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<th>Holistic evaluation of field-scale denitrifying bioreactors as a basis to improve environmental quality.</th>
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Abbreviations:
sustainability index (SI)
dissolved reactive phosphorus (DRP)
greenhouse gas (GHG)
dissolved organic carbon (DOC)
particulate nitrogen (PN)
total organic carbon (TOC)
maximum admissible concentration (MAC)
total dissolved nitrogen (TDN)
woodchip (WC)
sandy loam soil (SLS)
global warming potential (GWP)
dissimilatory nitrate reduction to ammonium (DNRA)
weighting factor (WF)
hydraulic loading rate (HLR)

Abstract

Denitrifying bioreactors effectively convert nitrate-nitrogen (NO$_3$-N) to di-nitrogen and thereby protect water quality in agricultural landscapes. In the present study, the performance of a pilot-scale bioreactor (50 m long, 5 m wide and 2 m deep) containing seven alternating cells, filled with either sandy loam soil or lodgepole pine woodchip, and with a novel zig-zag flow pattern, was investigated. The influent water had an average NO$_3$-N concentration of 25 mg L$^{-1}$. The performance of the bioreactor was evaluated in two scenarios. In scenario 1, only NO$_3$-N removal was evaluated, whereas in scenario 2, NO$_3$-N removal, ammonium-N (NH$_4$-N) and dissolved reactive phosphorus (DRP) generation was considered. These data were used to generate a ‘sustainability index’ (SI) – a number which evaluated the overall performance taking these parameters into account. When the bioreactor performance was evaluated in scenario 1, it was a net reducer of contaminants, but it transformed into a net producer of contaminants in scenario 2. Inquisition of the data using these scenarios meant that an optimum bioreactor design could be identified. This would involve the reduction of the filter length such that it comprised only two cells – a single sandy loam soil cell, followed by a woodchip cell, which would remove NO$_3$-N, reduce greenhouse gas (GHG) emissions and DRP losses. An additional post-bed chamber containing media to eliminate NH$_4$-N may be added to this bioreactor. Scenario modelling such as that proposed in this paper, should ideally include GHG in the SI, but as different countries have different emission targets, future work should concentrate on the development of geographically appropriate weightings to facilitate the incorporation of GHG into a SI.

Keywords: denitrifying bioreactor; sustainability index; greenhouse gas; nitrate.
Introduction

A denitrifying bioreactor is an artificial nitrogen (N) sink in which an organic carbon (C) source (e.g. woodchip (WC)) is used to reduce nitrate (NO$_3$) in surface/subsurface drainage or groundwater flow systems (Cameron and Schipper, 2010). Research on denitrifying bioreactors (Schipper et al., 2010; Christianson et al., 2011) has focused on NO$_3$ removal, despite the fact that anthropogenic activities such as agriculture produce NO$_3$, as well as a range of other pollutants. Moreover, biophysical and biogeochemical processes occurring within denitrifying bioreactors frequently generate other contaminants such as nitrous oxide (N$_2$O), ammonia (NH$_3$), carbon dioxide (CO$_2$) and methane (CH$_4$), through ‘pollution swapping’ (Fenton et al., 2014). This issue has been discussed in the literature (e.g. Grennan et al., 2009; Elgood et al., 2010; Schipper et al., 2010; Woli et al., 2010; Shih et al., 2011; Warneke et al., 2011; Healy et al., 2012; 2014), but denitrifying bioreactors designed to control pollution swapping, such as permeable reactive interceptors, have only been examined at laboratory-scale (Fenton et al., 2014; Ibrahim et al., 2015).

