

Denitrification in a hyporheic riparian zone controlled by river regulation in the Seine river basin (France)

Journal:	<i>Hydrological Processes</i>
Manuscript ID:	HYP-08-0012.R1
Wiley - Manuscript type:	Research Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Curie, Florence; Université Pierre et Marie Curie, UMR Sisyphe Ducharne, Agnès; Université Pierre et Marie Curie, UMR Sisyphe Sebilo, Mathieu; Université Pierre et Marie Curie, UMR BIOEMCO Bendjoudi, Hocine; Université Pierre et Marie Curie, UMR Sisyphe
Keywords:	hyporheic zone, denitrification, regulated river, nitrate, riparian zone, isotopic biogeochemistry



view

1
2
3 Denitrification in a hyporheic riparian zone controlled by river regulation in the
4 Seine river basin (France)
5
6
7
8
9

10 F. Curie¹, A. Ducharne¹, M. Sebil², H. Bendjoudi¹
11

12 ¹ Université Pierre et Marie Curie, CNRS, UMR Sisyphe, Paris, France
13

14 ² Université Pierre et Marie Curie, UMR BIOEMCO, Paris, France
15
16

17 **Keywords:** Hyporheic zone, denitrification, regulated river, nitrate, riparian zone, isotopic
18 biogeochemistry.
19
20
21
22
23

24
25 F. Curie, UMR Sisyphe, CNRS / Université Pierre et Marie Curie, case 105, 4 place Jussieu, Paris,
26 75252, France.
27 (florence.curie@ccr.jussieu.fr}
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 Abstract:
4
5

6 The purpose of this paper is to study denitrification and the conditions for its
7 development in a hyporheic zone. The study site is the riparian zone of a former branch of the
8 Seine River, where the river stage is kept almost constant during the year by hydraulic
9 regulation. Hydrological and geochemical surveys were performed by monitoring four wells,
10 ten shorter piezometers and the river over a 15-month period. The water fluxes originating
11 from the chalky hillsides and the river converge in a zone parallel to the river that acts as a
12 drainage flow path through the floodplain. The riparian zone between this flow path and the
13 river shows an important depletion of nitrate during the summer and autumn period, which
14 cannot be explained by a simple mixing of waters coming from the river and the chalky
15 hillsides. It can be attributed to denitrification as it occurs when oxygen concentration is
16 below 2 mg/l, and goes along with a consumption of dissolved organic carbon and a decrease
17 of redox potential. The river completely controls these hydro-geochemical conditions. It also
18 keeps the wetness of the riparian zone almost constant, which allowed us to isolate the high
19 temperatures in summer and autumn as an important triggering factor for denitrification,
20 through its influence on the reaction rate and oxygen deficits. We also found a small isotopic
21 enrichment of nitrate, suggesting that denitrification occurs after diffusion of nitrate through
22 the sediment and riparian zone matrix, which is consistent with the hyporheic functioning of
23 the study site.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

I – Introduction

Riparian zones are buffer strips of land on either side of a stream that may be regarded as an ecotone at the transition between the terrestrial and the aquatic ecosystems (Malanson, 1993). These zones can play an important role in the control of water quality by functioning as a natural sink for sediments and nutrients (Bruner *et al.*, 1994; Burt and Pinay, 2005). Numerous studies have focused on nitrate removal in the riparian zones (Hill, 1996) because these buffers appear to be a natural solution to reduce the risk of eutrophication and to safeguard drinking water supplies (Burt *et al.*, 1999). Indeed, the two major processes responsible for nitrate removal, denitrification, which converts nitrate into nitrogen gas, and uptake (by the vegetation and the soil biomass), are favored in these zones by the presence of water and vegetation. The buffering functions of wetlands which cover globally 6% of land area (Lefeuvre, 2000) explain the attention denoted to their preservation. In the Seine river basin, a recent study based on the computation of a topographic index estimated that potential wetlands cover 11% of the Seine basin (Curie *et al.*, 2007).

In early studies of interaction between the river and the alluvial groundwater, the stream corresponded essentially to a pipe receiving unidirectional water and nutrient fluxes from the catchment and functioning as a conduit for transport isolated from adjacent geologic material (Bencala, 1993; Hinkle *et al.*, 2001). Biological processes could occur in the riparian zone before reaching the river or within the stream. These concepts have recently evolved to recognize more complex interactions between the groundwater and the river (Ward, 1989) with the emergence of the concept of hyporheic zone (Jones and Holmes, 1996). The hyporheic zone is defined as a continuum containing water originating from both the groundwater table and the river channel. The extent of this zone is very variable according to the stream order (Hinkle *et al.*, 2001), the morphology and characteristics of the river (Hill *et al.*, 1998), and the season (Hinkle *et al.*, 2001).

1
2
3 The purpose of this paper is to study denitrification and the hydrogeochemical
4 conditions of its development in a hyporheic zone where the hydrologic functioning and the
5 wetness conditions are controlled by a regulated river.
6
7
8
9

10 11 II – Materials and methods

12 13 1 – Study area

14
15
16 The study was carried out in the riparian zone of the Beauregard stream, which flows
17 in the large alluvial floodplain (about 2.5 km width) of the Seine River (France) upstream
18 from the confluence of rivers Aube and Seine (Figure 1). The Beauregard stream is a former
19 branch of the Seine River, parallel to the course of the Seine River. It is a part of a complex
20 network of interconnected streams, heavily regulated by sills, sluices, and inflows from a
21 massive reservoir (205 million m³) constructed upstream from the study site in 1966 to reduce
22 the level of floodwater and sustain low flows in the Seine. As a result, the water levels of the
23 Beauregard are almost constant during the year, with a variation of only 7 cm from January
24 2005 to June 2005.
25
26
27
28
29
30
31
32
33
34
35
36

37 The hydrological and geochemical survey of the riparian zone was performed by
38 monitoring four almost equidistant wells (W1 to W4) located along a transect across a
39 topographic profile from the chalky hillsides down to the stream (Figure 2). The thickness of
40 the alluvium increases gradually from the hillsides to the river, where it reaches five meters.
41 These four wells have a depth of 20 meters and present a succession of 1-meter slotted screen
42 and riser pipes that allows water sampling at different depths. They are positioned so as to
43 study the influence of different land uses on denitrification. The wells W1 and W2 are located
44 downstream from a cultivated field, and the two other wells are placed in a forested zone,
45 downstream from a pond for well W3 and from a fallow for well W4, which is closest to the
46 stream. This instrumentation was completed during the survey by the installation of ten
47 shorter piezometers (P1 to P10) (3-meter depth) in the vicinity of the river (Figure 3).
48
49
50
51
52
53
54
55
56
57
58
59
60

2 – Sampling and analysis

Weekly measurements and water samples were taken at the four wells over a period of 15 months, from April 2004 to June 2005. The Beauregard stream was also monitored each week from October 2004 to June 2005. In July and August 2005, two surveys were conducted on the four wells, the ten piezometers and the river.

