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Effects of over-winter green cover on groundwater nitrate and dissolved organic carbon concentrations beneath tillage land

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HIGHLIGHTS

► We study groundwater $NO_3^- - N$ and DOC in tillage under over-winter cover treatments.
► Mustard treatment significantly reduced $NO_3^- - N$ and increased DOC in groundwater.
► This was not observed under natural regeneration treatment.
► Observed DOC increase is potentially important for groundwater denitrification.

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ABSTRACT

Application of over-winter green cover (e.g. cover crops) as a measure for reducing nitrate losses from tillage land has been frequently investigated, especially in the unsaturated zone. Monitoring of groundwater is less common in these studies. Studies on groundwater responses to different land treatments can be challenging because they can be influenced by various conditions, such as recharge, seasonal variations, and aquifer properties, often occurring at different time scales than surface water processes. The aim of this study was to evaluate groundwater nitrate ($NO_3^- - N$) and dissolved organic carbon (DOC) concentration responses to different over-winter green covers: mustard, natural regeneration and no cover. A field experiment was designed and run for three years on tillage land underlain by a vulnerable sand and gravel aquifer in the south-east of Ireland. Results showed that over-winter green cover growth on tillage land can be an effective measure to reduce groundwater $NO_3^- - N$ concentrations. A significant decrease in groundwater $NO_3^- - N$ concentrations was observed under the mustard cover compared to no cover. All treatments, including no cover, showed a decline in groundwater $NO_3^- - N$ concentrations over time. A significant increase in groundwater DOC was also observed under the mustard cover. Although the overall groundwater DOC concentrations were low, the increased DOC occurrence in groundwater should be accounted for in carbon balances and could potentially enhance groundwater denitrification in cases where aquifer conditions may favour it.

1. Introduction

Elevated nitrate (NO_3^-) concentrations in water can potentially impact human health, and also contribute to eutrophication of waters (Stark and Richards, 2008). Excessive NO_3^- leaching to groundwater is often associated with intensive tillage farming, especially in spring sown systems where land is left fallow over-winter (Neill, 1989). Two well-known important processes for reducing NO_3^- losses from tillage land are plant nitrogen (N) uptake (e.g. via cover crops) and denitrification which is, among others, considerably influenced by the presence of organic carbon (C).

The role of over-winter green cover (e.g. cover crops) growth as a mitigation measure to reduce NO_3^- leaching losses during the winter recharge period has been recognized and frequently studied (e.g. Aronsson, 2000; Bergström and Jokela, 2001; Francis et al., 1998; Hansen and Djurhuus, 1997; Hooker et al., 2008; Kaspar et al., 2007; Shepherd et al., 1993; Shepherd and Lord, 1996; Shepherd, 1999; Tonitto et al., 2006). Many of these studies estimate the effect on groundwater quality indirectly through unsaturated zone monitoring rather than directly through groundwater observations from the saturated zone using piezometers. However, in order to investigate the continuity from the unsaturated zone through to the saturated zone, the direct monitoring of groundwater responses is important.

The excess NO_3^- can also undergo denitrification processes in both the unsaturated and saturated zones. In subsoils the dissolved organic matter represents an energy source for denitrifying organisms

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(Jahangir et al., 2012a). Dissolved organic carbon (DOC) is thought to be one of the major limiting factors for groundwater microbial denitrification (Buss et al., 2005). The potential for groundwater denitrification in relation to groundwater DOC quantity and quality is a subject meriting further research. A review by Spalding and Exner (1993) reported some studies in which a sufficient amount of DOC was percolating to the shallow groundwater, suggesting possible NO_3^- loss via denitrification. In contrast, Siemens et al. (2003) argue that this is unlikely due to, among other reasons, low bioavailability of leached dissolved organic matter. DOC can have a complex role in soil biogeochemical processes. For example, DOC quality can affect microbial seasonal variations (Cannavo et al., 2004a). Many studies on dissolved organic matter have been conducted on soils using laboratory experiments and fewer under field conditions, with frequent contradiction between both (Kalbitz et al., 2000). Often only incomplete and sometimes contradictory information can be found regarding the effect of land use and management practices on the dissolved organic matter in soils (Chantigny, 2003). Studies on forest soils dominate the literature, but a limited number of such studies have been done on agricultural systems (McTiernan et al., 2001; Vinther et al., 2006).

Both NO_3^- and DOC can undergo temporal and seasonal variations in a shallow aquifer (Clay et al., 1996); thus, studies on the effect of land practices in agricultural systems on groundwater quality can be challenging. The geologic composition of sediment strata, climatic conditions and recharge play an important role in the groundwater quality responses. The design of groundwater field experiments can be difficult due to groundwater flow, which prevents statistical randomisation of field experiments. Therefore, groundwater field experiments need to be large in size, hydrogeologically uniform as much as possible, and with a design that minimises lateral groundwater flow between different treatments. Issues of time trends and lag times in water quality responses to farming practices also need to be considered (Fenton et al., 2009; Meals et al., 2010). Petry et al. (2002) also stress the importance of understanding the influence of agricultural catchment hydrological controls on nutrient fluxes and concentrations.

Our approach in this study was to investigate the groundwater quality under experimental treatment plots in a three year field experiment specifically designed for groundwater monitoring. The main objective of this study was to investigate the effect of different over-winter green cover treatments (mustard, natural regeneration and no cover) on groundwater NO_3^- and DOC concentrations. This study further aimed to investigate the temporal and seasonal dynamics of the groundwater NO_3^-, DOC and the accompanying groundwater physico–chemical parameters.

2. Materials and methods

2.1. Study site and experimental setup

The experiment was conducted under a temperate maritime climate in Teagasc, Oak Park Research Centre, Co. Carlow in south-eastern Ireland near the River Barrow, on an area under continuous tillage (spring cereals). Detailed information on the study area including results from hydrogeological investigations prior to experiment establishment is provided in Premrov et al. (2008). Information on effective rainfall and climatic conditions for the duration of experiment is summarised in Table 1. The average annual precipitation during 2002 to 2008 was 818 mm. The long term annual precipitation during 1961 to 2001 was 838 mm, measured at the Met Éireann weather station in Kilkenny, located c. 40 km south-east from the experimental site (data-source: Met Éireann, The Irish Meteorological Service).The site has shallow, well drained Cambisol soil based on the FAO Reference Soil Group classification (FAO, 2001) which is very prone to leaching due to its highly gravelly and sandy texture (Conry and Ryan, 1967; Thorn, 1983). The soil at the experimental field (Sawmills Field) is gravelly and sandy (Premrov, 2011). The soil is underlain by fluvioglacial sands and gravels of Pleistocene age; the investigations were focused on this vulnerable sand and gravel aquifer. The aquifer is recharged by effective rainfall, and groundwater discharges as baseflow in the River Barrow (Daly 1981, GSI 2002). The sediment sequence contains some localised clay/silt lenses, which were shown to be discontinuous at the selected experimental field and thus not representing a significant barrier for solute transport (Premrov et al., 2008; Premrov et al., 2009a).