Fenton et al. (2014) proposed that denitrifying bioreactors should be analyzed holistically, taking all losses into account. They presented a sustainability index (SI), using inlet and outlet data, which identifies the “losses” in the system. Positive and negative balances of each parameter indicate either removal or production of the parameter of interest. This analysis indicates which parameters require additional interventions for the system to be environmentally sustainable. Complete removal of nutrients without pollution swapping is the ultimate goal, but thresholds imposed by environmental legislation may not be so stringent. Therefore, a SI may be developed for various scenarios, taking water, gaseous emissions, or both, into account. Healy et al. (2014) adopted this method of analysis in the
evaluation of laboratory denitrifying bioreactors containing various C-rich media, and found that the SI varied depending on the scenario examined. Analyzing NO₃ only, there was a net removal in the bioreactors. When all measured water quality parameters (NO₃, ammonium (NH₄) and dissolved reactive phosphorus (DRP)) were taken into account, there was a net release of contaminants from all bioreactors, which substantially increased when greenhouse gases (GHG) were included in the analysis.

The objectives of this study were: (1) to investigate this method of analysis at a much larger scale using a novel outdoor, pilot-scale denitrifying bioreactor (2) to illustrate how a SI and may be used to develop a permeable reactive interceptor, which minimizes pollution swapping.

Material and Methods

Denitrifying bioreactor design

A concrete tank (10 m long × 5 m wide × 2 m deep), with internally flanged 0.2 m-deep base panels, was laid on a concrete plinth (Fig. 1). The base of the tank was lined with heterogeneous clay textured soil. Non-reactive, high density polyethylene plastic sheets were sealed into the clay liner to create seven equally sized cells. The plastic sheets were positioned such that solute migration was forced into a zig-zag pattern to increase the hydraulic retention time, although dead zones were inevitably created. The cells in the tank were filled with either lodgepole pine woodchip (WC1-3) or sandy loam soil (SLS) (SLS1-4) (Fig. 1). Water was pumped into the tank and discharged from the denitrifying bioreactor outlet into an artificial drainage system.
The WC used had a particle size ranging from 10 to 50 mm. Healy et al. (2012, 2014) and Ibrahim et al. (2015) observed high dissolved organic carbon (DOC) effluent concentrations in the early stages of operation of a denitrifying bioreactor. Therefore, prior to placement in the pilot-scale bioreactor, the WC was spread in a uniform layer (10 long × 5 wide × 0.2 m deep) in a clean, concrete holding area and regularly power-hosed using a mains water supply over nine days. To determine potential losses from the media cells and the clay liner, samples were tested for total N (TN) and total C (TC) using a thermal conductivity detector, following combustion and separation in a chromatographic column, and the total P (TP) content was determined by inductively coupled plasma emission spectroscopy (ICP-ES) after aqua regia digestion.

Water, dissolved gas and surface emission instrumentation and monitoring

The SI was conducted using inlet/outlet data, whereas the provenance of losses within the bioreactor was measured using nests of multi-level piezometers (inner diameter 0.05 m), installed at 12 positions within the denitrifying bioreactor (Fig. 1). Each nest had sampling ports at 0.1 m, 0.4 and 0.7 m below the surface. A fully screened piezometer, through which influent water was injected into the denitrifying bioreactor, was installed in SLS1 (Fig. 1). In each nest, gas impermeable tubing, with an inner diameter of 5 mm, was installed to the center of the screen interval. At the surface level, a three-way stop cock and 50 ml-capacity syringe (Fenton et al., 2011) was used to extract multi-level water and dissolved gas samples.

The denitrifying bioreactor was saturated, and influent potable mains water was pumped continuously from a storage compartment (Fig. 1) into position 0 from August 2011, at a rate of 0.2 to 0.3 m³ d⁻¹. The characteristics of the mains water are shown in Table 1. Water temperature in the denitrifying bioreactor was typically between 12 -14°C at all depths, the
pH was 6.3-7.2, and the electrical conductivity (EC) was 229-820 µS cm$^{-1}$. On March 22, 2012 (210 days after the start of operation), the NO$_3$-N concentration of the influent water was modified to a target concentration of 25 mg L$^{-1}$, by adding potassium nitrate (KNO$_3$) salt in the storage compartment and mixing thoroughly. This target influent concentration was maintained until the end of the study (August 2012). The outlet was another fully screened piezometer positioned at position 12 (SLS4; Fig 1).

