

The role of groundwater characteristics in catchment recovery from nitrate pollution

S. M. Dunn, W. G. Darling, C. Birkel and J. R. Bacon

ABSTRACT

The effectiveness of measures to mitigate nitrate concentrations in surface and groundwater depends not only on their suitability for reducing nitrate leaching, but also on characteristics of groundwater transport that may cause a lag in achieving recovery. The recovery of a catchment within a Nitrate Vulnerable Zone in the east of Scotland has been assessed using a combined monitoring and modelling approach. Understanding of the dominant hydrological processes was developed through a programme of monitoring of surface and groundwater bodies. Age dating of groundwater samples, using dissolved atmospheric trace gases (CFCs and SF₆) underpinned the conceptualisation of groundwater transport and a lumped dispersion model was applied to the data to estimate mean solute transit times. High spatial variability in the groundwater dating made it difficult to estimate catchment means, but the range was estimated to lie between 15 and 60 years. A catchment hydrology and nitrate model was used to explore the effect of simple changes in land management on reducing nitrate concentrations, as well as associated time scales of recovery. The study has helped improve understanding of the role of groundwater in catchment recovery and given an indication of the scale of agricultural changes required to achieve different levels of pollution mitigation.

Key words | catchment, diffuse pollution, groundwater, nitrate, recovery, transit time

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INTRODUCTION

Four regions, covering 14.2% of the land area of Scotland, were designated as Nitrate Vulnerable Zones (NVZs) in 2002–2003 to fulfil the requirements of the European Nitrates Directive (91/676/EEC). These areas were identified as having groundwater where nitrate levels exceed, or are likely to exceed, the level of 11.3 mg l⁻¹ NO₃-N set in the Directive. Agricultural sources have been identified as the single most important cause of diffuse N pollution in Scotland (Scottish Environment Protection Agency 2007) and an NVZ Action Programme (Scottish Statutory Instrument 2003, updated in 2008) sets out rules for farmers managing land that drains to water bodies within the NVZs. The measures in the Action Programme are based on implementation of good agricultural practice, and aimed at achieving a reduction in concentrations of nitrate in surface and groundwater. Experiences from the USA have been that over a period of four decades, most

projects aimed at mitigation of diffuse pollution in watersheds have reported little improvement in water quality even after extensive implementation of best management practices (Meals *et al.* 2010). Numerous factors have contributed to the failure of such projects and the effectiveness of an action programme might be considered to comprise of three key elements: (a) the degree of uptake of the measures by land managers, (b) the suitability of the measures for reducing losses of nitrate from the soil zone, and (c) the residence time within groundwater which can cause a lag between implementation and environmental recovery (Kronvang *et al.* 2008). A comprehensive understanding of catchment processes is required to evaluate the latter two components of effectiveness, both to predict the magnitude of reduction in concentrations that can be expected and the time scale over which this recovery might be observed.

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In many areas, data pertaining to groundwater transport processes and quality are sparse. Where historical measurements are available they are usually limited to a few sampling points and are frequently inadequate for interpretation of trends in water quality. Owing to industrial activity, a range of atmospheric pollutants has entered groundwater systems during the past 70 years, and where the emissions history of these pollutants is known, their concentrations in groundwater can be used to provide a measure of residence time. Atmospheric tracers that are commonly used include tritium (^3H) (e.g. Schlosser *et al.* 1988; Clark & Fritz 1997), chlorofluorocarbons (CFCs) (e.g. Busenberg & Plummer 1992) and sulphur hexafluoride (SF_6) (e.g. Busenberg & Plummer 2000). Each of the tracers has a range of uncertainties associated with its application, so it is common for analyses to be based on more than one tracer in order that robust interpretations can be made (Bauer *et al.* 2001; Plummer *et al.* 2001; Kaown *et al.* 2009). By making some assumptions about the nature of the transit time distribution of groundwater transport, the tracer data can also be used to help develop simple lumped models to describe the system (Osenbruck *et al.* 2006). Groundwater age dating has been used to explore the lag times in recovery from N pollution in several studies. Galeone (2005) found that N applied to the land in a small watershed reached springs in 2–3 years but took in the region of 15–39 years for groundwater to reach the stream channel. Tomer & Burkart (2003) used groundwater dating techniques in conjunction with a paired catchment experiment to assess the effects of large inputs of N fertiliser to one catchment. Results confirmed that it would take many years before management changes would take effect in the groundwater. In a large scale study of the Geer basin in Belgium, Urban *et al.* (2010) found by measuring tritium that the key factors in the distribution and evolution of nitrate were travel times from the recharge zone and mixing between groundwater of different ages, rather than land use which was quite uniformly distributed across the basin. Kaown *et al.* (2009) also found that groundwater residence time and recharge rate played as important a role in the spatial distribution of nitrate concentrations as land use patterns in their study area. Most previous age dating studies have been undertaken in a geological setting characterised by thick deposits of porous rock (e.g. loess or chalk aquifers) where

groundwater recharge is important and aquifer travel times are known to be significant. However, as is the case in Scotland, many smaller groundwater aquifers can also be important in the context of water supply yet much less is understood about their potential responsiveness to changes in management.

The Lunan catchment in E. Scotland has been the focus of a collaborative catchment study between the Scottish Environment Protection Agency (SEPA), the Macaulay Land Use Research Institute (MLURI – now the James Hutton Institute) and the Scottish Agricultural College (Vinten *et al.* 2010). Surface water bodies within the catchment are currently classified by SEPA as ranging from moderate to bad and the groundwater bodies as poor. The catchment lies within an NVZ and concentrations of nitrate in the groundwater, an important drinking water resource, frequently exceed the EU Drinking Water Limit of $11.3 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$. One of the activities undertaken in the catchment study has been an exploration of the significance of hydrological processes in determining how the catchment will recover from diffuse pollution by nitrates.

A baseline hydrogeological study of the Vale of Strathmore (Ó Dochartaigh *et al.* 2006) has assessed the principal characteristics of groundwater flow in the Lower Devonian Sandstone aquifer that underlies the Lunan catchment. The study highlights the importance of fracture flow in dominating groundwater movement in a largely productive aquifer. The study also undertook a limited age dating assessment based on nine groundwater samples from boreholes across the region. The results of this indicated a range of ages of the water from modern to around 40 years old. Few other hydrogeological studies to assess groundwater ages have been undertaken in Scotland and consequently little is known about how rapidly groundwater might be expected to recover from diffuse pollution. The only published study of this type by MacDonald *et al.* (2003) assessed the age and quality of groundwater in the sandstone and breccia aquifer of the Dumfries region in south west Scotland. There they found that the aquifer quality could be explained by a mix of pre-1950s and modern water in varying proportions, and that nitrate concentrations in the aquifer could be expected to continue to rise as the proportion of pre-1950s groundwater diminishes over time. However, the Dumfries aquifer differs from the

Vale of Strathmore in that intergranular flow is more important and groundwater would be expected to be significantly older overall.

