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Time lag: a methodology for the estimation of vertical and horizontal travel & flushing timescales to nitrate threshold concentrations in Irish aquifers

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Abstract

The Water Framework Directive (WFD) in Europe aims, *inter alia*, to achieve at least "good" water quality status by 2015 by mitigating the causes of pollution. However, with the implementation of programmes of measures in 2012, many catchments may not achieve good water quality status within this timeframe due to the time lag of nutrient transport from source to receptor via hydrological and hydrogeological pathways. An appraisal of catchment time lag issues offers a more realistic scientifically based timescale for expected water quality improvements in response to mitigation measures implemented under the WFD. A simplified methodology for the calculation of nitrate time lag in a variety of Irish hydrogeological scenarios is presented, based on unsaturated vertical and aquifer flushing times required to reach environmental quality standards. Horizontal travel time is estimated for first occurrence of nutrients in a surface water body. The results show that achievement of good water quality status in the Republic of Ireland for some waterbodies may be too optimistic within the current timeframe of 2015 targets but improvements are predicted within subsequent 6 and 12 year cycles.

Keywords: nitrate, time lag; Water Framework Directive; uncertainty analysis

1. Introduction

Under the European Union (EU) Water Framework Directive (WFD; 2000/60/EC, OJEC, 2000), River Basin District managers must implement Programmes of Measures (POM) by 2012, within a catchment, where an individual waterbody has been classified as below good status or are at risk of not reaching at least "good ecological status" by 2015. The mitigation of agricultural pollution, notably the transfer of nitrogen (N) and phosphorus (P) from diffuse and point sources, will be part of a suite of mitigation measures to tackle eutrophication in waterbodies throughout the EU.

It is widely documented in the literature that many waterbodies in Europe will not achieve the desired water quality status by 2015 due to catchment buffering and long transit times (Cherry et al., 2008). Many River Basin District plans have now reset achievement targets for "good status" to more realistic time reporting periods beyond this timeframe. It is important to note that such time shifts may not be based on hydrological time lags but instead on socio-economic delays. For example, present time lags may be calculated based on practical delays such as: extensive time periods for total implementation of POM in a catchment, or obtaining capital and planning permission to complete a capital projects such as construction of a waste water treatment facility. Also, the choice of POM and their efficacy within a catchment will have an effect on time lag.

Hydrological delays may occur where diffuse nutrient transfer predominates in hydrogeological pathways. This delayed hydrological response is also referred to as memory effect, time delay or time lag, and has been highlighted previously (Worrall and Burt, 1999; Bechmann et al., 2008; Iital et al., 2008; Wahlin and Grimvall, 2008) and occurs as nitrate leaching pathways between soils, groundwaters and rivers are generally long and complex (Collins and McGonigle, 2008). Such hydrological time lags also depend on soil/subsoil type, bedrock geology/hydrogeology and climatic factors such as rainfall (Stark and Richards, 2008). The components of hydrological time lag as used in this paper are vertical travel time through the unsaturated zone and flushing of a nitrate contaminated aquifer to below a specified EU water quality target. Time lag through the European aquifer typology (carbonate, unconsolidated, sandstone and hard rock aquifer groups) classification system devised by Wendland et al. (2008) estimated nutrient residence times ranging from days to >1000 year. In many countries, the current estimated time lags of groundwater quality to changes in N inputs are not realistic for baseflow-dominated systems or chalk catchments, where significant retardation of chemicals can occur. Model simulations suggest that groundwater nitrate concentrations in such systems will not decline for several decades after input has been reduced or stopped, and that increases resulting from historical nutrient loading are inevitable within the short term (Jackson et al., 2008; Vertés et al., 2009).

