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Groundwater Quality Impacts from a Full-Scale Integrated Constructed Wetland

by Mawuli Dzakpasu, Miklas Scholz, Rory Harrington, Valerie McCarthy, and Siobhán Jordan

Abstract
The concept of integrated constructed wetlands (ICW) promotes in-situ soils to construct and line wetland cells. The integrity of soil material, however, may provide a potential pathway for contaminants to flow into the underlying groundwater. This study assessed the extent of groundwater quality deterioration due to the establishment of a full-scale ICW system treating domestic wastewater in Ireland. The ICW is located at Glaslough in Co. Monaghan, Ireland. It consists of two sedimentation ponds and a sequence of five shallow vegetated wetland cells. The ICW cells were lined with 500-mm thick local subsoil material, which comprised a mixture of alluvium, organic soils, tills, and gravel. Groundwater samples and head data were collected from eight piezometers, which were installed around the ICW cells. The groundwater and wetland water samples were analysed for water quality parameters such as bulk organic matter, nutrients, and pathogens. Overall, the quality of groundwater underlying the ICW system recorded some contamination with bulk organic matter and some inorganic nutrients. Significantly higher contaminant concentrations were recorded in monitoring wells upgradient and near to the distal wetland cells than downgradient ones, which were near to the proximal cells. For the downgradient piezometers, concentrations seldomly exceeded the natural background levels. Detailed analyses through the application of chemometrics models indicated that the source of contamination was largely of geogenic origin. Findings suggest that ICW systems pose a minimal risk to the groundwater quality; the greatest risk was associated with the distal wetland cells.

Introduction
The concept of integrated constructed wetlands (ICW) has been developed over the last two decades by the ICW Initiative of the Irish Department of Environment, Heritage, and Local Government. The concept of ICW endeavoured to achieve water treatment, landscape fit, and biodiversity enhancement targets through an innovative wetland design methodology (Scholz et al. 2007). Characterized by a series of interconnected free water surface flow constructed wetland cells, which incorporate the concept of restoration ecology (Jordan et al. 1987), ICW systems specifically mimic the structure and processes of natural wetlands (Scholz et al. 2007). In addition, ICW systems have shallow water depths (10–30 cm) and contain many plant species. This facilitates microbial and animal diversity (Nygaard and Ejmeas 2009; Jurado et al. 2010), and generally, is aesthetically appealing, which enhances recreation and amenity values.

ICW systems are traditionally built by utilizing resources from the site so that they will not require the installation of expensive artificial liners such as plastic or concrete to impede wastewater infiltration, and the consequent contaminants loading into the nearby groundwater system. The local onsite subsoil materials are reworked and compacted to form a low permeability liner for the ICW cells. Typically, ICW cells are underlain by at least 1.0 m of subsoil, with the upper 0.5 m enhanced where highly permeable subsoil is encountered, to hydraulic conductivity of $1 \times 10^{-6}$ m/s (Dunne et al. 2005a, 2005b; Harrington et al. 2007; Scholz et al. 2007; Carty et al. 2008). However, because the soil is a dynamic system that has been known to transmit water contaminants through its pore space, the question of wastewater infiltration from ICW cells as a potential source of groundwater pollution has often been raised. Particularly in Ireland, concerns are raised regarding the movement of nitrogen compounds into local drinking water supplies, where approximately 26% of all the drinking water supply is provided by groundwater (EPA 2008). Ultimately, groundwater flow can transport the nutrient-rich infiltration water to surrounding and nearby surface waters, where water quality degradation may occur (Hathaway et al. 2010).

In a previous study, Dzakpasu et al. (2012) noted infiltration rates of $4.3 \times 10^{-6}$, $3.7 \times 10^{-6}$, and $1.0 \times 10^{-4}$ m/s, respectively, through the cell liners of the first three ICW cells during the first 18 months of operation. Infiltration water originating from the ICW cells may potentially contain relatively high concentrations of organic carbon compounds, nutrients (mostly nitrogen and phosphorus), and pathogens. Such inputs to the groundwater may cause pollution or pose a risk to public health. While excess organic carbon compounds could impact the groundwater quality negatively, its presence in groundwater, nonetheless, plays important roles in controlling geochemical processes by acting as proton donors/acceptors and as pH buffers, by affecting the transport and degradation of pollutants, and by participating in...
mineral dissolution/precipitation reactions. Dissolved and particulate organic carbon compounds may also influence the availability of nutrients and serve as a carbon substrate for microbially mediated reactions (Aiken 2002). Nitrogen compounds, on the other hand, may be microbially oxidized to form nitrate (NO$_3^-$-$N$), excessive amounts of which are of a great concern to public health (WHO 2008).

Nonetheless, NO$_3^-$-$N$ often occurs naturally in groundwater, typically with a baseline not exceeding 2 mg/L (Wakida and Lerner 2005). Therefore, groundwater wells with NO$_3^-$-$N$ concentrations of 3–10 mg/L may indicate input from external sources (Power and Schepers 1989); excessive concentrations mostly being associated with water quality degradation (Canter and Knox 1985; Koh et al. 2007). Furthermore, although typically nontoxic, P compounds can considerably decrease the quality of water resource systems. Ortho-P and NO$_3^-$-$N$ are often, the limiting nutrients that could stimulate the growth of aquatic plants, most notably algae, leading to eutrophication problems and the consequent loss of recreational and commercial values of water systems (Cloern 2001; Khan and Ansari 2005; Akpor and Mutchie 2011).