The investigated shallow fluvioglacial sand and gravel aquifer is underlain by a deeper Carboniferous limestone aquifer (Conry, 2006; Daly, 1981). However, the focus of this study was on the overlying fluvioglacial deposits, due to their potential importance as a pathway for transport of pollutants to surface water receptors (Fenton et al., 2009). The overlying sand and gravel deposits at the experimental area in Oak Park extend only to a depth of c. 10 to 15 mbgl (Jahangir et al., 2012b). This corresponds to an average saturated zone thickness of c. 10 m [after taking into consideration the depth to the saturated zone at the experimental field (Premrov, 2011)]. Therefore, the size of treatment plots in this study (of c. 1.5 ha/plot) is estimated as relatively large compared to a relatively moderate thickness of the investigated fluvioglacial sand and gravel aquifer.

Details of the experimental design are described previously by Premrov et al. (2007). In brief, the experiment included establishment of three over-winter green cover treatment plots (c. 1.5 ha/plot in

Table 1
Summary of climatic conditions for the duration of experiment [estimation of effective rainfall is based on daily soil–water balance using Premrov et al. (2010a); data-source: Teagasc, Oak Park on-site weather station, Met Éireann, The Irish Meteorological Service].

Year	Mean temperature[a] [°C]	Minimum temperature[a] [°C]	Maximum temperature[a] [°C]	Rainfall [mm/year]	Actual evapo–transpiration [mm/year]	Effective rainfall [mm/year]
2002	9.7	−1.1	18.7	914	435	478
2003	10.0	−1.7	22.1	599	424	175
2004	10.0	−1.1	20.2	787	505	284
2005	10.2	−1.1	20.4	732	490	240
2006	10.4	−0.8	21.4	909	495	415
2007	10.5	−1.2	20.5	844	504	340
2008	9.6	−1.6	19.5	946	540	413
2009[b]	6.8[b]	3.1[b]	10.5[b]	373[b]	189[b]	175[b]

[a] Daily temperature.
[b] Period: 1/01/2009–19/05/2009. Yearly values not available.

size, within the 10 ha Sawmills Field, Fig. 1a): 1. mustard cover crop (M), 2. natural regeneration (NR) i.e. the regeneration of natural vegetative growth including growth of weeds, grasses and cereal volunteers, and 3. no cover (NC) — i.e. treatment sprayed each year with herbicide in autumn after the harvest of spring cereals.

The treatment plots were established each year after the harvest of spring cereals, with the first establishment in 2006. The treatment plots were applied during the three over-winter seasons: 2006/2007, 2007/2008 and 2008/2009. Spring cereal crops were grown from c. March to August each year (i.e. spring wheat in 2006 and spring barley in 2007, 2008 and 2009). Fertilisers (inorganic N fertiliser and KCl) were applied at the field (information on N and Cl^- fertiliser application rates is important because both NO_3^- – N and Cl^- were monitored in the groundwater). The fertilisers applied during 2004 to 2009 were mainly in the inorganic form [inorganic N fertiliser "Super Nett" (27%N + 3.7%S) and KCl]; cattle slurry was applied once in 2004. Different crops were cultivated prior to the start of this experiment in 2004 and 2005 resulting in the range of annual N rates 212.0 to 287.0 kg/ha N and Cl^- rates 142.9 to 171.1 kg/ha Cl^- (including Cl^- from slurry). During the experiment the annual fertiliser application rate for N ranged from 115.0 to 135.0 kg/ha, and for Cl^- from 34.5 to 90.7 kg/ha. The N fertiliser rate in 2006 was slightly lower than in other years as spring wheat was grown in experimental area prior to the start of the experiment. The N fertiliser rates in 2007 to 2009 were 135 kg/ha and the Cl^- application rates varied slightly between years due to the varying soil potassium requirements determined by soil testing.

The plots and groundwater monitoring network were orientated parallel to the dominant groundwater flow direction (north-east to the south-west towards the river; Fig 1a), avoiding any unsuitable areas, such as the areas with possible aquifer semi-confinement or unsuitable past land use (Premrov et al., 2007), to ensure hydrogeological homogeneity of the experiment, and to minimise the lateral flow between treatments and the surrounding farm land. The orientation and location of treatment plots (Fig. 1a) show that M and NC affect the areas outside the monitored treatments; NR affects Plots 1 and 2 equally. NR outside the Plot 3 has also a function of a "buffer" zone against the potential effects from surrounding land.

The soil at the field (corresponding mainly to A horizon) was described as a sandy loam with gravel stones (Premrov, 2011) and it was observed to cover the whole Sawmills Field. Sediments that were collected from the borehole drillings (below A horizon) were also described and analysed, and the parameter Cu (coefficient of