Hydrological time lags in response to agricultural policy and practice in Europe have differed considerably. For example in several major Eastern European rivers there has been a remarkable lack of response to dramatic decreases in the use of commercial fertilisers since the late 1980’s (Grimvall et al., 2000). Large amounts of organic N can accumulate in soil during periods of higher application rates. Therefore nitrogen losses from agricultural runoff will decline very slowly, even though fertiliser inputs have been reduced (Grimvall et al., 2000; Löfgren et al., 1999). State supported agriculture ceased in Finland and Poland in the late 1980's and early 1990's respectively. This led to reduced fertilizer usage but riverine water quality still continued to deteriorate in some areas. In Denmark, intensive application of fertilizers and leaching of nitrate from the soil to groundwater began in the late 1950s. This increased until groundwater nitrate concentrations stabilised in 1980 (Postma et al., 1991). Stringent Danish measures have resulted in a decline in nitrate leaching from the root zone. Determining improvements in Danish ground, coastal and estuarine water is improbable at present, as a result of the time lag factor (Nimmo Smith et al., 2007). A reduction in Denmark's surface water nitrate concentrations has been identified between 1992 and 2002, but this has taken > 20 years (Kronvang et al., 2009).

In Ireland, 102 groundwater bodies (representing 13.3% of the land area of Ireland) are designated poor status due to elevated groundwater P (Daly, 2009). Where this P is being transported to groundwater from diffuse agricultural sources by diffuse recharge then the recharge principals are similar to nitrate but there will be greater uncertainty as P can be retarded, through adsorption, along its migration pathway due to its non-conservative nature (Corbett et al., 2000). This uncertainty reflects the accumulation of high levels of P in soils and the sorption/desorption processes that occur along the groundwater recharge pathway (Dillon et al., 2003). Schulte et al. (2010) showed that it may take many years for elevated soil P concentrations to be reduced to agronomically and environmentally optimum levels. The extent of these delays were predominantly related to the relative annual P-balance (P balance relative to total P reserves) while the onset of reductions in excessive soil P levels may be observed within five years, this reduction is a slow process and may take years to decades to be completed. In Ireland, only two groundwater bodies (0.3%) have been classified at poor status due to elevated nitrate concentrations in groundwater (Daly, 2009). This is based on a mean annual threshold concentration of 37.5 mg NO_3^- L^{-1} where there is a sustained upward trend. There is a potential for further groundwater bodies to be classified as “poor” in time if the environmental quality standard (EQS) is lowered. In the future the EQS for groundwater nitrate maybe reduced to combat eutrophication in surface and estuarine waters where N limitation to aquatic plant ecology is identified. The EQS for dissolved inorganic N in estuaries has been set at 2.6 mg N L^{-1} (S.I. 272 of 2009). In Ireland, at time of writing there is no EQS in place for rivers.

The objective of this paper is to estimate the hydrological time lag between implementation of nitrate mitigation measures in 2012 and improvement in groundwater quality using a simplified methodology in a variety of Irish hydrogeological scenarios (Table 1).

2. Materials & Methods

This study links a number of modelling approaches to estimate the time lag between implementing measures to reduce nitrate loss to groundwater and the subsequent changes in groundwater and surface water quality. The travel time of the pathway between the soil surface and shallow groundwater (vertical pathway travel time) is estimated based on matrix flow through the vadose zone (Section 2.1). The vertical pathway is the time required for recharge to reach shallow groundwater and either displace or dilute the *in situ* groundwater nitrate concentrations. Where a surface water receptor has elevated nitrate concentrations then the travel time between the groundwater body and the surface water must be accounted for. Horizontal travel time (Section 2.2) estimates the time required for groundwater migration between recharge and discharge, but is not part of the total time lag calculation. Instead it indicates first breakthrough of nutrients from groundwater to surface water. The time required for elevated groundwater nitrate to decrease to acceptable levels (flushing) in response to mitigation measures is estimated based on displacement. The time lag between mitigation measure implementation and groundwater body response is the cumulative travel time in vertical and flushing time lags above. For surface water receptors the time lag is the cumulative time of the hydrological pathways to the river channel. Finally, uncertainty analysis for vertical and flushing time lags is carried out.

2.1 Vertical pathway travel time in soil/subsoil

A range of subsoil thicknesses were used: <1m, <3m, 3 - 5 m, 5 - 10 m and >10 m. Such thicknesses were also used by Misstear et al. (2009) when making initial estimates of groundwater recharge from groundwater vulnerability mapping. Vertical travel time is based on matrix flow through these depths of overburden. Where a watertable exists within this overburden, travel times may be shorter (e.g. perched watertable in glacial till) or where the watertable is within the deeper aquifer travel times may be longer e.g. Karst limestone.