Water samples were collected from the inlet and outlet, and from all nests (longitudinal and vertical profiles), over a 5-month period (February to August 2012, 14 sampling dates). Water samples were collected in 50 ml polyethylene screw top bottles. Unfiltered and filtered samples (0.45 µm filter membrane) were collected. Nitrate-N, NH$_4$-N, dissolved organic nitrogen (DON), particulate nitrogen (PN), DRP and dissolved unreactive P (DUP) were analyzed on a Thermo Konelab 20 analyzer (Technical Lab Services, Ontario, Canada). Dissolved Organic Carbon (DOC) concentrations were analyzed on a TOC analyzer (TOC-V series, Shimadzu, Kyoto, Japan). pH, EC (µS cm$^{-1}$), temperature (ºC) and oxidation redox potential (ORP) were measured using a multi-parameter Troll 9500 probe (In situ, CO, U.S.A.) with a flow-through cell.

Triplicate water samples were collected for all sampling events to identify potential denitrification in the screened interval of each piezometer, based on dissolved N$_2$ and the N$_2$/argon (Ar) ratio (Kana et al., 1998). The samples were transferred from the syringe to a 12 ml Exetainer® (Labco Ltd., U.K.), filled from the base of each container, overfilled, and then sealed with a butyl rubber septum to avoid any air entrapment. Samples were then placed upside down under water (below the average groundwater temperature of 12ºC) in an ice box, transported to the laboratory, and kept in a dark cold room at 4ºC prior to analysis. Dissolved
N₂ and Ar were analyzed using membrane inlet mass spectrometry at groundwater temperature (Kana et al., 1998).

To analyze dissolved gases (presented as N₂O-N, CO₂-C and CH₄-C), water samples were collected periodically in 160-ml glass serum bottles. The bottles were capped and evacuated prior to the sampling. Twenty ml of sample water was injected into the bottles, and then helium gas was filled to bring back to atmospheric pressure. After equilibration, the headspace was sampled and analyzed by gas chromatography equipped with an electron capture detector (N₂O-N analysis), a flame ionization detector (CH₄-C analysis) and a thermal conductivity detector (CO₂-C analysis) (CP-3800, Varian, Inc. USA) using Ar as a carrier gas (Jahangir et al., 2013).

Greenhouse gases from the bioreactor surface were measured using the static chamber method (Hutchinson and Mosier, 1981; Smith and Dobbie, 2001). Chambers consisted of a stainless steel structure with two components, a collar base (0.41 m × 0.41 m), and a lid (0.41 m × 0.41 m × 0.41 m), with a volume of 0.068 m³ above ground level. To provide a gas-tight seal, the collar base was filled with water. Chamber position was as in Fig. 1. Twenty ml samples were drawn through a rubber septum (Becton Dickinson, UK) 20 min and one hour after closure (Becton Dickinson, UK) using a 20 ml polypropylene syringe with a hypodermic needle (BD Microlance 3, Becton Dickinson, UK) and injected into pre-evacuated 7 ml screw-cap septum glass vials (Labco, UK). Gas concentration was quantified using gas chromatography (see above). As fluxes are calculated from gas accumulation within the chamber over time, samples were collected at four time-points per chamber (0, 15, 30 and 45 min after lid closure).
Sustainability Index and Damage Cost Approach

All parameters are expressed in g m\(^{-2}\) (of bioreactor surface area) d\(^{-1}\). A SI is then created by summation of all parameters (Fenton et al. 2014):

\[
SI = a(B_{\text{N}_\text{O}_3}) + b(B_{\text{NO}_x}) + c(B_{\text{CH}_4}) + d(B_{\text{CO}_2}) + \text{etc.}..... [1]
\]

