Dynamics and Fluxes of Nutrients in Surface and Groundwaters in a Cultivated Karstic Basin in the Jura Mountains

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Abstract

This study aims at characterizing spatiotemporal variability of the fate of nutrients in the karst basin of the Loue River in the French Jura Mountains. The long-term temporal analysis (40 years) shows that the NO_3 increase from 1970s to the 1990s followed by a no-trend period in 2000s. The changes are linked to the usage of mineral fertilizers. The short-term analysis shows that the degree of aquifer saturation at the beginning of the hydrological cycle is a key factor to assess NO_3 mobilization during the recharge events. Contrary to nitrate, the PO_4 concentrations are disconnected from agricultural practices and are probably the consequence of point-source contaminations from domestic wastewater. Annual loads were estimated on 5 sub-basins in order to characterize the spatial variability of water contamination. Difference in fluxes for each sub-basin highlighted the most impacted reaches, providing information on hydrological units where anthropogenic pressure is highest. A correlation of NO_3–N loads with the surface area of main crops using highest level of fertilization and tillage (field crops, temporary grasslands) is proposed, highlighting the environmental impact of most intensive agricultural practices (inventoried in a small area covering less than 10% of the whole basin). This study illustrates complex interactions between agricultural practice and hydrological function and gives first insight into the fate of nutrients in karst environment.

Introduction

Excess nitrogen (N) and phosphorous (P) in surface water and groundwater cause chronic changes in aquatic ecosystems. Despite some studies in the last decade (Mahler et al. 2008; Huebsch et al. 2014; Lorette et al. 2018), the case of karst basins is generally poorly documented in the literature. Morphological and hydrological properties of karst aquifers can limit retention and remediation, and favor fast transfers at the outlet. Environmental consequences of anthropogenic pressures are then likely to be intensified in karst basins.

Rivers in the Jura massif (Eastern France) are fed mainly by karst springs that drain the plateau. That context favors complex karst–river interactions, making difficult the understanding of hydrological behavior of basins (Dörfliger et al. 2004; Charlier et al. 2014). Although population and agricultural activity are relatively moderate compared to other intensive cultivated territories in France, the water contamination seems to be promoted by the vulnerability of the karst environment.

The Loue River in the Jura massif is important for tourism, fishing, and drinking water supply (Besançon for example) and has become an observatory for the fate of nutrients in karst basins. The aim of this paper is to present first results about the characterization of dynamics and fluxes of nutrients in waters and to investigate the relationships between agricultural practice and water contamination. Based on a monitoring network surveying nutrient concentrations and water flow, a temporal analysis of concentrations at short (1 year, daily frequency) and long term (40 years, monthly to seasonal frequency) as well as (2) a spatial analysis of fluxes at the sub-basin scale in relation to agricultural practices has been carried out.

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Site and Data Available

The study site is the Loue–Lison basin (1100 km^2) in the French Jura Mountains (Fig. 1a). The climate is temperate and displays a strong influence of mountainous areas in the eastern border. Precipitation averages 1400–1700 mm/year. The recharge area is characterized by a carbonate plateau of Jurassic limestones cross cut by 150 m deep valleys (Fig. 1b). Loue and Lison rivers are mainly fed by groundwater originating from several karst aquifers (Charlier et al. 2014). Two main springs located in the upstream zone, the Loue and Lison springs with a mean annual discharge Q_{mean} of about 9 and 7.5 m^3/s, respectively, generate more than 1/3 of the river flows at the basin outlet (Q_{mean} = 47 m^3/s). In addition, numerous lateral karst springs contribute to the surface flows. Surface runoff is usually limited to small marly areas in the downstream zone of the basin. The Loue spring is partly recharged by losses from the Doubs River

that lead to dry up some river reaches during low-water periods in summer.