In this study, age dating of groundwater samples has been undertaken, using dissolved atmospheric trace gases, to underpin the conceptualisation of groundwater transport in the catchment. The groundwater transport conceptualisation has then been linked with a catchment model to simulate flow and nitrate behaviour in the catchment. This model has been used to explore some simple scenarios of nitrate mitigation, in order to quantify their effectiveness and the time scales over which recovery of ground and surface water bodies might be expected to occur.

STUDY AREA

Physical characteristics

The Lunan Water drains an area of 134 km² from its source near the town of Forfar to the North Sea at Lunan Bay. A map of the catchment is shown in Figure 1 and physical and topographical characteristics are summarised in Table 1. The Lunan is a lowland agricultural catchment with a maximum elevation of 250 m, but with most of the area lying along a flat broad valley. Some 77% of the area

Table 1 | Physical and topographical characteristics of the Lunan catchment above Kirkton Mill gauging station

Topography	Area (km ²)	122
	Mean elevation (m)	97
	Max elevation (m)	250
	Min elevation (m)	1
	Mean slope (°)	2.9
	Max slope (°)	45
Land use	Arable (%)	77
	Grassland (%)	14
	Forest (%)	10
Soils	Humus iron podzol	42
	Brown forest soils	33
	Mineral alluvial	12
Bedrock geology	Dundee Flagstone Formation (%)	74
	Montrose Volcanic Formation (%)	24
Superficial geology	Glacial till (%)	79
	Glacio-fluvial deposits (%)	21
Hydrology	Mean annual rainfall (2000–2008) (mm)	820
	Estimated evapotranspiration (2000–2008) (mm)	400
	Stream flow Kirkton Mill (2000–2008) (mm)	467

is used for arable agriculture with spring barley, winter wheat, and winter barley dominating. The remainder of the land use is mainly forestry and grassland with only a few small settlements within the catchment.

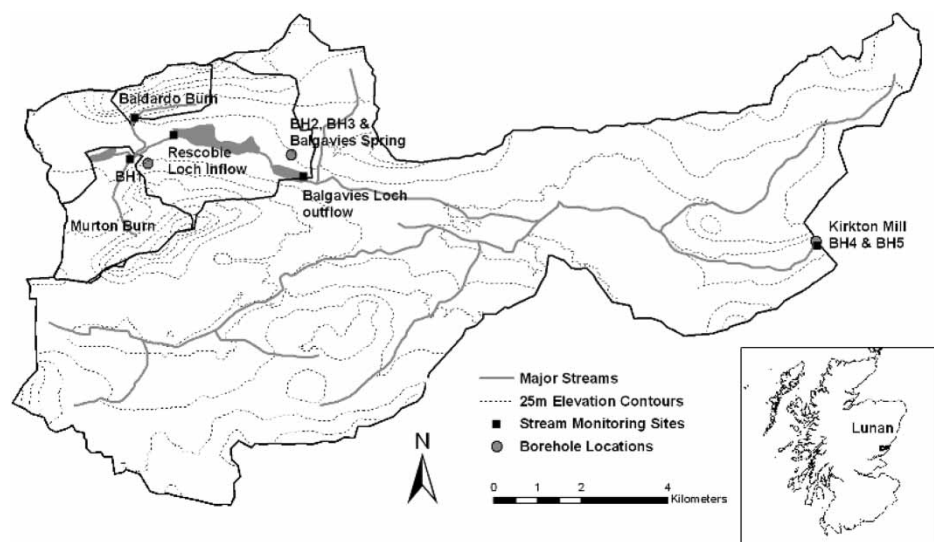


Figure 1 | Map of the Lunan catchment showing relief, stream network and locations of sampling points.

Average annual rainfall for 2000–2008 was 820 mm quite uniformly distributed throughout the year. Estimated annual evapotranspiration is around 400 mm. The main stream of the Lunan Water is gauged at Kirkton Mill (representing 122 km² of the catchment) by SEPA, where the average annual runoff for 2000–2008 was equivalent to 467 mm.

The catchment is underlain by Lower Devonian sandstone with two principal formations present: the Dundee Flagstone Formation intercalated with northwest-southwest trending bands of the Montrose Volcanic Formation. The Dundee Formation has been classed as a highly productive aquifer by the British Geological Survey and supports a combination of intergranular and fracture flow (Browne *et al.* 2001). However the intergranular permeability is quite low and downhole geophysical logging has indicated that the fracture permeability dominates groundwater flow (Ó Dochartaigh *et al.* 2006). From 5–25 m below ground, fracture spacings have been measured at 0.65 m decreasing to a lower density at greater depth. The Montrose Volcanic Formation consists of early Devonian andesite, basaltic andesite, volcanoclastic conglomerate and sandstone. It has been classed as an aquifer of low productivity where fracture flow dominates (Browne *et al.* 2001).

The bedrock is overlain by glacial till with a typical thickness of 4.5 m encountered by SEPA during borehole drilling operations in the area (Le Feuvre & Fitzsimons 2010). The glacial till is considered to contain little usable groundwater. Along the course of the Lunan Water there are glacio-fluvial deposits which are generally less than 10 m thick and locally overlain by alluvium deposits. These deposits have been classified as intergranular and highly productive by the British Geological Survey.

Relatively freely draining podzols and brown forest soils have developed on the glacial till over much of the catchment and these facilitate groundwater recharge. However, around 30% of the soils are gleyed with impeded drainage. Many soils have been under-drained to improve their agricultural potential which also facilitates the generation of near-surface runoff via lateral flow pathways.

Monitoring

A range of monitoring activities has been ongoing in the catchment since 2007. SEPA installed five boreholes for

groundwater monitoring at three locations, with paired boreholes at two of the sites. The details of the boreholes are given in Table 2 and their locations shown in Figure 1. SEPA have undertaken regular monthly sampling of these boreholes for hydrochemical analysis. In addition, stable isotopes of water ($\delta^{18}\text{O}$ and δD) have been measured every 2–3 months, by infrared laser spectroscopy, and periodic samples have been taken for age dating using the dissolved atmospheric gas tracers, CFC and SF₆. Age dating samples were also collected from a further three sites including: a surface spring (BS) close to boreholes BH2 and BH3, believed to be recharged by superficial groundwater; the Lunan Water at Kirkton Mill (LW) and the Baldardo Burn at Wemyss (BB). Three sets of dating samples were taken in November 2007, November 2008 and August 2009, in accordance with a methodology developed by Oster (1994). Concentrations were determined by the British Geological Survey using the gas chromatographic method of Bullister & Weiss (1988). This method uses cryogenic pre-concentration of dissolved CFCs and SF₆ prior to measurement by electron capture detector (ECD).

