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Deep denitrification: Stream and groundwater biogeochemistry reveal contrasted but connected worlds above and below

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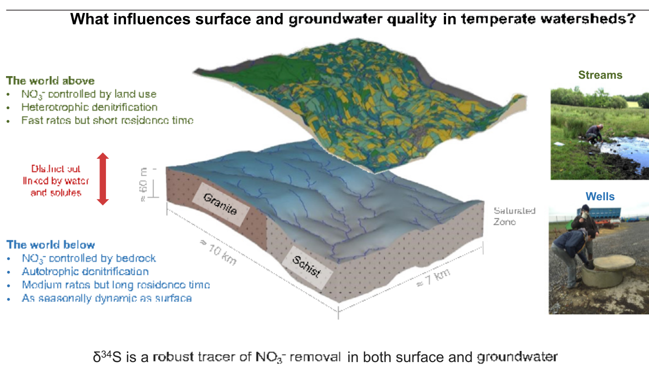
HIGHLIGHTS

- Disparate processes create opposite chemical patterns in surface and subsurface.
- C, N, and S patterns reflect both mixing and separation at watershed scales.
- Groundwater is as or more dynamic than surface water for many parameters.
- $\delta^{34}S$, DSi and CFCs provide robust nutrient retention and residence time proxies.

GRAPHICAL ABSTRACT



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ABSTRACT

Excess nutrients from agricultural and urban development have created a cascade of ecological crises around the globe. Nutrient pollution has triggered eutrophication in most freshwater and coastal ecosystems, contributing to a loss in biodiversity, harm to human health, and trillions in economic damage every year. Much of the research conducted on nutrient transport and retention has focused on surface environments, which are both easy to access and biologi-cally active. However, surface characteristics of watersheds, such as land use and network configuration, often do not explain the variation in nutrient retention observed in rivers, lakes, and estuaries. Recent research suggests subsur-face processes and characteristics may be more important than previously thought in determining watershed-level nutrient fluxes and removal. In a small watershed in western France, we used a multi-tracer approach to compare surface

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and subsurface nitrate dynamics at commensurate spatiotemporal scales. We combined 3-D hydrological modeling with a rich biogeochemical dataset from 20 wells and 15 stream locations. Water chemistry in the surface and subsurface showed high temporal variability, but groundwater was substantially more spatially variable, attributable to long transport times (10–60 years) and patchy distribution of the iron and sulfur electron donors fueling autotrophic denitrification. Isotopes of nitrate and sulfate revealed fundamentally different processes dominating the surface (heterotrophic denitrification and sulfate reduction) and subsurface (autotrophic denitrification and sulfate production). Agricultural land use was associated with elevated nitrate in surface water, but subsurface nitrate concentration was decoupled from land use. Dissolved silica and sulfate are affordable tracers of residence time and nitrogen removal that are relatively stable in surface and subsurface environments. Together, these findings reveal distinct but adjacent and connected biogeochemical worlds in the surface and subsurface. Characterizing how these worlds are linked and decoupled is critical to meeting water quality targets and addressing water issues in the Anthropocene.

1. Introduction

Excess nutrients from human activities have created a cascade of ecological crises that threaten humankind and ecosystems around the globe. The nutrients that have constrained primary productivity and heterotrophic growth for most of Earth's history—nitrogen (N) and phosphorous (P)—now saturate many environments along the terrestrial-aquatic-marine gradient, including soils, rivers, lakes, groundwater, and oceans (Pinay et al., 2018; Van Meter et al., 2018; Kolbe et al., 2019; Jane et al., 2021; Dai et al., 2023; Davidson et al., 2023). This widespread nutrient overload (eutrophication) causes immense damage to ecological food webs and human society, making it one of the most pressing and costly environmental issues of our day (Diaz and Rosenberg, 2008; Steffen et al., 2015b; Le Moal et al., 2019; Ward et al., 2018). Globally, approximately 80 % of freshwater and coastal ecosystems are experiencing some level of anthropogenic eutrophication (Galloway et al., 2003; Frei et al., 2020; Stoddard et al., 2016; Brahney et al., 2015; Dai et al., 2023).

In response to this nutrient crisis, progress has been made in some regions to stem the flood of anthropogenic nutrients, largely through the control of nutrient point sources such as wastewater discharge from humans and livestock (Abbott et al., 2018b; Ehrhardt et al., 2019; Yang et al., 2019). Additionally, many countries have implemented practical and regulatory measures to reduce nutrient pollution, though the results remain mixed (Poisvert et al., 2017; Dupas et al., 2018; Van Meter et al., 2018; Sabo et al., 2021b). However, as human activities now directly affect 77 % of the ice-free land surface (Watson et al., 2018; Abbott et al., 2019a), nutrient concentrations and fluxes continue to rise in much of the world (Seitzinger et al., 2010; Bouwman et al., 2013; Stoddard et al., 2016; Le Moal et al., 2019; Frei et al., 2021).

To identify effective solutions to the eutrophication crisis, we need to understand the sources and fates of nutrients added by humans to the Earth system. For example, agricultural activities account for approximately 85 % of the human nutrient load globally (Smil, 1999; Galloway et al., 2004; Bouwman et al., 2009; Campbell et al., 2017). However, only half of the nutrients applied in fertilizers is taken up by crops (Smil, 1999; Liu et al., 2010; Foley et al., 2011), with most of the nutrient waste occur-ring in areas of intensive agriculture in Asia, Europe, and North America (Foley et al., 2011; Sabo et al., 2021b). In agricultural areas where nutrient inputs exceed nutrient uptake of harvested crops, there are three general fates for excess nutrients: accumulation in the soil, leaching into groundwa-ter or surface water, or conversion to gaseous forms via denitrification for N (Aquilina et al., 2012a; Sebilo et al., 2013; Van Meter et al., 2016; Poisvert et al., 2017; Minaudo et al., 2019; Peterjohn and Correll, 1984). While understanding the relative importance of these fates in different socio-ecological contexts is crucial to solving eutrophication, it is also exceedingly difficult at medium to large scales. On one end of this scaling problem, plot-scale experiments in a single component of the watershed (e.g., the riparian zone or soil layer) are often unrelated to watershed-level fluxes (Pinay et al., 2015, 2018; Heiner et al., 2022; Ebeling et al., 2021; Basu et al., 2022). On the other end, watershed-scale observations often do not have the spatial resolution to identify what characteristics or practices are effective at reducing nutrient waste (Abbott et al., 2018b; Thomas and Abbott, 2018; Frei et al., 2020; Van Meter et al., 2021).

While most interventions to improve water quality are associated with surface or near-surface environments (e.g. riparian zones, surface waters, and soils), there is growing evidence that catchment-level nutrient retention is strongly influenced by subsurface characteristics (Aquilina et al., 2018; Kolbe et al., 2019; Frei et al., 2020; Pauwels et al., 2000; Böhlke, 2002; Duncan et al., 2015; Fan et al., 2020; Nguyen et al., 2022a; Lupon et al., 2023). Because hydrological residence time in the subsurface far exceeds the surface (Gleeson et al., 2016; Cook and Herczeg, 2012; Green et al., 2011), time lags or "legacies" are created between the input and out-put of excess nutrients (Van Meter and Basu, 2017; Ehrhardt et al., 2019; Guillaumot et al., 2021; Basu et al., 2022). This provides extended opportunities for physical and biological processes to take up or transform nutrients and other solutes traveling through aquifers (Oldham et al. 2013; Abbott et al., 2016; Dehaspe et al., 2021). However, subsurface environments have long been considered as less dynamic than surface environments (Li et al., 2017), where rapid biogeochemical processes are easily observable (McClain et al., 2003; Bernhardt et al., 2017). This paradigm of a "quiet world beneath" has recently been challenged on multiple fronts.

Advances in hydrological modeling, inferential methods, and direct observations now show that the subsurface is biogeochemically active and temporally dynamic (Ben Maamar et al., 2015; Long et al., 2016; Marçais et al., 2018; Kolbe et al., 2019; Bochet et al., 2020). However, the relative influence of subsurface and surface activity on watershed-scale nutrient dynamics remains uncertain. Because of logistical challenges and disciplinary divides (Li et al., 2017; Kolbe et al., 2019; Krause et al., 2022), relatively few studies characterize biogeochemistry in both the surface and deep subsurface (e.g., >10 m) at watershed scales, complicating direct comparison of the spatiotemporal dynamics and dominant processes in these environments. Yet, there is evidence from the shallow subsurface that these interactions are important across scales (Krause et al., 2014; Helton et al., 2015; Lee-Cullin et al., 2018; Wen et al., 2020; Guillaumot et al., 2021; Lupon et al., 2023).

In this context, we collected water samples over several years from streams and aquifers in small watersheds (<50 km^2) in a region of intensive agriculture in western France. Using a multi-proxy framework combined with previous hydrological research from this area (Abbott et al., 2016; Kolbe et al., 2016; Marçais et al., 2018; Thomas et al., 2019), we investigated the interaction of hydrological residence time, land-use, and biogeochemical processing in surface and subsurface environments. We were motivated by three general questions. First, how do spatial and temporal variability regimes differ between the surface and subsurface environments in this region? Second, what processes regulate nutrient dynamics as water travels through various watershed components (i.e., streams, vadose zones, and aquifers)? Third, what are the management implications of these observations of watershed-scale ecohydrology in the surface and subsurface? To address these questions, we focused on the transport and transformation of nitrate (NO_3^-), one of the most common nutrients associated with eutrophication and one of the costliest regarding environmental remediation, particularly in this region (Thomas et al., 2019; Abbott et al., 2018b; Heiner et al., 2022; Dupas et al., 2018). We analyzed a broad range of elements (e.g., carbon, sulfur, and silicon), proxies (e.g., isotopes, dissolved gases, and rare earth elements), and other data (e.g., historical land use, 3-D hydrological modeling, and reconstructed nutrient inputs) to characterize the surface and subsurface at the watershed scale.

