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# 1 Deep denitrification: stream and groundwater biogeochemistry

## 2 reveal contrasted but connected worlds above and below

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25 **Key words:** Nitrogen, Sulfur, Silica, Carbon, Groundwater, Surface Water, Denitrification, Environmental  
26 Tracers, Residence Time, Nitrate Removal, Wells

### 27 Key points

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

33 **Abstract**

34 Excess nutrients from agricultural and urban development have created a cascade of ecological crises  
35 around the globe. Nutrient pollution has triggered eutrophication in most freshwater and coastal  
36 ecosystems, contributing to a loss in biodiversity, harm to human health, and trillions in economic  
37 damage every year. Much of the research conducted on nutrient transport and retention has focused on  
38 surface environments, which are both easy to access and biologically active. However, surface  
39 characteristics of watersheds, such as land use and network configuration, often do not explain the  
40 variation in nutrient retention observed in rivers, lakes, and estuaries. Recent research suggests subsurface  
41 processes and characteristics may be more important than previously thought in determining watershed-  
42 level nutrient fluxes and removal. In a small watershed in western France, we used a multi-tracer  
43 approach to compare surface and subsurface nitrate dynamics at commensurate spatiotemporal scales. We  
44 combined 3-D hydrological modeling with a rich biogeochemical dataset from 20 wells and 15 stream  
45 locations. Water chemistry in the surface and subsurface showed high temporal variability, but  
46 groundwater was substantially more spatially variable, attributable to long transport times (10–60 years)  
47 and patchy distribution of the iron and sulfur electron donors fueling autotrophic denitrification. Isotopes  
48 of nitrate and sulfate revealed fundamentally different processes dominating the surface (heterotrophic  
49 denitrification and sulfate reduction) and subsurface (autotrophic denitrification and sulfate production).  
50 Agricultural land use was associated with elevated nitrate in surface water, but subsurface nitrate  
51 concentration was decoupled from land use. Dissolved silica and sulfate are affordable tracers of  
52 residence time and nitrogen removal that are relatively stable in surface and subsurface environments.  
53 Together, these findings reveal distinct but adjacent and connected biogeochemical worlds in the surface  
54 and subsurface. Characterizing how these worlds are linked and decoupled is critical to meeting water  
55 quality targets and addressing water issues in the Anthropocene.

56

## 57 **1 Introduction**

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

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

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

98 While most interventions to improve water quality are associated with surface or near-  
99 surface environments (e.g. riparian zones, surface waters, and soils), there is growing evidence  
100 that catchment-level nutrient retention is strongly influenced by subsurface characteristics  
101 (Aquilina *et al* 2018, Kolbe *et al* 2019, Frei *et al* 2020, Pauwels *et al* 2000, Böhlke 2002, Duncan

102 *et al* 2015, Fan *et al* 2020, Nguyen *et al* 2022a, Lupon *et al* 2023). Because hydrological  
103 residence time in the subsurface far exceeds the surface (Gleeson *et al* 2016, Cook and Herczeg  
104 2012, Green *et al* 2011), time lags or “legacies” are created between the input and output of  
105 excess nutrients (Van Meter and Basu 2017, Ehrhardt *et al* 2019, Guillaumot *et al* 2021, Basu *et*  
106 *al* 2022). This provides extended opportunities for physical and biological processes to take up  
107 or transform nutrients and other solutes traveling through aquifers (Oldham *et al* 2013a, Abbott  
108 *et al* 2016, Dehaspe *et al* 2021). However, subsurface environments have long been considered  
109 as less dynamic than surface environments (Li *et al* 2017), where rapid biogeochemical  
110 processes are easily observable (McClain *et al* 2003, Bernhardt *et al* 2017). This paradigm of a  
111 “quiet world beneath” has recently been challenged on multiple fronts.

112 Advances in hydrological modeling, inferential methods, and direct observations now  
113 show that the subsurface is biogeochemically active and temporally dynamic (Ben Maamar *et al*  
114 2015, Long *et al* 2016, Marçais *et al* 2018, Kolbe *et al* 2019, Bochet *et al* 2020). However, the  
115 relative influence of subsurface and surface activity on watershed-scale nutrient dynamics  
116 remains uncertain. Because of logistical challenges and disciplinary divides (Li *et al* 2017, Kolbe  
117 *et al* 2019, Krause *et al* 2022), relatively few studies characterize biogeochemistry in both the  
118 surface and deep subsurface (e.g., >10 m) at watershed scales, complicating direct comparison of  
119 the spatiotemporal dynamics and dominant processes in these environments. Yet, there is  
120 evidence from the shallow subsurface that these interactions are important across scales (Krause  
121 *et al* 2014, Helton *et al* 2015, Lee-Cullin *et al* 2018, Wen *et al* 2020, Guillaumot *et al* 2021,  
122 Lupon *et al* 2023).

123 In this context, we collected water samples over several years from streams and aquifers  
124 in small watersheds (<50 km<sup>2</sup>) in a region of intensive agriculture in western France. Using a

125 multi-proxy framework combined with previous hydrological research from this area (Abbott *et*  
126 *al* 2016, Kolbe *et al* 2016, Marçais *et al* 2018, Thomas *et al* 2019), we investigated the  
127 interaction of hydrological residence time, land-use, and biogeochemical processing in surface  
128 and subsurface environments. We were motivated by three general questions. First, how do  
129 spatial and temporal variability regimes differ between the surface and subsurface environments  
130 in this region? Second, what processes regulate nutrient dynamics as water travels through  
131 various watershed components (i.e., streams, vadose zones, and aquifers)? Third, what are the  
132 management implications of these observations of watershed-scale ecohydrology in the surface  
133 and subsurface? To address these questions, we focused on the transport and transformation of  
134 nitrate ( $\text{NO}_3^-$ ), one of the most common nutrients associated with eutrophication and one of the  
135 costliest regarding environmental remediation, particularly in this region (Thomas *et al* 2019,  
136 Abbott *et al* 2018b, Heiner *et al* 2022, Dupas *et al* 2018). We analyzed a broad range of elements  
137 (e.g., carbon, sulfur, and silicon), proxies (e.g., isotopes, dissolved gases, and rare earth  
138 elements), and other data (e.g., historical land use, 3-D hydrological modeling, and reconstructed  
139 nutrient inputs) to characterize the surface and subsurface at the watershed scale.

## 140 **2 Methods**

### 141 **2.1 Site description and experimental design**

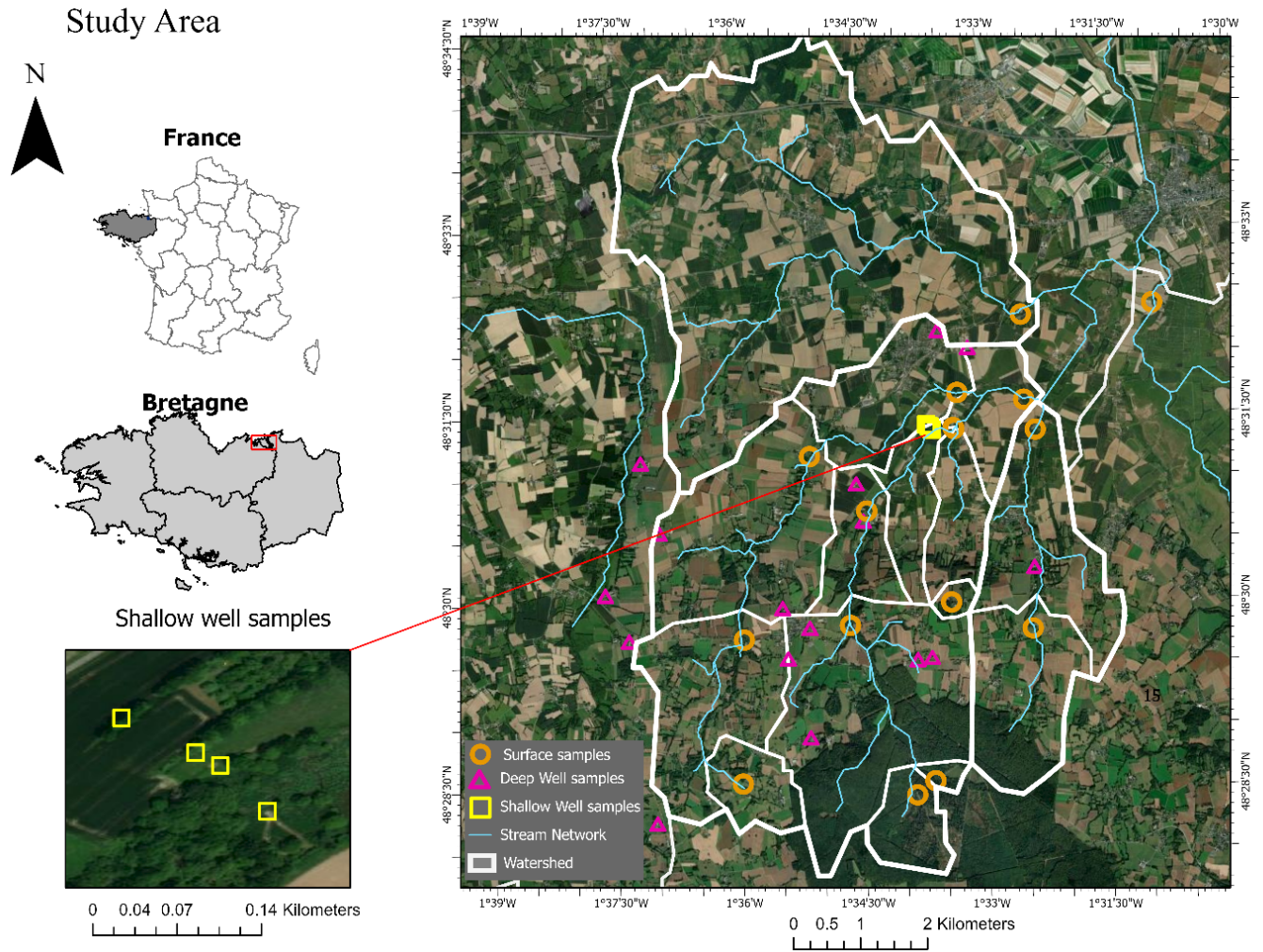
142 This study was conducted within the Zone Atelier Armorique research area, which is part  
143 of the Long-term socio-ecological research (LTSER) network (Thomas *et al* 2019). The history,  
144 socioecological characteristics, and available data from this LTSER are described in detail by  
145 Thomas *et al* (2019). The research area is in northeast Brittany in northwestern France. Brittany  
146 has a temperate oceanic climate (category “Cfb”: temperate, no dry season, warm summer,  
147 following Kottek *et al* 2006) and extensive livestock and row-crop agriculture (Thomas *et al*