Based on Fenton et al. (2009) and Lee and Casey (2005) the unsaturated vertical subsurface travel time (Tt in a certain period of ER) can be calculated from equation 1.

$$Tt = \frac{d}{ER/(\eta_e/100)} \qquad [1]$$

Where ER (m) is mean annual effective rainfall (rainfall-actual evapotranspiration) for a known period and can be estimated for permanent grassland systems in Ireland using the hybrid model developed by Schulte et al. (2005), η_e (%) is average effective porosity (assuming it is a time and space averaged effective porosity) and d is total depth of the unsaturated zone (m) during the same period. A range of η_e values (2.5 to 40%) were taken as indicative of various scenarios found in the literature. In general Kilfeather and Van der Meer (2008) found low η_e values for County Laois, Midlands, Ireland but η_e in immature tills were higher giving a range from 1 to 18.9% (pores greater than 25 µm).The mean η_e of 7% is indicative of tills in Ireland, provided immature tills are included. However, a mean of 5% is more appropriate when immature tills are excluded. This could be low if pores >15 µm are considered effective as in Lind and Nyborg, (1998). Till η_e ranges from 2.5 to 32% (pores greater than 15 µm) were found in Sweden (Lind and Nyborg, 1998). Where immature tills were excluded η_e ranged from 3 to 10%. In sandy silty un-weathered Fennoscandian lodgement tills η_e varied from 5 to 10% or less in clayey tills (Haldorsen and Krüger, 1990). Such immature till values are low under Irish conditions but are included in the range to be inclusive of all tills. Gibbons et al. (2006) reported subsoil average pore velocities of 6, 7 and 11 mm day^{-1} and the corresponding depths of infiltration would be 2.1, 2.5 and 4.0 m year^{-1} when multiplied over a calendar year. However, recharge and saturated soil porosity does not occur on all days and therefore the pore velocity should be multiplied by the average number of days where soil pores are saturated.

Gibbons et al. (2006) concluded that the mean residence time is determined by the recharge (ER and additional irrigation application rates) rate and the water-filled pore space, and not by the K_{sat} that is in the range of 160-1130 mm day^{-1}. This range is at least 40 times greater than the mean rainfall rate of 3-4 mm day^{-1} during the winter season. Misstear et al. (2008) estimated vertical travel times of recharge through 20 m of low K_{sat} clay till with η_e of 40% to be over 250 years.

Three typical Irish ER quantities (600, 800 and 1000 mm yr^{-1}) were selected for the estimation of the vertical travel time, based on Schulte et al. (2006). Mean rainfall in Ireland is 1150 mm yr^{-1}. The model estimates ER as a function of soil moisture deficit and evapotranspiration taking antecedent conditions into account. The zero flux plane method is incorporated in this hybrid model, where evaporation occurs above the zero flux plane and below which water moves to the watertable by capillary or gravity effects. On this plane no hydraulic gradient (*dh/dx*) exists. Drainage rate increases with saturation. The *dh/dx* also increases proportionally with moisture content.

These unsaturated zone *Tt* were compared to saturated zone velocities (v m day^{-1}) calculated using effective Darcian velocity (Equation 2):

$$v = -K_{sat} \frac{1}{\eta_e} \frac{dh}{dx} \qquad [2]$$

Where K_{sat} is either within a range of literature values for tills (Misstear et al. 2008; Lind and Lundin 1990) or can be estimated using slug injection or pumping tests (Bouwer and Rice, 1976), *dh/dx* (50%) is the estimated vertical hydraulic gradient for a point (Mulqueen, 2005). A similar approach was used previously by Helmke et al. (2005) to investigate nitrate transport to groundwater in four Iowa till units.

