

USING STREAM FLOW AND CHEMISTRY DATA TO ESTIMATE CATCHMENT SCALE GROUNDWATER AND NITRATE FLUXES

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Abstract

Groundwater is the dominant flow path carrying land surface recharge, including dissolved contaminants, to surface waters draining a catchment. The dominance of the groundwater pathway poses a challenge to management of water quality in agricultural catchments, because groundwater quantity and quality are difficult and expensive to monitor, and groundwater assimilative capacity for nitrate is generally unknown. On the other hand, rainfall and evapotranspiration as inputs, and stream flow and nitrate concentration as outputs, can be recorded relatively easily, especially if inexpensive in-stream nitrate sensors can be developed.

The eigenmodel approach has previously been used to estimate the land surface area and groundwater discharge contributing to stream flow in a small hill catchment. We extended this approach to explain seasonal patterns of nitrate and silica concentrations observed in the Toenepi Stream, which drains a lowland dairying catchment near Morrinsville, and to estimate the water and nitrate fluxes driving these observations.

The resulting model (“StreamGEM”) was calibrated for the four-year period 1 April 2007 to 31 March 2011, and cross-validated using data from the period 1 April 1995 to 31 March 1997. Estimated discharge, nitrate concentration (as nitrate-N) and nitrate load from near-surface, fast groundwater, and slow groundwater flowpaths were then calculated.

On an annual basis, stream flow was dominated by discharge from fast, shallow groundwater. In summer however, slow, deeper groundwater dominated both flow and chemistry.

The total catchment input load (at the bottom of the root zone) was estimated to be 40 kg N ha⁻¹ y⁻¹ nitrate nitrogen (NO₃-N). Nitrate attenuation in the groundwater components accounted for 20 kg N ha⁻¹ y⁻¹ of this, with the remaining 50% being discharged to the stream. At the catchment scale, nitrate assimilation appears to occur dominantly in the shallower flow near the redox boundary, despite the strongly reduced conditions and much lower nitrate concentrations found in the deeper groundwater.

The ability to estimate catchment water and nitrate fluxes from weather and in-stream data offers an inexpensive and potentially widely applicable tool for improved management of New Zealand’s land and water resources. Current research focuses on ascertaining in which type of catchments StreamGEM can be applied successfully.

Introduction

All agricultural systems are characterised by significant inputs as well as losses of nutrients. Losses of nitrate are particularly difficult to manage, as the anion is highly mobile and leaches rapidly to contaminate the underlying groundwater that subsequently discharges to environmentally sensitive surface waters. This means that nitrate losses cannot be effectively managed by riparian exclusion zones or vegetation strips that are more effective in reducing the transfer of contaminants that are predominantly transported by surface runoff (e.g. sediment, phosphorus, microbes). Furthermore, the large volume relative to flow rate of many groundwater systems means that leached nitrate can be stored and may continue to be discharged to surface waters long after leaching losses have been reduced by introduction of improved land management.

A mitigating factor is that in some situations nitrate leached into groundwater may be denitrified (Stenger et al., this issue), predominantly to harmless dinitrogen gas (N_2). For denitrification to occur, oxygen-depleted conditions, suitable electron donors (e.g. carbon, pyrite) and a microbial community with the metabolic capacity for denitrification are required. As nitrate is not necessarily conserved in the groundwater system, it is essential to understand not only the flow paths, but also any attenuation processes possibly occurring along them. This will allow defensible cause–effect relationships to be established, which are needed for improved resource management.

Modelling and management of agricultural nutrient losses is often done on a catchment basis, in order to make use of the natural hydrological boundary conditions implied by catchment topography and geology. Most catchment modelling is done using distributed or semi-distributed models, which require detailed land use and physical data, that is not always available outside research sites. At the same time, these models have tended to focus on the more easily observed overland/near-surface runoff and channel flow, with groundwater hydrology typically being greatly simplified, despite groundwater being the main conduit for nitrate from the land surface to streams and lakes.

Temporal changes in the relative contributions of overland/near-surface flow and groundwater discharge may also be reflected in the chemistry of the stream water. Stewart et al. (2007) showed how weekly samples from Pukemanga Stream, analysed for oxygen-18, silica, tritium and sulphur hexafluoride, provided additional evidence for the dominance of groundwater flow. The longer transit times associated with water flowing along deeper flow paths is reflected in lower concentrations of tritium and reactive ions, and higher concentrations of silica, relative to overland/near-surface flow water.

The ability to link stream water chemistry with catchment land use is therefore of particular interest, for the information it provides on catchment-scale land use impacts as well as nutrient attenuation processes along the various flow paths. Time-series records of stream nitrate can provide the basis for development and calibration of a model that encompasses multiple flow paths through the catchment, with different dynamic response times and chemical signatures. Analysis of predicted flows and concentrations can then provide estimates of catchment-scale nitrate loads and denitrification along each flow path.

