Temporal analysis of groundwater nitrate concentrations from wells in Prince Edward Island, Canada: application of a linear mixed effects model

Victoria S. Benson · John A. VanLeeuwen · Henrik Stryhn · George H. Somers

Abstract Changes in nitrate concentration in groundwater from wells in Prince Edward Island, Canada were investigated over time using two datasets. Temporal trends in groundwater nitrate concentrations were assessed annually during 1981–1996 (1,299 observations), and both seasonally and monthly during 1988–1991 (1,868 observations). Data were analysed using linear mixed models with random effects and correlation structures. The average nitrate concentration in the monthly dataset was 3.99 mg/L as NO_3–N, with January, May, and November concentrations being higher (p=0.018). A seasonal effect was present when season was combined with land use type in an interaction term (p=0.004). Wells located in agricultural areas had greater nitrate concentrations than urban areas, which in turn, had greater values than low human-impact areas. Row-cropped areas had higher groundwater nitrate concentrations in the summer, whereas manure storage areas were higher in the spring and autumn. Nitrate in groundwater in areas with low human impact and with centralized sewage disposal infrastructure remained relatively low and stable throughout the seasons. There was no significant annual trend (p=0.954), but for individual sites, 9.6% significantly increased in nitrate concentration over time, and 6.6% significantly decreased over time.

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Résumé Les variations des concentrations en nitrates dans les eaux de puits situés sur l'Ile Prince Edward, au Canada, ont été étudiées dans le temps, en utilisant deux lots de données. Les évolutions temporelles des concentrations en nitrates dans les eaux souterraines ont été évaluées annuellement de 1981 à 1996 (1,299 observations), et à la fois mensuellement et saisonnièrement de 1988 à 1991 (1,868 observations). Plusieurs modèles linéaires mixtes ont été utilisés pour analyser les données, avec des effets aléatoires et des structures de corrélation. La concentration moyenne en nitrates sur les données mensuelles était de 3.99 mg/L d'azote, les mois de janvier, mai et novembre présentant des concentrations plus élevées (p=0.018). La combinaison des saisons et du type d'occupation du sol sous un terme corrélatif a fait apparaître une influence saisonnière (p=0.004). Les puits situés en zones agricoles présentaient des concentrations en nitrates plus élevées que ceux situés en zones urbaines, qui eux-même avaient des concentrations plus élevées que les zones faiblement anthropisées. Les teneurs en nitrates étaient plus élevées en été dans les zones de culture en ligne, et au printemps et en automne dans les zones de stockage du fumier. Dans les secteurs peu anthropisés, équipés d'infrastructures de collecte des eaux usées, les concentrations dans les eaux souterraines restaient relativement basses et stables le long de l'année. Aucune tendance annuelle significative n'a été décelée (p=0.954); cependant, sur tous les sites pris individuellement, 9.6% présentaient un augmentation significative des concentrations en nitrates dans le temps, et 6.6% présentaient au contraire une diminution.

Resumen Mediante la utilización de dos conjuntos de datos, se ha investigado la evolución temporal de la concentración de nitratos en las aguas subterráneas a partir de pozos en Prince Edward Island, Canadá. Las series temporales en las concentraciones de nitratos fueron medidas anualmente durante 1981–1996 (1,299 medidas), y además de forma estacional y mensual durante 1988–1991 (1,868 medidas). Los datos fueron analizados usando modelos lineales mixtos de efectos aleatorios y estructuras de correlación. La concentración media de nitratos en el conjunto de datos mensuales fue de 3.99 mg/L como NO_3–N, con concentraciones mayores en Enero, Mayo y Noviembre (p=0.018). Se observa un efecto estacional cuando la estación se combina con el tipo de

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uso del suelo en un término de interacción (p=0.004). Los pozos localizados en áreas agrícolas presentaron unas mayores concentraciones de nitratos que las zonas urbanas, las cuales tuvieron mayores concentraciones que las zonas con bajo impacto antrópico. Las zonas con cultivos en surco presentaron mayores concentraciones de nitratos en el agua subterránea en verano, mientras que las áreas de almacenamiento de abonos presentaron valores más altos en primavera y otoño. El agua subterránea en las áreas en las que el impacto humano es bajo y que cuentan con infraestructura centralizada de depuración se mantiene en niveles relativamente bajos y estables en todas las estaciones. No se observó una tendencia anual significativa (p=0.954), aunque en algunas estaciones individuales las concentraciones de nitratos se incrementaron significativamente en un 9.6% y decrecieron significativamente en un 6.6% en otras.

Keywords Agriculture · Canada · Groundwater monitoring · Statistical modeling · Water supply

Introduction

Nitrate contamination of groundwater is increasing in frequency and severity on a worldwide scale and nitrate is possibly the most widespread contaminant in the world today (Gulis et al. 2002). It is an escalating public health concern, especially where intensive agricultural production is practiced. In North America and Western Europe, intensive agriculture is considered to be the main source of water pollution by nitrate (WHO 2004). In Prince Edward Island (PEI), Canada, high nitrate concentrations in groundwater appear to be more highly correlated with the use of inorganic fertilizers than manure inputs to the soils (Young et al. 2002). Unsewered urban areas without sewerage infrastructure also have high nitrate concentrations in groundwater (Barber et al. 1996).