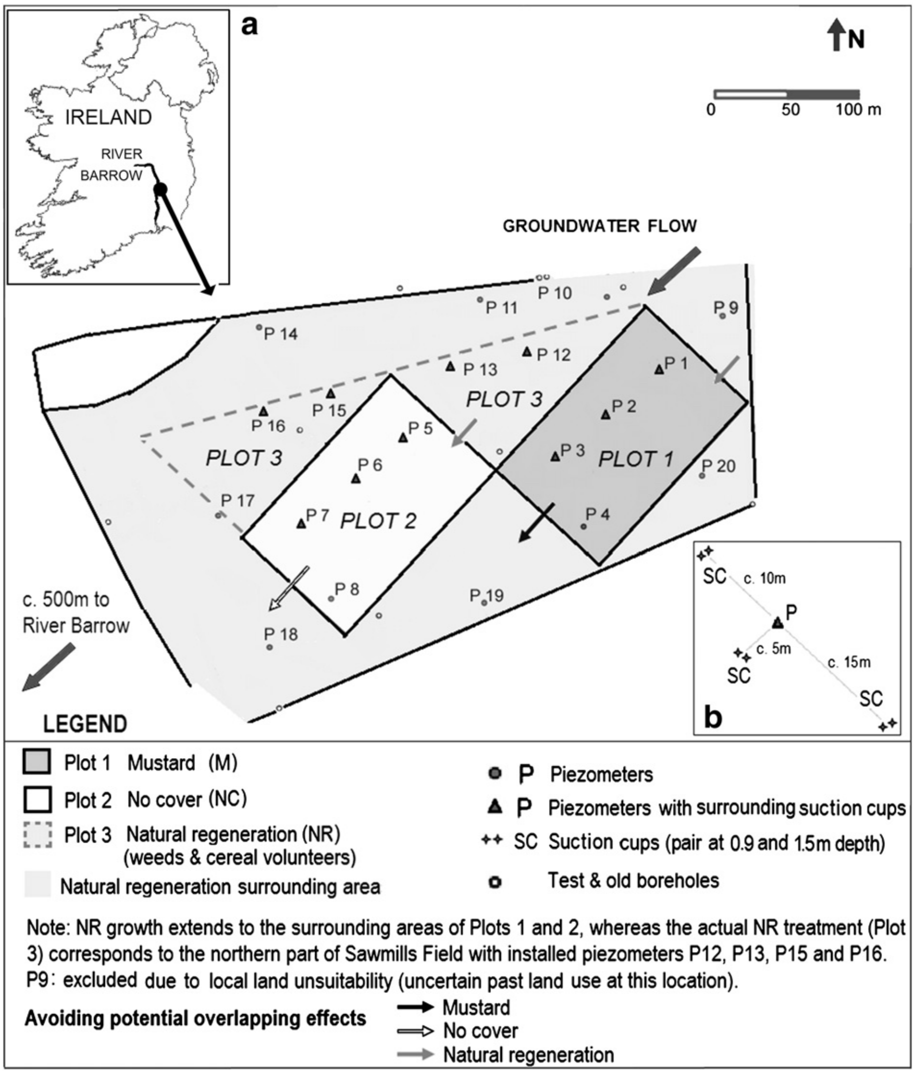

Fig. 1. Schematic illustration of the groundwater experiment (Sawmills Field): (a) position of the instrumented treatment plots relative to the groundwater flow direction; (b) position of the installed pairs of suction cups surrounding each selected piezometer [Top left (schematic presentation of site location in Ireland) — adapted from http://d-maps.com/pays.php?lib=ireland_maps&num_pay=198&lang=en (d-maps.com, 2012); (a) — adapted from Premrov et al. (2007, 2009a), with permission].

uniformity) was obtained for different layers of these sediments (Premrov, 2011). Obtained Cu values were analysed using one way ANOVA in R version 2.11.1 (The R Foundation for Statistical Computing, 2010) and they showed no significant difference in sediments beneath the three treatment plots. The hydrogeological investigation confirmed the suitability of the established groundwater experiment in terms of its hydrogeological homogeneity (with dominance of sand and gravel under the treatments) and its orientation relative to the main groundwater flow direction (Premrov, 2011).

The hydrogeological investigations also confirmed relatively short solute travel times through the unsaturated zone (Premrov et al., 2009a) with the possible impact of land surface activities on shallow groundwater quality within a single season, depending on climatic conditions (Premrov, 2011). For example, a tracer test showed 70 days for vertical tracer transport from the ground surface to the water table at 1.8 m (based on the first tracer detection) (Premrov et al., 2009a); (corresponding to vertical tracer movement of 0.03 m per day); and 175 days for lateral tracer transport over a distance of 81 m through the saturated zone, following the main groundwater flow direction towards the river (Premrov et al., 2009a); (corresponding to lateral tracer movement of 0.46 m per day). This indicates that the shallow sand and gravel aquifer can potentially represent an important pathway for transport of water soluble pollutants to the nearby surface water receptor (i.e. River Barrow, c. 500 m south-west of the experimental site).

2.2. Field and laboratory methods

The groundwater monitoring network consisted of 20 piezometers (12 piezometers under different treatments and 8 surrounding piezometers, with P9 excluded, as explained in Fig. 1a). Piezometer pipes (Van Walt, UK) screened across the groundwater level were installed in the sand and gravel aquifer to a depth of c. 4 mbgl following the U.S. Geological Survey guidelines and standard procedures (Lapham et al., 1997). Further methods of borehole drilling, piezometer installation, levelling and mapping using a Geographic Positioning System (GPS) instrument, and water level (WL) measurements are explained in Premrov et al. (2008).

In addition, unsaturated zone nitrate leaching was investigated using pairs of ceramic suction cups (SDEC, Reignac sur Indre, France) installed at 0.9 and 1.5 mbgl following the methodology described in Hooker et al. (2008). Suction cups were installed vertically surrounding each of 10 selected piezometers within treatment plots (see Fig. 1a and b). In this groundwater experiment, the unsaturated zone monitoring locations (Fig. 1a) were designed to coincide with the saturated zone monitoring locations, and therefore did not adhere to randomised plot designs [these are the subject of a separate unsaturated zone study with a larger number of land use permutations in a neighbouring field (Premrov, 2011)]. Suction cups had to be secured before spring ploughing by removing the suction tubing above the soil surface and sealing them. The tubing was re-installed in each autumn. Soil solution samples were taken fortnightly over each winter sampling period.

Groundwater was sampled after removing 3 well volumes using a peristaltic pump. Samples were filtered in the field using 0.45 μm filters (Filtropur S 0.45, Sarstedt, Germany). Regular sampling of groundwater was done from the start of the experiment in November 2006 until early March 2009 at one to two week intervals for NO_3^- – N analysis, whereas sampling for DOC was done c. once monthly from April 2008 to March 2009. DOC was also analysed on samples from selected dates prior to April 2008 that had been preserved by freezing. Suction cups were sampled for soil solution NO_3^- – N analysis fortnightly from c. November until early May the following year for the first two over-winter seasons (2006/2007 and 2007/2008) following the methodology described in Hooker et al. (2008). Further details on groundwater and soil solution sampling are provided in Premrov et al. (2008). All samples were transported in cool boxes and stored at c. 4 °C until laboratory analysis, which was generally performed within 24 to 48 h of sampling. Groundwater physico–chemical parameters [pH, temperature (T), redox potential (Redox), electrical conductivity (EC) and dissolved oxygen (DO)] were measured on site c. once monthly from May 2008 onwards using a Troll 9500 probe (In-Situ Inc., USA) and flow-through cell attached to the peristaltic pump on low purging speed.

