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1 **Vertical change in dissolved organic carbon and oxygen at the water table**
2 **region of an aquifer recharged with stormwater:**
3 **biological uptake or mixing?**

4
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1 **Key words:** DOC, dissolved oxygen, aquifer sediment respiration, groundwater, vadose zone,
2 stormwater infiltration

3
4 **Abstract:**

5 Decreases in dissolved organic carbon (DOC) and dissolved oxygen (DO) with increasing
6 depth below the groundwater table are often considered as evidence for aerobic respiration;
7 however they may reflect mixing of infiltrating water and groundwater. We found that
8 groundwater DOC concentration was on average 0.3 mg C l^{-1} higher and DO concentration
9 $1.5 \text{ mg O}_2 \text{ l}^{-1}$ lower at recharge sites replenished with stormwater than at reference sites fed by
10 direct infiltration of rain water from the land surface. Groundwater DOC increased and DO
11 decreased with increasing vadose zone thickness (VZT) at both recharge and reference sites.
12 There was no significant interaction between the effects of stormwater infiltration and VZT.
13 Vertical changes in DOC and DO below the groundwater table at recharge sites could account
14 for by simple mixing of infiltrating stormwater and groundwater. Moreover, aquifer sediment
15 respiration (SR) was not significantly higher at recharge sites than at reference sites.
16 However, slow filtration column experiments showed that SR increased significantly with an
17 increasing supply of easily biodegradable DOC. We conclude that the observed reduction in
18 DOC below the groundwater table at recharge sites was essentially due to water mixing rather
19 than biological uptake because of the low biodegradability of DOC and short transit time of
20 stormwater in the upper layers of groundwater. Our results highlight the need to distinguish
21 between the effect of hydrological and biological processes on DOC and DO patterns below
22 the groundwater before conclusions are made on the efficiency of groundwater in degrading
23 surface-derived DOC.

24

1 **Introduction**

2

3 Groundwater ecosystem metabolism depends on transport of organic substances and electron
4 acceptors from the surface (Chapelle 1993). The supply of dissolved organic carbon (DOC) to
5 groundwater is usually low because the mineral soil horizons and the vadose zone intercept
6 most of the DOC solubilized in the humic soil layer (Michalzik et al. 2001; Neff & Asner
7 2001; Cannavo et al. 2004; Goldscheider et al. 2006) (Fig. 1). Weak DOC supply was shown
8 to limit the rate of several biogeochemical processes in groundwater including aerobic
9 respiration (Baker et al. 2000), nitrification (Holmes et al. 1994), and denitrification (Starr &
10 Gillham 1993; Siemens et al. 2003) and might also constrain the abundance and diversity of
11 invertebrate assemblages (Datry et al. 2005). The residence time of water, environmental
12 conditions (e.g. temperature, moisture, water flux) and the strength of attenuation processes in
13 the soil and vadose zone interact in a complex way to control the amount of DOC reaching the
14 groundwater table (Kalbitz et al. 2000). Several studies found an inverse relationship between
15 the concentration of DOC in groundwater and vadose zone thickness (VZT), indicating
16 vadose flowpaths with longer residence time exhibited more DOC retention (Pabich et al.
17 2001; Jardine et al. 2006; McMahon & Chapelle 2008). The relationship between
18 groundwater DOC concentration and the percolation rate of infiltrating water is unclear
19 because higher water fluxes simultaneously reduce the transit time of water, dilute soil DOC
20 solution, and potentially stimulate microbial activity in response to increased soil moisture
21 (Amiel et al. 1990; Kalbitz et al. 2000).

22

23 The soil DOC leached to groundwater is retained onto aquifer sediments and consumed by
24 microorganisms as groundwater moves either vertically or horizontally away from the

1 recharge zone (Malard & Hervant 1999). The concentration of dissolved oxygen (DO) in
2 groundwater decreases with decreasing VZT (McMahon & Chapelle 2008) and shallow
3 water-table aquifers typically exhibit higher vertical loss rates of DOC and DO than deep
4 water-table aquifers (Malard & Hervant 1999; Pabich et al. 2001). These are strong arguments
5 in favor of a biological degradation of DOC in the upper groundwater layers. However, the
6 losses of DOC and DO with increasing depth below the groundwater table or increasing
7 distance from stream in downwelling areas cannot be taken in isolation as proof of aerobic
8 respiration because they may be caused by other factors, including the mixing of distinct
9 water sources and the spatio-temporal variability of the source and sink of DOC and DO
10 (Rutherford & Hynes 1987; Malard & Hervant 1999; Sobczak & Findlay 2002; Wassenaar &
11 Hendry 2007). For example, water mixing rather than denitrification was reported to explain
12 the apparent change in nitrate concentration in a number of aquifers (Howard 1985;
13 McMahon & Bohlke 1996; Pinay et al. 1998). The significance of water mixing in generating
14 declining gradients of DOC and DO is more likely to be enhanced at sites where groundwater
15 is being rapidly recharged, either naturally or artificially, with surface water. Indeed, high
16 recharge rates generate pronounced variation in the proportion of infiltrating water with
17 increasing depth below the water table (Foulquier et al. 2009). In addition, they increase
18 groundwater flow velocity, thereby limiting the biological uptake of DOC per distance unit.

19

20 The present study aimed to disentangle the effect of water mixing and biological uptake
21 on spatial variation in the concentrations of DOC and DO at the water table region of an
22 aquifer artificially recharged with stormwater. Measurements were conducted at recharge sites
23 fed artificially with stormwater and reference sites fed exclusively by the natural infiltration
24 of rainwater. We hypothesized that the reduction in DOC and DO concentration with
25 increasing depth below the groundwater table at sites recharged with stormwater reflected

1 water mixing rather than an *in situ* biological uptake of DOC. First, we tested the influence of
2 VZT and recharge by measuring DOC and DO concentrations in groundwater beneath a range
3 of VZTs at multiple recharge and reference sites. Second, a mixing model was used to
4 determine whether vertical gradients of DOC and DO at recharge sites could be accounted for
5 by a simple mixing of infiltrating stormwater and groundwater. Third, we examined
6 differences in aquifer sediment respiration (SR) among recharge and reference sites and
7 evaluated the biodegradability of DOC leached to groundwater by comparing SR measured in
8 the field with that obtained in the laboratory with a control supply of easily biodegradable
9 DOC.

10

11 **Material and methods**

12 *Study sites*

13

14 Study sites were located in the eastern aquifer of the Lyon metropolitan area, France (Fig.
15 2A). The aquifer (catchment area: 314 km²) consisted of 3 corridors separated by moraine
16 hills of low hydraulic conductivity (10^{-5} - 10^{-8} m s⁻¹) (BURGEAP 2001; Detry 2003a). Aquifer
17 corridors consisted of highly permeable glaciofluvial sediments (hydraulic conductivity: 10^{-3} -
18 10^{-2} m s⁻¹) and were drained by the Rhône River. The glaciofluvial deposit consisted of
19 extremely heterogeneous sediments containing on average $1.2 \pm 0.7\%$ of silt and clay (grain
20 size < 0.08 mm), $23.5 \pm 5.1\%$ of sand (2–5 mm), $10.3 \pm 3.4\%$ of gravel (2–5 mm), and $65.1 \pm$
21 6.6% of pebble (> 5 mm) (Malard et al. 2005). The aquifer was artificially recharged with
22 stormwater at multiple locations to compensate for reduced natural recharge caused by the
23 sealing due to urban surfaces. Artificial groundwater recharge with stormwater represented at

1 least 10 % of the annual flux of groundwater which was estimated at 69.1 million m³ (Giry
2 1997; Foulquier et al. 2009).

3

4 Monitoring sites

5 Twenty one sites were selected with a VZT ranging from 1.7 to 28.2 m (Fig. 2A). Twelve
6 recharge sites were in groundwater areas artificially recharged by stormwater infiltration
7 basins, and 9 reference sites in groundwater areas fed exclusively by direct infiltration of rain
8 water from the land surface. The stormwater infiltration basins rapidly infiltrate (< 2 days)
9 large quantities of runoff water collected during rainfall events from residential, commercial
10 and/or industrial catchments into the aquifer (Barraud et al. 2002). Catchment areas and
11 surface areas of the infiltration basins ranged from 2.5 to 285 ha and 0.08 to 1 ha, respectively
12 (Table 1). The annual groundwater recharge below each stormwater system was estimated as
13 follows:

14

$$15 \quad \text{Groundwater recharge (m}^3 \text{ of stormwater m}^{-2}\text{)} = P \times RC \times CA_{IB} / SA_{IB}$$

16 where:

17 P (m): annual precipitation (0.835 m ± 0.125 m; n=38 years, 1970-2007)

18 RC (%): runoff coefficient on urban catchment (0.35)

19 CA_{IB}: catchment area of the infiltration basin (m²)

20 SA_{IB} (m²): surface area of the infiltration basin

21

22 The annual groundwater recharge below stormwater basins averaged 89 ± 56 m³ of
23 stormwater m⁻² (n=11 basins) (Table 1). For comparison, the annual groundwater recharge at
24 reference site was estimated at 0.24 m³ of rainwater m⁻² (i.e. 29 % of annual precipitation)
25 (BURGEAP 1995). All recharge and reference sites were equipped with monitoring wells

1 with a perforated casing intersecting the first 5 meters below the groundwater table. At
2 recharge sites, monitoring wells were in the immediate downstream vicinity of infiltration
3 basins in order to intersect the stormwater plume flowing into groundwater.