where \(B_x\) denotes the net loss (either positive or negative) of a specific contaminant from the denitrifying bioreactor, and \(a, b, c, \text{etc.}\) are weighting factors (WF) that depend on the context of the analysis (e.g. legislative, environmental, geographical). The rationale of Fenton et al. (2014) was used to calculate the WFs. In the current study, two scenarios are examined. For scenario 1, in countries or geographical areas where only NO\(_3\)-N concentration is considered, the WF for NO\(_3\) is set to 1, while the other measured parameters are set to zero. For scenario 2, in which NO\(_3\)-N, NH\(_4\)-N and DRP are considered, the maximum admissible concentration (MAC) for these parameters is used to determine the WFs. In Ireland, for example, the MAC for molybdate-reactive P (MRP = DRP in the current study) and NH\(_4\)-N in rivers is 35 \(\mu\text{g L}\(^{-1}\) and 65 \(\mu\text{g L}\(^{-1}\), respectively, while NO\(_3\)-N in estuaries should not exceed 2.5 mg L\(^{-1}\) (Bowman, 2009). As DRP is the most sensitive parameter in this scenario, the WFs for DRP, NH\(_4\)-N and NO\(_3\)-N are set to 1, 0.538 (35/65) and 0.014 (35/2500), respectively. Calculating a WF for GHGs is more problematic, as there is no MAC for GHGs and, moreover, individual countries have very different targets in terms of their GHG commitments. For example, under the EU 2020 Climate and Energy Package (EC, 2012), the Republic of Ireland must reduce GHG emissions by 20% by 2020, whereas developing countries, such as China and India, have no international commitments in terms of emissions reduction. As a result, the WF for GHG used in the SI should reflect the relative importance of GHG limits in
terms of national policy objectives, and be set at a level that is nationally appropriate in terms of policy relative to other pollutants.

A damage cost approach was also used, which assigned a cost to each of the water quality and GHG parameters examined in terms of damage to the environment and human health (Eory et al., 2013; Anon, 2014). For the water parameters, the costs per tonne (converting from pounds sterling to euro at the time of writing) were €916 (NO\textsubscript{3}-N), €61553 (P) and €2458 (NH\textsubscript{4}-N) (Eory et al., 2013). A cost per year was assigned to scenarios 1 and 2 by substituting the unit costs for each pollutant as WFs in Eqn. 1. These values were multiplied by 365 to give yearly equivalents.

Results and Discussion

Media and woodchip washing

The WC had higher TN content than the clay liner and SLS cells (Table 2). However, the TP of the clay liner, WC and SLS were low, and were reflective of P-deficient agronomic grassland soils. In previous studies (Healy et al., 2014), there were considerable C, N and P losses from bioreactors immediately after the start of operation. In the current study, the concentrations of the NH\textsubscript{4}-N and DRP concentrations in the drainage water decreased from ~7 to <1 mg L\textsuperscript{-1} over the two washing periods, but were still relatively high, considering the TP content of the WC. This suggests that washing of the WC prior to installation in the bioreactor is an efficient means of reducing losses.

Carbon, Nitrogen and Phosphorus

The DOC and dissolved CH\textsubscript{4}-C concentrations were higher at the outlet than at the inlet of the denitrifying bioreactor (Fig. 2), and were highest in deep flow paths (Fig. 3), as a result of
prolonged interaction of water with the woodchip media. The highest dissolved CO$_2$-C and
CH$_4$-C concentrations (501 and 26 mg L$^{-1}$, respectively, Fig. 3) were measured in deep flow
paths, which is indicative of lower redox conditions at this depth.

Water temperature in the denitrifying bioreactor was typically between 12-14 ºC at all depths,
with pH ranging from 6.3 to 7.2, and EC ranging from 229 to 820 µS cm$^{-1}$. Nitrate-N and
DON concentrations were reduced within the denitrifying bioreactor, but NH$_4$-N
concentrations were higher at the outlet (Fig. 4). Most of the reduction of the NO$_3$-N occurred
in SLS1 and WC1 of the bioreactor (Fig. 5). It was also in these cells also that the highest
N$_2$/Ar (55 at the outlet of WC1; Fig. 5) and dissolved N$_2$O-N concentrations (1000 µg L$^{-1}$ at
the outlet of WC1; Fig. 5) were measured. This probably indicates that partial and full
heterotrophic denitrification occurred in these two cells, as a result of bioavailable DOC, a
sufficient supply of O$_2$ for N$_2$O formation, and short water transit-times. Dissolved organic
nitrogen concentrations increased from below detection to a maximum of 10 mg L$^{-1}$ after
amendment of the inlet water with KNO$_3$, but remained below 0.9 mg L$^{-1}$ at the outlet for the
entire study period (Fig. 4). Longitudinal patterns in the ORP decreased from positive values
in SLS1 to negative values in WC3, but increased in SLS2 (maximum increase of -121 to 111
mV) (data not shown).