Groundwater and soil solution total oxidised N (TON) concentrations were determined on a Thermo Konelab discrete analyser (Thermo Scientific, Finland), with a detection limit of 0.25 mg/l for total oxidised N. Samples were also analysed for NO_2^-, NH_4^+, dissolved reactive phosphorus (DRP), and Cl^-. NO_3^- – N was calculated by subtracting NO_2^- – N from TON. In addition, a groundwater sample batch was analysed on a TOC-V instrument (Shimadzu, Japan) for total N (TN) which showed that c. 96.2% of TN was NO_3^- – N.

The groundwater DOC concentration was determined on a TOC-V instrument (Shimadzu, Japan). DOC analysis performed on frozen samples was statistically verified on a full sample batch vs. analysis on fresh samples and no significant difference was found (t-test, $p>0.05$). The DOC analysis result is referred to as non-purgeable organic carbon (NPOC), which was determined by first eliminating the inorganic C from samples via acidification and bubbling through by sparging gas and the remaining C was measured (Brennan, 2009; Shimadzu Corporation, 2003). The detection of low DOC concentrations using NPOC method was possible down to the method detection limit of 0.05 mg/l.

In addition to regular c. monthly groundwater DOC analysis, a single groundwater sample batch was sampled in September 2009. These samples were analysed on a Varian Cary Eclipse Fluorescence Spectrophotometer (Varian Inc., USA) after the Raman water calibration to obtain the excitation emission matrix (EEM) profile of dissolved organic matter (mainly DOC due to low presence of organic N). EEM was used to determine the humification index (HIX) applying the methodology adapted from Zsolnay (2003) and Cannavo et al. (2004b), described in Premrov et al. (2010b).

Green cover plant biomass (0.5 m × 0.5 m area) was sampled each year (10 random samples per treatment) prior to spring ploughing. Plant Kjeldahl digestate was analysed on a Burkard Series 2000 continuous segmented flow analyser (Uxbridge, UK) to obtain the N% of the plant dry matter. Poor over-winter plant growth occurred in 2009 and consequently some samples had to be bulked together for the plant N analysis.

2.3. Statistical analysis and computation of effective rainfall

The effects of green cover treatments on groundwater solute concentrations and groundwater physico–chemical parameters were assessed by fitting generalised linear mixed models (GLMM). The models were fitted to the average responses over time for each treatment (i.e. 4 piezometers per treatment for three treatments: M, NC, and NR; see Fig. 1a) using SAS (SAS Version 9.1), Glimmix procedure. A GLMM contains random effects in addition to the usual fixed effects. A random effect was included to account for non-independence due to the spatial correlation of piezometers. The structure of the variance–covariance matrix for the random effect was selected using a variogram fitted to the data from all P piezometers (P1 to P20 with the exception of P9, see Fig. 1a) which were GPS positioned. Alternative structures were compared using Akaike's Information Criterion and the Gaussian structure was selected as the best fit. The correlations between the groundwater solute concentrations, groundwater levels (which depend on recharge) and major physico–chemical groundwater parameters were also evaluated.

The treatment effect on plant dry biomass and plant N uptake was analysed using the Welch two-sample t-test using R version 2.11.1 (The R Foundation for Statistical Computing, 2010). Effective rainfall (Table 1) was computed using the soil moisture deficit (SMD) crop model by Premrov et al. (2010a) and daily measured input

Table 2
Dry matter plant biomass and plant N uptake by M and NR.

Year	Cover (n = 10 per treatment)	Dry matter biomass ± S.E.[a] (kg/ha)	N uptake ± S.E.[a] (kg N/ha)
2007	M	1196 ± 101.1	31 ± 1.5
	NR	1223 ± 180.9	24 ± 2.1
	M[a] vs. NR	p = 0.806[d]	**p<0.05**[b,d]
2008	M	3371 ± 242.8	81 ± 5.3
	NR	1659 ± 211.4	39 ± 6.2
	M vs. NR	**p<0.001**[b,d]	**p<0.001**[b,d]
2009	M	158 ± 24.8	6 ± 0.8
	NR	87 ± 34.9	3 ± 1.1
	M vs. NR[c]	p = 0.120[d]	**p<0.05**[d]

[a] S.E. - Standard error.
[b] Significant p values highlighted in bold (significance at 0.05 level); logarithm transformations and statistical analysis done on g N/m^2 (original measurements); means transformed to kg N/ha.
[c] Normality (Shapiro–Wilk test) after natural logarithm data transformation at 0.005 level (i.e. p > 0.005).
[d] Welch two-sample t-test.

parameters from the on-site weather station. The model predicts soil moisture deficit (SMD) and effective rainfall for a free draining arable soil under spring cereal cultivation in Ireland. It is a dynamic, deterministic, model that uses water-mass balance daily time-step calculation (Premrov et al., 2010a). The SMD crop model was developed on the basis of an SMD grassland model by Schulte et al. (2005), and it includes additional design of a crop model component, model calibration and validation against the field data Premrov et al. (2010a). Results from hydrogeological investigations by Premrov (2011) proved a linear relationship between groundwater level (WL) and effective rainfall after taking into account the time lag necessary for the response of WL to the effective rainfall.

3. Results and discussion

3.1. Over-winter green cover effects

3.1.1. N uptake

N uptake by mustard (M) was significantly higher than by natural regeneration (NR) in all three years of the experiment (Table 2). Annual N uptake by M ranged from 6 to 81 kg N/ha (Table 2). The over-winter plant biomass was significantly higher in M treatment compared to NR only in one of the three years (2007/2008). The results from this experiment showed that the N uptake by NR growth was close to uptake rates found for some other popular cover crops, i.e. rye and ryegrass (>30 kg N/ha) as reported by O'Keeffe et al. (2005). Cover crop N uptake differed between years and was highest in 2007/2008 which is in agreement with the low $NO_3^- - N$ concentrations in soil solution (Fig. 2) and in groundwater (Fig. 3) during that time. The rates of N uptake by both M and NR were within the cover crop N uptake ranges reported in some other studies: e.g. up to 35 kg N/ha (Allison et al., 1998) and >50 kg N/ha (O'Keeffe et al., 2005) for mustard crop; up to 126 kg N/ha (Thorup-Kristensen et al., 2009) for winter wheat.

Autumn soil N uptake by cover crops and their ability to capture N through the winter period is a crucial factor in reducing the over-winter nitrate leaching losses; thus, it is important that cover crop growth is commenced as early as possible (Thorup-Kristensen et al., 2009). According to Feaga (2004) there is a risk of reduced efficiency of cover crops during large rainfall events if the cover crop rooting system is not properly established at the time. In this experiment, the mustard cover crop was sown in mid-September each year.