Several published studies such as Dunne et al. (2005a, 2005b), Mustafa et al. (2009), Kayranli et al. (2010), Dong et al. (2011), and Dzakpasu et al. (2011) have indicated that ICW systems can provide an effective method of wastewater treatment for both point and diffuse sources. Nevertheless, the question still remains as to whether the use of local soil materials to line ICW cells is capable of providing effective protection to the underlying and associated groundwater. Furthermore, limited studies have been carried out concerning the potential infiltration of water contaminants from full-scale constructed wetlands into groundwater systems.

The research aim addressed by this paper was to assess the groundwater quality near a full-scale ICW system treating domestic wastewater. The specific objectives were (1) to evaluate the temporal and spatial extent of groundwater contamination near the ICW system and (2) to identify the possible sources of contamination in the groundwater and assess the contributions, thereof, of contaminant sources on the groundwater quality parameters by using chemometrics models. Chemometrics is the field of extracting information from multivariate chemical data using mathematical and statistical methods.

### Materials and Methods

#### Study Site Description

The ICW treatment system at the centre of the study is located within the walls of the Castle Leslie Estate at Glaslough in County Monaghan, Ireland (06°53’37.94” W, 54°19’6.01” N). The site is surrounded by woodland and therefore, required sensitive development in terms of landscape fit, and biodiversity, amenity, and habitat enhancement.

The ICW (Figure 1) comprises a small pumping station, two sedimentation ponds, and a sequence of five shallow and vegetated wetland cells. Hydraulic characteristics of the wetland cells are presented in Table 1. The ICW

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**Table 1**

<table>
<thead>
<tr>
<th>ICW Section</th>
<th>Area (m$^2$)</th>
<th>Depth (m)</th>
<th>Total Volume (m$^3$)</th>
<th>Effective Volume (m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.45</td>
<td>128.3</td>
<td>85.5</td>
</tr>
<tr>
<td>Sedimentation pond 2</td>
<td>365</td>
<td>0.45</td>
<td>164.3</td>
<td>109.5</td>
</tr>
<tr>
<td>Cell 1</td>
<td>4664</td>
<td>0.42</td>
<td>1958.9</td>
<td>1399.2</td>
</tr>
<tr>
<td>Cell 2</td>
<td>4500</td>
<td>0.38</td>
<td>1710.0</td>
<td>1350</td>
</tr>
<tr>
<td>Cell 3</td>
<td>12660</td>
<td>0.32</td>
<td>4051.2</td>
<td>3798</td>
</tr>
<tr>
<td>Cell 4</td>
<td>9170</td>
<td>0.36</td>
<td>3301.2</td>
<td>2751</td>
</tr>
<tr>
<td>Cell 5</td>
<td>1460</td>
<td>0.29</td>
<td>423.4</td>
<td>423.4</td>
</tr>
<tr>
<td>Total wetland</td>
<td>33104</td>
<td></td>
<td>11737.3</td>
<td>9916.6</td>
</tr>
</tbody>
</table>
system was commissioned in October 2007 to treat sewage from Glaslough village and to improve the water quality of the Mountain Water River, which flows through the site. The Mountain Water River is within the catchment area of the Blackwater River in Monahan.

The design capacity of the ICW system is 1750 p.e. (105 kg BOD/d). The functional water area of the ICW cells is 3.25 ha (HLR of 0.54 cm/d) within a curtilage area of 6.74 ha. The wetland cells was used to construct the base of the wetland cells and was compacted to a thickness of 500 mm to form a low permeability liner. A site investigation conducted in September 2005 indicated a soil coefficient of permeability of 9 x 10^-11 m/s (IGSL Ltd., Business Park, Naas, Co. Kildare, Ireland). The soils at the study area comprise a mixture of coarse and fine-grained materials, namely alluvium, organic soils, tills, and gravel. Subsoil samples collected from the first 2 m near the sedimentation ponds were classified as sandy gravelly clay; whereas those collected near cell 1 and cell 2 were classified as sandy silt and silty clay, respectively (IGSL Ltd., Business Park, Naas, Co. Kildare, Ireland). Typically, the mineral content of the soils is in the following range: Al³⁺, 4.1–5.0%; Fe²⁺, 2.01–2.5%; Ca²⁺, 0.301–0.45%; Na⁺, 0.501–0.65%; K⁺, 0.751–1.00%; Mg²⁺, 0.41–0.5%; Organic C, 6.1–10%; and pH, 5.01–5.5 (Fay et al. 2007). The main ICW system is flanked by the Mountain Water River and the Glaslough Stream (Figure 1).

Influent primary domestic wastewater from the village is pumped directly into a receiving sedimentation pond. The system contains two sedimentation ponds that can be used alternately so that one can be desludged without interrupting the whole treatment process. The purpose of the sedimentation ponds is to retain the suspended solids contained in the influent wastewater. In this way, the build-up of sludge in the wetland cells, which could otherwise decrease the capacity of the cells, is prevented. From the sedimentation pond, the wastewater subsequently flows by gravity sequentially through the five earthen-lined cells. The effluent of the last cell discharges directly into the adjacent Mountain Water River.