In WC2, SLS3 and WC3 (sampling points 6 – 12), NO$_3$-N concentrations were below
detection, while N$_2$/Ar and dissolved N$_2$O-N concentrations decreased (Fig. 5). After
modification with KNO$_3$, NH$_4$-N generally increased from inlet to outlet (Fig. 5), and the
highest concentrations were observed in the deep water flow paths.
In Warneke et al. (2011) NH₄ ranged from <0.0007 mg L⁻¹ to 2.12 mg L⁻¹ and NO₂ concentrations ranged from 0.0018 mg L⁻¹ to 0.95 mg L⁻¹. Such concentrations were thought not to infer anammox as a likely mechanism for NO₃ removal in the denitrification bed. The increase in NH₄ has several plausible origins. These include dissimilatory nitrate reduction to ammonium (DNRA), suggested by Healy et al. (2014) to occur in denitrifying bioreactors where the media has a high C/N ratio (e.g. >12). DNRA is also energetically favored over denitrification in reducing conditions, where NO₃ becomes limited as an electron acceptor. Such a process is known to occur in artificially drained fields, where heavy textured soil with moderate permeability enables transformation to NH₄ from NO₃ (Necpalova et al., 2012). An alternative is ammonification of organic N compounds in the woodchip and release to the fluid phase, which is supported by corresponding increases in P. Such processes, together with the release of NH₄ from the SLS and WC, may contribute to an increase in NH₄-N concentrations. In the present study much of the NH₄ stems from within the bioreactor, illustrated by the high levels of NH₄ when compared with NO₃ in the pre-spike phase. This correlates well with the methane production, which could be a product of anaerobic N mineralization. However, in terms of removal of NO₃ when concentrations begin to drop, we propose that DNRA would be favored over NO₃ immobilization as given a choice, microbes preferentially use NH₄ over NO₃ for growth, as it is much more energy efficient to do so.

Before installation, washing of the woodchip media showed consistently high release of DRP concentrations. Over the entire study period, DRP, DUP and PP concentrations were higher at the outlet than the inlet (Fig. 4), but these concentrations decreased over time. The longitudinal data indicates that the WC cells (WC1 and WC2) were the source of DRP (Fig. 5). In addition, the heterogeneous clay liner, given its relatively high P content (Table 2), could have contributed to the P loss at specific locations.
Greenhouse gas emissions to the atmosphere

The N$_2$O-N (Fig. 6) emissions were greater in the first three cells (maximum N$_2$O-N emission of 70.0 mg N$_2$O-N m$^{-2}$ d$^{-1}$ in WC1), and were likely linked to partial denitrification. This also indicated that anoxic, as opposed to anaerobic conditions, prevailed in these cells. In contrast, CH$_4$-C and CO$_2$-C emissions (Fig. 6) peaked towards the outlet of the denitrifying bioreactor, and were linked to lower ORP at this position. Warneke et al. (2011) measured average surface emissions of N$_2$O-N and CO$_2$-C of 79 $\mu$g m$^{-2}$ min$^{-1}$ (or 113.2 mg m$^{-2}$ d$^{-1}$, comparable to current study) (reflecting 1% of the removed NO$_3$-N) and 12.6 mg m$^{-2}$ min$^{-1}$, respectively. Observed methane emissions were considerably higher than those reported for stream bed denitrifying bioreactors containing woodchip (Elgood et al., 2010), but were on a par with emissions from column studies (Healy et al., 2012) and indeed were in the lower range of values reported for landfill systems (Chanton and Liptay, 2000).