This paper describes the application of such an inverse modelling approach to estimate the relative contributions of near-surface drainage and groundwater discharge to stream flow and nitrate fluxes in a closed catchment. This approach is based on the calibration of a simple, lumped (i.e. non–distributed) process model (Streamflow Generation EigenModel,

‘StreamGEM’), which sacrifices spatial detail in favour of analytical tractability. As well as facilitating model calibration for interpretation of stream information, this approach allows meaningful modelling of catchments with limited available spatial or geological information.

The model is applied to analysis of water and nitrate time-series data taken from the Toenepi Stream, which drains a lowland dairying catchment in the Waikato region of New Zealand’s North Island. Stream silica data is also included in the calibration, as a useful surrogate for water age.

Site Description

The Toenepi Stream drains a small catchment (15.1 km², elevation 40-130 metres above sea level) north-west of Kiwitahi in the Waikato region of New Zealand. The catchment is characterised by lowland alluvial plains in the central portion of the catchment and at the outlet, with the remainder of the catchment consisting mainly of rolling downlands and some hill country in the headwater area. Most of the properties in the catchment are intensive pastoral dairy farms (average 3.1 cows ha⁻¹), complemented by a small number of pastoral drystock farms. In 2003, the dairy land received an average of 99 kg N ha⁻¹ y⁻¹ fertiliser (Stenger et al., 2008).

Intensive monitoring of the surface water (since 1995) and groundwater (since 2002) in this catchment has been motivated by concerns about present and future effects of pastoral dairy farming intensification on water quality (Wilcock et al., 1999; Stenger et al., 2008).

Stream discharge from the catchment (at the Tahuroa Road bridge) has been monitored continuously since June 1995, with the exception of the periods of April 1997–October 1998 and November 2001–February 2002 (Wilcock et al., 1999, 2006). Instantaneous flow rate (L s⁻¹) was recorded at 15 minute intervals. Stream ammonia and nitrate concentrations were measured weekly from March 1995–April 1997, and then monthly from October 1998 until March 2011 (Wilcock et al., 1999, 2006). Stream silica concentrations were measured at irregular intervals from August 2007 (Stenger et al., 2009). Stream chemistry at the catchment outlet shows a strong seasonal pattern, with high nitrate and low silica concentrations in the winter, when high flow rates are typical, contrasting with low nitrate and high silica concentrations in the summer, when low flow conditions prevail (Fig. 1; Wilcock et al., 1999, 2006; Morgenstern et al., 2010).

Despite the long history of intensive dairying, and moderately high nitrate concentrations in the stream, observations of shallow groundwater (less than 3 m below ground surface) reported by Stenger et al. (2008) found generally low levels of nitrate (80% of the 843 samples taken between December 2002 and December 2004 were below the Australia and New Zealand Environment and Conservation Council trigger value of 0.44 mg NO₃-N L⁻¹ for eutrophication of surface water). In addition, persistent vertical stratification was subsequently observed within the groundwater underlying well-drained soils, with a relatively thin uppermost, oxidised and nitrate-bearing (5-10 mg L⁻¹ NO₃-N) zone overlying the reduced and nearly nitrate-free (less than 0.5 mg L⁻¹ NO₃-N) deeper groundwater. The consistently low nitrate concentrations in this deeper groundwater are considered to be partly due to recharge prior to commencement of agricultural land use and partly to denitrification occurring in the groundwater system (Stenger et al., 2008).