The wetland cells were planted in a club pattern, and the main ones were *Carex riparia* Curtis, *Phragmites australis* (Cav.) Trin. ex Steud., *Typha latifolia* L., *Iris pseudacorus* L., and *Glyceria maxima* (Hartm.) Holm. This currently includes a complex mixture of *Glyceria fluviatilis* (L.) R.Br., *Juncus effusus* L., *Sparganium erectum* L. emend Rchb, *Elisma natans* (L.) Raf., and *Scirpus pendulus* Muholder.

### Installation of Monitoring Wells

Eight cassagrande (standpipe) piezometers were constructed around the ICW cells (labelled WS-1 to WS-F on Figure 1) in May 2011. The drilling of piezometers was done by using a hydraulic percussion drilling rig (IGSL Ltd., Business Park, Naas, Co., Kildare, Ireland). Depths of these wells ranged from 3 to 5 m below land surface (Table 2). PVC standpipes of 50 mm diameter, typically consisting of a solid casing down to the depth of the overburden, and a screened casing within the water bearing zone, were set into the ground. A filter medium consisting of washed peat gravel was constructed in the well annulus at the base and around the screened casing to prevent soil material from entering the wells. A seal of bentonite pellets was installed in the well annulus at the base of the solid casing to a thickness of at least 0.5 m, and the well annulus at the surface was sealed using cement grout and a steel cover.

### Groundwater Sampling

Groundwater samples were collected weekly between May 2011 and April 2012, from the eight piezometers placed within the ICW system (Figure 1). Before a sample was taken each week, the water level in each piezometer was recorded using an electronic dip meter (Geotechnical Instruments Ltd., Leamington Spa, UK). The groundwater sampling involved purging the well to remove stagnant and contaminated water within the piezometer that may not be representative of in situ groundwater quality. Three times the volume of water contained in the well casing was purged using a WP 9012 submersible groundwater purging pump (Global Water, Gold River, California, USA). Water samples were collected immediately after purging using 2 L polyethylene bottles and transported directly to the laboratory for immediate analysis. Samples for microbiological analyses were collected in 120 mL pre-sterilized polystyrene bottles and transported to the laboratory in cooled insulated boxes.
Wetland Water and Hydrological Monitoring

A suite of automated sampling and monitoring instrumentation such as the ISCO 4700 Refrigerated Automatic Wastewater Sampler (Teledyne Isco, Inc., Nebraska, USA) was used for weekly wetland water sampling (Figure 1). Additionally, all flows into and out of each ICW cell were measured and recorded with Siemens Electromagnetic Flow Meters FM MAGFLO and MAG5000 (Siemens Flow Instruments A/S, Nordborg, Denmark) and their allied computer-linked data loggers. Mean flows were recorded at a 1-min interval frequency. A weather station is located beside the inlet pump sump to measure local temperature, precipitation, and evapotranspiration.

Water Quality Analysis

The water samples were analysed weekly for several parameters including the 5-days at 20°C N-allylthiourea biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total nitrogen (TN), ammonia–nitrogen (NH₃-N), nitrate–nitrogen (NO₃-N), total phosphorus (TP), and molybdate reactive phosphate (MRP; equivalent to soluble reactive phosphorus). All analyses were carried out at the Monaghan County Council wastewater laboratory, using kits supplied by HACH Lange (HACH Company, Loveland, Colorado, USA), and by following the standard operating procedures for the HACH DR/2010 portable data logging spectrophotometer (HACH Company 2000) or the standard methods for examination of water and wastewater (APHA 1998).

The BOD, was determined by APHA Method 5210 B (APHA 1998), using the respirometric (manometric) BOD OxiTop system (WTW GmbH, Weilheim, Germany), whereas COD was measured by the reactor digestion method, followed by colorimetric analysis (HACH Method 8000). NH₃-N and NO₃-N were determined by the Nessler method (HACH Method 8038) and the cadmium reduction method (HACH Method 8171), respectively, whereas MRP was determined by the ascorbic acid method (HACH Method 8048). Low range TN (HACH Method 10071) and high range TN (HACH Method 10072) were determined following persulfate digestion. TP was determined by the acid persulfate digestion Test ‘N Tube Method (HACH Method 8190).

Other ancillary water quality parameters such as water pH, temperature, oxidation–reduction potential (ORP), dissolved oxygen (DO), and electrical conductivity (EC) were measured onsite by using a WTW Multi 1970i portable multi-parameter meter and WTW ProfiLine Cond 197i portable conductivity meter (WTW GmbH, Weilheim, Germany).

Samples for microbiological and chloride analyses were transported to the Waterford County Council wastewater laboratory and analysed within 24 h of collection. Total coliforms and Escherichia coli were analysed using the membrane filter method (APHA Method 9222).

Statistical Analyses

Data distributions were tested for normality by using the Shapiro–Wilk Normality Test (Shapiro and Wilk 1965). Statistically significant differences were all determined at α = 0.05, unless stated otherwise. Comparisons of means were by paired samples t-tests and one-factor analysis of variance (ANOVA). Tukey’s HSD (Honestly Significant Difference) tests were applied for post-ANOVA pair-wise comparisons to identify significant differences among means. Exploratory factor analysis and principal component analysis (PCA) were employed to identify possible factors/sources of contamination in the groundwater and to estimate the contributions of the possible factors/sources identified on the concentrations of the measured physicochemical parameters. The raw analytical data set were primarily standardized through a z-scale transformation in order to avoid misclassification due to the wide differences in data dimensionality. All statistical analyses were performed by using Minitab 16 (Minitab Inc., State College, Pennsylvania, USA) and IBM SPSS Statistics 21 (IBM Corporation, Armonk, New York, USA).