2. Methods

2.1. Site description and experimental design

This study was conducted within the Zone Atelier Armorique research area, which is part of the Long-term socio-ecological research (LTSER) network (Thomas et al., 2019). The history, socioecological characteristics, and available data from this LTSER are described in detail by Thomas et al. (2019). The research area is in northeast Brittany in northwestern France. Brittany has a temperate oceanic climate (category "Cfb": temperate, no dry season, warm summer, following Kottek et al., 2006) and extensive livestock and row-crop agriculture (Thomas et al., 2019; Frei et al., 2020; Poisvert et al., 2017). The study catchment occurs on the Armorican massif, which is composed of metamorphic and igneous rock, primarily granite, schist, and micaschist (Aquilina et al., 2012a; Goderniaux et al., 2013b; Kolbe et al., 2016). The mean annual temperature is 11.2 °C, and the mean annual rainfall is 910 mm, which is relatively well distributed throughout the year, and mean potential evapotranspiration is 690 mm (Thomas et al., 2019). Because of the high infiltration capacity and relatively gentle precipitation, there is little artificial drainage (e.g., tile drains), but there are ditches and hedgerows around many fields, some of which have been present since Medieval times (Thomas and Abbott, 2018; Baudry et al., 2000; Forman and Baudry, 1984). The main land use is agriculture, with around 80 % of the region covered by row crops, pastureland, and indoor animal husbandry (pigs, poultry, and cows). This gives Brittany one of the highest densities of livestock in France and Europe (Gascuel-Odoux et al., 2010; Poisvert et al., 2017; Kim et al., 2019). The intensive agriculture in this region has created widespread and persistent eutrophication of streams, estuaries, and groundwater (Dupas et al., 2018; Moatar et al., 2017; Minaudo et al., 2019). However, improved nutrient management, particularly the reduction of point sources (e.g., wastewater and feedlot effluent) and decreases in fertilizer application have resulted in declining N and P concentrations in many Brittany watersheds (Dupas et al., 2018; Poisvert et al., 2017; Aquilina et al., 2012b; Gu et al., 2021; Abbott et al., 2018b).

To characterize the dominant hydrological and biogeochemical processes in the surface and subsurface, we collected samples for chemical analysis from 16 agricultural wells (28–94 m deep; hereafter deep wells), 4 research piezometers (<10 m deep; hereafter shallow wells), and 15 surface water locations within Le Guyoult and the Couesnon watersheds (Fig. 1). From December 2014 to April 2016, we performed seven sampling campaigns to capture temporal variability in the surface and subsurface. To

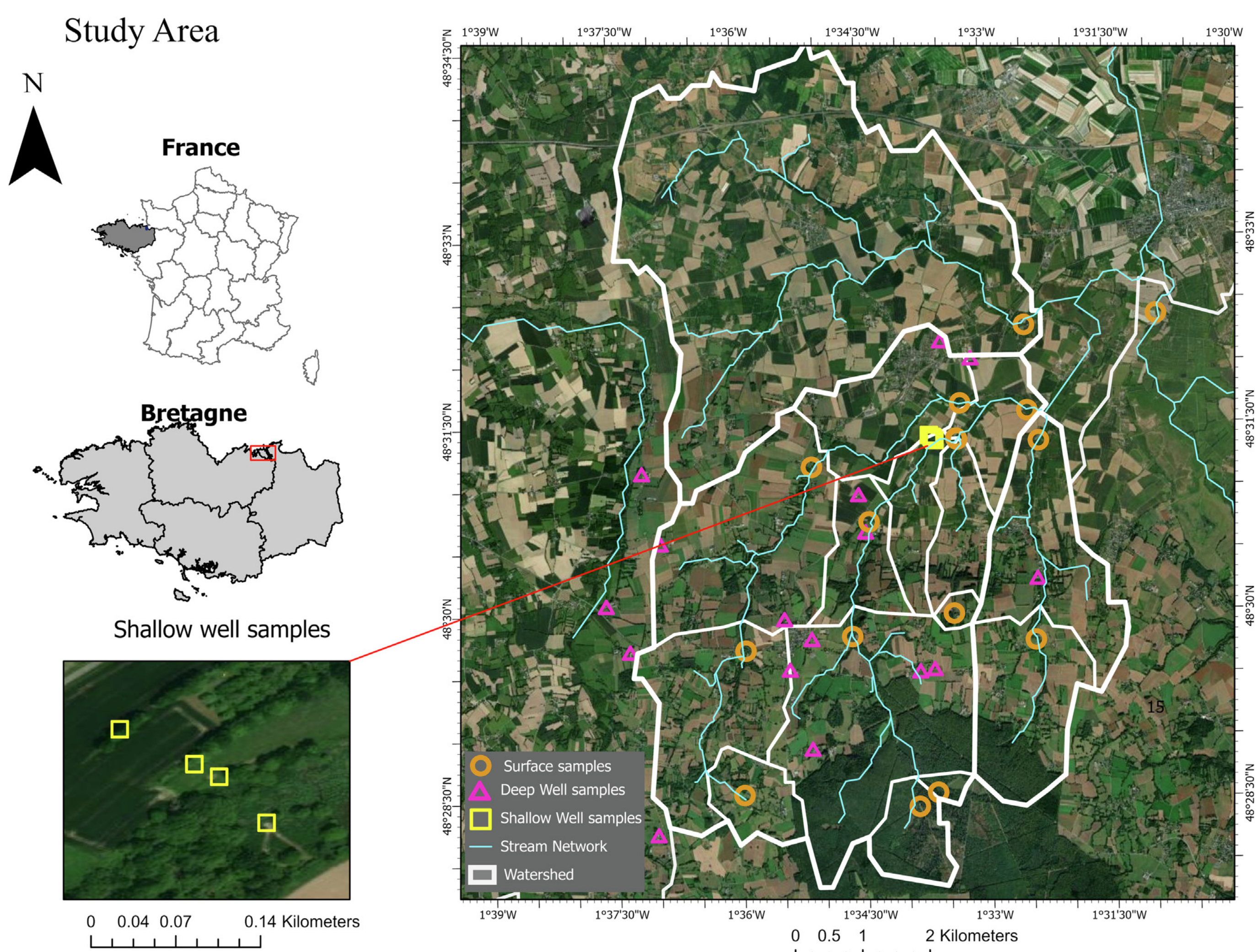

Fig. 1. Map of the study area near the Zone Atelier Armorique Long-term socio-ecological research (LTSER) site. Le Guyoult watershed to the west is a tributary of the larger Couesnon watershed to the east. The white lines indicate the subcatchment boundaries based on topographic delineation.

maximize the spatial extent of surface and groundwater sampling, not all the sites were visited during every campaign, and the mean number of return visits per site was four.

2.2. Estimating nitrate removal

Nitrate removal was estimated based on the concentration of excess N_2 dissolved in the groundwater. The detailed procedure for calculating nitrate removal is described fully in Kolbe et al. (2019) and Vautier et al. (2021). Briefly, in a groundwater environment, the concentration of excess N_2–i.e., above the expected concentration—can indicate the amount of NO_3^- removed by denitrification because equilibration with the atmosphere is not possible (Aeschbach-Hertig et al., 1999; Ayraud et al., 2006; Böhlke, 2002). After correcting for atmospheric partial pressure and temperature with the observed Ar concentration, the sum of the excess N_2 and remaining NO_3^- allow calculation of the concentration of NO_3^- that reached the water table (Kolbe et al., 2019; Böhlke, 2002). Combined with estimates of groundwater residence time, this can allow the reconstruction historical NO_3^- inputs (Kolbe et al., 2019; Aquilina et al., 2012b).

Though land use in specific parcels of the catchment has varied substantially in the past (Barbe et al., 2020), crop rotations have created a reasonably uniform N input time series at the catchment scale (Kolbe et al., 2019). Because this method only accounts for NO_3^- removed after the water lost contact with the atmosphere (i.e., in the saturated zone), it accounts implicitly for biogeochemical removal or retention in the unsaturated zone (Thomas and Abbott, 2018; Basu et al., 2022). For our purposes, this is an advantage over more common nutrient surplus estimates, which account for overall disequilibrium in N and P but not vadose-zone removal (Van Meter et al., 2016; Sebilo et al., 2013; Poisvert et al., 2017).

