Nitrogen patterns in subsurface waters of the Yzeron stream: effect of combined sewer overflows and subsurface–surface water mixing

A. M. Aucour, T. Bariac, P. Breil, P. Namour, L. Schmitt, R. Gnouma and P. Zuddas

ABSTRACT

Urbanization subjects streams to increased nitrogen loads. Therefore studying nitrogen forms at the interface between urban stream and groundwater is important for water resource management. In this study we report results on water δ^{18}O and nitrogen forms in subsurface waters of a stream (Yzeron, France). The sites studied were located upstream and downstream of combined sewer overflows (CSO) in a rural area and a periurban area, respectively. Water δ^{18}O allowed us to follow the mixing of subsurface water with surface water. Dissolved organic nitrogen and organic carbon of fine sediment increased by 20–30% between rural and periurban subsurface waters in the cold season, under high flow. The highest nitrate levels were observed in rural subsurface waters in the cold season. The lowest nitrate levels were found in periurban subsurface waters in the warm season, under low flow. They corresponded to slow exchange of subsurface waters with channel water. Thus reduced exchange between surface and subsurface waters and organic-matter-rich input seemed to favor nitrate reduction in the downstream, periurban, subsurface waters impacted by CSO.

Key words | CSO, hyporheic, nitrogen, oxygen isotopes, stream, subsurface water

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INTRODUCTION

Urbanization increases nitrogen loading in streams, potentially degrading water quality. A critical issue is thus to investigate N processing in urban streams in view of minimizing the nitrogen loading (Grimm *et al.* 2005; Wenger *et al.* 2009; O'Driscoll *et al.* 2010; Pickett *et al.* 2011). An important zone for N retention and transformation is the zone below the streambed in which water exchange occurs between subsurface and surface waters (the hyporheic zone) (Jones & Holmes 1996). The inflow of surface water into the streambed and its mixing with subsurface waters has been shown to be of major importance for N redox reactions in streams (Lefebvre *et al.* 2004; Storey *et al.* 2004). Investigation of N processing at urban stream–aquifer interfaces is thus needed, especially in areas impacted by nitrogen and organic pollution.

When studying nitrogen processing at the stream–aquifer interface, it is highly relevant to follow the mixing between subsurface and surface waters. The water δ^{18}O has been widely used to trace the river–aquifer interactions in large basins (Négrel *et al.* 2003). In small basins of temperate streams, water δ^{18}O variations are mainly driven by the seasonal change in δ^{18}O of rain (Rozanski *et al.* 1982). Contrasts in δ^{18}O between surface and subsurface reflect differences in water residence time and could provide the proportion of surface water at the stream–aquifer interface.

In the present study, we investigated nitrogen (organic N, NO_3^-, NO_2^-, NH_4^+) changes in subsurface waters in relation with subsurface–surface water mixing and combined sewer overflow (CSO) inputs. The studied stream

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(Yzeron) was sampled upstream and downstream from several CSO units, in a rural and periurban area, respectively. CSO present elevated levels of ammonium and labile organic matter and we aimed to test whether they affect the organic and inorganic nitrogen budgets of subsurface waters. Mixing of subsurface water with surface water, which is a key process in the system, was followed using water $\delta^{18}O$. The specific questions addressed were as follows. (i) Does mixing differ between upstream rural and downstream periurban sites? (ii) Does the organic nitrogen content of sediments and subsurface waters increase downstream from CSO? (iii) Do organic nitrogen and carbon content and/or mixing with surface water affect the nitrate pattern in subsurface waters?

HYDROLOGICAL AND GEOMORPHOLOGICAL CONTEXT

The Yzeron basin is located west of Lyon, an urban area with a population of about 1.7 million (Figure 1). From west to east, in the downstream direction, the stream drains a granito-gneissic mountain that is a forested-agricultural area, a granito-gneissic plateau that is mostly a periurban area, and glacial and fluvial foothills that correspond to the urban area. Groundwater is limited to a steep-sided aquifer in colluvio-alluvial deposits that extend at depths up to several metres. Residential periurban areas are served by a combined sewer system connected to a wastewater treatment plant located outside the basin. The main interceptor of the sewer system with its CSO units runs alongside the stream.

