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Loire River eutrophication mitigation (1981–2011) measured by seasonal nutrients and algal pigments

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Abstract The Loire River basin is very sensitive to eutrophication due to its multiple-channel morphology, summer low flows, high water temperatures, and high exposure to nutrient inputs from agriculture and urban sources. The seasonal variation of nutrients and chlorophyll-a from the river headwaters to the estuary (1012 km) was studied by harmonic analysis for three periods between 1981 and 2011. The Upper Loire does not present significant seasonal variations. The eutrophication level of the Middle and Lower Loire, favoured by hydroclimatic conditions, is responsible for significant seasonal amplitude of algal pigments, nutrients and physico-chemical variables. In the Middle Loire, the summer phosphate minimum (15 μg L^{-1}) is controlled by algal uptake, and the summer nitrate minimum (0.8 mg-N L^{-1}) is attributed to algal uptake and denitrification. The 1991 European Directives had an impact on phosphorus levels, but nitrate levels kept increasing slightly, showing a lack of appropriate agro-environmental measures in the Loire River basin.

Key words Loire River; eutrophication; nutrients; seasonality; phosphate; nitrate

INTRODUCTION

In the 1960s, agricultural intensification and rising urban pressures started to cause phosphorous and nitrogen increases in European surface waters (EEA, 2001). The nutrient bioavailability contributed to dramatic development of eutrophication in surface water bodies. Despite the implementation of the European Directives (EEC, 1991a,b) to control eutrophication and nutrient loadings into receiving waters, the recovery of water quality is limited by the time required for nitrates to be transferred from the soil to running waters (Jackson *et al.*, 2008; Bouraoui & Grizzetti, 2011). It is known that improvement of agricultural practices may improve water quality after several decades (Behrendt *et al.*, 2000; Howden *et al.*, 2010). Surface water quality is also affected by the variation of hydro-climatic conditions (Floury *et al.*, 2012). In Europe, both climatic models and observations show a general rise in air and water temperature (Moatar & Gailhard, 2006; Whitehead *et al.*, 2009). Models predict the increase of river flow variability with low flow reduction in summer, intensifying the risk of droughts (Whitehead *et al.*, 2009). Therefore, better control of nutrient fluxes and prediction of how eutrophication would change with global warming becomes essential.

Decrease of the river nutrient levels is observed in European basins such as the River Elbe (Lehmann & Rode, 2000), the River Seine (Billen *et al.*, 2007) and the River Thames (Howden *et al.*, 2010), and is attributed to an improvement of wastewater treatment and to better agricultural practices. However, primary production is still at a high level, proving that diffuse sources of nutrients are still significant. Moreover, it seems that nutrient inputs are supposed to increase with global warming (Bouraoui *et al.*, 2002).

The River Loire basin covers 20% of the French territory. Its area is 110 000 km^2. Urban and agricultural pressures are significant: 4.2×10^6 inhabitants equivalent are mainly concentrated near the main river course; 70% of the basin area is devoted to agriculture activities (Oudin, 2009). The Loire River has been considered eutrophic since at least 1980 when the first chlorophyll measurements were made (Crouzet, 1983; Meybeck *et al.*, 1988; Etcheber *et al.*, 2007), with chlorophyll-a concentration exceeding 150 μg L^{-1} during the summer period in the Middle Loire (Lair, 2001). The morphology of this part of the river favours excessive algal development. Its multiple channels slow the water flow. Summer low flows can reach critical low levels, although two dams support low levels in the Upper Loire (Fig. 1). As a consequence, average water depth can be low, contributing to warming and better lighting, and inducing high photosynthesis rates. Recently, Floury *et al*. (2012) presented the effects of global warming on the River Loire as seen from the Orléans experimental monitoring station (Middle Loire). Climatic variability explains only 20% of the long-term variations in major water quality variables, and the notable decline of chlorophyll since 1998 contradicts the expected development with global warming. The local-scale changes influencing nutrient inputs are dominating the current trend.

The objectives of our study were to analyse the eutrophication control factors (nutrients, water discharge and temperature) at the seasonal scale for the whole river course (1012-km long) over a period of 30 years (1981–2011). This paper is based on the River Loire water quality datasets (total algal pigments, nutrients and physico-chemical variables) from the French National Water Quality Survey (Réseau National de Bassin, RNB).