The maximum acceptable concentration (MAC) for nitrate in drinking water has been set at 50 mg/L NO_3 (equivalent to 11.3 mg/L NO_3–N) by the World Health Organization (WHO 2002) and 45.00 mg/L NO_3 (~10 mg/L NO_3–N) in Canada and the United States (Health Canada 1992). European Union guidelines recommended that drinking water concentrations should not exceed 5.56 mg/L NO_3–N, due to the possible health risks associated with nitrate exposure (Van Maanen et al. 2000). Elevated nitrate concentrations in drinking water have been associated with methemoglobinemia in newborns and infants less than 6 months of age (Gelberg et al. 1999). Links to other adverse health effects have also been suggested, but are inconclusive (Bukowski et al. 2001; Duncan et al. 1997; McKinney et al. 1997; Van Maanen et al. 2000). Hereafter, nitrate will refer to nitrate–nitrogen (NO_3–N).

North American background concentrations of nitrate in groundwater are estimated to be no more than 3 mg/L (Spalding and Exner 1993) in areas with relatively low human impact. In PEI, nitrate concentrations of 0.1–2 mg/L are thought to represent background levels, with these values determined from low human-impact, 'pristine' watersheds (Young et al. 2002). Elevated nitrate concentrations in PEI are considered to be primarily due to agricultural practices taking place on almost half of the island's land area, with potato and livestock farming predominant (Somers 1992).

Groundwater in PEI is of particular importance not only because of the 100% reliance on this source as the drinking water supply, but also because its discharge represents 60–70% of the island's surface water. Thus, protection of groundwater quality is important not only for human and animal health but also for the environment due to concerns over eutrophication of surface water, caused by nutrient enrichment. Because of the contribution of baseflow to surface water, attempts to control surface water chemistry will not be successful if groundwater is left unmanaged.

Much of the scientific literature suggests that nitrate levels in groundwater have been generally increasing over time, unless there has been a change in local land use practices (Somers 1998; Trojan et al. 2003). In a recent analysis on groundwater nitrate concentrations in PEI, land use type did influence nitrate concentrations, however, temporally, there was no significant annual variation within the 5 years of data analyzed (Benson et al. 2006). Seasonal trends have also been evident in some studies, but, similar to annual trends, they typically depend on other factors, namely surrounding land use, groundwater recharge rate, local climate, and well depth and construction (Maila et al. 2004; Scheytt 1997; Somers 1998). However, many of these studies have not investigated variable interactions, and have not examined these relationships while taking into account the hierarchical nature of the data (e.g. the clustering of months within years, and years within sites), or the autocorrelation structure between months, seasons or years.

The main objective of this study was to identify annual and/or seasonal/monthly trends in historical nitrate concentrations in PEI groundwater, while accounting for land use, clustered data, and temporal autocorrelation, where possible. In order to reach this objective, two different datasets were used for the analyses: one addressing seasonal and monthly variation over 3 years, and the other addressing annual variation over a 16-year study period.

Study area

Prince Edward Island (PEI) is an island located on the eastern coast of Canada, and is approximately 5,656 km^2 in area (Fig. 1). The topography reaches a maximum height of 120 m above sea level, and is characterized by gentle rolling hills. The geology consists mainly of fractured sandstone bedrock overlain by a thin layer of fine sandy loam soils. As this top layer is very porous, the groundwater is susceptible to contamination, especially

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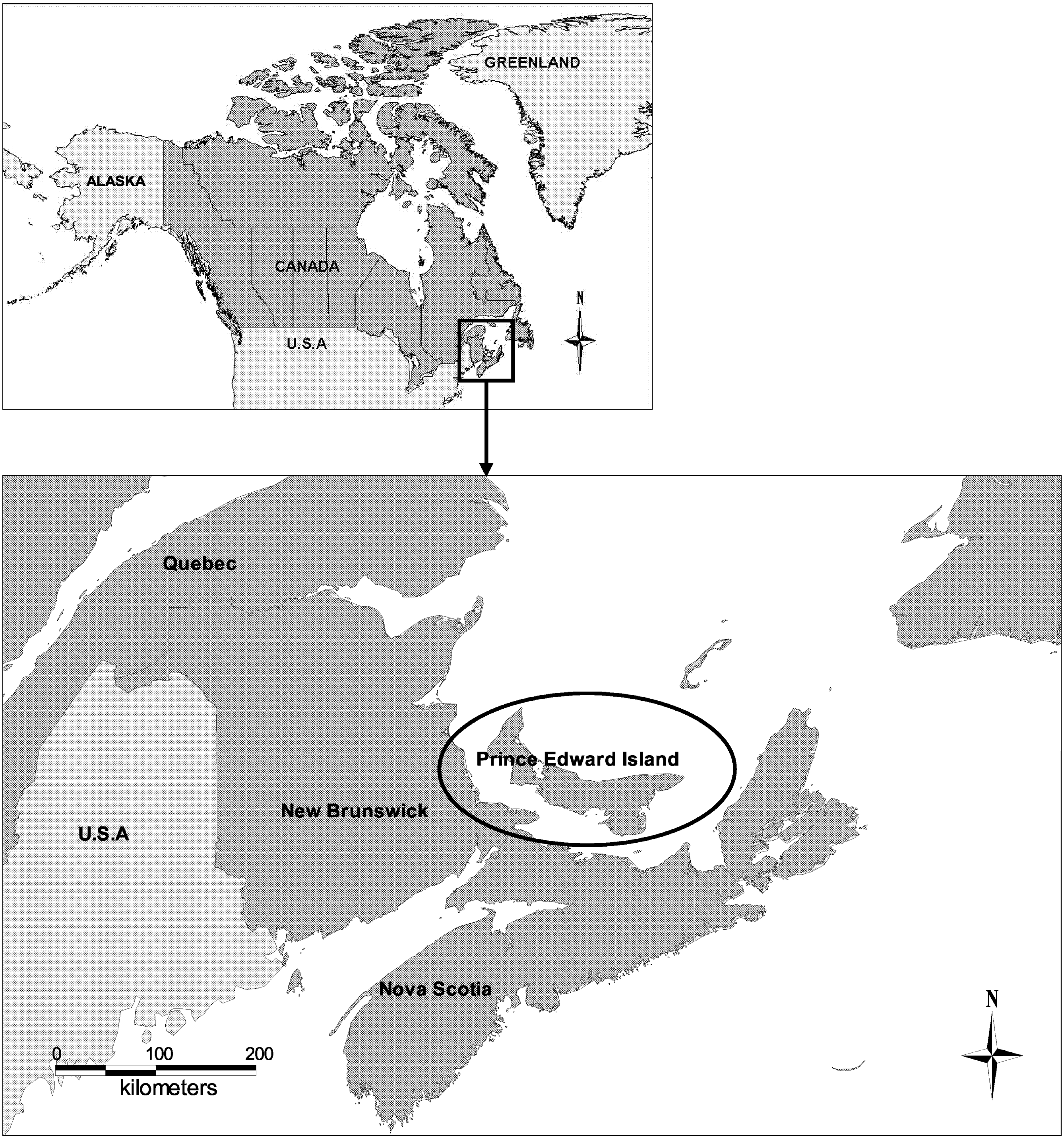