Travel time (year) for saturated conditions ($Tt_{(sat)}$) can be calculated from the total unsaturated zone depth (d (m)) using Equation 3.

$$Tt_{(sat)} = \frac{d}{v} \qquad [3]$$

2.2 Horizontal travel time in upper aquifer/shallow groundwater

Horizontal travel times under saturated conditions, although not included in time lag calculation, will indicate the first breakthrough of nutrients at a surface water receptor. Here, piston flow is assumed under steady state conditions. Flows in the saturated zone are a function of the K_{sat} and the potential dh/dx, which in most cases is gravitational. In the saturated zone, K_{sat} remains constant at a particular location but varies spatially, due to the heterogeneity of the aquifer and between different aquifers and geological units. K_{sat} may also vary due to anisotropies in the aquifer. Horizontal travel time estimation (groundwater velocity), was calculated by effective Darcian linear velocity, v (m day^{-1}) as per Eqn. 2. This calculation will estimate the first occurrence of breakthrough at a surface water body and is only indicative of the shortest travel times. Time lag will always be longer than this value.

Indicative values of K_{sat}, for gravel ranges from 10^2 to 10^3 m day^{-1} and when mixed with sand ranges from 5 to 10^2 m day^{-1}. Addition of clay lenses reduces K_{sat} and the range is from 10^{-3} to 10^{-1} m day^{-1}. The relationship between K_{sat}, particle size and dh/dx in sand and gavels was investigated thoroughly by Mulqueen (2005), indicating that larger proportions of finer material within a gravel reduces K_{sat} drastically. Fenton et al. (2009) estimated travel times in a sand and gravel aquifer ranged from months to decades due to the presence or absence of clay lenses. Johnson, (1967) gives a list of representative values of specific yield (S_y) for a variety of materials and presents a starting point for gravels 23-25%, limestone – 14% (high for Ireland) and till from 6 to 16%. Misstear et al. (2008) estimated S_y parameters based on recharge coefficients –values ranged from 17 to 36% but when extreme values were omitted a more realistic value of 19% was chosen for sand and gravels. Interestingly using a mean S_y of 13% produced unrealistically low recharge coefficient from 40 to 80%. In two synclinal aquifers in the Cork harbour area in southern Ireland, η_e of 1% was found but can be much higher locally (Allen and Milenic, 2001). Similar η_e values are seen in the Waulsortian (2.5%) (Anon, 2005) and Ballysteen limestones (1%) of north Cork, Ireland.

2.3 Aquifer Flushing times

Nutrient mixing in the aquifer can be estimated using Equation 4:

$$\text{Nitrate}_{(\text{MIX})} = \frac{\text{Recharge} * \text{Nitrate}_{(\text{R})} + \text{Storage} * \text{Nitrate}_{(\text{I})}}{\text{Recharge} + \text{AquiferT}} \qquad [4]$$

where Nitrate $_{(\text{MIX})}$ is the nitrate concentration in the aquifer after mixing, this is the input concentration for the next time step of the mixing model; Recharge is recharge in (m) over an area (m^2); Nitrate $_{(\text{R})}$ is the nitrate concentration (mg L^{-1}) in the recharge, multiplication of these two parameters gives a contaminant flux entering the aquifer; Storage is storage in the aquifer based on the thickness of the aquifer (m), unit width of the aquifer and specific yield (S_y); Nitrate $_{(\text{I})}$ is the initial nitrate concentration (mg L^{-1}) in the aquifer and AquiferT is aquifer thickness in (m).

For the examples presented the aquifer is 100 m thick, unit width of 1 m, recharge taken was 0.4 m and S_y of 0.02. The recharge concentrations used were 25, 30 and 35 mg NO_3^- L^{-1}. The model was re-run over incremental time steps (each time step is the equivalent of 0.1 of a year) until the mean annual nitrate threshold value of 37.5 mg NO_3^- L^{-1} was reached.

The minimum time required to reduce groundwater nitrate concentrations below the mean annual threshold of 37.5 mg NO_3^- L^{-1} is calculated by cumulating the vertical and flushing times and adding these to the WFD measures implementation year 2012. A range of times was estimated by varying aquifer specific yields of two bedrock aquifers (S_y of 0.01 and 0.02) and a gravel aquifer (S_y - 0.2) each with unsaturated zone depths of 3, 5 and 10 m.

2.4 Uncertainty analysis

In order to reflect the spatial (and in the case of effective rainfall, temporal) variability of the model input parameters, we applied Monte Carlo analyses to compute the probability density distributions for the unsaturated zone travel time and for the aquifer flushing times.