MONITORING STATIONS AND METHODS

River Loire water quality monitoring has been performed since 1971 by the Loire River basin authority (AELB) from the headwaters to the estuary (Atlantic Ocean). Between the source and the estuary, 69 monitoring stations were identified on a 1012 km stretch. Only 19 stations are monthly sampled (or bi-monthly for some of the variables) between 1981 and 2011, and were selected to be analysed in this paper. The River Loire can be divided into three parts: the Upper Loire (451 km, 10 stations) extends from the headwaters to the confluence with the River Allier (Fig. 1). From there, the Middle Loire (307 km, 6 stations) extends to the confluence with the River Cher and receives inputs from small tributaries. In contrast, the Lower Loire (110 km, 3 stations) receives inputs from important tributaries (Cher, Indre, Vienne and Maine rivers) doubling the river basin area over only 110 river km (Table 1). The hydrological regime of the Loire is pluvial with some nival influences because of the high headwater elevation (3% of the basin area exceeds 1000 m).

Water quality databases from regulatory surveys (water temperature, pH, total pigments (chlorophyll-a + pheopigments), nitrate ($N\text{-}NO_3^-$), phosphate (soluble reactive phosphorus, SRP) and total phosphorus (TP) concentrations are available online on the OSUR website (http://osur.eau-loire-bretagne.fr/exportosur/Accueil). River flow datasets originate from the national database "Banque Hydro" (http://www.hydro.eaufrance.fr/). In order to validate the datasets, temporal behaviour and concentration *versus* discharge relationships were analysed and compared with previous studies carried out during targeted periods (Grosbois *et al*., 2001). The separation between living algal biomass and algal detritus depends on the protocol used. This protocol may have evolved over the 30 years. Therefore, we worked with the total pigments, which increased the robustness of the data (Meybeck *et al*., 1988).

Seasonal analysis was performed after segmentation of the dataset into three periods where nutrients and pigments variations are more homogenous. Those three periods were defined both from Floury *et al*. (2012) results and our own analysis: (a) 1981–1995, (b) 1996–2004 and (c) 2005–2011. The dataset in each period permitted the comparisons to be made (data number varied from 90 to 135 per river reach on average). Fourier harmonic analysis was then computed on each variable to fit by multiple regressions the *a*, *b* and *c* coefficients of the seasonal cycle equation: $f(t) = a + b \cdot \cos\left(\frac{2\pi t}{T}\right) + c \cdot \sin\left(\frac{2\pi t}{T}\right)$, where T is the period of the seasonal cycle (e.g. 365 days), and $\Delta S = 2\sqrt{b^2 + c^2}$ its amplitude. The mean and the extremes (minimum and maximum) of the cycle were also of interest. Some variables may have more complex cycles (two peaks in the season), and need to be fitted with a Fourier function of the second order:

$$f(t) = a + b \cdot \cos\left(\frac{2\pi t}{T}\right) + c \cdot \sin\left(\frac{2\pi t}{T}\right) + d \cdot t \cdot \cos\left(\frac{4\pi t}{T}\right) + e \cdot t \cdot \sin\left(\frac{4\pi t}{T}\right)$$

An additional analysis was performed on seasonal means. We defined summer from April to October and winter from November to March. We attributed uncertainties on calculated seasonal