4

5 Well-cluster sites

6 Recharge sites 1 and 2 were equipped with one cluster of 5 wells that were successively
7 installed at depths of 1, 2, 3, 4 and 5 m below the groundwater table (Fig. 2B). At each site,
8 the wells were located downstream of the infiltration basin and intersected the groundwater
9 zone that was artificially recharged with stormwater. They were installed with an engine-
10 operated hammer and were separated from each other by a distance of less than 2 m (Fig. 2B).
11 The well casings were made of PVC or transparent Plexiglas® (inner diameter: 6 cm) and
12 were screened at their lower end over a height of only 0.5 m (Datry et al. 2003b; Foulquier et
13 al. 2009).

14

15 Sites 3 to 5 were instrumented with 6 clusters of 5 wells that were successively installed at
16 depths of 10, 30, 50, 70 and 90 cm below the groundwater table. At each site, three replicate
17 well clusters were located upstream of the infiltration basin and three other replicate clusters
18 were located in the immediate downstream vicinity of the basin. The upstream well clusters
19 intersecting the groundwater zone that was not recharged with stormwater were used as
20 reference sites while the downstream well clusters were used as recharge sites because they
21 intersected the stormwater plume induced by the infiltration basins. Distances between the 3
22 replicate clusters did not exceed 10 m and wells within each replicate cluster were separated
23 from each other by a distance of 0.5 m. All wells were constructed of 3.8 cm inner diameter
24 steel pipe with a screen of 13 cm in height (hole diameter: 0.5 cm) at their lower ends. They
25 were installed at the desired depths using a vibrating electric-powered hammer.

1 *Effect of VZT and recharge on DOC and DO concentrations*

2

3 Groundwater samples were collected from the 21 monitoring sites on four occasions (October
4 2001 and April, June and October 2002) to test for the effect of VZT and recharge with
5 stormwater on the concentrations of DOC and DO in groundwater. Groundwater was
6 collected at a depth of 1 m below the water table by pumping each well with a pneumatic
7 piston pump equipped with 2 inflatable packers (discharge rate $\sim 10 \text{ l min}^{-1}$) (UWITEC
8 Company, Mondsee, Austria). The first 50L of pumped water were discarded as rinse to
9 ensure purging at least 3 times the well volume. We checked that specific conductance and
10 DO stabilized during well purging. After well purging, water was collected in 0.1-L burned
11 glass bottles for the determination of DOC and DO was measured with an O₂ meter (WTW
12 OXI 330 meter, Weilheim, Germany) whose readings had been previously checked with the
13 Winkler method. Water samples were stored at 4°C, brought within 4h to the laboratory, and
14 filtered through a 0.45 μm membrane filter. Depth of the water table was measured in each
15 well with a contact gauge (KL 010, OTT Messtechnik, Kempten, Germany).

16

17 DOC was determined using a carbon analyser (multi N / C[®] 3100, Analytik Jena, Jena,
18 Germany) based on thermocatalytic oxidation (850 °C) of organic carbon and infrared
19 detection of CO₂. We used an automatic selection outlier method in which repeated injection
20 of the same water samples was carried out until the coefficient of variation between any 2
21 injections was less than 2 %. The reproducibility of measurements calculated from repeated
22 analyses of in-house standard (K-Phtalate solution, 1 mg C l⁻¹) was better than $\pm 0.05 \text{ mg C l}^{-1}$
23 (1 σ).

24

25 *Vertical profiles of DOC and DO concentrations in groundwater*

1
2 Changes in the concentration of DOC, DO, and chloride (Cl^-) and specific conductance at
3 depth below the water table were determined by collecting groundwater from well clusters on
4 3 rainfall events (October 2003, 2004 and 2005) and 3 dry-weather periods (October 2003,
5 2004 and 2005) at site 1, 3 rainfall events (November 2001 and March and June 2002) and 3
6 dry-weather periods (November 2001 and March and November 2002) at site 2, and one
7 rainfall event at sites 3-5 (September 2006). Chloride and specific conductance were used as
8 tracers to detect depth variation in the relative proportion of stormwater into groundwater
9 because Cl^- concentration and specific conductance of stormwater (ca $5 \text{ mg Cl}^- \text{ l}^{-1}$, $100 \mu\text{S cm}^{-1}$
10 $^{-1}$) were much lower than those of groundwater (ca $22 \text{ mg Cl}^- \text{ l}^{-1}$, $> 500 \mu\text{S cm}^{-1}$). Chloride was
11 determined by ion chromatography on water samples collected in polypropylene bottles.
12 Specific conductance was measured in the field with a portable meter (WTW LF 330,
13 Weilheim, Germany). The groundwater sampling procedure at sites 1 and 2 was the same as
14 those described above. At sites 3 to 5, groundwater was pumped from the 6 well clusters with
15 a suction piston pump (discharge rate: 10 l min^{-1}). The first 10 L of pumped water were
16 discarded as rinse to ensure purging at least 3 times the well volume. Samples of stormwater
17 were collected in the infiltration basins.

18
19 Concentration of DO in groundwater was recorded at 1-hr intervals for one year in well
20 clusters at sites 1 and 2 to determine differences in oxygen depth profile among multiple
21 rainfall events. An YSI 600 XLM multiparameter logger (Yellow Springs Instrument Co.,
22 Yellow Springs, Ohio) equipped with three probes measuring specific conductance,
23 temperature and DO was positioned at screen depth in each well. Loggers were transported to
24 the laboratory every 15 to 21 days for data transfer, data examination, probe maintenance and
25 calibration. On several occasions we checked that measurements provided by the loggers were

1 similar to those made on groundwater samples collected from the wells. Rainfall and air
2 temperature data (1-hr intervals) for sites 1 and 2 were obtained from the nearest station of the
3 Meteorological Survey of the city of Lyon.

4

5 *Effect of recharge and depth below groundwater table on SR and sedimentary organic carbon*

6

7 Aquifer sediment was collected from upstream and downstream well clusters at sites 3 to 5
8 during one rainfall event (n=90 samples) to test for the effect of recharge and depth below the
9 groundwater table on sediment respiration (SR) and sedimentary organic carbon (SOC).
10 Sediment for respiration and SOC measurements was obtained by pumping because of the
11 difficulty in recovering uncontaminated sediment cores at depth into this glaciofluvial aquifer
12 (Malard et al. 2005). A mixture of water and sediment was extracted using a hand piston
13 pump from each well (UWITEC Company, Mondsee, Austria). After sediment settling, at
14 least 0.5 L of sediment was collected in polypropylene containers that were stored at ~ 20 °C
15 and brought within 4 h to the laboratory for analysis. The sediment was sieved wet through a
16 1-mm sieve and respiration was measured using the slurry technique (Furutani et al. 1984).
17 About 10 g of wet sediment with 5 mL of groundwater collected in the wells were placed in
18 150 mL flasks. The samples were incubated under aerobiosis at 20 °C, in the dark under a
19 gentle shaking. At t = 3 h and t = 6 h, CO₂ gas was collected and then measured by gas
20 chromatography on a MTI 200 microcatharometer (Agilent, Santa Clara, CA, USA). Dry
21 weights of sediment were determined after drying at 60 °C and SR was expressed as ng of
22 CO₂ g⁻¹ sediment dry weight (DW) h⁻¹.

23 SOC was measured on replicate samples of 0.25 g that were placed in pre-combusted ceramic
24 boats, dried at 50 °C and treated with 2M HCl to remove inorganic carbon. Acid treatment
25 consisted of repeated additions of small quantities of acid (up to 400 µL) with the samples

1 being dried in a warming oven at 50 °C between each acid addition. The incremental addition
2 of acid continued until there was no visual evidence of effervescence. The organic carbon
3 content of sediment was then determined using a carbon analyser (multi N / C[®] 3100,
4 Analytik Jena, Jena, Germany) based on thermocatalytic oxidation (900 °C) of organic carbon
5 and infrared detection of CO₂. Replicate sediment samples were analyzed until the coefficient
6 of variation between any 2 replicate samples was less than 10 %. The reproducibility of
7 measurements calculated from repeated measurements of calcite powder (4.2 mg CaCO₃; 120
8 g C kg⁻¹) was better than ± 26.5 µg C (1 σ).

9

10 *Sediment respiration under controlled supply of BDOC*

11

12 Slow filtration column experiments were conducted to assess the biodegradability of DOC
13 leached to groundwater by comparing SR measured under field condition with that obtained
14 under controlled supply of BDOC. In addition, they enabled to test our ability to detect
15 differences in SR in response to DOC enrichment despite sediment disturbance caused by
16 sediment collection and sieving. Columns had an inner diameter of 10 cm and consisted of
17 two experimental modules (10 cm high) topped by a third module of 5 cm in height
18 (Mermillod-Blondin et al. 2005) (Fig. 3). They were filled with inert gravel and fresh sand to
19 a height of 15 cm. About 10 cm of water was left above the sediment surface. Gravels (grain
20 size: 5-8 mm) were cleaned with deionized water and dried at 60°C. Fresh sand (grain size
21 100-1000 µm) was collected at a depth of 1 m below the bed of a gravel pit intersecting the
22 water table of the glaciofluvial aquifer using the Bou-Rouch method (Bou & Rouch 1967).
23 Masses of gravel (500 g, 500 g and 400 g) and sand (150 g, 150 g and 120 g) were alternately
24 introduced into the columns to obtain a heterogeneous porous media.