Fig. 1 Location of study area, Prince Edward Island, Canada

considering the island's high water table and high groundwater recharge rate (PEI Government 2004, 2005; Somers 1998).

An estimated 20,000–25,000 rural private wells supply water to over half of the population in PEI. The remainder of the population obtains drinking water from the same groundwater source, but is serviced by central water supply systems (Young et al. 2002).

Methodology

Data acquisition

The data used to assess seasonal and monthly variation were associated with up to 37 water samples per site, taken monthly from December 1988 to December 1991. These samples were taken from 54 different sites located across PEI, grouped by land use. The sites were originally

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selected to assess the effect that land use has on groundwater nitrate concentrations, with 9 wells in each of 6 land-use categories. The 6 land uses under study were: "pristine" areas (non-cropped), row cropped areas (for example, potatoes), non-row cropped areas (for example, wheat), feedlot areas with on-site manure storage, areas with on-site sewage disposal, and areas with central sewage infrastructure (Somers 1998). Available data for each sample included site identification, nitrate concentration in mg/L, land use type, month, and year. A total of 1,868 nitrate measurements were in the dataset, providing an average of 35 results per site (130 values were missing).

For the assessment of annual groundwater nitrate concentration variation, the data used were from samples collected annually (where possible) over a 16-year period beginning in 1981. The samples were originally collected as part of a routine island-wide survey assessing the drinking water chemistry of public institutions. The institutions were both privately and government-owned, and their water was supplied by a well located on the property. Institutions included schools, senior citizen homes, campgrounds, national parks, and many more. Available data for each sample included site identification, nitrate concentration in mg/L, and year. Due to logistical reasons and time constraints, sampling each of the sites every year was not always possible. In addition, no data were available for any of the sites during the year 1992. In total, 167 institutions were sampled during this time, collectively contributing 1,299 samples.

For both datasets, all samples were analyzed by flow injection analysis colorimetry (using the QuikChem Series 8000, Flow Injection Analysis) at the provincial laboratory of the Department of Environment, Energy and Forestry. The detection limit of nitrate was 0.10 mg/L N.

Statistical analyses for monthly/seasonal trends

A 3-level hierarchical model (monthly measurements within seasons, and seasons within years) with linear mixed effects (Pinheiro and Bates 2000) was created to assess possible monthly or seasonal effects on groundwater nitrate concentrations. A linear mixed model retains 3 of the 4 model assumptions of a linear regression model (equal variance across the range of predicted outcome values; normal distribution of the model residuals; and a linear relationship between the outcome and each continuous variable; linearity was not a concern in this study as no predictors were continuous). A major advantage of a linear mixed model is that if the observations are not independent (the fourth assumption of linear regression, for example, repeated nitrate measurements from the same site are not independent of each other), the model is adjusted to account for the effects of clustering using a random effect variable in a hierarchical model. An additional assumption of the linear mixed models is that all random effects are normally distributed (Dohoo et al. 2003a). Each part of the model is described in turn. The top 2 levels, represented by site and year within site random effects, accounted for clustering of years within sampling sites and for clustering of monthly samples within years, respectively. The lowest level of the model represented the error term (month) of the nitrate observations. Due to limited data within this dataset, only the following fixed effects on nitrate concentrations were investigated: land use type, year, season, and month, as well as an interaction between season and land use type. For this interaction, season was represented by averaging three months within each season. For example, the winter estimate was composed by averaging the January, February and March estimates.