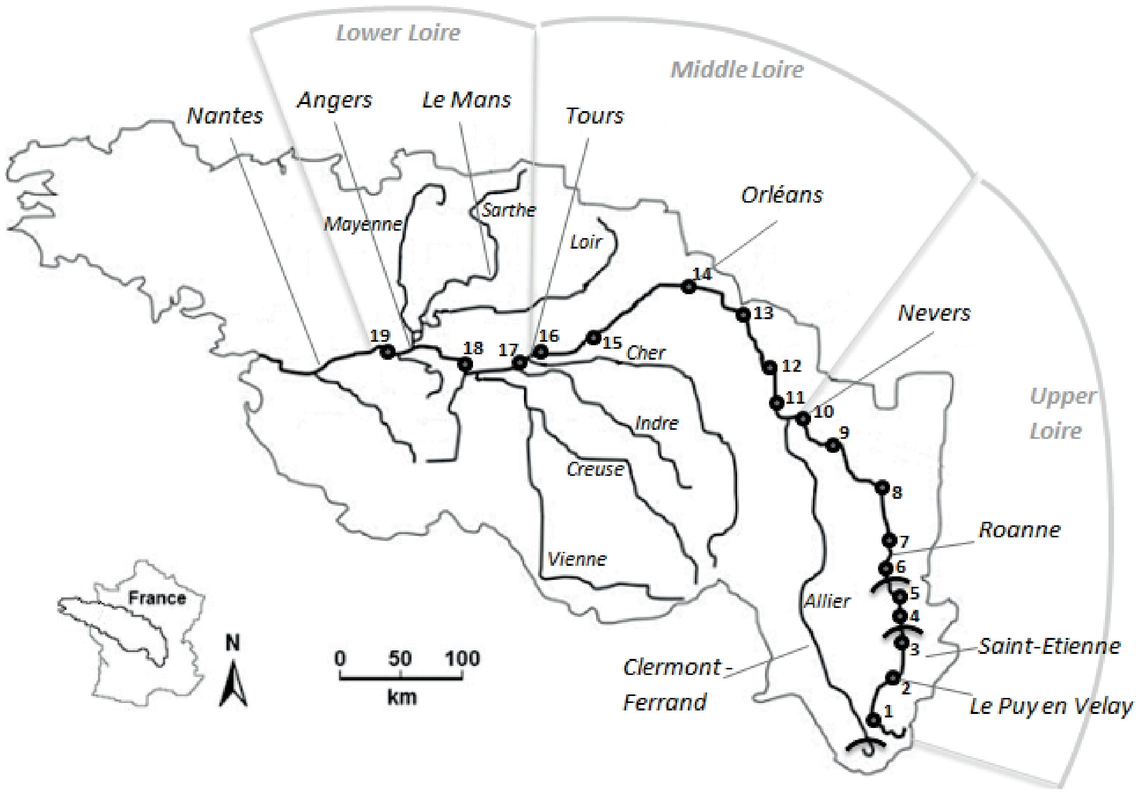

Fig. 1 Location of the Loire River, main urban areas and monitoring sites. Thick circles are the stations. Two major reservoirs are located in the Upper Loire.

Table 1 Monitoring sites. Kilometric point (KP), distance from the source (km); D.A., drained area (10^3 km^2); Q, mean river flow (m^3 s^{-1}).

	← Upper Loire (451 km) →									← Middle Loire (307 km) →						← Lower Loire (110 km) →		
Station	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
KP (km)	50	92	150	200	224	273	292	344	417	451	465	500	564	633	712	772	785	822	895
D.A. (10^3 km²)	-	1.3	3.2	4.2	5.0	6.6	7.5	12.5	16.5	18.2	32.6	-	-	37.0	40.6	42.1	-	81.2	108.6
Q (m^3 s^{-1})	4	-	34	-	44	61	-	-	-	190	-	266	327	387	-	-	-	593	859

Stations : 1 = Goudet, 2 = Le Puy, 3 = Bas en Basset, 4 = Veauchette, 5 = Feurs, 6 = Villerest, 7 = Briennon, 8 = La Motte St Jean, 9 = Decize, 10 = Nevers, 11 = Fourchambault, 12 = St Satur, 13 = Gien, 14 = Orléans – Jargeau, 15 = Chaumont, 16 = Villandry, 17 = Langeais, 18 = Saumur, 19 = La Possonière – Montjean.

means depending on sampling frequency, which is specific for each variable. We used Monte-Carlo random draw on daily data at the pilot station Orléans (station 14) to assess these uncertainties (Moatar & Meybeck, 2005). Uncertainties on seasonal means varied between 10% (nitrate) and 30% (SRP) in summer, and between 6% (nitrate) and 10% (SRP) in winter.

RESULTS AND DISCUSSION

Seasonality of variables and their longitudinal evolution

The more pronounced the seasonality of a variable, the more accurate is the curve fitting (Table 2). The correlations between data and fitted curves were significant (p-value <0.05) for all variables except TP and SRP, for which correlations were significant only for some river reaches. As a consequence, seasonality is considered non-significant for SRP in the Upper Loire and for TP in

Table 2 Seasonality curves fitted for water temperature, total pigmentation, nitrate, phosphate and total phosphorus.