Conversion to a permeable reactive interceptor

The SIs calculated for the entire bioreactor are presented in Table 3. In scenario 1, where NO$_3$-N only was considered, the denitrifying bioreactor was successful in remediating NO$_3$-N (SI of 0.121 g m$^{-2}$ d$^{-1}$). This is comparable to SIs calculated for laboratory denitrifying bioreactors containing various C-rich media, in which SIs of between 0.81 and 1.46 g m$^{-2}$d$^{-1}$ were measured (Healy et al., 2014). However, when other water quality parameters (scenario 2) were factored in, similar to Healy et al. (2014), the denitrifying bioreactor transformed from a net reducer of contaminants to a net producer of contaminants (SI of $-0.00011$ g m$^{-2}$d$^{-1}$; Table 3).
SLS1 and WC1 of the denitrifying bioreactor (Fig 1) were successful in removing NO₃, but were also sources of other contaminants of NH₄ and GHGs. While these contaminants did not peak until the influent water reached the subsequent cells, the longitudinal data collected from the bioreactor (Figs 3, 5 and 6), combined with the calculated SIs (Table 3), suggest that the present unit could be converted to a permeable reactive interceptor (Fenton et al., 2014) by reduction to three cells: the existing first two cells (SLS1, WC1), followed by a post bed cell containing media, such as zeolite, which would be capable of reducing NH₄, thereby mitigating DRP and GHG emissions caused by bioreactor P losses and N limitation further on in the bioreactor. The likely DRP losses requiring sequestration from inlet DRP will be small, as indicative drainage DRP concentrations in the vicinity are < 0.01 mg/L. The performance of this new configuration could then be assessed by performing a new SI calculation. Recalculating the SI based on this smaller configuration gives 0.112 and -0.002, for Scenarios 1 and 2, respectively.

Recommendations for the future

It should be noted that while the idea of understanding pollution swapping is of course important, the precise nature of the input variables/weighting needs to be developed further. A consensus needs to be reached across the research community which reflects different scenarios. The SI is context-specific and dependent upon the selected weighting factors, which, in turn, should be informed by national and international environmental policy priorities.

Important considerations for the future when using this approach are cost and time. In this study, each sampling event lasted four days, and a team of three people were needed in the field to complete all the multilevel piezometer and multi-parameter sampling. In addition to
training costs of the personnel, consumable, labor and analysis costs were extensive (total costs were in excess of €40,000 over the total study duration). Of course, such costs are associated with intense analyses required for a research project. On a commercial farm site, the dimensions and monitoring system will inevitably vary and therefore costs will be lowered. Depending on the parameters analyzed, a denitrifying bioreactor may either negate costs (if only water quality parameters are measured) or cause damage to the environment (particularly if GHG emissions are considered) (Table 3). When modifying a denitrifying bioreactor to a permeable reactive interceptor to reduce contaminant losses (e.g. reduction of N₂O losses thereby eliminating indirect losses from NO₃ leaching), the cost of environmental damage should also be considered within a life cycle analysis. This will also allow easy comparison with other systems.

Acknowledgments
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Captions for Figures

Fig. 1 Schematic top view of the denitrifying bioreactor (top). Cross section of the tank along multi-level piezometer locations (bottom). Sampling point 0 is the inlet and 12 is the outlet. CL refers to the clay liner. Black square is 0.1 m, black circle is 0.4 m and black triangle is 0.7 m below the filter surface.

Fig. 2. Dissolved organic carbon (DOC), HCO$_3^-$, dissolved CO$_2$-C and dissolved CH$_4$-C at the inlet (black circles) and outlet of the bioreactor (white circles). The influent water was modified with KNO$_3$ on March 22, 2012.

Fig. 3. Longitudinal (1-12 sampling points, as per Fig 1) and vertical profiles (at depths of 0.7m (box), 0.4 m (triangle), and 0.1 m (cross)) of DOC, dissolved CO$_2$-C and CH$_4$-C in the bioreactor before modification of the inlet water with KNO$_3$ (February 2012 - top row) and after spiking (July 2012). Circle indicates inlet (0) concentrations.