25

1 Experiments were performed at constant temperature ($15 \pm 0.5^\circ\text{C}$) in the dark. The columns
2 were supplied from the top with reconstituted water ($96 \text{ mg NaHCO}_3 \text{ l}^{-1}$, 39.4 mg CaSO_4
3 $2\text{H}_2\text{O l}^{-1}$, $60 \text{ mg MgSO}_4 \cdot 7\text{H}_2\text{O l}^{-1}$ and 4 mg KCl l^{-1} , $19 \text{ mg Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O l}^{-1}$, US EPA 1991)
4 using a peristaltic pump controlling a constant infiltration flow rate of 2 ml min^{-1} . This flow
5 rate corresponded to the average groundwater recharge rate estimated at recharge sites.
6 Columns were operated as fully saturated to mimic moisture conditions in groundwater.
7 Supplied water was aerated to maintain concentrations of DO between 8.5 and 9.5 mg l^{-1} at
8 the inlet of the columns throughout the experiment. Three concentrations of sodium acetate
9 (i.e. 0.5 mg , 1.5 mg and $2.5 \text{ mg C-NaCH}_3\text{COOH l}^{-1}$), an easily biodegradable form of DOC,
10 were applied to the columns with three replicate columns per concentration. Water sampling
11 for DOC determination and oxygen measurements were made at four depths (5 cm above the
12 sediment surface, and 1 , 5 and 10 cm below the sediment surface) by means of lateral water
13 derivation outlets on days 6, 10, 14, 18, 22 and 26 after the start of the experiments. For DO
14 measurements, an oxygen micro-sensor probe (Unisense, Aarhus, Denmark) was directly
15 connected to the lateral water derivation, thereby preventing any contact with atmospheric
16 oxygen. On day 26, the columns were dismantled and 3 sediment layers (0 - 2 , 4 - 6 and 9 - 11 cm
17 below the sediment surface) were collected for the determination of SR and SOC. Analytical
18 procedures for these 2 parameters were the same as those described above.

19

20 *Data analysis*

21

22 Linear regression analyses were performed to evaluate the relationships between VZT and
23 concentrations of DOC and DO in groundwater. We used the average concentrations of DOC
24 and DO from groundwater samples collected over the 4 sampling dates at 21 monitoring sites
25 to avoid a pseudoreplication effect (i.e. unjustified increase in the degree of freedom).

1 Analysis of covariance (ANCOVA) was used to determine whether the relationships differed
2 between recharge and reference sites. The design was a 2 (i.e. recharge versus reference sites)
3 by 1 (i.e. VZT in m) analysis.

4

5 A two-end member mixing model based on measured concentrations of chloride was used to:
6 (i) determine vertical change in the proportion of inflow stormwater in groundwater at
7 recharge sites and (ii) to test whether the observed vertical changes in DOC and DO below the
8 groundwater table could be accounted for by a simple mixing of water sources. Water
9 sampled at each depth below the groundwater table during rainfall events was assumed to be a
10 mix of pre-event groundwater and inflow stormwater infiltrating through the vadose zone.
11 The relative proportion at depth x of water from depth $x-1$ was calculated using the following
12 formula:

$$13 \quad f_{x-1} = (C_x - C_{g_x}) / (C_{x-1} - C_{g_x})$$

14 where f_{x-1} was the proportion at depth x of water from depth $x-1$, and C_x , C_{g_x} and C_{x-1}
15 represented the chloride concentrations of post-event groundwater, pre-event groundwater,
16 and water collected at depth $x-1$, respectively. Chloride was used as a conservative tracer
17 (Triska et al. 1993). The proportion f_{x-1} was used to calculate the concentrations of DOC and
18 DO at each depth under the assumption of a simple mixing of water sources. Concentrations
19 in upstream well clusters (sites 3 to 5) and groundwater collected during dry weather periods
20 (sites 1 and 2) were used as pre-event groundwater concentrations. Concentrations of DOC
21 and DO in stormwater collected in the infiltration basins were used as input concentrations in
22 the model for calculating DOC and DO concentrations in the uppermost layer of groundwater.
23 Calculated concentrations were plotted against measured concentrations and were compared
24 using a Wilcoxon paired test. In order to test the validity of our mixing model, we checked

1 that the calculated/measured ratio of specific conductance, which was also expected to behave
2 as a conservative tracer, did not significantly differ from 1.

3

4 We used continuous measurements of DO at sites 1 and 2 to examine differences in the
5 vertical gradient of DO between cold and warm seasons. Warm and cold seasons
6 corresponded respectively to months with higher and lower mean air temperature than the
7 annual air temperature.

8

9 Analysis of variances (ANOVA) was used to test for the effect of recharge and depth below
10 the water table on SR and SOC using data collected at well cluster sites 3 to 5 (n=90 wells). A
11 nested design with sites, recharge nested in sites and depth as main effects was used in order
12 to avoid confounding between-site variation with variation induced by recharge. The
13 interactions between depth and recharge nested in sites as well as between depth and sites
14 were also tested. ANOVA was performed to test for the effect of an increasing supply of
15 BDOC on SR and SOC using data from the slow filtration column experiments. The design
16 was a 3 (BDOC concentrations of 0.5, 1.5, and 2.5 mg C l⁻¹) by 3 (depths of 1, 5 and 10 cm
17 below the sediment surface) analysis. We examined the relationship between SR and the
18 removal rate of DOC and DO in the slow filtration columns. The removal rate in each
19 sediment layer (i.e. 0-2, 4-6 and 9-11 cm below the sediment surface) was calculated using
20 data obtained on day 26 of the experiments as follows:

21

$$22 \quad RR = (\Delta_C \times Q) / (V \times P)$$

23 Where:

24 RR: Removal rate of DOC and DO in mg l⁻¹ sediment h⁻¹

25 Δ_C : Difference in DOC or DO concentration (mg l⁻¹) between 2 consecutive depths

1 Q: water discharge (l h^{-1}) through the sediment layer

2 V: volume of the sediment layer (l)

3 P: porosity

4

5 Statistical analyses were performed using R (R Development Core team 2006) and the

6 Statistica 6[®] software package (Statsoft Inc., Tulsa, Oklahoma, USA). Significance for all

7 statistical tests was accepted at $\alpha < 0.05$.

8

9 **Results**

10

11 *Effect of VZT and recharge on DOC and DO concentrations*

12

13 Groundwater DOC concentration varied from 0.1 to 3.1 mg C l^{-1} and averaged $1 \pm 0.6 \text{ mg C l}^{-1}$

14 ¹ (n=228), whereas that of stormwater averaged 4.6 ± 1.9 (n=34; range: 2.5 - 11). DOC was

15 negatively correlated and DO was positively correlated with VZT at both reference and

16 recharge sites (Fig. 4). DOC was significantly higher (p=0.0107) and DO was significantly

17 lower (p=0.0429) at recharge sites than at reference sites (Fig. 4, Tables 2 & 3). The increase

18 in DOC and decrease in DO averaged 0.3 mg C l^{-1} and $1.51 \text{ mg O}_2 \text{ l}^{-1}$, respectively. Near

19 anoxic conditions (i.e. $\text{DO} < 1 \text{ mg O}_2 \text{ l}^{-1}$) occurred at only 2 out of 11 recharge sites. The

20 slopes of the regressions between VZT and DOC and DO concentrations did not differ

21 between reference and recharge sites, indicating that the effect of recharge did not depend

22 upon VZT.

23

24 *Vertical profiles of concentration at recharge sites*

25

1 DOC decreased with increasing depth below the groundwater table but vertical gradients were
2 typically more pronounced at recharge sites 1, 2 and 3 characterized by a distinct vertical
3 reduction in the proportion of infiltrating stormwater (Fig. 5, Table 3). There was almost no
4 variation in DOC concentration with depth at sites 4 and 5, which showed little vertical
5 change in the proportion of infiltrating stormwater. Wilcoxon matched pairs test indicated no
6 difference ($n=72$, $p=0.13$) between measured values of specific conductance and those
7 calculated with the mixing model based on chloride concentrations (Fig. 6). There were also
8 no differences ($p>0.05$) between calculated and measured concentrations of DOC at sites 1
9 and 3 (Figs 5 & 6). At site 2, measured concentrations of DOC were significantly lower than
10 calculated concentrations ($n=12$; $p=0.03$) but the difference was no longer statistically
11 significant ($n=9$, $p=0.17$) when data at depth of 1 m below the groundwater table were
12 excluded from the analysis. Vertical changes in DO below the groundwater table at recharge
13 sites could also be accounted for by a simple mixing of infiltrating stormwater and
14 groundwater (Figs 5 & 6). At sites 2, 3, 4 and 5 measured concentrations of DO did not
15 significantly differ ($p>0.05$) from calculated concentrations. At site 1, measured
16 concentrations of DO were significantly lower than calculated concentrations ($n=15$, $p=$
17 0.047) but the difference was no longer statistically significant ($n=12$, $p=0.21$) when data at
18 depth of 1 m below the groundwater were excluded from the analysis. Vertical profiles of DO
19 at sites 1 and 2 exhibited a clear seasonal shift (Fig. 7), although DOC concentration always
20 decreased with depth during recharge events (sites 1 and 2 in Fig. 5). DO concentration
21 decreased with depth during cold recharge events (i.e. cold rains), whereas it increased during
22 warm recharge events.