Loire reach	Water temperature (°C)			Total pigments (µg L^{-1})			N-NO$_3$ (mg L^{-1})			P-PO$_4$ (µg L^{-1})			total P (µg L^{-1})		
	1981-1995	1996-2004	2005-2011	1981-1995	1996-2004	2005-2011	1981-1995	1996-2004	2005-2011	1981-1995	1996-2004	2005-2011	1981-1995	1996-2004	2005-2011
Upper *n*	115	106	72	86	68	47	115	106	72	116	106	72	97	106	72
Middle *n*	162	166	104	182	158	82	368	185	103	352	185	103	282	185	103
Lower *n*	159	144	109	105	104	70	159	144	108	158	144	108	133	140	108
Upper R² (%)	85	88	88	19	10	16	30	36	44	8	12	11	3	7	11
Middle R² (%)	88	87	87	50	56	25	56	74	53	24	44	21	3	8	13
Lower R² (%)	88	88	89	48	28	40	65	67	66	30	35	17	5	11	14
Upper m	12.1	12.5	12.6	24	19	8	1.4	1.5	1.5	135	93	64	254	155	93
Middle m	13.6	13.6	14.0	81	74	23	1.7	1.9	2.1	84	40	33	242	147	61
Lower m	13.6	14.1	14.1	105	73	34	2.3	2.7	2.5	98	66	41	282	184	93
Upper ΔS	17.7	17.7	17.5	34	-	14	**0.8**	**1.0**	**1.0**	-	-	-	-	-	-
Middle ΔS	17.9	17.7	18.5	143	128	37	**2.2**	**2.3**	**1.8**	**72**	**47**	**23**	-	-	-
Lower ΔS	16.8	17.1	17.8	168	102	59	**3.4**	**3.3**	**2.8**	**97**	**81**	**27**	**129**	**81**	**42**

Note: *n* is the data number, R² the squared correlation coefficient for the fitted curves, m is the mean, ΔS the cycle amplitude. Shadow cells: the correlation between data and fitted curves is not significant (p-value > 0.05). Bold font: the minimum occurs in the summer (nitrate, SRP and TP).