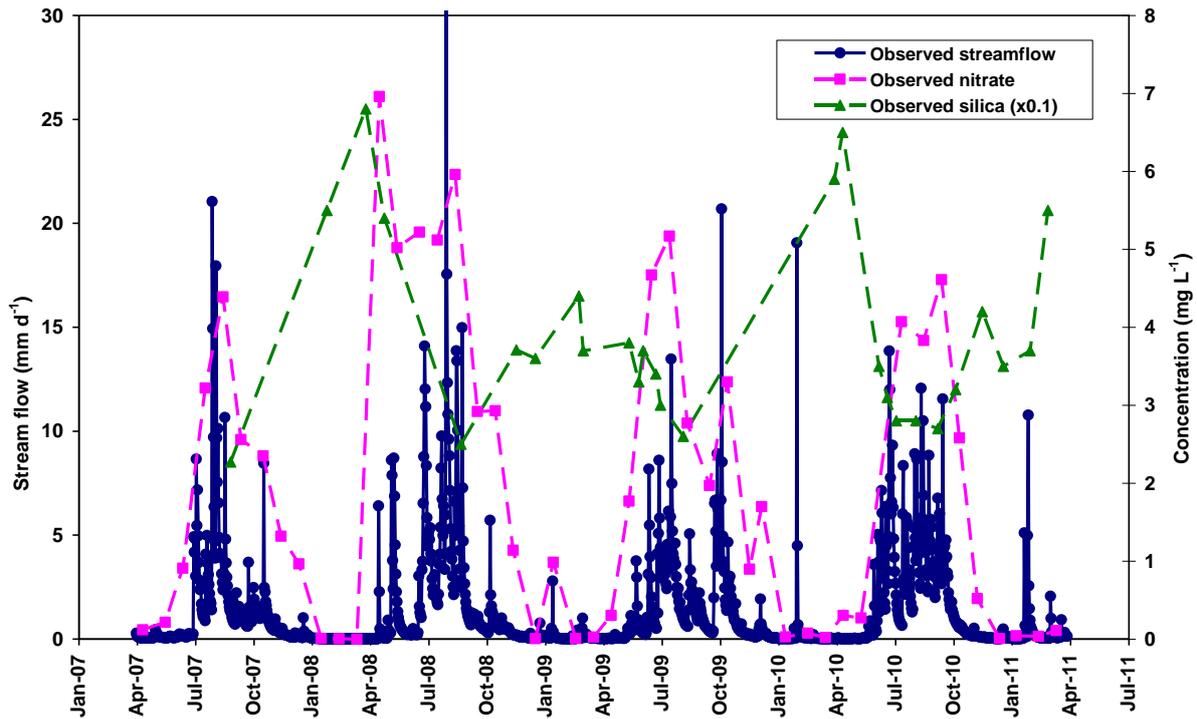


Figure 1. Stream flow (mm d^{-1} over the catchment area), nitrate-nitrogen (mg L^{-1}), and silica ($\text{mg L}^{-1} \times 0.1$) observations collected at Toenepi Stream catchment outlet weir.

The stratified groundwater observations suggest the existence of two distinct groundwater zones at a catchment scale; one shallower, predominantly oxidised, nitrate bearing and rapidly draining to the stream, and the other slightly deeper, consistently reduced, denitrified, and draining more slowly. The shallower groundwater is thought to reside in the young, friable volcanic ash beds that overlie substantially older and argillised ones (Stenger et al., 2008). The existence of this redox stratification also raises the question of how much nitrate gets denitrified in the groundwater system between the recharge locations and discharge into Toenepi Stream.

Methods

These observations motivated the development of a lumped catchment-scale model, StreamGEM (Streamflow Generation EigenModel). StreamGEM uses climate and stream data to characterise water and nitrate fluxes through these two groundwater zones, and to estimate attenuation of nitrate in the subsurface prior to discharge into the stream.

The original eigenmodel developed by Bidwell et al. (2008) considered soil water content (W), drainage-excess overland and near-surface flow entering the stream network directly (N), the passage of drainage water through the vadose zone (V), and groundwater response modelled using the linearised Boussinesq equation (“eigenmodel”). On the basis of the groundwater observations described in the previous section, in the present model groundwater response was subdivided into two reservoirs with different hydraulic response times and chemical signatures. These were a relatively shallow, “fast” reservoir (F), recharged from the vadose zone, and a slightly deeper, “slow” reservoir (S), recharged from

the fast reservoir (Fig. 2). “Fast” and “slow” here refer to the expected hydrometric response times of the two reservoirs.

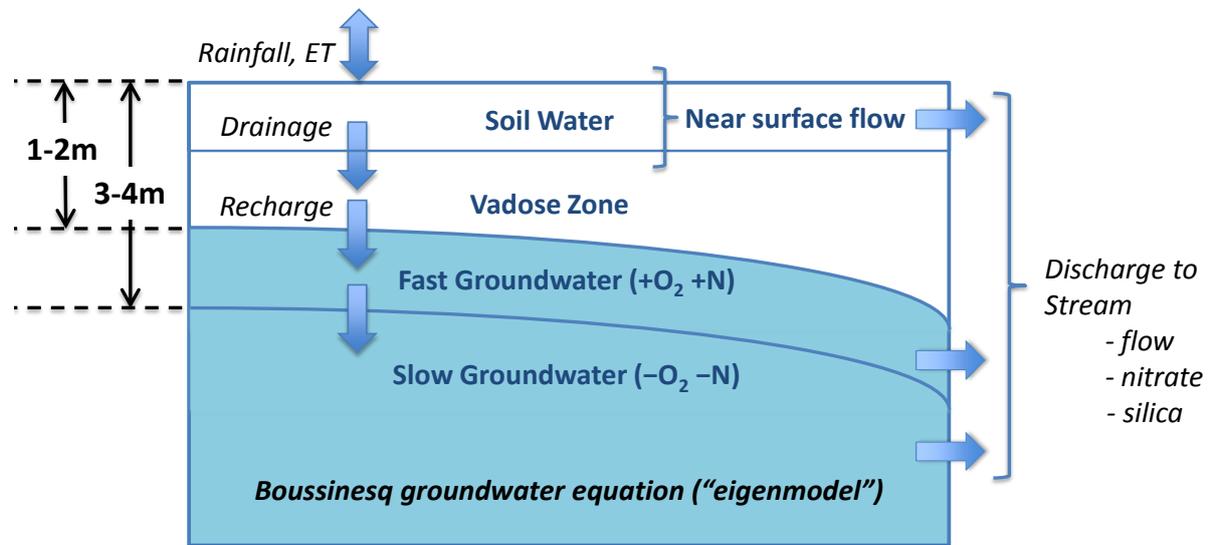


Figure 2. Schematic showing water reservoirs (Soil water, Near surface flow, Vadose zone, Fast groundwater, Slow groundwater) and flows simulated in the StreamGEM model.