23

24 *Effect of recharge and depth below groundwater table on SR and SOC*

25

1 SR varied greatly among sites 3-5 but was not significantly higher in downstream well
2 clusters than in upstream well clusters nor did it decrease with increasing depth below the
3 water table (Fig. 8, Table 3). A non significant effect ($p=0.140$) of groundwater recharge with
4 stormwater on SR was observed although DOC was significantly higher ($p<0.001$) and DO
5 was significantly lower ($p<0.001$) in downstream well clusters than in upstream well clusters
6 (Table 3). SOC was significantly higher in downstream well clusters but there were no
7 differences among depths (Table 3).

8

9 *Response of SR to DOC enrichment under controlled conditions*

10

11 SR increased significantly ($p<0.001$) with increasing BDOC supply and decreased with depth
12 ($p=0.014$) (Fig. 9, Table 4). The increase in sediment respiration was typically more
13 pronounced in the first cm of sediment. SR with a supply of BDOC ($SR=547 \pm 601 \text{ ng CO}_2 \text{ g}^{-1}$
14 dry sediment weight h^{-1}) was on average 4.3 times higher than that measured under field
15 conditions ($SR=127 \pm 206 \text{ ng CO}_2 \text{ g}^{-1}$ dry sediment weight h^{-1}). SR resulted in a steep
16 decreasing gradient in the concentration of DOC and DO in the slow filtration columns. The
17 removal rates (RR) of DOC and DO increased significantly with increasing BDOC supply and
18 were linearly correlated with SR (RR_{DOC} in mg C l^{-1} sediment $\text{h}^{-1} = 0.003 \times \text{SR}$, $n=27$, $r^2=0.64$,
19 $p<0.001$; $RR_{\text{DO}}=0.006 \times \text{SR}$, $n=27$, $r^2=0.72$, $p<0.001$) (Table 4). The molar ratio of consumed
20 O_2 to removed C equaled 0.65 and did not vary among depths (RR_{DO} in $\text{mol O}_2 \text{ l}^{-1}$ sediment h^{-1}
21 $= 0.65 \times RR_{\text{DOC}}$, $n=27$, $r^2=0.95$, $p<0.001$). SOC did not significantly increase ($p=0.944$) with
22 increasing BDOC supply but it was significantly higher ($p<0.001$) in the first cm of sediment
23 (Fig. 9, Table 4).

24

25 **Discussion**

1

2 *Effect of VZT and recharge on DOC and DO concentrations*

3

4 Our finding that groundwater DOC concentration decreased and DO increased with increasing
5 VZT corroborated the results of recent studies conducted in several aquifers of the United
6 States (Pabich et al. 2001; McMahon & Chapelle 2008). A longer residence time of water in
7 the vadose zone enabled an increasing amount of soil-derived DOC to be removed from
8 solution either by adsorption or respiration. The subsequent mineralization of the remaining
9 soil DOC fraction leached to groundwater probably accounted for the observed positive
10 relation between DO concentration and VZT (McMahon & Chapelle 2008). The diffusion of
11 oxygen through the vadose zone and into the saturated zone was another process that might
12 have influenced DO concentration in groundwater. However, Neale et al. (2000) showed that
13 the reaeration flux rate decreased with increasing VZT. The linear relationships between DOC
14 and DO concentrations and VZT observed in this study differed from exponential
15 relationships reported for several aquifers of the United States for which the reduction rate in
16 DOC was much higher for VZT less than 2 to 3 m (Pabich et al. 2001; McMahon & Chapelle
17 2008). This difference was essentially due to a lack of DOC measurements for VZT < 2 m
18 because of the scarcity of shallow water-table sites in the glaciofluvial aquifer of the Lyon
19 City.

20

21 The increase in groundwater DOC concentration at recharge sites was caused by localized
22 infiltration of stormwater enriched in organic matter during runoff on urban catchments (Pitt
23 et al. 1999). Stormwater also leached DOC as it percolated through the infiltration beds. Slow
24 filtration column experiments showed that the concentration of DOC in stormwater could
25 increase by 10 to 40 mg C l⁻¹ as it percolated through bed sediments of recharge sites 1 and 2

1 (Datry et al. 2003c; Larmet 2007; Nogaro et al. 2007). Two distinct, albeit not mutually
2 exclusive, mechanisms could account for the observed reduction in groundwater DO at
3 recharge sites. The first mechanism was the mineralization in groundwater of an excess of
4 labile DOC brought by infiltrating water (Pabich et al. 2001). The second mechanism did not
5 necessitate a supply of labile DOC but corresponded to groundwater recharge with
6 stormwater that had been depleted of DO during its transit through the infiltration bed (Datry
7 et al. 2003c, 2004; Foulquier et al. 2009). Both mechanisms could also explain why the effect
8 of recharge on DOC and DO concentrations did not appear to depend on VZT. The first
9 mechanism implies that an increased amount of labile DOC reached the groundwater at
10 recharge sites but this amount and the resulting DO consumption in groundwater was
11 controlled by VZT in the same way as at reference sites. The second mechanism implies that
12 excess DOC leached to groundwater at recharge sites was poorly biodegradable and did not
13 stimulate microbial respiration. In addition, replenishment of groundwater with oxygen-poor
14 stormwater decreased DO concentration at all recharge sites independently of VZT.

15

16 *Significance of water mixing on vertical gradient of DOC and DO*

17

18 Results of the mixing model strongly indicated that decreasing gradients of DOC were
19 essentially due to a decrease in the proportion of DOC-rich infiltrating water with increasing
20 depth below the groundwater table. This was consistent with the lack of DOC attenuation with
21 depth at recharge sites 4 and 5, which were characterized by a constant proportion of newly
22 infiltrating stormwater at all depths. DOC concentration was not markedly affected by
23 biological uptake or adsorption within the first meter below the groundwater table. Our
24 conclusion that groundwater was not a sink of DOC was based on the assumption that the
25 mixing model provided a reasonable estimate of concentrations expected if only mixing

1 processes were important. This assumption was robust because the calculated/measured ratio
2 of specific conductance that was expected to be conservative did not significantly differ from
3 1. Results of the mixing model also depended on our estimates of chloride, DOC and DO
4 concentrations for each water source and depth. The only major uncertainty was the
5 concentration of DOC and DO of infiltrating water reaching the uppermost layer of
6 groundwater. The mixing model probably overestimated the attenuation of DOC and
7 consumption of DO in the uppermost layer of groundwater because stormwater was assumed
8 to reach groundwater with DOC and DO concentrations equaled to those measured in the
9 infiltration basins. In any case, this uncertainty did not affect the model calculations at
10 subsequent depths.

11

12 The mixing model satisfactorily explained vertical gradients of DO in recharge areas even in
13 cases when declines in DOC were accompanied by a concomitant loss in DO. Moreover, we
14 found that DO evolved independently of the DOC decline because it alternatively increased
15 and decreased with depth during winter and summer rainfall events. This implied that DO
16 gradients were controlled by the concentration of infiltrating water reaching the groundwater
17 table rather than by in situ consumption of DO in groundwater. Datry et al. (2004) and
18 Foulquier et al. (2009) suggested that the dynamics of DO in groundwater below stormwater
19 infiltration basins might be strongly influenced by temperature-induced changes in the rate of
20 oxygen consumption in infiltration beds. Summer warming of the bed probably stimulated
21 microbial respiration, thereby leading to a downward flow of oxygen-poor stormwater. Datry
22 et al. (2003c) and Nogaro et al. (2007) showed that oxygen uptake in filtration columns filled
23 with sediment collected in infiltration beds at recharge sites 1 and 2 could lead to near anoxic
24 conditions at a depth of only 5 cm below the water sediment interface. Reaeration of
25 infiltrating water due to O₂ diffusion in the vadose zone was probably minimal because the

1 high stormwater infiltration rate (i.e. $0.014 \text{ l m}^{-2} \text{ s}^{-1}$) rapidly led to pore space saturation with
2 water (Refsgaard et al. 1991; Le Coustumer & Barraud 2007; Goutaland et al. 2008).
3 Groundwater DO depletion below stormwater infiltration basins was reported in a number of
4 studies but the causal mechanisms remained unclear (Fischer et al. 2003). Determining the
5 relative significance of replenishment with deoxygenated but DOC-poor water and *in situ* DO
6 consumption due to a supply of labile DOC is of paramount importance because these two
7 processes may result in dissimilar changes in the rate of microbial terminal electron acceptor
8 processes in groundwater (e.g. denitrification, iron reduction).