Diagnostic graphs of homoskedasticity (equal variance between all combinations of the predictors) and normality of the residuals, were assessed visually because statistical tests were not available in the software, and it is recommended that they should only be used to supplement a graph, not represent the main assessment criteria (Dohoo et al. 2003b). The top level of the hierarchy, site, was assessed first, followed by year, and then finally the residuals of the actual observations (Langford and Lewis 1998).

The natural logarithm (+1) transformation was necessary to improve normality of the model residuals. This transformation also improved homoskedasticity. The residuals at the top 2 levels, site and year, remained normal when the log transformation of nitrate concentration was used. Without the constant of 1 added, the log transformations of nitrate concentrations were not normally distributed. Variance components, explaining the proportion of the variation occurring at different levels of the hierarchy were also assessed.

To determine if there was monthly or seasonal autocorrelation in nitrate concentrations in the above model, the residuals of 1 month were compared to the fitted values of the previous month in order to assess the time lags in the data. This was done using a correlation matrix in Stata 8 (Stata Corp 2004). Autocorrelation was present between months within sites, with a correlation value of 14 and 13% for months within 1–2 months of each other, respectively. Various correlation structures were investigated to take into account the autocorrelation present, including: compound symmetry (CS), autoregressive [AR(1)], and autoregressive moving average [ARMA (1,1)]. The CS correlation structure assumes the same correlation between all pairs of observations (nitrate values). Conversely, the AR(1) and the ARMA(1,1) correlation structures assume that the correlation between two observations decreases with increasing time between the two observations. The AR(1) structure has a sharper decrease in correlation over time than the ARMA(1,1) (Dohoo et al. 2003a).

Autocorrelation was also present between seasons that were up to 3 lags apart, with percent correlation between the fitted values and residuals of 10.8, 9.9, and 6.7% for seasons 1, 2 and 3 lags apart, respectively. Consequently, the same 3 correlation structures were also explored for seasonal autocorrelation in the following linear mixed regression modeling in order to improve the final model's

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goodness-of-fit. Model comparison of different fixed effects was assessed by likelihood ratio tests (Pinheiro and Bates 2000). The Akaike's Information Criteria (AIC) and likelihood ratio test were examined for the decision on best autocorrelation structure. The AIC statistic is used to compare how well statistical models fit the data when the models are not nested (i.e. nested models have some of the same predictors, or use similar correlation structures), but each model must have the same number of observations. The model with the lowest value is considered the better model. Conversely, the likelihood ratio test was used to compare nested correlation structures—e.g. CS and ARMA (1,1)—with the value closest to 0 being the preferred model (Dohoo et al. 2003a,c).

Interaction variables between main effects were created and investigated for their association with groundwater nitrate concentrations. A significant interaction between 2 variables assumes that the effect of 1 variable depends on the value of the other variable, therefore neither variable should be interpreted independently of the other.

To assist in understanding the relationships between nitrate concentrations and year, season, month, and land use type, the data were summarized by calculating and graphing expected nitrate concentrations by year, by season, by month, and by land use type. Back transformed least square means (LSM) gave an expected value (median) for each category within a categorical variable, with all other variables in the model being held at their mean values. The addition of 1 to each nitrate value also avoided the problem of working with negative log values (Rodvang et al. 2004).

Statistical analyses for annual trends

Initially, each site was individually assessed to determine if a site increase or decrease in nitrate concentration was evident over time. Using a paired *t*-test, the average of the first 3 nitrate concentrations from each site was compared to the average of the last 3 measurements to detect a significant difference between initial and final sample years at each site. A total of 23 of the sites contained less than 6 measurements, so the first and last 2 measurements were compared for these sites. Due to substantial missing data in the dataset, it was not possible to compare average nitrate concentrations with the same temporal interval length for each site in a consistent manner. Three samples were chosen so as to generate a stable estimate, and choosing the first 3 and the last 3 samples at each site helped to maximize the temporal interval between comparisons.

A 2-level hierarchical model with linear mixed effects was created to assess possible annual effects on groundwater nitrate concentrations. The top level, represented by site random effects, accounted for clustering of years within sampling sites. The lowest level of the model represented the error term (year) of the nitrate observations again. The residuals were again not normally distributed, and therefore nitrate, the outcome, was transformed to the natural logarithm scale (+1). Again, due to limited data within this dataset, only 2 variables were available for analyses: site as a random effect, and year as a fixed effect. Variance components explaining the proportion of the variation occurring at different levels of the hierarchy were again assessed.

To determine if there was annual autocorrelation in nitrate concentrations in the above model, the residuals of 1 year were compared to the fitted values of the previous year, using Stata 8 (Stata Corp 2004). Autocorrelation was not present when assessing the lags; however, correlation structures were still investigated. The repeated measures correlation structures explored were the CS, AR(1) and ARMA(1,1) matrices. Model choice was achieved using the AIC statistic. Again, the data were summarized by calculating average nitrate concentrations (using LSM), by year, in order to assist understanding the relationships between nitrate concentrations and year. Model assumptions were assessed using the statistical package MLwiN (Beta version 2; Rashbash et al. 2003), and all final analyses were carried out in SAS 8.02 (SAS Institute 2001).

Results

Monthly/seasonal results

The mean and median nitrate values for all observations were 3.99 and 3.30 mg/L, respectively, with an interquartile range of 1.90 to 5.20 mg/L. The maximum nitrate concentration was 15.50 mg/L. Descriptive statistics of nitrate concentrations by each predictor (year, season, month, and land use) are provided in Table 1.