The StreamGEM model is specified as a system of linear differential equations, which can be solved analytically for stress periods over which the model inputs (rainfall, evapotranspiration) remain constant. Fixed-length stress periods (hourly, daily, etc.) are a special, but useful case. In this study, the time step is 1 day and volume/area units are mm (over the catchment area of 15.1 km²). The model is implemented in Microsoft Excel.

While some temporal variation is evident in the field data (Stenger et al., 2009), as a first approximation the nitrate and silica concentrations associated with the near-surface, fast and slow groundwater discharge in the model were assumed to be constant with time. These concentrations were estimated by model calibration to the stream chemistry data. Attenuation of discharged nitrate due to hyporheic or in-stream uptake was not modelled, on the basis that Wilcock et al. (1999) found stream nitrate concentrations to be similar between three widely spaced sampling sites, implying that in-stream attenuation processes are relatively small in this catchment.

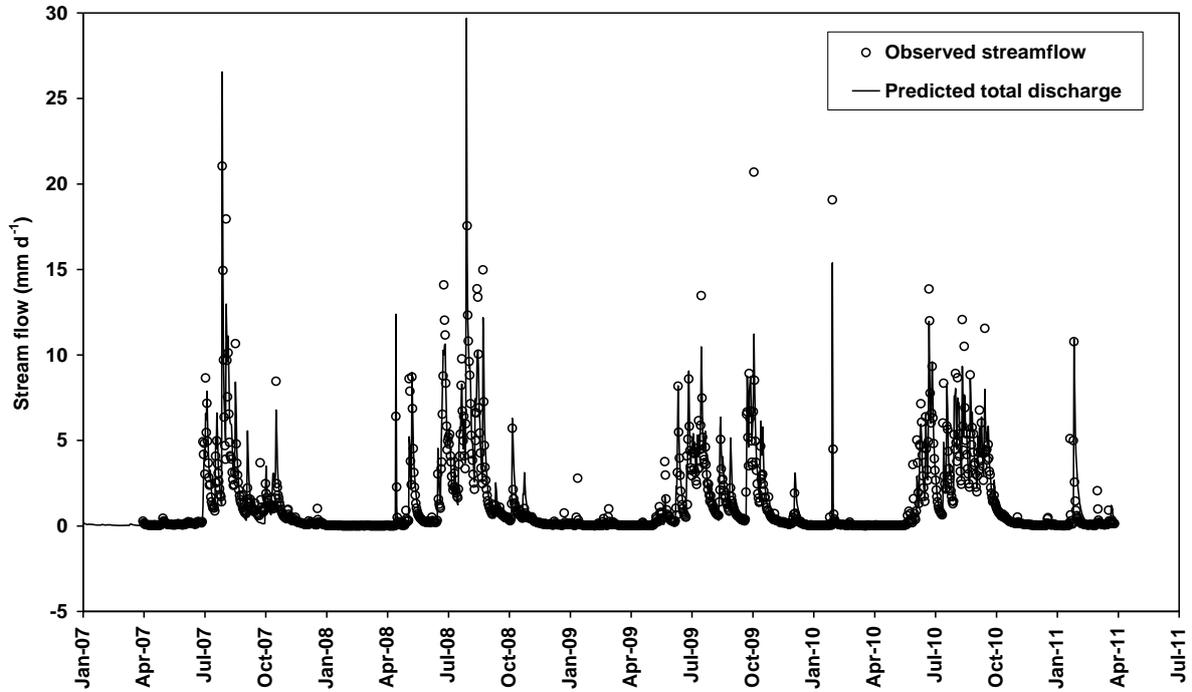
A Visual Basic implementation of the PIKAIA 1.2 genetic algorithm optimiser (Charbonneau, 2002; Pelletier, 2002) was used to calibrate the model to stream flow and chemistry data collected at the Toenepi catchment outlet during the four-year period 1 April 2007 to 31 March 2011, and to estimate the model parameters. Cross-validation was subsequently carried out by comparing model predictions with independent data from the period 1 April 1995 to 31 March 1997, during which stream nitrate was measured weekly (Wilcock et al., 1999). However, no silica measurements were available for this period.