9

10 *Effect of DOC supply on SR*

11

12 The lack of stimulation of SR at recharge sites was congruent with our observation that the
13 decrease in DOC and DO concentrations with depth essentially reflected mixing of infiltrating
14 water and groundwater. Studies of biological activity along subsurface flowpaths in which
15 DOC loss was observed provided equivocal results with some studies but not all reporting a
16 concomitant decrease in SR, bacterial activity or abundance (Findlay et al. 1993; Marmonier
17 et al. 1995; Ellis et al. 1998; Battin 2000, Craft et al. 2002; Sobczak & Findlay 2002).
18 Stormwater reaching groundwater was probably a source of low biodegradable DOC since
19 slow filtration column experiments demonstrated that SR was extremely sensitive to an
20 increase in BDOC supply. The increase in SR within slow filtration columns enabled an
21 increasing quantity of dissolved acetate (up to $1 \text{ mg C l}^{-1} \text{ sediment h}^{-1}$) to be almost totally
22 removed within only 10 cm of sediment. Baker et al. (1999) found that acetate injected into
23 hyporheic sediment of Rio Calaveras stream, New Mexico, with an initial concentration of 7.9
24 mg C l^{-1} stimulated aerobic and anaerobic respirations and was entirely consumed along
25 flowpath length $< 50 \text{ cm}$. In the present study, the more labile fraction of DOC was likely to

1 be intercepted in the soil and vadose zone, leaving only the refractory fraction to reach the
2 underlying groundwater. Pabich et al. (2001) found that the DOC loss rate as a function of
3 depth below groundwater table in Cape Cod, USA decreased with increasing VZT indicating
4 that DOC was either less labile or sorbable under thicker vadose zones. The low DOC
5 concentration ($< 2 \text{ mg C l}^{-1}$) and the lack of stimulation of SR in groundwater at recharge sites
6 characterized by high stormwater infiltration rate and VZT $< 3 \text{ m}$ indicated that the soil and
7 vadose zone were very efficient in retaining DOC either by mineralization or adsorption. The
8 increase in sediment moisture associated with stormwater infiltration could stimulate
9 microbial activity, thereby enhancing microbial degradation of DOC in the soil and vadose
10 zone (Kalbitz et al. 2000; Marschner & Kalbitz 2003). Amiel et al. (1990) pointed out that the
11 biological degradation of sewage derived DOC in the vadose zone was more efficient under
12 saturated conditions prevailing below infiltration ponds than under unsaturated conditions
13 prevailing below land irrigated with wastewater effluent.

14
15 Adsorption of dissolved organic matter onto mineral particles, its retention by microbial
16 extracellular polymeric substances and its assimilation into bacterial biomass might also
17 contribute to reduce DOC concentration along groundwater flowpaths (Kaplan & Newbold
18 2000). Unlike microbial respiration, these mechanisms were expected to result in a decreasing
19 gradient of SOC with depth. SOC was significantly higher at recharge sites than at reference
20 sites but it did not exhibit any decreasing trend with depth that might have indicated a
21 preferential retention of DOC in the uppermost layers of groundwater. In slow filtration
22 columns, the first cm of sediment which exhibited the highest removal rates of BDOC and
23 DO also had a distinctively higher SOC concentration. SOC accumulation within this
24 uppermost layer probably reflected a biological retention and/or assimilation of BDOC rather
25 than a physical adsorption of BDOC onto mineral particles because our C to O₂ molar ratio of

1 0.65 effectively corresponded to values reported in the literature for microbial degradation of
2 BDOC (Bauerfind 1985; Pusch & Schwoerbel 1994; Roy et al. 1999). Baker et al. (1999) did
3 not observe any acetate sorption onto aquifer sediment samples of Rio Calaveras that were
4 incubated for 30 min in acetate solutions with concentrations ranging from 1 to 100 mg C l⁻¹.

5
6 Our conclusion that vertical gradient of DOC and DO at recharge sites was essentially due to
7 water mixing might seem to contradict our interpretation of a positive relation between DO
8 and VZT being caused by mineralization of DOC leached to groundwater at reference sites.
9 Depending on the biodegradability of DOC leached to groundwater at recharge sites, the
10 contact time of water with sediment in the upper layers of groundwater could be too short to
11 result in a detectable decreasing trend in DOC and DO with depth. At site 1, the vertical
12 velocity of stormwater in the upper layers of groundwater during rainfall events was found to
13 average 7 m day⁻¹ based on phase difference between time series of specific conductance at
14 multiple depths below the groundwater table (Foulquier et al. 2009). This vertical velocity
15 was 10 times higher than that estimated at reference sites using a three-dimension model of
16 groundwater flow in the glaciofluvial aquifer (Chastanet et al. 2008). Kalbitz et al. (2003)
17 who conducted out 90-day liquid incubation experiments with DOC from diverse soil samples
18 found a mean residence time of 3.3 to 8.9 days for the labile DOC pool and 0.3 to 12.5 years
19 for the stable DOC pool.

20
21 Our results suggest that non retentive processes such as water mixing or differential residence
22 time of water can lead us to over-estimate the ability of groundwater to act as a sink of DOC
23 being transported through the vadose zone. They highlight the need for detailed studies of
24 coupled hydrological and biogeochemical processes for determining the DOC retention
25 capacity of the upper layers of groundwater. Current research in this glaciofluvial aquifer is

1 examining the relationship between DOC composition as evaluated by excitation-emission
2 fluorescence spectroscopy (Kalbitz et al. 2003) and SR in the upper layers of groundwater
3 under different recharge conditions.

4

5

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7

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16

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5 dissolved oxygen. Ground Water 45:447-460

6

7 .

1

Figure captions

2 Figure 1: Fate of DOC during infiltration of surface water in the soil, vadose zone and
3 groundwater. Vertical change in DOC concentration below the groundwater table may
4 either result from water mixing or biological uptake of DOC in groundwater.

5

6 Figure 2: **A.** Locations of recharge sites (stormwater infiltration basins) and reference sites. **B.**
7 Cross sectional illustration of well clusters at site 1 to 5.

8

9 Figure 3: Schematic diagram of a slow filtration column and description of the sampling
10 procedure.

11

12 Figure 4: Relationships between the concentrations of dissolved organic carbon (DOC) and
13 dissolved oxygen (DO) in groundwater and vadose zone thickness at reference sites (left
14 panels) and recharge sites (right panels).

15

16 Figure 5: Changes at depth below the groundwater table in: 1) the relative proportion of
17 stormwater into groundwater (left panels); 2) measured (black circles) and calculated
18 (white circles) concentrations of dissolved organic carbon (DOC) (middle panels) and; 3)
19 measured (black circles) and calculated (white circles) concentrations of dissolved oxygen
20 (DO) (right panels). Horizontal bars show ± 1 standard deviation for 3 rainfall events at
21 sites 1 and 2 and 3 replicate wells at sites 3 to 5.

22 Figure 6: Calculated values from the two-end member mixing model based on chloride
23 concentrations versus measured values for specific conductance (Sp. Cond.), dissolved
24 organic carbon (DOC), and dissolved oxygen (DO). Values (n=72) were from all sites,

1 dates and depths. White symbols correspond to the uppermost depth. The line indicates
2 1:1 equivalence relationships.

3

4 **Figure 7:** Vertical gradients of dissolved oxygen below the groundwater table at recharge sites
5 1 and 2 before (grey circles) and after (black circles) rainfall events during the warm (left
6 panels) and cold (right panels) seasons. Horizontal bars show ± 1 standard deviation for
7 multiple rainfall events (n = 5 warm events and 5 cold events at site 1; n = 6 warm and
8 cold events at site 2).

9

10 **Figure 8:** Changes at depth below the groundwater table in sediment respiration (SR) and
11 sedimentary organic carbon (SOC) in upstream (white square) and downstream (black
12 circles) well clusters at sites 3 to 5. Horizontal bars show ± 1 standard deviation for 3
13 replicate wells.

14

15 **Figure 9:** Vertical gradients of sediment respiration (SR), sedimentary organic carbon (SOC),
16 dissolved organic carbon (DOC) and dissolved oxygen (DO) at day 26 in slow filtration
17 columns supplied with water containing 0.5 (upper panels), 1.5 (middle panels) and 2.5
18 (lower panels) mg C - sodium acetate l⁻¹.

19

20 **Table 1:** Characteristics of recharge (below stormwater infiltration basins) and reference sites.

21 Recharge at reference sites was derived only from the natural infiltration of rainwater
22 (0.24 m³ m⁻²).

23 **Table 2:** Results of analysis of covariance for testing the effect of recharge and vadose zone

24 thickness (VZT) on the concentrations of dissolved organic carbon (DOC) and dissolved
25 oxygen (DO).

1

2 Table 3: Results of nested analysis of variance for testing the effect of recharge and depth

3 below the groundwater table on the concentrations of dissolved organic carbon (DOC) and

4 dissolved oxygen (DO) in groundwater, sediment respiration (SR) and sedimentary

5 organic carbon (SOC).

6

7 Table 4: Results of analysis of variance for testing the effect of an increasing supply of labile

8 dissolved organic carbon (DOC as sodium acetate) and depth on removal rates of

9 dissolved organic carbon (RR-DOC) and dissolved oxygen (RR-DO) in slow filtration

10 columns, sediment respiration (SR) and sedimentary organic carbon (SOC).