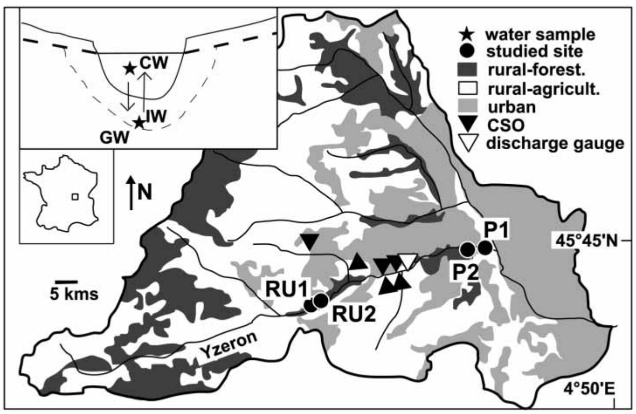

Figure 1 | Map of the Yzeron stream basin showing the reaches studied, the CSO and the discharge gauge. The inset schematically represents the relationship between the channel water (CW) and groundwater (GW) components in the interstitial waters (IW) studied.

The stream was sampled upstream and downstream from several CSO units at rural (RU1, RU2) and periurban (P1, P2) reaches. The valley bottom has a width of about 100 m at RU1 and P1 and about 20 m at RU2 and P2 (Schmitt *et al.* 2011). The stream flows in its natural channel with bankful width and depth from 10 to 15 m and from 1 to 2 m, respectively. For a given width of the valley bottom, riffle frequency and streambed slope are higher in the rural reaches than in the periurban ones: riffles cover at RU-1 54% of reach longitudinal profile versus 33% at P1, 72% at RU-2 versus 61% at P2. The mean bed slope is 3.3% at RU2 versus 1.4% at P2, 1.2% at RU1 versus 0.5% at P1. The moderately high specific stream power (12 to 72 W m^{-2}) prevents macrophyte development.

SAMPLING AND ANALYTICAL METHODS

Sampling was performed at baseflow (Figure 2). Stream discharge during sampling was lower in the warm season

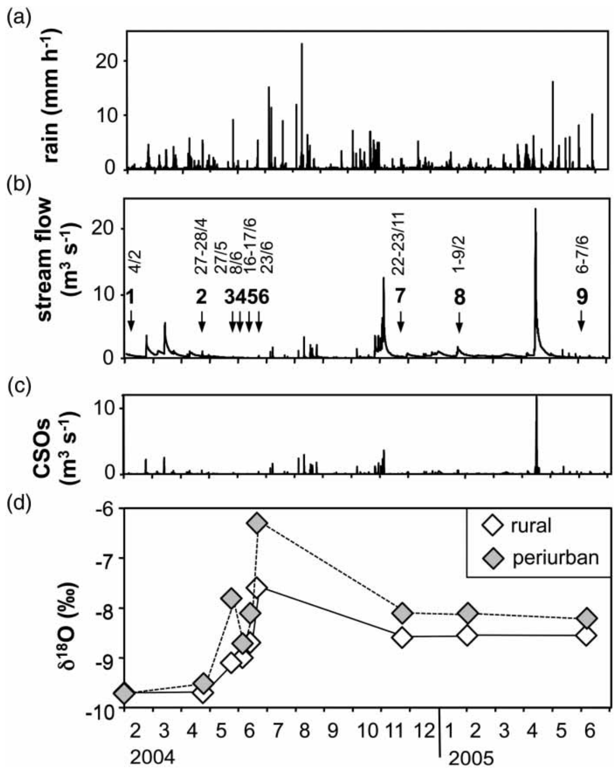

Figure 2 | Hourly rainfall (a), stream flow (b), estimated CSO flow (c) and channel water $\delta^{18}O$ (d) as a function of times. Arrows (with number and date) show the samplings. Stream flow was monitored at discharge gauge located downstream from CSO (Figure 1) and CSO discharge was estimated from stream flow time series. The method of estimation (Braud *et al.* 2013) and statistics on rainfall and CSO discharge are given in Supplementary material 1 (available online at http://www.iwaponline.com/wst/068/531.pdf).

(0.01 to 0.07 $m^3 s^{-1}$) than in the cold season (0.2 to 0.5 $m^3 s^{-1}$). Cumulative rainfall amounts for the last three days before sampling was generally low, less than 4 mm. Exceptions were the samplings of May 27, 2004 and June 23, 2004 that occurred several hours (14–18 hours and 9–11 hours respectively) after heavy storms with cumulative rainfall amount of 12–13 mm. The estimated CSO flow (Figure 2) represented 16% of the stream flow measured for the whole period from January 2004 to June 2005 and only 11% during the low-water period.