148 2019, Frei *et al* 2020, Poisvert *et al* 2017). The study catchment occurs on the Armorican massif,  
149 which is composed of metamorphic and igneous rock, primarily granite, schist, and micaschist  
150 (Aquilina *et al* 2012a, Goderniaux *et al* 2013b, Kolbe *et al* 2016). The mean annual temperature  
151 is 11.2°C, and the mean annual rainfall is 910 mm, which is relatively well distributed  
152 throughout the year, and mean potential evapotranspiration is 690 mm (Thomas *et al* 2019).  
153 Because of the high infiltration capacity and relatively gentle precipitation, there is little artificial  
154 drainage (e.g., tile drains), but there are ditches and hedgerows around many fields, some of  
155 which have been present since Medieval times(Thomas and Abbott 2018, Baudry *et al* 2000,  
156 Forman and Baudry 1984). The main land use is agriculture, with around 80% of the region  
157 covered by row crops, pastureland, and indoor animal husbandry (pigs, poultry, and cows). This  
158 gives Brittany one of the highest densities of livestock in France and Europe (Gascuel-Odoux *et*  
159 *al* 2010, Poisvert *et al* 2017, Kim *et al* 2019). The intensive agriculture in this region has created  
160 widespread and persistent eutrophication of streams, estuaries, and groundwater (Dupas *et al*  
161 2018, Moatar *et al* 2017, Minaudo *et al* 2019). However, improved nutrient management,  
162 particularly the reduction of point sources (e.g., wastewater and feedlot effluent) and decreases in  
163 fertilizer application have resulted in declining N and P concentrations in many Brittany  
164 watersheds (Dupas *et al* 2018, Poisvert *et al* 2017, Aquilina *et al* 2012b, Gu *et al* 2021, Abbott *et*  
165 *al* 2018b).

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



171 variability in the surface and subsurface. To maximize the spatial extent of surface and  
172 groundwater sampling, not all the sites were visited during every campaign, and the mean  
173 number of return visits per site was four.



174  
175 **Figure 1.** Map of the study area near the Zone Atelier Armorique Long-term socio-  
176 ecological research (LTSER) site. Le Guyoult watershed to the west is a tributary of the  
177 larger Couesnon watershed to the east. The white lines indicate the subcatchment  
178 boundaries based on topographic delineation.

## 180 **2.2 Estimating nitrate removal**

181 Nitrate removal was estimated based on the concentration of excess  $N_2$  dissolved in the  
182 groundwater. The detailed procedure for calculating nitrate removal is described fully in Kolbe *et al*  
183 *al* 2019 and Vautier *et al* 2021. Briefly, in a groundwater environment, the concentration of  
184 *excess*  $N_2$ —i.e., above the expected concentration—can indicate the amount of  $NO_3^-$  removed by  
185 denitrification because equilibration with the atmosphere is not possible (Aeschbach-Hertig *et al*  
186 1999, Ayraud *et al* 2006, Böhlke 2002). After correcting for atmospheric partial pressure and  
187 temperature with the observed Ar concentration, the sum of the excess  $N_2$  and remaining  $NO_3^-$   
188 allow calculation of the concentration of  $NO_3^-$  that reached the water table (Kolbe *et al* 2019,  
189 Böhlke 2002). Combined with estimates of groundwater residence time, this can allow the  
190 reconstruction historical  $NO_3^-$  inputs (Kolbe *et al* 2019, Aquilina *et al* 2012b).

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

## 199 **2.3 Proxies of hydrology and biogeochemistry**

200 To assess the degree of biogeochemical attenuation of nutrients and the relative  
201 importance of nutrient loading versus nutrient removal, we measured the concentrations and

202 stable isotope ratios of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) and  $\text{SO}_4^{2-}$  ( $\delta^{34}\text{S}$ ). Stable isotopes can indicate the  
203 nutrient source and the degree of biogeochemical processing (Lehmann *et al* 2003, Mariotti *et al*  
204 1981, Malone *et al* 2018).  $\text{NO}_3^-$  isotopes have been widely analyzed because  $\text{NO}_3^-$  is a dominant  
205 form of nitrogen in nutrient saturated ecosystems (Aber *et al* 1998), organic and industrial  
206 fertilizers have distinct initial  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  (Lohse *et al* 2013, Denk *et al* 2017, Bedard-Haughn  
207 *et al* 2003), and denitrification (both heterotrophic and autotrophic) strongly fractionates  $\text{NO}_3^-$   
208 isotopes, increasing the residual  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  relative to the initial values prior to denitrification  
209 (Hosono *et al* 2014, Malone *et al* 2018, Ayraud *et al* 2006, Pauwels *et al* 2010). Therefore, we  
210 predicted that watersheds with isotopically enriched  $\text{NO}_3^-$  would have higher N attenuation  
211 (Lehmann *et al* 2003) or alternatively that they would have received primarily organic fertilizer  
212 (Bedard-Haughn *et al* 2003).

213 Sulfur isotopes have been used extensively in geochemical studies of processes ranging  
214 from the evolution of the Earth's atmosphere to bacterial and archaeal dissimilatory  $\text{SO}_4^{2-}$   
215 reduction (Canfield 2001, Farquhar and Wing 2003). For the purposes of this study, we were  
216 particularly interested in  $\delta^{34}\text{S}$ , which can be increased by  $\text{SO}_4^{2-}$  reduction after depletion of  $\text{NO}_3^-$   
217 (e.g., in highly reduced wetland habitats) and decreased by  $\text{SO}_4^{2-}$  production in aquifers during  
218 autotrophic denitrification (Hosono *et al* 2014, Abbott *et al* 2016). Consequently, we predicted  
219 that  $\delta^{34}\text{S}$  of  $\text{SO}_4^{2-}$  would be higher in watersheds where surface processes dominate  $\text{NO}_3^-$   
220 removal, whereas  $\delta^{34}\text{S}$  would be lower when groundwater processes were relatively more  
221 important.

222 We used a combination of tracers to assess water residence time, including  
223 chlorofluorocarbons (CFCs), sulfur hexafluoride ( $\text{SF}_6$ ), and dissolved silica (DSi). CFCs and  
224  $\text{SF}_6$  have been commonly used as tracers of water age due to their high detectability and low

225 reactivity in aqueous environments (Abbott *et al* 2016, Cook and Herczeg 2012, Busenberg and  
226 Plummer 1992, Wilson and Mackay 1996). However, these anthropogenic gases cannot be used  
227 to quantify the age of surface waters because they readily equilibrate with the atmosphere when  
228 groundwater resurfaces. DSi has been shown to strongly correlate with subsurface residence time  
229 (Marçais *et al* 2018, Becker 2013) and has been used to measure surface water ages in previous  
230 studies in this area (Frei *et al* 2020). Though the concentration of DSi can be influenced by  
231 terrestrial and aquatic plant uptake in surface waters, we assumed conservative transport given  
232 the short residence time and relatively high concentration of DSi in these headwater streams  
233 (Marçais *et al* 2018, Delvaux *et al* 2013, Carey *et al* 2019, Abbott *et al* 2018b).