PCA is concerned with establishing which linear components exist within the data set and how a particular variable might contribute to a component (Field 2009). This is achieved by transforming the original data variables into new, uncorrelated (orthogonal) variables (axes), called the principal components (PC), which are linear combinations of the original data variables (Shrestha and Kazama 2007). The PC provides information on the most meaningful patterns, which describe whole data sets, affording data reduction with minimum loss of original information (Vega et al. 1998; Helena et al. 2000; Shrestha and Kazama 2007). These PC’s are obtained by multiplying the original correlated variables with a list of coefficients (loadings or weightings) called eigenvectors. Thus, PC’s are weighted linear combinations of the original data variables, and can be expressed as shown in Equation 1.

\[ Z_j = a_{i1}x_{ij} + a_{i2}x_{ij} + a_{i3}x_{ij} + \ldots + a_{im}x_{nj} \]  

(1)

where Z is the component score, a is the component loading, x is the measured value of variable, j is the sample number, i is the component number, and m is the total number of variables.

Factor analysis (FA) then extracts the eigenvalues and eigenvectors from a covariance/correlation matrix of the original data variables, which are subsequently rearranged in a manner that better explains the structure of the underlying system that produced the data set, and further reduces the contributions of less significant variables obtained from PCA (Shrestha and Kazama 2007). The new group of variables, known as variifactors, are extracted through rotating the axis defined by PCA. The correlation coefficient matrix measures how well the variance of each constituent can be explained by relationships with each of the others. The correlation coefficients are computed as shown in Equation 2.

\[ r_{xy} = \frac{\sum(x-x_m)(y-y_m)}{\sqrt{\sum(x-x_m)^2\sum(y-y_m)^2}} \]  

(2)

where the correlation coefficients \( r_{xy} \) is simply the sum (overall samples) of the products of the deviations of the \( x \)- and \( y \)-measurements on each sample, from the mean values of \( x \) and \( y \), respectively, for the complete set of samples (Liu et al. 2003).

Overall, FA yields the general relationships among measured variables by showing multivariate patterns that
may help to classify the original data (Liu et al. 2003). Equation 3 indicates FA.

\[ z_y = a_1f_1 + a_2f_2 + a_3f_3 + \ldots + a_mf_m + e_y \]

(3)

where \( z \) is the measured variable; \( a \) is the factor loading; \( f \) is the factor score; \( e \) is the residual term accounting for errors or other source of variation; \( i \) is the sample number; and \( m \) is the total number of factors.

In this study, PCA of the standardized groundwater quality data set was performed to extract significant principal components, which were further subjected to varimax rotation (a varimax rotation is a change of coordinates used in PCA and FA that maximizes the sum of the variances of the squared loadings, i.e., squared correlations between variables and factors) to generate the varifactors. Exploratory FA, a statistical method used to uncover the underlying structure of a relatively large set of variables (Field 2009) was applied, which allowed for a better understanding of the complex set of variables by reducing them into a smaller number of factors. Projections of the original variables on the subspace of the principal components, known as factor/component loadings, were used to determine the relative importance of a variable as compared to other variables in a particular principal component and may not necessarily reflect the importance of the component itself (Ouyang et al. 2006). The terms “strong,” “moderate,” and “weak,” as applied to factor/component loadings, refer to absolute loading values of >0.75, 0.75–0.50, and 0.50–0.30, respectively (Liu et al. 2003).

**Results and Discussion**

**Piezometer Hydrographs and Seasonal Fluctuations**

The groundwater level monitoring provided insight regarding the response of water levels in the aquifer underneath the ICW system to changing hydrologic conditions. All of the piezometers displayed certain similarities, whereby the groundwater level in all piezometers showed variations in response to seasonal influences, with a clear recharge and natural discharge process evident in most instances. The relatively wet conditions that prevailed at the ICW site during the monitoring period saw a general upward trend in groundwater levels, with periodic minor recharge events associated with larger precipitation events. Recharge events showed a rather quick response to larger precipitation events (Figure 2), with many of the piezometers...

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**Figure 2** (a-f). Groundwater table elevation for monitoring wells within the integrated constructed wetland (ICW) system plotted in relation to bed invert level of individual ICW cells and total daily precipitation.
generally exhibiting uniform increases in water levels following such precipitation events. Therefore, recharge to the aquifer seemed to originate from precipitation that infiltrated through the soil and percolated to the water table. Nevertheless, in the Blackwater catchment where the ICW system is located, Misstear and Brown (2010) noted that groundwater recharge mainly occurred indirectly through the fractured bedrock, which provide conduits for lateral flow from upgradient areas and that direct recharge through the overlying till was only approximately 26 mm or 5% of the annual effective rainfall. This possibly explains the relatively quick increase of the groundwater table elevation to larger precipitation events that occurred during the monitoring period. At all other times during the monitoring period when precipitation was relatively low, fairly constant groundwater levels were recorded (Figure 2), with a relatively higher water table elevation being recorded during winter months.

The groundwater levels in most of the piezometers were at all times higher than the invert (base interior) levels of the wetland cells. The significance of the level of the groundwater table in this instance is that water will flow from the wetland into the aquifer and thus degrade groundwater quality once the level of the groundwater table fell below the wetland cell invert level, albeit; the flow distance must be taken into account. In a review of the risk of groundwater pollution by onsite sanitation in developing countries, Lewis et al. (1980) noted that the groundwater quality tend to depend on the vertical separation allowed between the base of the pit latrines and the groundwater table elevation.