2.3. Proxies of hydrology and biogeochemistry

To assess the degree of biogeochemical attenuation of nutrients and the relative importance of nutrient loading versus nutrient removal, we measured the concentrations and stable isotope ratios of NO_3^- ($\delta^{15}N$ and $\delta^{18}O$) and SO_4^{2-} ($\delta^{34}S$). Stable isotopes can indicate the nutrient source and the degree of biogeochemical processing (Lehmann et al., 2003; Mariotti et al., 1981; Malone et al., 2018). NO_3^- isotopes have been widely analyzed because NO_3^- is a dominant form of nitrogen in nutrient saturated ecosystems (Aber et al., 1998), organic and industrial fertilizers have distinct initial $\delta^{15}N$ and $\delta^{18}O$ (Lohse et al., 2013; Denk et al., 2017; Bedard-Haughn et al., 2003), and denitrification (both heterotrophic and autotrophic) strongly fractionates NO_3^- isotopes, increasing the residual $\delta^{15}N$ and $\delta^{18}O$ relative to the initial values prior to denitrification (Hosono et al., 2014; Malone et al., 2018; Ayraud et al., 2006; Pauwels et al., 2010). Therefore, we predicted that watersheds with isotopically enriched NO_3^- would have higher N attenuation (Lehmann et al., 2003) or alternatively that they would have received primarily organic fertilizer (Bedard-Haughn et al., 2003).

Sulfur isotopes have been used extensively in geochemical studies of processes ranging from the evolution of the Earth's atmosphere to bacterial and archaeal dissimilatory SO_4^{2-} reduction (Canfield, 2001; Farquhar and Wing, 2003). For the purposes of this study, we were particularly interested in $\delta^{34}S$, which can be increased by SO_4^{2-} reduction after depletion of NO_3^- (e.g., in highly reduced wetland habitats) and decreased by SO_4^{2-} production in aquifers during autotrophic denitrification (Hosono et al., 2014; Abbott et al., 2016). Consequently, we predicted that $\delta^{34}S$ of SO_4^{2-} would be higher in watersheds where surface processes dominate NO_3^- removal, whereas $\delta^{34}S$ would be lower when groundwater processes were relatively more important.

We used a combination of tracers to assess water residence time, including chlorofluorocarbons (CFCs), sulfur hexafluoride (SF6), and dissolved silica (DSi). CFCs and SF6 have been commonly used as tracers of water age due to their high detectability and low reactivity in aqueous environments (Abbott et al., 2016; Cook and Herczeg, 2012; Busenberg and Plummer, 1992; Wilson and Mackay, 1996). However, these anthropogenic gases cannot be used to quantify the age of surface waters because they readily equilibrate with the atmosphere when groundwater resurfaces. DSi has been shown to strongly correlate with subsurface residence time (Marçais et al., 2018; Becker, 2013) and has been used to measure surface water ages in previous studies in this area (Frei et al., 2020). Though the concentration of DSi can be influenced by terrestrial and aquatic plant uptake in surface waters, we assumed conservative transport given the short residence time and relatively high concentration of DSi in these headwater streams (Marçais et al., 2018; Delvaux et al., 2013; Carey et al., 2019; Abbott et al., 2018b).

2.4. Gas sampling and analysis

CFC and SF6 measurements were taken at the Plateform Condate Eau from University of Rennes 1. We collected water in steel ampoules (40 mL for CFC and 300 mL for SF6) by pumping with a MP1 Grunfoss pump in the borehole. After stabilization, we measured the conductivity, pH and dissolved O_2 using a custom sensor manifold preventing contact with the atmosphere (Hach, Loveland CO, USA; model HQ440d multi; Fig. S1), and the ampoules were rinsed with three times their volume of water and closed (Labasque et al., 2014). CFC and SF6 concentrations were determined by a purge and trap extraction coupled to a GC/ECD (Busenberg and Plummer, 1992, 2000; Labasque, 2020). Uncertainties are around 3 % for young groundwaters for CFC, 10 % for SF6, and 20 % for CFC on old (>50 years) groundwaters. The major dissolved gases (He, Ne, Ar, N_2, CO_2, CH_4) were sampled in 500 mL glass flasks and analyzed by headspace extraction followed by μGC/TCD measurements, following (Sugisaki and Taki, 1987). Uncertainties are around 5 % for Ne and He and 3 % for other gases.

2.5. Solute and isotope collection and analysis

At each site, we collected a 5 L sample of water for immediate sensor readings and eight smaller samples for laboratory analyses. For the laboratory analyses, we immediately filtered subsamples using a 50 mL syringe and two 250 mL filter towers. We used a 0.2 μm cellulose acetate syringe filter to prepare samples for the analysis of cations, rare earth elements (REE), and NO_3^- isotopes. Molybdate reactive phosphorous (MRP) concentration was determined colorimetrically via reaction with ammonium molybdate (Murphy and Riley, 1962), with a precision of ± 4 μg l^{-1} (Gu et al., 2018). Nitrate isotope samples were frozen immediately and shipped to the UC Davis Stable Isotope Facility for analysis of $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- by bacterial denitrification assay (McIlvin and Casciotti, 2011). Isotope ratios of $\delta^{15}N$ and $\delta^{18}O$ were determined by measuring N and O using a ThermoFinnigan GasBench + PreCon trace gas concentration system connected to a ThermoScientific Delta V Plus isotope-ratio mass spectrometer (Bremen, Germany) with a precision of ± 0.4 ‰ and 0.5 ‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively. Cations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700×, Santa Clara, USA, relative uncertainties ± 5 %). We quantified dissolved organic carbon (DOC; Shimadzu TOC-5050A, Kyoto, Japan, precision ± 5 %), which is often considered a master variable influencing physicochemical conditions in aqueous environments (Zarnetske et al., 2018; Abbott et al., 2016). Because DOC is the electron donor for both aerobic respiration and heterotrophic denitrification (Hosono et al., 2014; Sebilo et al., 2019), high DOC can enhance NO_3^- removal, and high NO_3^- can accelerate DOC oxidation (Abbott et al., 2016; Kolbe et al., 2019). This two-way interaction contributes to the strong negative stoichiometric relationship between NO_3^- and DOC observed in surface and groundwaters globally, including in this region (Taylor and Townsend, 2010; Frei et al., 2020).

To determine SO_4^{2-} isotopes, we filtered water samples on a Millipore™ system using 0.45 μm cellulose acetate filters. Filtered solutions were then heated to 70 °C and a 5 % solution of barium chlorate was added drop-to-drop to precipitate dissolved SO_4^{2-} as barium sulfate ($BaSO_4$). Sulfur isotope composition of SO_4^{2-} was measured using a VarioPYROcube™ elemental analyzer in combustion mode interfaced in continuous-flow mode with an Isoprime™ isotope ratio mass spectrometer at the Laboratoire de Géologie de Lyon (CNRS UMR 5276, University Claude Bernard Lyon 1). $BaSO_4$ from water samples was analyzed by weighing 3 aliquots of 250 μg in tin foil capsules. Measurements were calibrated against the three $BaSO_4$ international standards NBS127, IAEA-SO-5 andIAEA-SO-6. The standard deviation of $\delta^{34}S$ measurements was close to 0.3 ‰. Data are reported as $\delta^{34}S$ vs. V-CDT.

2.6. Spatial analysis

Using detailed land-use time series from the LTSER (Barbe et al., 2020), we calculated the dominant land use type for each parcel from 1993 to 2013 (except 1995; Fig. 1). We converted all the land use shapefiles to raster files with a cell size of 15 m. We then used "majority" in cell stat to calculate the value of the most common land use through time. For the cells that had no historical data, we used the 2013 values (i.e., the most recent values). Similar land-use types were clustered into 4 groups: row crops, developed land, natural landscapes, and pastureland. The row crops category included corn, wheat, and other ploughed crops. Developed land included asphalt roads, unpaved roads, buildings, and railroad tracks. Natural landscapes consisted of forested and riparian areas. The last category pastureland consisted of grazing pastures and abandoned lands.

We intersected the land use raster with contributing watershed area for stream locations and the contributing area of the deep wells, which had been calculated in previous work (Kolbe et al., 2016). We excluded the shallow wells from this analysis because all the sampling points were contained in the same subcatchment and therefore could not be differentiated by land use (see Thomas et al., 2019 for a detailed analysis of the shallow wells).

2.7. Statistical analysis

We used Pearson and Spearman correlations to quantify relationships among and within biogeochemical and landscape parameters (Malone et al., 2018). We calculated both parametric (r) and nonparametric (rho) correlation coefficients for different reasons. The Spearman correlations (rho) are rank based, providing a robust metric of the overall association across sites. Conversely, the Pearson correlations (r) provide full weight to extreme values, which can be influential in determining overall watershed behavior. For example, small portion of the watershed (i.e., a single or a few sites) can control source or sink dynamics for a given parameter (Bernhardt et al., 2017; McClain et al., 2003; Abbott et al., 2018a; Lee et al., 2022). For both Spearman and Pearson correlations, we used a decision criterion of $\alpha = 0.05$. To compare variability in surface and subsurface environments, we calculated the mean and its standard error of the spatial and temporal coefficients of variation (CV) for each parameter. This allowed us to compare whether there was more variation for a given parameter in the surface or in the subsurface. We conducted all analysis and visualizations in the R statistical computing software environment (R Core Team, 2022).

3. Results

3.1. Spatiotemporal dynamics in the surface and subsurface

The water chemistry of wells and streams indicated both contrasts and connectivity of the surface and subsurface water. The subsurface showed larger variations in most physicochemical parameters compared to the surface sites, except for temperature, pH, and DOC, which are strongly influenced by seasonal drivers at the surface (Fig. 2). For most parameters, including the nutrients which are the focus of this study, the stream values fell between the deep and shallow wells (Fig. 2). The N parameters grouped closer to deep wells, but the P, S, and Si parameters grouped closer to shallow wells, suggesting a combination of mixing and biogeochemical attenuation at watershed scales.