In addition to the groundwater monitoring, measurements of surface waters have also been made. High resolution hydrological (15 min) and isotope (daily) monitoring was focussed on two locations in the catchment: the downstream gauging station at Kirkton Mill (SEPA site), and a small 2 km² tributary of the Baldardo Burn in the upper catchment. Birkel *et al.* (2011) present the data from these sites. Bi-weekly or monthly samples of stream water at a range of sites in the catchment have been analysed for a suite of hydrochemical parameters, including nitrate concentrations. Samples taken by the Macaulay Institute were analysed for nitrate using a Skalar method based on cadmium reduction. After dialysis, samples are buffered at pH 8.2 and passed through a column containing

Table 2 | Groundwater sampling points

Location	Borehole	Geology	Screened depth (m)
Murton	BH1	Solid	24–30
Balgavies	BH2	Solid (shallow)	9–15
Balgavies	BH3	Solid (deep)	21–27
Kirkton Mill	BH4	Solid	34–40
Kirkton Mill	BH5	Drift	11–14

copper-cadmium to reduce the nitrate to nitrite. The nitrite is converted to a highly coloured azo dye which is measured at 540 nm. SEPA samples were analysed for total oxidised nitrogen (TON) and nitrite using the 'Blue Book' standard method (SCA 1981). Nitrate was calculated by subtracting nitrite from TON. Precipitation was measured using a tipping-bucket gauge at the Mains of Balgavies Farm, adjacent to BS (Figure 1) and was also available from a Meteorological Office gauge near Forfar.

Prior to 2007, SEPA measured flows at Kirkton Mill at 15 min resolution and monitored stream water quality at Kirkton Mill and downstream of Balgavies Loch on a monthly basis, with nitrate measured as described above.

GROUNDWATER TRANSIT TIME ESTIMATION

Data interpretation

Raw data values for measured CFC-11, CFC-12 and SF₆ concentrations are presented in Table 3. SF₆ is particularly sensitive to the presence of 'excess air' (EA) incorporated during recharge, which can elevate concentrations well above the equilibrium values on which the dating method depends (Busenberg & Plummer 2000). Sandstones with primary porosity typically have EA values of ~ 3 ccSTP kg⁻¹ (Wilson *et al.* 1994). Although no EA values have been measured on the Lunan groundwaters, as mentioned above, the local aquifer has a well-developed fracture permeability which typically results in higher amounts of EA (Wilson & McNeill 1997). Therefore an EA component of 5 ccSTP kg⁻¹, slightly higher than that of the sandstone,

has been assumed for all groundwater samples. This translates to an SF₆ correction factor of 0.67. Reported data were also converted to equivalent atmospheric mixing ratios in units of pptv (parts per trillion by volume).

Examination of the data indicated that four samples had 'over-modern' concentrations of CFC-12 and nine samples had similarly elevated concentrations of CFC-11, indicating the presence of minor contamination, probably from agricultural or light industrial pollution. Contamination renders samples unsuitable for age dating purposes, so these analyses have been excluded from further interpretation with regard to the CFCs. Comparison of concentrations of CFC-11 against CFC-12 for non-contaminated samples indicated a good correlation in terms of the historic dating. Since the temporal evolution of their atmospheric concentration is also very similar, only the CFC-12 data have been further interpreted.

Various factors such as recharge elevation, unsaturated zone thickness and recharge temperature need to be factored into the interpretation of both CFC and SF₆ data (Plummer & Busenberg 1999). In the present case, the low relief of the catchment above sea level and relatively thin unsaturated zone have been discounted as having a significant effect. However, data have been corrected to account for a mean recharge temperature of 8.5 °C, estimated from daily air temperature data.

The corrected data for CFC-12 and SF₆ are plotted in Figure 2. The curve on the graph depicts the historic relationship between atmospheric SF₆ and CFC-12 and thus would give an indication of the ages of the water samples, if they had been transported by piston flow. The straight line joining present day atmospheric concentrations

Table 3 | Raw measurements of CFC-12 (pmol l⁻¹), CFC-11 (pmol l⁻¹) and SF₆ (fmol l⁻¹) in borehole (BH1-BH5), spring (BS) and surface water (LW and BB) samples

Analysis	Date	BH1	BH2	BH3	BH4	BH5	BS	LW	BB
CFC-11	Nov 07	1.37	6.40	4.19	5.55	4.8	7.9	10.6	x
	Nov 08	1.76	10.4	7.55	7.00	6.9	7.33	16.8	13.2
	Aug 09	1.40	4.70	4.62	5.44	4.01	4.84	4.8	6.93
CFC-12	Nov 07	0.49	2.31	3.01	3.28	2.56	3.75	3.3	x
	Nov 08	0.77	4.17	3.11	3.14	3.09	3.37	6.24	5.56
	Aug 09	0.52	1.67	1.95	2.76	1.46	1.83	2.45	3.03
SF ₆	Nov 07	0.59	1.98	6.53	0.75	1.48	1.63	1.79	x
	Nov 08	0.75	2.25	4.67	1.14	1.06	2.44	1.96	1.75
	Aug 09	0.68	0.81	3.32	0.71	1.01	1.45	1.89	1.34

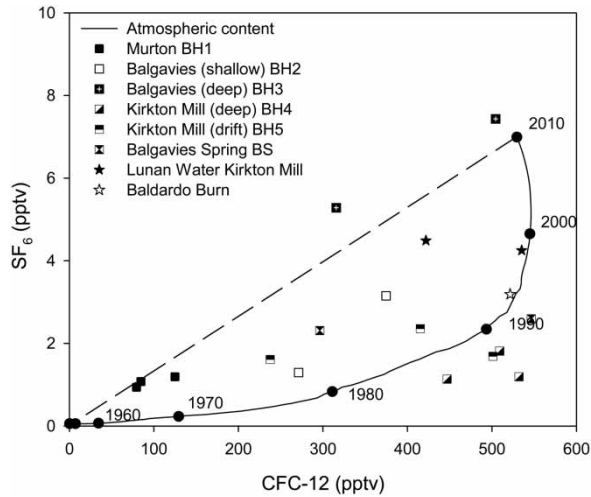


Figure 2 | CFC-12 and SF₆ for each sample plotted together with a curve depicting the time-course relationship of atmospheric CFC-12 to SF₆. The dashed line represents simple mixing between modern and pre-1950s water.

with 0 indicates where the data points would be expected to lie, if the waters were comprised of a simple mix of pre-1950s water with recent recharge. If the data were error free, all values should fall within the bounds of the envelope created by these two lines. The data indicate a large scatter of different ages of water sampled. However, there is some consistency in the clustering of values for different sites and the values of SF₆ for individual sites are almost constant for all sites except BH3. All data points except those from BH1 and BH3 lie far to the right of the simple mixing line between pre-1950s and modern water indicating that there must be some interaction between an older (immobile) groundwater fraction and a young (mobile) fraction within the system. Some of the data points fall to the right of the piston flow curve indicating an error in either the CFC-12 measurement or the SF₆ but it is not possible to determine which value is correct. This has implications for dating of these samples. The samples taken in 2009 generally had lower CFC-12 and SF₆ content. These samples were taken during the summer (August) compared with the 2007/2008 samples which were taken in late autumn (November). During the summer, it is to be expected that little active recharge will be taking place, suggesting that the difference between these values and those from 2007/2008 might reflect the fraction of groundwater being actively and rapidly transported during the autumn. The concentrations of trace gases in four out of five groundwater sample points

and the spring reflect atmospheric concentrations between 1970 and 1990. The remaining point, BH3, appears largely characteristic of modern water, suggesting rapid recharge by fracture flow at this location. The surface water samples are apparently younger than the groundwaters, indicating atmospheric SF₆ concentrations from the mid to late 1990s though this may be the result of partial atmospheric re-equilibration.