For the Monte Carlo analysis of the unsaturated zone travel time, we assumed a uniform distribution of effective rainfall between 600 mm a^{-1} and 1000 mm a^{-1}, a uniform distribution of thickness of the unsaturated zone between 0 m and 15 m, and a lognormal distribution of the effective porosity, with a mean porosity of 1.800 and a standard deviation of 0.784, based on combined empirical data from Kilfeather et al.

(2008) and Lind and Lundin (1990). To quantify the spatio-temporal variability in aquifer flushing times, we developed 8 scenarios Table 1.

In addition, to reflect the variability of nitrate concentrations of the recharge entering each of these aquifers, we subjected each of these scenarios to a Monte Carlo analysis with a uniform distribution of initial nitrate concentrations. We assumed a best-case scenario, in which the POM are fully effective and nitrate concentrations in all recharge are below the guideline value of 37.5 mg L^{-1}. Therefore, we assumed that incoming nitrates concentrations were uniformly distributed from a maximum of 37.5 mg L^{-1} to a minimum of half this value.

3.0 Results

3.1Vertical pathway *Tt* in soil/subsoil

A comparison of methods to estimate vertical flux time is presented in Table 2. Methods 1 (Gibbons et al., 2006), 2 (Gibbons et al., 2006) and 3 (Fenton et al., 2009) all gave similar estimated travel times through varying unsaturated thicknesses ranging from 0.5 years through 0.5 m unsaturated zone thickness to 9.3-10.8 years for 10 m unsaturated zone thickness. Method 4 based on Darcian flux under saturated conditions, gave much shorter *Tt*, compared with methods from 1 to 3, of 0.2 and 4.7 years for 0.5 and 10 m unsaturated zone thickness. These times (method 4) reflected the fastest *Tt* thresholds. As other methods involved some form of unsaturated conditions, *Tt* were slower. The K_{sat} of tills varies considerably e.g. sandy silty tills in Scandinavia range from 5 x 10^{-9} m s^{-1} to 5 x 10^{-4} m s^{-1}(Lind and Lundin, 1990). The scenarios covered in this paper represented K_{sat} of moderate permeability tills ranging from 5 x 10^{-8} m s^{-1} to 5 x 10^{-4} m s^{-1}(Donal Daly, *pers comm.*). Clay tills can have low permeability ($<10^{-9}$ m s^{-1}) e.g. at a site in Northern Ireland (Phillips et al., 2007) or comparable tills found in Saskatchewan Canada (from 10^{-11} to 10^{-12} m s^{-1}) (Shaw and Hendry, 1998) due to the high η_e.

The results in Table 2 confirm that the unsaturated travel times are generally 50% longer than the equivalent $Tt_{(sat)}$. The unsaturated zone models all seem to be providing similar estimates of *Tt* to the saturated zone but these times are highly dependent on the input parameters of ER and η_e. There are negative relationships between ER quantity/η_e and *Tt*.

Vertical *Tt* in tills of different depths to the saturated zone were estimated for a range of ER quantities and η_e to identify the likely ranges of *Tt* that can be expected under heterogeneous till properties and meteorological conditions in Ireland (Table 3). Tills may be saturated and unsaturated at different times of the year, so ER only occurs on a set number of days per year. *Tt* would be expected to vary spatially within catchments due to a combination of till property variation and ER quantities. In areas with lower permeability soils, a proportion of ER would be expected to run laterally over the soil surface or at shallow depths within the soil. The results of this lateral movement would be decreased ER amounts, which would increase the travel time to groundwater in these areas. Conversely areas where lateral flow re-infiltrates in to the soil would have shorter travel times due to increased quantities of drainage water.

Table 3 presents *Tt* for recharge to move through tills and sand and gravels. For tills receiving 0.4 m ER, estimated *Tt* were 1, 0.7 and 0.5 m yr^{-1} for η_e of 40, 30 and 20%.

Below such η_e values of 20%, *Tt* times are faster compared to $Tt_{(sat)}$ conditions as presented in Table 1. There is a positive relationship between ER and *Tt*. Depths indicative of sand and gravels are 1.5 to 5 m of unsaturated subsoil at 0.4, 0.8 and 1 m ER at η_e of 10, 15, 20 and 30%. The *Tt* again is influenced by ER. High η_e and low ER result in slower *Tt* compared to the $Tt_{(sat)}$ equivalent. The $Tt_{(sat)}$ indicates an upper threshold for Eqn.1.

