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Sources and fates of NO_3^- and PO_4^{3-} in an alluvial plain wetland - Insights from the Auzon oxbow and the alluvial aquifer of the Allier (Auvergne, France)

Cyril Aumar^{a,b,e,*} , H el ene Celle^a, M elanie Quenet^{a,c}, Olivier Voldoire^c, Elisabeth Allain^c, Alexandre Garreau^c, Nicolas Caillon^d, Pierre Nevers^a, Jean-Luc Devidal^e, Gilles Mailhot^b, Aude Beauger^c

^a Universit e de Franche-Comt e, CNRS, Chrono-environnement, F-25000, Besan on, France

^b CNRS, SIGMA, Institut de Chimie de Clermont-Ferrand, Universit e Clermont Auvergne, 63000, Clermont-Ferrand, France

^c GEOLAB - UMR 6042 UBP & CNRS, 4 Rue Ledru, 63000, Clermont-Ferrand, France

^d Universit e Grenoble Alpes, CNRS, IRD, Grenoble INP (Institute of Engineering), IGE, Grenoble, France

^e Universit e Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, 63000, Clermont-Ferrand, France

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ABSTRACT

The continental hydrosystems of wetlands play fundamental socio-economic and environmental roles in all aquatic environments. These ecosystems, when located at the interface between surface and groundwater, such as oxbows, are of crucial importance in regulating water and nutrient flows. They help control water quality and provide ideal habitats for often fragile species. The transfer of contaminants into the different compartments of the groundwater-wetland-river continuum is difficult to characterize because they are most often of different types and origins within the same hydrosystem. The objective of this study is to characterize water quality and water exchange using a multi-tracer approach combining monthly hydrochemical monitoring, isotopic characterization of NO_3^- molecules ($\delta^{18}\text{O}_{\text{NO}_3}$ and $\delta^{15}\text{N}_{\text{NO}_3}$) and concentration of chemical micropollutant particles. This methodology is applied to a fluvial annex of the Allier River, the Auzon oxbow hydrosystem, subject to moderate environmental and anthropogenic pressure (low level of industrialization and urbanization, mixed conventional farming). Nitrate (NO_3^-) and phosphate (PO_4^{3-}) concentrations do not behave in the same way over time: NO_3^- has a seasonal dynamic, whereas phosphates are disconnected from the hydrological regime. Some subsystems of the Auzon oxbow are undergoing denitrification, demonstrating the importance of preserving these environments for their nutrient regulation potential. As for chemical micropollutants and PO_4^{3-} , the low overall concentration of these two contaminants, coupled with the high dilution potential of the Auzon oxbow hydrosystem, means that average concentrations remain within acceptable standards for surface waters. Based on these results, the Auzon hydrosystem is maintaining good ecological quality despite nutrient flows from multiple sources. The multi-tracer approach used in this study demonstrates its effectiveness in determining the origin of nutrients, and it could be applied to other studies in contexts where environmental and societal pressures are significantly higher.

1. Introduction

Wetlands, including oxbows, play a fundamental socio-economic and ecological role by efficiently controlling river discharge (flood prevention and low water adaptation) and improving water quality. They provide major ecological services as ecological niches and reproduction areas (Bullock and Acreman, 2003; Keddy, 2010; Maltby and Acreman, 2011; Mitsch and Gosselink, 2000). These wetlands are increasingly

crucial as nature-based solutions to address ecological issues and hydrological concerns caused by climate change (Davidson, 2014; Erwin, 2009; Goyette et al., 2023; Mitsch et al., 2013). However, to fully leverage their benefits, it is essential to understand their hydrological aspects in detail, as their connectivity with surface water and groundwater determines water quality and, consequently, their ecological properties (Borrette et al., 1998; Hunt et al., 1996; McLaughlin et al., 2019). Each wetland is unique and influenced by its own complexity

* Corresponding author. Universit e de Franche-Comt e, CNRS, Chrono-environnement, F-25000, Besan on, France.

E-mail address: Cyril.aurmar@uca.fr (C. Aumar).

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(Amoros and Bornette, 2002).

The interface between the aquifer and the river is considered a key zone for sustainable water management (WWAP /UN-Water, 2018), as it constitutes a transition area with transverse flows between aquatic and terrestrial environments (Dahm et al., 1998). This zone hosts biogeochemical processes that participate in natural contaminant removal within the hyporheic zone (Conant et al., 2004; Smith et al., 2005) and riparian areas (Aguiar Jr et al., 2015; Hill, 2019). Major contaminants degrading surface water and groundwater quality often include fertilizers, industrial synthetic chemicals, phytosanitary products, or pharmaceuticals (EEA, 1999; Hooda et al., 2000; Delpla et al., 2009). Numerous studies focus on nitrogen and phosphorus cycles (EEA, 2015), which are vital for living organisms but can harm the ecological balance in surface waters through eutrophication when in excess (Boeykens et al., 2017). Nitrate (NO_3^-) can be very harmful to human health, prompting various actions to reduce NO_3^- pollution, such as the Nitrates Directive (EC, 1991a,b) and the Water Framework Directive (EC, 2000) in Europe. For phosphate (PO_4^{3-}), which is the main nutrient favoring eutrophication (Boeykens et al., 2017), some actions have been promoted to reduce the concentration, such as the Urban Waste Water Treatment Directive and also the Water Framework Directive (EC, 2000).

Wetlands, whether artificial (Hammer, 2020; Wu et al., 2015) or natural (Cheng et al., 2020; Ingersoll and Baker, 1998; Hansen et al., 2018), are increasingly cited as solutions to problems associated with wastewater and contaminants in natural environments. Studies discuss the dynamics of NO_3^- and PO_4^{3-} concentrations using a spatial (Lasagna et al., 2016; Puig et al., 2017) or temporal approach (Randall and Mulla, 2001; Yue et al., 2023), but rarely both, in association with environmental tracers capable of identifying the biogeochemical processes involved. Contamination from NO_3^- , and to a lesser extent PO_4^{3-} , is often associated with agricultural pollution (Kendall et al., 2007; Widory et al., 2005; Power and Schepers, 1989) and tends not to consider chemical micropollutants from other sources.

Considering the issues surrounding nutrient regulation, it is essential to study wetland dynamics and the processes at work in these aquatic environments. In this study, we investigate the origin, dynamics, and fate of nutrients (NO_3^- and PO_4^{3-}) in a wetland located at the interface between several water bodies along a groundwater-wetland-river continuum. Auzon oxbow hydrosystem is a unique site comprising a wetland (a river annex) on the banks of the Allier River in the Haute-Loire department (France). Quenet et al. (2019) previously studied this site to identify the connections between the Allier alluvial aquifer, the wetland, and the Allier and Vendage rivers, which constitute the Auzon hydrosystem. Additionally, this study site is located in a diverse agricultural context, between intensive and extensive farming, in a moderately populated rural area, where nutrient flows sometimes exceed French environmental standards (Phyt'eauvergne, 2014).

In this manuscript we present firstly, a spatiotemporal analysis of nutrient fluxes in the Auzon hydrosystem. The coupling of spatial and temporal approaches over such an extended period (4 years) is unusual for this type of study. Secondly, NO_3^- isotope analysis following a sampling campaign (March 2018) was used to identify the origin and fate of NO_3^- in the hydro(geo)logical context. Thirdly, the analysis of chemical micropollutants in the waters of the Auzon hydrosystem was correlated with the analysis of PO_4^{3-} concentrations to identify their origin. The data from all three parts are discussed below, and used to create a conceptual model for the remediation of water flows in this type of riparian wetland.

2. Study area description

2.1. Location and climate

The Auzon oxbow is a fluvial annex of the Allier River, formed during two flood events in 1988 and 1989 (Beauger, 2008). It extends over a

length of 400 m downstream within the Allier River catchment, which itself covers a total area of 14,310 km² (Fig. 1). The Allier River originates at 1423 m above sea level at the La Moure de Gardille summit in the French Massif Central and flows northward for 410 km, joining the Loire River at the Bec d'Allier near Nevers. The Allier River is considered one of the last wild rivers in Europe, featuring active hydro-morphological dynamics, but it is also impacted by anthropogenic activities (Arfeuillère et al., 2023).

During the 1990–2020 period, the Allier watershed experienced a temperate climate with relatively hot summers (average temperatures above 23 °C in July and August) and cold winters (average temperatures of –2 to –3 °C from December to February, Lefort et al., 2022). In the Auzon oxbow study area, rainfall occurs primarily between May and October, with an average cumulative precipitation of 423 mm, contributing to an annual average precipitation of 692 mm (Lefort et al., 2022).

2.2. Geological and hydrogeological background

Upstream of Vieille-Brioude, the Allier riverbed is steep-sided and composed of Variscan crystalline formations (Korobova et al., 1997). Downstream, the Allier flows over the Tertiary sedimentary formations of the Limagne basin, characterized by marl and limestone deposits. This graben geomorphology led to the formation of the Allier alluvial aquifer, which is an unconfined alluvium layer 8–12 m in thickness and 100–4000 m wide (Lasnier and Marchand, 1982; Labbe et al., 2023). The Allier alluvial groundwater is a major freshwater resource for the Auvergne region, providing over 40% of the drinking water supply and a significant portion of water for agricultural irrigation (Mohammed, 2014; Mohammed et al., 2014). The alluvial groundwater is characterized by moderate electrical conductivity, neutral pH, and a calcium bicarbonate water type (Négrel et al., 2003, 2004; Mohammed et al., 2014; Quenet et al., 2019).

The study site, the Auzon oxbow hydrosystem (Fig. 1), includes the oxbow itself, the Allier River, its tributary the Vendage River, and the alluvial aquifer, which can reach a thickness of 10 m and is limited to the edge of the crystalline plateau domain. The Auzon oxbow was created by the capture of a former anthropogenic gravel pit during two flood events in 1988 and 1989. Currently, the Auzon oxbow is an active floodplain oxbow, as it remains connected to the Allier River through its downstream end. It has a total length of about 560 m and can be divided into three geomorphological parts (Beauger et al., 2015; Quenet et al., 2019): the upstream zone, disconnected from the Allier River at the surface but connected via an underground paleochannel; the hydrodynamically stable intermediate zone; and the downstream zone, characterized by the confluence of the oxbow with the Allier River at its downstream end. Quenet et al. (2019) demonstrated that the dynamics of the Auzon oxbow hydrosystem are governed by lateral inputs from the Allier River on its right bank and alluvial groundwater on its left bank during low flow periods. During high flow periods, the Allier River paleochannel connects to the oxbow, allowing water from the oxbow to infiltrate into the alluvial aquifer.