Lumped dispersion modelling

In practice, few groundwater bodies could be expected to be characterised by a simple mix of 'old' and 'new' water, but rather are comprised of a continuous distribution of ages. Schilling & Wolter (2007) estimated a range of ages from 2 days to 308 years with a mean of 10.1 years based on the spatial and topographic structure of their catchment and estimates of hydraulic characterisation of sub-surface properties. Similarly, Bester *et al.* (2006) concluded from an experiment tracing Cl⁻ from road salt in groundwater, that travel times in the sub-surface were highly heterogeneous. Zuber *et al.* (2005) found that unique solutions using lumped parameter models to describe groundwater transport are seldom available even if simple box models adequately describe the real flow pattern, but are useful for obtaining an idea of possible age distributions. In this study, the representation of groundwater transport processes was explored further through application of a simple dispersion model. There are various mechanisms by which hydrodynamic dispersion can take place including the heterogeneous recharge of groundwater in a glaciated environment and the variable path length of lateral flow in the saturated zone. Einsiedl *et al.* (2009) argued that the dispersion model can be used to describe the transit time of tracer particles in a dual-porosity fissured-porous system provided that the transit times of the mobile fraction are sufficiently slow (~2–3 years) to permit diffusion into the immobile water of the rock matrix. The distribution of tracer within the mobile and immobile fractions then depends only on the relative pore volumes of the two fractions. These mobile and immobile fractions can be considered analogous to the fracture and inter-granular flow pathways proposed by Le Feuvre & Fitzsimons (2010), and according to the dispersion model these pathways

interact. To explore the properties of the Lunan groundwater system and their relationships with concentrations of dissolved atmospheric trace gases, the dispersion model was applied using a simple convolution method:

$$C_{out}(t) = \int_0^{\infty} C_{in}(t - \tau)g(\tau)d\tau \quad (1)$$

where $C_{out}(t)$ is the output concentration at time t , $C_{in}(t)$ is the recharge concentration at time t and $g(\tau)$ is the transit time distribution function.

The dispersive transit time distribution function is given by:

$$g(\tau) = \frac{1}{\sqrt{4\pi P_D^* \tau / T^*}} \frac{1}{\tau} \exp \left[-\frac{(1 - \tau/T^*)^2}{4P_D^* \tau / T^*} \right] \quad (2)$$

where τ is the transit time of a single particle through the system, P_D^* is the apparent dispersion parameter and T^* is the mean transit time of the tracer. Note that in a system dominated by rapid fracture flow, the transit time of water will be much shorter than the tracer transit time.

In order to apply this model using CFC-12 and SF₆ as tracers, a historic time-series of meteorological and atmospheric data was constructed from 01/01/1967–31/12/2008. Following the method presented by McGuire *et al.* (2005), input concentrations were weighted by effective precipitation to account for temporal differences in recharge. Daily precipitation measurements were available from a rain gauge at Forfar. Evapotranspiration estimates were based on current day measurements and used in combination with the precipitation data to estimate effective precipitation. Concentrations of atmospheric CFC-12 and SF₆ were based on historic observations for the Northern hemisphere (Busenberg & Plummer 2006).

The sensitivity of the model was explored through application using a range of different values for the parameters P_D^* and T^* , the results of which are illustrated in Figure 3. This figure illustrates that the tracer response is significantly more sensitive to the value of T^* than to P_D^* . Therefore, if we assume a value of $P_D^*=0.5$ estimates of T^* can be made for each borehole according to the mean measured CFC-12 and SF₆ content for 2007–2009. A similar approach was adopted by Kaown *et al.* (2009) to fit a dispersive model of

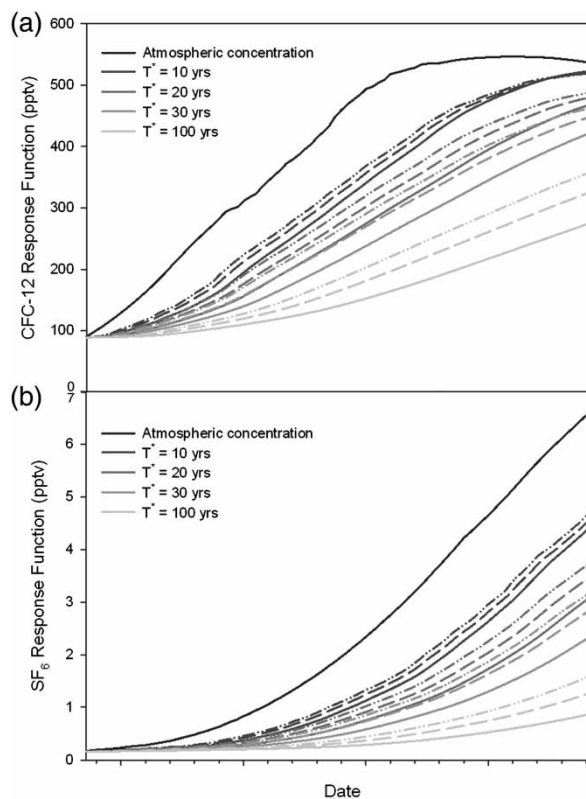


Figure 3 | Groundwater response functions for (a) CFC-12 and (b) SF₆ obtained by applying a range of dispersion models to historic concentrations of the atmospheric trace gases. Solid lines represent results with $P_D^*=0.3$, dashed lines $P_D^*=0.5$ and dotted-dashed lines $P_D^*=0.7$.

residence times to tritium and CFC-113 data for a small agricultural catchment in Korea.

Table 4 presents the results of modelled estimates of T^* for each monitoring site. Note that the mean tracer transit time for a dispersion model is significantly skewed by the tail of the distribution, such that a high proportion of the tracer will have a transit time shorter than the mean value. The results of the dispersion analysis reveal

Table 4 | Estimated mean transit times of tracer (yrs) based on application of a dispersion model with $P_D^*=0.5$ and fitted to the mean of 2007–2009 measurements of CFC-12 and SF₆.

Tracer	BH1	BH2	BH3	BH4	BH5	BS	LW	BB
CFC-12	>500	100	30	12 ^a	52	35	15	10
SF ₆	132	36	Not pos ^b	95	62	31	12	22

^aSamples possibly contaminated with CFC-12.