## 234 **2.4 Gas sampling and analysis**

235 CFC and SF<sub>6</sub> measurements were taken at the Plateform Condate Eau from University of  
236 Rennes 1. We collected water in steel ampoules (40 ml for CFC and 300 ml for SF<sub>6</sub>) by pumping  
237 with a MP1 Grunfoss pump in the borehole. After stabilization, we measured the conductivity,  
238 pH and dissolved O<sub>2</sub> using a custom sensor manifold preventing contact with the atmosphere  
239 (Hach, Loveland CO, USA; model HQ440d multi; Fig. S1), and the ampoules were rinsed with  
240 three times their volume of water and closed (Labasque *et al* 2014). CFC and SF<sub>6</sub> concentrations  
241 were determined by a purge and trap extraction coupled to a GC/ECD (Busenberg and Plummer  
242 1992, 2000, Labasque 2020). Uncertainties are around 3% for young groundwaters for CFC,  
243 10% for SF<sub>6</sub>, and 20% for CFC on old (>50 years) groundwaters. The major dissolved gases  
244 (He, Ne, Ar, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>) were sampled in 500 ml glass flasks and analyzed by headspace  
245 extraction followed by  $\mu$ GC/TCD measurements, following (Sugisaki and Taki 1987).  
246 Uncertainties are around 5% for Ne and He and 3% for other gases.

247

## 248 2.5 Solute and isotope collection and analysis

249 At each site, we collected a 5 L sample of water for immediate sensor readings and eight  
250 smaller samples for laboratory analyses. For the laboratory analyses, we immediately filtered  
251 subsamples using a 50 mL syringe and two 250 mL filter towers. We used a 0.2  $\mu\text{m}$  cellulose  
252 acetate syringe filter to prepare samples for the analysis of cations, rare earth elements (REE),  
253 and  $\text{NO}_3^-$  isotopes. Molybdate reactive phosphorus (MRP) concentration was determined  
254 colorimetrically via reaction with ammonium molybdate (Murphy and Riley, 1962), with a  
255 precision of  $\pm 4 \mu\text{g l}^{-1}$  (Gu *et al* 2018). Nitrate isotope samples were frozen immediately and  
256 shipped to the UC Davis Stable Isotope Facility for analysis of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  by  
257 bacterial denitrification assay (McIlvin and Casciotti 2011). Isotope ratios of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  were  
258 determined by measuring N and O using a ThermoFinnigan GasBench + PreCon trace gas  
259 concentration system connected to a ThermoScientific Delta V Plus isotope-ratio mass  
260 spectrometer (Bremen, Germany) with a precision of  $\pm 0.4\text{‰}$  and  $0.5\text{‰}$  for  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ,  
261 respectively. Cations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS;  
262 Agilent 7700 $\times$ , Santa Clara, USA, relative uncertainties  $\pm 5\%$ ). We quantified dissolved organic  
263 carbon (DOC; Shimadzu TOC-5050A, Kyoto, Japan, precision  $\pm 5\%$ ), which is often considered  
264 a master variable influencing physicochemical conditions in aqueous environments (Zarnetske *et*  
265 *al* 2018, Abbott *et al* 2016). Because DOC is the electron donor for both aerobic respiration and  
266 heterotrophic denitrification (Hosono *et al* 2014, Sebito *et al* 2019), high DOC can enhance  $\text{NO}_3^-$   
267 removal, and high  $\text{NO}_3^-$  can accelerate DOC oxidation (Abbott *et al* 2016, Kolbe *et al* 2019).  
268 This two-way interaction contributes to the strong negative stoichiometric relationship between  
269  $\text{NO}_3^-$  and DOC observed in surface and groundwaters globally, including in this region (Taylor  
270 and Townsend 2010, Frei *et al* 2020)

271 To determine  $\text{SO}_4^{2-}$  isotopes, we filtered water samples on a Millipore™ system using  
272 0.45  $\mu\text{m}$  cellulose acetate filters. Filtered solutions were then heated to 70°C and a 5% solution  
273 of barium chlorate was added drop-to-drop to precipitate dissolved  $\text{SO}_4^{2-}$  as barium sulfate  
274 ( $\text{BaSO}_4$ ). Sulfur isotope composition of  $\text{SO}_4^{2-}$  was measured using a VarioPYROcube™  
275 elemental analyzer in combustion mode interfaced in continuous-flow mode with an Isoprime™  
276 isotope ratio mass spectrometer at the Laboratoire de Géologie de Lyon (CNRS UMR 5276,  
277 University Claude Bernard Lyon 1).  $\text{BaSO}_4$  from water samples was analyzed by weighing 3  
278 aliquots of 250  $\mu\text{g}$  in tin foil capsules. Measurements were calibrated against the three  $\text{BaSO}_4$   
279 international standards NBS127, IAEA-SO-5 and IAEA-SO-6. The standard deviation of  $\delta^{34}\text{S}$   
280 measurements was close to 0.3‰. Data are reported as  $\delta^{34}\text{S}$  vs. V-CDT.

## 281 **2.6 Spatial analysis**

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

292 We intersected the land use raster with contributing watershed area for stream locations  
293 and the contributing area of the deep wells, which had been calculated in previous work (Kolbe

294 *et al* 2016). We excluded the shallow wells from this analysis because all the sampling points  
295 were contained in the same subcatchment and therefore could not be differentiated by land use  
296 (see Thomas *et al* 2019 for a detailed analysis of the shallow wells).

## 297 **2.7 Statistical analysis**

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

## 312 **3 Results**

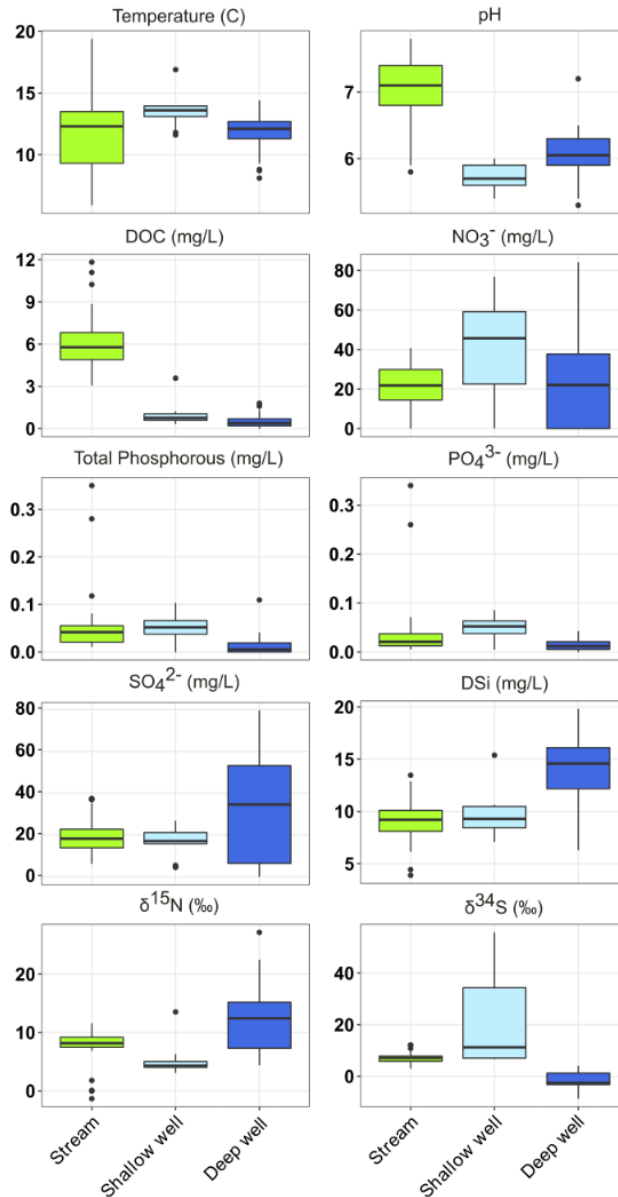
### 313 **3.1 Spatiotemporal dynamics in the surface and subsurface**

314 The water chemistry of wells and streams indicated both contrasts and connectivity of the  
315 surface and subsurface water. The subsurface showed larger variations in most physicochemical

316 parameters compared to the surface sites, except for temperature, pH, and DOC, which are  
317 strongly influenced by seasonal drivers at the surface (Fig. 2). For most parameters, including the  
318 nutrients which are the focus of this study, the stream values fell between the deep and shallow  
319 wells (Fig. 2). The N parameters grouped closer to deep wells, but the P, S, and Si parameters  
320 grouped closer to shallow wells, suggesting a combination of mixing and biogeochemical  
321 attenuation at watershed scales.