Measurements and samples were taken in well W1 at a 5 meter depth and in the three other wells (W2, W3 and W4) at different depths ranging between 2.5 and 7 meters, as detailed in Figure 2, so as to study the possible differences between alluvium and fractured chalk. In situ measurements were always performed before the sampling by introduction of sensors into the wells. The depth of the water table was measured first, before dissolved oxygen concentration, redox potential and temperature. Samples were taken with a double packer system (Lerner and Teutsch, 1995), which allowed us to isolate the sampling zone between the packers and to minimize purge volumes. Before sampling, the volume isolated by the packer in the well was pumped three times to ensure that samples were representative of the undisturbed water table (Jacks and Norrström, 2004). Water samples intended for laboratory analyses of dissolved organic carbon, isotopic composition and major ions were filtered in the field through 0.2 μm filters.

Total alkalinity was determined by titration with sulphuric acid (APHA, 1985) on non-filtered water samples. Major anions and cations were analysed by ion chromatography with a Dionex DX100 connected to an autosampler AS3500. The results of these analyses were validated against the computation of the ion balance. The samples with an error higher than 10% were not taken into account during analysis of the results. Of the 453 water samples, only 4.5% were excluded. Dissolved organic carbon was analysed by a Shimadzu TOC-5000A Total Organic Carbon Analyzer connected to a Shimadzu ASI-5000A Autosampler and the reported concentration of dissolved organic carbon corresponds to the mean of four

1
2
3 sample replicates. Isotopic composition of nitrate-nitrogen ($\delta^{15}\text{N-NO}_3^-$) was measured by
4
5 isotope ratio mass spectrometer (IRMS) following the method described by Sebilo *et al.*
6
7 (2004) with an analytical accuracy of $\pm 0.2 \text{ ‰}$. Nitrogen ratios are expressed with delta
8
9 notation ($\delta^{15}\text{N-NO}_3^- \text{ ‰}$), defined as:

$$\delta_{\text{sample}} (\text{‰}) = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] * 1000$$

12
13 where R is the isotopic ratio $^{15}\text{N}/^{14}\text{N}$ of a sample and a reference material, respectively. The
14
15 international standard for N is atmospheric nitrogen, for which R the ratio $^{15}\text{N}/^{14}\text{N}$ is 0.003676
16
17 (Mariotti, 1982).
18
19
20
21
22
23

24 III – Results

25 1 – Hydrological functioning

26
27 Water fluxes in the riparian zone were explored by different means in this study. At
28
29 first, we created piezometric maps from the water levels measured in all the piezometers and
30
31 in the stream during the spring and the summer 2005. The piezometric curves were obtained
32
33 by linear interpolation between the measurements points. The water level in the river is
34
35 approximately one meter above the alluvial water-table. The gradient between the river and
36
37 the alluvial water table is linked to the regulation of the stream flow by the Seine reservoir
38
39 that maintains the river level throughout the year, including summer. The fluxes coming from
40
41 the watershed and the river converge to a zone parallel to the river, which acts as a drainage
42
43 flow path in the riparian zone (Figure 3).
44
45
46
47
48
49

50
51 The ten piezometers were installed during the spring 2005, so that in the preceding
52
53 winter, levels of the alluvial water table were only known in the four wells. During the winter
54
55 period (January 2005 to March 2005), the water level in the river was always above the levels
56
57 of water in the wells but the difference was less marked than in summer (60 cm instead of 1
58
59 m). Thus, piezometric maps in winter are probably very similar to those of summer, with the
60

1
2
3 same flow directions, converging from the river and the hillsides to a draining zone parallel to
4
5 the river between wells W4 and W3.
6
7

8 To better understand the hydrodynamics of the site, chloride was measured as a natural
9
10 tracer of water fluxes. This element is chemically conservative and is not involved in the
11
12 biological processes occurring in the water bodies (Hill *et al.*, 1998). The only source of
13
14 chloride that is likely to increase the concentration of this element in our study zone is the use
15
16 of chloride fertilizers in the field located between the wells W1 and W2 (Figure 2). The
17
18 chloride concentration remained almost constant during the year in the four wells and in the
19
20 stream (Figure 4a). The concentration tended to increase from well W1 to well W3, most
21
22 likely linked to the use of fertilizers in the field located between W1 and W2. In the stream,
23
24 chloride concentrations were lower than in the groundwater, whatever the sampled well. In
25
26 particular, the well near the river (W4) had chloride concentrations between those of the river
27
28 and the well W3, indicating a mixing of waters coming from the river and the chalky hillsides.
29
30 There were no significant variations in the concentration with the depth of sampling in the
31
32 wells except in W4 near the river, where the values of chloride increased with the depth,
33
34 showing that the contribution of the river decreases with depth. The mixing of waters was
35
36 confirmed by the map of chloride concentration during the summer period (16/08/2005).
37
38 Concentrations in the piezometers near the river were significantly lower than in the others,
39
40 according to the student test with a significance level of 0.01 (Figure 5). This supports the
41
42 proposition that the zones in the vicinity of the river have the hydrological functioning of a
43
44 hyporheic zone and contain water originating from both the groundwater table and the river
45
46 channel.
47
48
49
50
51
52
53

54 55 56 2 – Geochemical functioning

57 58 59 a – Nitrate concentrations 60

1
2
3 To analyse seasonal variations of nitrate concentrations, two periods of time were
4 defined (Figure 6):
5

6
7
8 - a period going from 14th December 2004 to 26th April 2005 (winter and spring)
9 called “high nitrate period” (HiN).
10

11
12 - a period going from 11th October 2004 to 7th December 2004 and from 11th May
13 2005 to 16th August 2005 (summer and autumn) called “low nitrate period” (LoN).
14

15
16
17 The HiN period corresponds to the time when the nitrate concentrations in the well W4 are
18 high (generally above 25 mg/l) and higher than those of the river. The LoN period has the
19 opposite characteristics. The wells W3, W2 and W1 are not located precisely along the same
20 water pathway but they are at an increasing distance from the river and the parallel draining
21 zone (Figure 3). In these wells, nitrate concentrations are constant during the year, without
22 any difference between the LoN and HiN periods (Figure 4b). In W2 and W3, there are no
23 differences with respect to sampling depth. The sample from well W1, at the interface
24 between the alluvial plain and the hillside, is representative of the nitrate concentration from
25 the hillside and nitrate concentration increases until W3, as the pathway within the cultivated
26 alluvial plain becomes longer.
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 In the river, nitrate concentrations are lower than in the three first wells and exhibit
42 seasonal differences with a decrease during the LoN period, which can be linked to aquatic
43 macrophytes development, denitrification or plant uptake in the contributing watershed, as the
44 LoN period largely encompasses the summer and autumn seasons.
45
46
47
48
49