2.3. Land use and anthropogenic contamination

Land use at the site includes intermittent cow grazing on the right bank (RB), while the left bank (LB) is used for cereal production. The alluvial plain adjacent to the oxbow on the LB is divided into parcels dedicated to market gardening and small-scale crop production. Agricultural activities are more intensively developed on the neighboring agricultural plateau, which is an aquifer that likely contributes partially to the alluvial groundwater system. Additionally, the Vendage River provides an average annual discharge of about 50 L/s. It is partially fed by the discharge from the Cohade wastewater treatment plant (WWTP) (Fig. 1b) and has been identified as a poor-quality river with chemical micropollutant pollution and NO_3^- - PO_4^{3-} concentrations that exceed

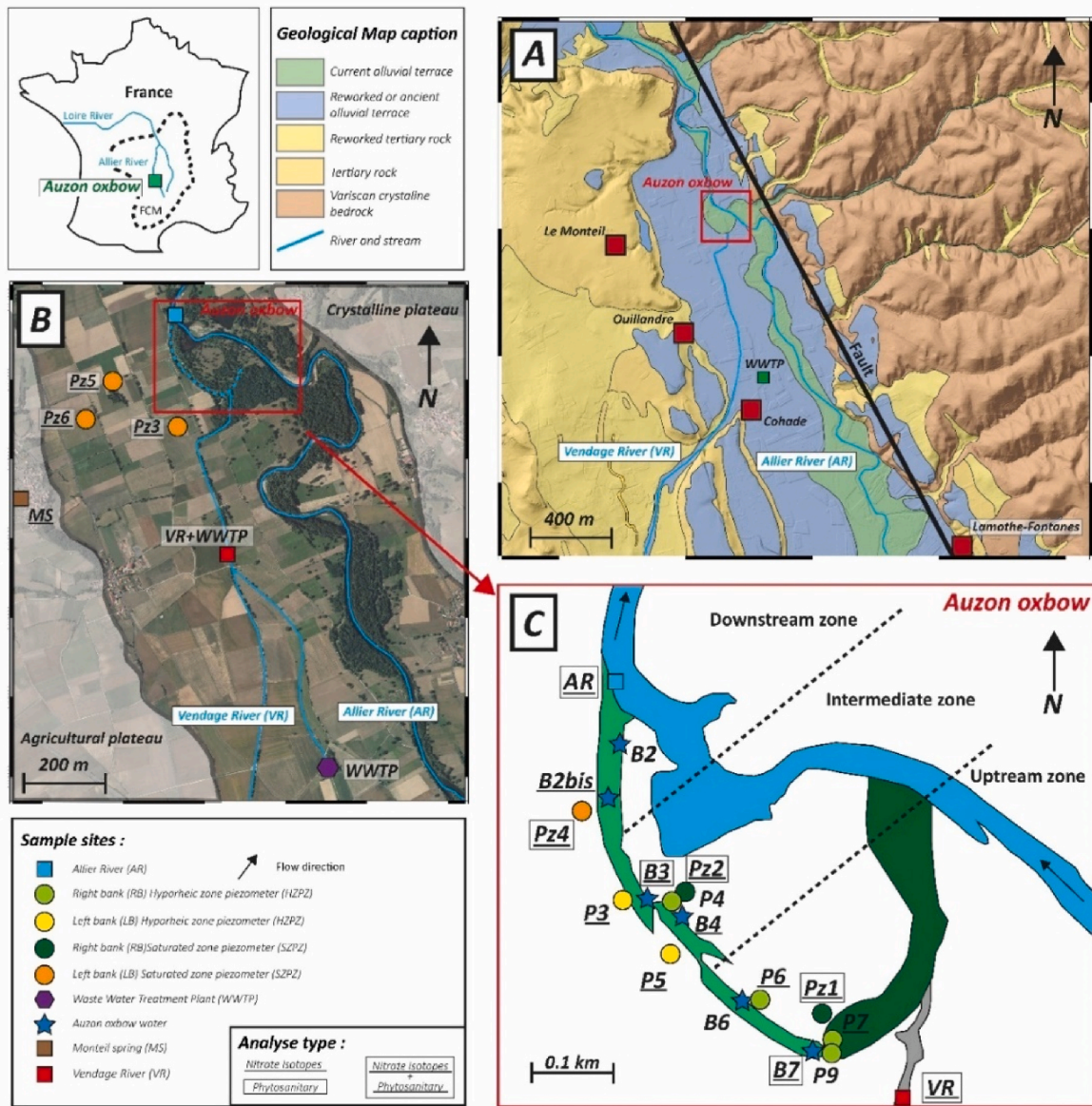


Fig. 1. Location of the Auzon oxbow and the sampling sites at different scales (French Massif Central, Brioude basin, Cohade agricultural plain and the Auzon oxbow). (A) Geological map of Cohade region; (B) Alluvial plain of Allier river and Vendage river with all external tributaries (VR + WWTP, MS) of the Auzon oxbow and piezometer in the alluvial aquifer (Pz3, Pz5 and Pz6); (C) Enlargement of the Auzon oxbow hydrosystem with all sample sites in the river (AR and VR), in the hyporheic zone (P3, P4, P5, P6, P7, P9), in the aquifer (Pz1, Pz2 and Pz4) and in the oxbow (B2, B2bis, B3, B4, B6 and B7).

European quality standards for aquatic environments (Phyt'eauvergne, 2014). The Vendage River reaches the study area south of the oxbow without any visible surface interaction with it (Fig. 1c), although Palma et al. (2020) demonstrated a potential seasonal connection using a Dissolved Organic Matter (DOM) balance.

3. Material and methods

3.1. Sampling network

The following sites were monitored to evaluate the water quality of the Auzon oxbow (Fig. 1):

- Auzon oxbow (B2, B2bis, B3, B4, B6, and B7);
- Allier (AR) and Vendage Rivers (VR);
- alluvial aquifer through six observation wells, covering the entire thickness of the local alluvial aquifer (Pz1 to Pz6);

- hyporheic zone of the alluvial plain through seven piezometers adjacent to the oxbow and implanted at depths ranging from 0.92 to 1.85 m (P3, P4, P5, P6, P7, and P9).
- Monteil spring (MS) representing the agricultural plateau aquifer which is assumed to partially feed the alluvial groundwater;
- Cohade wastewater treatment plant (WWTP); VR + WWTP represents the discharge from the WWTP diluted by the water of the Vendage River.

3.2. Field protocol and ion analysis

Surface waters and the Monteil spring were sampled directly using polypropylene containers. Groundwater was sampled using a Cole Parmer Masterflex I/S pump for hyporheic zone piezometers and a 12 V standard PVC narrow-diameter submersible pump for the observation wells. For each groundwater sample, stagnant water in the borehole was purged before sampling, and physicochemical parameters (electrical conductivity (EC), temperature, and pH) were monitored until they

stabilized.

Forty-four sampling campaigns were conducted at the 22 sites within the Auzon oxbow hydrosystem on a monthly basis from July 2014 to April 2018, apart from in February and December 2017 when the alluvial plain was flooded. Electrical Conductivity (EC), pH, and water temperature were measured *in situ* using a WTW multi 340i. Dissolved oxygen was determined with a Troll 9500 multiparameter instrument equipped with an RDO Sensor. HCO_3^- concentrations were determined directly in the field using a HACH Digital Titrator with sulfuric acid (0.1600 N and 1.600 N) and Bromocresol Green-Methyl Red Indicator (Hach method 8203). Samples were collected in clean, sterile 180 mL polypropylene containers with polyethylene caps after rinsing the bottles twice with the water to be sampled. All collected samples were transported and stored at 4 °C before analysis. Anions and cations were analyzed within 3 day at UMR 6042 CNRS Clermont Auvergne University (France) using a Thermo Fisher Scientific Dionex DX120 ionic chromatography for anions (F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) and a Thermo Fisher Scientific Dionex ICS1100 ionic chromatography for cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}).

3.3. Nitrate isotope and micropollutant analysis

Since the 1990s and early 2000s, nitrogen and oxygen isotopes of NO_3^- molecules have been used to identify NO_3^- sources in surface water and groundwater (Kendall, 1998; Böttcher et al., 1990; Widory et al., 2005; Kendall et al., 2007; Fenech et al., 2012; Matiatos et al., 2021; Puig et al., 2017; Petelet-Giraud et al., 2021; Harris et al., 2022). Nitrogen and Oxygen isotopes are effective tracers for understanding the nitrogen cycle in nature, particularly from soils to groundwater. Processes such as immobilization, mineralization, nitrification, anammox and denitrification will modify the $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ isotopic signatures of natural or anthropogenic NO_3^- inputs through fractionation (Robinson, 2001; Zhang et al., 2020). Each process is linked to a specific change in isotopic ratios, which can then be used to identify the different phenomena and determine the mobility of nitrogen in the environment.

In March 2018, a specific campaign to investigate NO_3^- dynamics was carried out at 16 sampling points on the site: the Allier and Vendage Rivers, four locations in the oxbow (B2bis, B3, B4, and B7), one spring on the agricultural plateau (the Monteil spring), five piezometers in the alluvial aquifer (PZ1, PZ3, PZ4, PZ5, PZ6) and four samples in the hyporheic zone (P3, P5, P6, and P7) (Fig. 1). For these points, in addition to the usual protocol, isotopic measurements of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ were carried out at UMR 5001 CNRS Grenoble Alpes University (IGE, France) using the bacterial denitrifier method (Casciotti et al., 2002; Morin et al., 2008; Kaiser et al., 2007). Samples were filtered with 0.45 μm membrane filters in the field, placed in 60 mL HDPE bottles, half-filled, and then frozen prior to analysis. The $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ isotope ratios were analyzed using a Thermo Finnigan MAT 253 IRMS and corrected for any isotopic effects related to the procedure by simultaneous analysis of the respective IAEA international reference materials (USGS 32, USGS 34, and USGS 35). Isotopic data were reported in the standard delta notation in parts per thousand relative to Atmospheric Air (AIR) for $\delta^{15}\text{N}_{\text{NO}_3}$ and Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}\text{O}_{\text{NO}_3}$. Detailed analytical procedures for isotopic measurements of NO_3^- molecules can be found in Bourgeois (2017) and Morin et al. (2008).

Of the 22 sampling sites, 12 were also selected for chemical micropollutant screening: the Allier River, the Vendage River, B3, B7, the six wells, WWTP, and VR + WWTP (Fig. 1b). Chemical micropollutant screening was performed by the COFRAC accredited Eurofins Laboratory (Eurofins Hydrologie Est, Maxéville: NF EN ISO/IEC 17025:2005 COFRAC 1–0685). Water samples were collected following Eurofins protocols, allowing for five different injections making it possible to screen 597 molecules for each sample site. Following Eurofins Laboratory protocols, samples were stored in icehouses provided by the laboratory; they were sent for analysis on the day of the campaign, and

analyzed the following day. The package chosen with Eurofins included various types of chemical micropollutants: agricultural (phytosanitary, fungicides, insecticides), urban (resins, paints), and industrial (resins, plasticizers). Analytical methodologies are described in the analytical report for each compound analyzed in the samples in Supplementary Materials 1.