Separating the combined variability shown in Fig. 2 into spatial and temporal CV revealed several surprising patterns (Fig. 3). Throughout the watershed and through time, stream chemistry showed relatively less variation, with no parameters exceeding a mean CV of 75 % (Fig. 3). Conversely, the shallow wells and especially the deep wells showed greater spatial and temporal variability, including several parameters with >100 % variation (Fig. 3). We note that CV is expressed as a percentage, representing proportional change rather than absolute change. For example, stream environments showed more absolute range in DOC concentration (Fig. 2), but because the mean DOC was much higher than in the subsurface sites, the DOC CV was lower in streams (Fig. 3).

Spatial variation generally exceeded temporal variation across site types (i.e., most parameters plotted below the 1:1 line in Fig. 3), though this was notably not the case for NO_3^- in deep wells and SO_4^{2-} and water age in all wells (see Section 3.3 for detailed water age results). N and S isotopes

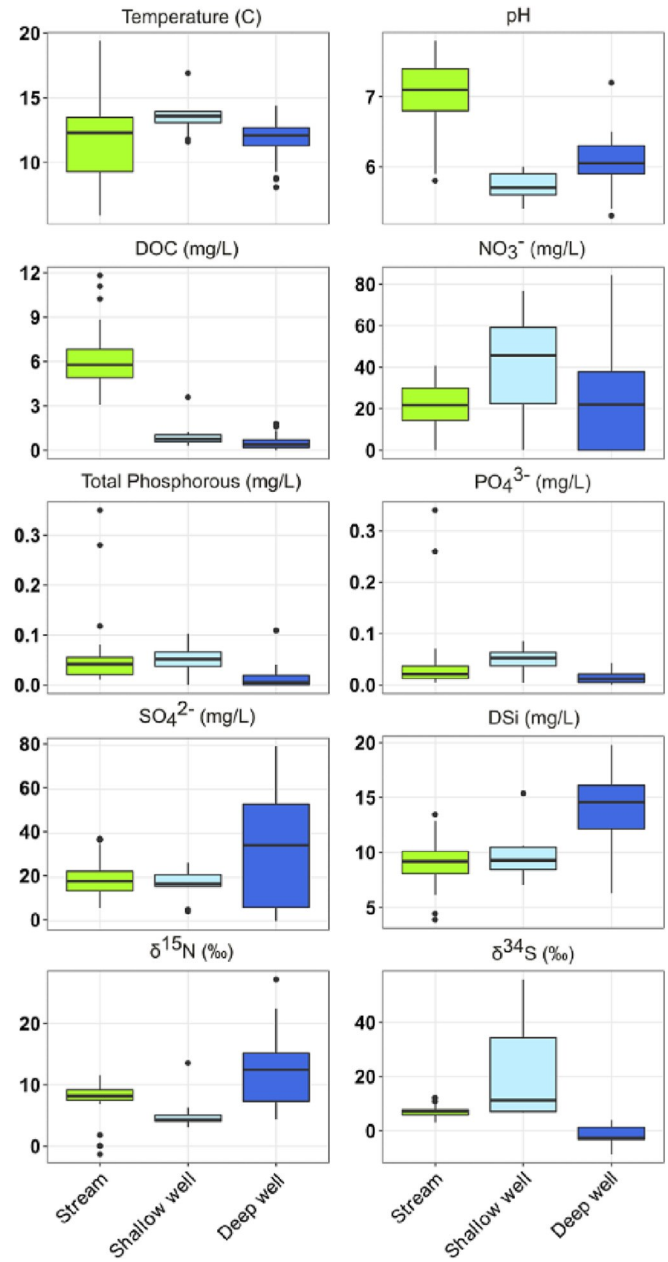

Fig. 2. The distribution of several physicochemical parameters in the streams, shallow wells, and deep wells sampled in this study. The parameter and units are shown above each plot. The boxplots represent the median, interquartile range (IQR), points within 1.5-times the IQR, and outliers beyond 1.5-times the IQR. Because each site and sampling event are included as individual points, the ranges represent the combined spatial and temporal variability.

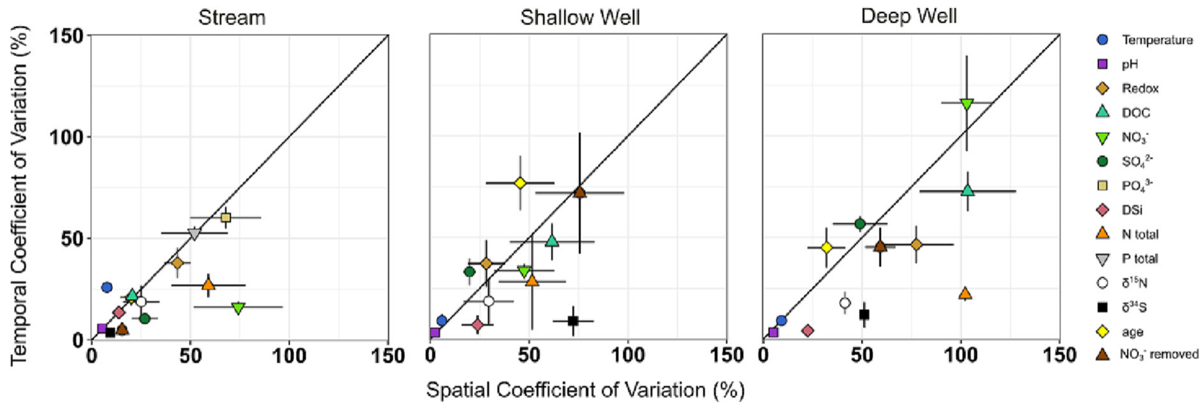

Fig. 3. The spatial and temporal coefficients of variation for physicochemical parameters in streams, shallow wells, and deep wells (mean ± SE).

tended to be substantially less variable than N and S concentrations, suggesting that hydrological dilution rather than changes in nutrient source or processing accounted for variability in concentrations.

Mapping NO_3^- concentration and removal showed the contrasts in spatial patterns between the surface and subsurface more explicitly (Fig. 4). In the stream network, NO_3^- concentration was relatively homogeneous, increasing gradually from the forested uplands in the south to the more intensively cultivated landscapes in the north of the watershed (Fig. 4). Conversely, groundwater NO_3^- concentration showed extreme variation throughout the watershed, with sites only meters apart showing up to 70 mg/L differences in concentration. Similarly, the percentage of NO_3^- removed was much more variable for groundwater, while the stream network showed a moderated pattern similar to the groundwater mean (Fig. 4).

3.2. Isotopic and dissolved tracers

The isotopes and solutes provided clues about the causes of the surprising spatiotemporal patterns. There were opposite relationships between isotope signatures and NO_3^- removal in the streams and deep wells, with mixed patterns in the shallow wells (Fig. 5A & B). In the deep wells, NO_3^- removal was positively correlated with $\delta^{15}N$, as expected due to fractionation during denitrification. The opposite pattern existed in the surface water where $\delta^{15}N$ was negatively correlated with NO_3^- removal, though the correlation was only significant for the Pearson coefficient, indicating that a few extreme values were driving the relationship (Fig. 5A & B). Indeed, the low NO_3^- and low $\delta^{15}N$ stream sites occurred in the forested south of the watershed (Fig. 4), likely indicating a non-fertilizer N source (e.g., atmospheric deposition or natural N fixation). We note that the percentage N removal for these sites was likely overestimated because our reconstructed N input assumed similar land use for each subcatchment, which is not the case for forested sites that have never been under cultivation.

In general, $\delta^{34}S$ was a better proxy of NO_3^- concentration and removal, with $\delta^{15}N$ showing fewer and weaker relationships (Fig. 5). $\delta^{34}S$ was positively correlated with NO_3^- removal in the surface but negatively correlated in the deep wells (Fig. 5C & D), in line with our hypotheses about S reduction in the surface and S release from autotrophic denitrification in the subsurface.

Contrary to our predictions, DOC was not correlated with most NO_3^- and SO_4^{2-} parameters, and when correlations existed, they were typically weak (Fig. S2). Across site types, there was a significant negative correlation between $\delta^{34}S$ and SO_4^{2-} concentration (Fig. 6). Some of the highest $\delta^{34}S$ values we are aware of were observed in the shallow well sites that occurred in the riparian wetland (Fig. 1). Together these patterns suggest that different processes are controlling nutrient retention in the surface and subsurface, with heterotrophic denitrification and sulfur reduction dominating in the surface and autotrophic denitrification in the subsurface.

3.3. Residence time and nutrient removal

We combined gaseous and dissolved residence time tracers to allow estimation of mean water age in both the surface and subsurface. There was a high correlation (r = 0.96, rho = 0.95) between water residence times derived from DSi concentrations with residence times calculated using CFCs and SF6 (Fig. 7). This allowed us to use DSi to estimate mean residence time in surface water environments where gaseous tracers are not effective.

The deep wells showed the longest residence time, with a median age of 42 years and a mean age of 36 years. Shallow well water was the youngest, with a median age of 23.5 years and a mean age of 20.5 years (Fig. 7B). The stream water was slightly older than the shallow well water with a median age of 25 years and a mean age of 24.4 years, indicating a mix of shallow and deep groundwater sources. The streams were more homogeneous in age (interquartile range of 20–28 years) than either the shallow (2–30 years) or deep wells (17–46 years; Fig. 7).