Figure 1: Foulquier *et al.*

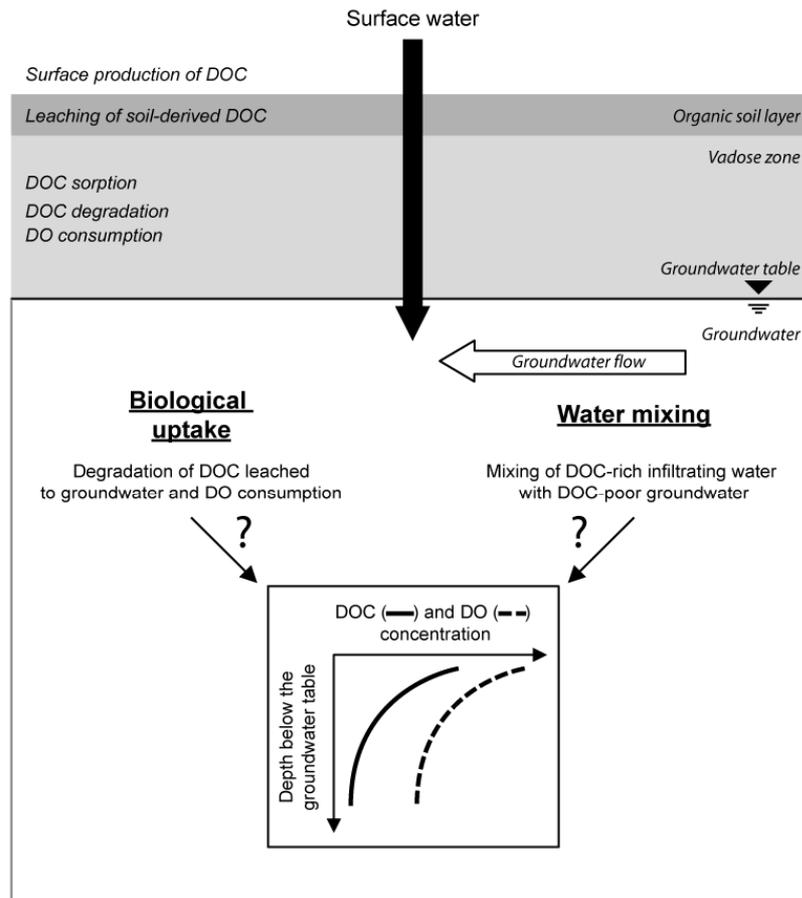


Figure 1: Fate of DOC during infiltration of surface water in the soil, vadose zone and groundwater. Vertical change in DOC concentration below the groundwater table may either result from water mixing or biological uptake of DOC in groundwater.

1

Figure 2: Foulquier *et al.*

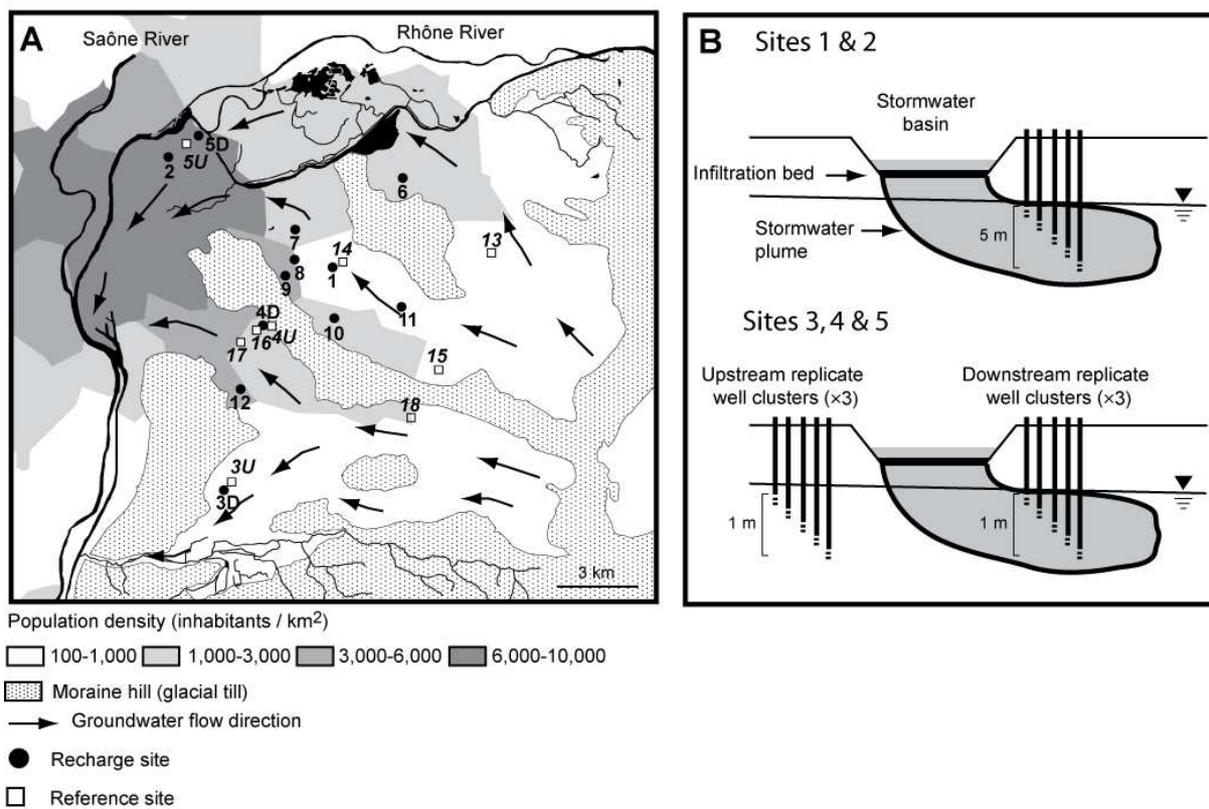
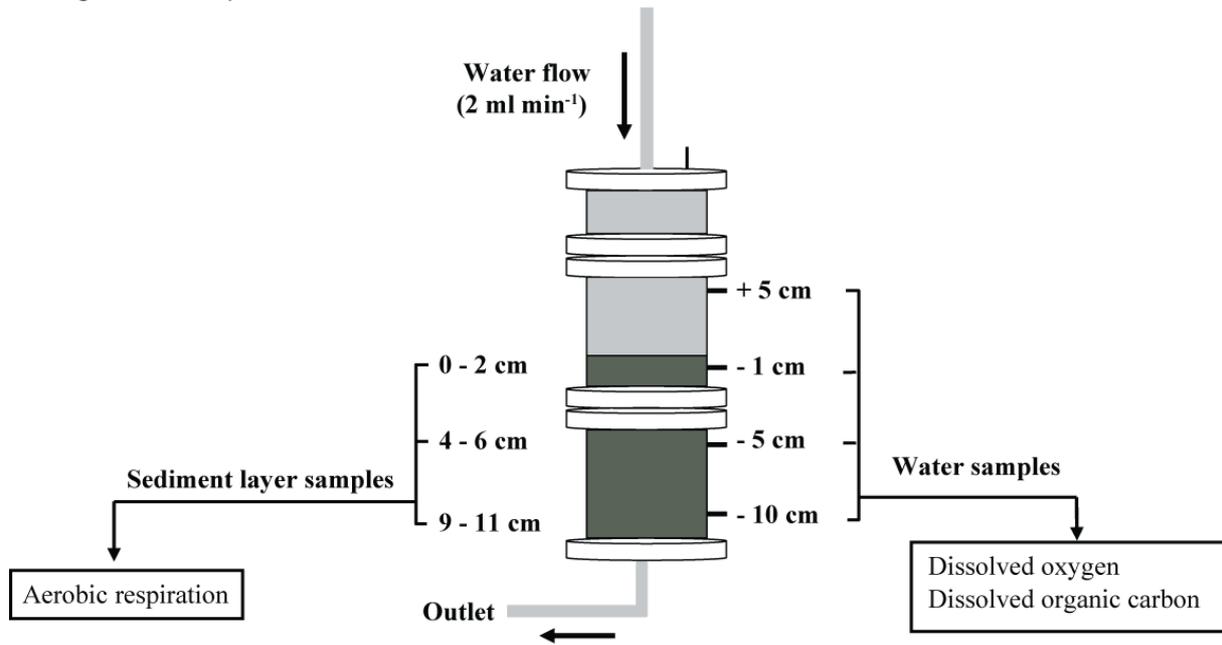


Figure 2: A. Locations of recharge sites (stormwater infiltration basins) and reference sites.