50 In the well closest to the stream (W4), nitrate concentrations show smaller values in
51 the LoN than in the HiN period like in the river. Three mechanisms can explain this depletion
52 of nitrate during the LoN period: (1) mixing of waters coming from the river and the chalky
53 hillsides, (2) local plant uptake and (3) denitrification.
54
55
56
57
58
59
60

1
2
3 Two wells (W4 and W3) are located in similarly forested zones, where plant uptake
4 can reduce nitrate concentration. In well W3, no decrease of nitrate concentration was
5 measured during the LoN period, which suggests that plant uptake can be ruled out at this
6 local scale. In well W4, there is a mixing of waters coming from both the hillsides and the
7 river as previously shown by our chloride analysis. If mixing alone explained the nitrate
8 decrease observed near the river, nitrate concentrations in well W4 should be between those
9 of the river and the well W3. This is the case during the HiN period, but during the LoN
10 period, nitrate concentrations in W4 are lower than in both the river and W3, which can only
11 be explained by denitrification.
12
13
14
15
16
17
18
19
20
21
22
23
24
25

26 b – Denitrification conditions

27
28 In addition to a source of nitrate (coming in W4 from the hillside and the river),
29 denitrification requires both an organic carbon source and anoxic conditions (Sirivedhin and
30 Gray, 2006). It is a competitive process to aerobic respiration and can occur even with low
31 levels of dissolved oxygen (Mariotti, 1986). The upper limit of dissolved oxygen
32 concentration that allows denitrification is not precisely known but most authors agree on a
33 value between 0.2 and 2 mg/l (Nakajima *et al.*, 1984; Trevors, 1985).
34
35
36
37
38
39
40
41

42 The high concentrations of dissolved oxygen in wells W1, W2 and W3 do not permit
43 denitrification (Figure 4c). Only the well W4, during the LoN period, displays dissolved
44 oxygen concentrations lower than 2 mg/l. The concentration of dissolved oxygen increases
45 with the distance to the river (Figure 7). This again suggests a mixing between waters rich in
46 oxygen, coming from the hillside and depleted water coming from the river. The zone
47 inducing the depletion of oxygen must be located between the open river water where the
48 concentrations are high and the piezometers close to the river such as W4. It is likely that the
49 river water loses its dissolved oxygen content when it seeps into the anoxic sediments to
50
51
52
53
54
55
56
57
58
59
60

1
2
3 flow to the riparian zone. The low levels of oxygen induced by the river sediment create a
4 potential for denitrification in the sediment or in the riparian zone in vicinity of the river.
5
6

7
8 The presence of organic carbon is also necessary for denitrification, as it that plays the
9 role of electron donor. Only a few analyses of dissolved organic carbon (DOC) were
10 performed from 21st June to 22nd November 2004, during the LoN period (Figure 8).
11 Concentrations in wells W1, W2 and W3 were low and rather constant during the study
12 period. In contrast, in well W4, especially at the 3-meter depth, the organic matter was smaller
13 from July to October compared to higher concentrations in June and November. DOC in well
14 W4 can either be produced in situ by decomposition of organic matter or be supplied by the
15 river. In both cases, contributions of DOC come from the surface, which explains the higher
16 concentrations at the 3-meter than at 5 and 7-meter depths in well W4. The wells W4 and W3
17 are located in a forested zone, which could be a source of DOC. The well W3, however, even
18 at 2.5 meters, does not show concentrations of DOC as high as in well W4, which suggests
19 that the forested zone could not be the principal source of DOC in W4. The river, in contrast,
20 shows high concentrations of DOC, which could explain those of the well W4 by mixing.
21 This is true locally at the beginning of winter 2004, when the DOC concentrations at the three
22 sampling depths in W4 range between those of the rivers and of wells W1 to W3,
23 representative of the water flowing from the chalky hillsides.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44

45 As complementary analysis, we also considered year-long surveys at two stations of
46 the national water quality monitoring network (Réseau National de Bassins). Both are on the
47 main branch of the Seine River, Verrière being upstream from the site, and Méry-sur-Seine
48 being downstream (Figure 1). The DOC concentrations at these sites are above those in wells
49 W1, W2 and W3 throughout the year during the survey period and show a maximum in
50 spring. The seasonal variations of DOC in the rivers and in W4 are likely explained by the
51 mineralization of organic matter for the high values, and by heterotrophic consumption, by
52
53
54
55
56
57
58
59
60

1
2
3 means of either respiration or denitrification, for the lower values. The differences between
4 the Seine River stations and the study site (showing higher riverine concentration over the 2-
5 month shared period) can be explained by the location of the Beaugard stream inside a
6 forested zone, the leaching of wastewater upstream from the study site or differences between
7 the DOC measuring protocols. In any case, the DOC required to achieve denitrification is
8 present in W4 and is probably mainly provided by the river.
9

10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
High temperatures enhance biological reactions and limit oxygen diffusion in the
water, which promotes the denitrification process (Sirivedhin and Gray, 2006). The well W4
displayed important seasonal variations of temperature at the 3-meter depth with high water
temperatures during the LoN period (Figure 9). The amplitude of these variations decreased
with depth (from 3 to 7-meter) and with the distance to the river (from W4 to W1). The
temperature variations in W4 were smoothed, shifted and attenuated in comparison to those of
the river. This confirms the mixing of waters in the vicinity of the river as previously shown
by chloride analysis. These higher temperatures can enhance denitrification in W4 during the
LoN period, when the denitrification conditions are met, in particular low dissolved oxygen
concentration.

The denitrification process is related to a decrease of redox potential and occurs, in
theory, between +100 and +400 mV (Reddy and D'Angelo, 1994). These limit values are very
large and give only a general frame because others reactions can occur simultaneously in the
field and modify these theoretical redox conditions (Lindberg and Runnells, 1984). In W1,
W2 and W3 wells, the redox potentials were constant throughout the year and with
measurement depth, at around 400 mV (Figure 4d). This value was also found in the well W4
during the HiN period, but the redox decreased markedly to values around 200 mV during the
LoN, providing additional evidence for denitrification in W4.

c – Isotopic evidences

1
2
3 To verify that nitrate depletion near the river is due to denitrification, isotopic
4 measurements were conducted on water sampled in the river, in the well W3 at 2.5-meters and
5 in the well W4 at the three sampling depths (3, 5 and 7 meters) (Figure 10). These
6 measurements were performed on samples taken at one date during the HiN period
7 (15/02/2005), when the decrease in nitrate concentrations between W3 and the river was
8 probably explained by the sole mixing of waters from the hillside and the river, and at one
9 date in the LoN period (09/11/2004), when the nitrate concentrations in W4 were lower than
10 those of the river suggesting denitrification.
11
12
13
14
15
16
17
18
19
20
21