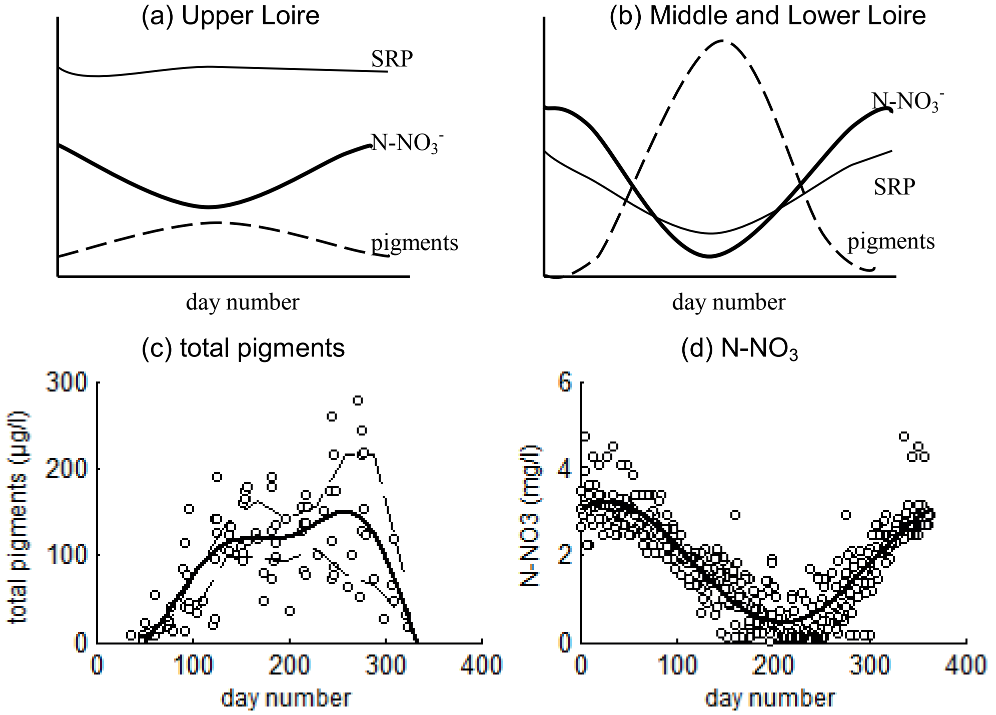

Fig. 2 Conceptual cycles observed for pigments and nutrients (NO_3 and SRP) depending on the river reach. (a) Upper Loire, (b) Middle and Lower Loire. Seasonal cycles for (c) total pigmentation at station 16 (1996–2004), (d) nutrients at station 10 (1981–2011). Observed values are the circles, thick line is the adjustment, dotted lines are 75 and 25 percentiles.

the Upper and Middle Loire. Seasonality had different dynamics depending on the river reach, the variable considered and the period (see Table 2 and Fig. 2). It is generally well expressed for the Middle and Lower Loire, and is less explicit for the Upper Loire.

Temperature cycles are very clear and very similar for the three river sections (16.8 to 18.5°C). they increase slightly (+0.6 to +1°C) in the Middle and Lower sections between 1981–1995 and 2005–2011.

In the Upper section, phosphate concentrations (SRP) reach a maximum of 500 µg $P\text{-}PO_4^{3-}$ L^{-1} (station 4) during summer low flow resulting from the urban inputs of two cities Le Puy and St Etienne (400 000 inhabitants equivalent). The seasonality of total phosphorus is not significant. Nitrate seasonality (variations between 1 and 2 mg N L^{-1}) is also less important, with a minimum reached in summer. The pigment seasonality is very low and decreases from 34 to 14 µg L^{-1} between 1981–1985 and 2005–2011. Below the last reservoir (station 6) the algal pigment concentration increases as a result of enhanced primary production in two reservoirs (Grangent and Villerest) (Abonnyi *et al*., 2011).

In the Middle Loire, seasonal features become more and more pronounced for SRP concentrations with a minimum occurring in summer (Fig. 3). Over the 1981 to 2004 period, the amplitude of SRP seasonal cycles increased going downstream, while the mean values decreased. The amplitude of nitrate cycles with very low summer levels kept increasing going downstream. Algal proliferation was extreme in this section with total pigments over 180 µg L^{-1} at station 16 by the end of summer during the 1981–1995 period, and was responsible for partial nitrate uptake and phosphate reduction in summer. The amplitude of nitrate cycles from station 11 onwards (Middle and Lower Loire) was 2.5 mg $N\text{-}NO_3^-$ L^{-1}, and corresponding pigments, using the Redfield ratio, equal to 460 µg L^{-1}. The maximum algal pigments observed are almost five times lower; the riverine denitrification process, still incompletely understood in the Loire River, could explain the seasonal nitrate reduction.

In the Lower Loire, all variables showed an increased seasonality. The highest nitrate seasonal variations occurred at the very last station with seasonal cycles means reaching 3.47 mg $N\text{-}NO_3$ L^{-1} and an amplitude of 4.27 mg $N\text{-}NO_3$ L^{-1}. Summer nitrate levels increased in this downstream section suggesting that nitrate uptake by phytoplankton or riverine denitrification were less important. Eutrophication seems to be less severe in the Lower Loire than in the Middle reach, and this is in agreement with Abonyi *et al*. (2012).

Despite the inputs of the Lower Loire tributaries, which are less eutrophic than the Loire itself, total pigments levels are still very high. Another eutrophication marker, the seasonal pH, confirms these observations: the high values of pH are linked to eutrophication due to changes of carbonate species balance during photosynthesis. In the Upper Loire, where the algal biomass is limited, pH does not exceed 7.6 for the whole year. In the Middle and Lower sections it rises to pH9 in summer, and seasonal variations are important. Then, the acidic Vienne River (Grosbois *et al*., 2001) contributes to decrease it by one pH unit.

