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High frequency records of nutrients and algal biomass pigments for deciphering biogeochemical processes in the Loire River (France)

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Abstract

A high temporal hydro-biogeochemical monitoring based on daily discharges and Total Suspended Solids concentrations and on a three-day frequency survey of nutrients (NO_3^-, PO_4^{2-}, SiO_2) and algal biomass pigments was carried out during 2012 at three strategic stations in the Loire River. In a context of a strong eutrophication history, this survey aimed at observing temporal variability and deciphering biogeochemical processes at a fine temporal scale such as nutrients uptake by different phytoplankton species, P-limitation, N losses, and the impact of hydrological events on algal biomass.

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Introduction

The Loire River basin covers 20% of the French territory. Its estuary is known for being the most impacted by hypoxia in France with zones of low oxygen (~10%) approximately 30 km in length during several weeks. The Loire was found to suffer from extreme eutrophication during the 1980s when bio-available nutrients reached high concentrations[1] (150 µg P-PO_4^{2-}/L) in both the Middle and Lower Loire systems, leading to extensive development of algal biomass (summer chlorophyll *a* average > 150 µg/L). Recent papers based on the regular monitoring survey[2, 3] (carried out by the Basin Authority) have observed that controlling direct P inputs since the 1990's is more likely to be the cause of a spectacular decline of algal pigments in the Middle and Lower Loire from a summer

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chlorophyll *a* average of 150 µg/L, to 50 µg/L. These previous works also called into question the validation of research interpretation based on monthly frequency sampling. This present study proposes assessing the different biogeochemical processes involved in the Loire River during the year 2012 based on high sampling frequency, at three strategic stations.

1. Study area and localization of sampling sites

Station 1 is located at Saint-Satur (SS), in the upper part of the Loire catchment (Fig. 1). The headwater catchment is a mountainous area, and the Loire main stream runs through narrow gorges and valleys. Below the confluence with the Allier River, the geomorphology of the Middle Loire favours algal development: the valleys become wider with multiple channels, slowing down flow velocity[4]. As a consequence, average water depth can be low in the summer (0.60 m), contributing to warming and lighting up the water column.

Situated at Cinq-Mars-La-Pile (CM), station 2 corresponds to the outlet of the Middle Loire Corridor: between the Allier-Loire confluence, the river receives no significant tributaries but some groundwater inputs from the Beauce aquifers where agricultural pressure is intense[3]. Station 3 at Montjean (MJ) is located at the basin outlet (110000 km^2), before the estuarine influence.

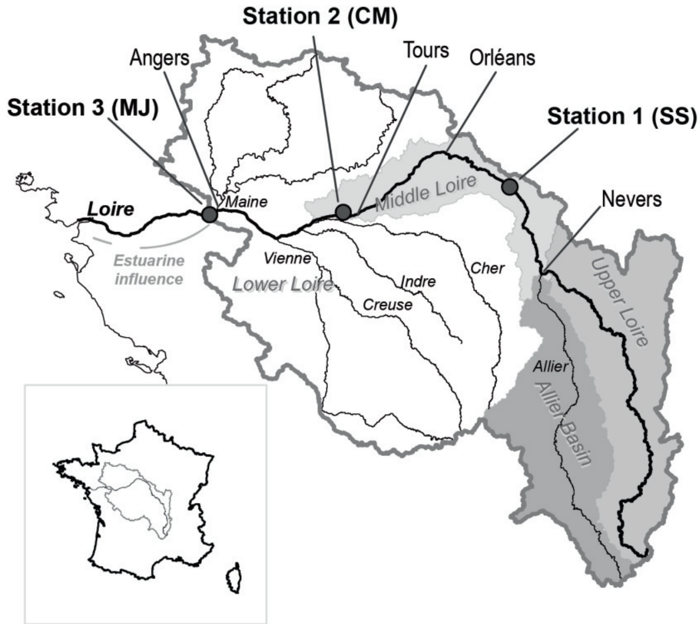

Fig. 1. Basin situation, location of sampling sites and major cities.

Urban pressure is significant: 8 million people live in the Loire Basin (INSEE 2008), mainly concentrated near the main river course. This pressure is known to be responsible for direct phosphorus inputs in the Loire River[5]. Diffuse nutrient sources are also significant since agricultural pressures are intense: arable land represents 30% of the whole catchment at station 3.

2. Sampling

Samples were collected every three days according to the same procedure at each station. Water was sampled from a bridge in the main river channel. Filtrations were made on-site with 0.45 µm cellulose acetate membrane filters for chemical parameters, and with 0.7 µm glass filter (Whatmann GFF), previously burned at 500°C during 6 hours for chlorophyll-a. Nutrients (N, P) were measured on filtered and unfiltered water in order to determine different forms. Silica was only measured in the dissolved phase. Water samples were stored in polypropylene tubes. Aliquots for P (dissolved inorganic and particulate P) and for dissolved organic nitrogen were acidified to pH = 2 with Suprapur grade nitric acid (Merck). After water filtration, filters for chlorophyll-a determination were stored at -80°C.