1 B. Cross sectional illustration of well clusters at site 1 to 5.

Figure 3: Foulquier *et al.*



1 Figure 3: Schematic diagram of a slow filtration column and description of the sampling procedure.

Figure 4: Foulquier *et al.*

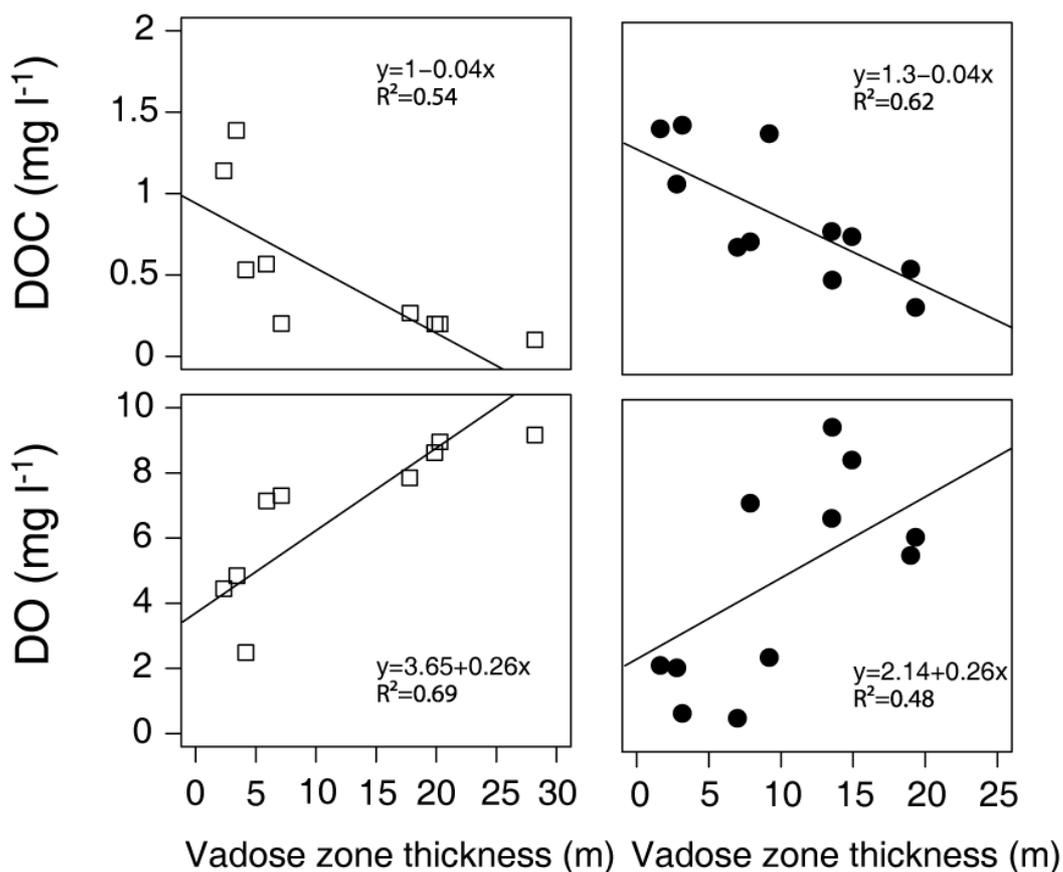


Figure 4: Relationships between the concentrations of dissolved organic carbon (DOC) and dissolved oxygen (DO) in groundwater and vadose zone thickness at reference sites (left panels) and recharge sites (right panels).

1

Figure 5: Foulquier *et al.*

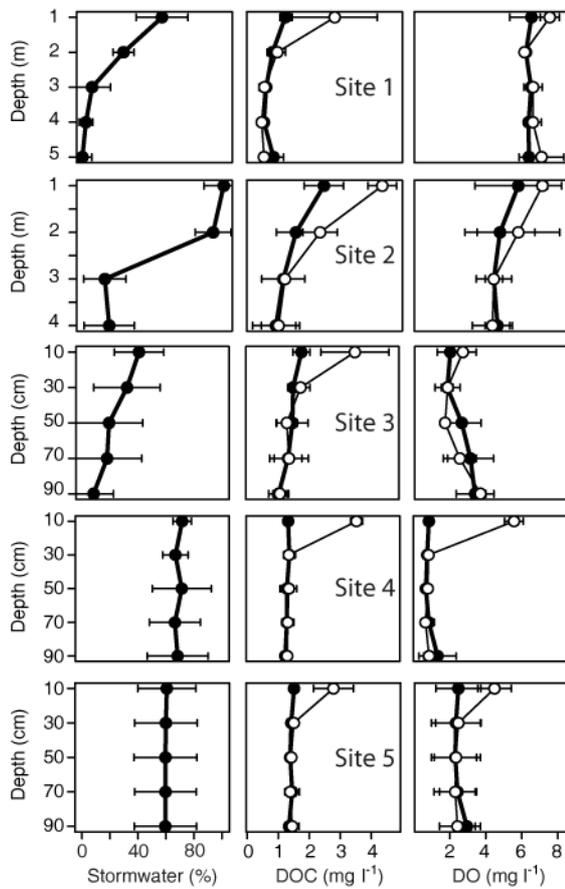


Figure 5: Changes at depth below the groundwater table in: 1) the relative proportion of stormwater into groundwater (left panels); 2) measured (black circles) and calculated (white circles) concentrations of dissolved organic carbon (DOC) (middle panels) and; 3) measured (black circles) and calculated (white circles) concentrations of dissolved oxygen (DO) (right panels). Horizontal bars show ± 1 standard deviation for 3 rainfall events at sites 1 and 2 and 3 replicate wells at sites 3 to 5.

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Figure 6: Foulquier *et al.*

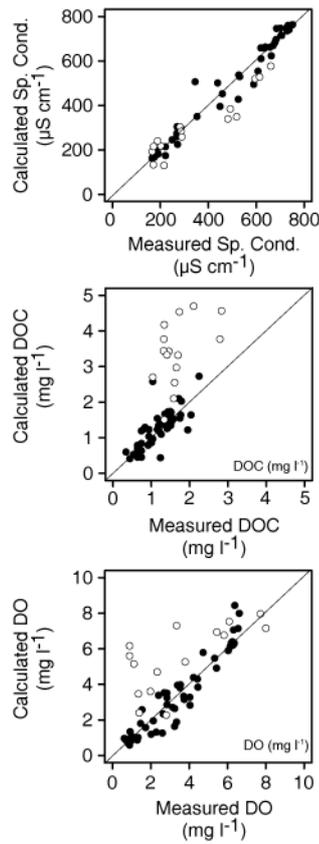


Figure 6: Calculated values from the two-end member mixing model based on chloride concentrations versus measured values for specific conductance (Sp. Cond.), dissolved organic carbon (DOC), and dissolved oxygen (DO). Values ($n=72$) were from all sites, dates and depths. White symbols correspond to the uppermost depth. The line indicates 1:1 equivalence relationships.

1

Figure 7: Foulquier *et al.*

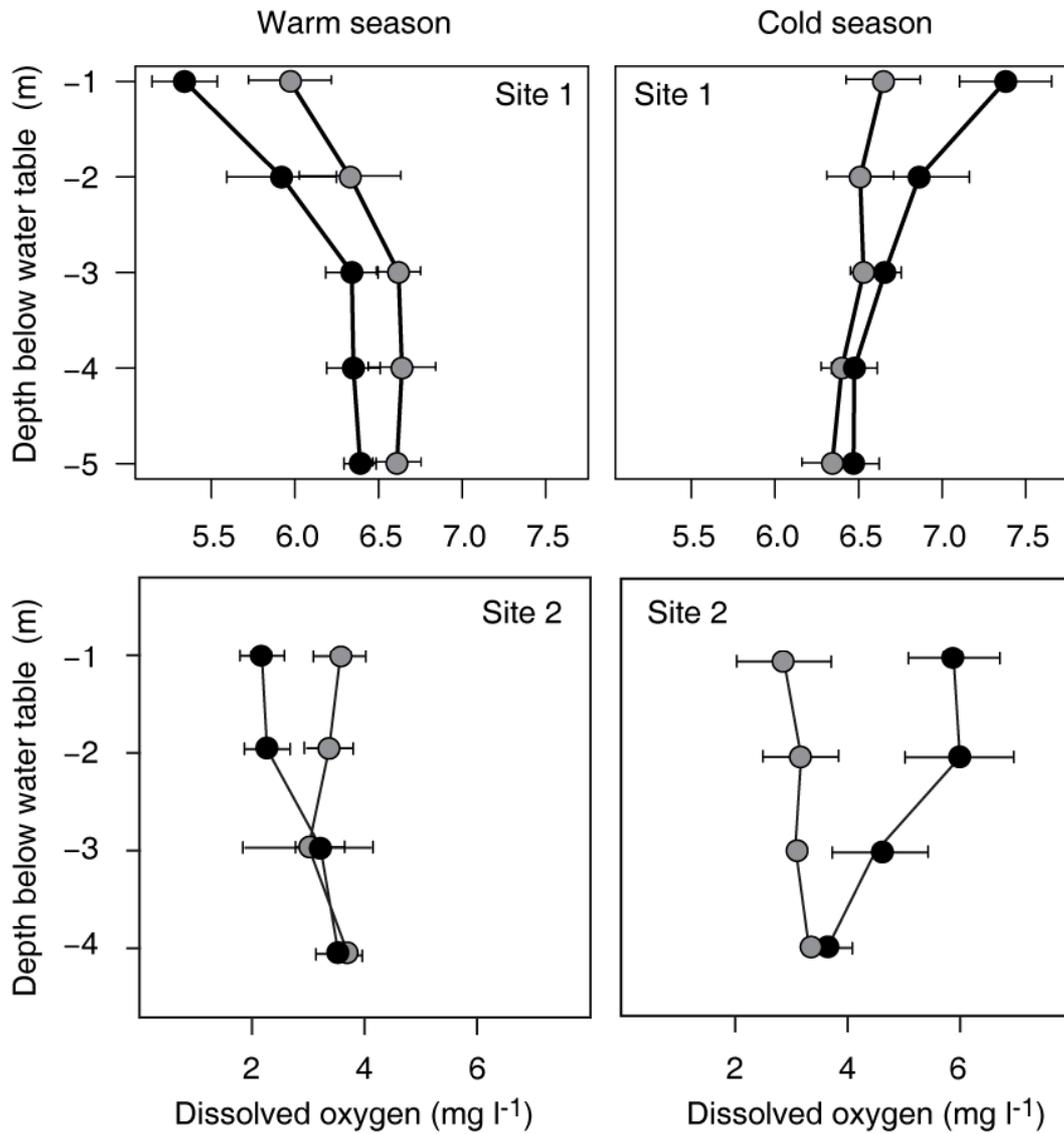


Figure 7: Vertical gradients of dissolved oxygen below the groundwater table at recharge sites 1 and 2 before (grey circles) and after (black circles) rainfall events during the warm (left panels) and cold (right panels) seasons. Horizontal bars show ± 1 standard deviation for multiple rainfall events ($n = 5$ warm events and 5 cold events at site 1; $n = 6$ warm and cold events at site 2).