4. Results

4.1. Spatio-temporal characterization of PO_4^{3-} and NO_3^- contamination in the Auzon oxbow hydrosystem

Results of the 44 sampling campaigns are summarized in Table 1 in the form of minimum, maximum and average concentration values for PO_4^{3-} and NO_3^- for each sample. Table 2 shows major element concentrations, physicochemical data (EC, pH, T and RDO) and isotopic ratios from the NO_3^- analysis for each sample from the March 2018 campaign. In this section, PO_4^{3-} and NO_3^- dynamics will be discussed using two approaches: (a) spatial analysis to determine the location of contaminants; (b) temporal analysis to compare PO_4^{3-} and NO_3^- concentrations with hydrological conditions during the period 2014–2018.

a) Spatial distribution of NO_3^- and PO_4^{3-} contamination.

Fig. 2 shows mean concentrations of PO_4^{3-} and NO_3^- based on 44 sampling campaigns conducted between 2014 and 2018, as well as concentrations recorded during the March 2018 campaign.

The Allier River (AR) is characterized by low NO_3^- and PO_4^{3-} concentrations, with maximum NO_3^- and PO_4^{3-} concentrations reaching 6.97 mg/L and 0.15 mg/L, respectively, and means of 3.37 mg/L and 0.06 mg/L, respectively. In comparison, the Vendage River (VR) exhibits the highest NO_3^- and PO_4^{3-} concentrations (except for Monteil spring for NO_3^-), with a maximum NO_3^- concentration of 40.81 mg/L and a maximum PO_4^{3-} concentration of 3.51 mg/L, with respective averages of 16.99 mg/L and 1.17 mg/L. In terms of NO_3^- , the Vendage River shows acceptable concentration ranges with respect to surface water quality standards (REEE-ESC (2019): <50 mg/L for NO_3^-). However, PO_4^{3-} concentrations exceed maximum and average standards (REEE-ESC (2019): <0.1 mg/L for PO_4^{3-}). Monteil spring is characterized by low PO_4^{3-} concentrations, despite a maximum of 4.08 mg/L recorded in August 2015. On average, the PO_4^{3-} concentration is 0.05 mg/L and is relatively constant. Nitrate concentrations are high, with a maximum value of 120.99 mg/L and an average of 97.77 mg/L.

Hyporheic zone waters (P2, P4, P6, P7, P9 for RB and P3, P5 for LB) exhibit notable differences between the two banks. The RB is characterized by low levels of NO_3^- and PO_4^{3-} (average $[\text{NO}_3^-] < 3$ mg/L, $[\text{PO}_4^{3-}] < 0.3$ mg/L), whereas LB waters appear to be more contaminated, with an average NO_3^- concentration close to 22 mg/L and a maximum value of 46.1 mg/L at P3. PO_4^{3-} concentrations are also high, with an average of 0.15 mg/L and maximum values of 0.73 mg/L for P3 and 0.8 mg/L for P5. The groundwater samples (PZ1, PZ2, PZ3, PZ4, PZ5, PZ6) display similar disparities in average and maximum concentrations to the hyporheic zone samples, particularly between the two banks (RB and LB). Groundwater in the RB area is characterized by low NO_3^- concentrations (max <5 mg/L, average of 1 mg/L). For the LB, NO_3^- concentrations are higher, ranging from 3 mg/L (PZ3) to 15 mg/L for PZ3, PZ4, and PZ5, indicating heterogeneous contamination within the alluvial aquifer itself. Regarding PO_4^{3-} , the groundwater is slightly contaminated, with average concentrations consistently below 0.1 mg/L.

Finally, the oxbow waters (B2, B2bis, B3, B4, B6, and B7) generally have low concentrations of NO_3^- and PO_4^{3-} . The only high value is the maximum concentration in PO_4^{3-} recorded at B7 (0.5 mg/L), while the NO_3^- concentration never exceeds 10 mg/L.

The spatial representation of the data shows that the March 2018 campaign is representative of the observations made during the 44

Table 1

Average, minimum and maximum values for NO_3^- and PO_4^{3-} concentrations for all 22 sample sites for surface water, hyporheic waters and groundwaters of the right bank and the left bank for the 44 campaigns.

Sample ID		NO3-	PO43-	Sample ID		NO3-	PO43-	Sample ID		NO3-	PO43-
Surface water		mg/L		Right Bank		mg/L		Left bank		mg/L	
AR	Av.	3.37	0.06	P2	Av.	2.89	0.05	P3	Av.	25.44	0.14
	Min.	1.24	0.02		Min.	0.03	0.01		Min.	11.08	0.05
	Max.	6.97	0.15		Max.	10.47	0.11		Max.	46.13	0.73
B2	Av.	2.15	0.08	P4	Av.	0.20	0.04	P5	Av.	20.16	0.16
	Min.	0.22	0.02		Min.	0.03	0.02		Min.	13.25	0.02
	Max.	6.67	0.13		Max.	0.90	0.09		Max.	34.41	0.80
B2bis	Av.	1.94	0.07	P6	Av.	1.64	0.06	Pz3	Av.	3.01	0.06
	Min.	0.18	0.03		Min.	0.04	0.01		Min.	0.06	0.01
	Max.	7.99	0.13		Max.	6.53	0.39		Max.	17.11	0.16
B3	Av.	1.65	0.07	P7	Av.	2.35	0.30	Pz4	Av.	12.1	0.09
	Min.	0.15	0.02		Min.	0.23	0.04		Min.	3.39	0.01
	Max.	7.59	0.13		Max.	7.46	0.79		Max.	23.71	24.00
B4	Av.	1.76	0.07	P9	Av.	0.42	0.06	Pz5	Av.	4.34	0.09
	Min.	0.26	0.01		Min.	0.04	0.01		Min.	0.07	0.02
	Max.	7.59	0.17		Max.	4.35	0.19		Max.	15.45	0.25
B6	Av.	1.38	0.07	Pz1	Av.	0.78	0.07	Pz6	Av.	4.08	0.09
	Min.	0.06	0.02		Min.	0.05	0.01		Min.	1.13	0.02
	Max.	6.70	0.15		Max.	3.96	0.17		Max.	7.68	0.52
B7	Av.	2.34	0.11	Pz2	Av.	1.23	0.06	MS	Av.	97.77	0.45
	Min.	0.83	0.02		Min.	0.06	0.01		Min.	88.95	0.05
	Max.	9.01	0.54		Max.	4.84	0.12		Max.	120.59	4.08
VR	Av.	16.99	1.17								
	Min.	0.07	0.26								
	Max.	40.81	3.51								

sampling campaigns on the scale of the whole the Auzon oxbow hydrosystem (Fig. 2). Phosphate concentrations are higher than the natural signal (more than 0.015 mg/L) for all the samples. These concentrations are not alarming, however, as they are generally below 0.1 mg/L (the limit for surface water to be considered of good quality under French regulations, REEE-ESC (2019)).

b) Temporal evolution of NO_3^- and PO_4^{3-} concentrations in the Auzon oxbow hydrosystem

In this section, timeseries for PO_4^{3-} and NO_3^- concentrations are presented along with the records of the Allier River discharge rate at Vieille-Brioude (12 km south of the study site, data available on www.hydro.eaufrance.fr), the piezometric level in the alluvial aquifer at Cohade ("Puits des Crozes", BSS001WJPR, data available on www.ades.eaufrance.fr), and the amount of rainfall recorded at Fontanes (10 km south, data available on www.donneespubliques.meteofrance.fr). This additional data is used to determine the influence of the hydrological regime on contaminant transport dynamics. Figs. 3 and 4 show the evolution of NO_3^- and PO_4^{3-} concentrations for seven samples divided into two groups: surface waters (AR, VR, B2, and B7, Fig. 3) and hyporheic water/groundwater (MS, P3, PZ4).

For the Allier River (Fig. 3), the NO_3^- concentration trend follows the discharge rate curve, with concentration peaks in late winter/early spring. Similarly, periods of low NO_3^- concentration occur during low-

water periods. For PO_4^{3-} , no distinct dynamics are observed, with the concentration remaining relatively stable, showing no significant increase or decrease. The same dynamic is observed for waters upstream and downstream of the oxbow (B7 and B2), with seasonal fluctuations for NO_3^- and no significant variation for PO_4^{3-} , except for B7 in spring 2016. B2 reacts synchronously with the Allier River (Fig. 3), while B7 sometimes shows a delay, as for the winters of 2015 and 2018. The Vendage River (Fig. 3) is seasonally close to quality limits for NO_3^- and consistently exceeds standards for phosphates. As with the Allier River, NO_3^- peaks in the Vendage River are also associated with the end of the winter period, whereas phosphate peaks do not appear to be correlated with the Allier's hydrological regime.

For groundwater (Fig. 4), concentrations are not primarily dependent on variations in the piezometric level of the alluvial water table, which follows the flow of the Allier River in a buffered manner (Quenet et al., 2019; Labbe et al., 2023). In the Monteil spring (Fig. 4), which is the most contaminated sample in terms of NO_3^- and the only one beyond water quality ranges, the temporal dynamics of NO_3^- and PO_4^{3-} concentrations do not follow any seasonal pattern. There are relatively stable, high NO_3^- concentrations, with an isolated increase during the winter of 2015/2016. A peak in PO_4^{3-} concentration was also observed during this winter. Nitrate and phosphate concentrations at PZ4 (Fig. 4) remain stable, apart from during the winter of 2016/2017, when there is an increase in NO_3^- concentration, although PO_4^{3-} concentrations remain stable throughout the monitoring period. Finally, PO_4^{3-} concentrations

Table 2

Concentrations of major elements (Na^+ , Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}), Charge Balance Error (CBE) for each sample, data for physicochemical parameters (EC, pH, $\text{O}_2(\text{d})$), $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ during March 2018 campaign.