NO_3^- tended to be higher in younger water, i.e., there was a negative correlation between mean water age and NO_3^- concentration in shallow and deep wells (Fig. 8A). This implies that either NO_3^- loading has increased through time or that older sites have less NO_3^- because of cumulative removal. The latter is suggested by the positive correlation between water age and $\delta^{15}N$ in deep wells, though the relationship is less clear in shallow wells and streams (Fig. 8B). For streams and shallow wells, water age was positively correlated with NO_3^- removal (Fig. 9). We note that because the stream water comes from shallow and deep groundwater in this system, the stream removal values are cumulative (i.e., most of the removal is happening in the deep and shallow wells before flowing into the stream; Fig. 9).

3.4. Nutrient sources

In stream environments, NO_3^- concentration was positively correlated with percentage of row crop agriculture in the subcatchment and negatively correlated with the amount of natural land cover types (Fig. 10). However, no such relationships were detected in deep wells, where NO_3^- concentration was not correlated with land use in the contributing area (Fig. 10). This lack of correlation could be due to a combination in uncertainty in the determination of contributing areas, temporal changes in land use over the ~40 years of transit time, and heterogeneous rates of removal of NO_3^- during transit through the aquifer.

4. Discussion

In this study we characterized biogeochemical and hydrological processes in the surface and subsurface at the same spatiotemporal scales to explore watershed-level controls on nutrient retention and removal. We

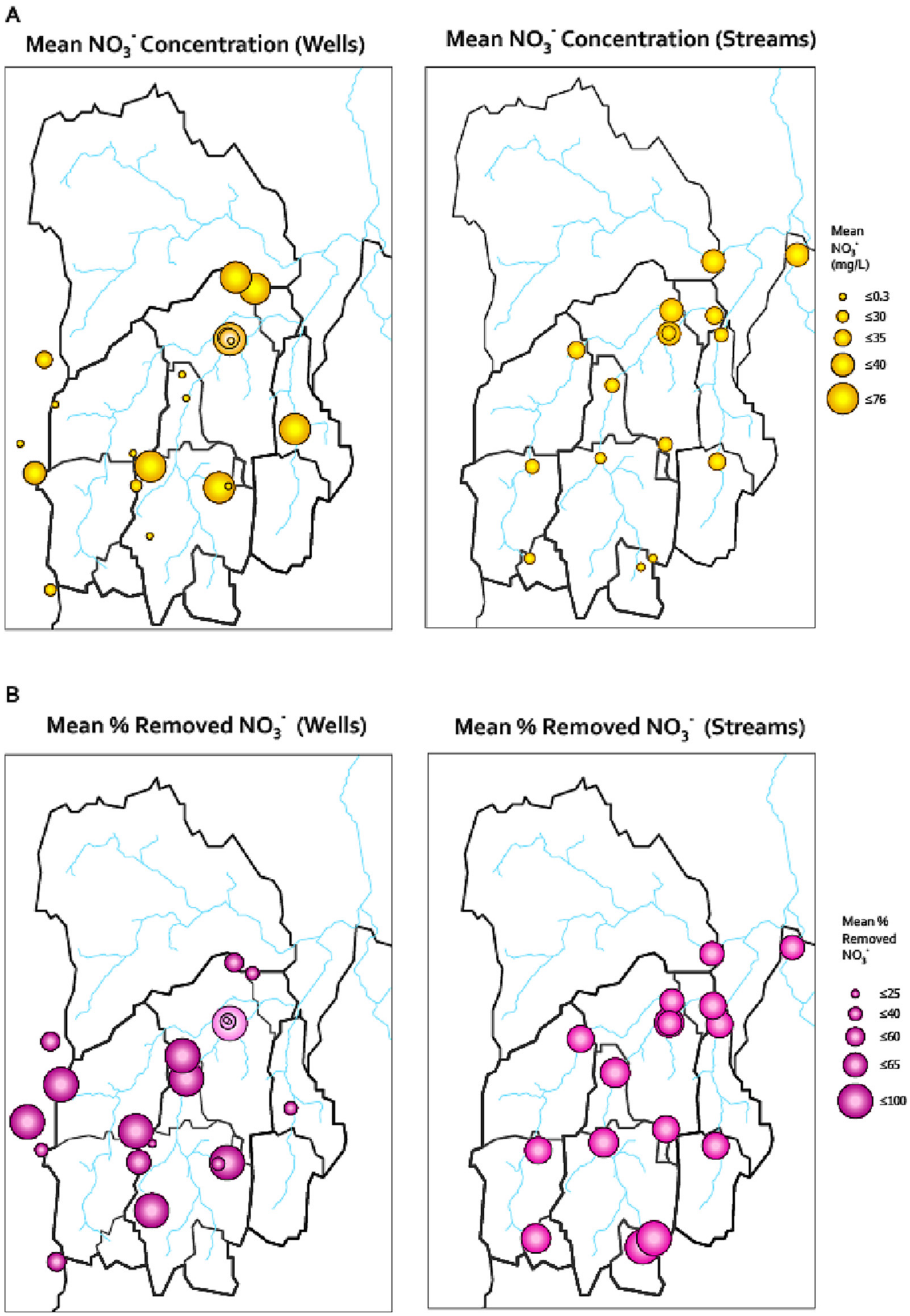

Fig. 4. NO_3^- concentration (A) and percent removal (B) in subsurface (left) and surface (right) environments. Average across time for each site, showing spatial variation of chemical parameters. NO_3^- removal was calculated based on the difference between the reconstructed NO_3^- input and the observed concentration (methods).

used a multi-proxy approach to identify dominant NO_3^- removal processes and characterized spatiotemporal variation in streams and groundwater. We observed highly distinct but linked biogeochemical "worlds" above and below the surface, which interacted to determine watershed-level nutrient dynamics. In the following paragraphs, we compare these results with studies from this and other regions and explore potential management implications.

4.1. Deepening our thinking to address water-energy-food crises

Because of disciplinary differences in methods and processes, groundwater and surface water environments are often considered individually, especially at watershed scales (Bochet et al., 2020; Abbott et al., 2018a; Leibundgut et al., 2009; Krause and Bronstert, 2007; Duncan et al., 2015; Knee et al., 2018). Groundwater biogeochemistry and hydrology have

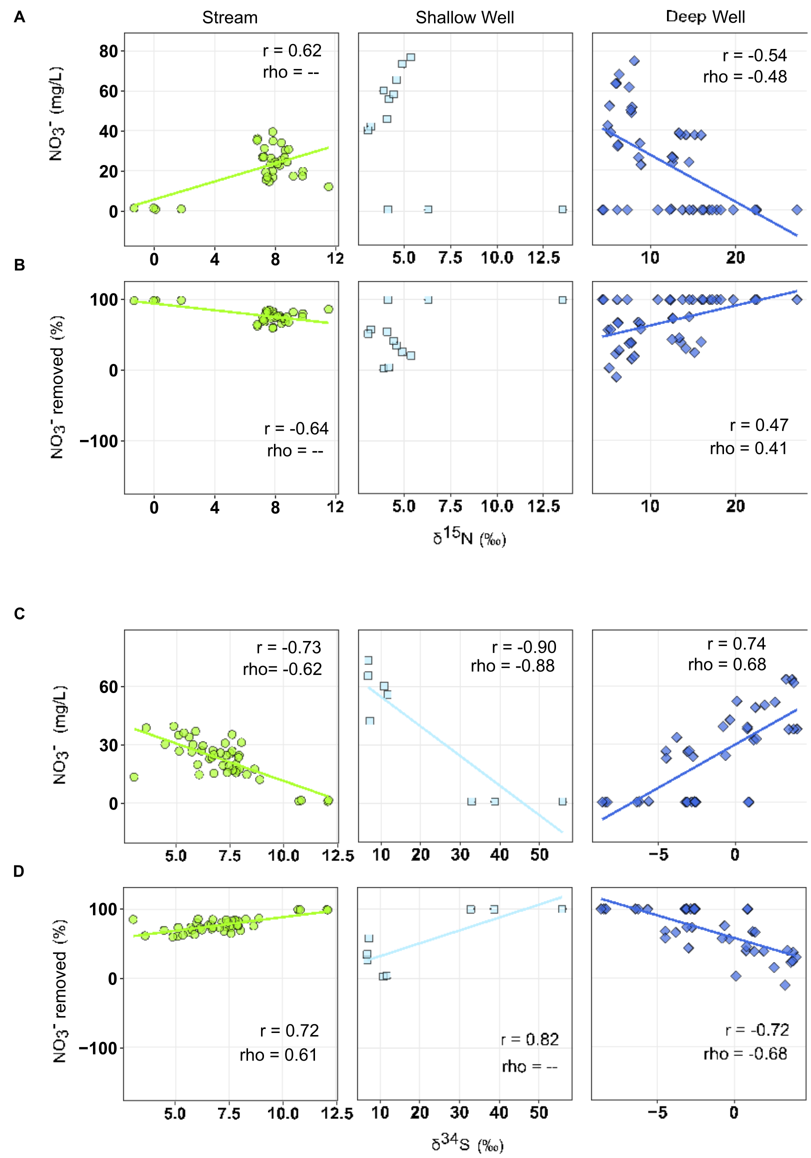

Fig. 5. Relationships of $\delta^{15}N$ and $\delta^{34}S$ with NO_3^- concentration and removal. Linear fit lines are shown for convenience to indicate a significant relationship—either Pearson (r) or Spearman (rho)—at α = 0.05.

long been areas of focus in hydrogeology and critical zone science, but they have not received as much attention in ecosystem ecology and nutrient management (Chorover et al., 2007; Krause et al., 2022; Goderniaux et al., 2013a; Li et al., 2021, 2017; Brookfield et al., 2021). Because attaining surface water quality goals depends on the overall watershed response (including the subsurface), this disconnect needs to be addressed (Van Meter et al., 2021; Vautier et al., 2021; Heiner et al., 2022; Basu et al., 2022; Lupon et al., 2023). Additionally, global water security and aquatic habitat conservation increasingly depend on hydrochemical understanding of groundwater-surface water interactions (Hartmann et al., 2021; Jasechko and Perrone, 2021; Wine, 2022; Gleeson et al., 2020).