The mean ± SD water level in piezometers WS-F and WS-B were 54.06 ± 0.37 m OD and 51.42 ± 0.25 m OD, respectively (Figure 2). Piezometer WS-F is located approximately 100 m upgradient from ICW cell 1, whereas WS-B is located about 0.5 m downgradient (Figure 1). The invert level of the ICW cell is 52.46 m OD. The water level in piezometer WS-B was well below the invert level of the ICW cell during the monitoring period (Figure 2). The water level in piezometer WS-F (control) also exceeded the ICW cell invert level.

Piezometers WS-1 and WS-D are located approximately 0.5 m from the influent and effluent points of ICW cell 2, respectively. The invert level of the ICW cell is 52.50 m OD. The groundwater levels in the piezometers were 51.61 ± 0.26 m OD and 52.93 ± 0.16 m OD, respectively, for WS-1 and WS-D. The water level of piezometer WS-D was higher than the ICW cell invert level during the monitoring period. The fact that the invert level of this ICW cell sat below the groundwater elevation in the piezometer indicated that there was groundwater flow into the wetland. In this regard, minimal influence and possibly no contamination from this ICW cell to the groundwater quality might be expected. In addition, for piezometer WS-E, which is located about 0.5 m from the effluent of ICW cell 3, the groundwater level (52.88 ± 0.20 m OD) exceeded the ICW cell invert level slightly (52.56 m OD) at all times during the monitoring period, also suggesting a minimal influence from this cell on groundwater quality at this point. The groundwater level in piezometer WS-D, located about 30 m from the influent of cell 3, also exceeded the invert level of the cell at that point, and would be less likely to receive effluent from that cell. Nevertheless, glacial till is frequently known to be dense, restricting hydraulic conductivity through the soil (Hart et al. 2006). The presence of till in the study area (having a hydraulic conductivity of $9 \times 10^{-11} \text{ m/s}$) potentially exerts some pressure on the groundwater, creating some confinement. Therefore, the water level recorded in most piezometers at the ICW site represents the potentiometric surface level rather than the groundwater table elevation. Conlon et al. (2005) noted that if a well is completed in an aquifer confined by overlying materials of low permeability, groundwater in the aquifer may be under sufficient pressure to cause the water level in the well to rise above the top of the aquifer. A contour map of heads in such a confined aquifer defines a water level surface that shows the horizontal direction of flow in the confined aquifer.

The invert levels of ICW cells 4 and 5 are 52.41 m OD and 52.37 m OD, respectively. Piezometer WS-2 is located near the effluent point of cell 4, whereas piezometer WS-C is located near that of cell 5. The average water level in piezometer WS-2 (52.95 ± 0.13 m OD) was found to be slightly higher than the ICW cell invert level. On the contrary, the water level in piezometer WS-C, fell at 51.35 ± 0.27 m OD far lower than the ICW cell invert level. This suggests a greater influence of that ICW cell on the groundwater at that point.

Contaminant Concentrations in Groundwater

Nitrogen Contamination in Groundwater

Nitrogen in the groundwater underneath the ICW system was recorded mainly as ammonia. The overall average of ammonia (NH₄-N) for all sample points accounted for more than 80% of the total N recorded in the groundwater. The range for NH₄-N was 0.01–12.6 mg/L, for all sample points, with over 60% of the total results falling below the WHO recommended threshold for odour and taste concentrations (WHO 2008). Total N and NH₄-N persisted quite strongly in piezometers WS-E, WS-D, and WS-2 (Table 3), and tended to decrease significantly ($p < 0.05$) in concentration from piezometers upgradient of the groundwater flow direction to the downgradient piezometers. When compared with each other, there was also a significant ($p < 0.05$) variation in total N and NH₄-N concentrations, in all of the downgradient piezometers (i.e., WS-A, WS-B, WS-C, and WS-1). In addition, the concentrations in the control piezometer, which was constructed outside of the ICW system were found to be generally similar to that in all the downgradient piezometers. This indicated that concentrations in the downgradient piezometers rarely exceeded the natural background levels.

On the other hand, the concentrations of NO₃-N recorded for all the piezometers were rather low and accounted for less than 10% of the total N recorded in the groundwater. The range for NO₃-N was 0–1.7 mg/L for all sample points, with all of the total results falling far below the WHO recommended threshold for drinking water; nitrate could cause health problems at concentrations above 50 mg/L NO₃ or 10 mg/L NO₃-N (WHO 2008).

The presence of NH₄-N at higher than the natural (geogenic) levels of 0.2 mg/L (WHO 2008) is an important
Table 3
Contaminant Concentrations in Groundwater Recorded Near the Integrated Constructed Wetland (ICW) System Between May 2011 and April 2012

<table>
<thead>
<tr>
<th></th>
<th></th>
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<tbody>
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<td></td>
<td>Mean</td>
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<td>SD†</td>
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<tr>
<td>pH</td>
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<tr>
<td></td>
<td>SD†</td>
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<td>EC† (μS/cm)</td>
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<td>68</td>
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<td>125</td>
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<td>Dissolved oxygen (mg O₂/L)</td>
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<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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**Note:**

1. Electrical conductivity.
2. Oxidation-reduction potential.
3. Molybdate reactive phosphate.
4. Most probable number.
5. Standard deviation.