^bSamples possibly contaminated with terrigenic SF₆.

heterogeneity and significant variation in mean transit times of groundwater, ranging from recent to greater than 100 years.

The tracer transit time (T^*) can be related to the transit time of water (T) according to the following equation:

$$T^* = \left(\frac{\eta_m + \eta_{im}}{\eta_m} \right) \times T \quad (3)$$

where η_m represents the mobile (fracture) porosity and η_{im} represents the immobile (matrix) porosity. Assuming a value of $\eta_{im}=0.14$ based on measurements of a borehole near Forfar (Ó Dochartaigh *et al.* 2006), and an estimate of $\eta_m=0.01$ for the fracture porosity based on measurements of fracture spacing (Le Feuvre & Fitzsimons 2010), the mean transit time of water can be estimated as $T=T^*/15$. This would indicate mean transit times for the water ranging from around 1–10 years for the various boreholes, i.e. showing quite high hydraulic responsiveness consistent with observed fracture flow dynamics.

In aquifer systems where intergranular flow dominates, there is commonly a relationship between the age of water and depth of sampling. However in this study, groundwater in one of the deeper boreholes (BH3) appears to be largely modern and is significantly younger than water sampled from an adjacent shallower borehole (BH2). This supports the theory that fracture flow is very important, indicating in this case that BH3 is co-incident with fracturing in the rock and that modern water is being locally recharged. Similarly, there is little apparent difference in ages of the water in the two boreholes at Kirkton Mill (BH4 and BH5), although during the drilling of BH4, BH5 became artesian. This suggests that there is a direct hydraulic connection of the aquifer at this location (Entec 2007) and we cannot be confident about the depth of water being sampled in BH4. Given the proximity of BH4 and BH5 to the Lunan Water (~5 m distant) it seems likely that they give a good representation of the characteristics of groundwater being discharged to the surface stream. The spring at Balgavies is likely to be supplied by the shallower groundwater flow pathway through superficial deposits, identified by Le Feuvre & Fitzsimons (2010), and is characterised by water intermediate in age between the streams and deeper system.

CATCHMENT PROCESSES AND MODELLING RECOVERY

Surface and groundwater processes

A conceptualisation of hydrological processes in the Lunan catchment has been presented by Birkel *et al.* (2010, 2011). The conceptualisation was based on high temporal resolution of hydrometric (15 min) and isotopic (daily) data from a range of surface water sampling points. Some of these data are illustrated in Figure 4. Data from a small sub-catchment, the Baldardo Burn (see Figure 1), indicated an unclosed water balance, with a loss of approximately 100–200 mm per year of the net precipitation, assumed to recharge the regional groundwater aquifer. The presence of this deep groundwater flow pathway is supported by closure of the water balance for the catchment at Kirkton Mill (see Figure 4(a) for a comparison) and is consistent with the underlying geology of the catchment. Assuming the recharge in the Baldardo Burn sub-catchment is representative of the contribution of net precipitation to deep groundwater in the catchment as a whole, these figures indicate a deep groundwater contribution of somewhere between 25 and 50% of the total catchment runoff. The isotope data (Figure 4(b) – note separate scale for precipitation $\delta^2\text{H}$) indicated the occurrence of a rapid flow pathway during storm events, highlighted by sharp fluctuations in stream isotope measurements, which is most likely facilitated by agricultural drainage. They also indicated that the lochs in the upper Lunan catchment, draining approximately 17% of the area, have an important effect on mixing of water (not shown here). A further interpretation of flow pathways by SEPA (Le Feuvre & Fitzsimons 2010), based on hydrogeological data including permeabilities and major ions and an analysis of the river Base Flow Index, suggests a comparable groundwater contribution to flow at Kirkton Mill of around 46%.

Nitrate in the Lunan catchment

Measured nitrate concentrations in surface and groundwater samples are shown in Figure 4(c) and (d). Figure 4(c) shows groundwater concentrations for the five

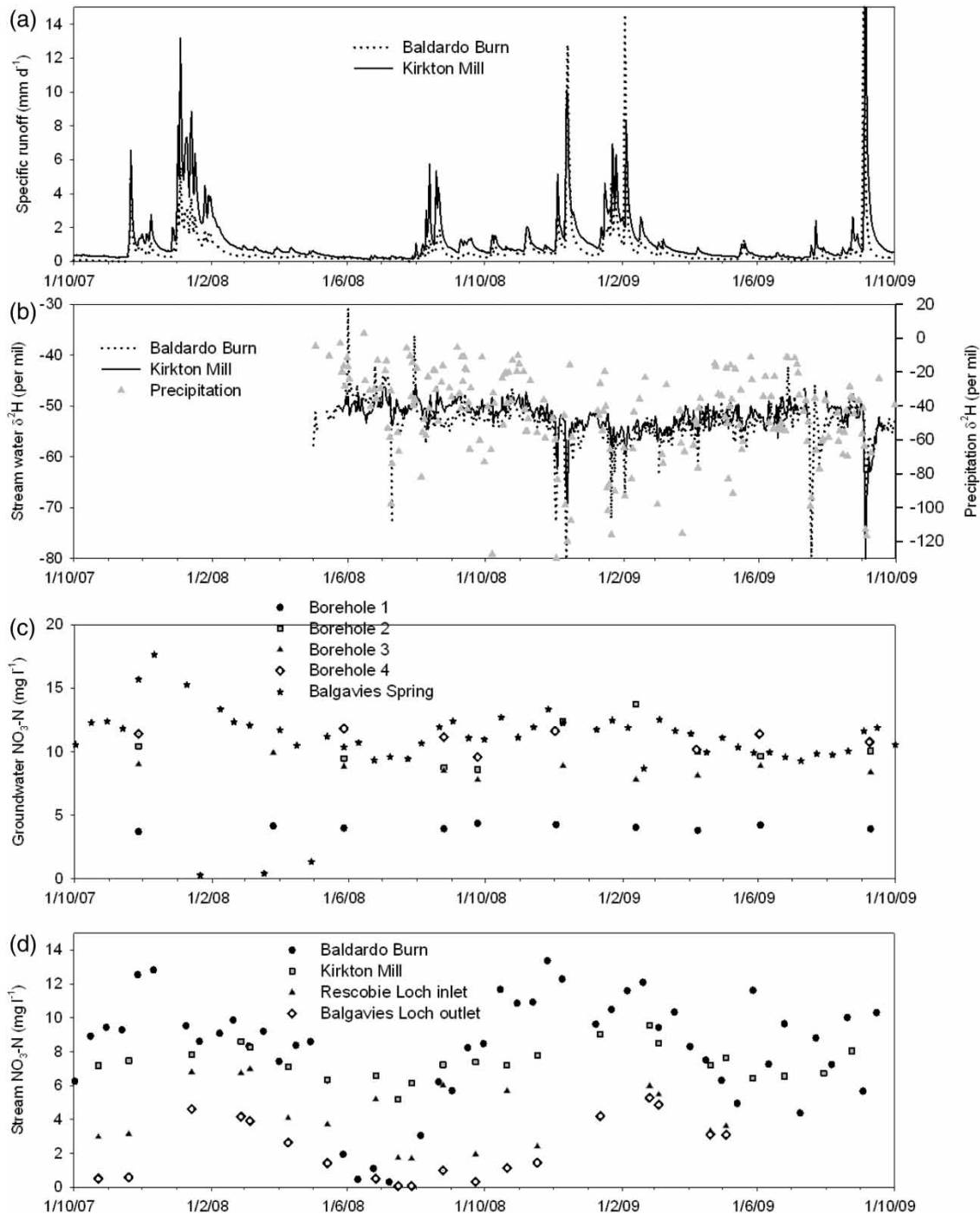


Figure 4 | Monitoring data from the Lunan catchment including (a) specific discharge, (b) daily $\delta^2\text{H}$ measurements from precipitation and stream water, (c) groundwater nitrate concentrations and (d) stream nitrate concentrations.