Leaching during the summer months and extreme temperatures or other climatic conditions can also influence the over-winter green cover growth. Schroder et al. (1996) concluded from a long-term 6-year study that plant N uptake (for rye and grass cover crops) was more a function of the winter temperatures than the available mineral nitrogen in the soil. The poor plant N uptake observed in this study during the winter 2008/2009 (Table 2) may have resulted from 1. high rainfall during the summer and the harvest-season in 2008 [205 mm effective rainfall 01/06/2008 to 30/09/2008], resulting in poor germination and in less available soil N (due to leaching) for green cover establishment and growth; 2. low winter temperatures (minimum −1.6 °C), with frost known to be able to cause plant biomass losses (Vos and van der Putten, 1997).

3.1.2. $NO_3^- - N$

Mean groundwater nitrate ($NO_3^- - N$) concentrations over the three year period were 18.0 mg/l for the mustard (M) cover crop, 22.4 mg/l for natural regeneration (NR), and 23.9 mg/l for the no cover (NC) treatment. Mean groundwater $NO_3^- - N$ concentrations were significantly lower under M than under NC (p<0.05; Table 3). This was not observed under NR treatment.

Reductions in groundwater nitrate concentrations from this field experiment are compared with some results from other studies performed on cover crops in Table 4. The observed $NO_3^- - N$ groundwater reductions from this experiment (based on the 3-year mean values) were found to be either relatively close to or somewhat below the reductions found in some examples with comparable climates (Table 4). The broad range in nitrate reductions in the groundwater achieved using various cover crops reported in the literature is not surprising, considering that crop type and growth, and various other environmental conditions will influence the results.

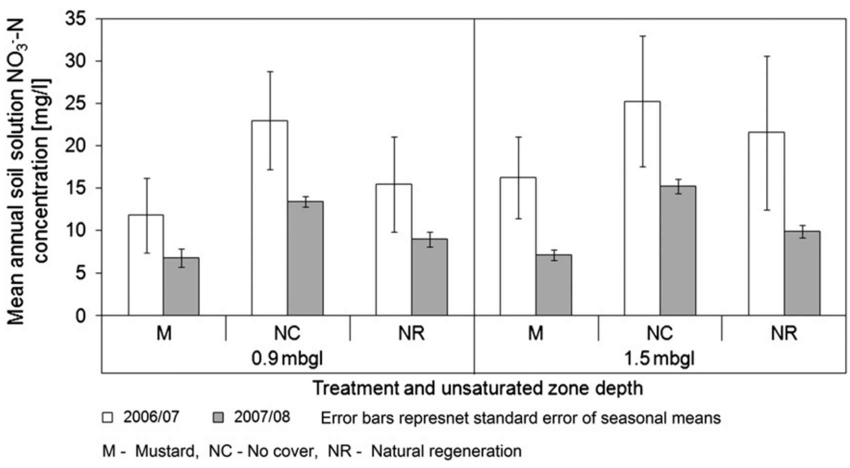

Fig. 2. Mean annual unsaturated zone soil solution $NO_3^- - N$ concentrations at 0.9 and 1.5 mbgl for different treatments in 2006/2007 and 2007/2008 seasons.