Given how different the skillsets are for surface and subsurface measurements and modeling, we believe the best way to deepen our watershed approaches is through collaborations. We call on researchers and research-funding agencies to encourage such collaboration. There are many watershed-focused projects from around the world that can be used as models for next steps in integrating surface and groundwater hydrochemistry, ecology, and sustainability in the Anthropocene (Oldham et al. 2013; Mu et al., 2020; Krause et al., 2022; Lee-Cullin et al., 2018; Marçais et al., 2022; Musacchio et al., 2020). However, many watershed observatories and interdisciplinary approaches are threatened or underfunded (Laudon et al., 2017; Arènes et al., 2018; Brooks et al., 2015; Linton, 2008, 2014; Thomas et al., 2019). Increased investment is needed not only for basic research but also (and perhaps primarily) for community participation and education (Abbott et al., 2018b, 2023; Ben-zvi-Assarf and Orion, 2005; Basu et al., 2022). In the Anthropocene, the lack of understanding of watershed processes is a major obstacle to achieving sustainable practices central to the water-energy-food nexus (Albrecht et al., 2018; Zhang et al., 2018; Biggs et al., 2015; Abbott et al., 2019b).

4.2. Integrated sampling reveals contrasted but connected worlds above and below

An important theme from collaborative work linking surface and subsurface environments is that the world beneath is not stable or calm. Groundwater environments are commonly characterized as homogeneous and slow, lacking the diversity and energetic gradients to support dynamic biogeochemistry (Bochet et al., 2020; McClain et al., 2003; Cardenas, 2015). Evidence from work around the world shows that the view of a quiet world beneath is not accurate (Marçais et al., 2022; Ben Maamar et al., 2015; Zhang et al., 2015; Jasechko et al., 2017; Green et al., 2011).

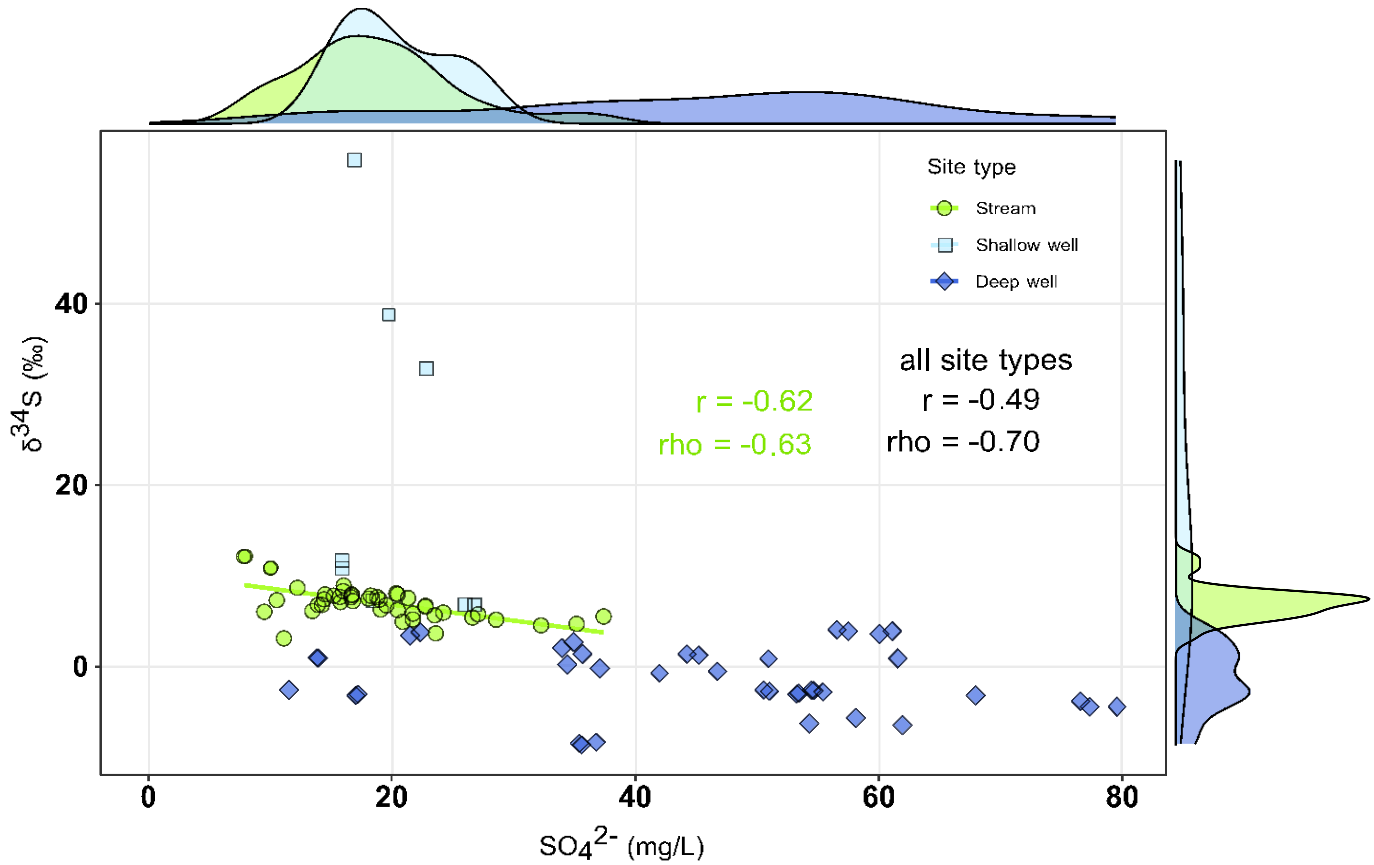

Fig. 6. The relationship between $\delta^{34}S$ and SO_4^{2-} for streams, shallow wells, and deep wells. The two subsurface site types showed more variation in $\delta^{34}S$, bracketing the stream water samples, which resembled a mix of the two contributing flow paths (i.e., deep groundwater and shallow soil/riparian water).

Indeed, there is a growing consensus that catchment-level nutrient removal may depend largely or primarily on subsurface characteristics that are often temporally dynamic (Aquilina et al., 2018; Kolbe et al., 2019; Frei et al., 2020; Bochet et al., 2020; Long et al., 2016; Brookfield et al., 2021; Hosono et al., 2014).

For the watersheds in our study, the subsurface appears to be the epicenter of denitrification rather than a biogeochemical afterthought, likely because of the combination of longer residence times and relatively abundant electron donors (Oldham et al. 2013; Pu et al., 2014).

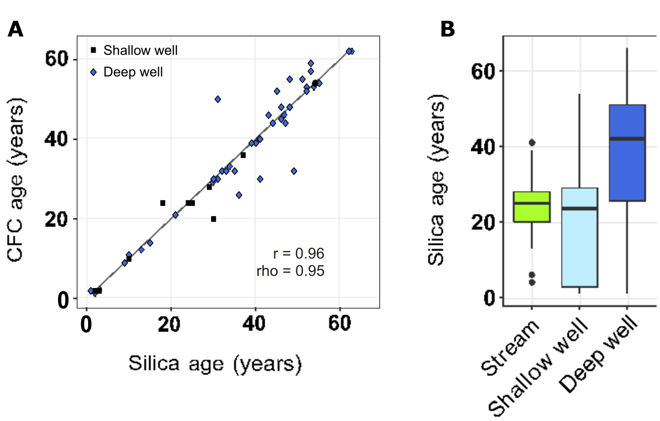

Fig. 7. Estimates of mean water age. Because the dissolved anthropogenic gas measurements are only effective in the subsurface, we calculated the relationship between silica-derived and CFC-derived water ages for shallow and deep groundwater environments only.

Groundwater environments are home to most of Earth's bacterial and archaeal biomass (Bar-On et al., 2018), and the combination of biological and hydrological factors can create extreme spatial and temporal variation in groundwater reaction types and rates (Bochet et al., 2020; Ben Maamar et al., 2015). Because groundwater and surface-water environments are constantly exchanging water, energy, and material, the failure to adequately characterize subsurface processes likely explains some of the difficulties in predicting nutrient fluxes and recovery patterns at watershed scales (Kolbe et al., 2019; Frei et al., 2021; Van Meter et al., 2018; Brookfield et al., 2021).

The relatively low variance we observed for many surface parameters demonstrates another interesting implication of surface-subsurface interactions. In Brittany, as in many temperate regions, surface water is comprised of water mixing from the shallow and deep groundwater (Marçais et al., 2018, 2022; Thomas and Abbott, 2018). While the processes and solute concentrations in the groundwater system are highly variable, they become mixed as they enter the surface environment through riparian zones and diffuse groundwater flux to streams (Krause et al., 2022; Pinay and Haycock, 2019; Le Moal et al., 2019; Cardenas, 2015). Given the short transit times in the surface, this results in a homogenized signature; as the surface water travels farther and faster, it integrates a larger spatial scale and reflects a larger landscape patch (Abbott et al., 2018a; Dupas et al., 2019). While this reduces the ability of streams to mitigate high nutrient loading (i.e., stream and riparian retention cannot offset watershed-wide nutrient excess), it reinforces the role of streams as integrators of watershed processes, creating valuable sentinels of change, particularly when monitored in a quantitative, multi-proxy way (Moatar et al., 2020; Frei et al., 2020; Helton et al., 2011; Pinay et al., 2018; Brookshire et al., 2009; Cole et al., 2007; Shogren et al., 2021; Casas-Ruiz et al., 2023, 2017).