boreholes and the spring at Balgavies Farm, and [Figure 4\(d\)](#) shows concentrations for several surface water locations. The data support the designation of the catchment as a

NVZ with concentrations commonly exceeding 11.3 mg l^{-1} $\text{NO}_3\text{-N}$ in three of the five boreholes, as well as the Balgavies spring. BH1 has a much lower nitrate concentration than

other locations and displays very little temporal variability. It is notable that the CFC-12 and SF₆ data for this site indicated that the groundwater was apparently much older than the other locations and major ion data also support this (Le Feuvre & Fitzsimons 2010). This may mean that the nitrate concentrations have not yet risen to the levels of leaching associated with the 1980s and 1990s and could be expected to increase over time.

The surface water monitoring also shows heterogeneity in nitrate concentrations across the catchment. Upstream of Rescobie Loch, average nitrate inputs from the upper catchment appear to be quite low despite high concentrations measured in the Baldardo Burn. In-stream processes, such as uptake and de-nitrification, appear to occur within the loch system resulting in even lower concentrations at the outflow of Balgavies Loch downstream. However, nitrate concentrations at Kirkton Mill, some 10 km downstream, are much higher. The streams generally have higher nitrate concentrations in winter, probably reflecting flushing of excess N from the soil under wet conditions.

Catchment model

Based on: (a) the preceding analysis of groundwater characteristics, (b) the conceptualisation of hydrological processes and (c) the observations of nitrate variability, a framework for modelling the hydrological and nitrate behaviour in the catchment was constructed as illustrated in Figure 5. The details of the model structure and its application are presented in Dunn *et al.* (2011). The STREAM model (Dunn *et al.* 2007) was used to represent the key runoff generation processes in the catchment, which were then combined with a simple loch mixing model and the lumped dispersion model for the groundwater transport.

Measured flows from the Baldardo Burn and Kirkton Mill were available for calibration of the hydrological model. The nitrate model is based on a daily calculation of excess nitrate available for leaching, with key components of the model parameterised as follows:

1. Fertiliser inputs and crop uptakes were based on recommended levels and previous estimates for different crop types (Dunn *et al.* 2004).
2. Timing of inputs and uptake were based on known management with calibration of relative amounts of autumn versus spring fertilisation to fit the observed nitrate signal.
3. Atmospheric deposition was assumed constant throughout the year with a total annual input of 8 kg ha⁻¹.
4. Parameter ranges for soil mineralisation and de-nitrification rates, K_{\min} and K_{denit} , were selected to give an approximate balance of the N cycle and to give cumulative totals comparable with those estimated for other areas (e.g. Wade *et al.* 2002).
5. The parameter determining in-stream processing of nitrate was calibrated to fit the observed data, whilst retaining a level of consistency across the whole catchment.

The calibration method involved Monte-Carlo sampling of parameters from broad initial ranges with simulations evaluated against a set of objective functions for simulation of flow and nitrate concentrations in the Baldardo Burn catchment for the period October 2007–October 2009. The selected objective functions were: Nash Sutcliffe (NS) efficiency of flow, NS log (flow), NS nitrate concentration, NS nitrate load, flow % bias, nitrate load % bias, flow root mean square error (RMSE) and nitrate concentration RMSE. Parameters that gave the best overall simulation for Baldardo Burn were then transferred to the full catchment

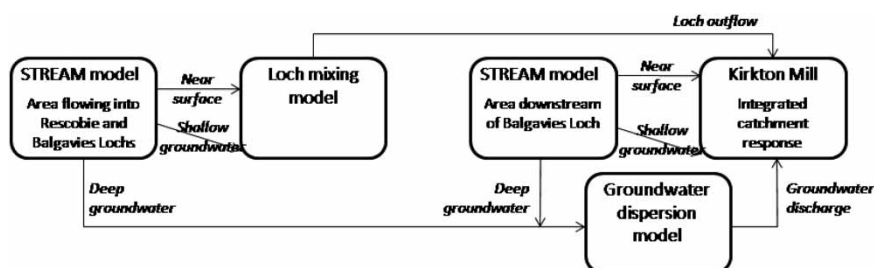


Figure 5 | Model components linked to form integrated model of the Lunan catchment.

simulation. Results of the calibrated simulations are shown in Figures 6(a)–(f). Nitrate simulations were subsequently validated at two sites for the period from October 2000–October 2006 as shown in Figures 6(g) and (h). Statistics for the calibration and validation at Baldardo Burn and Kirkton Mill are summarised in Table 5. Without measurements of flow it is not possible to calculate most of the objective functions for the other sub-catchments but values for the nitrate concentration RMSE are shown on Figure 6. Visually it can be seen that the model simulations for other locations successfully reproduced the key characteristics of the nitrate response both spatially and temporally. The differences in concentrations between the sites were found, through the modelling, to reflect: differences in land use in the upper catchment (Figures 6(a) and (b)); mixing and de-nitrification in the loch system (Figures 6(c) and (d)); and higher concentration groundwater contributions discharging in the lower catchment (Figures 6(e) and (f)). The greater errors in the simulation of N loads for the Kirkton Mill catchment compared with Baldardo Burn suggest that further calibration of the model to individual sub-catchments could be beneficial but has not yet been undertaken.

Land use change scenarios

Following successful validation, the model can be used to explore the sensitivity of the catchment response to different scenarios of land use change and management. The following set of four (hypothetical) scenarios were designed to examine both: (a) the effect of the groundwater residence times on rate of recovery, and (b) the sensitivity of nitrate leaching to changes in land use:

1. A uniform reduction of 10% in concentrations of leached nitrate (to simulate the effect of the groundwater delay in recovery, in isolation from other effects).
2. A change of 20% of the area of arable land to grassland.
3. A removal of 20% of the arable land from productive agriculture.
4. A modification to the K_{\min} parameter to achieve a reduction in soil mineralisation, as a surrogate for exploring limitations in available soil organic matter.