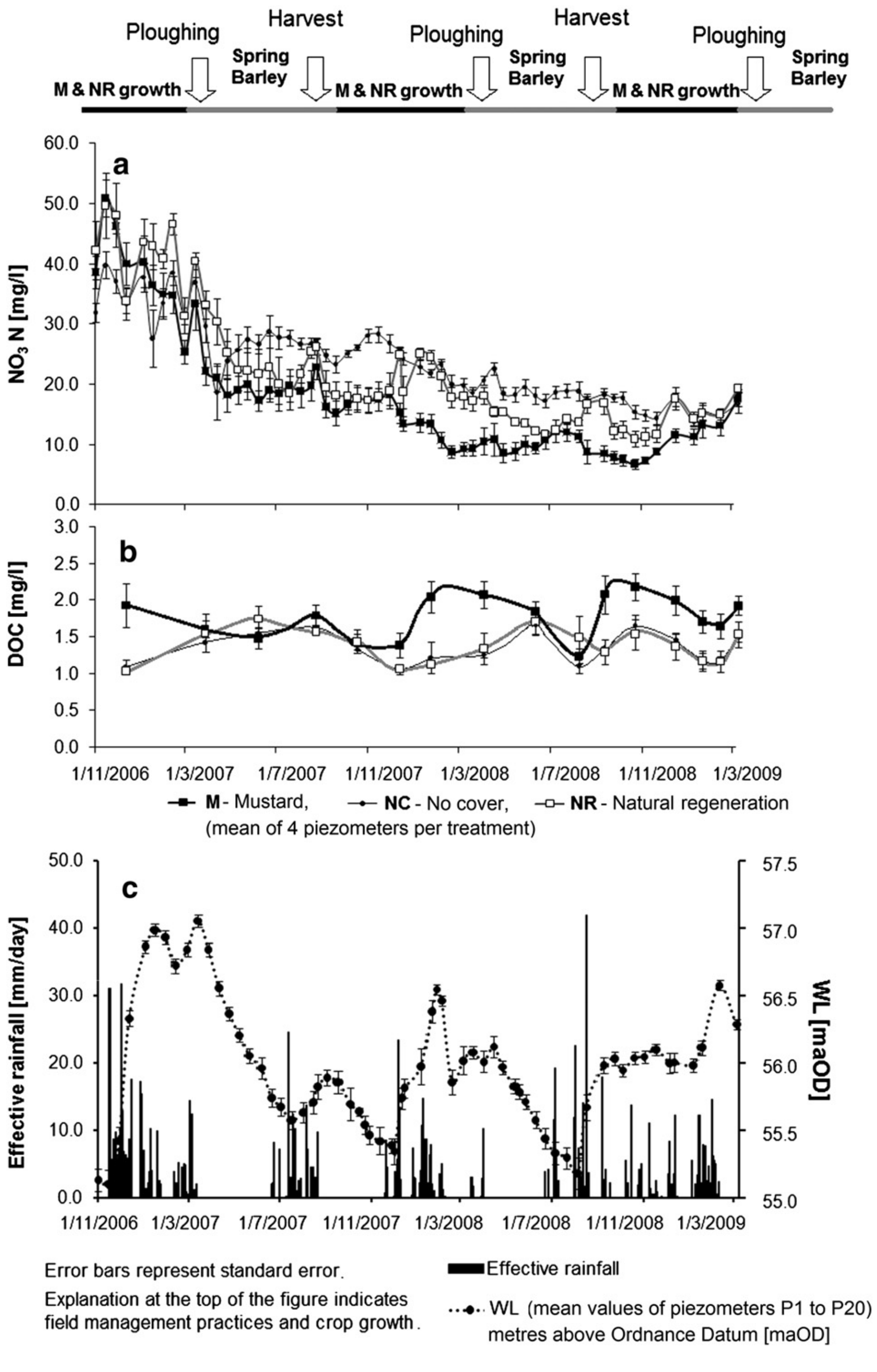

Fig. 3. Groundwater nitrate [NO_3^- – N] (a) and dissolved organic carbon [DOC] (b) concentrations over time under the three green cover treatments in relation to seasonal variability depending on effective rainfall and groundwater level [WL] (c); [DOC concentrations (b) and the illustration/explanation indicating field management/crop growth (top) were initially reported in conference proceedings (Premrov et al., 2009b; used with permission)].

The NO_3^- – N reductions observed in the groundwater results were mirrored by the unsaturated zone monitoring, which also found the lowest over-winter mean NO_3^- – N concentrations under M treatment for both sampling seasons 2006/2007 and 2007/2008 (Fig. 2). Mean soil solution NO_3^- – N concentrations were lower in 2007/2008 compared to 2006/2007 which was also observed in the groundwater.

Elevated groundwater NO_3^- – N concentrations, initially observed in 2006 (Fig. 3a), generally exceeded the drinking water (DW) limit [11.3 mg/l NO_3^- – N; (European Communities, 1998)] by more than three times. These concentrations then gradually decreased during the next two sampling years (2007/2008 and 2008/2009): i.e. the groundwater NO_3^- – N concentrations under M treatment decreased to <20 mg/l from c. September 2007 on, and they decreased to close to or below the DW limit during c. February to mid-December 2008; for NC and NR treatments they decreased to <20 mg/l from c. February/May 2008 on (Fig. 3a). Although the mean values (Table 3) exceeded the DW limit, Fig. 3a shows an overall consistent drop of NO_3^- – N concentrations in the groundwater over time. The NO_3^- – N concentrations under M dropped below the DW limit during the second over-winter season 2008 (Fig. 3a).

Table 3
Treatment means of groundwater solute concentrations and physico–chemical parameters presented along with standard errors of differences (S.E.D.), and comparisons of treatment means conducted using t-tests derived from the GLMM applied to each response (averaged over the time from 2006 to 2009).

	Cover[a]	Mean	Comparing covers	S.E.D.[b]	Test of difference t_{15}[c]	p-value
NO_3^- – N [mg/l]	M	18.0	M vs. NR		−1.99	0.065
	NR	22.4	M vs. NC		−2.67	**0.018**
	NC	23.9	NR vs. NC	2.23	−0.68	0.510
DOC [mg/l]	M	1.78	M vs. NR		2.4	**0.030**
	NR	1.38	M vs. NC		2.62	**0.019**
	NC	1.35	NR vs. NC	0.163	0.22	0.832
Cl − [mg/l]	M	26.2	M vs. NR		−0.28	0.785
	NR	27.1	M vs. NC		−1.36	0.193
	NC	30.8	NR vs. NC	3.36	−1.09	0.294
T [°C]	M	10.17	M vs. NR		0.12	0.904
	NR	10.14	M vs. NC		0.93	0.365
	NC	9.94	NR vs. NC	0.250	0.81	0.429
pH	M	7.69	M vs. NR		−2.53	**0.023**
	NR	7.92	M vs. NC		−4.18	**0.001**
	NC	8.07	NR vs. NC	0.091	−1.65	0.121
EC [µS/cm]	M	480.7	M vs. NR		1.95	0.070
	NR	459.1	M vs. NC		1.75	0.100
	NC	461.3	NR vs. NC	11.09	−0.2	0.846
DO [mg/l]	M	10.05	M vs. NR		0.37	0.717
	NR	9.90	M vs. NC		0.04	0.967
	NC	10.03	NR vs. NC	0.388	−0.33	0.748
Redox [mV]	M	208.2	M vs. NR		2.58	**0.021**
	NR	200.5	M vs. NC		4.61	**0.0003**
	NC	194.6	NR vs. NC	2.95	2.03	0.061

[a] Over-winter green cover treatments.
[b] S.E.D. is the standard error of the difference between two treatment means; it is calculated using linear contrasts with the Glimmix procedure in SAS.
[c] t_{15} (t-value, degrees of freedom 15); significant contrasts ($p<0.05$) are highlighted in bold. Comparisons of treatment means are conducted using t-tests derived from the GLMM applied to each response (averaged over time), with treatment included as a fixed effect and a Gaussian random effects structure to allow for non-independence of wells due to spatial correlation.

Table 4
Reductions in NO_3^- – N concentrations from this experiment compared with some examples from the literature.

Study	Over-winter green cover	Reduction NO_3^- – N by (%)
This experiment; groundwater (3-year study)	Mustard natural regeneration	25%[a] 6%[a]
Meisinger et al. (1991); groundwater (1-year study)	Rye	c. 29%[a]
McLenaghen et al. (1996); deep unsaturated zone (80-day study)	Mustard	44%[a]
Staver and Brinsfield (1998); unsaturated zone and groundwater (7-year study)	Rye	c.80% (unsaturated zone)[b,d] c. 50–75% (groundwater)[c,d]
Feaga (2004) and Feaga et al. (2010) water flux to groundwater[e] (11-year study)	Variety of cover crops (rye, triticale, rye/wheat hybrid, common vetch/ triticale)	c. 29 to 41%[a,d,f] (depending on fertiliser type)

[a] Compared to fallow/no cover/bare soil.
[b] Reduced annual nitrate leaching losses.
[c] After 7 years of cover crop use: rye 7 years, fallow 3 years.
[d] Calculated from reported results.
[e] Passive capillary samplers (below root zone) at 1.2 m dept.
[f] Annual reductions.

3.1.3. Groundwater DOC and physico–chemical parameters

The low mean groundwater DOC concentrations observed in this study (<3 mg/l; Table 3, Fig. 3b) were in agreement with the expected low organic C content of glacial and fluvioglacial stratified sediments, based on the reported DOC values for selected UK lithologies — e.g. sands and gravels; Carboniferous limestone (UK Environmental Agency data reported in Buss et al., 2005). Lower soil organic carbon content is also known to be more generally typical for long term arable cropping systems than for grassland or forest soils (e.g. Chantigny, 2003; Gregorich et al., 1995). The longer the duration of arable cropping, the greater is the decrease in the soil water extractable and labile organic C content (Haynes, 2000; Saviozzi et al., 1994). Soil C is known to be present in subsoil horizons at low concentration; however according to a review by Schmidt et al. (2011), this C can be still important because it represents >1/2 of the global soil C stocks (Jobbagy and Jackson, 2000).