Indicator of possible bacterial and faecal (human or animal) pollution (WHO 2003). Therefore, the relatively high NH₄–N concentrations recorded in some upgradient piezometers during the current study indicate the presence of an immediate source of organic or faecal pollution. However, it is also noted that anaerobic groundwater may contain up to 3 mg/L NH₄–N (WHO 2008) and that natural concentrations of up to 3 mg/L of NH₄–N could be found usually in strata rich in humic substances or iron or in forests (Dieter and Möller 1991; Tilaki and Kahe 2012). Because the ICW site was originally a forestland, which was redeveloped, it is possible that the high NH₄–N concentrations recorded in some of the piezometers may have geogenic origin. In addition, the borehole logs from the affected piezometers indicated the presence of organic material in the stratigraphy of the site. Besides, Fay et al. (2007) estimated that the soils at the ICW site contain about 2.5% of Fe²⁺ and about 10% of organic carbon. These findings are consistent with the assertion that groundwater with naturally higher NH₄–N contents could occur in strata rich in humic substances or iron or in forests (Dieter and Möller 1991; Tilaki and Kahe 2012).

Moreover, there was a slight reduction in N concentrations during recharge events, which generally occurred during high precipitation events. The relative decreases in N concentrations during such recharge events suggest possible...
dilution of N in the groundwater. This indicates that the source of N contamination can be found within the immediate surroundings of the sampling points. The recharge events were also associated with a rise in the groundwater table elevation, which exceeded the wetland cell invert levels, consequently discharging groundwater into the wetland cells. Thus, the wetlands were less likely to influence the groundwater quality. The differences in chloride concentrations, which were lower in the groundwater than that in the wetlands, further affirm this.

When compared (Figure 3), the quality of the wastewater contained in ICW cells 1 and 2, and the sedimentation ponds showed significantly higher (p < 0.05) concentrations of N than that in the groundwater at some of the sampling points; WS-A, WS-B, WS-1, and WS-D (Figure 1). At other sampling points (WS-E and WS-2), the concentrations of
N in the groundwater were slightly higher than those contained in the nearby cells of the ICW system. For example, the concentration of N in the most contaminated piezometer (WS-E) was 10.2 ± 1.14 mg N total/L, 8.1 ± 1.72 mg NH₄–N/L, and 0.6 ± 0.41 mg NO₃–N/L; BOD₅ was 17 ± 6.9 mg/L. This piezometer is located upgradient of the effluent point of ICW cell 3, which contained 5.1±4.26 mg N total/L, 4.0 ± 4.38 mg NH₄–N/L, 0.6 ± 0.30 mg NO₃–N/L, and 10 ± 4.7 mg BOD₅/L. It seems evident from here that the concentrations of N were generally higher in the groundwater at this point than that in the ICW cell, and therefore, N contamination was likely not originating from the ICW cell. On the other hand, the ICW cell that contained the most contaminated wastewater is the sedimentation pond. The piezometer closest to this ICW cell is WS-A (downgradient). The concentrations of N in the piezometer at that point were 1.6±0.60 mg N total/L, 0.7±0.10 mg NH₄–N/L and 0.3±0.58 mg NO₃–N/L; BOD₅ was 7±1.4 mg/L, whereas the concentrations of N in the ICW cell were 61±24.11 mg N total/L, 42±13.66 mg NH₄–N/L and 3.5±2.90 mg NO₃–N/L; BOD₅ was 308±16 mg/L. It seems evident that the concentrations of N were generally higher by quite a large margin in the ICW cell at this point than in the groundwater. Findings were similar for all the other piezometers, which are downgradient to the other proximal ICW cells. Overall, N contamination in the groundwater was higher in piezometers WS-E, WS-D, and WS-2, which are located upgradient and closer to the distal ICW cells containing the least contaminated wastewater compared to piezometers WS-A, WS-B, and WS-1, which are downgradient and closer to the proximal ICW cells containing the most contaminated wastewater. Thus, the proximal ICW cells pose a minimal risk to the groundwater quality.

**Geochemical Fingerprinting of Nitrogen Contamination in Groundwater**

Groundwater contamination with N includes several sources, which are frequently not evident, and sometimes occur with multiple sources. As chloride is ubiquitous to domestic wastewater and not subject to adsorption, ion exchange or oxidation–reduction reactions, it is commonly a useful and reliable chemical indicator of groundwater faecal contamination (McQuillan 2004; Canter and Knox 1985). Besides, nitrate is relatively mobile in soil and groundwater because, unlike ammonium, nitrate does not adsorb onto soil or aquifer geologic materials, and only precipitates as a mineral under dry conditions (Uhlman and Artiola 2011). Thus, nitrate tends to persist for long periods, sometimes migrating great distances downgradient from the source (Taylor 2003).

The correlations of chloride with nitrate and dissolved organic carbon, which is otherwise distinctive for extremely low levels of major ions, consequently, often suggest contamination with wastewater (Foster 1990). Therefore, chloride and nitrate-N can be useful indicative parameters for identifying the source of groundwater contamination. The correlation between chloride and nitrate in an area of known faecal contamination generally shows a linear increase in chloride concentrations with increasing nitrate. McQuillan (2004) made a comparison of the correlation of groundwater nitrate and chloride concentrations from three different types of contaminant sources and indicated that groundwater contaminated by faecal material contained slightly lower concentrations of both nitrate and chloride than dairy sources, whereas groundwater contaminated by evaporative concentration of rainwater beneath ephemeral streams contained relatively lower concentrations (consistent with local meteoric water).