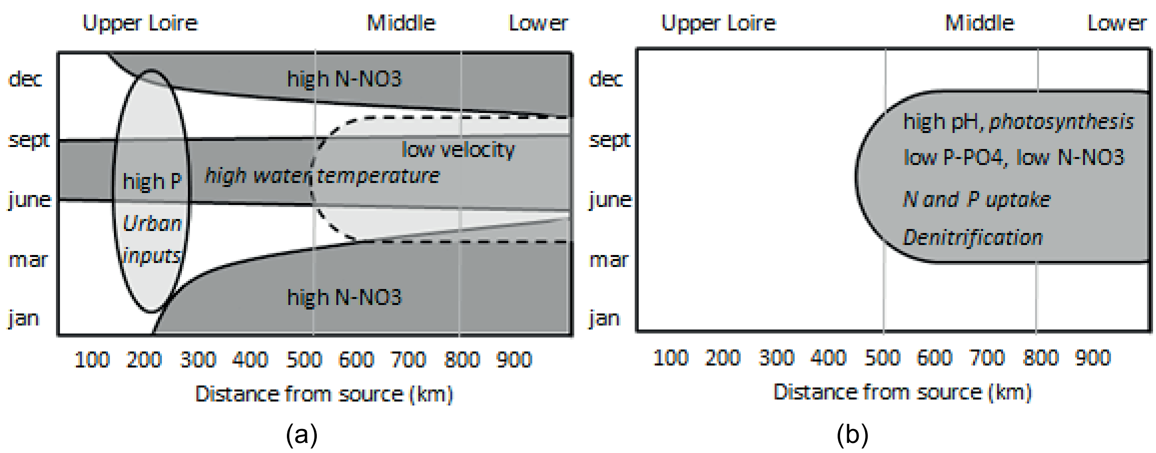

Fig. 3 Conceptual spatiotemporal domains of a) eutrophication controls (water temperature, velocity, nutrients inputs); b) eutrophication effects on summer nutrients and pH.

Long-term spatial gradients analysis

The longitudinal dynamics were similar over the 30 years, but the concentration levels were substantially modified (Fig. 4). Most remarkable is the spectacular drop in phosphate and TP between periods: varying from 250 to 300 µg TP L^{-1} in 1981–1995, TP significantly decreased to reach an average of 60–90 µg L^{-1} during the last period (2005–2011). This large reduction illustrates the efforts made to control and reduce phosphorus from point sources (wastewater treatment improvements and change in agricultural practices) linked with the implementation of the European Directives (EEC, 1991b).

However, the Upper Loire maintains high concentration levels of SRP showing that the high anthropogenic pressure keeps impacting the river. In contrast to notable phosphorus reduction on the whole river, summer nitrate concentrations remain stable in the Upper Loire, and show a significant increase for the Middle and Lower Loire between 1981 and 2011. In parallel, seasonal amplitudes for nitrate and phosphate were reduced. Winter nitrate concentration slightly increased in both the Middle and the Lower Loire, showing that nitrate bioavailability is rising. We have not observed any effects resulting from the implementation of the European Nitrate Directive (EEC,