For each scenario, the relative proportions of individual crops within the arable land area (e.g. winter barley, winter

wheat, ware potatoes, grass over or under 5 years) were maintained in line with recent historic practice. The scenario simulations were based on the meteorological record from Oct 2000–Oct 2006. Initial conditions were established from 6 years of simulation prior to implementation of the scenario change. The met data were then cycled over the same 6 year block with the scenario change applied, and the groundwater model was run for a period of 100 years until it approached a steady-state. Combination of the long-term groundwater simulation with cycled results from the remainder of the model permitted the long-term evolution of concentration in both the groundwater and stream to be simulated. All scenarios set values for parameters of the groundwater dispersion model as $P_D^*=0.5$ for the apparent dispersion parameter and $T^*=30$ years for the solute mean transit time. These parameters represent intermediate values in the range of those calculated from the groundwater dating (Table 4).

Results from the scenario simulations are illustrated in Figure 7 in terms of time-series of nitrate concentrations in groundwater and in the stream at the downstream gauging site of Kirkton Mill. The parameter set assigned by the model calibration simulated the fraction of deep groundwater contributing to stream flow as 25% of the total catchment runoff. A further 42% of the runoff was simulated as a shallow groundwater flow, with a rapid (<2 years) mean transit time, with the remaining 33% following a near surface flow path. Note that this simulation represents one specific model realisation from those identified as acceptable for Baldardo Burn through the application of Monte-Carlo simulations. Other parameter sets may simulate slightly differing proportions of runoff by each flow pathway (Birkel *et al.* 2011), despite the use of multiple objective functions for model calibration.

In terms of the temporal response, it can be seen from Figure 7 that for each scenario, the groundwater concentrations would reduce steadily during the 20 years following implementation of the scenario. Within the first 10 years the concentrations would drop by 52% of their final decrease, and by 20 years would drop by 83% of their final decrease. The streamwater would be expected to achieve 80% of its final drop in concentration within 2 years, but then take much longer to achieve full recovery from the deep groundwater contribution. This long tail to the recovery of the

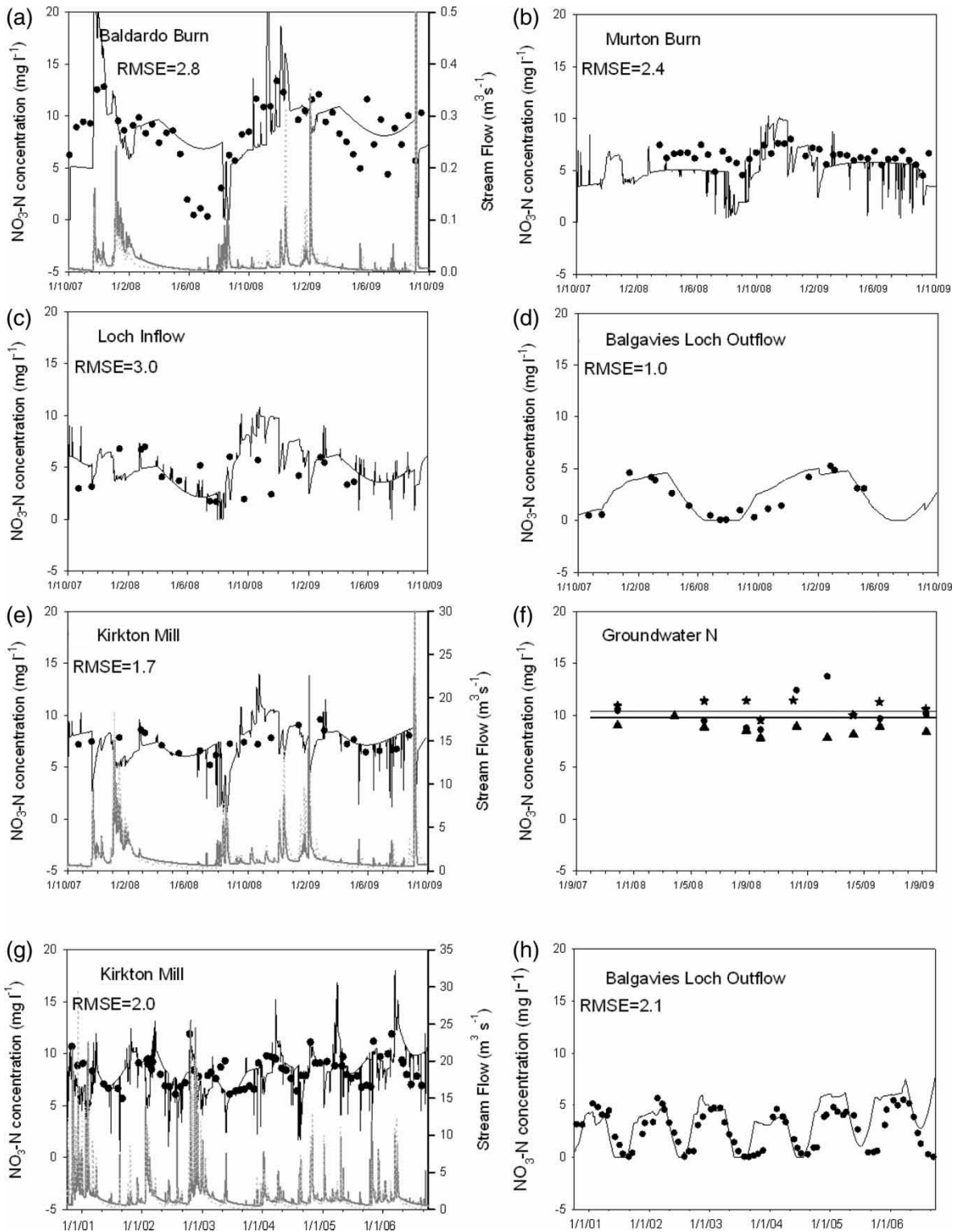


Figure 6 | Results of model calibration simulations for Oct 2007–Oct 2009 at 5 stream sites (a)–(e) and for groundwater recharge (f), and model validation simulations for Oct 2000–Oct 2006 at two stream sites (g) and (h).