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





331

332

**Figure 2.** The distribution of several physicochemical parameters in the streams, shallow

333

wells, and deep wells sampled in this study. The parameter and units are shown above

334

each plot. The boxplots represent the median, interquartile range (IQR), points within

335

1.5-times the IQR, and outliers beyond 1.5-times the IQR. Because each site and

336

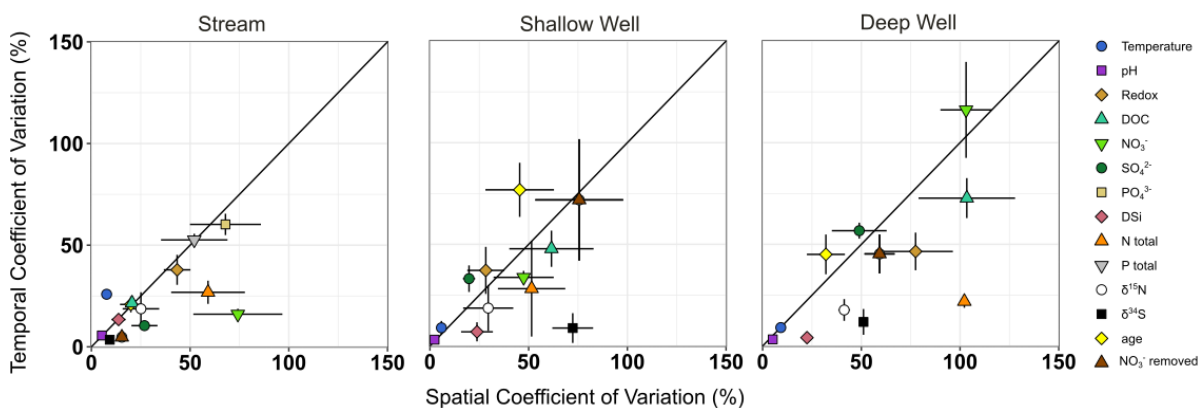
sampling event are included as individual points, the ranges represent the combined

337

spatial and temporal variability.

338 Spatial variation generally exceeded temporal variation across site types (i.e., most  
 339 parameters plotted below the 1:1 line in Figure 3), though this was notably not the case for  $\text{NO}_3^-$   
 340 in deep wells and  $\text{SO}_4^{2-}$  and water age in all wells (see section 3.3 for detailed water age results).  
 341 N and S isotopes tended to be substantially less variable than N and S concentrations, suggesting  
 342 that hydrological dilution rather than changes in nutrient source or processing accounted for  
 343 variability in concentrations.

344



345

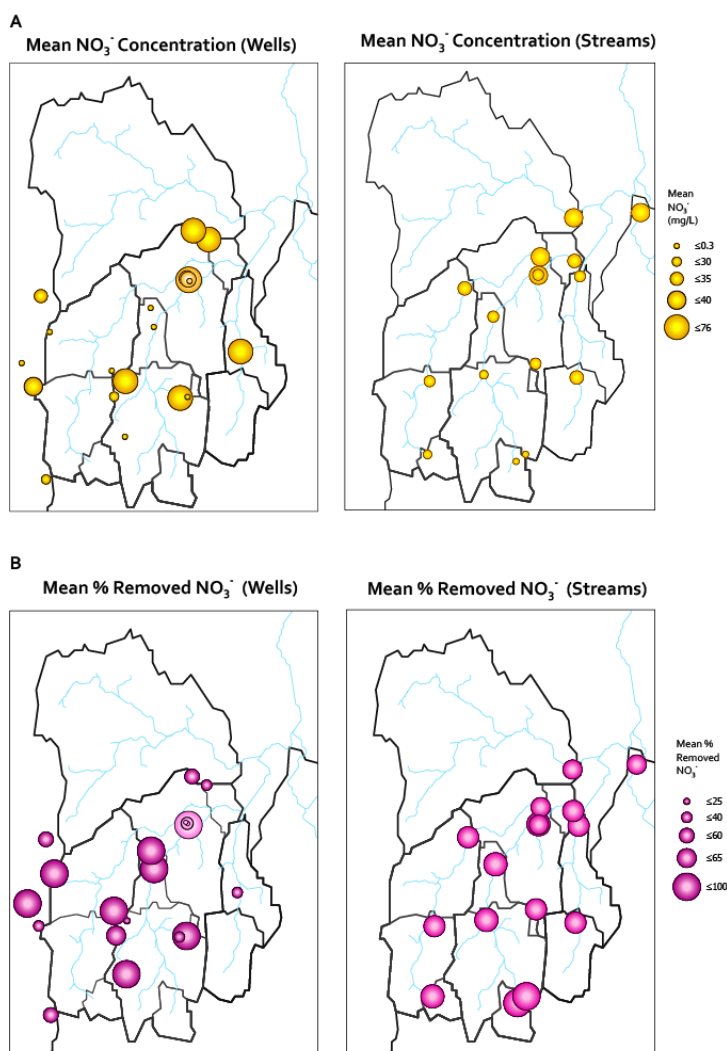
346 **Figure 3.** The spatial and temporal coefficients of variation for physicochemical  
 347 parameters in streams, shallow wells, and deep wells (mean  $\pm$  SE).

348

349 Mapping  $\text{NO}_3^-$  concentration and removal showed the contrasts in spatial patterns  
 350 between the surface and subsurface more explicitly (Fig. 4). In the stream network,  $\text{NO}_3^-$   
 351 concentration was relatively homogeneous, increasing gradually from the forested uplands in the  
 352 south to the more intensively cultivated landscapes in the north of the watershed (Fig. 4).  
 353 Conversely, groundwater  $\text{NO}_3^-$  concentration showed extreme variation throughout the  
 354 watershed, with sites only meters apart showing up to 70 mg/L differences in concentration.

355 Similarly, the percentage of  $\text{NO}_3^-$  removed was much more variable for groundwater, while the  
356 stream network showed a moderated pattern similar to the groundwater mean (Fig. 4).

357



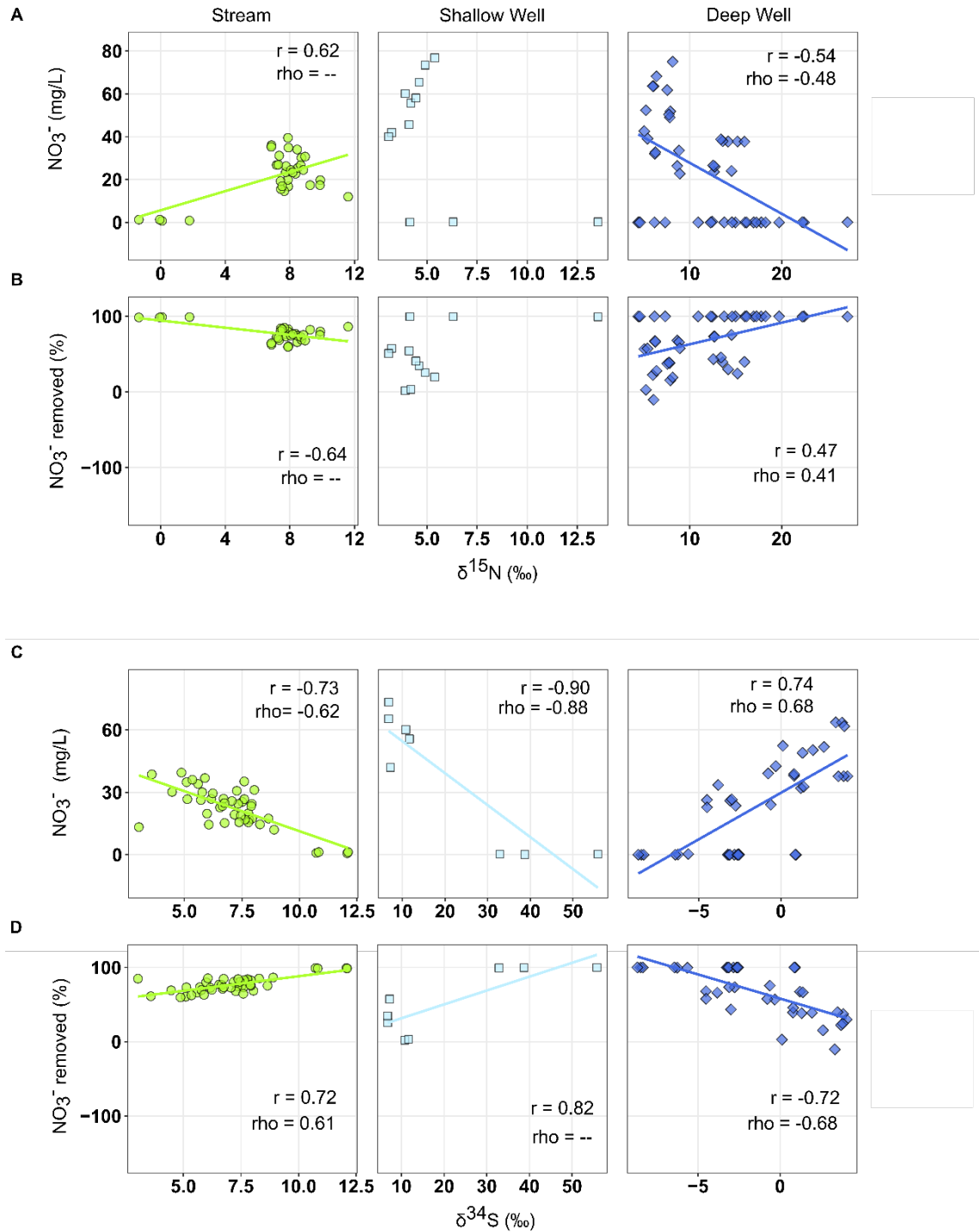
358

359 **Figure 4.**  $\text{NO}_3^-$  concentration (A) and percent removal (B) in subsurface (left) and  
360 surface (right) environments. Average across time for each site, showing spatial variation  
361 of chemical parameters.  $\text{NO}_3^-$  removal was calculated based on the difference between the  
362 reconstructed  $\text{NO}_3^-$  input and the observed concentration (methods).