Type of water bodies	ID	Na+	Cl-	NO3-	PO43-	SO42-	NH4+	CBE	O2(d)	pH	EC	$\delta^{15}\text{N}(\text{NO}_3)$	$\delta^{18}\text{O}(\text{NO}_3)$	
		(mg/L)						%				($\mu\text{S}/\text{cm}$)	(‰)	
Surface water	AR	5.95	10.95	5.32	0.03	6.38	0.06	2	11.2	7.09	100	6.15	4.69	
	B2	13.72	30.67	0.94	0.03	16.58	0.13	2	8.4	7.04	325			
	B2bis	14.65	33.76	0.65	0.05	18.40	0.14	2	8.3	6.86	343	18.55	17.09	
	B3	14.63	32.91	0.76	0.06	16.03	0.12	2	8.4	7.1	319	19.10	14.64	
	B4	14.40	31.48	0.62	0.07	15.21	0.15	2	8.5	7.1	307	18.88	15.51	
	B6	13.12	27.39	0.44	0.09	13.57	0.11	1	9.0	7.14	242			
	B7	8.93	15.93	2.68	0.01	9.03	0.08	2	5.0	6.67	173	12.36	6.48	
	VR	25.47	56.51	20.99	0.48	27.31	0.83	0	11.4	7.72	497	11.10	5.85	
	VR + WWTP	25.18	57.19	21.06	0.35	27.55	0.77	3	10.9	7.74	514			
	WWTP	36.36	86.83	0.21	4.50	35.12	20.47	1	7.9	7.12	872			
Right Bank	P2	10.16	29.54	0.12	0.02	55.79	0.06	2	2.3	6.69	410			
	P4	16.11	41.42	0.05	0.02	6.73	0.67	2	2.2	6.75	389			
	P6	19.33	54.23	0.50	0.07	24.22	0.12	2	1.1	6.87	411	28.28	24.92	
	P7	9.97	17.95	2.44	0.28	8.96	0.09	2	3.5	6.67	183	13.28	4.28	
	P9	24.39	58.44	0.15	0.03	19.40	0.10	2	2.3	6.61	420			
	PZ1	22.08	45.06	1.26	0.07	24.97	0.14	2	0.4	6.82	369	44.69	24.07	
	PZ2	16.21	46.13	0.33	0.02	20.63	0.44	2	1.8	6.84	461			
Left Bank	P3	16.60	67.44	20.46	0.08	76.08	0.12	1	2.4	6.96	771	14.71	9.07	
	P5	18.78	75.43	17.87	0.07	69.78	0.11	1	2.2	6.89	807	17.17	18.87	
	PZ3	20.95	78.04	4.03	0.04	80.28	0.18	1	0.4	7.00	857	18.45	30.78	
	PZ4	14.92	55.33	11.72	0.10	59.29	0.17	3	1.5	6.99	698	17.76	15.71	
	PZ5	19.06	78.71	1.81	0.06	87.43	0.18	2	1.3	7.1	995	18.24	12.37	
	PZ6	26.22	77.018	5.08	0.085	121.41	0.26	1	0.3	7.3	1068	53.81	35.00	
Agricultural plateau GW	MS	11.51	63.35	100.36	0.29	67.27	0.11	0	nd	6.95	858	12.17	6.01	



Fig. 2. Nitrate and phosphate concentration maps based on the concentrations recorded during the 44 sampling campaigns on the Auzon oxbow. (A) Mean NO_3^- concentrations during the 2014–2018 period; (B) NO_3^- concentration during the March 2018 campaign; (C) Mean PO_4^{3-} concentrations during the 2014–2018 period; (D) PO_4^{3-} concentration during the March 2018 campaign.

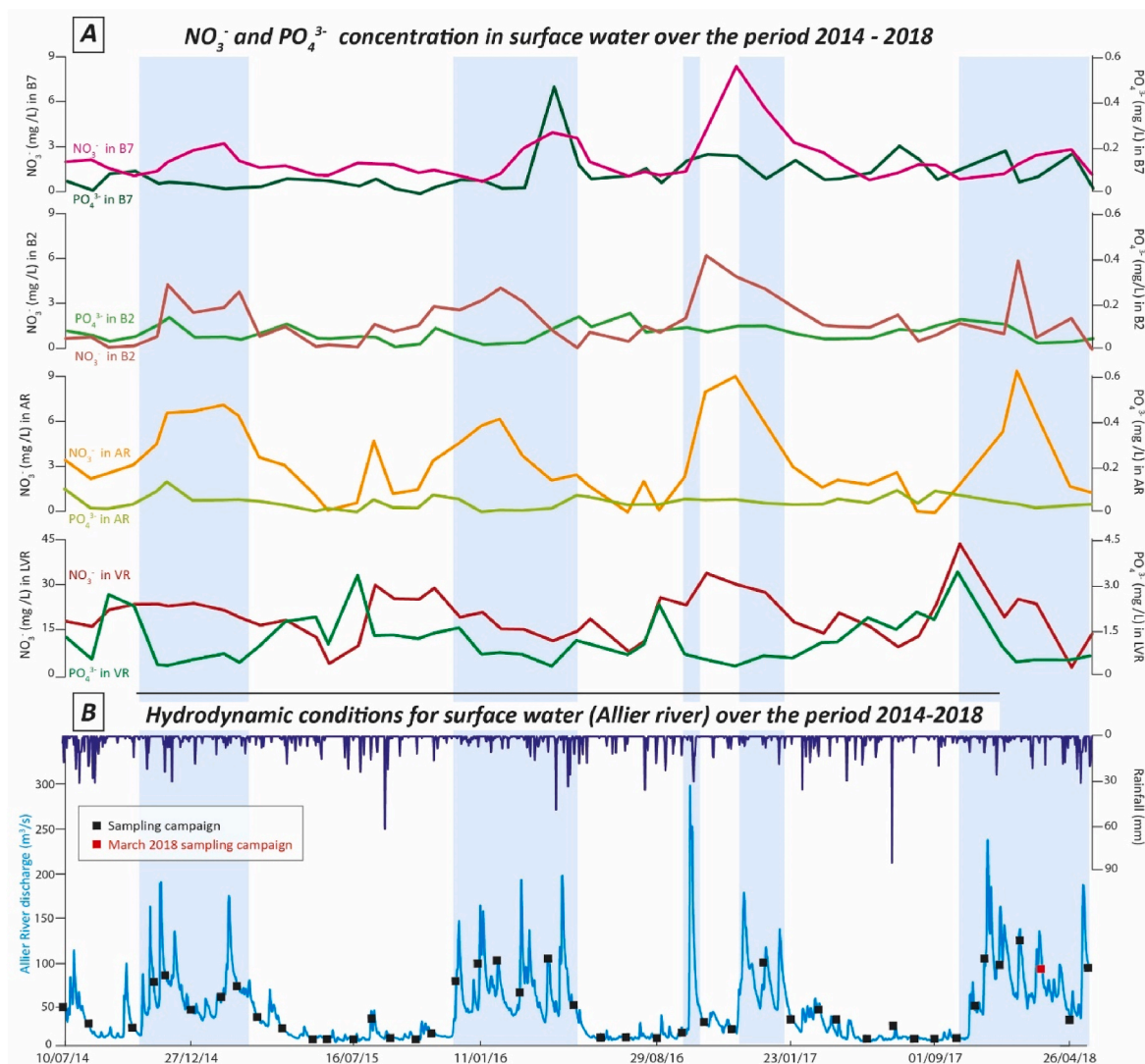


Fig. 3. Nitrate and phosphate concentration time-series in surface waters. These timeseries are cross-compared with rainfall at Fontanes and with the Allier discharge rate at Vieille Brioude (43, France).

in P3 (hyporheic zone, Fig. 4) are stable except for some peaks recorded in the autumn of 2014 and the summer of 2016. Nitrate concentrations do not follow any seasonal dynamics either, except for some peaks observed in the autumn of 2015 and the winter of 2016–2017.

The approach proposed here has its limitations in the sampling step for NO_3^- and PO_4^{3-} concentrations, particularly given the reactivity of the environment and the heterogeneous distribution of rainfall. Nevertheless, it provides a first-order understanding of contaminant dynamics as a function of hydrological and rainfall regimes.

4.2. Identifying NO_3^- origins in the Auzon oxbow hydrosystem from $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$

To identify the origins of NO_3^- in the Auzon oxbow hydrosystem, we analyzed 16 sampling points for N and O isotopes of NO_3^- ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$). These sampling points were selected to represent the different water bodies in the study area: surface water, oxbow water, hyporheic zone water, and groundwater from each bank. The sampling campaign was conducted in March 2018 to coincide with the seasonal NO_3^- concentration increases in late winter/early spring. Isotope ratios of each sample, coupled with their NO_3^- and phosphate concentrations, are presented in Table 2 and illustrated in Fig. 5a and b $\delta^{15}\text{N}_{\text{NO}_3}$ signatures for all samples ranged from +6.2 ‰ (Allier River) to +53.8 ‰ (Pz6), and

$\delta^{18}\text{O}_{\text{NO}_3}$ ranged from +4.3 ‰ (P7) to +30.8 ‰ (Pz3), with NO_3^- concentrations ranging from 0.6 mg/L (B4) to 100.4 mg/L (Monteil spring).

Fig. 5b identifies the origin of NO_3^- in water from their isotopic content ($\delta^{18}\text{O}_{\text{NO}_3}$ and $\delta^{15}\text{N}_{\text{NO}_3}$) by comparison with classical isotope values for all potential NO_3^- sources (Kendall et al., 2007): chemical fertilizers (Vitória et al., 2004), soil NO_3^- , manure, and wastewater or other organic fertilizers (Widory et al., 2004).

The Allier River has a $\delta^{15}\text{N}_{\text{NO}_3}$ value consistent with an organic soil nitrogen origin, whereas the $\delta^{15}\text{N}_{\text{NO}_3}$ of MS and VR are characteristic of manure or sewage origins (Kloppmann, 2003; Widory et al., 2005). Kendall et al. (2007) demonstrated that for isotopic compositions similar to those observed in AR, NO_3^- can originate from multiple sources (as a result of mixing). The $\delta^{15}\text{N}_{\text{NO}_3}$ of P3 (hyporheic zone) also indicated an NO_3^- origin from manure or sewage. Samples B2bis, B3, B4, P6, Pz1, and Pz6, with values higher than +8 ‰ and +15 ‰, are grouped along a trend of 0.71 for all 16 samples. This type of alignment, in addition to the low NO_3^- content of the samples, is consistent with natural denitrification processes (Kendall et al., 2007; Aravena and Robertson, 1998; Bailly et al., 2011; Böhlke et al., 2006; Böttcher et al., 1990; Bourke et al., 2019; Cey et al., 1999; Minet et al., 2017; Singleton et al., 2007; Wunderlich et al., 2013). Three samples, P5, Pz3, and Pz4, lie outside this trend and the fields for the sources, with higher $\delta^{18}\text{O}_{\text{NO}_3}$ values.