Overall mean DOC concentrations were 1.78 mg/l under M, 1.38 mg/l under NC and 1.35 mg/l under NR. Mean groundwater DOC concentration was significantly higher under M treatment than under NC and NR ($p<0.05$; Table 3). Fig. 3b shows higher DOC concentrations observed under M during the over-winter growth period compared to the other two treatments. The effects of the treatments become more pronounced and obvious after the winter cover growth period when DOC concentrations under M exceeded those under NC and NR (between January and March/April of 2008 and 2009; Fig. 3b).

Although the observed increase in groundwater DOC under M cover crop compared to the other two treatments was quite low in absolute terms (c. 0.4 mg/l DOC), it was nevertheless statistically significant (Table 3). A variety of factors may have contributed to enhancing the C pool below the M cover crop in this experiment (e.g. possible presence of plant litter originating from the green cover, plant root exudation, possible differences in the stimulation of microbial activity or productivity etc. under different treatments).

DOC was not monitored in the unsaturated zone in this experiment due to questionable suitability of ceramic suction cups for DOC sampling (Buckingham et al., 2008). Contradictory examples can be found in the literature in regard to cover crop effect on DOC leaching. For example Walmsley et al. (2011) found that cover crop in combination with non-inversion tillage did not increase DOC leaching losses (mustard; unsaturated zone <0.5 mbgl) in a spring cereal production on a sandy loam soil in south-east Ireland. In contrast, Vinther et al. (2006) observed an increase in the amount of leached DOC under a cover crop compared to bare soil (perennial ryegrass; unsaturated zone 0.3 to 0.9 m depth), and a decrease in DOC concentrations with depth in sandy loam soil in Denmark in a spring cereal production (after ploughed grass-clover) followed by cover crops.

The single sample batch, for which HIX values of DOC were determined, provided the following results: HIX of 1.92 (M), and 1.90 (NR, NC); DOC of 1.67 mg/l (M), 1.18 mg/l (NR) and 1.22 mg/l (NC). The groundwater HIX (<2.0) showed that most of the organic compounds in the groundwater correspond to small organic molecules (Cannavo et al., 2004b). The results from this study are generally comparable to the low HIX values found by Cannavo et al. (2004a) on a tillage site with high vulnerability to groundwater pollution by agricultural practices (HIX of c. 2 at 1–2 m unsaturated zone depth).

The results of measured groundwater physico–chemical parameters are provided in Table 3. Green cover treatments had significant effects on both pH and Redox, whereas there was no significant effect on T, EC and DO. Generally high DO levels were observed in the groundwater with mean values close to 10 mg/l. M had significantly lower groundwater pH and Redox compared to both NR and NC. The significant relationship between green cover treatment and groundwater pH (with the slightly lower pH under M) (Table 3) could be due to the higher DOC concentrations (i.e. possibly due to the presence of additional organic acids). The high groundwater DO (Table 3, Fig. 4) is typical for a shallow air-saturated groundwater (Buss et al., 2005); whereas the observed Redox was slightly lower than expected [DO >1 mg/l should generally have a redox potential of >300 mV (Krešić, 2007)].

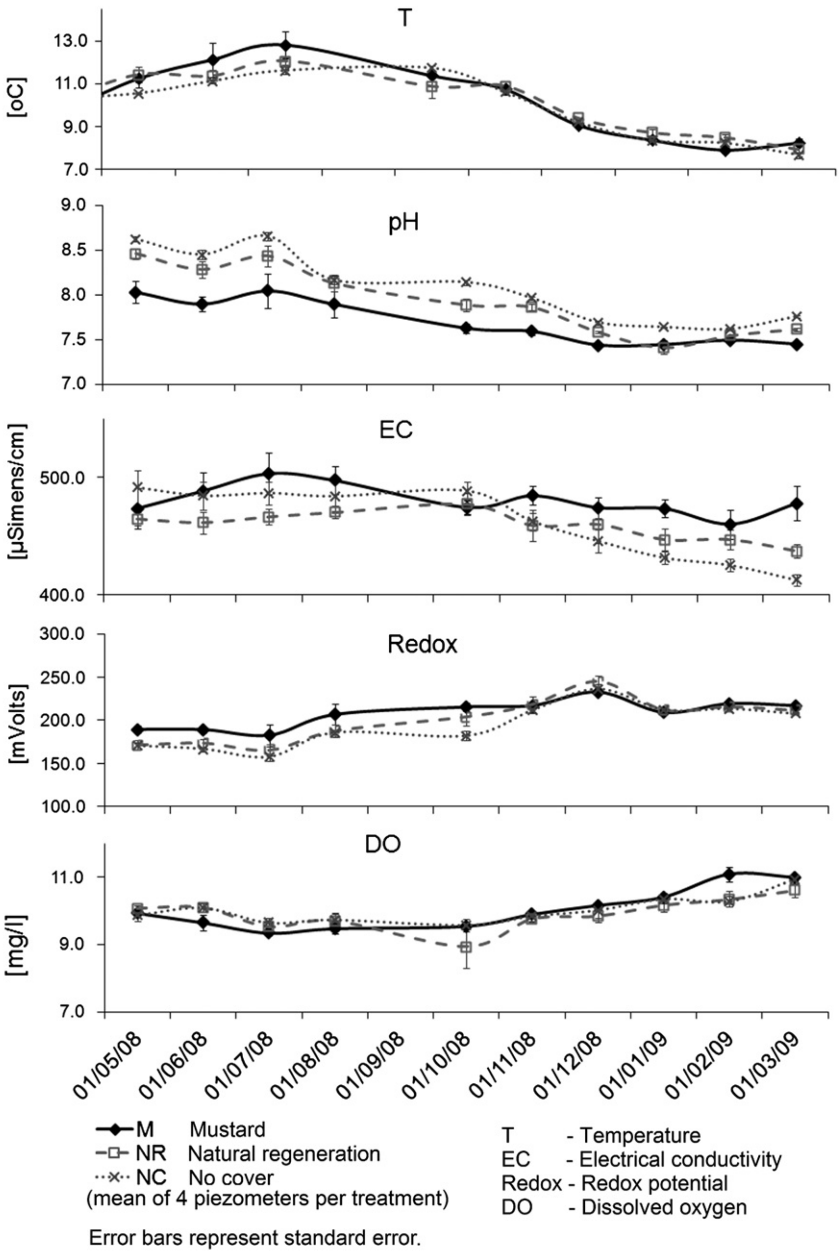

Fig. 4. Groundwater physico–chemical parameters under different treatments during May 2008 to March 2009.

