explain the phytoplankton diminution: it was necessary to introduce the effect of grazing by a benthic lamellibranch, *Corbicula fluminea*. The role played by this invasive clam definitely needs to be assessed, as it has propagated dramatically in the Loire Basin since 1990 (Brancotte and Vincent, 2002).

The relationship between the winter nitrate levels and the percentage of the catchment under arable land is strong (Fig. 2), illustrating the fact that nitrate levels originate mainly from diffuse agricultural sources. Such diffuse sources are seasonal with less transfer of nitrate from the drainage basin in summer, but the Fig. 3 clearly indicates the influence of phytoplankton uptake on the nitrate seasonal cycle: nitrate minimum were reached where algal pigments concentrations were maximum, i.e. in the Middle and Lower sectors. Besides, the slight increasing trend in nitrate could partly be explained by the delayed response of the environment to external changes (Behrendt et al., 2002; Howden et al., 2010). According to Bouraoui and Grizzetti (2008), nitrogen application in the Loire basin has increased during the period 1991–2004, showing a lack of appropriate agro-environmental methods, or a delay in implementing the

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1991 European Nitrates Directive. Further investigations on this are needed and the development of a N-surplus model would explain better why nitrate levels remain this high in the Loire Basin.

5.2 Nutrient limitation variation since 1980

The N : P molar ratio allows to determine whether the system studied is under nitrate or phosphate limitation (Koerselman and Meuleman, 1996; Ludwig et al., 2009). Under 14, the system is limited by N; over 16, the ecosystem is considered under P limitation. In-between, N and P availabilities are sufficient or the ecosystem is co-limited by N and P.

In the Loire River, a slight increase in annual concentrations of nitrate during the last 30 years while phosphate decreased greatly resulted in the modification of the N : P molar ratio. In the Middle Loire, the annual average ratio kept on increasing since 1980 (Fig. 5). In summer during the 1980s, the lowest values observed were occasionally under the Redfield limitation but most of the time over it. These results suggest that the system has always been P limited and occasionally not limited by N nor P. Since 1998, the system never reached again the Redfield limit and remained in the P-limitation domain as a result of reducing significantly phosphorus direct inputs. Similar variations were observed in other river systems (e.g. the Ebro, Rhone, Po, Danube, Ludwig et al., 2009; the Seine, Billen and Garnier, 2007; the Mississippi, Turner et al., 2003) where similar trends in NO_3^- and PO_4^{3-} concentrations were recorded.

The Lower Loire presented a N : P molar ratio trajectory through the last 30 years very similar to the Middle segments, with Redfield ratios at station 21 increasing from 72 in 1980 to 190 in 2012. In the Upper Loire, it presented an increasing trend as well but stayed relatively low (from 16 in the 1980s to 26 in 2012 on average).

The N : P ratio was subjected to a significant seasonality. Its pattern and strength has changed from low seasonal variations during the 1980s and a minimum reached in summer to a well-defined seasonality since 2002 in the Middle and Lower reaches

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with a maximum reached in summer, reinforcing the P limitation characteristic of the Loire River.

The ratio in summer apparently started to decrease since 2008, but this is unfortunately due to the fact that the quality of analysis of PO_4^{3-} has reduced, increasing the quantification limit from $10 \mu\text{g PL}^{-1}$ before 2008 to $30 \mu\text{g PL}^{-1}$ afterwards.

This analysis suggested an explanation for the apparent shift in seasonal phases of algal pigments (late summer blooms no longer occur, described in Sect. 3.2): in the 1980s, the algal development was not controlled by bioavailability of nutrients and the algal growth limitation was probably hydrologic and climatic. Since the system is always P limited, algae growth would empty in-stream available phosphate and not be able to develop any longer even if hydrologic and climatic conditions remain favorable.

5.3 Daily O_2 and pH amplitudes as indicators of eutrophication mitigation

The delta O_2 and delta pH seasonal amplitudes decreased greatly since 1990: around 7mg L^{-1} in 1990–1995, delta O_2 amplitude declined down to 2.5mg L^{-1} . Similarly, from a seasonal amplitude at 0.5 pH unit, delta pH seasonal amplitude was maximum in 1998 (0.7) and went down to 0.3 since 2007. These descending trends are linked to the apparent decrease of algal biomass: the seasonal amplitude of algal pigments explained 80 % of the seasonal variations of delta O_2 and only 59 % for delta pH amplitudes. Continuous records of O_2 and pH take into account the whole in-stream primary activity, that is to say not only the phytoplankton respiration but also macrophytes and periphyton activities. While total pigments concentrations kept on declining since 1991, delta O_2 and delta pH stopped decreasing suggesting that a non-phytoplanktonic activity was rising. Besides, one would expect that since phytoplankton biomass declined, water column irradiance increased and macrophyte abundance would have risen. We unfortunately lack data about macrophyte and periphyton developments in the Loire River, but the biological reserve Saint-Mesmin located near Orléans City (station 15) studied the development of macrophyte species