22 Natural stable isotopic compositions of nitrate-nitrogen ($\delta^{15}\text{N-NO}_3^-$) in W4, in
23 particular at 3 meters depth, were systematically higher than those in the well W3 and the
24 river. The enrichment in ^{15}N could be due to denitrification, to the mixing of waters with
25 different $\delta^{15}\text{N-NO}_3^-$ or to input of wastewater. The well W4 is supplied by the river and the
26 waters coming from the chalky hillsides, which both have smaller isotopic compositions than
27 W4, so that mixing cannot explain these high values of $\delta^{15}\text{N-NO}_3^-$. To our knowledge, there is
28 no leaching of human or animal wastewater near the study site that could contribute to the
29 enrichment in ^{15}N in W4. Only the denitrification can thus produce this enrichment in ^{15}N (by
30 isotopic fractionation) and the low values in nitrate concentrations in the well near the river.
31
32
33
34
35
36
37
38
39
40
41
42
43

44 When denitrification occurs without renewal of the substrate (closed system), the
45 isotopic composition of the substrate can be calculated using the “Rayleigh equation”:
46
47
48

$$\delta_S(t) = \delta_{S0} + \epsilon \ln S_t/S_0$$

49
50 where δ_{S0} is the isotopic composition of the nitrate at the initial time, ϵ the isotopic
51 enrichment factor (expressed in ‰), S_0 and S_t are the concentrations of the nitrate at time zero
52 and t, respectively.
53
54
55
56
57

58 Given the concentration and the related isotopic composition of nitrates, it is possible
59 to calculate the isotopic enrichment factor:
60

$$\varepsilon = [\delta_S(t) - \delta_{S0}] / \ln S_t/S_0$$

The denitrification process can occur from nitrate molecules that are either provided locally (one-phase denitrification) or after diffusion of nitrates through the sediment (two-phase denitrification). These two types of denitrification can be distinguished using stable isotope measurements (Sebilo, 2003). Denitrification leads to a negative isotopic enrichment factor as $\delta^{15}\text{N-NO}_3^-$ increases when nitrate concentration decreases, but it is more negative in case of one-phase denitrification (-18 ‰) than in a two-phase denitrification (-1.5 to -3.6 ‰) (Lehmann *et al.*, 2003; Sebilo *et al.*, 2003).

The isotopic enrichment factors have been calculated among the three sampling depths in W4 from either the river or the well W3 (at 2.5 m, representative of the chalky hillsides) (Figure 10). The enrichment factors for residual nitrates in W4 are within the same range of small values, between - 2.8 ‰ and -3 ‰, which is indicative of a two-phase denitrification process. This result is consistent with the hyporheic functioning of the study area, in which nitrate is denitrified during its percolation through the anoxic zone, with an isotopic fractionation controlled by the diffusion of riverine water through the sediment and the riparian zone.

IV – Conclusion

The riparian studied zone along the Beauregard River is fed by a river that dilutes the waters coming from the chalky hillsides, hence defining a hyporheic zone. This kind of hydrological functioning has already been observed in the alluvial plain of the Seine River, close to the study site, at the confluence between the rivers Aube and Seine during the high flow period (Bendjoudi *et al.*, 2002). In most cases reported in the literature, inverse water fluxes toward the river occur temporarily, but in our study site, the hyporheic functioning occurs all year long, even during the low-flow period in summer. This hydrological specificity

1
2
3 is linked to the management of the Seine River and its tributaries by the numerous locks and
4
5 dams maintaining constant river levels.
6
7

8 The riparian zone shows an important depletion of nitrate during the so-called LoN
9
10 period that goes from 11th October 2004 to 7th December 2004 and from 11th May 2005 to
11
12 16th August 2005. The decrease cannot be explained by a simple mixing of waters coming
13
14 from the river and the chalky hillsides because these two water sources have higher nitrate
15
16 concentrations than the riparian well W4 during the LoN period. The decrease can be most
17
18 convincingly attributed to denitrification, as demonstrated by several pieces of evidence. The
19
20 decrease of nitrate in well W4 during the LoN period comes along with concentrations of
21
22 dissolved oxygen lower than 2mg/l, a consumption of dissolved organic carbon, a decrease of
23
24 the redox potential, and an increase of the $\delta^{15}\text{N-NO}_3^-$ of nitrate. The related enrichment is in a
25
26 low range that corresponds to a two-phase denitrification, which is consistent with the
27
28 hyporheic functioning.
29
30
31
32
33

34 At our study site, the denitrification process in the vicinity of the river during the LoN
35
36 period (summer and autumn) is completely controlled by the conditions established by the
37
38 river, which provides waters with low level of dissolved oxygen, high content in organic
39
40 carbon and high temperatures. Since river levels are constant all year long, the seasonal
41
42 variation of the denitrification is not linked to the wetness conditions of the zone but to the
43
44 temperature variations. The higher water temperatures, during the summer and autumn
45
46 seasons that more or less correspond to the LoN period, act directly on denitrification by
47
48 activating the reaction rate and indirectly by limiting the diffusion of dissolved oxygen, what
49
50 produces the anoxia required by denitrification.
51
52
53
54

55 Thus, the particular hydrological functioning of the study site implies that the waters
56
57 coming from both the watershed and the river are denitrified in the riparian zone. The
58
59 resulting purified water is probably drained to the hydrographic network somewhere
60

1
2
3 downstream where the river level decreases, as it cannot accumulate in the riparian system.
4
5 As denitrification is the only way to permanently remove nitrate, the hyporheic studied zone
6
7 has a positive influence on the quality of downstream riverine water. It is all the more
8
9 important as similar hyporheic conditions can potentially exist in many zones in the Seine
10
11 basin. Indeed, rivers levels in the Seine basin are regulated by numerous locks and dams and
12
13 by three massive reservoirs (Seine, Aube and Marne), which can influence as much 1000 km
14
15 of downstream streams.
16
17

18
19
20 The hyporheic functioning studied here, however, is not entirely natural, and this calls
21
22 for further investigation. In particular, the aim of river management authorities is, at present,
23
24 to return to a more natural state in the river control to comply with the European Water
25
26 Framework Directive, and the Agence de l'Eau Seine Normandie (AESN) has plans for
27
28 removing a significant number locks and dams that regulate the low-order streams. What will
29
30 happen if the river hydrology is allowed to return to a more natural state? This type of
31
32 modification may diminish the denitrification functioning of some hyporheic riparian zones
33
34 that are currently maintained by the river stage control, in particular during the low flow
35
36 period in summer. How much nitrate will go un-denitrified after these modifications? In this
37
38 framework, modeling would certainly be very helpful to guide decision by allowing to assess
39
40 the impact of river control scenarios on the hydrological functioning of such riparian zones
41
42 and its consequences on the denitrification.
43
44
45
46
47
48
49

50 Acknowledgements

51
52
53 This study was supported by the PIREN-Seine research programme. We wish to thank
54
55 Samia Aloui (UMR Sisyphe) for field samplings and measurements and Emmanuel Aubry
56
57 (UMR Bioemco) for the DOC analyses and Valérie Plagnes (UMR Sisyphe) for valuable
58
59 discussions on major element analyses.
60