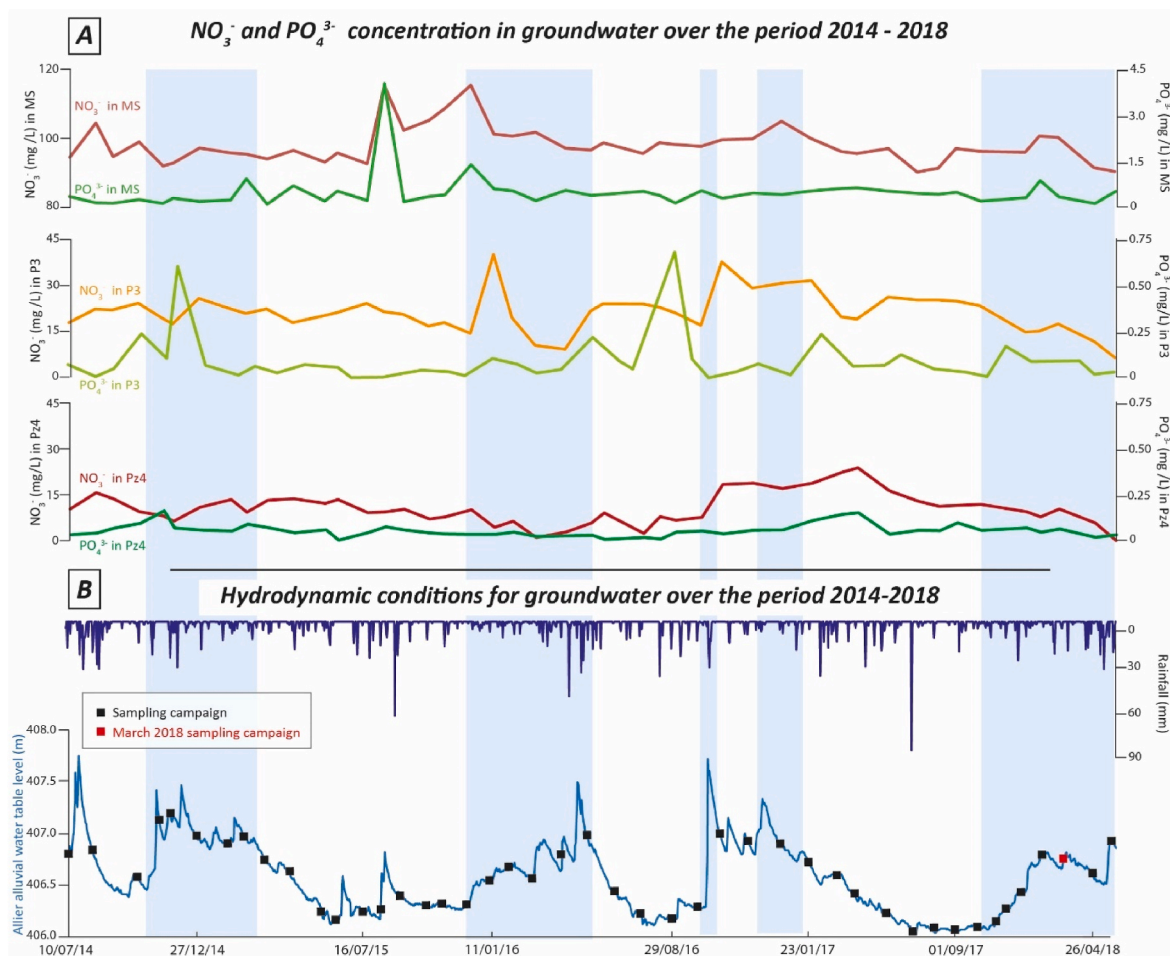


Fig. 4. Time-series NO₃⁻ and PO₄³⁻ concentration in groundwater (Pz4), in hyporheic zone water (P3) and in agricultural plateau water (MS). These time-series are cross-compared with rainfall at Fontanes (43, France) and piezometric levels in the alluvial aquifer at Cohade (43, France).

4.3. Screening of chemical micropollutants

To determine the origin of PO₄³⁻ in the Auzon oxbow hydrosystem, we combined the analyzed PO₄³⁻ concentrations with chemical micropollutant data. All analyses were performed at the end of the sampling campaign in March 2018. This approach also makes it possible to assess the water quality across the various sub-systems of the Auzon oxbow hydrosystem in terms of chemical micropollutants.

The contamination of surface waters by chemical micropollutants is both seasonal and long-lasting, similar to NO₃⁻ contamination but occurring at different times (Mohammed et al., 2014; Phyt'eauvergne, 2014). The window for applying manure or synthetic fertilizers is controlled by weather conditions at the end of winter and sometimes in autumn. In contrast, the application of chemical micropollutants occurs in spring for crop treatment and in late summer or autumn for land preparation for planting (Chambre d'Agriculture 43, 2018).

a) Chemical micropollutants detected in the waters of the Auzon hydrosystem

Sampling for the chemical micropollutants was conducted in March 2018, at the beginning of the application period. The screening revealed the presence of 14 molecules out of the 590 analyzed for across all 12 samples (Table 3), indicating a low diversity of contaminants. To discuss the origins (industrial, urban, agricultural) and transfer of these molecules within the Auzon oxbow study site, it is essential first to determine the origin for each molecule detected in the majority of samples.

Four of the detected molecules are associated with industrial and urban areas. Diethylhexylphthalate (DEHP) is a plasticizer used in the production of plastics for both medical applications (blood bags, consumables) and everyday items (food plastics). This compound is considered as toxic component because it is an endocrine disruptor (similar to bisphenol A) and a potential carcinogen (Caldwell, 2012; Ye et al., 2014). N-Butylbenzenesulfonamide (NBBS) is a plasticizer used in the industrial sector for the polymerization of polyamide compounds, identified as having significant neurotoxic properties (Waidyanatha et al., 2020). m + p Cresol is a natural or synthetic resin used in industry as a sealing agent, a natural aroma in agro-industry, or as a fragrance in the cosmetics industry. This compound is linked to liver and kidney problems (Rong et al., 2022; Vanholder et al., 1995). Benzotriazole is an anticorrosive additive commonly found in industrial coolants or de-icers (Cotton and Scholes, 1967).

Ten of the detected molecules are typically associated with agricultural or gardening activities. Of these ten chemical micropollutants, four are purely related to agricultural activities. Dinoterb is a herbicide used in corn crop treatment, but banned for all other crop types in France (Belbachir et al., 1980; Beulke and Malkomes, 2001). Metoxuron and Chlortoluron are herbicides used for cereal crops such as wheat, barley, and rye (Klusmeier et al., 1989; Guo et al., 2016). Chloridazon, or Pyrazon, banned in France since 2021, was a herbicide used for corn and wheat crops (Bisewska et al., 2012). The other six molecules are primarily associated with gardening activities or green space maintenance, thus having urban or peri-urban origins. Metaldehyde is a molluscicide used for slug and snail control (Castle et al., 2017). Imidacloprid, an

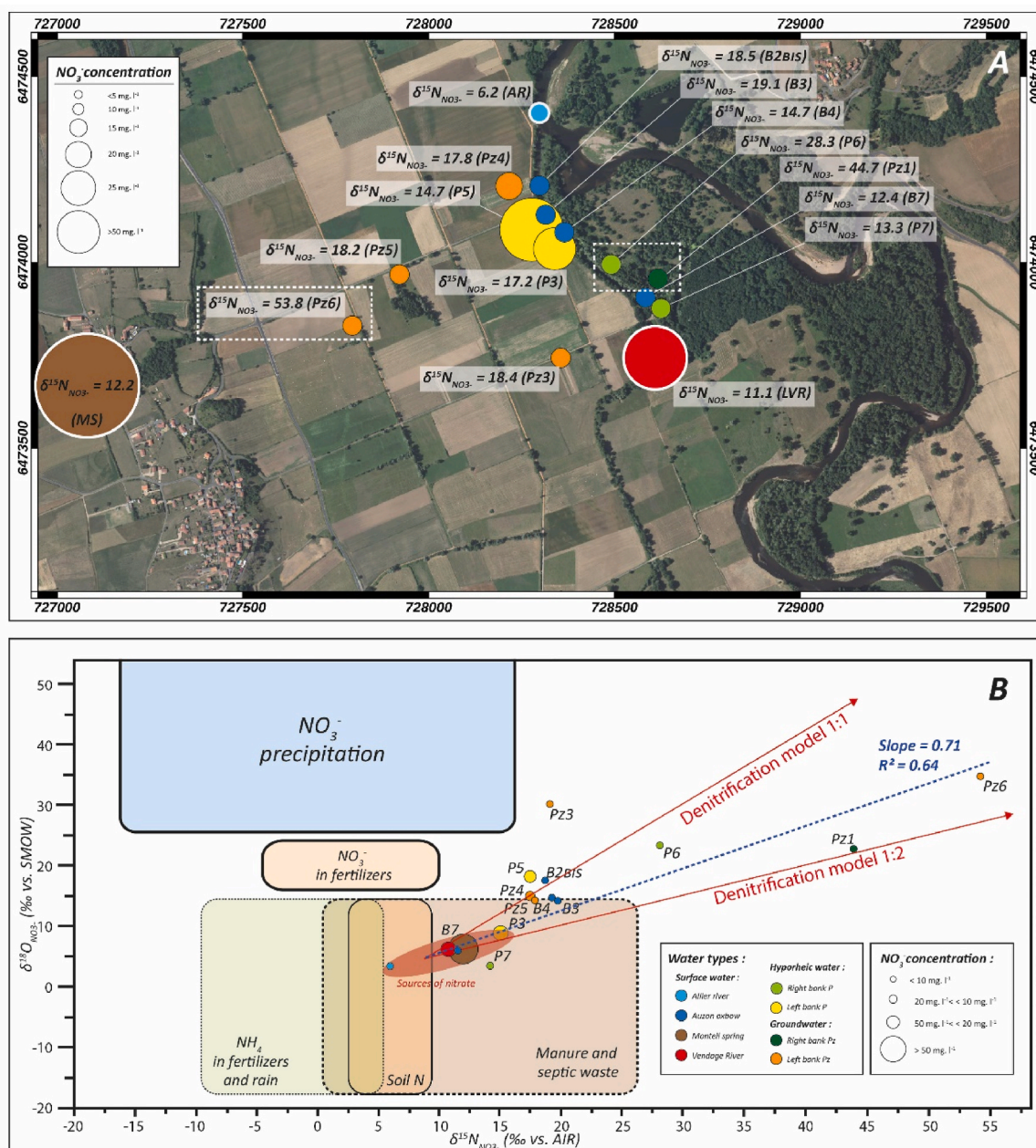


Fig. 5. (A) $\delta^{15}\text{N}_{\text{NO}_3}$ isotopic ratios for sites sampled during the March 2018 campaign. (B) $\delta^{15}\text{N}_{\text{NO}_3}$ vs $\delta^{18}\text{O}_{\text{NO}_3}$ plot for all 16 analyses together with the fields for $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ for atmospheric deposition, fertilizer input, or nitrification from various sources of NH_4 and organic matter (atmosphere and fertilizers, soil, manure and wastewater; derived from Kendall et al., 2007).

insecticide from the neonicotinoid family, is used for seed treatment, aphid control, and in treatments against fleas and ticks in pets (Tisler et al., 2009). Thiabendazole is a fungicide present in seed treatments, fruit and vegetable storage, and treatment of livestock buildings (Robinson et al., 1978). Propiconazole is a fungicide used for treating wooden structures (Gilley and Fletcher, 1997). Glyphosate, along with its metabolite AMPA, is a herbicide used for weed control in agriculture or gardening in urban areas (Carlisle and Trevors, 1988; Malik et al., 1989).

b) Spatial distribution and concentration in chemical micropollutants

As a reminder, the regulatory level for chemical micropollutants is approximately 0.1 $\mu\text{g/L}$ (EC, 1998) according to French regulations for untreated water used for drinking water. Quality limits are about 2 $\mu\text{g/L}$

per individual substances and 5 $\mu\text{g/L}$ for all pesticides combined (EC, 1998). Thus, in terms of total concentration (Fig. 6), two samples exceed the authorized limit for rivers and groundwater intended for drinking water: WWTP and the Allier River. WWTP waters are the most concentrated in chemical micropollutants and present the highest number of molecules of urban origin, including Dinoterb. Wastewater Treatment Plant (WWTP) waters are subsequently diluted by the Cohade stream and then by the Vendage River before joining the Auzon oxbow hydrosystem. Examining the concentrations of individual substances that exceed the French regulations for drinking water (Table 3), NBBS is found in significant concentrations at all sampled points and exceeds the individual authorized concentration in the Allier River, PZ2, and PZ6. m + p cresol is found in high concentrations at only one point, WWTP. These two types of molecules stay in the environment for a long time, and require highly developed removal processes (Panigrahy et al.,

Table 3
Chemical micropollutant screening results for March 2018 campaign. Numbers in bold are those that exceed the French standards in number of molecules or in concentration of individual molecules.