Channel (surface), interstitial (subsurface) waters and sediments were sampled for $\delta^{18}O$ and nitrogen analysis between June 23, 2004 and June 2005 (samplings 6–9). Previously, we collected for $\delta^{18}O$ measurements (i) channel waters (samplings 1–5) and (ii) interstitial waters along longitudinal rural and periurban reach profiles (sampling 5). Interstitial waters and sediments were taken at a depth of 50 cm below the streambed surface with a Bou-Rouch pump. The samples were immediately sieved through 160 μm mesh. Water and particles <160 μm were separated by centrifugation at 4 °C shortly after sampling. The O_2 content was measured in the field with a Horiba-U-22XD sensor.

The $\delta^{18}O$ were determined by equilibration with CO_2 using an automated ISOPREP 18 device coupled to a FISONS-OPTIMA mass spectrometer. The $\delta^{18}O$ allows calculation of the fraction of A in the water mixture (mix) between A and B following:

$$f = (\delta^{18}O_{mix} - \delta^{18}O_B)/(\delta^{18}O_A - \delta^{18}O_B) \quad (1)$$

Nitrate was measured by ionic chromatography, NH_4^+ and NO_2^- by spectrophotometry, fine sediment organic nitrogen (ON) by the Kjeldahl method and dissolved organic nitrogen (DON) by the difference between Kjeldahl nitrogen and NH_4^+. Dissolved organic carbon was determined using acid-persulfate oxidation and organic carbon (OC) with an elemental combustion analyzer.

RESULTS AND DISCUSSION

Exchange of interstitial with channel waters: oxygen isotope constraints

We performed a preliminary investigation (i) of temporal variation in channel $\delta^{18}O$ and (ii) of spatial variation in interstitial water $\delta^{18}O$ before our main study of $\delta^{18}O$ and nitrogen forms conducted from June 23, 2004 to June 2005. We found significant ^{18}O enrichment of channel waters between April and June 2004 (Figure 2(c)), in agreement with seasonal $\delta^{18}O$ variation in temperate precipitations (Rozanski et al. 1982). In late spring 2004, water $\delta^{18}O$ could thus be used to discriminate between recent stormwater and older groundwater.

Spatial variations in $\delta^{18}O$ of interstitial waters were investigated on June 16–17, 2004, under low flow (Figure 3). Rural interstitial waters presented a narrow $\delta^{18}O$ range (−9.1 to −8.7‰ except for one point at −8.4‰) with the channel at −8.7‰. Thus the rural channel and interstitial waters did not differ in isotopic compositions and all samples showed good mixing of interstitial waters with channel water. Periurban interstitial waters showed a wider range of $\delta^{18}O$ (−8.8 to −7.4‰). The values close to −8.1‰ indicated an inflow of channel water (measured at −8.1‰). They were mostly located in the upstream part of riffles. Interstitial waters with higher $\delta^{18}O$ values were close to channel water collected during the previous storm event of May 27, 2004 and have a possible residence time of about three weeks in the sediments. They were located in pools. Interstitial waters with lower $\delta^{18}O$ values were