Results

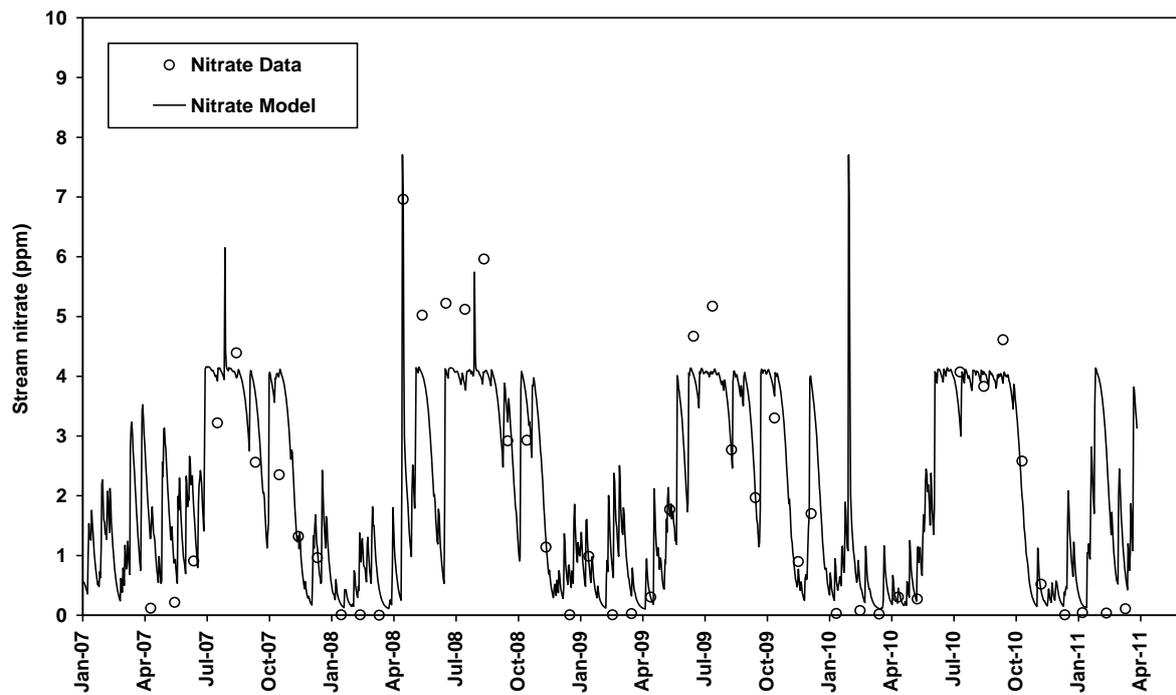
The calibrated Nash-Sutcliffe model efficiencies (Nash and Sutcliffe, 1970), E , for the three datasets were 0.90 for stream flow, 0.81 for nitrate, and 0.67 for silica, indicating a good

calibration (Fig. 3). (The Nash-Sutcliffe model efficiency statistic is similar to the familiar coefficient of determination statistic, R^2 , and indicates the proportion of variation in the data that is explained by the model.) The cross-validation model efficiencies were 0.71 for stream flow and 0.76 for nitrate. Further details of model calibration and validation, including uncertainty analysis, are presented in Woodward et al. (2013).

(a)



(b)



(c)