The observed high groundwater DO and low DOC indicates that denitrification may be unlikely to occur at this site. Relevant microbial species would generally require oxygen concentrations as low as 0.7 to 0.01 mg/l (8 °C), (Krešić, 2007). The high DO and low DOC suggest that carbon could already be used prior to denitrification due to the oxidation of DOC [10.3 mg O_2/l uses up c. 3.8 mg C/l (Buss et al., 2005)]. However, it should be noted that these values relate to groundwater abstracted by the peristaltic pump (on low purging speed), and it is possible that there may be localised anoxic microenvironments within the aquifer corresponding to small pockets of lower permeability sediment, which might provide potential locations for denitrification. Also, although high DO concentrations may be typical for the shallow saturated zone of this type of highly permeable fluvioglacial deposit, other aquifers/sediments can contain lower DO levels. In such situations the increase of DOC via green cover could be a beneficial factor enhancing groundwater denitrification.

Table 5
Correlation coefficient matrix of monitored groundwater solute concentrations, physico–chemical parameters and WL.

$NO_3^- - N$	**0.66**							
DOC	−0.05	**−0.24**						
WL	**0.41**	0.05	−0.10					
T	**−0.50**	**−0.25**	0.09	**−0.72**				
pH	**−0.28**	0.12	**0.21**	**−0.56**	**0.55**			
EC	0.05	**0.17**	−0.06	**−0.43**	**0.55**	**−0.28**		
DO	**0.22**	0.08	**0.22**	**0.36**	**−0.55**	**−0.30**	**−0.52**	
Redox	**0.28**	−0.08	**−0.26**	**0.52**	**−0.51**	**−0.88**	**−0.31**	**0.23**
	Cl^-	$NO_3^- - N$	DOC	WL	T	pH	EC	DO

Correlations (Pearson) based on the data from P piezometers (P1–P20, with exception of P9; Fig. 1a) from 3-year monitoring period. Values set in bold are significant at $p<0.05$.

3.1.4. Other monitored groundwater constituents

Mean groundwater chloride (Cl^-) concentrations over the 3-year period under different treatments showed no statistically significant difference (Table 3). Cl^- is a mobile ion which undergoes less assimilation than NO_3^-, but plants can also uptake some Cl^- (White and Broadley, 2001). However, no significant difference in Cl^- was observed among different plant treatments in this experiment. The lowest $NO_3^- - N/Cl^-$ ratio was observed under M, reflecting the lowest groundwater $NO_3^- - N$ concentrations of the three treatments. Mean groundwater $NH_4^+ - N$ and DRP concentrations over the period of 3 years detected under all treatments were below the method detection limits of 0.09 mg/l for $NH_4^+ - N$ and 0.005 mg/l for DRP.

3.2. Seasonal and temporal effects

Seasonal variability was observed in some groundwater results. The over-winter green cover growth periods overlapped with the winter groundwater recharge periods (Fig. 3) with both having an effect on the groundwater. Correlations between the monitored groundwater solute concentrations, physico–chemical parameters and WL are provided in the correlation coefficient matrix in Table 5 (with WL being a function of effective rainfall as explained in Section 2.3). The groundwater Cl^- was significantly correlated with WL (since green cover did not have significant effect on it; Table 3); whereas $NO_3^- - N$ and DOC were not significantly correlated with WL (Table 5), which indicated that they were more strongly influenced by green cover treatment effects than by recharge. In addition WL was negatively correlated with T, pH and EC and positively correlated with DO and redox. The increase in groundwater DOC concentrations reflects the period of the presence of M cover crop treatment. DOC increase occurred in the spring of 2008 and 2009 (before ploughing of mustard, usually in March) with a slight time delay (Fig. 3b). This delay is in agreement with the observed time delay from a Br^- tracer experiment at this site [i.e. c. 70 to 160 days for vertical transport from the ground surface to the saturated zone (Premrov et al., 2009a), which is also strongly dependent on the amount of effective rainfall]. Groundwater physico–chemical parameters in this shallow aquifer also varied seasonally: T and pH were higher in summer than in winter (Fig. 4), with T and pH being positively correlated (Table 5). This can be explained by lower CO_2 solubility at higher T (Appelo and Postma, 2005).

The temporal pattern of elevated concentrations (under all treatments) at the beginning of groundwater monitoring in 2006 with a gradual decrease in the concentrations over the time was observed for both $NO_3^- - N$ and Cl^-, but not for DOC concentrations (Fig. 3). This observed temporal pattern may have been due to climatic conditions and groundwater recharge or due to the higher annual rate of fertilisation prior to the start of this experiment, or both.

4. Conclusions

This three year field experiment showed that the establishment of over-winter green cover, with sufficient growth and N uptake, such as mustard cover crop in this experiment, on tillage land during the over-winter recharge period can be a good measure for reducing nitrate leaching losses from tillage land to groundwater. In this experiment, a significant reduction in groundwater $NO_3^- - N$ concentrations was observed under the M (mustard), compared to NC (no cover). Nitrate observations from the unsaturated zone under M (at 0.9 and 1.5 m deep) were in agreement with the groundwater results.

A significant increase in groundwater DOC concentrations was also observed under the M over-winter cover crop. Although the overall observed groundwater DOC concentrations were small, they should be still accounted for in carbon balances. The increased groundwater DOC concentrations under M may potentially enhance groundwater denitrification (in localised anoxic microenvironments within this aquifer or in aquifers with less permeable deposits and lower DO) thereby further reducing groundwater nitrates.

Temporal and seasonal patterns were observed in the groundwater results reflecting the meteorological factors and over-winter green cover treatments — i.e. observed were elevated groundwater $NO_3^- - N$ concentrations at the beginning of the experiment with a gradual decrease over time; seasonal increase in groundwater DOC concentrations was observed in spring (reflecting the period of the presence of mustard cover crop treatment with a time delay). Seasonal variability and groundwater recharge influenced the groundwater physical–chemical parameters. The sustained decrease in groundwater $NO_3^- - N$ concentrations over the three year experimental period requires further long term investigation to assess the environmental driver.

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