Phytosanitaires screening results					Sample sites												
Origin	Molecule name	Nature type	LQ	Unit	Groundwater						Surface water					Wastewater	
					PZ1	PZ2	PZ3	PZ4	PZ5	PZ6	Allier River	B3	B7	LVR	V + C	WWTP	
Industrial	N-Butylbenzenesulfonamide	plasticizer	< 0,1	(µg/l)	0.940	2.300	1.500	1.300	1.700	2.700	5.900	0.630	1.600	1.000	1.600	1.100	
	DEHP	plasticizer	< 0,5			1.100										0.700	
	Benzotriazole	detergent	< 0,1											0.100			0.800
Urban agriculture	m + p-Cresol	synthetic resins	< 0,1													4.500	
	Glyphosate (1)	herbicide	< 0,02											0.068	0.080	0.870	
	AMPA	metabolite (1)	< 0,02								0.029			0.210	0.170	0.530	
Agricultural	Imidacloprid	insecticide	< 0,005													0.015	
	Thiabendazole	fungicide	< 0,005													0.011	
	Propiconazole	fungicide	< 0,005													0.012	
	Dinoterb	herbicide	< 0,005			0.054		0.051	0.025	0.010	0.038	0.049	0.032	0.062		0.025	
	Chloridazon (Pyrazon)	herbicide	< 0,005				0.005		0.006								
	Chlortoluron	herbicide	< 0,005											0.009	0.008		
	Metoxuron	herbicide	< 0,005											0.010	0.011		
	Metaldéhyde	molluscicide	< 0,02											0.120	0.150		
		Number of molecules				1	3	2	2	3	2	3	2	2	8	6	10
		Total concentration			(µg/l)	Err:522	Err:522	Err:522	Err:522	Err:522	Err:522	Err:522	Err:522	Err:522	Err:522	Err:522	Err:522
	Agricultural molecules			(µg/l)	0.000	0.054	0.005	0.051	0.031	0.010	0.038	0.049	0.032	0.201	0.169	0.025	
	Urban agriculture molecules			(µg/l)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.029	0.000	0.000	0.278	0.250	
	Industrial molecules			(µg/l)	0.940	3.400	1.500	1.300	1.700	2.700	5.900	0.630	1.600	1.100	1.600	7.100	
	Nitrate			(mg/l)	1.3	0.3	4.0	11.7	1.8	5.1	5.3	0.8	2.7	21.0	21.06	0.21	
	Phosphate			(mg/l)	0.07	0.02	0.04	0.10	0.06	0.09	0.03	0.06	0.10	0.48	0.35	4.51	

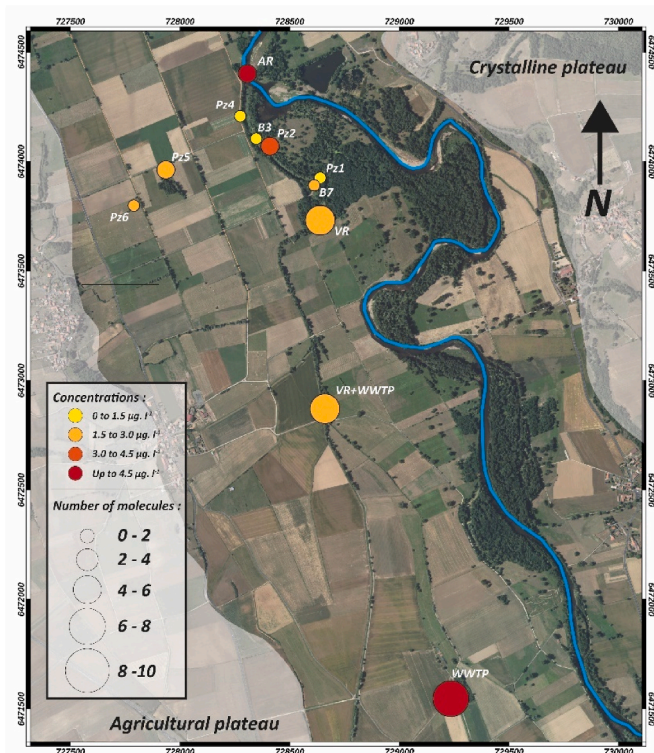


Fig. 6. Concentrations of all chemical micropollutants during the March 2018 campaign.

2022). The disappearance of these molecules in the environment can be attributed to the dilution of WWTP waters. Except for the Allier River and WWTP, other points show slight contamination in these molecules with regard to the French regulations. However, all points present NBBS contamination, which represents up to 100% of the quantity of active substances in one sample (Pz1).

Substances identified as being of urban origin, apart from NBBS, are present in VR + WWTP and VR, which corresponds to the water body excluding the Allier River and WWTP, with the highest quantity of chemical micropollutants. Dinoterb and Benzotriazole appear between the VR + WWTP sample and VR. Benzotriazole is likely present in VR + WWTP but below the detection limit. Dinoterb undoubtedly originates from local agricultural activity near VR. AMPA is found at high levels in WWTP, Allier River, VR + WWTP, and VR. The concentration of Glyphosate metabolite in the Vendage River raises questions because it is similar to that in WWTP despite significant dilution. Thus, AMPA and to a lesser extent Glyphosate are present in VR but diluted, making it difficult to determine whether their origin is agricultural or urban. AMPA is also found in the Allier River, indicating a regional dispersion of this molecule (Phyt'eauvergne, 2014; Mohammed et al., 2014). As previously mentioned, the water quality of the Vendage River is impacted by agricultural activity and constitutes the most degraded water body in the study area. Active substances found in these waters originate from the entire Vendage watershed, not just from the Cohade WWTP. Finally, Pz2, along with WWTP, are the only samples in which DEHP is found, indicating local contamination. Pz2 is also contaminated by Dinoterb and Chloridazon, confirming an agricultural origin for the contamination. The quality of the waters of B7 in the upstream part of the oxbow and B3 downstream is impacted by NBBS and Dinoterb. NBBS concentration is higher in B7, likely due to a possible contribution from the Allier River through the paleochannel (Quenet et al., 2019).

5. Discussion

5.1. Sources and transport of contaminants in the Auzon oxbow

a) Sources and origins of NO_3^- in the study area

In terms of dynamics, the Allier River is a reactive system, with a clear correlation between rainfall events and increase in flow (Quenet et al., 2019; Labbe et al., 2023). There is a shift component at the end of winter due to snowmelt, which increases river flow over an extended period. Thus, the flow of the Allier serves as a proxy for the local and regional hydrodynamic context, enabling the characterization of contaminant flows over time at various scales. As shown in Section 4.1, NO_3^- concentrations in surface waters follow the hydrological regime. Increases in NO_3^- are explained by leaching of manure or soil during the winter on both local (Vendage River) and regional (Allier River) scales. These phenomena are well-documented and directly associated with agricultural practices worldwide (Böhlke, 2002) and through more localized monitoring (Dejaifve, 2003; Widory et al., 2004).

For groundwater, although NO_3^- concentrations increase during the aquifer recharge period, no clear trend aligns with surface water patterns. Nitrate concentrations are spatially variable and cannot be explained by a simple mixing law between groundwater from the alluvial aquifer, water from the hillsides of the alluvial plain, and water from the Allier, as demonstrated by Mohammed et al. (2014). Results in Section 4.2 indicate that NO_3^- is of agricultural origin and primarily comes from the Vendage River watershed, the hillsides of the alluvial plain (agricultural plateau, Monteil spring), and the Allier River. They are transported by surface water (Allier and Vendage rivers), the hyporheic zone (P3 and P5), or the aquifer in the case of local contamination (Pz4).

b) PO_4^{3-} : agricultural or urban origin?

Based on the results in Section 4.1, PO_4^{3-} contamination is more episodic and does not follow the overall hydrological regime. Locations of these PO_4^{3-} concentration anomalies are not systematically consistent with NO_3^- contamination, indicating a different origin for the contamination. Phosphates origin is therefore considered to be localized, with input coming from either the local application of phosphate fertilizers or from malfunctioning of the wastewater treatment plant (WWTP) during extreme weather events (overflow). These cases are well-known and common in small rural catchments (Carey and Migliaccio, 2009) or in the presence of intermittent streams (Castelar et al., 2022). According to analyses from the March 2018 campaign (Table 2), PO_4^{3-} in the Vendage River likely originates from the WWTP, which discharges a PO_4^{3-} concentration of 4.5 mg/L.