When month and season were assessed in separate models, autocorrelation between months or seasons was controlled, using an ARMA(1,1) correlation matrix. With both season and month in the same model, the most appropriate correlation structure to fit the autocorrelation expressed in the data was again the ARMA(1,1) matrix, with an AIC of −1,826. The other 2 structures, CS and AR (1), had higher AIC values (−1,659 and −1,820, respectively).

With both season and month in the model, the main effects of land use type, year, and month were significant factors affecting groundwater nitrate concentrations in PEI (p values of <0.001, 0.011, and 0.018, respectively, with a p value being significant at 0.05), as shown in Table 2. Estimates and standard errors of nitrate concentrations for the different months are not shown in Table 2 because the table would be very large, and so are shown in Fig. 2, using back-transformed LSM and then subtracting 1.

Season was not significant (p=0.764); however, the interaction term between season and land use was highly significant (p=0.004), and therefore remained in the final model. With this interaction, land use and season cannot be interpreted separately. Figure 3 demonstrates the land use and season interaction, using back-transformed estimated nitrate values (LSM-1). Nitrate concentrations were higher in autumn and winter for locations with non-row crops and on-site sewage disposal, higher in spring and

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Table 1 Descriptive statistics of groundwater nitrate concentrations from 54 sites in Prince Edward Island, Canada (1988–1991), by year, season, month and land use

Variable	Level	Number of observations	Mean value (mg/L)	Median value (mg/L)	Range (mg/L)
Year	1988	52	3.99	2.80	0.10–14.00
	1989	616	3.86	3.30	0.10–14.00
	1990	596	4.14	3.50	0.10–15.50
	1991	604	3.98	3.30	0.10–15.00
Season	Winter	464	3.98	3.40	0.10–15.50
	Spring	448	3.95	3.50	0.10–15.50
	Summer	453	4.03	3.20	0.10–15.00
	Autumn	503	3.99	3.30	0.10–14.00
Month	January	155	4.08	3.40	0.10–15.50
	February	154	3.97	3.50	0.10–12.50
	March	155	3.90	3.30	0.10–14.00
	April	142	3.80	3.55	0.10–15.50
	May	151	4.04	3.50	0.10–14.50
	June	155	4.01	3.40	0.10–15.00
	July	152	3.95	3.10	0.10–15.00
	August	149	4.04	3.20	0.10–15.00
	September	152	4.10	3.25	0.10–15.00
	October	154	3.95	3.30	0.10–14.00
	November	150	4.02	3.40	0.10–14.00
	December	199	4.00	3.30	0.10–14.00
Land use type	Row-crop	316	6.49	6.00	2.10–15.00
	Non-row crop	306	3.95	3.80	0.70–10.50
	Manure storage sites	309	5.43	5.00	1.60–14.00
	On-site sewage disposal	310	4.27	3.60	0.10–15.50
	Central sewage disposal	321	2.60	2.60	0.10–6.50
	Pristine	306	1.17	1.20	0.10–6.00

autumn for locations with manure storage, and higher in summer for locations with row crops. Central sewage disposal and pristine land uses had little seasonal variation in nitrate concentrations.

Almost 92% of the variation of nitrate concentrations was between sites, with only 0.4% between years (within sites). The remainder of the variation was residual, unexplained variation between months within years.

Annual results

The mean and median nitrate values for all observations were 2.40 and 1.90 mg/L, respectively, with an inter-quartile range of 1.00–3.20 mg/L. The maximum concentration was 14.00 mg/L. Descriptive statistics of nitrate concentrations, by year, are provided in Table 3. Individual site analysis showed that 9.6% of the sites had significantly increased and 6.6% significantly decreased 3-year average nitrate concentrations at the $p<0.05$ level, when comparing the first 3 years with the last 3 years of

Table 2 Random effects model analysis of the monthly and seasonal effect on groundwater nitrate concentrations from 54 sites in Prince Edward Island, Canada (1988–1991)

Variable	Estimate	Standard error[a]	p value[b]
Fixed effects[c]			
Month	–	–	0.018
Year			0.011
1988	2.97	0.15	
1989	3.10	0.14	
1990	3.25	0.14	
1991	3.16	0.14	
Land use type			<0.001
Row-crop	5.84	0.37	
Non-row crop	3.51	0.37	
Manure storage	4.84	0.37	
On-site sewage disposal	3.35	0.37	
Central sewage disposal	2.24	0.37	
Pristine	0.92	0.37	
Land use and season interaction	–	–	0.004
Correlation parameters[d]			
Rho	0.55	0.066	
Gamma	0.37	0.031	
Random effects[e]			
Site	0.23	0.05	
Year (site)	0.001	0.0008	
Error	0.02	0.001	

[a] Standard error of estimate
[b] Significant at 0.05
[c] Back transformed Least Square Means, interpreted as median nitrate values
[d] ARMA(1,1) within-site correlation
[e] Variances of random effects