Fig. 4. Nitrogen (NO$_3$-N, NH$_4$-N, dissolved N$_2$O, DON, N$_2$/Ar, PN) and P (DRP, DUP and PP) at the inlet (black circles) and outlet of the bioreactor (white circles). The influent water was modified with KNO$_3$ on March 22, 2012.

Fig. 5. Longitudinal (1-12 sampling points, as per Fig 1) and vertical profiles (at depths of 0.7m (box), 0.4 m (triangle), and 0.1 m (cross)) of NO$_3$-N, NH$_4$-N, N$_2$/Ar ratios, dissolved N$_2$O-N, and DRP in the DB before modification of the inlet water with KNO$_3$ (February 2012 - top row) and after spiking (July 2012). Circle indicates inlet (0) concentrations.

Fig. 6. Example longitudinal N$_2$O-N, CH$_4$-C and CO$_2$-C surface emissions as measured from static chambers at the media surface in the denitrifying bioreactor before NO$_3^-$ spiking (February 2012 - a) and after spiking (June 2012 - b and July 2012 - c).
Table 1. Characteristics of the influent water to the denitrifying bioreactor.

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<th>Ammonium-N</th>
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<th>Total phosphorus</th>
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Table 2. Concentrations of TN, TP and TC within the denitrifying bioreactor used in this study.

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<th>TC</th>
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<td>WC</td>
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<td>Clay liner</td>
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<td>SLS</td>
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Table 3. Inlet and outlet mass fluxes (g m\(^{-2}\) (surface area) d\(^{-1}\)) of NO\(_3\)-N, NH\(_4\)-N, and DRP in the bioreactor when operated at steady-state, based on data from 14 sampling events. Scenario 1 and 2 considers reductions (positive values) and emissions (negative values) when NO\(_3\)-N only is considered (Scenario 1), and when NO\(_3\)-N, NH\(_4\)-N and DRP are considered (Scenario 2). Weighting Factors applied as per Section 2.5.

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<th>SI Full (g m(^{-2}) d(^{-1}))</th>
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† Using costs tabulated in Eory et al. (2013)
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Fig. 2. Dissolved organic carbon (DOC), HCO₃, dissolved CO₂-C and dissolved CH₄-C at the inlet (black circles) and outlet of the bioreactor (white circles). The influent water was modified with KNO₃ on March 22, 2012.
Fig. 3. Longitudinal (1-12 sampling points, as per Fig 1) and vertical profiles (at depths of 0.7m (box), 0.4 m (triangle), and 0.1 m (cross)) of DOC, dissolved CO$_2$-C and CH$_4$-C in the bioreactor before modification of the inlet water with KNO$_3$ (February 2012 - top row) and after spiking (July 2012). Circle indicates inlet (0) concentrations.
Fig. 4. Nitrogen (NO$_3$-N, NH$_4$-N, dissolved N$_2$O, DON, N$_2$/Ar, PN) and P (DRP, DUP and PP) at the inlet (black circles) and outlet of the bioreactor (white circles)). The influent water was modified with KNO$_3$ on March 22, 2012.
Fig. 5. Longitudinal (1-12 sampling points, as per Fig 1) and vertical profiles (at depths of 0.7m (box), 0.4 m (triangle), and 0.1 m (cross)) of NO$_3$-N, NH$_4$-N, N$_2$/Ar ratios, dissolved N$_2$O-N, and DRP in the DB before modification of the inlet water with KNO$_3$ (February 2012 - top row) and after spiking (July 2012). Circle indicates inlet (0) concentrations.
Fig. 6. Example longitudinal N$_2$O-N, CH$_4$-C & CO$_2$-C surface emissions as measured from static chambers at the media surface in the denitrifying bioreactor before NO$_3^-$ spiking (February 2012 - a) and after spiking (June 2012 - b and July 2012 - c).