On the overall basin, land use is dominated by forest (49%) and permanent grassland (36%) for dairy cows (milk and cheese production) (Fig. 1c). However, at the sub-basin scale, a spatial variation is observed with an increase in land uses that use mineral fertilizers in the downstream area: cereal and field crops (up to 6%), as well as temporary grassland (up to 13%). There are four main application periods of fertilization over a year (including both mineral and organic fertilizers). Applications in March–April represent about 2/3 of the total applied amount for crops and grasslands. A second application period occurs between May and July after the first hay cut. In September–October, composted or evolved manures are spread mostly before autumnal crops. In the same time, manure and slury pits are emptied before the cold season for application in grasslands. In winter, composted and evolved manures are spread on grasslands.
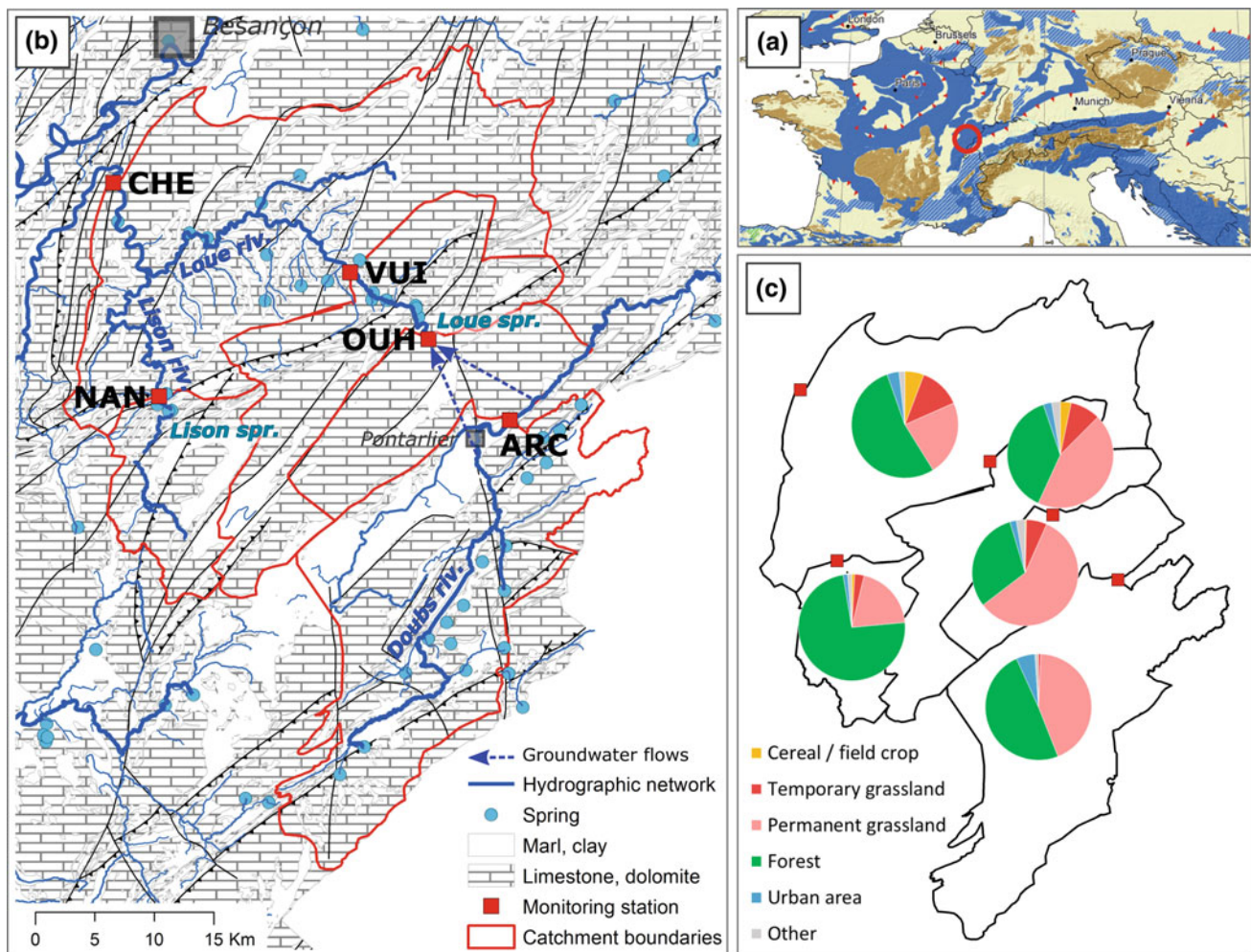