References:

- 1
2
3
4
5
6
7
8 Bencala KE. 1993. A perspective on stream-catchment connections. *Journal of the North*
9 *American Benthological society* **12**: 44-47.
- 10 Bendjoudi H, Weng P, Guérin R, Pastre JF. 2002. Riparian wetlands of the middle reach of
11 the Seine river (France): historical development, investigation and present hydrologic
12 functioning. A case of study. *Journal of hydrology* **263**: 131-155.
- 13 Böttcher J, Strebel O, Voerkelius S, Schmidt HL. 1990. Using isotope fractionation of nitrate-
14 nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy
15 aquifer. *Journal of hydrology* **114**: 413-424.
- 16 Brunet RC, Pinay G, Gazelle F, Roques L. 1994. Role of the floodplain and riparian zone in
17 suspended matter and nitrogen retention in the Adour River, south-West France.
18 *Regulated Rivers: Research and management* **9**: 53-63.
- 19 Burt T, Pinay G. 2005. Linking hydrology and biogeochemistry in complex landscapes.
20 *Progress in Physical geography* **29**: 297-316.
- 21 Burt TP, Matchett LS, Goulding KWT, Webster CP, Haycock NE. 1999. Denitrification in
22 riparian buffer zones: the role of floodplain hydrology. *Hydrological processes* **13**:
23 1451-1463.
- 24 Curie F, Gaillard S, Ducharne A, Bendjoudi H. 2007. Geomorphological methods to
25 characterise wetlands at the scale of the Seine watershed. *Science of the Total*
26 *Environment* **375**: 59-68.
- 27 Hill AR. 1996. Nitrate removal in stream riparian zones. *Journal of environmental quality* **25**:
28 743-755.
- 29 Hill AR, Labadia CF, Sanmugadas K. 1998. Hyporheic zone hydrology and nitrogen
30 dynamics in relation to the streambed topography of a N-rich stream. *Biogeochemistry*
31 **42**: 285-310.
- 32 Hinkle SR, Duff JH, Triska FJ, Laenen A, Gates EB, Bencala KE, Wentz DA, Silva SR. 2001.
33 Linking hyporheic flow and nitrogen cycling near the Willamette River - a large river
34 in Oregon, USA. *Journal of hydrology* **244**: 157-180.
- 35 Jacks G, Norrström A-C. 2004. Hydrochemistry and hydrology of forest riparian wetlands.
36 *Forest ecology and Management* **196**: 187-197.
- 37 Jones JB, Holmes RM. 1996. Surface-subsurface interactions in stream ecosystems. *Trends in*
38 *ecology and evolution* **11**: 239-242.
- 39 Lefeuvre JC, Fustec E, Barnaud G. 2000. De l'élimination à la reconquête des zones humides.
40 In *Fonctions et valeurs des zones humides*, Fustec E, Lefeuvre JC (eds). Dunod, Paris;
41 1-16.
- 42 Lehmann MF, Reichert P, Bernasconi SM, Barbieri A, McKenzie A. 2003. Modelling
43 nitrogen and oxygen isotope fractionation during denitrification in a lacustrine redox-
44 transition zone. *Geochimica et Cosmochimica Acta* **67**: 2529-2542.
- 45 Lindberg RD, Runnells DD. 1984. Ground water redox reactions: an analysis of equilibrium
46 state applied to Eh measurements and geochemical modeling. *Science* **225**: 925-927.
- 47 Malanson GP. 1993. *Riparian landscapes*. Cambridge University Press: Cambridge.
- 48 Mariotti A. 1982. Apports de la géochimie isotopique à la connaissance du cycle de l'azote.
49 Thèse de l'Université Pierre et Marie Curie, Paris, 476 pp.
- 50 Mariotti A. 1986. La dénitrification dans les eaux souterraines, principes et méthodes de son
51 identification : une revue. *Journal of hydrology* **88**: 1-23.
- 52
53
54
55
56
57
58
59
60

- 1
2
3 Nakajima M, Hayamizu T, Nishimura H. 1984. Effect of oxygen concentration on the rates of
4 denitrification and denitritification in the sediments of an eutrophic lake. *Water*
5 *Research* **18**: 335-338.
6
7 Reddy KR, D'Angelo EM. 1994. Soil processes regulating water quality in wetlands. In
8 *Global Wetlands: Old World and New*, Mitsch WJ (ed). Elsevier Science; 309-324.
9
10 Sebilo, M. 2003. Utilisation du traçage isotopique naturel pour caractériser et quantifier les
11 processus de nitrification et de dénitrification à l'échelle du réseau hydrographique de
12 la Seine, Thèse de l'Université Pierre et Marie Curie, Paris, 128 pp.
13
14 Sebilo M, Billen G, Grably M, Mariotti A. 2003. Isotopic composition of nitrate-nitrogen as a
15 marker of riparian and benthic denitrification at the scale of the whole Seine River
16 system. *Biogeochemistry* **63**: 35-51.
17
18 Sebilo M, Mayer B, Grably M, Billiou D, Mariotti A. 2004. The use of the "ammonium
19 diffusion" method for $\delta^{15}\text{N-NH}_4^+$ and $\delta^{15}\text{N-NO}_3^-$ measurements: Comparison with
20 others techniques. *Environmental Chemistry* **1**: 99-103.
21
22 Sirivedhin T, Gray KA. 2006. Factors affecting denitrification rates in experimental wetlands
23 : Field and laboratory studies. *Ecological Engineering* **26**: 167-181.
24
25 Trevors JT. 1985. The influence of oxygen concentrations on denitrification in soils. *Applied*
26 *Micobiology and Biotechnology* **23**: 152-155.
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

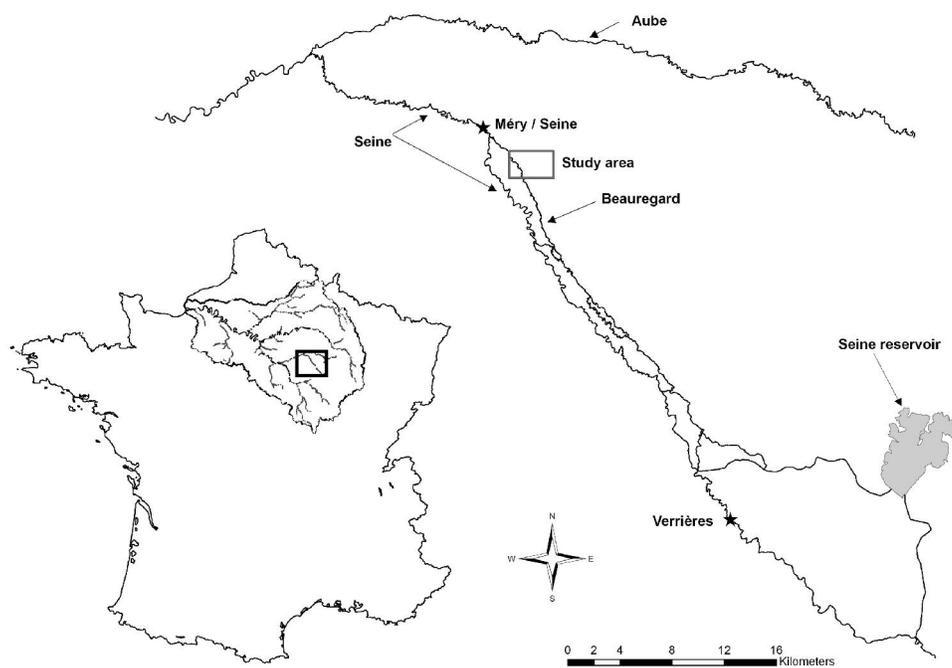


Figure 1: Location map of the study area. The study site is located in the rectangle and the two RNB stations (Méry/Seine and Verrière) are depicted by a star.
237x167mm (300 x 300 DPI)