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since 1998 on 24 river sections (60 m long by 5 m width) and showed the increasing abundance and biodiversity of such aquatic plants since 2002. Two species were dominant, *Myriophyllum spicatum* and *Ranunculus fluitans*.

5 A major change occurred in the seasonal patterns of daily maximum of dissolved O₂. From a maximum reached in June or July at least between 1990 and 2001, the seasonal pattern of daily maximum shifted dramatically to a maximum reached in winter. On the contrary, daily O₂ and pH minimum always reached their maximum in winter and their minimum in summer (due to biomass respiration). Such a spectacular change in daily O₂ maximum because of a declining eutrophication has never been
10 shown in other major European rivers.

When unusual late floods occurred, higher flow velocity, increased turbidity and reduced water column irradiance probably disrupted the well-established dominance of production/respiration cycles. Therefore both dissolved oxygen and pH levels dropped for a few days. Such episodes happened in 1992 (event described in Moatar et al., 2009), 1998 and 2008.
15

5.4 What's driving N-uptake variations?

In the Middle Loire between stations 10 and 15 (170 km away), there were no major tributaries or significant urban area enabling the comparison of summer nutrients and chlorophyll *a* concentrations (Table 6). Besides, station 15 is located upstream of the locally known Beauce aquifers inputs rich in nitrate contents because of an intense agricultural pressure. Algal pigments remained higher downstream, and as expected both summer nitrate and phosphate were lower at the downstream station. Hence, the differences between the two stations were negative. If one considers Redfield ratios (C : N : P : Si = 106 : 16 : 1 : 40 mol) and C : chl *a* = 37 based on the study of Loire phytoplankton by Descy et al. (2011), the potential uptake of nitrate and phosphate by
20 the algal biomass can be calculated from chl *a* datasets (Table 6).
25

The calculated algal uptake explained well the observed difference of PO₄³⁻ between the two stations, except the last decade where lesser data quality probably explain

a lower value. The calculated uptake was singularly not covering the total NO_3^- decrease between the two stations, only reaching 63 % in the 1980s, higher during the 1990s when phytoplankton biomass developed the most (83 %), and back to 62 % the last decade. This study reveals that algal biomass measured by chlorophyll *a* cannot account now for more than 65 % of the observed nitrate loss. It then should impact the seasonal variations of nitrate with predictable lower amplitudes when N-uptake reduces. Indeed, seasonal amplitudes of nitrate did not decrease significantly in the Middle Loire while the decline of algal biomass started since the 1990s and was generalized to the whole basin since 2002 (Sect. 4.3) and N-inputs have been shown to be a slightly increasing diffuse source.

Several hypotheses can be invoked to face this result:

1. The role played by the fixed aquatic vegetation on the river biogeochemistry is very significant as massive developments of macrophytes were observed during the last decade. Besides, macrophytes are known to get nutrients contained in the water compartment as well as in the sediments (Carignan and Kalff, 1980; Hood, 2012). Hence, during low PO_4^{3-} concentration in summer, macrophyte growth is not limited by the in-stream nutrient limitation. Despite this, delta O_2 and delta pH descending trends at station 19 corresponded well to the generalized decline in algal biomass, suggesting that the apparent nitrate loss cannot be attributed totally to aquatic vegetation.
2. The terrestrial vegetation has developed considerably since 1980. A recent work studied the variation of the active width (i.e. the non-vegetalized width of the river section) of both the Middle and Lower Loire since the 1990s (Braud and Latapie, 2012). The analysis of aerial images shot in 1995 and in 2010 allowed assessing potential changes in the active width alongside the river channel between the stations 10 and 21 of the present paper. Most of the River Loire showed a spectacular increase of vegetalization: the width of floodplain colonized by terrestrial woody vegetation between 1995 and 2010 was reaching 40 m on

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average in the Middle Loire, sometimes up to 180 m at several river sections. Nevertheless, the Lower Loire after station 19 presented no change during this period. The authors attributed this spectacular variation to the river bed incision, disconnecting sediment bars from the river flow and facilitating more the development of islands where pioneer vegetation would potentially grow and prosper (Fouzi, 2013).