(a) total pigments

(b) nitrate N-NO_3^-

(c) SRP

(d) total P

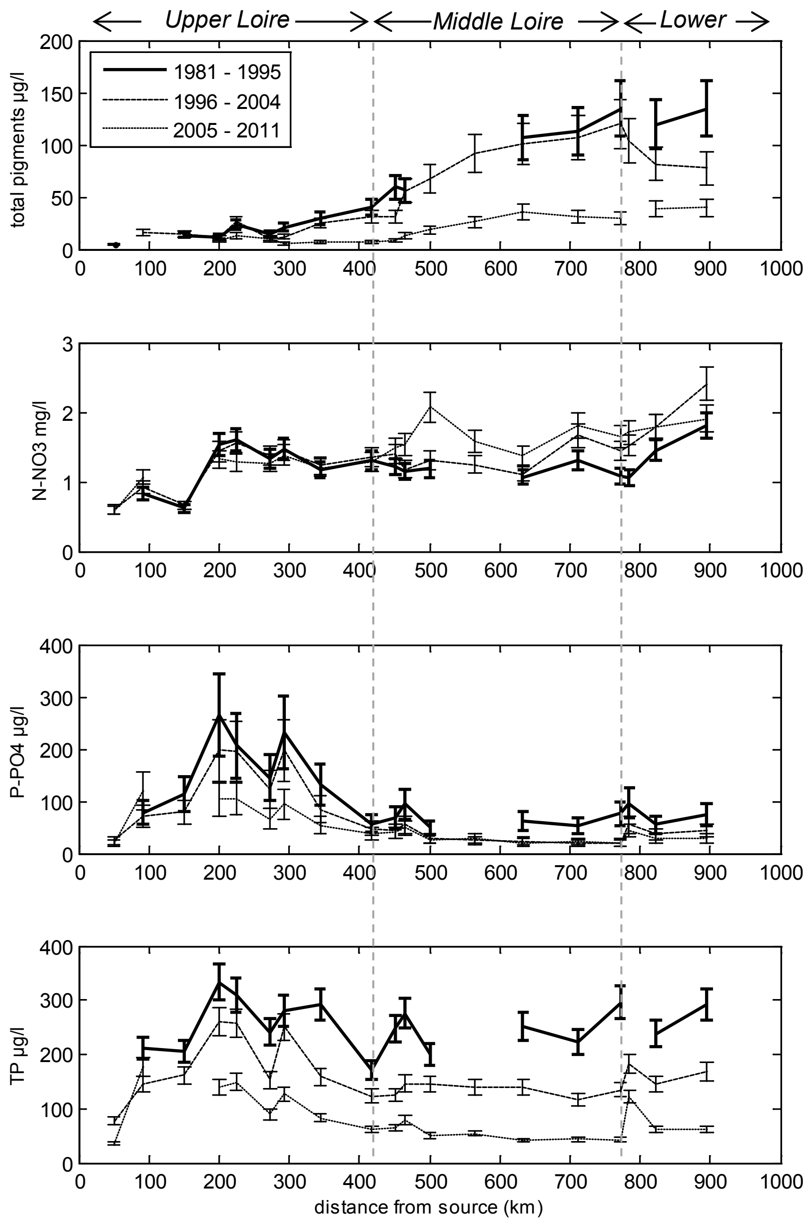

Fig. 4 Summer average longitudinal profiles in the River Loire from the headwaters to the estuary for three periods (1981–1995, 1996–2004, 2005–2011). Summer average concentrations of: (a) pigments, (b) nitrate, (c) SRP, and (d) total P.

1991a). In contrast, the pigments trend follows the phosphorus reduction: summer pigments averages were three times lower during 2005–2011 compared to the first period (Fig. 4). At station 16, the algal proliferation, which reached 200 µg L^{-1} of total pigments during 1981–1995, now does not exceed 50 µg L^{-1}.

CONCLUSION

The implementation of the European Directives on phosphorus reduction did decrease phosphorus levels in all sections of the Loire River by a factor of two since 1995. In contrast, winter nitrate has increased by almost 10% since 1995, despite the implementation of the Nitrate Directives (1991). Part of this is explained by the delayed response of the environment to external changes. However, according to Bouraoui & Grizzetti (2007), there was still an increase of nitrogen application in the Loire basin during the period 1991–2004, showing a lack of appropriate agro-environmental methods. Nutrients and eutrophication dynamics followed different patterns depending on the river reach: (a) the Upper section with the high phosphate level (>150 µg L^{-1}) from urban inputs and the high nitrate level (1.5 mg N L^{-1}) did not develop a high algal biomass. River flow velocity is most likely the cause for that; (b) extremely high algal pigments developed mostly in the lowest 420 km (Middle and Lower Loire), where velocity is lower, and reached levels similar to that for eutrophic lakes (200 µg pigments L-[1]) despite lower phosphorus levels (<100µg L^{-1}). The very high eutrophication level of the Middle and Lower Loire favoured by hydroclimatic conditions is responsible for a clear seasonal cycle of pigments, phosphate, nitrate (partial control), pH, oxygen, daily pH variations and daily oxygen variations (Moatar *et al*., 2009). This study demonstrates how different the sensitivity to nutrient enrichment is, depending on the river section. Physical and biological controls are also important. Eutrophication controls on river biogeochemistry (phosphates, particulate organic carbon, pH, dissolved oxygen, calcite precipitation), already described for a few stations (Meybeck *et al*., 1988; Moatar *et al*., 2009; Grosbois *et al*., 2010) will be investigated for the whole basin in our future research.

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