Fig. 1 **a** Location of Loue–Lison basin in the French Jura Mountains on the World Karst map (Karst aquifers in blue color—Chen et al. 2017), **b** hydrogeological map with the location of the 5 monitoring stations, **c** land use map for the 5 sub-basins

Daily precipitation and discharge are recorded by Météo-France and DREAL (*Direction Régionale de l'Environnement, de l'Aménagement et du Logement*) Burgundy Franche-Comté, respectively. Three data sets for NO_3 and PO_4 concentrations are used in this study (Fig. 2). Long-term data set (occasional analysis from 1970 to 2002) and mid-term data set (daily to biweekly analysis 2003–2012) of the Loue River at Chenecey-Buillon (CHE station) were provided by the Water Agency and the City of Besançon, respectively. Recent data set (daily to biweekly analysis from 2015 to 2017) was also collected from the QUARSTIC network (QUAlity of Rivers and Survey of nutrients in Franche-Comté; Charlier et al. 2018) at five monitoring stations (Fig. 1b): ARC station on the losing reach of the Doubs River at Arçon, OUH station at the Loue Spring at Ouhans, NAN station at the Lison Spring at Nans-sous-Sainte-Anne, VUI station on the Loue River, CHE station on the Loue River at the basin outlet. Agronomic data are provided by the Agricultural Association of the Doubs Department (CIA25-90). Spatial data of land uses are extracted from the land register (RPG 2014 database). In addition, temporal data of annual delivery amount of mineral fertilizers are estimated from data from the Union of Fertilizer Industries in Doubs department where the study site is located.

Results and Discussion

Evolution of Nutrient in Waters

At Multi-annual Scale

Figure 3 compares the annual evolution of the mean concentration of NO_3 and PO_4 at the basin outlet (CHE station) with the evolution of the delivery amount of mineral fertilizers (differencing those containing N and P). Standard deviation of concentrations indicates high intra-annual variations. Regarding the NO_3 global evolution, the increase from 3 to 7 mg L^{-1} in the 1970s to 1990s period is concomitant with the increase in delivery of mineral fertilizers. In the 2000s, NO_3 stops to increase when a significant decrease in delivery of fertilizers is observed. An unusual peak in 2003–2004 hydrological cycle appears after the extreme dry period in spring and summer 2003. No clear evolution is visible in PO_4, but two years (1982 and 2012) show high concentrations in waters (mean concentration >0.2 mg L^{-1}) without link with fertilizer amount. Indeed, contrary to NO_3, no relationships are observed with the delivery amount of fertilizers although fertilizer containing P shows a strong decrease since the 1980s.

Globally, changes to the annual NO_3 concentration may be explained partly by the intensity of crop mineral
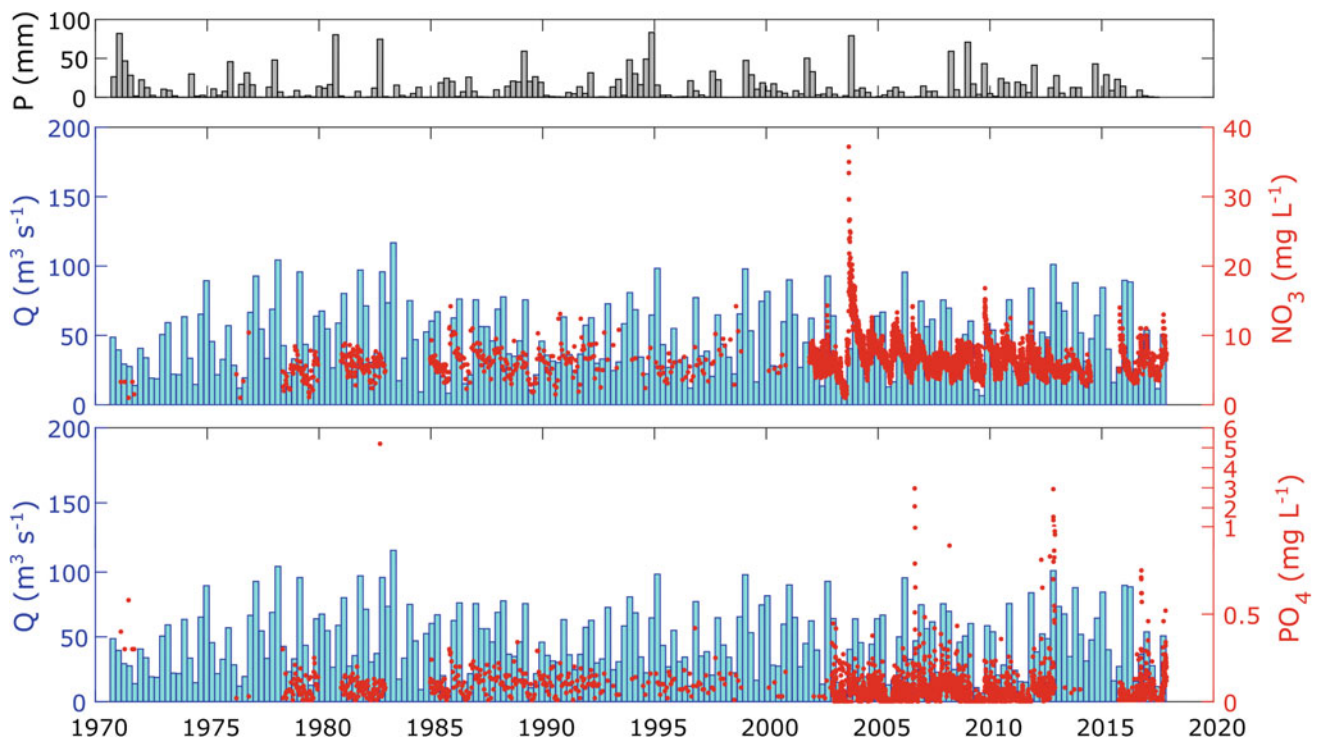