The concentrations of chloride recorded in this study ranged between 8.0 and 75.6 mg/L for all sample points, with all of the total results falling far below the WHO recommended threshold for taste concentrations (WHO 2008). Chloride was higher in piezometers WS-D, WS-C, and WS-1 (Table 3) and tended to decrease significantly (p<0.05) in concentration from the piezometers downgradient of the groundwater flow direction to the upgradient ones.

An evaluation of the correlation between chloride and nitrate in the groundwater at the ICW site recorded in all the eight sampling points over the entire period of monitoring (Figure 4) indicated a weak negative correlation (R² = 0.098), which was, however, statistically significant (p<0.05). This is not consistent with the correlation often found between chloride and nitrate in groundwater contaminated with faecal materials as indicated by Foster (1990) and McQuillan (2004). The concentrations of both nitrate and chloride were rather consistent with local meteoric water. This indicated that the N contamination recorded in some of the piezometers may not be originating from the ICW cells, and that indeed the source of contamination might have geogenic origin.

**Phosphorus Contamination in Groundwater**

Phosphorus in the groundwater underneath the ICW system occurred mainly in particulate form. The overall average of MRP for all sample points accounted for less than 15% of the total P recorded in the groundwater. The range for MRP...
was 0–0.45 mg/L for all sample points, with over 75% of the total results falling below the EQS for P in groundwater in Ireland, which is set at 0.03 mg/L (EPA 2003) or the threshold value for MRP in groundwater considered being at less than a “good” chemical status in Ireland, which is set at 0.035 mg/L (S.I. No. 9 of 2010). In this study, MRP persisted quite strongly and somewhat variable in piezometer WS-F, which is the control piezometer constructed outside of the ICW system (Table 3). The highest concentrations (around 0.07 ± 0.11 mg/L) were recorded in this piezometer. The average concentrations of MRP were quite similar in all the other piezometers. The same was true for total P, but the individual values were quite variable.

Overall, the patterns of P concentrations recorded in the groundwater across the sampling sites provide no indication of P contamination originating from the ICW cells. When compared with Figure 3, the quality of wastewater contained in the ICW cells was associated with significantly higher (p<0.05) concentrations of P than that in the groundwater at all sampling points. This suggested that either there was no P contamination originating from the ICW cells to the groundwater system underneath, or that any P contamination potentially originating from the ICW cells was being effectively attenuated in the sub-surface as a consequence of the sub-soil mineralogy. It is generally noted that P has the capacity to be adsorbed onto or form precipitates within mineral surfaces of soil particles (Gill et al. 2004), particularly clay, resulting in significantly lower P loads to the groundwater. Adsorbed P can further migrate into the interior of the minerals that adsorbed them, and therefore becoming even less available (Troeh and Thompson 2005).

**Organic Matter and Bacteriological Contamination in Groundwater**

The overall average of BOD, for all sample points accounted for approximately 35% of the COD recorded in the groundwater. The range for BOD, was 0–34 mg/L for all sample points, with over 75% of the total results falling below the recommended threshold values of greater than 10 mg BOD/L or 200 mg COD/L for water pollution due to wastewater discharges (Chapman and Kistmacht 1996).

The concentrations of BOD, and COD persisted quite strongly in piezometer WS-E (Table 3), which is upgradient to the ICW system, followed by WS-2. Furthermore, water samples from these two piezometers normally exhibited some colouration. Such coloration in water is primarily due to the presence of humic and fulvic acids associated with the humus fraction of soils (WHO 2008). As the borehole logs from these piezometers indicated the presence of a considerable amount of organic soils in the stratigraphy at that point and also, because the ICW site was originally a forestland, the presence of relatively high BOD5 and COD concentrations may be geogenically derived. Besides, the BOD5/COD ratios in both piezometers were found to be relatively lower (<0.3) than the range between 0.4 and 0.8 commonly found in domestic wastewaters (Srinivas 2008). Chapman and Kistmacht (1996) noted that unpolluted waters typically have BOD concentrations of 2 mg/L or less and COD of 20 mg/L or less. In terms of COD, piezometers WS-1, WS-A, WS-B, and WS-D actually fall into the class of unpolluted waters.

Additionally, the presence or absence of faecal indicator bacteria is a commonly used operational indicator of water quality. Coliform bacteria are the most prevalent genera used. In most waters, the predominant genus is Escherichia, with the detection of E. coli providing definite evidence of faecal pollution (APHA 1998; WHO 2008). Some members of the total coliform bacteria group, on the other hand, are commonly found in the environment (e.g., soil or vegetation) and are generally harmless. Consequently, if only total coliform bacteria are detected in water, the source may be environmental, and faecal contamination is not likely (Maia et al. 2012).

In this study, the total coliform count varied highly across sampling points (Table 3). Conversely, the E. coli count at all sample points were found to be <1 MPN 100 mL. This provided an indication that there may not have been a source of faecal contamination originating from the ICW cells to the groundwater and that organic material found in the stratigraphy of the ICW site at some sample points may be contributing to the high levels of total coliforms recorded.