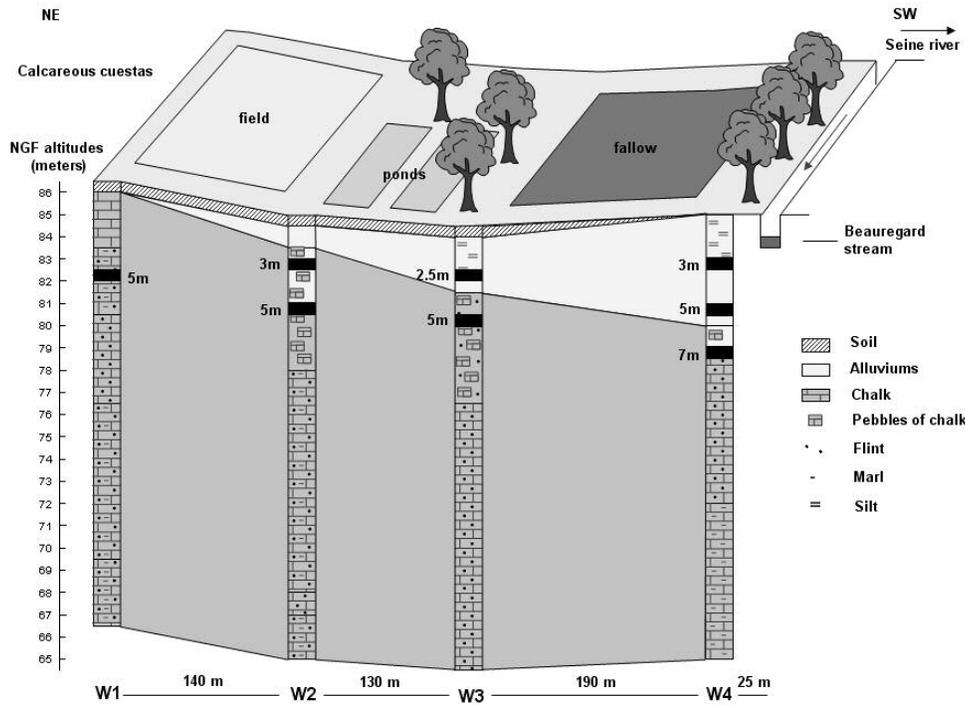
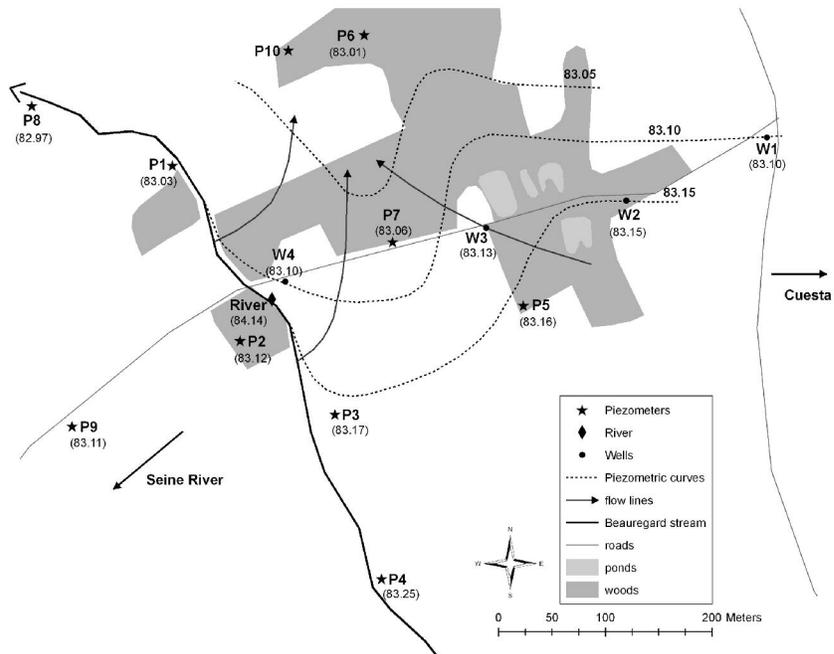


Figure 2: Schematic representation of the geology and landcover along the four wells of the study site. Rectangles correspond here to the different depths of measurements and water sampling.
320x236mm (72 x 72 DPI)

view



**Figure 3: Piezometric map at the date of 15th June 2005 with the location of wells and piezometers. The altitudes of the water table, indicated between brackets, are in NGF (French geodetic leveling norm).
237x167mm (300 x 300 DPI)**