Fig. 2 Hydrological (quarterly precipitation *P* and discharge *Q*) and nutrient (punctual records) time series in the Loue River at Chenecey-Buillon over the 1970–2017 period; the interval on the *y*-scale for PO_4 is changing above 1 mg L^{-1}
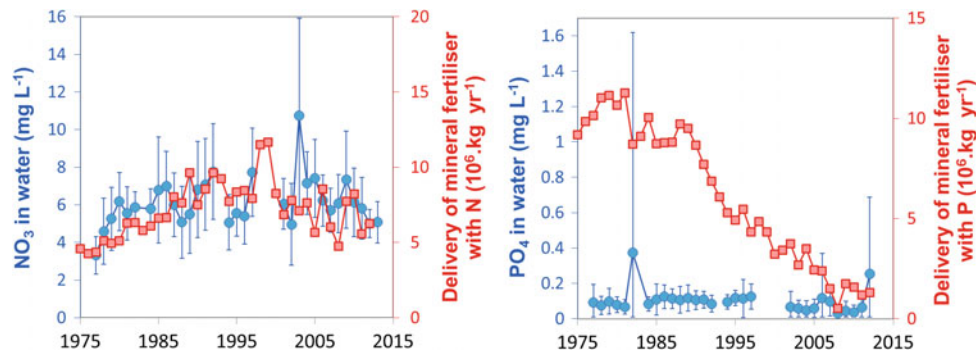
Fig. 3 Mean annual concentration (blue circles) of NO_3 (left) and PO_4 (right) at the CHE station plotted in parallel with the delivery amount of mineral fertilizer (red squares) containing N (left) and P (right) in the Doubs Department. Only years having more than 5 analyses are plotted; bars indicated s.d.

fertilization. As mineral fertilization is limited in grasslands by the cheese production (Comté) industry (cooperative union) as part of their quality insurance policy, the general NO_3 evolution observed at the basin outlet is probably the consequence of agricultural changes in only a small part of the cultivated fields used for cereals, field crops, and temporary grasslands, which represent less than 10% of the total area.

The PO_4 evolution in water is very different from NO_3 but is also different from global phosphorous trends at a larger scale. Indeed, phosphorus concentrations and loads strongly declined in main European rivers during the 1990s (Bouza-Deaño et al. 2008; Ludwig et al. 2009; Floury et al. 2012; Aguilera et al. 2015). But in our case, the severe decrease in mineral fertilization containing P is not followed by a decrease in PO_4 in water. Thus, following annual phosphorous budget given by Mainstone and Parr (2002) who showed that most of phosphorous origin is from wastewater treatment plants (WWTP), we hypothesis that the main origin of phosphorous contamination of the Loue River has a domestic origin. These results are coherent with some regional characterizations showing that the NO_3 dynamic in water was found to be a multifaceted process including agricultural practices, whereas that of PO_4 seemed to depend more on local impacts, such as urban and industrial activities (Aguilera et al. 2015).