3. The in-stream denitrification could play a significant role on this NO_3^- loss, but it is hard to speculate on this aspect without data. Further investigations are here necessary.

6 Conclusions

The Loire River is a relevant case of a river recovering from severe eutrophication by controlling phosphorus direct inputs.

This study highlighted how contrasted can be the different long term trajectories of algal pigment and nutrient concentrations in the different reaches of a eutrophic river and contributed to better understand the current biogeochemical functioning. Although the Upper Loire received the highest concentrations of phosphorus, the signs of eutrophication were expressed only in the lowest part of the Upper River because of its morphology. The Middle Loire is very favorable to eutrophication and the Lower reach functioning and trends remained close to the Middle Loire trajectory although it receives most of the tributaries inputs. Signs of eutrophication remained lower in the major tributaries than the main river stem, but it has been shown that their influence on the Loire River nutrient fluxes (and consequently on the algal biomass) at the confluences can reach up to 35 %.

This study also support the previous works on the Loire eutrophication, but the analysis of the long term changes in seasonality in this paper could bring more elements:

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1. The Loire River has always been under P limitation, explaining why controlling P inputs led to decreasing dramatically eutrophication across the whole basin.
2. The algal biomass uptake only accounted for $\approx 65\%$ of the nitrate loss where phytoplankton species grow the most and algal pigments and phosphate seasonal amplitudes declined drastically in a P-limited river system while nitrate amplitudes remained high. These observations are questioning the exact role played by denitrification, macrophytes and terrestrial vegetation on the nitrogen cycle.
3. Combined to algal pigments concentration time series, delta O_2 and delta pH are relevant metrics for studying eutrophication variations. High frequency records of algal pigments, O_2 and pH could potentially enable the separation between phytoplankton and macrophytes impacts on the river biogeochemistry.

Other recent changes should also be considered. For example, it would be interesting to investigate the impact of the development of *Corbicula* clams (Brancotte and Vincent, 2002) on the biogeochemistry of the Loire basin surface waters. A potential numerical model of the Loire basin eutrophication should not only take into account recent ecological changes (Descy et al., 2011; Ruelland et al., 2007), but also climate and land-use changes.

In addition, this study highlights the temporal variability of the different eutrophication metrics: in summer, the river biogeochemistry is essentially controlled by production/respiration processes. Thus, daily and seasonal variations are very significant and call into question the classical monthly survey recommended by national or international authorities.

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terrestrial vegetation and macrophytes details and data. Comments and suggestions by G. Pinay (Rennes 1 Univ.) and O. Coulon (AELB) significantly improved the manuscript.

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Table 1. Loire main stem stations characteristics. Kilometric point (KP): distance from headwaters; Drained area; Q: average annual discharge; population density in 2008; arable land as percentage of the drained catchment; API: agricultural pressure indicator = (pasture + forest)/(pasture + forest + arable land) expressed in percentage. See Sect. 1.2 for source information.

Station	Upper Loire								Middle Loire						Lower		
	1	2	3	4	5	6	7	8	9	10	11	13	15	17	18	20	21
KP (km)	44	92	200	224	273	292	344	417	451	465	500	564	633	712	772	822	895
Drained area (10^3 km^2)	0.5	1	4	5	7	8	13	15	18	33	34	36	37	41	43	82	109
Q ($\text{m}^3 \text{ s}^{-1}$)	6	10	–	47	67	–	89	–	180	300	320	327	–	360	366	680	850
Population density (inhab. km^{-2})	13	50	144	143	122	128	101	91	80	75	74	74	73	80	83	–	73
Arable land (%)	0.6	3	1	3	4	4	3	4	6	9	11	13	13	15	17	24	30
API (%)	99	97	99	96	96	96	96	96	93	90	89	87	86	84	82	75	69

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Table 2. Major tributaries station characteristics.

Station	A	B	C	D	E
Drained area (10^3 km^2)	14	13	33	21	22
Average discharge ($\text{m}^3 \text{ s}^{-1}$)	143	81	37	–	135
Population density (inhab. km^{-2})	67	52	76	55	82
Arable land (%)	13	36	52	25	49
API (%)	87	63	46	74	50

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Table 3. Long term trends at three stations representative of the Upper, Middle and Lower Loire.