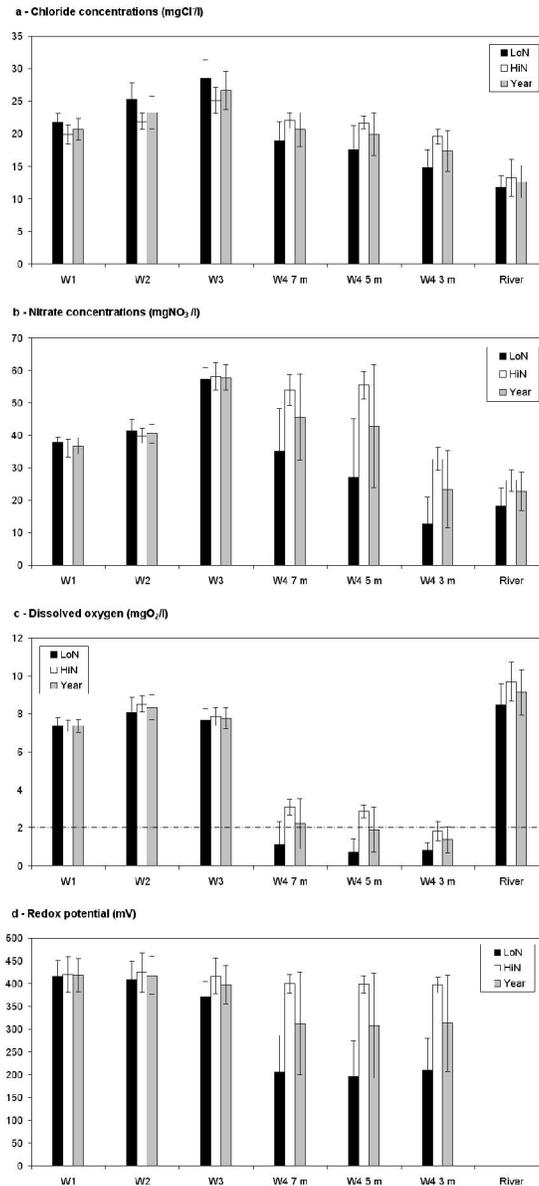


Figure 4: Mean concentrations (bars) and standard deviation (error bars) of (a) Chloride concentrations (mg/l), (b) Nitrate concentrations (mgNO₃-/l), (c) Dissolved oxygen levels (mgO₂/l) and (d) Redox potential (mV) in the four wells and in the river during the year (period of river survey), the LoN period and the HiN period (Figure 6).

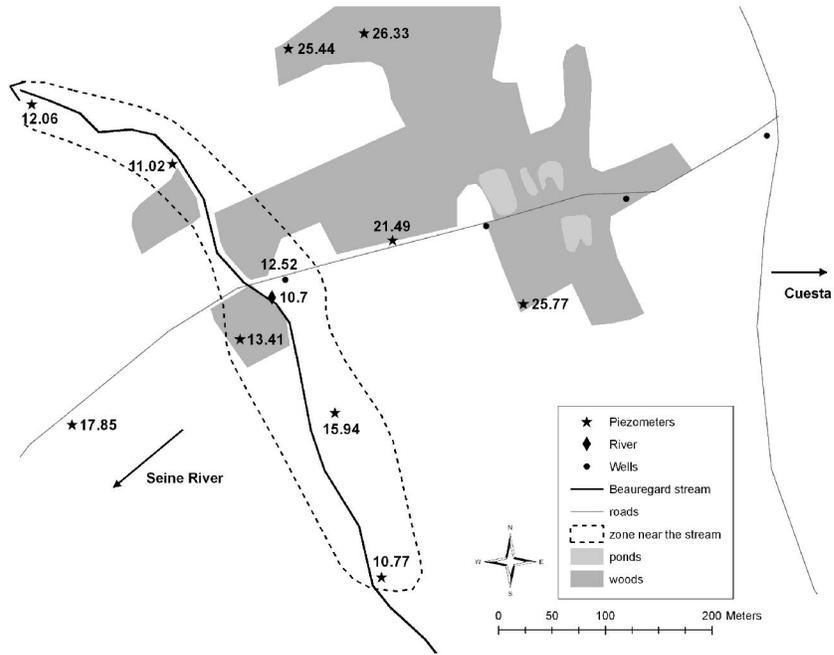


Figure 5: Chloride concentrations (mg/l) in well W4 and piezometers on 16th August 2005.
 237x167mm (300 x 300 DPI)

Review

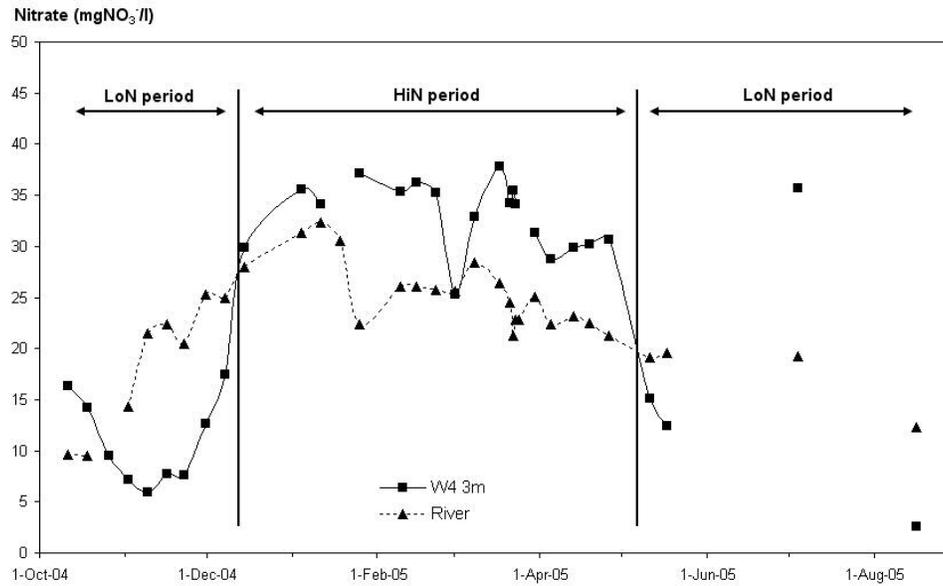


Figure 6: Nitrate concentration (mgNO₃-/l) in well W4 and in the river and definition of the “Low Nitrate” (LoN) and “High Nitrate” (HiN) periods used for averages in Figure 4. The LoN period goes from 11th October 2004 to 7th December 2004 and from 11th May 2005 to 16th August 2005 and counts between 10 and 13 water samples according to the measured parameters and sample points. The HiN period goes from 14th December 2004 to 26th April 2005 and counts between 14 and 16 water samples. The “year” period gathers the HiN and the LoN periods.

307x183mm (72 x 72 DPI)

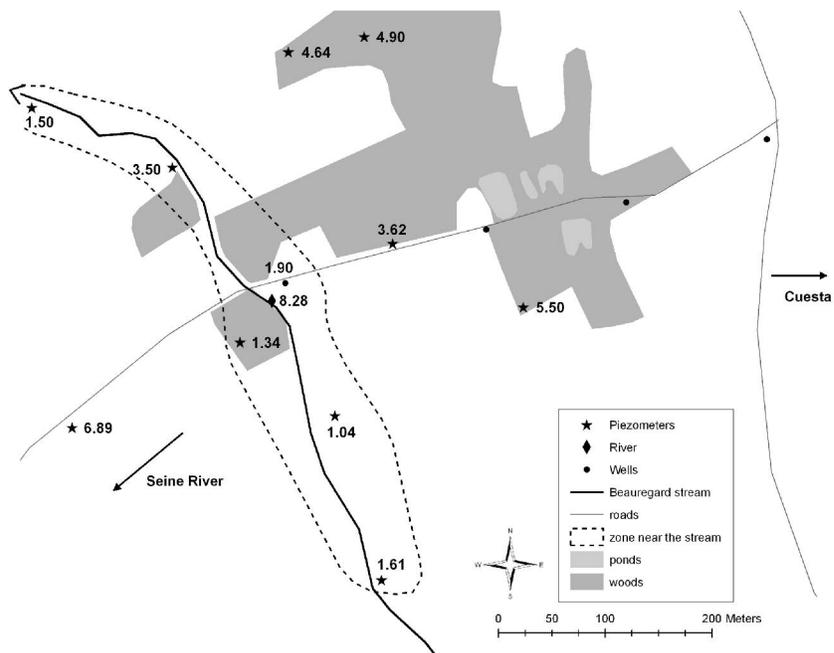


Figure 7: Dissolved oxygen concentrations (mgO₂/l) in well W4 and piezometers on 16th August 2005.
 222x157mm (300 x 300 DPI)