To confirm this origin, Fig. 7a shows a histogram of concentrations of chemical micropollutants of agricultural origin for each of the 16 sampling points, with average NO_3^- concentrations also plotted. Samples with the highest concentrations of agricultural-origin micropollutants also have the highest NO_3^- concentrations, confirming the agricultural origin of NO_3^- . Fig. 7b shows a histogram of the total concentration of chemical micropollutants from all sources, associated with the average PO_4^{3-} concentration for each sampling site. Phosphate concentrations are very low in all samples from the Auzon hydrosystem, except for those from VR, VR + WWTP, and WWTP. The high PO_4^{3-} concentration from WWTP, coupled with the absence of any agricultural-origin molecules in these waters, clearly demonstrates the urban origin of PO_4^{3-} .

c) Water transport and mixing: transfer and attenuation processes

The waters of the oxbow show an increase in NO_3^- at the end of winter or the beginning of spring, with concentration ranges similar to those of the Allier River. The Vendage River follows the same dynamic (either slightly ahead or synchronously), with higher NO_3^- concentration

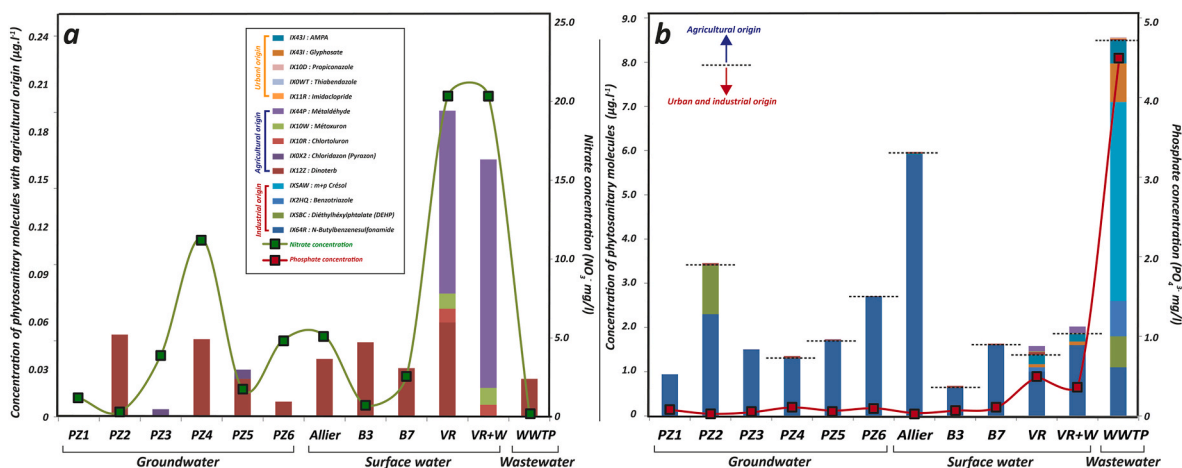


Fig. 7. Cumulative histogram of concentrations as a function of individual concentrations of active substances of agricultural origin a) and all origins (b). Nitrate concentration (on agricultural origin histogram) is represented by the green curve and phosphate concentration (on all origin histogram) by the red curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

ranges. To understand contaminant diffusion, it is necessary to characterize water transfer and mixing in the hydrosystem. Studying the interactions between different water bodies is essential to understanding the mixing and dilution phenomena that can occur in a hydrosystem, explaining chemical contrasts (Erostate et al., 2019; Grimmeisen et al., 2017).

Quenet et al. (2019) demonstrated the connections, based on hydrological conditions, between the Auzon oxbow, Allier River, and alluvial groundwater. During the March 2018 field campaign, the paleochannel between the Allier River and the upstream part of the Auzon oxbow was active. Moreover, several other relationships between water bodies can be noted: 1) from RB groundwater to the Auzon oxbow, 2) from the Allier River to the downstream part of the Auzon oxbow, and 3) from the Auzon oxbow to LB alluvial aquifer. Additionally, Palma et al. (2020) showed that the Vendage River can contribute to the Auzon oxbow through the Allier River paleochannel, thereby providing the oxbow with NO₃ during high flow regimes. Fig. 8, plotting Na⁺ vs SO₄²⁻, confirms water mixing in the Auzon hydrosystem based on various inputs: Allier River, Vendage River, and groundwater of the alluvial aquifer. A first mixing trend groups the waters of the Allier River, the Vendage River, and alluvial groundwater of the right bank. P9 concentrations are close to those of the Vendage River, while P7 is close to the

Allier River, providing two end-members.

The second mixing line evolves from the Allier River to Pz6, representing the alluvial groundwater end-member of the LB. This relationship between the Allier River and alluvial groundwater was noted by Mohammed et al. (2014), with a gradient from the border of the alluvial plain to the Allier River. The chemical content of Na⁺ and SO₄²⁻ in the Auzon oxbow water plots between these three end-members. B7 is close to the composition of the Allier River, while B2 and B2bis shift towards the Allier River/LB groundwater line. These observations confirm the conclusions of Quenet et al. (2019), which show that: 1) upstream, the Allier River feeds the Auzon oxbow (B7) through the paleochannel; 2) the alluvial aquifer feeds the oxbow in its median and downstream parts. In their study, Quenet et al. (2019) did not consider the impact of the Vendage River on the chemical composition of the waters of the Auzon oxbow hydrosystem. Fig. 8 demonstrates a clear relationship between the Vendage River and P9 through the Allier River paleochannel. According to this model, the waters of the oxbow should have higher NO₃ concentrations than observed, as they result from mixing between end-members that are richer in NO₃. Thus, concerning PO₄³⁻ concentration in oxbow waters, two phenomena potentially explain the low PO₄³⁻ concentrations:

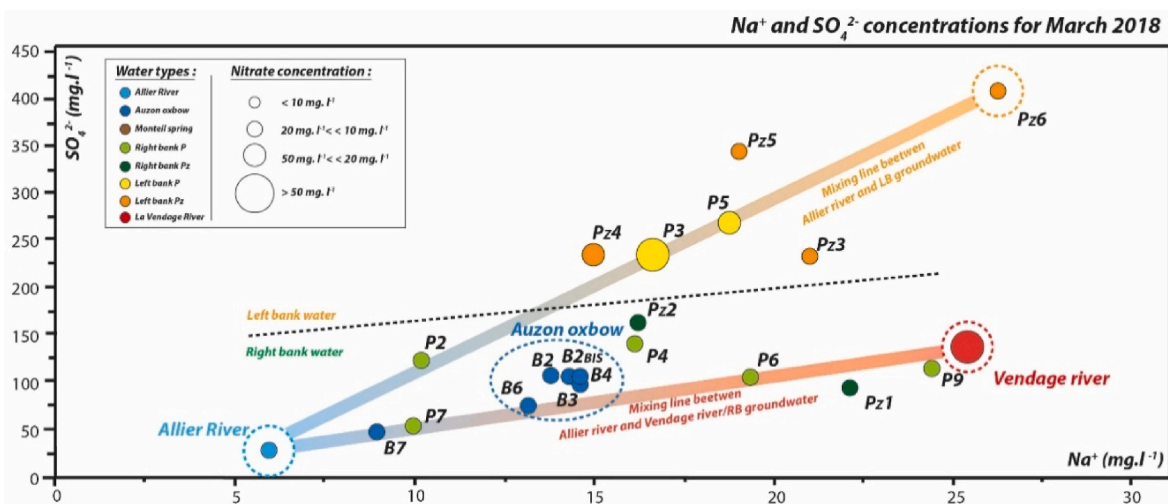


Fig. 8. Na⁺ vs SO₄²⁻ (in mg/L) for all samples for March 2018 campaign. Pz6, Vendage River and Allier River are end-members which explain Auzon Oxbow hydrosystem water interactions.

- An attenuation process due to dilution of Vendage River water (the source of PO_4^{3-} in the hydrosystem) in the upstream part by Allier River waters and in the downstream part by Allier River waters and groundwater of the alluvial aquifer (Quen et al., 2019).
- A storage effect of PO_4^{3-} by riparian wetlands, which can be partially released over several years (Howard-Williams, 1985; Audet et al., 2020; Walton et al., 2020).

5.2. The fate of NO_3^- in a complex hydrosystem: a dual denitrification process ?

As noted above, numerous interactions between water bodies of different chemical and isotopic compositions complicate the identification of biogeochemical processes (Kendall et al., 2007; Paredes et al., 2020). Nevertheless, isotope analysis of NO_3^- has shown that denitrification phenomena occur in this hydrosystem.

In Fig. 9, the $\delta^{15}\text{N}_{\text{NO}_3}$ of oxbow waters increases from upstream to downstream (+12.4‰ to +18.5‰), while NO_3^- concentrations decrease (2.7 mg/L to 0.7 mg/L). The isotopic signature of the oxbow waters shows a slight trend towards denitrification from upstream to downstream (Figs. 5b and 9). The denitrification capacity of oxbow-wetlands has been demonstrated in other similar studies on wetlands (Clément et al., 2002; Martínez-Espinosa et al., 2021). Furthermore, alluvial groundwater shows a wide range of $\delta^{15}\text{N}_{\text{NO}_3}$ values from +17.2‰ (Pz4) to +53.8‰ (Pz6). Denitrification occurs in two locations in the alluvial aquifer: between the oxbow and the Allier River (Pz1, RB) and at the edge of the alluvial aquifer near the agricultural plateau (Pz6, LB). These denitrification spots indicate that the alluvial aquifer can denitrify NO_3^- -rich water from the agricultural plateau, as well as waters from the Allier and Vendage rivers with lower NO_3^- concentrations. The isotopic signatures of other piezometers (Pz2, Pz3, Pz4, and Pz5) are explained by mixing between denitrified groundwater close to the agricultural plateau (Pz6) and groundwater from the southern part of the aquifer and the Allier River (Fig. 8). The subsurface piezometers in the hyporheic zone appear to be influenced by the chemistry of alluvial groundwater and local input from agricultural practices.

In addition to the complexity of water mixing described by Quenet et al. (2019) and discussed earlier in this study, non-homogeneous diffusion of water into the alluvial aquifer can affect the efficiency of biogeochemical processes like denitrification (Pittalis et al., 2018; Karlović et al., 2023). Groundwater flow modalities differ between the right and left banks due to geological differences. The right bank is composed of a paleochannel and recent alluvium, resulting from two flood events in 1988 and 1989 (which also formed the oxbow), with a higher permeability than the rest of the alluvial aquifer. Conversely, the left bank consists of a classic alluvial environment with a heterogeneous structure of fine (clay) to coarse (pebble) deposits (Sarris et al., 2018;

Teles et al., 2004). These spatial, lateral, and vertical heterogeneities result in varied reactivity (convection, dispersion, adsorption, degradation) of the alluvial environment to contaminants. The age of these alluvium deposits can influence their permeability. Indeed, the denitrification process during NO_3^- transfer depends on the distribution of flows within the aquifer, their residence time, and the reactivity of the environment, particularly regarding biogeochemical processes.

Denitrification processes occur in three distinct environments: the right bank, the left bank, and the wetland of the Auzon oxbow. In terms of biogeochemical processes and the physicochemical conditions of these reactions, denitrification in the alluvial aquifer is autotrophic, involving the oxidation of pyrite or biotite (Pauwels et al., 2000; Roques et al., 2018). The observed anaerobic conditions in the piezometers and the hyporheic zone confirm this. Denitrification processes in the wetland are heterotrophic, driven by the oxidation of available organic compounds in the environment. Palma et al. (2020) have demonstrated the presence of organic matter in the wetland waters of the Auzon oxbow. While this study does not characterize these processes in detail, it is noteworthy that, on the scale of a hydrosystem, both heterotrophic and autotrophic denitrification processes can coexist. Based on the results of this study, future measurements should include the redox conditions of the environment (which are absent from this dataset) to improve the characterization of the denitrification processes in the Auzon hydrosystem. Additionally, the analysis of trace elements, particularly Fe and Mn, could enhance our understanding of autotrophic denitrification processes.