### 363 3.2 Isotopic and dissolved tracers

364 The isotopes and solutes provided clues about the causes of the surprising spatiotemporal  
365 patterns. There were opposite relationships between isotope signatures and  $\text{NO}_3^-$  removal in the  
366 streams and deep wells, with mixed patterns in the shallow wells (Fig. 5A & 5B). In the deep  
367 wells,  $\text{NO}_3^-$  removal was positively correlated with  $\delta^{15}\text{N}$ , as expected due to fractionation during  
368 denitrification. The opposite pattern existed in the surface water where  $\delta^{15}\text{N}$  was negatively  
369 correlated with  $\text{NO}_3^-$  removal, though the correlation was only significant for the Pearson  
370 coefficient, indicating that a few extreme values were driving the relationship (Fig. 5A & 5B).  
371 Indeed, the low  $\text{NO}_3^-$  and low  $\delta^{15}\text{N}$  stream sites occurred in the forested south of the watershed  
372 (Fig. 4), likely indicating a non-fertilizer N source (e.g., atmospheric deposition or natural N  
373 fixation). We note that the percentage N removal for these sites was likely overestimated because  
374 our reconstructed N input assumed similar land use for each subcatchment, which is not the case  
375 for forested sites that have never been under cultivation.

376 In general,  $\delta^{34}\text{S}$  was a better proxy of  $\text{NO}_3^-$  concentration and removal, with  $\delta^{15}\text{N}$   
377 showing fewer and weaker relationships (Fig. 5).  $\delta^{34}\text{S}$  was positively correlated with  $\text{NO}_3^-$   
378 removal in the surface but negatively correlated in the deep wells (Fig. 5C & 5D), in line with  
379 our hypotheses about S reduction in the surface and S release from autotrophic denitrification in  
380 the subsurface.



381

382

**Figure 5.** Relationships of  $\delta^{15}\text{N}$  and  $\delta^{34}\text{S}$  with  $\text{NO}_3^-$  concentration and removal. Linear fit

383

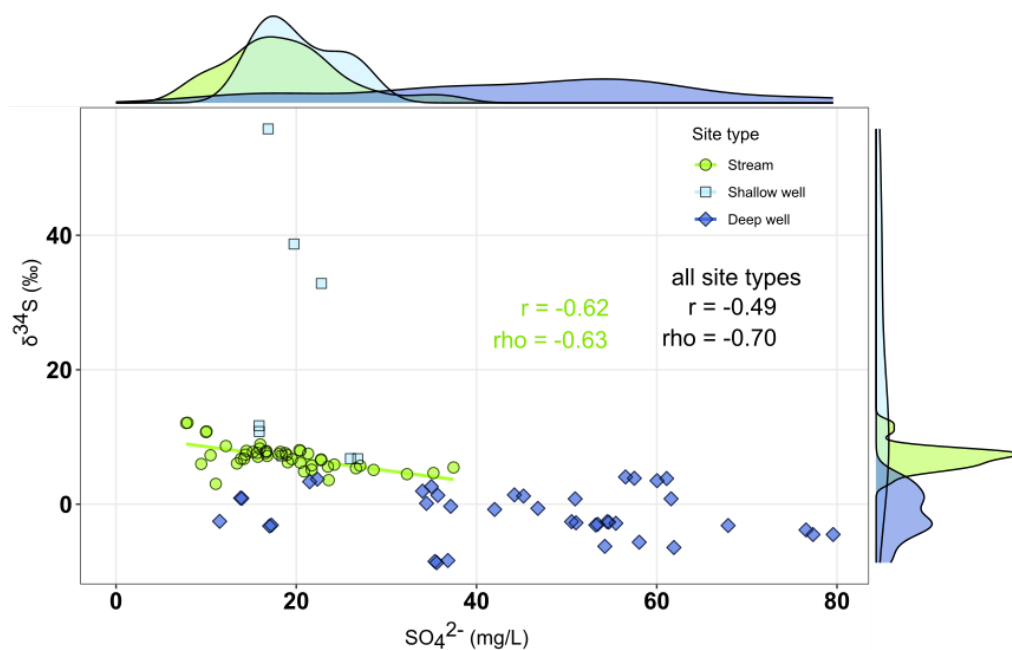
lines are shown for convenience to indicate a significant relationship—either Pearson ( $r$ )

384

or Spearman ( $\rho$ )—at  $\alpha = 0.05$ .

385 Contrary to our predictions, DOC was not correlated with most  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$   
386 parameters, and when correlations existed, they were typically weak (Fig. S2). Across site types,  
387 there was a significant negative correlation between  $\delta^{34}\text{S}$  and  $\text{SO}_4^{2-}$  concentration (Fig. 6). Some  
388 of the highest  $\delta^{34}\text{S}$  values we are aware of were observed in the shallow well sites that occurred  
389 in the riparian wetland (Fig. 1). Together these patterns suggest that different processes are  
390 controlling nutrient retention in the surface and subsurface, with heterotrophic denitrification and  
391 sulfur reduction dominating in the surface and autotrophic denitrification in the subsurface.

392



393

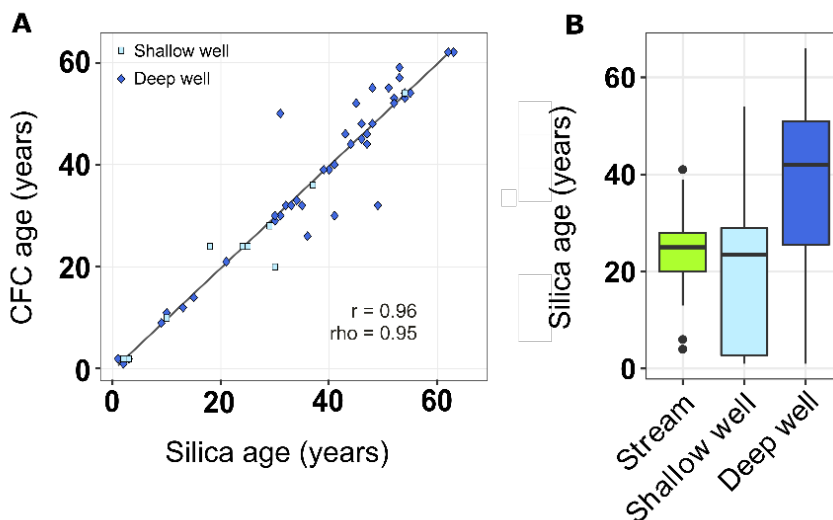
394 **Figure 6.** The relationship between  $\delta^{34}\text{S}$  and  $\text{SO}_4^{2-}$  for streams, shallow wells, and deep  
395 wells. The two subsurface site types showed more variation in  $\delta^{34}\text{S}$ , bracketing the stream  
396 water samples, which resembled a mix of the two contributing flow paths (i.e., deep  
397 groundwater and shallow soil/riparian water).