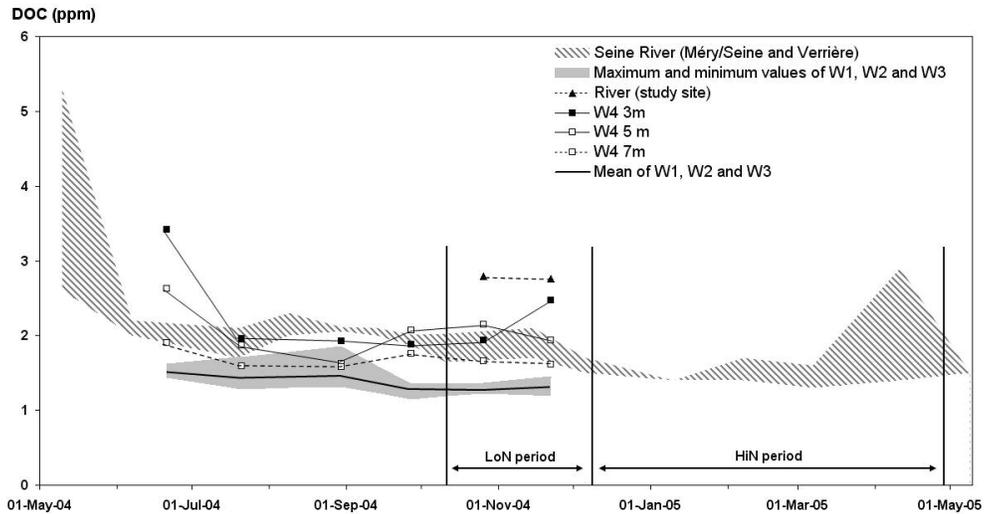


Figure 8: Dissolved organic carbon (DOC) in the four wells and in the river for the period going from 21st June to 22nd November 2004, during the LoN period. The hatched envelope corresponds to the DOC concentrations in the Seine River over an entire annual cycle, at two stations of the national water quality monitoring network (Réseau National de Bassins): Verrière being upstream from the site, and Méry-sur-Seine being downstream.

422x222mm (72 x 72 DPI)

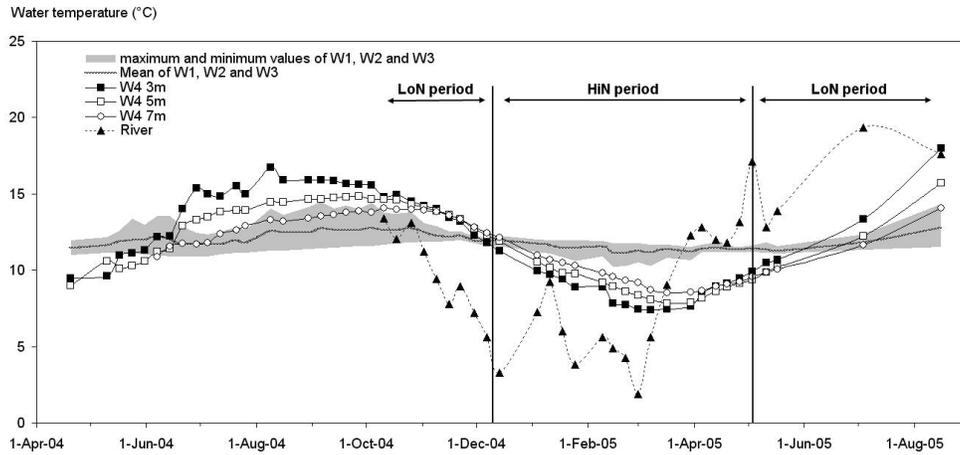


Figure 9: Water temperature in the four wells and in the river for the period of study.
473x220mm (72 x 72 DPI)

Peer Review

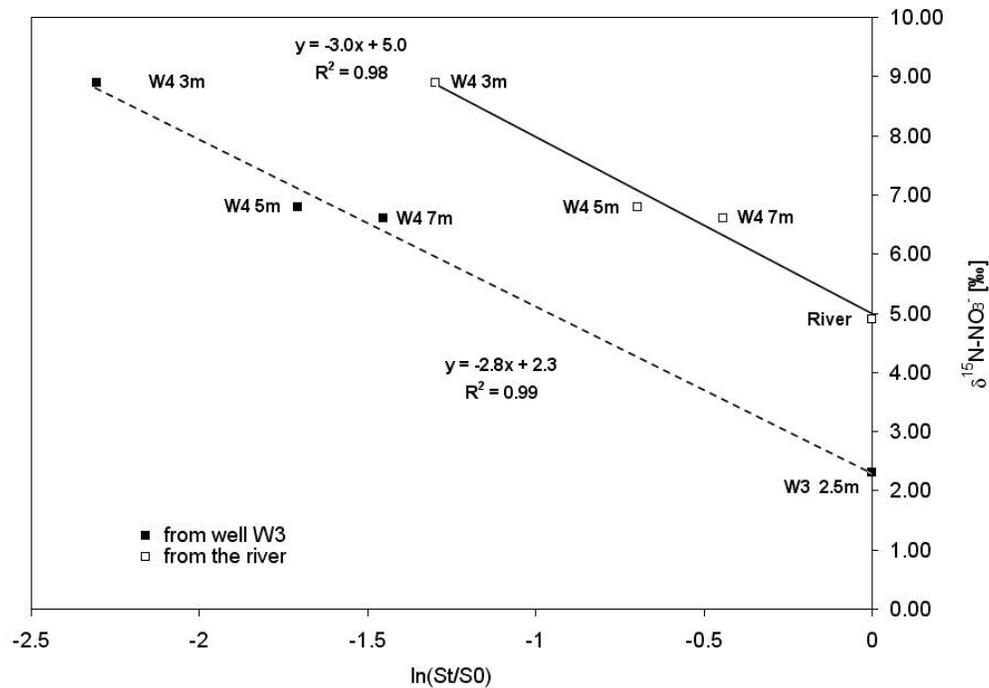


Figure 10: Calculation of isotopic enrichment factors (ϵ) for the well W4 (at the three sampling depths) if the water comes from the river (in solid line) or the well W3 (in dotted line). The enrichment factor is given by the slope of the equation $\delta_s(t) = \epsilon * \ln(S_t/S_0) + \delta_{s0}$ and is between -2.8 and -3.0 depending on the water sources.

316x220mm (72 x 72 DPI)