Table 5 | Summary of goodness of fit statistics for flow and nitrate calibration and validation simulations at Baldardo Burn and Kirkton Mill

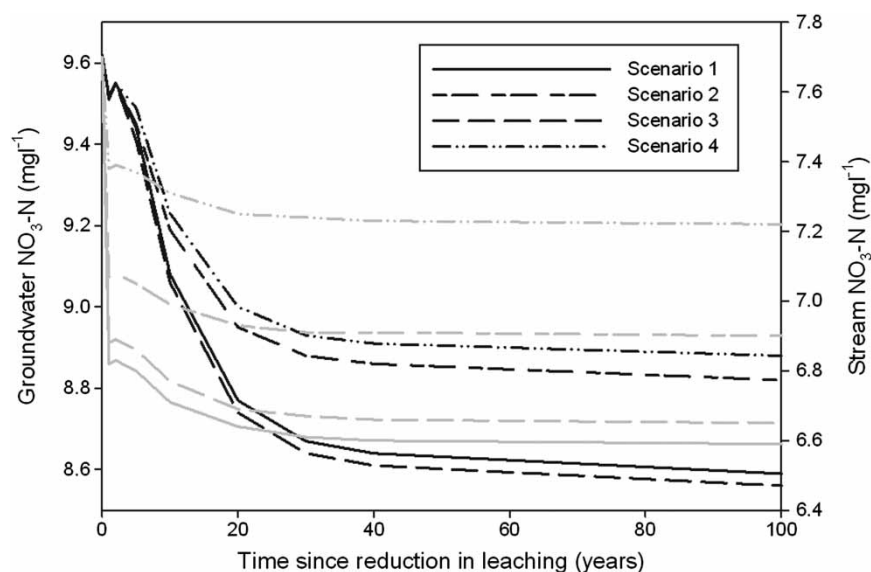
Objective function	Baldardo 2007–2009	Kirkton Mill 2007–2009	Kirkton Mill 2000–2006
NS flow	0.66	0.84	0.60
NS log (Flow)	0.61	0.68	0.55
% Bias flow	1.0	−4.0	−3.1
RMSE flow ($\text{m}^3 \text{s}^{-1}$)	0.02	1.8	1.7
NS N conc	0.18	−1.9	−0.7
NS N load	0.25	0.52	0.51
% Bias N load	−3.3	−14	−17
RMSE N conc (mg l^{-1})	2.8	1.7	2.0

surface water perhaps helps explain the solute mean transit times of 10–15 years estimated from the CFC-12 and SF₆ surface water samples, based on the dispersion model.

Acknowledging the uncertainty in the spatial average of groundwater transit times, some upper and lower bounds for recovery rates have also been made. Applying a lower estimate of the solute mean transit time of $T^*=15$ years, groundwater concentrations would drop by 73% of their final value within the first 10 years whereas with an upper estimate of $T^*=60$ years, they would only drop by 32% within the first 10 years. The time taken to achieve 90% of

the final drop in concentration (i.e. recovery) would take between 16 and 38 years.

In terms of the effectiveness of the scenarios in reducing nitrate losses, scenario (3), where 20% of arable land was removed from productive agriculture, gave very similar results to scenario (1), where leached nitrate was reduced uniformly by 10%. These scenarios lead to an eventual reduction of around 14% in the stream nitrate concentrations, but only 10% in groundwater concentrations. Scenario (2), where 20% of arable land was changed to grassland, followed a similar pattern but with slightly higher nitrate concentrations, as would be expected. Both scenario (2) and (3) showed similar patterns of decreases in the groundwater concentrations compared with the overall stream concentrations. Decreases in nitrate concentrations are not necessarily proportional to the % of land removed from agriculture, because of the non-linear relationship between N management and nitrate in runoff. Hutchins *et al.* (2010) found that whilst changes in land use in their UK study catchment could account for a 29% increase in nitrate losses, this was mitigated by in-stream processes which reduced the change in stream nitrate by around one third. Scenario (4), where the soil mineralisation rate was reduced, simulated a greater effect in reducing long term groundwater concentrations compared with the overall

**Figure 7** | Time-course of reduction in nitrate concentrations for groundwater (black lines) and stream water (grey lines) according to various management scenarios, based on a groundwater mean solute transit time of 30 years.

stream response. This reflects a loose relationship between groundwater recharge and mineralisation in terms of soil moisture, as higher rates of both processes occur under wetter conditions. The overall stream nitrate concentrations are proportionately less affected by the reduction in mineralisation rates, since runoff generation by the shallower flow paths continues under drier conditions. In all cases, the simulated concentrations of nitrate in groundwater were higher than the stream water average, because the timing of groundwater recharge coincides with the timing of highest nitrate losses and because there are no de-nitrification losses associated with the groundwater.

The sensitivity of nitrate concentrations to changes in land management at the catchment scale has also been explored in other studies. *Beaudoin et al. (2005)* applied a combined modelling and experimental approach to assess the value of a set of 'Good Agricultural Practices' including optimal fertiliser usage, use of catch crops and incorporation of straw. *Thieu et al. (2010)* assessed the effectiveness of land management practices including a conversion of fodder corn crop into grassland and the use of nitrogen trapping winter crops. Overall, land management changes of these types were estimated to generate a reduction of 14–23% nitrate losses at the river basin scale which, although significant, was still insufficient to achieve the required mitigation to meet EU targets. *Rode et al. (2009)* applied a range of different management scenarios to their model simulations, making some simplified assumptions about how the management would affect the N balance. The highest effectiveness was found for a scenario of converting 50% of arable land to pasture which lead to almost a 50% decrease in simulated N loads in two catchments.

Our model simulations predicted a mean deep groundwater concentration of around 10 mg l^{-1} prior to any changes in land use management. Although this figure is below the EU limit of 11.3 mg l^{-1} , in practice, spatial and temporal variability in groundwater concentrations across the catchment would mean that the EU limit is likely to be exceeded quite regularly (and indeed the data from borehole monitoring confirm this). Therefore it is necessary to have a target figure that is perhaps 20% lower than the 11.3 mg l^{-1} EU limit in order to ensure that concentrations remain consistently below that level. The level of reductions achieved by the different scenarios helps to

give an indication of the length of time and scale of changes that would be required before nitrate concentrations can be consistently lowered to a suitable value. Other studies (e.g. *Jackson et al. 2008*; *Orban et al. 2010*) have shown that the timelines for water quality improvement demanded by the EU Water Framework Directive are not realistic for chalk aquifers. This study indicates that the issue may be rather more extensive in terms of also being difficult to achieve in catchments of intermediate groundwater character, that have previously been little studied in the context of groundwater ages.

CONCLUSIONS

This paper has presented a first interpretation of groundwater characteristics in the Lunan catchment in eastern Scotland and their role in determining recovery from nitrate pollution. Measurements of the trace atmospheric gases CFC-12 and SF₆ in groundwater samples were used to estimate parameters of a simple lumped dispersion model to represent bulk groundwater transport processes in the catchment. The tracer data gave indicative estimates of water transit times that were highly variable between the sites where measurements were made. It was therefore difficult to make generalisations about the average behaviour across the catchment, but some scenarios were explored further to establish the likely range of recovery times. Simulation of the groundwater response to changes in inputs of nitrate indicated that a rapid initial reduction in concentrations would be followed by a much slower rate of improvement such that it will be some years after nitrate leaching has been reduced before the full effectiveness will be observed in the groundwater. Broad ranges for the mean groundwater transit time indicate that it would take between 16 and 38 years to achieve the 90% of the effect of any reduction in nitrate leaching. The Lunan Water itself would be expected to display a much more rapid initial response to reductions in leaching, but would also take some years before full recovery is achieved. Simple scenarios for changes in management gave an indication of the scale of reduction in nitrate leaching that might be expected according to the scale of the management changes.

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