1

Figure 8: Foulquier *et al.*

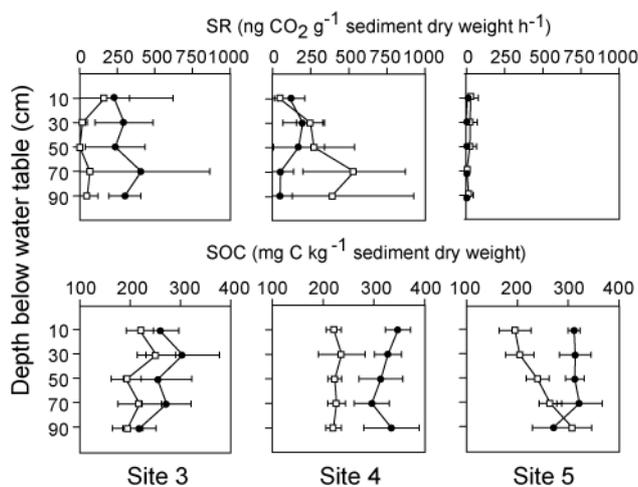


Figure 8: Changes at depth below the groundwater table in sediment respiration (SR) and sedimentary organic carbon (SOC) in upstream (white square) and downstream (black circles) well clusters at sites 3 to 5. Horizontal bars show ± 1 standard deviation for 3 replicate wells.

1

Figure 9: Foulquier *et al.*

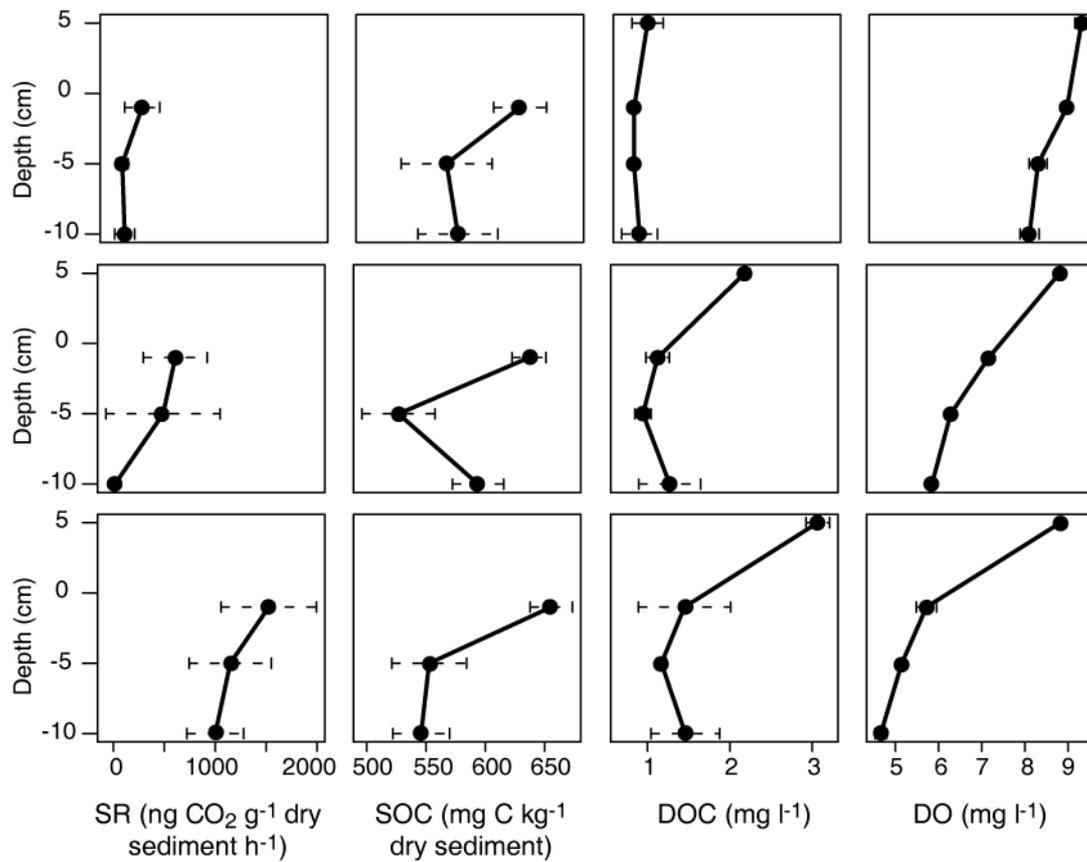


Figure 9: Vertical gradients of sediment respiration (SR), sedimentary organic carbon (SOC), dissolved organic carbon (DOC) and dissolved oxygen (DO) at day 26 in slow filtration columns supplied with water containing 0.5 (upper panels), 1.5 (middle panels) and 2.5 (lower panels) mg C - sodium acetate l⁻¹.

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Table 1: Foulquier *et al.*

Table 1: Characteristics of recharge (below stormwater infiltration basins) and reference sites. Recharge at reference sites was derived only from the natural infiltration of rainwater ($0.24 \text{ m}^3 \text{ m}^{-2}$)

Site	Type	Vadose zone thickness (m)	Catchment area (ha)	Basin area (ha)	Annual recharge ($\text{m}^3 \text{ m}^{-2}$)
1 *	Recharge	19.0	180.0	1.00	52.6
2 *	Recharge	2.8	2.5	0.08	9.7
3D *+	Recharge	1.7	100.0	0.40	73.1
4D *+	Recharge	3.2	270.0	0.39	202.3
5D *+	Recharge	2.8	2.5	0.08	9.7
6	Recharge	13.6	45.0	0.08	160.4
7	Recharge	15.0	51.0	0.12	119.7
8	Recharge	13.5	74.0	0.77	28.0
9	Recharge	9.2	33.7	0.11	89.5
10	Recharge	7.9	145.0	0.77	55.0
11	Recharge	19.3	50.0	0.15	97.4
12	Recharge	7.0	285.0	0.90	92.5
3U *‡	Reference	2.4			
4U *‡	Reference	3.5			
5U *‡	Reference	4.2			
13	Reference	28.2			
14	Reference	17.8			
15	Reference	20.3			
16	Reference	5.9			
17	Reference	7.1			
18	Reference	19.9			

* Well cluster sites

+ Downstream well clusters

‡ Upstream well clusters

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Table 2: Foulquier *et al.*

Table 2: Results of analysis of covariance for testing the effect of vadose zone thickness (VZT) and recharge on the concentrations of dissolved organic carbon (DOC) and dissolved oxygen (DO).

	df	DOC		DO	
		<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>
VZT	1	21.72	0.0003	17.70	0.0006
Recharge	1	8.33	0.0107	4.84	0.0429
Recharge × VZT	1	0.55	0.4705	1.34	0.2631
Error	16				

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Table 3: Foulquier *et al.*

Table 3: Results of nested analysis of variance for testing the effect of recharge and depth below the groundwater table on sediment respiration (SR), sedimentary organic carbon (SOC) and the concentrations of dissolved organic carbon (DOC) and dissolved oxygen (DO) in groundwater.

	df	SR		SOC		DOC		DO	
		<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>
Site	2	0.94	0.503	0.32	0.749	0.474	0.663	0.12	0.891
Recharge (Site)	3	2.21	0.140	17.36	< 0.001	52.40	< 0.001	109.59	< 0.001
Depth	4	0.93	0.492	0.33	0.853	3.79	0.050	12.12	0.002
Site × Depth	8	0.83	0.596	1.28	0.336	0.79	0.623	0.35	0.927
Recharge (Site) × Depth	12	1.10	0.378	1.69	0.091	1.04	0.429	0.90	0.551
Error	60								

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Table 4: Foulquier *et al.*

Table 4: Results of analysis of variance for testing the effect of an increasing supply of labile dissolved organic carbon (DOC as sodium acetate) and depth on sediment respiration (SR), sedimentary organic carbon (SOC) and removal rates of dissolved organic carbon (RR-DOC) and dissolved oxygen (RR-DO) in slow filtration columns.

	df	SR		SOC		RR-DOC		RR-DO	
		<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>
DOC supply	2	45.11	<0.001	0.06	0.944	4.43	0.027	101.78	<0.001
Depth	2	6.43	0.014	27.84	<0.001	41.07	<0.001	674.36	<0.001
DOC supply × depth	4	1.76	0.212	2.37	0.091	5.80	0.003	78.18	<0.001
Error	18								

1