At the Annual Scale

Two contrasted hydrological cycles have been selected to illustrate the infra-annual dynamic of NO_3 and PO_4 (Fig. 4). First, 2003–2004 (Fig. 4, left) has been chosen, because in September 2003 the highest NO_3 peak at the CHE station was recorded (37 mg L^{-1}) since the beginning of monitoring in 1970s (Fig. 2). The intra-annual NO_3 evolution shows a rapid and strong increase during first autumn recharge events, followed by a progressive decrease during winter, spring and summer to reach concentrations of few mg L^{-1} at

the end of the cycle. Despite high recharge events throughout the year, main peaks are recorded during autumn. This pattern is observed every year (Fig. 2) but with various decreasing slopes and peak intensities.

Second, 2016–2017 (right) is a mean year in terms of nutrient's concentrations. In that case, the intra-annual evolution of NO_3 at CHE station shows a similar behavior with highest values in autumn–winter, but NO_3 during recharge reaches a value of 11 mg L^{-1}. The comparison with the four other stations in the Loue basin is interesting because the pattern is globally similar. However, some differences are observed. While the intensity of NO_3 peak is similar for all stations of the Loue–Lison River (OUH, VUI, NAN, CHE), it is twofold lower for the ARC station in the Doubs River, in the losing reach feeding partly the Loue Spring. Moreover, the dynamics during spring and summer shows contrasting behavior along the river. The annual decrease is higher for ARC and especially VUI stations where concentrations reach the limit of quantification (0.5 mg L^{-1}). This NO_3 depletion over several weeks during periods of low-water levels is probably linked to a NO_3 consumption in favor of a biomass production (algal development) within these river reaches. This hypothesis is supported by a concomitant COT increase in the river as mentioned by Charlier et al. (2018). The progressive summer decrease is shorter at NAN station where we observe an earlier increase in concentrations from June, leading to NO_3 concentrations in the Lison Spring higher than other stations until September.

The PO_4 dynamics at the intra-annual scale does not show a clear annual pattern. Although, PO_4 peaks occur concomitantly to NO_3 peaks, as observed during winter 2003–2004 (Fig. 4, bottom left), PO_4 shows erratic daily peak intensities throughout the year. Peaks frequently exceed 0.2 mg L^{-1} and in some periods 0.5 mg L^{-1} (as in 2016–2017; Fig. 4—bottom right). The peak occurrence and intensity is not strictly related to high-water periods and many peaks occur during the low-water period, after rainfall