	Years	Annual median			Trend			Strength of trend 1980–2012 (%)		
		tot. pigmts $\mu\text{g L}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}	tot. pigmts $\mu\text{g L}^{-1} \text{ yr}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1} \text{ yr}^{-1}$	NO_3^- $\text{mg NL}^{-1} \text{ yr}^{-1}$	tot. pigmts	PO_4^{3-}	NO_3^-
Upper Loire Station 4	80–89	9	183	1.4	+2	+16	0.0	74	87	77
	90–01	12	169	1.8	0	–16	0.0			
	02–12	11	88	1.4	–1	–3	0.0			
Middle Loire Station 18	80–89	47	121	1.8	+3	–6	0.0	82	91	53
	90–01	83	58	1.9	–5	–3	+0.1			
	02–12	17	26	2.2	–5	–2	0.0			
Lower Loire Station 21	80–89	50	79	2.5	+5	+12	+0.3	83	76	71
	90–01	58	89	3.3	–9	–3	+0.1			
	02–12	14	37	2.6	–4	–5	–0.1			

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Table 4. Seasonality analysis and changes since 1980 at three stations representative of the Upper, Middle and Lower Loire.

	Years	Seasonal amplitude			Strength (%)			Amplitude trend		
		tot. pigmts $\mu\text{g L}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}	tot. pigmts	PO_4^{3-}	NO_3^-	tot. pigmts $\mu\text{g L}^{-1} \text{ yr}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1} \text{ yr}^{-1}$	NO_3^- $\text{mg NL}^{-1} \text{ yr}^{-1}$
Upper Loire Station 4	1980–1989	61	101	0.7	41	16	25	0.0	−0.2	+0.1
	1990–2001	114	107	0.9	31	33	38	−0.2	+0.7	0.0
	2002–2012	17	26	2.2	24	41	42	−1.2	+0.5	+0.1
Middle Loire Station 18	1980–1989	182	123	2.2	61	44	80	+7.8	−5.6	+0.1
	1990–2001	152	71	2.8	64	43	85	−9.8	−3.7	0.0
	2002–2012	57	38	2.1	55	47	84	−8.1	−2.1	0.0
Lower Loire Station 21	1980–1989	184	125	3.2	68	46	78	−2.7	+2.0	+0.4
	1990–2001	82	120	5.5	52	62	81	−9.6	−1.6	−0.2
	2002–2012	53	65	3.2	62	51	85	−1.1	−10.4	+0.1

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Table 5. Annual medians, DHR-model seasonal amplitudes and nutrients flux contributions of the main tributaries.

		Annual median			Seasonal amplitude			Nutrient flux contribution	
		tot. pigmts $\mu\text{g L}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}	tot. pigmts $\mu\text{g L}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}	PO_4^{3-}	NO_3^-
A	1980–1989	20	124	1.4	85	180	1.7	54 %	47 %
	1990–2001	23	83	1.5	134	112	2.1	44 %	43 %
	2002–2012	17	51	1.7	83	74	2.3	42 %	36 %
B	1980–1989	44	108	3.6	147	190	4.3	17 %	32 %
	1990–2001	61	79	4.1	197	181	5.9	31 %	37 %
	2002–2012	13	45	4.7	57	57	3.9	33 %	33 %
C	1980–1989	28	166	4.0	104	234	3.7	–	–
	1990–2001	44	90	4.2	109	144	5.0	–	–
	2002–2012	16	59	4.6	37	79	4.2	–	–
D	1980–1989	43	126	3.0	102	137	2.2	–	–
	1990–2001	50	68	2.7	107	87	2.8	–	–
	2002–2012	6	30	2.8	18	36	2.5	27 %	35 %
E	1980–1989	50	191	4.0	142	326	4.2	38 %	24 %
	1990–2001	62	181	4.4	132	236	8.1	33 %	23 %
	2002–2012	21	73	4.1	51	102	5.6	35 %	27 %

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Table 6. Nitrate and phosphate uptakes between stations 10 and 15 in the Middle Loire (170 km) using Redfield ratios on chlorophyll *a* concentrations. Numbers in brackets represent the uptakes in percentage of the observed concentration differences between the two stations.