398

399 **3.3 Residence time and nutrient removal**

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

405



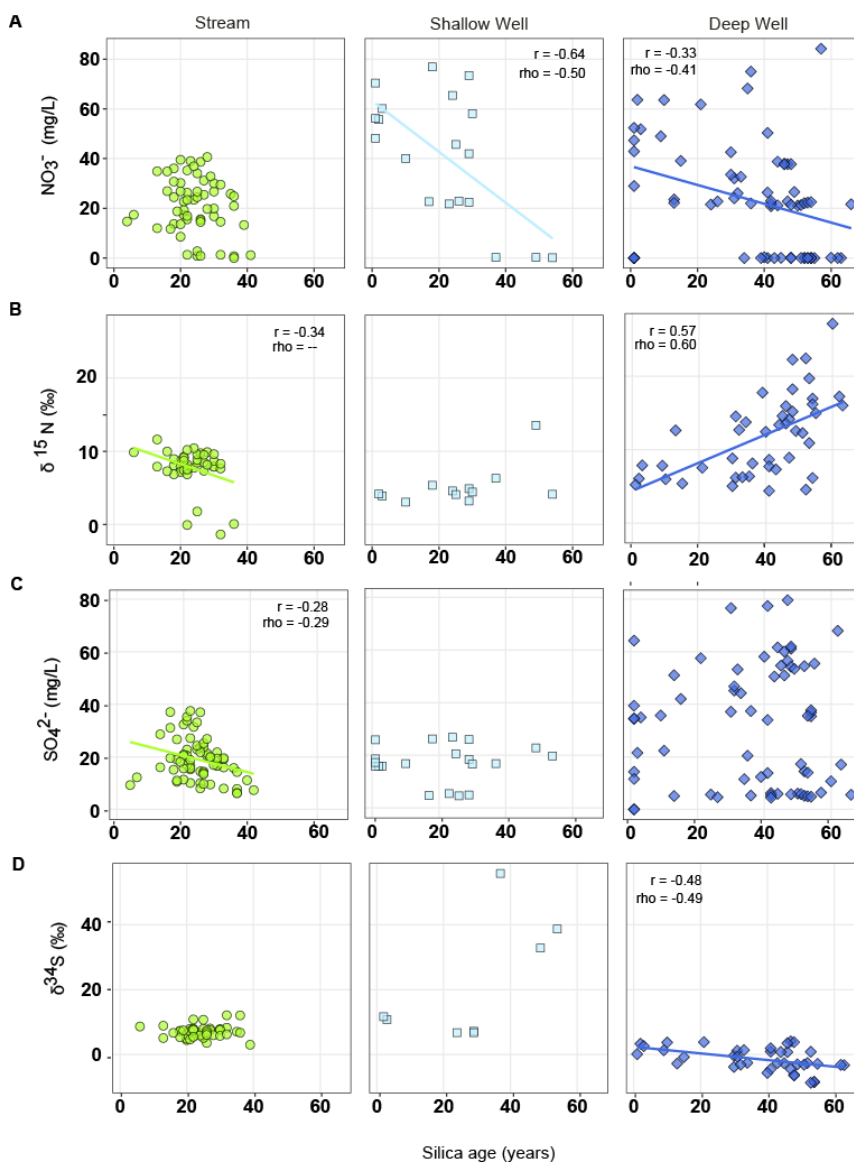
406

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

411

412 The deep wells showed the longest residence time, with a median age of 42 years and a  
413 mean age of 36 years. Shallow well water was the youngest, with a median age of 23.5 years and

414 a mean age of 20.5 years (Fig. 7B). The stream water was slightly older than the shallow well  
 415 water with a median age of 25 years and a mean age of 24.4 years, indicating a mix of shallow  
 416 and deep groundwater sources. The streams were more homogeneous in age (interquartile range  
 417 of 20-28 years) than either the shallow (2-30 years) or deep wells (17-46 years; Fig. 7).

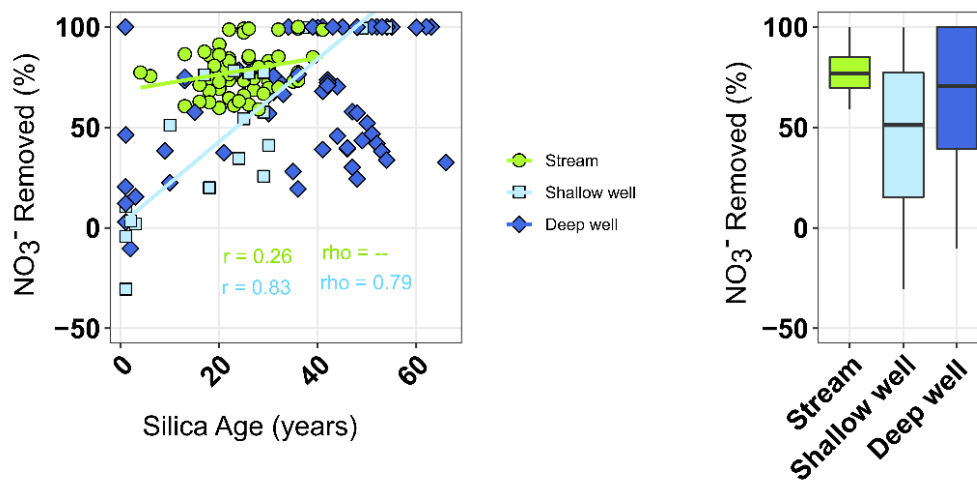


418  
 419 **Figure 8.** Relationships between mean water age and SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> isotopes and  
 420 concentrations in stream, shallow groundwater, and deep groundwater environments.



422  $\text{NO}_3^-$  tended to be higher in younger water, i.e., there was a negative correlation between  
 423 mean water age and  $\text{NO}_3^-$  concentration in shallow and deep wells (Fig. 8A). This implies that  
 424 either  $\text{NO}_3^-$  loading has increased through time or that older sites have less  $\text{NO}_3^-$  because of  
 425 cumulative removal. The latter is suggested by the positive correlation between water age and  
 426  $\delta^{15}\text{N}$  in deep wells, though the relationship is less clear in shallow wells and streams (Fig. 8B).  
 427 For streams and shallow wells, water age was positively correlated with  $\text{NO}_3^-$  removal (Fig. 9).  
 428 We note that because the stream water comes from shallow and deep groundwater in this system,  
 429 the stream removal values are cumulative (i.e., most of the removal is happening in the deep and  
 430 shallow wells before flowing into the stream; Fig. 9).

431



432

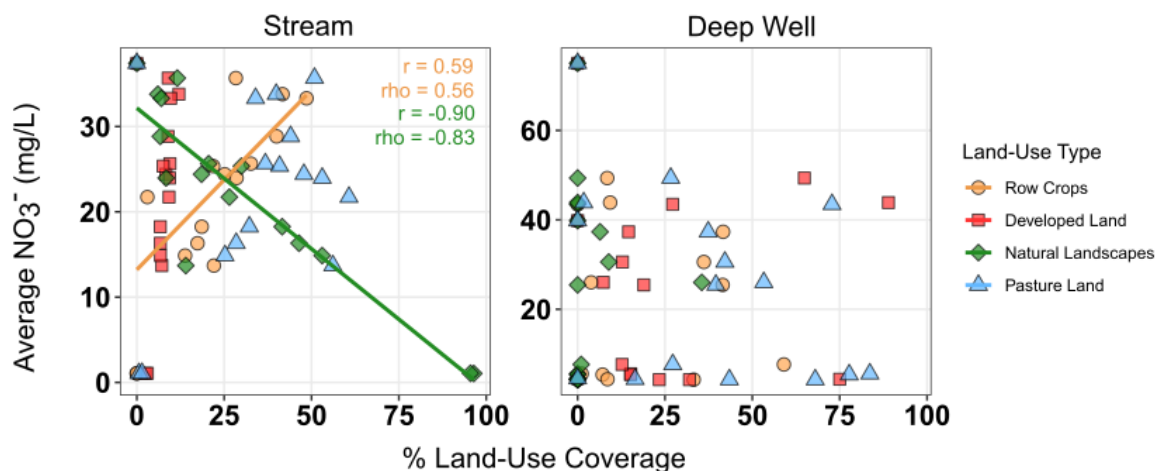
433 **Figure 9.**  $\text{NO}_3^-$  removal versus mean water age for streams, shallow wells, and deep  
 434 wells.  $\text{NO}_3^-$  removal represents the cumulative removal along the flow path starting with  
 435 input of  $\text{NO}_3^-$  to the water table.

436

437 **3.4 Nutrient sources**

438 In stream environments,  $\text{NO}_3^-$  concentration was positively correlated with percentage of  
439 row crop agriculture in the subcatchment and negatively correlated with the amount of natural  
440 land cover types (Fig. 10). However, no such relationships were detected in deep wells, where  
441  $\text{NO}_3^-$  concentration was not correlated with land use in the contributing area (Fig. 10). This lack  
442 of correlation could be due to a combination in uncertainty in the determination of contributing  
443 areas, temporal changes in land use over the  $\sim 40$  years of transit time, and heterogeneous rates of  
444 removal of  $\text{NO}_3^-$  during transit through the aquifer.

445



446

447 **Figure 10.** Correlation of  $\text{NO}_3^-$  and the percent of land-use cover for streams and deep  
448 wells. Shallow wells were omitted from this analysis as all shallow wells were contained  
449 within one subcatchment. Land-use coverage in the streams was calculated for the  
450 contributing subcatchment area. Land-use for deep wells was calculated from the well's  
451 contributing area based on prior hydrogeological modeling (Kolbe *et al* 2016).