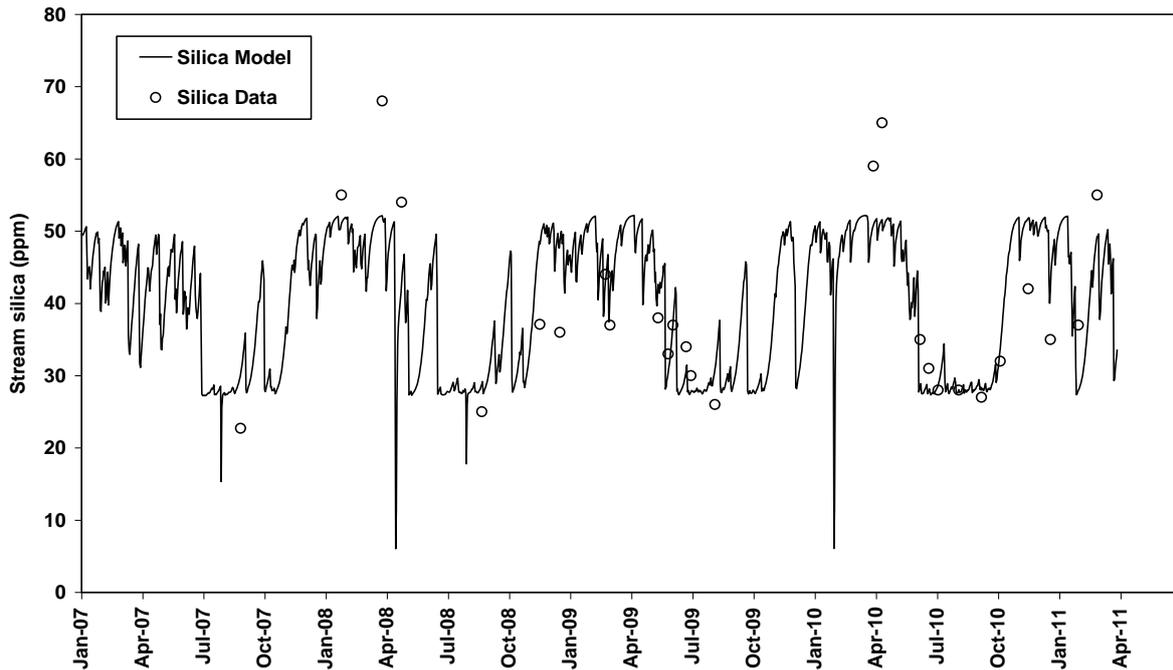
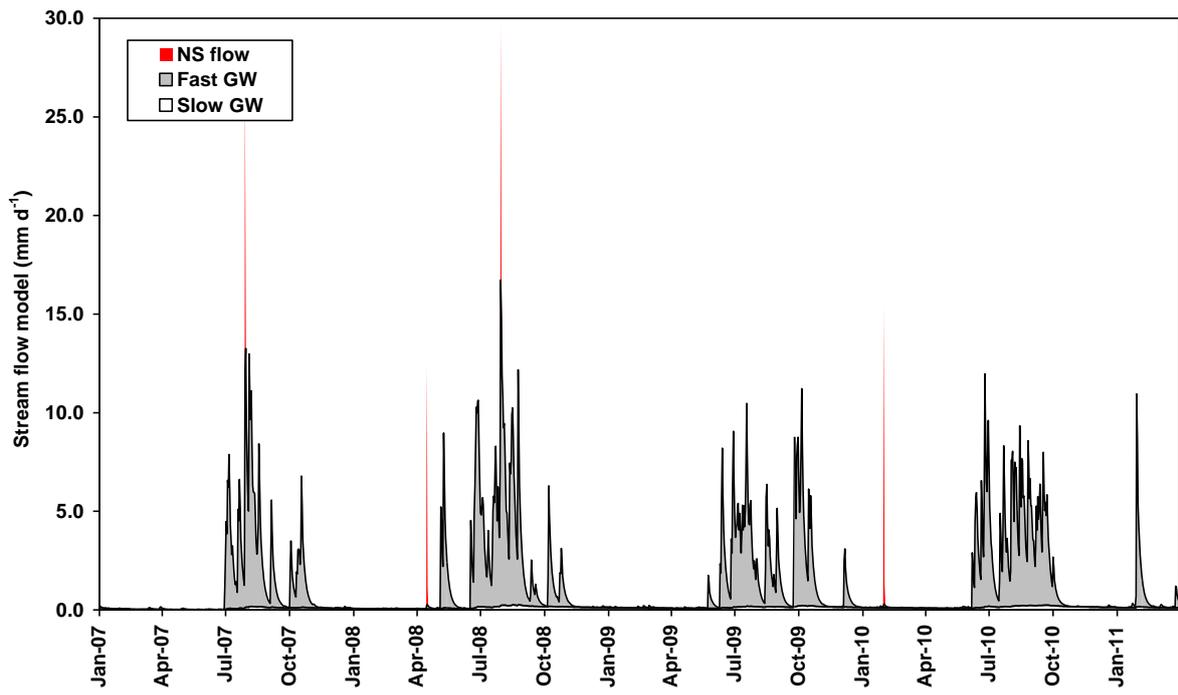


Figure 3. Calibrated prediction of (a) stream flow, (b) stream nitrate-nitrogen concentration, and (c) stream silica concentration.

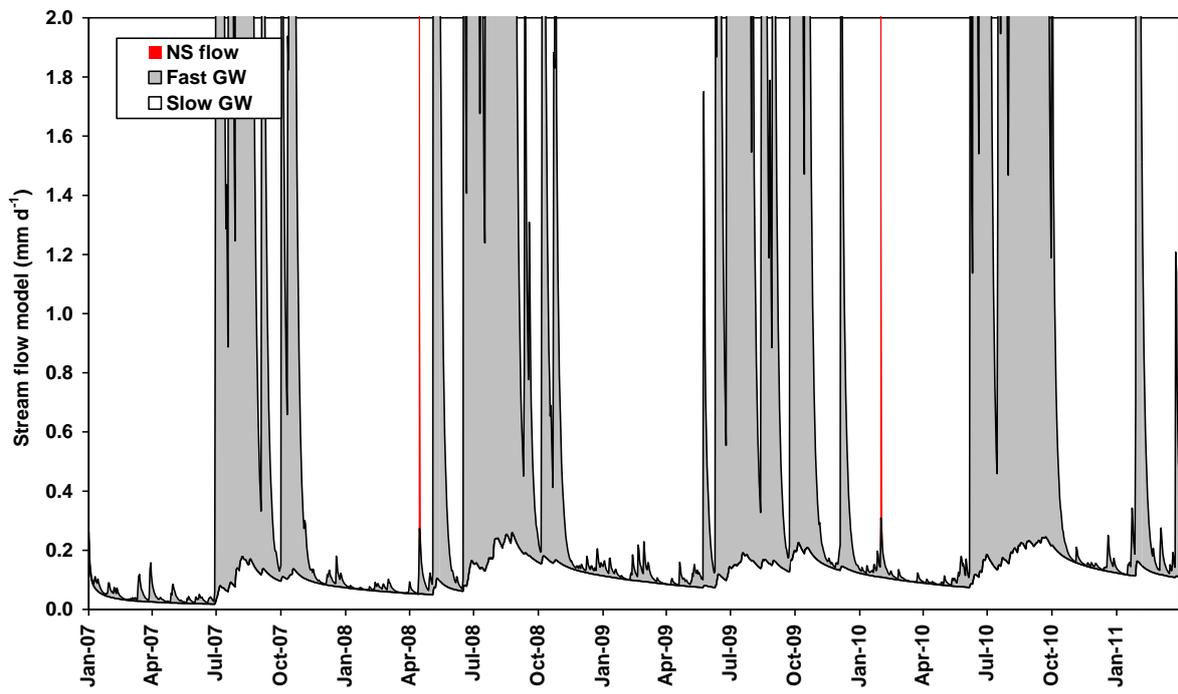
Analysis of the calibrated model allows separation of stream flow into its constituent sources (Fig. 4). Fig. 4a shows the contributions of stream flow generated by the different water reservoirs, Fig. 4b shows the low-flow portion of this chart in more detail, and Fig. 4c expresses this on a percentage basis. Notably, slow groundwater provides for a significant proportion of summer flow, even though its flow contribution is small on an annual basis. In contrast, the contribution of overland/near-surface (NS) flow is barely discernable on an annual basis, as it only contributes to total stream flow during a few major storm events (these can be identified as red spikes in Fig. 4).