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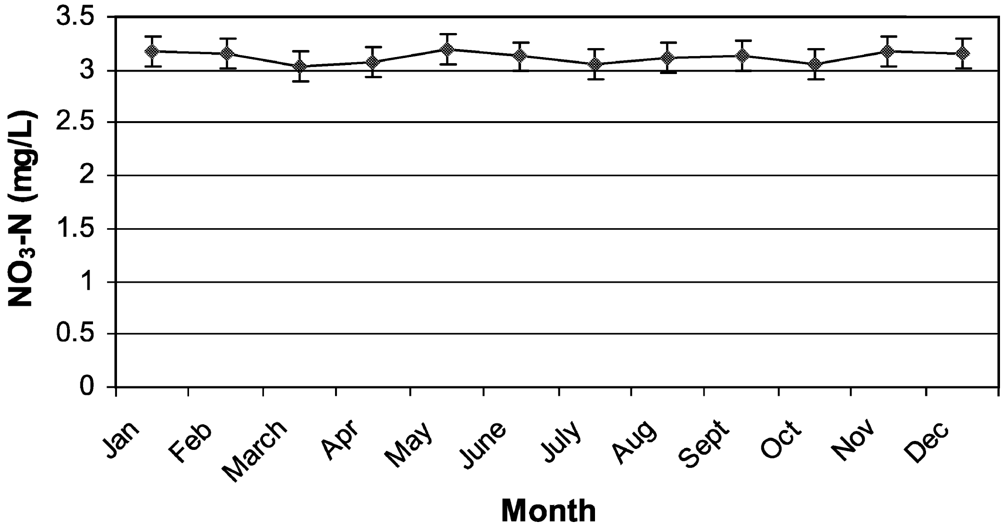

Fig. 2 Average monthly groundwater nitrate concentrations from 54 sites in Prince Edward Island, Canada (1988–1991), estimated from back-transformed least square means and then subtracting 1. The 95% confidence intervals are also shown (($\pm$))

test results. For the 23 sites that did not have 6 years of data, no sites had significant differences in 2-year average nitrate concentrations, when comparing the first 2 years with the last 2 years of test results.

The most appropriate correlation structure to fit the correlation expressed in the data was the ARMA (1,1) matrix, with an AIC of 370. The other two structures, CS and AR(1), had higher AIC values (524 and 388, respectively), and therefore fitted the data no better than the ARMA (1,1) matrix.

With site as a random effect, a year effect across all sites was not significant (p=0.954), as shown in Table 4. All years were compared to 1996, the reference value. Figure 4 shows estimated nitrate concentrations averaged across sites for each year, as estimated by back-transforming the LSM, and then subtracting 1. Average annual nitrate concentrations in PEI remained relatively constant across the 16-year period of the study. The majority of the variance (55.2%) was between sites, with the remaining 44.8% residing as unexplained variation between years within sites (Table 4).

Discussion

The objective of the study was to determine if there were temporal trends in groundwater nitrate concentrations in PEI. To determine yearly trends, appropriate annual water sampling and testing over a substantial number of years was required. Similarly, appropriate monthly sampling and testing was required for monthly trend determination. While these datasets were not ideal, in that there were substantial amounts of missing data in the datasets (51.4 and 6.5% for the yearly and monthly datasets, respectively) and limited supporting information on the sampled sites, the datasets were appropriate for determining the main goal of trend analyses.

Using up to 37 repeated measures of groundwater nitrate concentrations collected from 54 wells in 6

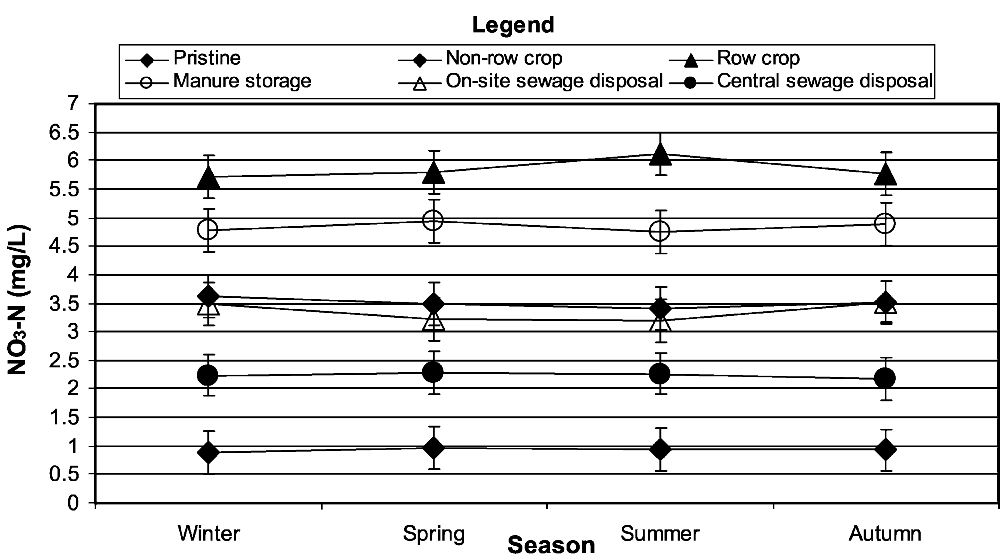

Fig. 3 Average seasonal groundwater nitrate concentrations, stratified by land use type, from 54 sites in Prince Edward Island, Canada (1988–1991), estimated from back-transformed least square means and then subtracting 1. The 95% confidence intervals are also shown (($\pm$))

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Table 3 Descriptive statistics of annual groundwater nitrate concentrations from 167 sites in Prince Edward Island, Canada (1981–1996)