**Factors Influencing the Variability in Groundwater Quality**

The PCA undertaken on the groundwater quality dataset showed that 82.3% of the data variance extracted was contained within the first four principal components. These four components had eigenvalues greater than or close to unity and explained 48.7%, 15.1%, 10.3%, and 8.2%, respectively, of the total variance extracted from the original data set. The main correlations between the respective variables determined by the PCA are given in Table 4. Figure 5 provides a biplot of PC1 and PC2. Factor/component loadings of the four principal components are presented in Table 5.

PC1, which explained 48.7% of the total variance, exhibited strong positive loadings for inorganic nutrients and organic-related parameters, namely NH₄,N, NO₃,N, total N, total P, BOD, and COD. It is evident from the component loadings of this principal component that the contamination recorded in the groundwater at some sample points was predominantly due to an organic source of contamination. This is because most of the parameters, which recorded high loadings on the principal component, are common to organic pollution and are also closely correlated (Figure 5), thereby confirming that they originated from the same source. Nevertheless, there was also a moderate negative loading of Cl⁻ on this principal component. This suggested that the source of contamination is not likely to be of faecal origin. The moderate negative correlation between Cl⁻ and NH₄,N, NO₃,N, total N, total P, BOD, and COD (Table 4) confirms this further. This provides evidence that the groundwater contamination recorded at some sample points during the course of the monitoring period as stated early on, may not be originating from the ICW cells. With respect to the N species, a positive correlation of nearby unity was recorded between total N and NH₄,N, with each also having strong positive loading scores on PC1. This indicated that the majority of N in the groundwater was primarily in the form of NH₄,N.

PC2, which explained 15.1% of the total variance, exhibited strong positive loadings for ORP, weak positive loading
Table 4
Correlation Matrix

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<th>pH</th>
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<th>NO₃-N</th>
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¹Water level.  
²Temperature.  
³Electrical conductivity.  
⁴Oxidation-reduction potential.  
⁵Dissolved oxygen.  
⁶Ammonia-nitrogen.  
⁷Nitrate-nitrogen.  
⁸Molybdate reactive phosphate.  
⁹Chemical oxygen demand.  
¹⁰Biochemical oxygen demand.

Figure 5. Component plot in rotated space.

for temperature and MRP, and strong negative loading for pH. Therefore, this component related to environmental conditions. Commonly, pH has a significant influence on the reactivity of phosphate, with lower pH increasing the level of reactive phosphate (Carroll and Goonetilleke 2005). Similarly, as the pH of water increases, the level of reactivity is reduced. The strong positive loading of ORP on this principal component further confirms this. Generally, the solubility of many elements in water depends on whether they are oxidized or reduced. Iron, for example, is more soluble in the reduced state than it is in the oxidized state (Nelson 2002). Therefore, as ORP drops, the groundwater will have higher concentrations of Fe²⁺ available for precipitation reactions with P.

Furthermore, PC3, which explained 10.3% of the total variance in the dataset, exhibited strong positive loadings for groundwater table elevation and dissolved oxygen and a moderate positive loading for electrical conductivity. Therefore, this principal component related to groundwater recharge events. Misstear and Brown (2010) noted that in the Blackwater catchment where the ICW system is located, groundwater recharge mainly occurred indirectly through the fractured bedrock, which provided conduits for lateral flow from upgradient. Consequently, groundwater recharge at the ICW site was potentially associated with an influx of oxygenated water from the surface during periods of such rapid recharge. The influx of oxygenated water may have subsequently resulted in increased concentrations of dissolved oxygen, pH, and ORP. These changes potentially led to decreases in concentrations of calcium and magnesium ions, heavy metals (particularly iron and manganese), hydrogen sulphide, ammonium and bulk organic parameters such as COD and BOD (EPA Victoria 2000). The weak negative correlations recorded between dissolved oxygen and both NH₃-N and total N (Table 4), and the moderate positive loading of electrical conductivity on this principal component (Table 5) provide strong evidence to confirm this. In general, the oxidation of an organic molecule can result in, for example, Fe or Mn, in a solid oxide mineral, being
dissolved into the groundwater in a reduced form as Fe$^{2+}$ or Mn$^{2+}$ (Nelson 2002) and potentially causing a corresponding increase in the electrical conductivity of the groundwater.

The PC4 explained 8.2% of the total variance in the dataset. This principal component exhibited a strong negative loading for temperature. Therefore, this component related well to seasonal temperature changes. There is a seeming negative effect of temperature on contaminant concentrations in the groundwater especially MRP, which also exhibited a moderate positive loading on this principal. It has been noted that the ability of soils to adsorb P was reduced at higher temperatures and that the rate of P desorption increases with increasing temperature (Sallade and Sims 1997a, 1997b; Mamo et al. 2005).

### Conclusions

Results from this study indicate some contamination with bulk organic matter and inorganic nutrients in the groundwater underlying the ICW system. Significantly higher contaminant concentrations were recorded in monitoring wells upgradient of the groundwater flow direction and near to the distal wetland cells than in the downgradient ones, which were near to the proximal cells. For the downgradient piezometers, concentrations rarely exceeded the natural background levels. Detailed analyses through the application of chemometrics models indicated that the source of contamination was largely of geogenic origin. Four possible factors were identified as causing the variations in groundwater quality at the ICW site namely, geogenically derived organic source of contamination, environmental conditions, groundwater recharge cycles, and seasonal variations in water temperature. Findings suggest that ICW systems pose a minimal risk to the groundwater quality and that the risk was highest for the distal wetland cells.

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