Fig. 4 Hydrological and nutrient's time series for two hydrological cycles: 2003–2004 (left) during which the highest nitrate concentration is observed at CHE station since 1970, and 2016–2017 (right) for which data from 5 stations over the basins are available. For more readability, y-scales for NO_3 and PO_4 are not the same for both hydrological cycles. Labels of stations referred to the map in Fig. 1b
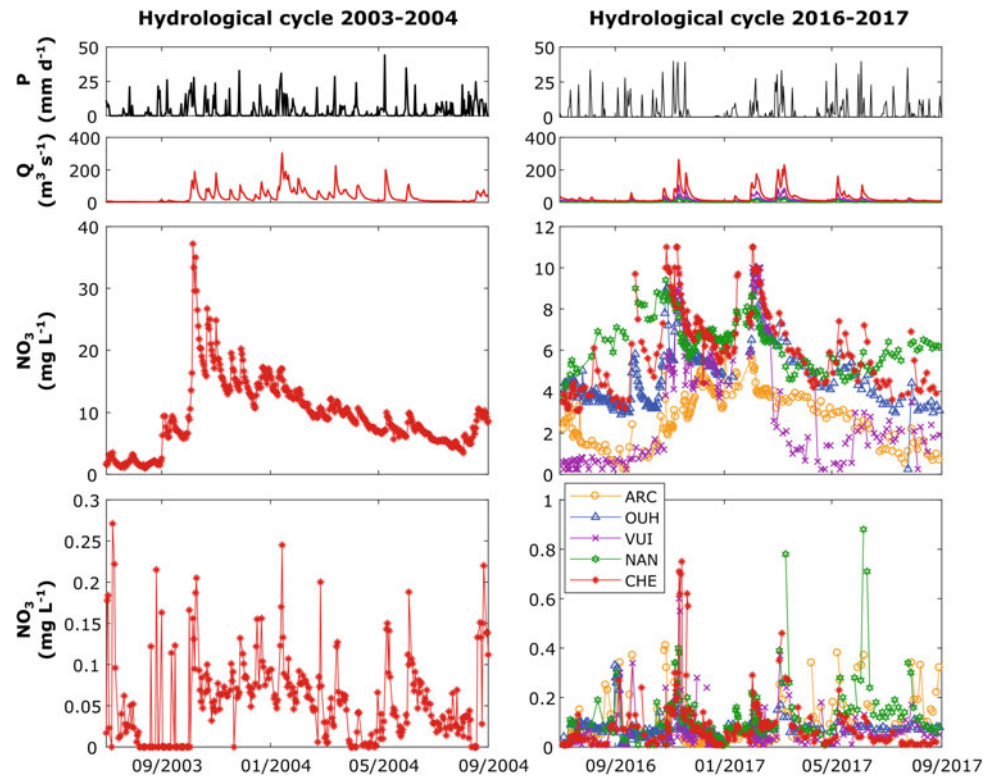
events that have a too low intensity to generate a flood. Apart from these periods, PO_4 is generally very low, close to the limit of quantification at 0.02 mg L^{-1}. The comparison with other stations over the basin (Fig. 4 bottom right) shows that the peak occurrence varies according to the river reaches, but the concentration remains in the same range between 0.2 and 0.8 mg L^{-1}.

As the highest NO_3 concentrations are generally observed during the autumn recharge events, we ask whether the antecedent hydrological conditions may explain the temporal variability of NO_3. The relationship between the annual NO_3 peak concentration and the minimum discharge recorded at the beginning of the hydrological cycle (as an indicator of the initial groundwater storage) has been plotted from 2002 to 2016 (Fig. 5). Data show that the lower the minimum discharge, the higher the following NO_3 peak. The relationship between these two variables can be fitted by a power-law function ($R^2 = 0.76$). This result means that the duration of the low-water period during summer is a key factor to explain nitrate mobilization in waters. As timing and amount of organic and mineral fertilizers are almost constant over the last decade, three hypotheses can be formulated to explain this relationship. First, driest periods are generally associated with lower agricultural yields, leading to a high amount of N in soil (Bloor and Bardgett 2012). This residual N that was not consumed by plants can be leached by infiltration waters in post-harvest periods. Second, first precipitations after a warm period may favor

mineralization of organic materials in soils, leading to enhance NO_3 leaching, as proposed by Mudarra et al. (2012). Third, a progressive desaturation of the karst aquifers during the summer may promote NO_3 storage in the soil/epikarst or aquifer which leaches during the first recharge events.
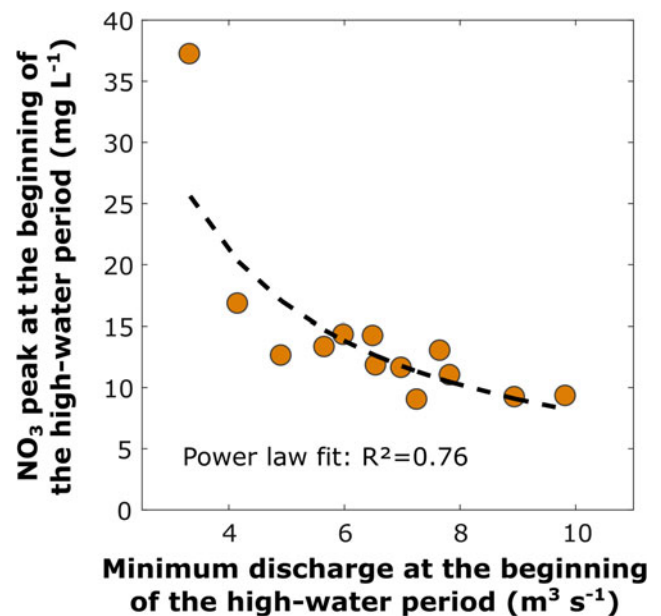