The average annual discharge from each reservoir was calculated for the calibrated model, and is summarized in Table 1. Over the period 1 January 2007 to 31 March 2011, overland/near-surface, fast groundwater and slow groundwater were estimated to contribute 2.5, 91.2 and 6.3% of annual flow respectively (Fig. 4a, 4b). On a time-basis, overland/near-surface flow was the dominant contributor to stream flow on only 0.4% of days, compared with 48.7% for fast groundwater and 50.9% for slow groundwater (Fig. 4c). Despite its low discharge rate, therefore, the slow groundwater reservoir plays a very significant role in determining stream water quality during the summer season.

(a)



(b)



(c)

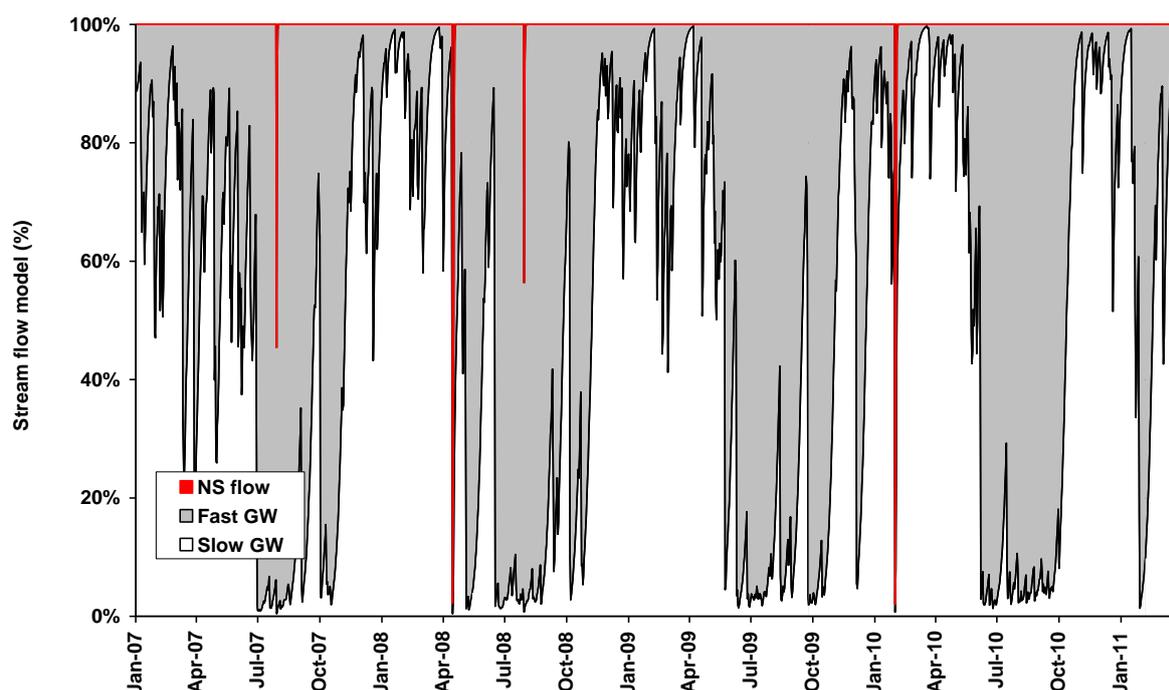


Figure 4. Modelled components of stream flow (a) from near surface (NS), fast groundwater (GW), and slow groundwater discharge, (b) truncated at 2 mm d^{-1} , and (c) on a percentage basis.

	Characteristic Response Time d	Annual Discharge mm y^{-1}	Annual Discharge %	Dominant Days %
Soil water				
Near-surface flow	0.46	13.4	2.5	0.4
Vadose zone	0.19			
Fast groundwater	4.0	493.0	91.2	48.7
Slow groundwater	390.0	34.2	6.3	50.9
Total		540.6	100.0	100.0

Table 1. Estimated hydrodynamic response time and annual discharge of water reservoirs from 1 April 2007 to 31 March 2011.