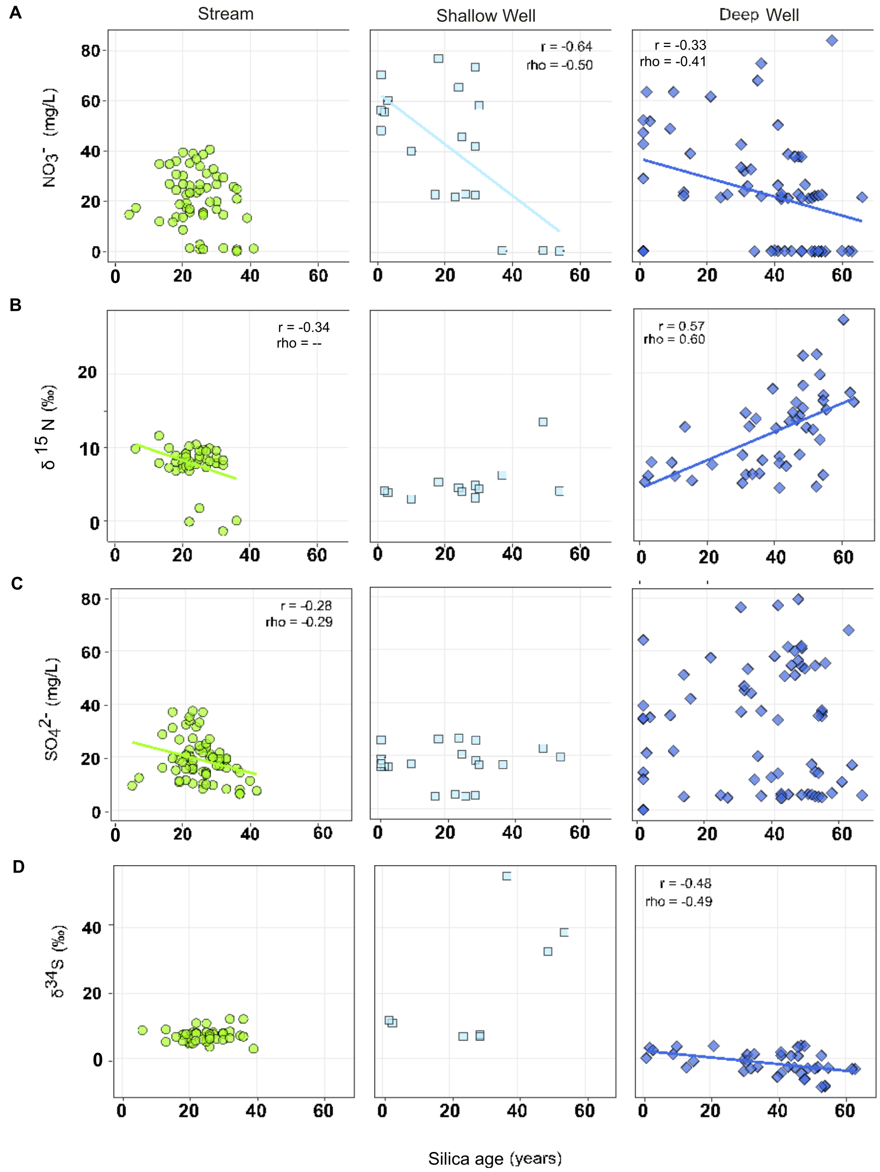

Fig. 8. Relationships between mean water age and SO_4^{2-} and NO_3^- isotopes and concentrations in stream, shallow groundwater, and deep groundwater environments.

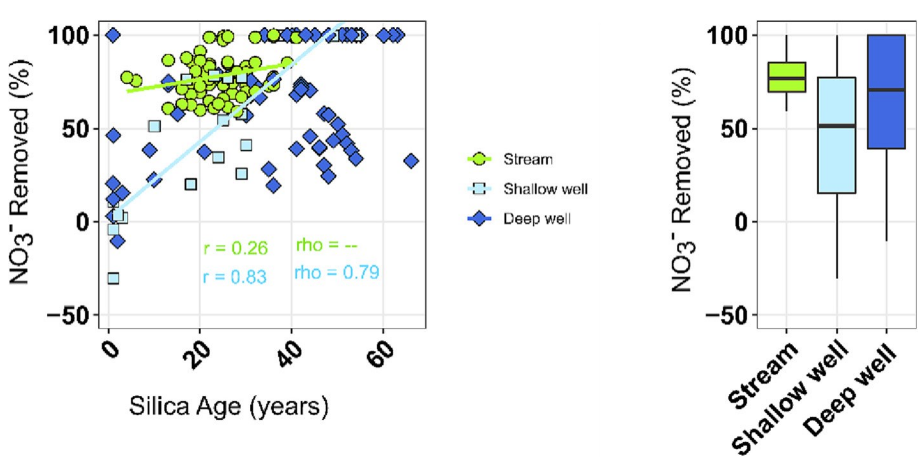

Fig. 9. NO_3^- removal versus mean water age for streams, shallow wells, and deep wells. NO_3^- removal represents the cumulative removal along the flow path starting with input of NO_3^- to the water table.

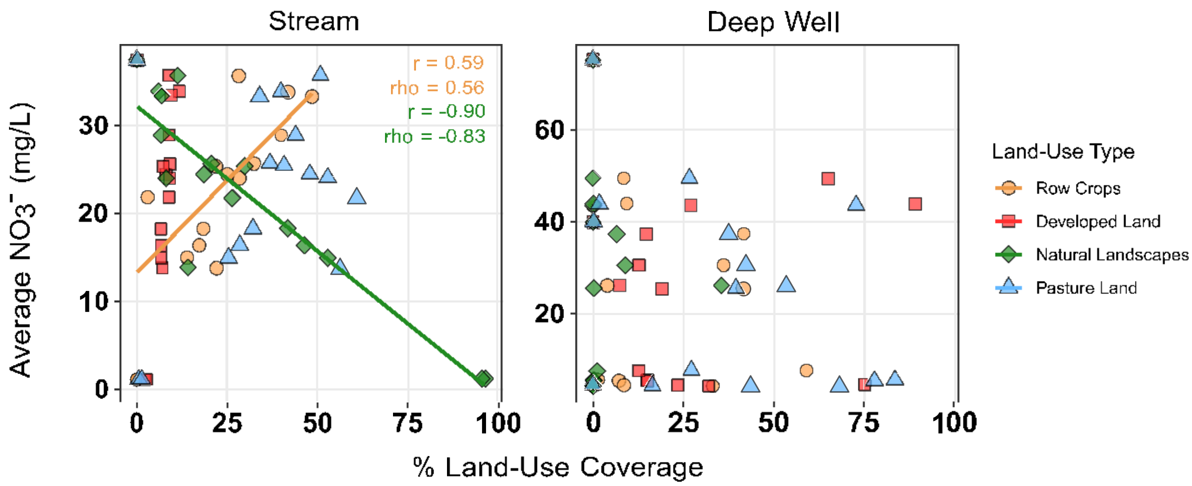

Fig. 10. Correlation of NO_3^- and the percent of land-use cover for streams and deep wells. Shallow wells were omitted from this analysis as all shallow wells were contained within one subcatchment. Land-use coverage in the streams was calculated for the contributing subcatchment area. Land-use for deep wells was calculated from the well's contributing area based on prior hydrogeological modeling (Kolbe et al., 2016).

4.3. Context-dependence of biogeochemical proxies in surface and subsurface environments

Biogeochemical proxies and tracers are indispensable tools to evaluate hydrological and ecological processes across scales (Pinay et al., 2015; Bernardie et al., 2018; Frei et al., 2020). Particularly when working at the watershed scale or when investigating groundwater environments where extensive physical exploration is impossible, proxies can reveal processes that are otherwise unobservable, including microbial metabolism, hydrological residence time, and weathering processes (Marçais et al., 2018; Kolbe et al., 2019; Leibundgut et al., 2009). Because proxies such as solutes, isotopes, and physicochemical attributes (e.g., temperature, pH, etc.) can reveal mass flux and processing, they have been used extensively to investigate the sources of nutrient pollution and to compare reactivity in different components of a watershed (Sebilo et al., 2013; Covino, 2017; Thomas and Abbott, 2018).