452

## 453 **4 Discussion**

454           In this study we characterized biogeochemical and hydrological processes in the surface  
455 and subsurface at the same spatiotemporal scales to explore watershed-level controls on nutrient  
456 retention and removal. We used a multi-proxy approach to identify dominant  $\text{NO}_3^-$  removal  
457 processes and characterized spatiotemporal variation in streams and groundwater. We observed  
458 highly distinct but linked biogeochemical “worlds” above and below the surface, which  
459 interacted to determine watershed-level nutrient dynamics. In the following paragraphs, we  
460 compare these results with studies from this and other regions and explore potential management  
461 implications.

### 462 **4.1 Deepening our thinking to address water-energy-food crises**

463           Because of disciplinary differences in methods and processes, groundwater and surface  
464 water environments are often considered individually, especially at watershed scales (Bochet *et al*  
465 *et al* 2020, Abbott *et al* 2018a, Leibundgut *et al* 2009, Krause and Bronstert 2007, Duncan *et al*  
466 2015, Knee *et al* 2018). Groundwater biogeochemistry and hydrology have long been areas of  
467 focus in hydrogeology and critical zone science, but they have not received as much attention in  
468 ecosystem ecology and nutrient management (Chorover *et al* 2007, Krause *et al* 2022,  
469 Goderniaux *et al* 2013a, Li *et al* 2021, 2017, Brookfield *et al* 2021). Because attaining surface  
470 water quality goals depends on the overall watershed response (including the subsurface), this  
471 disconnect needs to be addressed (Van Meter *et al* 2021, Vautier *et al* 2021, Heiner *et al* 2022,  
472 Basu *et al* 2022, Lupon *et al* 2023). Additionally, global water security and aquatic habitat  
473 conservation increasingly depend on hydrochemical understanding of groundwater-surface water  
474 interactions (Hartmann *et al* 2021, Jasechko and Perrone 2021, Wine 2022, Gleeson *et al* 2020).

475           Given how different the skillsets are for surface and subsurface measurements and  
476 modeling, we believe the best way to deepen our watershed approaches is through  
477 collaborations. We call on researchers and research-funding agencies to encourage such  
478 collaboration. There are many watershed-focused projects from around the world that can be  
479 used as models for next steps in integrating surface and groundwater hydrochemistry, ecology,  
480 and sustainability in the Anthropocene (Oldham *et al* 2013b, Mu *et al* 2020, Krause *et al* 2022,  
481 Lee-Cullin *et al* 2018, Marçais *et al* 2022, Musacchio *et al* 2020). However, many watershed  
482 observatories and interdisciplinary approaches are threatened or underfunded (Laudon *et al* 2017,  
483 Arènes *et al* 2018, Brooks *et al* 2015, Linton 2008, 2014, Thomas *et al* 2019). Increased  
484 investment is needed not only for basic research but also (and perhaps primarily) for community  
485 participation and education (Abbott *et al* 2018b, 2023, Ben-zvi-Assarf and Orion 2005, Basu *et*  
486 *al* 2022). In the Anthropocene, the lack of understanding of watershed processes is a major  
487 obstacle to achieving sustainable practices central to the water-energy-food nexus (Albrecht *et al*  
488 2018, Zhang *et al* 2018, Biggs *et al* 2015, Abbott *et al* 2019b).

#### 489 **4.2 Integrated sampling reveals contrasted but connected worlds above and below**

490           An important theme from collaborative work linking surface and subsurface  
491 environments is that the world beneath is not stable or calm. Groundwater environments are  
492 commonly characterized as homogeneous and slow, lacking the diversity and energetic gradients  
493 to support dynamic biogeochemistry (Bochet *et al* 2020, McClain *et al* 2003, Cardenas 2015).  
494 Evidence from work around the world shows that the view of a quiet world beneath is not  
495 accurate (Marçais *et al* 2022, Ben Maamar *et al* 2015, Zhang *et al* 2015, Jasechko *et al* 2017,  
496 Green *et al* 2011). Indeed, there is a growing consensus that catchment-level nutrient removal  
497 may depend largely or primarily on subsurface characteristics that are often temporally dynamic

498 (Aquilina *et al* 2018, Kolbe *et al* 2019, Frei *et al* 2020, Bochet *et al* 2020, Long *et al* 2016,  
499 Brookfield *et al* 2021, Hosono *et al* 2014).

500 For the watersheds in our study, the subsurface appears to be the epicenter of  
501 denitrification rather than a biogeochemical afterthought, likely because of the combination of  
502 longer residence times and relatively abundant electron donors (Oldham *et al* 2013b, Pu *et al*  
503 2014). Groundwater environments are home to most of Earth's bacterial and archaeal biomass  
504 (Bar-On *et al* 2018), and the combination of biological and hydrological factors can create  
505 extreme spatial and temporal variation in groundwater reaction types and rates (Bochet *et al*  
506 2020, Ben Maamar *et al* 2015). Because groundwater and surface-water environments are  
507 constantly exchanging water, energy, and material, the failure to adequately characterize  
508 subsurface processes likely explains some of the difficulties in predicting nutrient fluxes and  
509 recovery patterns at watershed scales (Kolbe *et al* 2019, Frei *et al* 2021, Van Meter *et al* 2018,  
510 Brookfield *et al* 2021).

511 The relatively low variance we observed for many surface parameters demonstrates  
512 another interesting implication of surface-subsurface interactions. In Brittany, as in many  
513 temperate regions, surface water is comprised of water mixing from the shallow and deep  
514 groundwater (Marçais *et al* 2018, 2022, Thomas and Abbott 2018). While the processes and  
515 solute concentrations in the groundwater system are highly variable, they become mixed as they  
516 enter the surface environment through riparian zones and diffuse groundwater flux to streams  
517 (Krause *et al* 2022, Pinay and Haycock 2019, Le Moal *et al* 2019, Cardenas 2015). Given the  
518 short transit times in the surface, this results in a homogenized signature; as the surface water  
519 travels farther and faster, it integrates a larger spatial scale and reflects a larger landscape patch  
520 (Abbott *et al* 2018a, Dupas *et al* 2019). While this reduces the ability of streams to mitigate high

521 nutrient loading (i.e., stream and riparian retention cannot offset watershed-wide nutrient  
522 excess), it reinforces the role of streams as integrators of watershed processes, creating valuable  
523 sentinels of change, particularly when monitored in a quantitative, multi-proxy way (Moatar *et al*  
524 2020, Frei *et al* 2020, Helton *et al* 2011, Pinay *et al* 2018, Brookshire *et al* 2009, Cole *et al* 2007,  
525 Shogren *et al* 2021, Casas-Ruiz *et al* 2023, 2017).

#### 526 **4.3 Context-dependence of biogeochemical proxies in surface and subsurface environments**

527 Biogeochemical proxies and tracers are indispensable tools to evaluate hydrological and  
528 ecological processes across scales (Pinay *et al* 2015, Bernardie *et al* 2018, Frei *et al* 2020).  
529 Particularly when working at the watershed scale or when investigating groundwater  
530 environments where extensive physical exploration is impossible, proxies can reveal processes  
531 that are otherwise unobservable, including microbial metabolism, hydrological residence time,  
532 and weathering processes (Marçais *et al* 2018, Kolbe *et al* 2019, Leibundgut *et al* 2009). Because  
533 proxies such as solutes, isotopes, and physicochemical attributes (e.g., temperature, pH, etc.) can  
534 reveal mass flux and processing, they have been used extensively to investigate the sources of  
535 nutrient pollution and to compare reactivity in different components of a watershed (Sebilo *et al*  
536 2013, Covino 2017, Thomas and Abbott 2018).

537 However, one of the fundamental assumptions about interpreting a tracer is that it will  
538 retain or conserve a portion of the signal imbued by the environment of interest as it travels to  
539 the location where it can be sampled (Abbott *et al* 2016, Aravena and Robertson 1998). If the  
540 tracer is completely consumed or modified, it can communicate no information about its source  
541 and the reactions it experienced during transport—unless, of course the product of its  
542 consumption can be measured, such as excess N<sub>2</sub> in this study (Kolbe *et al* 2019). Specifically,  
543 the limitations of using  $\delta^{15}\text{N}$  as a tracer for identifying nitrogen sources and transformations has

544 been well documented (Choi *et al* 2017, Robinson 2001). The  $\delta^{15}\text{N}$  signal is often used as an  
545 indicator of not only nitrogen cycles but also nitrogen origin. Our results suggest that  $\delta^{34}\text{S}$  is a  
546 more effective overall tracer of denitrification than  $\delta^{15}\text{N}$  as it is resilient to the conflicting signals  
547 and destructive interference that complicate  $\delta^{15}\text{N}$ . Sulfur and nitrogen cycles are connected in  
548 many ways, including through autotrophic denitrification and through redox dependence of both  
549 denitrification and sulfur reduction (Pu *et al* 2014, Aquilina *et al* 2018, Abbott *et al* 2016). It is  
550 therefore not surprising that information contained in  $\delta^{34}\text{S}$  could shed light on multiple aspects of  
551  $\text{NO}_3^-$  transport and degradation.