	Station 10 summer medians			Station 15 summer medians		
	chl <i>a</i> $\mu\text{g L}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}	chl <i>a</i> $\mu\text{g L}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}
1980–1989	41	96	1.1	80	55	0.7
1990–2001	33	70	1.3	81	30	0.9
2002–2012	11	47	1.3	24	20	1.2

	Difference between S10 and S15			Calculated Uptake using Redfield ratio	
	chl <i>a</i> $\mu\text{g L}^{-1}$	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}	PO_4^{3-} $\mu\text{g PL}^{-1}$	NO_3^- mg NL^{-1}
1980–1989	+40	−41	−0.41	−36 (88 %)	−0.26 (63 %)
1990–2001	+48	−40	−0.38	−43 (109 %)	−0.31 (83 %)
2002–2012	+13	−27	−0.13	−12 (42 %)	−0.08 (62 %)

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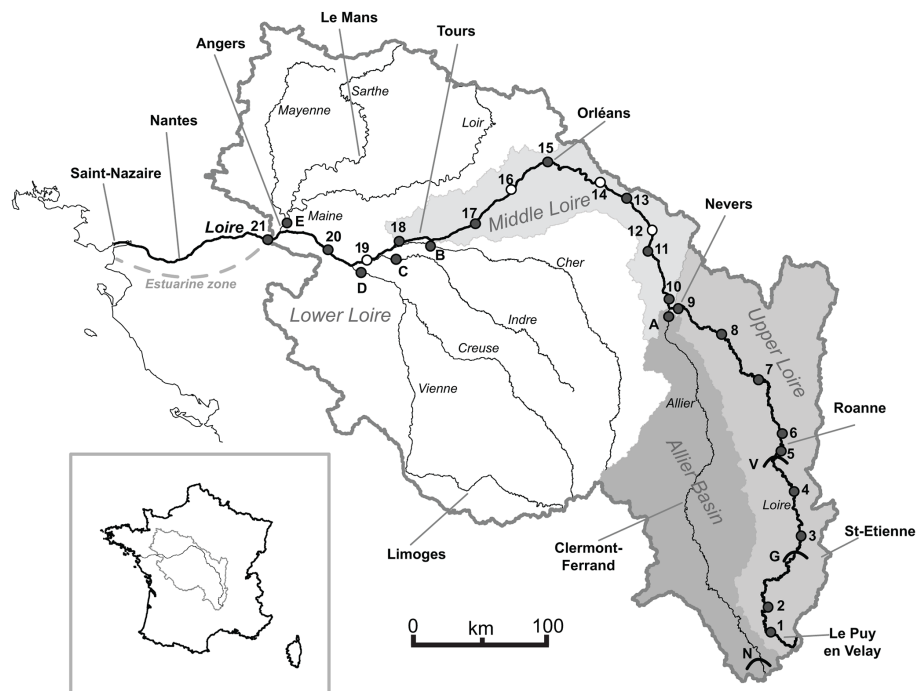


Figure 1. Loire River Basin. Dark circles: sites of regulatory surveys. White circles: nuclear Power Plants sampling sites. A to E: regulatory survey stations at tributaries outlets. G, V, N: three major dams, respectively Grangent, Villerest and Naussac. The estuarine influence begins downstream of station 21.

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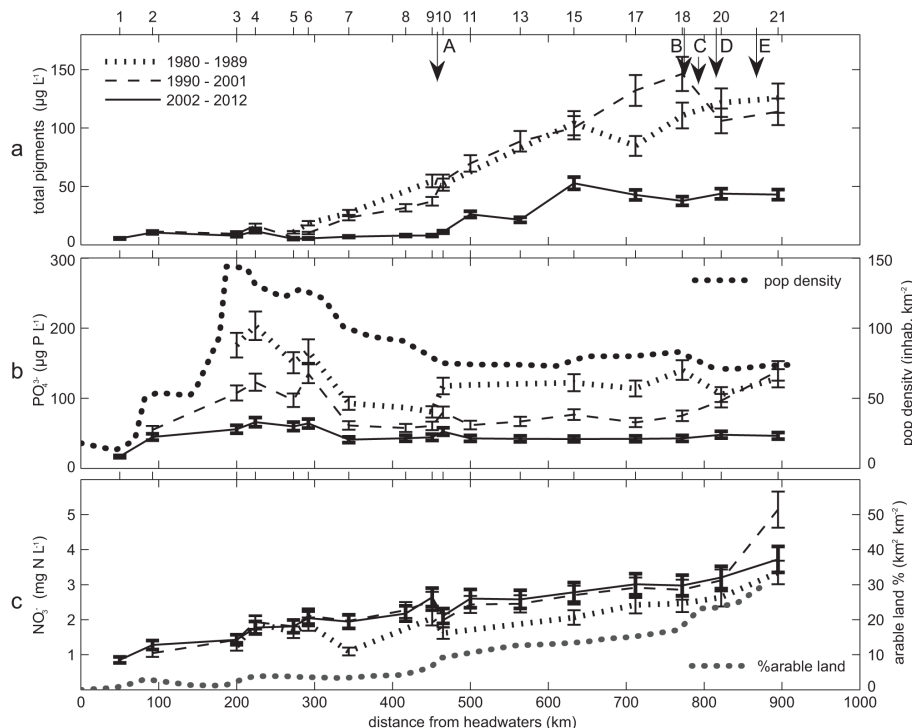