However, one of the fundamental assumptions about interpreting a tracer is that it will retain or conserve a portion of the signal imbued by the environment of interest as it travels to the location where it can be sampled (Abbott et al., 2016; Aravena and Robertson, 1998). If the tracer is completely consumed or modified, it can communicate no information about its source and the reactions it experienced during transport—unless, of course the product of its consumption can be measured, such as excess N_2 in this study (Kolbe et al., 2019). Specifically, the limitations of using $\delta^{15}N$ as a tracer for identifying nitrogen sources and transformations has been well documented (Choi et al., 2017; Robinson, 2001). The $\delta^{15}N$ signal is often used as an indicator of not only nitrogen cycles but also nitrogen origin. Our results suggest that $\delta^{34}S$ is a more effective overall tracer of denitrification than $\delta^{15}N$ as it is resilient to the conflicting signals and destructive interference that complicate $\delta^{15}N$. Sulfur and nitrogen cycles are connected in many ways, including through autotrophic denitrification and through redox dependence of both denitrification and sulfur reduction (Pu et al., 2014; Aquilina et al., 2018; Abbott et al., 2016). It is therefore not surprising that information contained in $\delta^{34}S$ could shed light on multiple aspects of NO_3^- transport and degradation.

In this study, we observed that even in cases of strong hydrological connectivity (Thomas and Abbott, 2018; Vautier et al., 2021), the biogeochemical signature of shallow wells, streams, and deep wells remained distinct. This was evidenced in the opposite relationships between $\delta^{34}S$ and NO_3^-, Cl^-, and NO_3^- as well as the contrasting spatiotemporal variability regimes for many parameters in the surface and subsurface. While we are not surprised that distinct biogeochemical reactions and physical conditions dominate surface and subsurface environments (Frey et al., 2014; Ben Maamar et al., 2015; Aquilina et al., 2018; Li et al., 2021), we were surprised by the abruptness of the transitions between these environments, even where we know hydrological connectivity exists (Kolbe et al., 2016; Le Lay et al., 2019b). Four non-exclusive hypotheses that could account for this disconnect are: 1. Surface-subsurface interfaces erase or substantially modify biogeochemical signatures (Krause et al., 2014), 2. Biogeochemical signatures persist across interfaces but are blurred by contrasting conditions in the new environment (Helton et al., 2011), 3. The mass balance of surface-subsurface exchanges is insufficient to substantially influence the conditions in either; i.e., inputs are diluted (Pinay et al., 2018; Le Moal et al., 2019), and 4. The groundwater contributing to the streams is different than the groundwater measured in wells dispersed across the aquifer; i.e., streams are deriving their water and solutes from near-stream rather than catchment-wide sources (Ågren et al., 2010; Gu et al., 2017).

Regardless of the cause, the contrasting chemistry of the surface and subsurface represents an ecological paradox and practical challenge. On the ecological side, these observations may suggest that surface and subsurface environments are largely disconnected and compartmentalized. Even in these wet watersheds in western France with relatively high hydrological connectivity, the interaction between groundwater and stream water chemistry is complex (Kolbe et al., 2016; Le Lay et al., 2019a). On the practical side, these observations demonstrate that proxy reactivity and hence information content are extremely context dependent (Abbott et al., 2016). This was, predictably the situation for the dissolved gases, which quickly equilibrate with the atmosphere after emerging to the surface (Ayraud et al., 2008; Vautier et al., 2021). However, we did not expect the same to hold for nutrients such as NO_3^-, DSi, and SO_4^{2-} (Lajtha, 2019; Lovett et al., 2018; Heiner et al., 2022). Together, these observations highlight how biogeochemical and physical processes can modify ecological signals on short timescales and medium spatial scales in surface environments and long timescales and small spatial scales in subsurface environments.

4.4. Was it my neighbor or my grandparents?

Understanding where nutrients originate and how they are transported through watersheds has ecological and interpersonal implications. Debates about who is responsible for water pollution in the surface and subsurface are likely as old as agriculture and urbanization (Snow, 1856). This is certainly the case in Europe, where local, national, and E.U. targets and regulations can have real environmental and legal consequences (Musacchio et al., 2020; Ebeling et al., 2021). Indeed, this issue was raised at a meeting with a farmer from this LTSER when he realized the importance of legacy nutrient loading in determining current-day water quality. During a landowner-researcher dinner, he exclaimed something along the lines of, "So you're telling me I have high nitrates because of my grandparents, not my neighbors?"

The integrated surface and subsurface sampling from our study and the Zone Atelier Armorique LTSER more broadly provides some perspective on these questions of nutrient legacies and pollutant transport (Thomas et al., 2019). Because of its low residence time and high lateral connectivity, the stream network acts much more like an equitable commons, where pollutant sources and sinks average out to create consistent conditions. Conversely, the subsurface is decidedly inequitable, with some areas laden with nutrient legacies that will last decades (Vautier et al., 2021), and other areas endowed with high nutrient removal capacity that will protect water quality despite high contemporary or historical loading (Aravena and Robertson, 1998). This highlights the challenge of assessing nutrient vulnerability or even characterizing four-dimensional nutrient sources and sinks (Hartmann et al., 2021; Kolbe et al., 2016). However, the linked nature of the subsurface and surface also illuminates a commonsense shortcut to reducing eutrophication, which we explore in the following section (Koh et al., 2018; Basu et al., 2022; Pinay et al., 2015; Frei et al., 2021; Poisvert et al., 2017; Sabo et al., 2021b).

4.5. Living within our nutrient means: focus on reducing nutrient loads

Since the Great Acceleration of the mid-20th century, humanity's capacity to create, collect, and distribute reactive nutrients has far exceeded the Earth system's ability to retain or remove them (Steffen et al., 2015b; Elser and Bennett, 2011; Vitousek et al., 1997; Steffen et al., 2015a). This global nutrient overload is at the root of many of the "syndromes" of the Anthropocene (Hale et al., 2016; Meybeck, 2003; Foley et al., 2011). Rather than reducing our overuse, it is tempting to try to reengineer the environment to tolerate our excesses. However, supercharging nutrient retention and removal has multiple limitations and side effects. For example, while the overapplication of fertilizer is relatively straightforward to monitor using national and regional nutrient inventories (Poisvert et al., 2017; Sabo et al., 2021a), we do not have reliable methods for predicting nutrient retention capacity at watershed or regional scales (Seitzinger et al., 2010; Pinay et al., 2015). At these scales, there are orders-of-magnitude variations in hydrological residence time and nutrient removal rates that do not correlate with known proxies (Hartmann et al., 2021; Burt, 2001; Burt and Pinay, 2005; Thomas et al., 2015; Bernhardt et al., 2017). The physical, chemical, and biological peculiarities of each watershed and watershed component—especially in the subsurface—precludes prediction of nutrient resilience or vulnerability (Pinay et al., 2015; Bernardie et al., 2018; Frei et al., 2020; Wolters et al., 2022). Even if we were able to measure nutrient retention reliably at a moment in time, this would not necessarily allow us to set sustainable nutrient loading thresholds because nutrient release depends on contemporary and historical conditions. For even a small watershed, nutrient transit times are often in the decades or centuries, creating a situation that is ecologically and politically untenable because of the lag between policy changes and ecosystem response (Sebilo et al., 2013; Basu et al., 2022; Van Meter et al., 2021; Nguyen et al., 2022b; Ascott et al., 2021). Seeking to supercharge removal by augmenting electron donors or modifying hydrology entails risks and tradeoffs as well (Pu et al., 2014; Roley et al., 2016; Aravena and Robertson, 1998). Finally, relying on microbial processes to remove excess NO_3^- can exacerbate climate change if the NO_3^- is partially denitrified into the greenhouse gas N_2O and not to the inert N_2 (Hallberg et al., 2022; Lu et al., 2022; Gerber et al., 2016).

These complexities indicate that relying on nutrient retention and removal to resolve nutrient pollution is a partial solution at best. Protecting natural zone of denitrification (e.g., groundwater aquifers and riparian zones) is highly desirable because of the multiple cobenefits (Pinay et al., 2018; Cheng et al., 2020), but it is clear that our capacity to load ecosystems with reactive nutrients far exceeds their ability to remove them. Reducing NO_3^- input into the soil and water is the most prudent action to reduce eutrophication (Wan et al., 2022). This can and should be done by implementing best management practices, and potentially limiting fertilizer application to cultivation of human food rather than feed for animal agriculture, decorative plants, and biofuels (Frei et al., 2021, 2020). In this case, the proverb holds: "An ounce of prevention is worth a pound of cure."

CRediT authorship contribution statement

Emilee Severe: Writing – original draft, Writing – review & editing, Visualization, Formal analysis. Isabella M. Errigo: Writing – original draft, Writing – review & editing, Visualization, Formal analysis. Mary Proteau: Writing – original draft, Writing – review & editing, Visualization, Formal analysis. Sayedeh Sara Sayedi: Writing – review & editing, Visualization, Formal analysis. Tamara Kolbe: Writing – review & editing, Methodology, Investigation. Jean Marçais: Methodology, Investigation. Zahra Thomas: Writing – review & editing, Methodology, Investigation. Christophe Petton: Methodology, Investigation. François Rouault: Methodology, Investigation. Camille Vautier: Writing – review & editing, Methodology, Investigation. Jean-Raynald de Dreuzy: Writing – review & editing, Methodology, Investigation. Florentina Moatar: Methodology, Investigation. Luc Aquilina: Writing – review & editing, Methodology, Investigation. Rachel L. Wood: Writing – review & editing. Thierry LaBasque: Writing – review & editing, Methodology, Investigation. Christophe Lécuyer: Writing – review & editing, Methodology, Investigation. Gilles Pinay: Conceptualization, Writing – review & editing, Methodology, Investigation. Benjamin W. Abbott: Conceptualization, Supervision, Visualization, Methodology, Investigation, Formal analysis, Writing – review & editing.

Data availability

The data are attached as a supplementary file.

Declaration of competing interest

The authors 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.scitotenv.2023.163178.

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