Variable	Level	Number of observations	Mean value (mg/L)	Median value (mg/L)	Range (mg/L)
Year	1981	51	2.16	1.40	0.20–9.00
	1982	30	2.21	1.55	0.20–10.00
	1983	34	2.73	1.70	0.20–9.50
	1984	49	2.21	1.70	0.20–12.00
	1985	68	2.32	1.80	0.20–7.00
	1986	62	2.64	2.10	0.20–9.00
	1987	86	2.12	1.80	0.10–7.90
	1988	71	2.57	1.80	0.10–9.00
	1989	102	2.27	1.65	0.10–8.00
	1990	99	2.43	2.03	0.10–7.50
	1991	116	2.45	2.10	0.20–13.50
	1992	.	.	.	.
	1993	150	2.39	2.00	0.10–14.00
	1994	155	2.36	1.90	0.10–11.96
	1995	131	2.47	2.00	0.10–8.30
	1996	95	2.50	2.00	0.10–9.30

different land uses in PEI, land use appeared to have a large effect on nitrate concentrations (Table 2). However, the land use effect was dependent on season.

Areas influenced by substantial human activity had higher nitrate concentrations than pristine areas. Figure 3 demonstrates that agricultural areas had higher concentrations than wells close to sewered areas, while pristine areas had the lowest nitrate values. This observation could be because fertilizer is added to many of the cropped areas, especially row-crops (for example, potatoes). Non-row cropped areas typically require less nitrate application (Jacques Whitford Environment Limited 2001); therefore, lower nitrate values in local well water would be expected. For example, potatoes are generally heavily fertilized at the start of the growing season—400 kg/ha of 18-46-0 (nitrogen–phosphorus–potassium)—and then another quantity of 500 kg/ha of 15-0-20 is added later into the growing season (PEI Government 2000). Spring grain crops are typically only fertilized at the start of the growing season at a rate of 300 kg/ha of 18-36-18 (PEI Government 2001).

Manure storage guidelines (Linkletter et al. 1999) were finalized in PEI in 1999 in order to limit effluent discharge and contamination of water resources. However, the nitrate measurements in this study were taken before the finalization of these guidelines, perhaps accounting for the relatively high nitrate concentrations in wells situated close to manure storage areas. It was also expected that areas with on-site septic systems would produce greater groundwater nitrate concentrations than areas with centralized sewage disposal systems because septic systems discharge on-site, while sewage collected by central sewer systems is discharged into rivers, estuaries, or open ocean environments, where it has no connection to, or impact on groundwater resources. The effect of land use on nitrate concentrations in PEI was also evident from a previous study (Benson et al. 2006). Other studies outside of PEI have also shown an association between groundwater nitrate concentrations and land use (Gardner and Vogel 2005; Levallois et al. 1998; Trojan et al. 2003).

Seasonal effects were only significant once they were expressed in an interaction term with land use. Groundwater nitrate concentrations in the summer were higher for row-cropped areas, but lower for non-row cropped and on-site sewage disposal areas. This is possibly because some of the fertilizer added to row crops is usually not taken up by the crops, or held in the soil, but leached out of the soils and into the nearby water-ways (Zvomuya et al. 2003) or into the underlying aquifers (MacLeod et al. 2002). This is particularly true for row crops where there is more bare soil before, during, and after the growing season compared to hay or pasture crops that tend to hold many of the nutrients in the soil and protect the land from the heavy rain, which may encourage erosion and leaching. Central sewage disposal and pristine areas remained relatively constant over seasons, perhaps because contamination from these land uses is much less intense. Nitrate concentrations in groundwater near manure storage areas were higher in the spring and autumn, which is when the manure is typically being spread on the land and when the crops on those lands are not rapidly growing (pre-planting or post-harvest). Freezing of manure in the winter may also reduce leakage of nitrate into groundwater, and frost in the ground may limit infiltration/discharge of nitrate to the underlying water table.

Table 4 Random effects model analysis of the annual effect on groundwater nitrate concentrations from 167 sites in Prince Edward Island, Canada (1981–1996)

Variable	Estimate	Standard error[a]	p value[b]
Fixed effect			
Year	–		0.954
Correlation parameter[c]			
Rho	0.91	0.10	
Gamma	0.72	0.18	
Random effects[d]			
Site	0.16	0.088	
Error	0.13	0.086	

[a] Standard error of estimate of variance component

[b] Significant at 0.05

[c] ARMA(1,1) within-site correlation

[d] Variances of random effects

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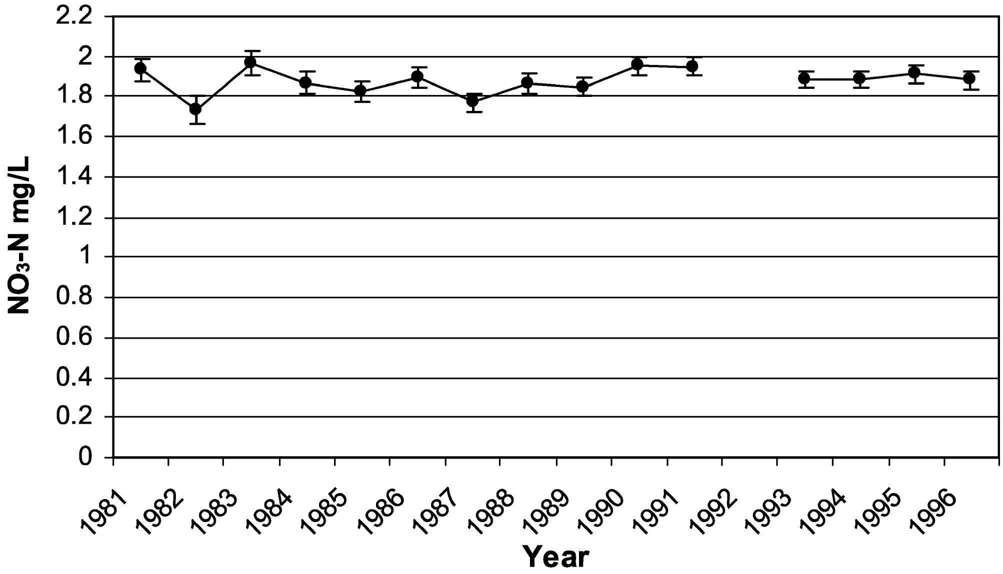