Figure 2. Longitudinal profiles of summer median total pigments **(a)**, winter median PO_4^{3-} **(b)** and NO_3^- **(c)**. Averages for three periods, in relation to % arable land (2006) and population density (2008) tested as eutrophication control variables. Uncertainty bars are due to sampling frequency. Arrows and capital letters (A to E) represent confluences with major tributaries (Fig. 1).

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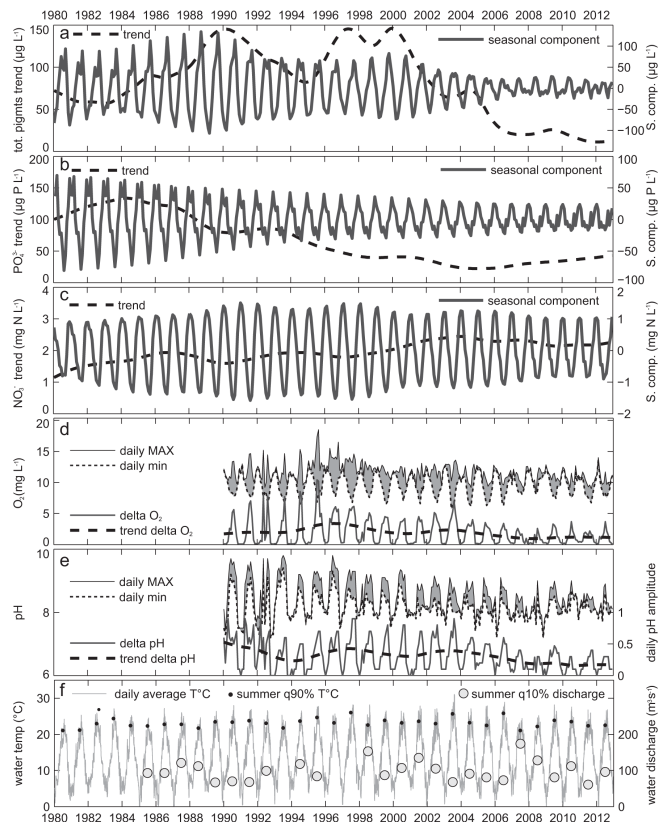


Figure 4. Trends and seasonal components at station 18 of algal pigments **(a)**, phosphate **(b)** and nitrate **(c)**. Corresponding time series of monthly medians of both daily min and max of O_2 **(d)** and pH **(e)** and their amplitude dynamics at station 19 (i.e. delta O_2 and delta pH). Daily average water temperature **(f)**, grey line) and summer percentile 90 % temperature (black dots) at station 19 and summer 10 % percentile discharge (white circles) at station 18 since 1980.



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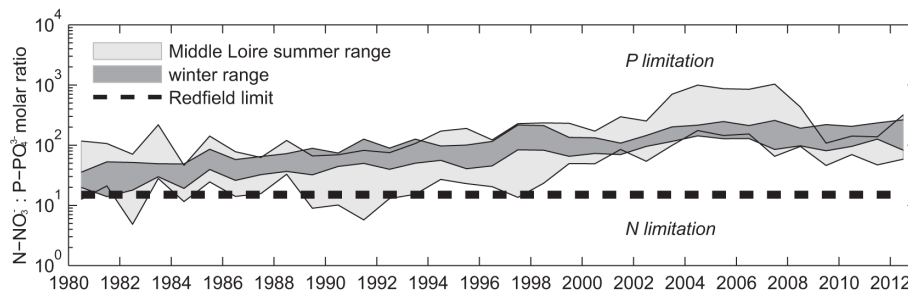


Figure 5. Variations of nitrate over phosphate molar ratios ranges during summer and winter in the Middle Loire since 1980 and compared to the Redfield limit (dotted line). Each patch is composed at the bottom by the percentile 10 % of the recorded data and percentile 90 % at the top.

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