552         In this study, we observed that even in cases of strong hydrological connectivity (Thomas  
553 and Abbott 2018, Vautier *et al* 2021), the biogeochemical signature of shallow wells, streams,  
554 and deep wells remained distinct. This was evidenced in the opposite relationships between  $\delta^{34}\text{S}$   
555 and  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ , as well as the contrasting spatiotemporal variability regimes for many  
556 parameters in the surface and subsurface. While we are not surprised that distinct  
557 biogeochemical reactions and physical conditions dominate surface and subsurface environments  
558 (Frey *et al* 2014, Ben Maamar *et al* 2015, Aquilina *et al* 2018, Li *et al* 2021), we were surprised  
559 by the abruptness of the transitions between these environments, even where we know  
560 hydrological connectivity exists (Kolbe *et al* 2016, Le Lay *et al* 2019b). Four non-exclusive  
561 hypotheses that could account for this disconnect are: 1. Surface-subsurface interfaces erase or  
562 substantially modify biogeochemical signatures (Krause *et al* 2014), 2. Biogeochemical  
563 signatures persist across interfaces but are blurred by contrasting conditions in the new  
564 environment (Helton *et al* 2011), 3. The mass balance of surface-subsurface exchanges is  
565 insufficient to substantially influence the conditions in either; i.e., inputs are diluted (Pinay *et al*  
566 2018, Le Moal *et al* 2019), and 4. The groundwater contributing to the streams is different than

567 the groundwater measured in wells dispersed across the aquifer; i.e., streams are deriving their  
568 water and solutes from near-stream rather than catchment-wide sources (Ågren *et al* 2010, Gu *et*  
569 *al* 2017).

570         Regardless of the cause, the contrasting chemistry of the surface and subsurface  
571 represents an ecological paradox and practical challenge. On the ecological side, these  
572 observations may suggest that surface and subsurface environments are largely disconnected and  
573 compartmentalized. Even in these wet watersheds in western France with relatively high  
574 hydrological connectivity, the interaction between groundwater and stream water chemistry is  
575 complex (Kolbe *et al* 2016, Le Lay *et al* 2019a). On the practical side, these observations  
576 demonstrate that proxy reactivity and hence information content are extremely context dependent  
577 (Abbott *et al* 2016). This was, predictably the situation for the dissolved gases, which quickly  
578 equilibrate with the atmosphere after emerging to the surface (Ayraud *et al* 2008, Vautier *et al*  
579 2021). However, we did not expect the same to hold for nutrients such as  $\text{NO}_3^-$ ,  $\text{DSi}$ , and  $\text{SO}_4^{2-}$   
580 (Lajtha 2019, Lovett *et al* 2018, Heiner *et al* 2022). Together, these observations highlight how  
581 biogeochemical and physical processes can modify ecological signals on short timescales and  
582 medium spatial scales in surface environments and long timescales and small spatial scales in  
583 subsurface environments.

#### 584 **4.4 Was it my neighbor or my grandparents?**

585         Understanding where nutrients originate and how they are transported through watersheds  
586 has ecological and interpersonal implications. Debates about who is responsible for water  
587 pollution in the surface and subsurface are likely as old as agriculture and urbanization (Snow  
588 1856). This is certainly the case in Europe, where local, national, and E.U. targets and  
589 regulations can have real environmental and legal consequences (Musacchio *et al* 2020, Ebeling



590 *et al* 2021). Indeed, this issue was raised at a meeting with a farmer from this LTSER when he  
591 realized the importance of legacy nutrient loading in determining current-day water quality.  
592 During a landowner-researcher dinner, he exclaimed something along the lines of, “So you’re  
593 telling me I have high nitrates because of my grandparents, not my neighbors?”

594 The integrated surface and subsurface sampling from our study and the Zone Atelier  
595 Armorique LTSER more broadly provides some perspective on these questions of nutrient  
596 legacies and pollutant transport (Thomas *et al* 2019). Because of its low residence time and high  
597 lateral connectivity, the stream network acts much more like an equitable commons, where  
598 pollutant sources and sinks average out to create consistent conditions. Conversely, the  
599 subsurface is decidedly inequitable, with some areas laden with nutrient legacies that will last  
600 decades (Vautier *et al* 2021), and other areas endowed with high nutrient removal capacity that  
601 will protect water quality despite high contemporary or historical loading (Aravena and  
602 Robertson 1998). This highlights the challenge of assessing nutrient vulnerability or even  
603 characterizing four-dimensional nutrient sources and sinks (Hartmann *et al* 2021, Kolbe *et al*  
604 2016). However, the linked nature of the subsurface and surface also illuminates a commonsense  
605 shortcut to reducing eutrophication, which we explore in the following section (Koh *et al* 2018,  
606 Basu *et al* 2022, Pinay *et al* 2015, Frei *et al* 2021, Poisvert *et al* 2017, Sabo *et al* 2021b).

#### 607 **4.5 Living within our nutrient means: focus on reducing nutrient loads**

608 Since the Great Acceleration of the mid-20<sup>th</sup> century, humanity’s capacity to create, collect,  
609 and distribute reactive nutrients has far exceeded the Earth system’s ability to retain or remove  
610 them (Steffen *et al* 2015b, Elser and Bennett 2011, Vitousek *et al* 1997, Steffen *et al* 2015a). This  
611 global nutrient overload is at the root of many of the “syndromes” of the Anthropocene (Hale *et al*  
612 2016, Meybeck 2003, Foley *et al* 2011). Rather than reducing our overuse, it is tempting to try to

613 reengineer the environment to tolerate our excesses. However, supercharging nutrient retention  
614 and removal has multiple limitations and side effects. For example, while the overapplication of  
615 fertilizer is relatively straightforward to monitor using national and regional nutrient inventories  
616 (Poisvert *et al* 2017, Sabo *et al* 2021a), we do not have reliable methods for predicting nutrient  
617 retention capacity at watershed or regional scales (Seitzinger *et al* 2010, Pinay *et al* 2015). At these  
618 scales, there are orders-of-magnitude variations in hydrological residence time and nutrient  
619 removal rates that do not correlate with known proxies (Hartmann *et al* 2021, Burt 2001, Burt and  
620 Pinay 2005, Thomas *et al* 2015, Bernhardt *et al* 2017). The physical, chemical, and biological  
621 peculiarities of each watershed and watershed component—especially in the subsurface—  
622 precludes prediction of nutrient resilience or vulnerability (Pinay *et al* 2015, Bernardie *et al* 2018,  
623 Frei *et al* 2020, Wolters *et al* 2022). Even if we were able to measure nutrient retention reliably at  
624 a moment in time, this would not necessarily allow us to set sustainable nutrient loading thresholds  
625 because nutrient release depends on contemporary and historical conditions. For even a small  
626 watershed, nutrient transit times are often in the decades or centuries, creating a situation that is  
627 ecologically and politically untenable because of the lag between policy changes and ecosystem  
628 response (Sebilo *et al* 2013, Basu *et al* 2022, Van Meter *et al* 2021, Nguyen *et al* 2022b, Ascott *et*  
629 *al* 2021). Seeking to supercharge removal by augmenting electron donors or modifying hydrology  
630 entails risks and tradeoffs as well (Pu *et al* 2014, Roley *et al* 2016, Aravena and Robertson 1998).  
631 Finally, relying on microbial processes to remove excess  $\text{NO}_3^-$  can exacerbate climate change if  
632 the  $\text{NO}_3^-$  is partially denitrified into the greenhouse gas  $\text{N}_2\text{O}$  and not to the inert  $\text{N}_2$  (Hallberg *et al*  
633 2022, Lu *et al* 2022, Gerber *et al* 2016).

634         These complexities indicate that relying on nutrient retention and removal to resolve  
635 nutrient pollution is a partial solution at best. Protecting natural zone of denitrification (e.g.,

636 groundwater aquifers and riparian zones) is highly desirable because of the multiple cobenefits  
637 (Pinay *et al* 2018, Cheng *et al* 2020), but it is clear that our capacity to load ecosystems with  
638 reactive nutrients far exceeds their ability to remove them. Reducing NO<sub>3</sub><sup>-</sup> input into the soil and  
639 water is the most prudent action to reduce eutrophication (Wan *et al* 2022). This can and should  
640 be done by implementing best management practices, and potentially limiting fertilizer  
641 application to cultivation of human food rather than feed for animal agriculture, decorative  
642 plants, and biofuels (Frei *et al* 2021, 2020). In this case, the proverb holds: “An ounce of  
643 prevention is worth a pound of cure.”

644

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