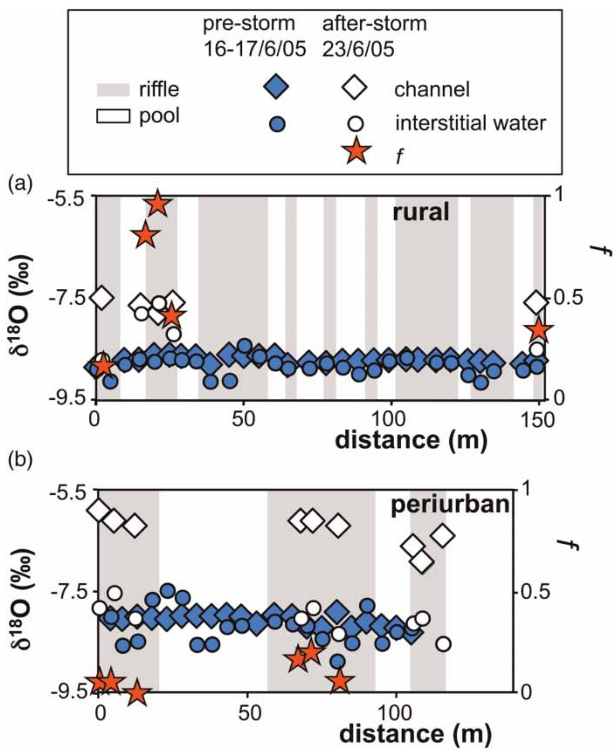

Figure 3 | $\delta^{18}O$ variations along reach longitudinal profile for pre-storm (June 16–17, 2004) and after-storm conditions (June 23, 2004). The $\delta^{18}O$ values of channel and interstitial waters allowed estimation of the fraction of 'new' channel water in interstitial waters (f) for June 23, 2004.

closer to those of the channel water from February to April (−9.6‰). They contained older winter rainfall and thus had longer residence times from about one to several months. They were mostly located in the downstream part of riffles. The δ^{18}O data thus indicated that periurban interstitial waters were fed by channel water in the upstream part of riffles and contain older groundwater in the downstream part as previously reported (Hendricks & White 1995).

Based on the above investigations, sampling for the main study of water δ^{18}O and nitrogen species was carried out in the middle, upstream and downstream parts of riffles. The sampling of June 23, 2004 (Figure 3) was performed 9–11 hours after a storm event. The stream channel was richer in ^{18}O compared to pre-storm conditions. Periurban interstitial waters (−8.5 to −7.8) kept pre-storm values, thus presenting slight mixing with 'new' channel water at a timescale of 9–11 hours. In contrast, the δ^{18}O value of rural interstitial waters rose, approaching that of channel water. The fraction of 'new' channel water in interstitial waters *f* was calculated using channel and pre-storm interstitial waters as end-members. It reflects the renewal of interstitial water with channel water over 9–11 hours and ranged from 0.21 to 1 in the rural reach (with a mean of 0.5) and from 0 to 0.20 in the periurban one (with a mean of 0.1). The most rapid exchange was found in the upstream part of the rural riffles, with *f* between 0.82 and 1, while the slowest exchange was in the downstream end of the periurban riffles (*f* down to 0).

In November 2004, under high flow, the values of rural interstitial waters fell between that of channel water and values that are richer in ^{18}O (Figure 4(a)). The ^{18}O-rich values can be related to groundwater derived from summer rains. The fact that interstitial waters differed from channel water indicated less efficient exchange between channel and interstitial waters (compared to June 2004). In contrast, most periurban interstitial waters matched channel water in November 2004, suggesting that they were fed by channel water (Figure 4(b)). For the last sampling campaign (June 2005), the δ^{18}O values (not shown) were close in channel and interstitial waters, making it difficult to follow mixing between the two compartments. The data for June 2004 and 2005 showed that ^{18}O tracing of mixing at the winter-to-summer transition was better when ^{18}O enriched stormwater reached surface waters, as in June 2004.

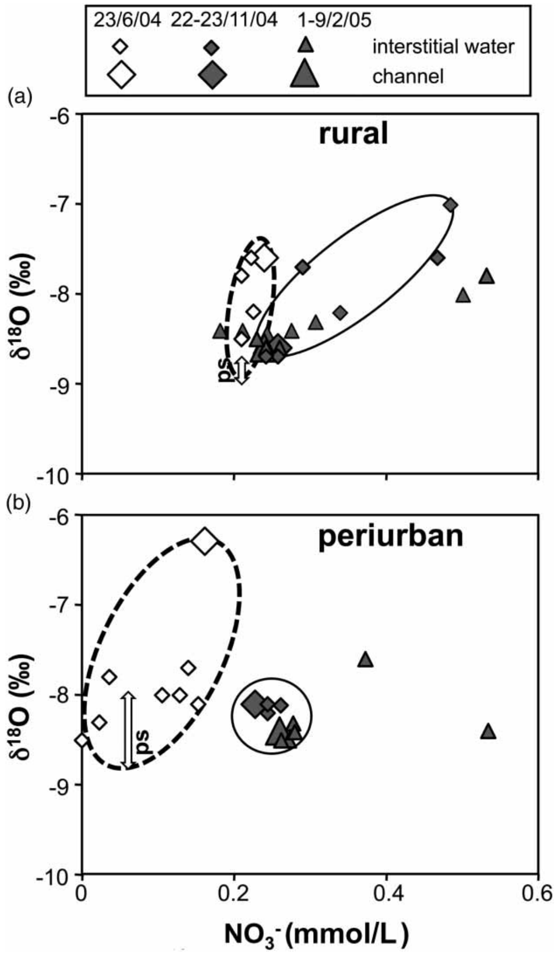

Figure 4 | Water δ^{18}O values versus nitrate concentrations. The dash outlined area shows the samples collected on June 23, 2004, the ps bar the δ^{18}O range of pre-storm interstitial waters. The black outlined area shows the samples collected in November 2004.