All the elements addressed in this discussion of the denitrification process and the attenuation of NO_3^- and PO_4^{3-} contamination are summarized in Fig. 10, which is a conceptual diagram of the functioning of the Auzon hydrosystem, including the Allier alluvial aquifer. The denitrification capacities of alluvial environments are well-known (McMahon and Böhlke, 1996; Haygarth et al., 2013; Harris et al., 2022), but have not previously been described for the Allier alluvial aquifer. From a water resource management perspective, this information is fundamental, given the importance of this resource for the Auvergne region. The results of this study could lead water managers to develop projects involving a controlled recharge of the aquifer using irrigation water or WWTP outflow water (REUSE project, Etteieb et al., 2013; Paruch, 2014; Crites et al., 2021), which often have high NO_3^- or PO_4^{3-} concentrations (Sexstone et al., 1985; Bouwer, 2002; Tweed et al., 2018; Harris et al., 2022). This study also highlights the importance of preserving riparian wetlands, which serve as biodiversity hotspots, protect river beds by limiting erosion, and improve water quality. The ecosystem services of these environments are recognized, but their significance for resource preservation is not necessarily well established.

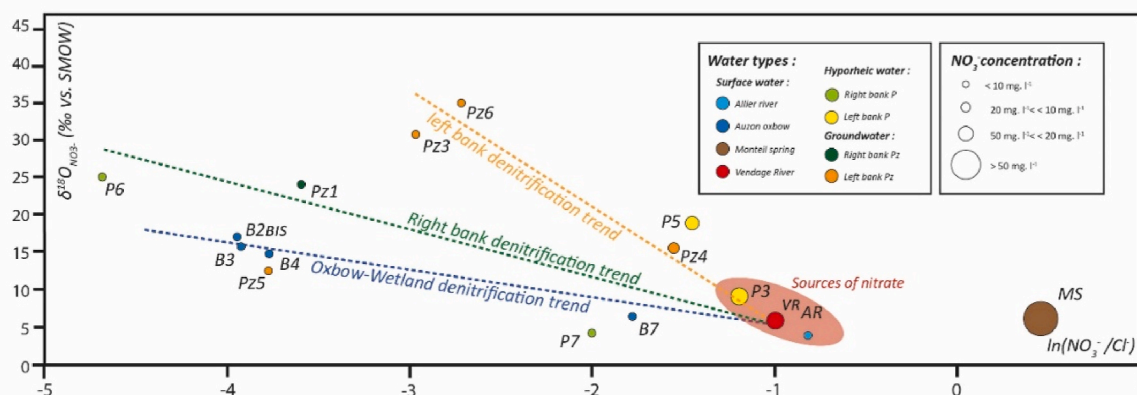


Fig. 9. $\delta^{15}\text{N}_{\text{NO}_3^-}$ vs $\ln(\text{NO}_3^-/\text{Cl}^-)$ for March 2018 campaign. P3, VR and AR are considered as sources for NO_3^- according to Fig. 5b. Denitrification trends are plotted for the groups of points for each denitrification process location: right bank, left bank and oxbow.

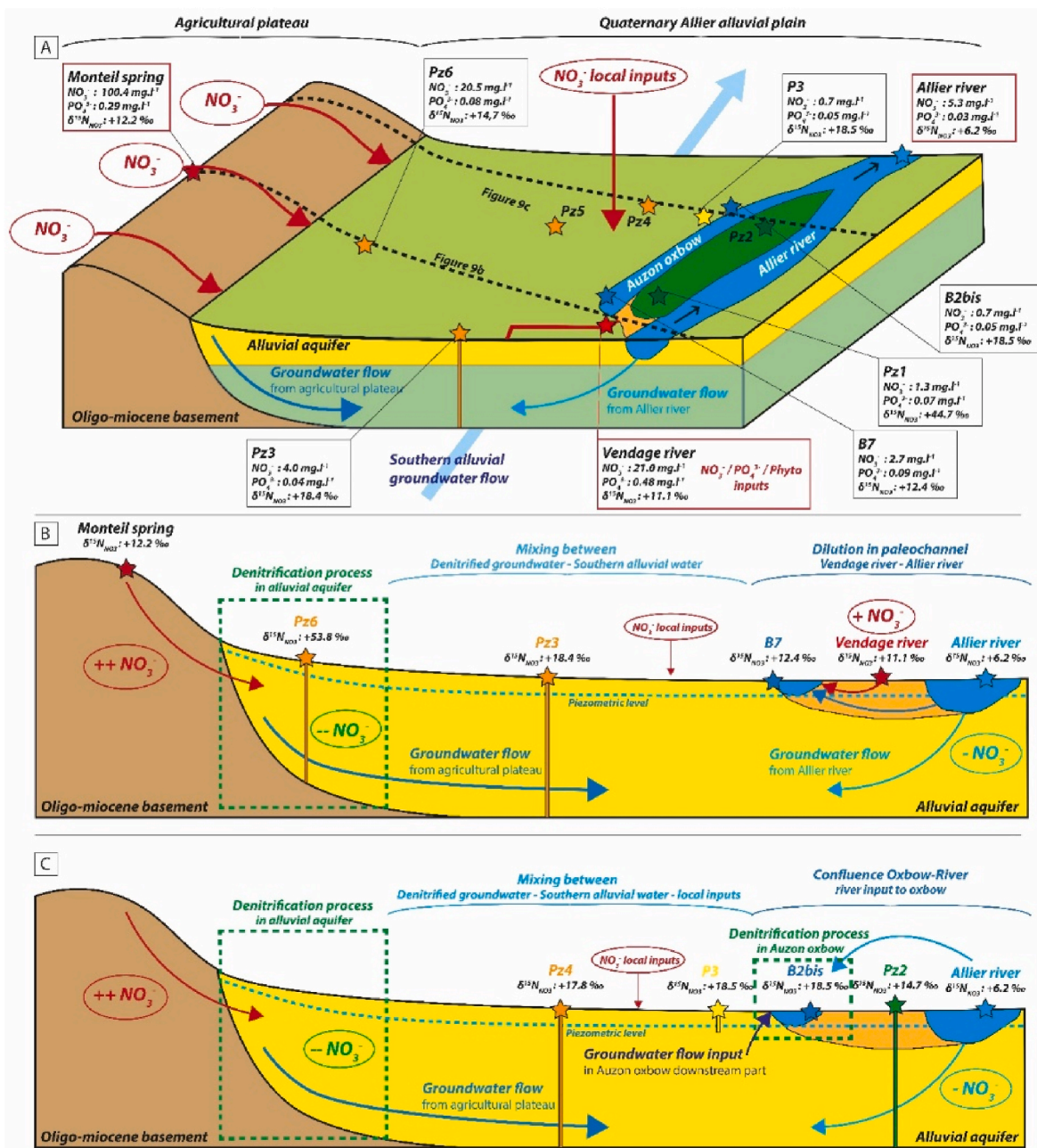


Fig. 10. Conceptual model of the Auzon oxbow hydrosystem, identifying sources of contamination, contaminant transport paths and interactions between water bodies. (A) Block diagram of the Auzon hydrosystem with sampling locations, NO_3^- and PO_4^{3-} concentrations and $\delta^{15}\text{N}_{\text{NO}_3}$ isotope ratio. (B) Cross-section through the upstream part and (C) the downstream part of the Auzon oxbow.

6. Conclusion and perspectives

The Auzon oxbow hydrosystem is composed of several sub-systems, including the oxbow itself, the Allier alluvial aquifer and the hillsides of its catchment area, and the surface waters represented by the Allier River (of which the oxbow is a fluvial annex) and the Vendage River. Firstly, hydrochemical monitoring of the water has revealed significant spatial heterogeneity in groundwater quality, as well as temporal variability. Nitrate concentrations generally lie within acceptable norms, with concentrations increasing at the end of winter due to leaching processes following seasonal patterns. Phosphate levels are not influenced by the hydrological regime, but some samples, including those from the Vendage River, have concentrations exceeding norms. This spatial and temporal information indicates different origins for these

two molecules.

Secondly, using isotope analysis of NO_3^- (N and O), we demonstrated the agricultural origin of NO_3^- , particularly related to manure spreading. The isotopes also reveal denitrification phenomena in two compartments of the Auzon oxbow hydrosystem: (1) the Allier alluvial aquifer, which denitrifies NO_3^- -rich hillside water and water flowing from the southern alluvial aquifer; (2) the oxbow, which denitrifies water from the Vendage River and NO_3^- -low water from the alluvial aquifer and the Allier River. The Auzon hydrosystem is thus a special site for the remediation of NO_3^- pollution, as it is the site of a dual denitrification process for water from the Allier and Vendage rivers, as well as water from the hyporheic zone or groundwater.

Thirdly, chemical micropollutant screening conducted on 12 samples shows concentrations of chemical micropollutants in some water bodies,

such as the Allier River and wastewater treatment plant (WWTP) waters. Cross-analysis between NO_3^- and PO_4^{3-} concentrations and chemical micropollutants of agricultural or urban/industrial origin clearly indicates the agricultural origin of NO_3^- and the urban/industrial origin of phosphates. Despite these findings, the water quality of the oxbow is very good, attesting not only to the site's sound ecological functioning but also to its fundamental role in regulating the flow of contaminants at the interface between different aquatic environments.

This multi-tracer approach highlights the importance of integrating different chemical parameters (water chemistry, isotopes, chemical micropollutants) to determine the origin and fate of contaminants. This methodology could be applied to other sites with varying environmental constraints (intensive agriculture, industrialization, polluted sites and soils) or with different challenges (drinking water, wastewater treatment plants, irrigation). The issue of water quality is widely discussed in the context of resource scarcity, particularly in alluvial environments, which are often subject to significant anthropogenic pressure. In this context, study sites close to the Auzon oxbow along the Allier River could be investigated, as the river and its associated alluvial aquifer represent one of the Auvergne's main water resources.

CRedit authorship contribution statement

Cyril Aumar: Writing – review & editing, Writing – original draft, Resources, Methodology, Investigation, Data curation. **Hélène Celle:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Mélanie Quenet:** Writing – original draft, Methodology, Investigation, Data curation. **Olivier Voldoire:** Resources, Methodology, Investigation. **Elisabeth Allain:** Resources, Investigation. **Alexandre Garreau:** Resources, Investigation. **Nicolas Caillon:** Resources, Investigation. **Pierre Nevers:** Resources, Investigation. **Jean-Luc Devidal:** Investigation. **Gilles Mailhot:** Validation, Supervision. **Aude Beauger:** Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Aude Beauger reports financial support was provided by Auvergne-Rhone-Alpes Region. Aude Beauger reports financial support was provided by European Regional Development Fund. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2024.106270>.

Data availability

Data will be made available on request.

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