Fig. 5 Relationships between the minimum discharge and the NO_3 peak at the beginning of the high-water period (from 2002 to 2016)

Other studies carried out in the Jura Mountains (Pronk et al. 2009; Cholet et al. 2019), showed fast NO_3 increase in springs after rainfall events. Such response was attributed as the consequence of a mobilization of NO_3 stored in the soil/epikarst by Huebsch et al. (2014). Finally, these new results show that the degree of aquifer desaturation is a key factor to assess the intensity of NO_3 mobilization during the main recharge events.

Spatial Distribution of N and P Load

Annual Loads

Annual loads of nitrate–nitrogen NO_3–N and of phosphate–phosphorous PO_4–P during the 2016–2017 hydrological cycle were estimated for each sub-basin. The annual load was calculated adding up daily loads estimated from discharge and concentration data sets. For intermediate sub-basins (delimited by two successive stations in a river reach) loads were estimated making the difference of annual loads between the downstream and the upstream stations. Annual loads expressed by surface unit are presented in Fig. 6.

Regarding NO_3–N, the downstream sub-basin of the Loue River (CHE station) has the highest loads (about 17 kg ha^{-1} year^{-1}). This is about 1.5 times more than the intermediate and upstream sub-basins (including the both Loue and Lison Springs at OUH and NAN stations, respectively) and about 7 times more than the Doubs River in the losing reach (ARC). Regarding PO_4–P, the downstream sub-basin (CHE station) is also the one with the highest loads (about 0.5 kg ha^{-1} year^{-1}), but in that case, the Lison Spring (NAN station) recorded also high PO_4–P loads. This is due to high PO_4 peaks recorded in summer (see green stars in Fig. 4—bottom right).

Impact of Agricultural Practices

In accordance with our first results highlighting a water contamination related to fertilization, we expect to describe the spatial variability of annual NO_3–N loads with agriculture. Figure 7 presents the annual NO_3–N loads at the sub-basin scale as a function of the main crops using fertilizers (expressed as a percentage of the total sub-basin