Spatial and temporal patterns of nitrogen

The concentrations of nitrogen forms, dissolved O_2 and OC and the ON-OC plots are given in Supplementary material 2 (available online at http://www.iwaponline.com/wst/068/531.pdf). DON increased significantly ($p < 0.01$) during the cold season from rural (0.054 ± 0.008 mmol/L, $n = 19$) to periurban interstitial waters (0.064 ± 0.014 mmol/L, $n = 17$), but not in the warm season. OC also showed a significant increase ($p < 0.05$) from rural (2.17 ± 1.15 g/100g, $n = 15$) to periurban (3.12 ± 1.11 g/100g, $n = 15$) fine sediments. In the warm season, under low flow, the decrease in periurban DON (0.044 ± 0.017 mmol/L, $n = 16$) evidenced reduced input and/or increased loss of DON. The above results likely reflected the input of OC-, ON-rich matter from CSO in periurban bed sediments and the degradation of this ON-pool in the warm season.

Nitrate varied by two orders of magnitude in interstitial waters (0.005 to 0.55 mmol/L) (Figure 5). The highest values were observed in interstitial waters during the cold season, the lowest values in periurban interstitial waters during the warm season. On average, nitrate decreased

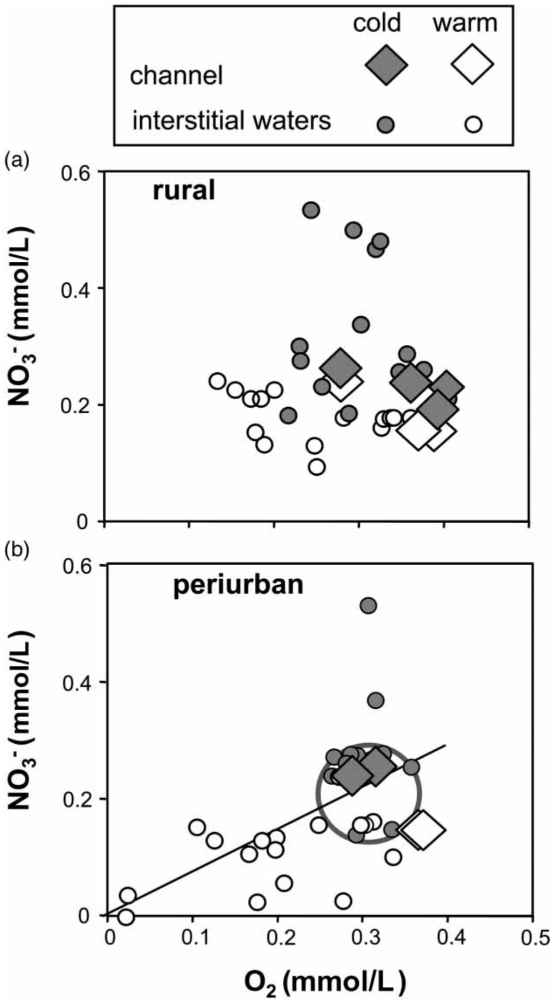

Figure 5 | Nitrate versus dissolved O_2 concentrations. The line represents the regression line between periurban nitrate and O_2 ($[NO_3^-] = 0.74\ [O_2] + 0.00$, $r = 0.58$, $p = 0.0007$, $n = 30$). Multiple regression using O_2 and sediment ON as independent variables ($[NO_3^-] = 0.58\ [O_2] + 0.32$ ON–0.03, $r = 0.63$, $p = 0.0011$, $n = 30$) slightly improved the variance explained.

significantly ($p < 0.01$) between the cold and warm season in rural interstitial waters (0.32 ± 0.12 mmol/L, $n = 15/0.18 \pm 0.04$ mmol/L, $n = 15$) as well as in periurban interstitial waters (0.27 ± 0.09 mmol/L, $n = 16$)/0.11 ± 0.06 mmol/L, $n = 15$). A significant decrease in nitrate was also found between rural and periurban interstitial waters in the warm season ($p < 0.01$).