3. Results and discussion

3.1. Description of annual water discharges

The Loire is under a pluvial regime, with some nival influences because of relatively high headwater elevation (3% of basin exceeds 1000 m). During 2012, daily water discharge at station 3 ranged between 130 and 2700 m^3/s. The flood which occurred during winter 2011/2012 corresponded to a mean hydrological event for the winter period. A spring-summer flood occurred in May/June 2012, making 2012 quite peculiar: the first event (flood of May) reached 2000 m^3/s at station 3 and corresponded to a five-year flood for this period. Despite an active hydrology in May and June, the flood recession leaded to low flows: discharge in mid-August ranged between 60 m^3/s at station 1 and 130 m^3/s at station 3.

Although both upstream stations (stations 1 and 2) are distant from 270 km, discharge remains quite similar because this reach receives no major inputs but mostly groundwater inputs (from Beauce aquifers). On the contrary, discharge pattern at station 3 can be different depending on the rain event location because the Loire receives 4 major tributaries (doubling the basin size) between stations 2 and 3.

3.2. Total Suspended Solids: origins and dynamics

Total Suspended Solids concentrations (TSS) presented a high temporal variability with values ranging between 0-150 mg/L at station 1, 0-130 mg/L at station 2 and 0-190mg/L at station 3. TSS followed the hydrodynamic conditions as a result of runoff and mechanical soil erosion. It remained higher at the basin outlet most of the time, despite few events when TSS concentration was higher at the upstream station. TSS originates mostly from soil erosion processes during significant hydrological events. In summer, it is partly composed of detrital rocks, of particulate organic matter when phytoplankton reaches high levels, and of neoformed precipitated calcite[3].

3.3. Nutrients dynamic

Nitrate concentrations respect an upstream-downstream gradient, concomitant with agricultural pressure that increases from upstream to downstream. In summer, the difference between stations 1 and 2 is probably due to Beauce aquifers inputs, where average nitrate is 14 mg N/L[3]. Nevertheless, nitrate pattern is quite similar for the three stations: maximum in winter (around 4 mg N/L) during significant hydrological events, and minimum in summer (1.7 mg N/L) due to the uptake of primary activity. Seasonal amplitude corresponds to 2.3 mg $N\text{-}NO_3^-/L$.

Dissolved inorganic P concentrations (DIP) had the same temporal pattern as nitrate (winter maximum, summer minimum), except at station 1 where levels remain quite high during summer (50 µg P/L) because of no significant algal activity. In winter, soil leaching processes explain the increasing of PO4 levels up to 50 µg P/L during winter 2011/2012 and 100 µg P/L the next year. There is a clear seasonality at stations 2 and 3, because of primary activity: the lowest value was 10 µg P/L at stations 2 and 3 in August.

Dec11 Jan12 Fev12 Mar12 Av12 May12 Jun12 Jui12 Aou12 Sept12 Oct12 Nov12

Fig. 2. Survey results during the year nov 2011 – nov 2012 at three stations.

Silica concentrations present a sharp decrease synchronous at the three stations and occurred in March-April. Its amplitude is high (7 mg $Si\text{-}SiO_2/L$) and we assume that it is linked to diatom growth favored by stable and low hydrology, nutrients availability, and slightly warm water temperature. The SiO_2 levels could have got back their initial value around 6 mg/L when diatoms decay occurred because of aging or water temperature increase.

3.4. Algal pigments: hydrological events disturbance and P- limitation

Algal pigments concentrations started to rise concomitantly with SiO_2 decrease by the end of February. It is probably the signal of diatom growth. Green algae started to develop and reached a maximum of 60 µg/L at stations 2 and 3, whereas it remained low at station 1. There was a great temporal variation during the summer: total pigments could be divided by a factor of ~3 from one day to another, because of a dynamic hydrological event. First, this decrease was due to dilution, but then phytoplankton decay occurred because of flow speed increase and suspended solids augmentation. Despite the disturbance caused, the River Loire was still able to develop 50 µg/L of total pigments within the Middle Loire corridor, evidencing the major role played by the river morphology.

Using Redfield ratios (106C / 16N / 1P / 40Si) and Descy *et al*. (2011) equivalence[6] (C:Chl. *a* = 37), the PO_4 seasonal amplitude corresponds potentially to the development of 45 µg Chl. *a* /L and the NO3 amplitude represents a potential of 350 µg Chl. *a*/L, five times the observed value. This shows that the Loire River is under P-limitation, and that there are clearly NO_3^- losses in the river water: riparian denitrification and uptake by macrophytes and periphyton are invoked to face such a difference. Denitrification is probably the main process removing nitrate in the alluvial channels, but further investigations are needed using N-isotope ratios[7] to confirm this hypothesis.

By the end of August, algal pigments dropped down to 10 µg/L when the river reached a P-limitation.

Conclusion and perspectives

Surveying nutrients and algal biomass at such a temporal scale allows observing and understanding better fine temporal biogeochemical processes. If we could decipher some of these (P-limitation, nutrient uptake, summer flood disturbance), several hypothesis need to be confirmed (riparian denitrification, macrophyte uptake), and further investigations are needed. Descy *et al.* (2011)[6] questioned the responsibility of the invasive *Corbicula* clam on the phytoplankton of the Loire River: would it be responsible for the apparent eutrophication decline? A numerical model adapted to the Loire River (currently in development) at high spatial and temporal discretization would contribute to evidence some of these processes.

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