Fig. 4 Annual groundwater nitrate concentrations from 167 sites in Prince Edward Island, Canada (1981–1996), estimated from back-transformed least square means and then subtracting 1. The 95% confidence intervals are also shown ((±))

Seasonal effects on groundwater nitrate concentrations have been observed in previous studies, but little information for monthly effects has been available. In the Gaza Strip, Asia, a seasonal effect was more noticeable in domestic wells than agricultural wells, however, only 2 samples were taken from each well, and just 1 year of data was used in the analyses (Maila et al. 2004). No seasonal effect was present in a large study conducted in Minnesota, USA, but a slight year effect was evident, especially with a sudden land use change (Trojan et al. 2003). In another study, no overall seasonal trend was apparent; however, there were some individual wells where seasonal fluctuation in nitrate concentrations was evident (Burkart and Kolpin 1993).

There was a significant temporal trend in the monthly dataset, both monthly and annually. However, graphically, the temporal trends, shown as LSM, were minor (Table 2 and Fig. 2). No general increase or decrease was noted over time, nor was a sinusoidal pattern significant in the monthly data. Furthermore, when looking at the variance components, very little of the variation was explained by year, only 0.4%. The majority, 92%, was explained by the site itself, suggesting that land use was responsible for much of the variation between nitrate observations. Some other factor may be causing the random fluctuations seen in the temporal variables. Such unmeasured variables could be well depth and construction (Spalding and Exner 1993), recharge rate, or precipitation. In PEI, the average well depth for a domestic well is approximately 30 m, but may vary from 15 to 60 m, depending on the depth of the water table.

Using 16 years of data collected from 167 institutions in PEI, a year effect was not significant (p=0.954), and autocorrelation between years was present. In this annual dataset, average annual nitrate concentrations ranged from 1.93 mg/L in 1981 to 1.88 mg/L in 1996, but fluctuated between 1.73 and 1.96 mg/L (Fig. 4). As no other variables were available for analysis, other factors affecting nitrate concentrations in groundwater such as land use, were not examined. Again, the majority of the variation was at the site level rather than in the residuals. Therefore, there was little evidence for an annual effect of groundwater nitrate concentrations in PEI. A total of 55.2% of the random variation was at the site level, with 44.8% in the error term. When sites were individually assessed for a significant change over time, a total of 9.6% of the sites significantly increased and 6.6% significantly decreased. This suggests that site level factors such as land use are perhaps more influential than province-wide factors.

Typically, the annual trend in groundwater samples reported in other studies has been a general increase over time, but often this was dependent on a number of factors such as climate, surrounding land use, well depth and age, and recharge rates (Overgaard 1984; Spalding and Exner 1993; Trojan et al. 2003). In Denmark, one study showed that the overall mean concentration trebled over a 20–30 year period, with specific regional effects (Overgaard 1984). A study in Alberta, Canada also noted a significant increase by 39% in nitrate concentrations over a 6-year period (Rodvang et al. 2004).

A year effect was present within the 3-year dataset for PEI, but 3 years of data was less appropriate for assessing annual trends than the 16-year dataset. There was a slight increase in groundwater nitrate concentrations during the period of 1988–1991 within the annual dataset, perhaps explaining the significant annual effect in the monthly dataset, but this temporal trend was not consistent within the 16-year annual dataset, producing no significant overall annual effect.

One interesting finding was that nitrate levels obtained for the annual dataset were lower than the monthly dataset. This could have been because wells at public institutions (annual dataset) may have been constructed to higher standards (i.e. more casing) than private wells (monthly dataset). Also, public institutions are more likely to be in a more urban setting, with less influence from agriculture and on-site septic systems on the local landscape.

Conclusion

In general, groundwater nitrate concentrations in PEI appeared to be influenced more by short-term temporal changes than yearly effects. In the dataset with monthly concentrations, a small monthly cyclic fluctuation over the 3 years was noted, but this pattern was not statistically significant when sine and cosine functions were added to the model. Land use greatly influenced nitrate concentrations, and this was dependent somewhat on the season. In general, agricultural land uses appeared to result in greater nitrate concentrations in groundwater than residential land uses, which in-turn were higher than pristine (low human-impact) areas.

The annual dataset analysis showed that nitrate concentrations did fluctuate somewhat, but no specific increase or decrease was apparent for the dataset overall. At the individual site level, 9.6% of the individual sites significantly increased, and 6.6% significantly decreased over time. In general, nitrate values for the sampled institutions were low and showed little variation, perhaps explaining why no specific yearly pattern was significant.

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