Concentrations of solutes in discharge water are also estimated during the calibration process (Table 2). Multiplying these by the water fluxes allows calculation of nitrate yield discharged annually from each reservoir. Annual nitrate-nitrogen yield was calculated as $1.0 \text{ kg N ha}^{-1} \text{ y}^{-1}$ from near surface flow, $19.1 \text{ kg N ha}^{-1} \text{ y}^{-1}$ from fast groundwater, and $0.03 \text{ kg N ha}^{-1} \text{ y}^{-1}$ from slow groundwater discharge, for a total yield of $20.1 \text{ kg N ha}^{-1} \text{ y}^{-1}$ and a total catchment load of $30.4 \text{ t NO}_3\text{-N y}^{-1}$. Annual nitrate discharge is therefore dominated by the fast groundwater flux. Near-surface flow results in very little nitrate entering the stream on an annual basis, because this pathway is significant only during major storm events (Table 1),

and slow groundwater discharge represents relatively small amounts of the total catchment discharge.

	Nitrate-N Concentration mg L⁻¹	Nitrate-N Yield kg ha⁻¹ y⁻¹	Nitrate-N Yield %	Nitrate-N Attenuation kg ha⁻¹ y⁻¹	Nitrate-N Attenuation %^b
Near-surface flow	7.4	1.0	4.9	^a	^a
Fast groundwater	3.9	19.1	94.9	18.8	46.1
Slow groundwater	0.1	0.03	0.2	1.3	3.3
Total		20.1	100.0	20.1	49.4

Table 2. Estimated nitrate yield and estimated attenuation of water reservoirs from 1 April 2007 to 31 March 2011.

^a Nitrate attenuation in Near-surface flow is assumed to be zero.

^b Percentage of total catchment input yield, estimated to be 40.2 kg N ha⁻¹ y⁻¹.

The estimated near-surface nitrate-nitrogen concentration of 7.4 mg L⁻¹ (Table 2) lies within the range of 7–11 mg L⁻¹ calculated by AgResearch for leachate from dairy farms in the catchment using the OVERSEER nutrient budgeting model (as quoted in Stenger et al., 2008) and concentrations measured in shallow groundwater underlying free-draining soils (Stenger, unpublished). Assuming that this represents the nitrate-nitrogen concentration in leachate draining from the root zone, an average nitrate-nitrogen yield across the catchment of 40.2 kg N ha⁻¹ y⁻¹ can be calculated (by multiplication by the annual discharge, 540.6 mm y⁻¹, Table 1). If no attenuation occurred along the water flow paths between the bottom of the root zone and the groundwater discharge into the stream, the resulting total catchment load would therefore amount to 60.8 t NO₃-N y⁻¹.

The lower nitrate-nitrogen concentrations estimated for the groundwater reservoirs (Table 2) relative to the near-surface and OVERSEER estimates, in line with the earlier groundwater investigations (Stenger et al., 2009), demonstrate that some degree of attenuation is taking place within the groundwater reservoirs. If the concentration differences between the reservoirs are interpreted as being due to denitrification alone, the annual denitrification in each reservoir can be calculated (Table 2). These calculations indicate that, as well as delivering 94.9% of the nitrate-nitrogen discharge to the stream, the fast groundwater reservoir also accounts for 93.0% of total attenuation (or 46.1% of the estimated land surface load). This finding indicates that conditions conducive to denitrification not only occur in the slow groundwater reservoir deemed to reside in the older argillised volcanic ash beds, but also in the overlying much more friable younger deposits.

Since low nitrate-nitrogen concentrations in the slow groundwater reservoir may be attributable to groundwater recharged prior to agricultural land use rather than denitrification, denitrification estimates in this reservoir can be considered as upper bounds only. Due to its low contribution to stream flow, nitrate attenuation in the slow groundwater reservoir accounts for a maximum of 3.3% of the potential load, notwithstanding the very low nitrate-nitrogen concentrations estimated for this reservoir.

Conclusions

Development of the Boussinesq equation has been motivated by the need to analyse catchment hydraulic response to recharge. Extensions of this model to include near-surface flow and differential chemistry between different flow paths has allowed this approach to be applied to study seasonal patterns in stream chemistry arising from changing dominance of different flowpaths in a small, lowland catchment dominated by intensive pastoral dairy farming. Analysis of field data using the “StreamGEM” model provided estimates of the size and hydraulic response times of the conceptual water reservoirs, and the contribution of each to nitrate attenuation within the groundwater system and nitrate discharge into the stream. These estimates were achieved with a simple model that has much smaller data demands than distributed catchment models, and thus has promise as a water and contaminant analysis tool for relatively data-poor catchments. Current work focuses on testing the applicability of the approach across a diverse range of catchments and on ascertaining the minimum period and frequency of catchment data required for meaningful analysis.

Acknowledgments

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