Nitrate was significantly related ($p = 0.01$) with O_2 and inversely related with ammonium for all the samples, and with O_2 and sediment ON in periurban samples (Supplementary material 3, available online at http://www.iwaponline.com/wst/068/531.pdf). The nitrate-dissolved O_2 plot (Figure 5) showed that the channel had higher dissolved O_2. Rural interstitial waters remained oxic with concentrations above 0.1–0.2 mmol/L whatever the season. Most periurban interstitial waters had O_2 and nitrate levels close to those of the channel during the cold season, confirming that they were fed by channel water. By contrast, in the warm season they showed the lowest NO_3^- and dissolved O_2 concentrations that were associated with the highest NH_4^+ concentrations.

We now discuss how the nitrate and dissolved O_2 of interstitial waters are affected by mixing with channel water and by periurban organic matter input. Under higher flow (November 2004), rural interstitial waters with highest nitrate levels had $\delta^{18}O$ fingerprints of local groundwater and should be derived from flow paths on adjacent hill slopes. The highest nitrate concentration of these waters can therefore be related to nitrate leaching. Under low flow (June 2004), water $\delta^{18}O$ showed high renewal of rural interstitial waters with channel water while interstitial water remained oxic with nitrate content similar to that of surface water (Figure 4). There was little if any apparent removal of nitrate from subsurface waters, probably because of high exchange between subsurface and surface waters.

Whereas the rural and periurban sites both presented high nitrate concentrations in channel water, their interstitial waters showed quite different seasonal patterns of nitrate. In the cold season, under high flow, water $\delta^{18}O$, dissolved O_2 and nitrate indicated that periurban interstitial waters were recharged by channel water and then bore high nitrate concentration. In the warm season, under low flow, a clear decrease in nitrate was found in periurban interstitial waters but not in the rural ones. It corresponded to slower renewal of interstitial waters by channel water as shown by water $\delta^{18}O$ in June 2004. Lower renewal was observed in the downstream part of riffles where interstitial waters had the longest residence time in bed sediments and presented the highest nitrate loss.

Several processes could explain the nitrate loss observed in the periurban interstitial waters in the warm season: (i) biological uptake in stream sediments, (ii) nitrate reduction (denitrification), (iii) mixing with groundwater poor in nitrate. It is unlikely that nitrate loss was due to uptake by macrophytes whose growth is hampered by the high stream specific power. Large nitrate loss occurred below the streambed and could thus not be explained by microphyte uptake. It could hardly be related to incorporation in the biomass of sediment as fine sediment ON content decreased between the cold and warm season ($0.28 \pm 0.11/0.20 \pm 0.07$ g/100 g). Reducing conditions were supported by low dissolved O_2 content, ammonium occurrence, nitrate loss and nitrate-O_2 correlation. Nitrate reduction (denitrification) occurs in stream subsurface waters when dissolved O_2 falls below 0.15 mmol/L (Lefebvre et al. 2004; Storey et al. 2004) and it is likely that aerobic respiration then produces anoxic microsites leading to denitrification. We could not decipher whether nitrate decreased strictly along the inflow of channel water into sediment interstices or along the groundwater flow, limited here to colluvio-alluvial deposits. Whatever the case, longer water residence time and degradation of labile organic matter seemed to favor nitrate decrease below the streambed, in agreement with previous works (Storey *et al*. 2004).

CONCLUSIONS

The Yzeron stream showed a downstream evolution in subsurface–surface water exchange between the upstream rural areas and downstream periurban areas impacted by CSO. This downstream evolution could be related to streambed slope, riffle frequency and to alluvial aquifer development. The DON and nitrate patterns in periurban subsurface waters were linked to the seasonal change in subsurface–surface water exchange. They showed high nitrate and DON in the cold season when surface waters recharged subsurface waters. In the warm season, slower exchange between periurban subsurface and surface waters seemed to drive nitrate reduction in subsurface waters. The OC and ON data supported the input of organic matter-rich particles and waters, possibly derived from CSO and fueling nitrate reduction in the periurban subsurface waters.

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