Fig. 6 Annual loads of NO_3–N (left) and PO_4–P (right) for the 5 sub-basins of the Loue–Lison during the 2016–2017 hydrological cycle
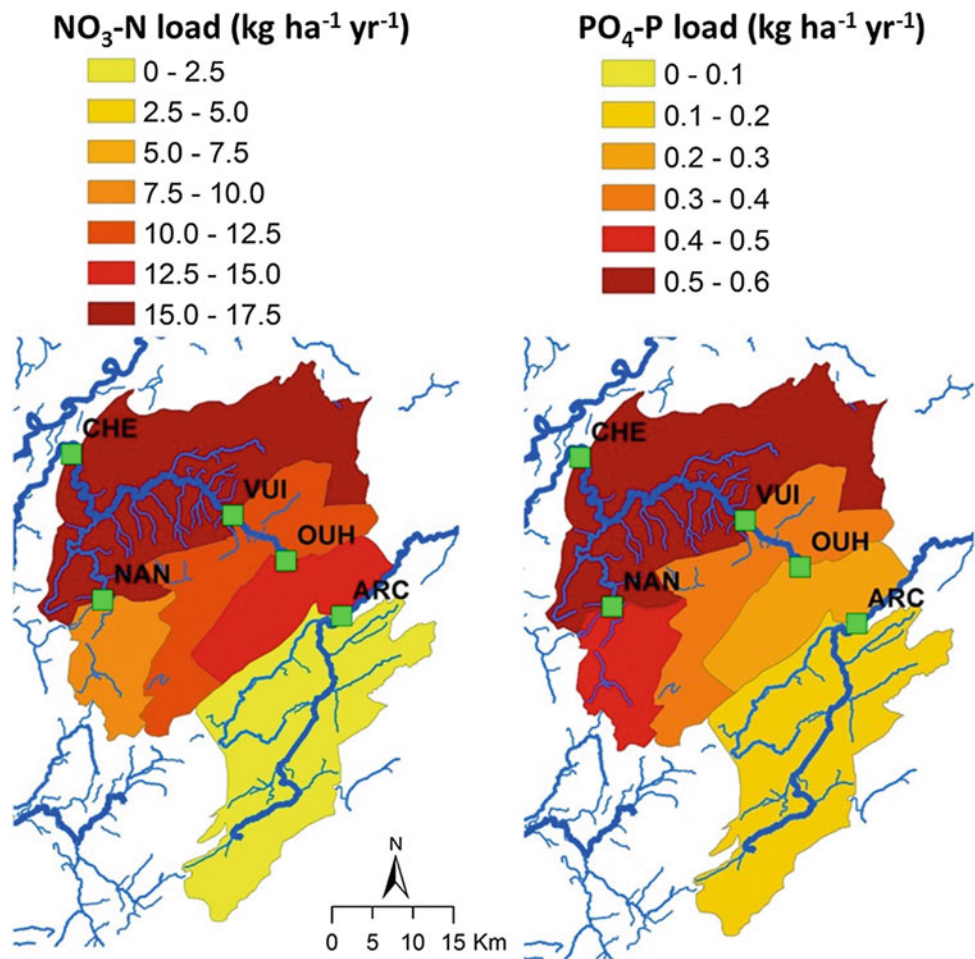
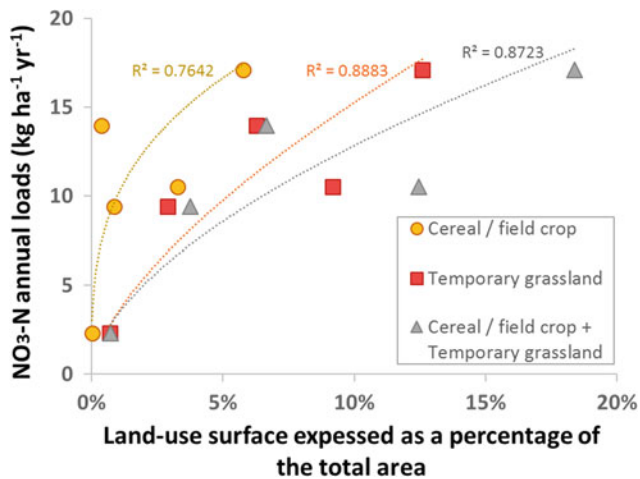**Fig. 7** NO$_3$–N loads during the 2016–2017 hydrological cycle versus surface of the main crops using fertilizers at sub-basin scale; R^2 refer to a power-law fit

area). The key land uses selected were those grouping cereal and field crops (yellow circle), and temporary grasslands (orange square). The combination of both was also tested (gray triangle). Good relationships were found for all three variables, but we should note that the temporary grassland seems to explain a little bit better the NO$_3$–N variability than cereals and field crops (r^2 = 0.89 vs. 0.76). The low number of stations (5 sub-basins) is not sufficient to characterize significantly the relationship and to conduct a thorough analysis differentiating the impact of cultural practices. However, it should be noticed that temporary grasslands cover twofold higher surface than cereal and field crops (7% against 3%), suggesting a probably high impact of those ones on the water quality of the Loue River. This result highlights the potential role of temporary grasslands (and cereals and field crops) in NO$_3$ leaching compared to permanent grasslands, which cover more than 1/3 of the surface basin (and for which no relationships was found with NO$_3$–N loads). This is coherent with observations at the field scale showing that grassland renovation (tillage) favors NO$_3$ leaching (Francis et al. 1995; Seidel et al. 2009).

Conclusion

Short- and long-term monitoring of NO$_3$ and PO$_4$ concentration in surface water and groundwater in the Loue basin (Jura Mountains) provides information on the evolution of the impact of anthropic activities at different time scales. The long-term NO$_3$ trend is related with the use of mineral fertilizers, while the short-term trend involves a more complex interaction between agricultural practices and hydrological

function. The changes in PO$_4$ are partly disconnected from agricultural practices and illustrate more probably point-source contaminations from domestic wastewater. The estimation of annual loads for each sub-basin showed the most impacted reaches. Contrasted flux gives information on hydrological units where anthropogenic pressure is the highest. Regarding nitrates, a link with agricultural practices is proposed, highlighting the role of the main crops using fertilizers on the spatial variability of water contamination.

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