The response surfaces in Fig. 1 presents estimated vertical *Tt* (years) for a range of η_e (ranging from 5 to 30%) over a range of annual ER amounts (ranging from 0.4 to 1 m yr^{-1}) and a range of depths of the unsaturated zone from 1 to 10 m. The vertical unsaturated zone *Tt* for η_e 30% (Fig. 1a) illustrates that as subsoil thickness increases to 10 m the *Tt* increases with decreasing ER. At low ER amounts of 0.4 m yr^{-1} the vertical *Tt* can reach approximately 20 years with unsaturated zone thicknesses up to 10 m. Less than 50% of the scenarios presented on the surface have *Tt* in excess of 4 years. When η_e is reduced to 20% (Fig. 1b) the *Tt* scenarios decrease although approximately 25% of the scenarios are still greater than 4 years. As η_e is reduced to 10% (Fig.1c) and 5% (Fig. 1d) many of the *Tt* scenarios are less than 4 years. All of the scenarios are likely to occur at the catchment scale with thinner soils at higher altitudes and subsoil depth increasing as altitude decreases into a valley towards a river. The integration of unsaturated zone depth, η_e and ER can provide catchment managers with more spatially explicit estimates and catchment specific mean time lags of groundwater quality improvements to mitigation measures.

3.2 Horizontal travel time

Horizontal travel times indicative of various geological scenarios are presented in Table 3. *Tt* are determined here in particular by the range of K_{sat}, S_y and *dh/dx* of 2%. The *Tt* indicates that migration in sand and gravel aquifers takes longer than all other aquifers to reach sediment at the base (Hyporheic zone) of the surface water receptor. This methodology provides the framework for a range of parameters to be inputted into such tables. An example here would be *dh/dx* – the figure taken here is 0.2, which of course will vary with K_{sat}. The length of the pathway here was kept the same for all scenarios but within a catchment this will inevitably also be a range of values. Such values are not as important as flushing times to achieve water quality targets but provide upper limits of travel time. Flushing timescales should be longer than first occurrence at a surface water receptor. Such values therefore present a lower range value for time lag.

3.3 Time to complete flushing of aquifer

The time it takes for complete flushing to occur should always be longer than the horizontal breakthrough time. However, reducing groundwater nitrate concentrations to below the mean annual threshold value of 37.5 mg NO_3^- L^{-1} may vary depending on the level of mixing and the horizontal pathway taken by the groundwater to the surface waterbody. A certain percentage of the ER will be separated into different pathways and pathway lengths with corresponding travel times. The nitrate concentration leaving the rooting zone and entering the system as recharge will also differ considerably. Assumptions have been made such as a) no natural attenuation or denitrification occurs and b) no vertical mixing. Of course separation into pathways may not be possible in regimes with high K_{sat} e.g. Karst limestone where travel times although fast may range several orders of magnitude.

In bedrock aquifers with S_y of 0.01 and mean nitrate concentration of 40 mg NO_3^- L^{-1}, the estimated time required to decrease to below the threshold value were 0.5, 0.8 and 1.8 years, for recharge nitrate concentrations of 25, 30 and 35 mg NO_3^- L^{-1}, respectively. Increasing the mean groundwater nitrate concentration to 50 mg NO_3^- L^{-1}increased these time lags to 1.8, 2.6 and 4.6 years for recharge nitrate concentrations of 25, 30 and 35 mg NO_3^- L^{-1}, respectively. Thus bedrock aquifers with low S_y of 0.01 have saturated zone time lags of between 0.5 and 4.6 years depending on the initial groundwater and recharge nitrate concentrations (Fig. 2a). Doubling the S_y of the aquifer doubles the flushing times which then range 1 to 3.6 years and 3.6 to 9.1 years for aquifer with mean initial groundwater nitrate of 40 and 50 mg NO_3^- L^{-1}, respectively (Fig. 2b).

For aquifers with higher S_y the time lags increase considerably. In Ireland, sand and gravel aquifers have the highest S_y typically in the range 0.15 to 0.2. At a typical S_y of 0.2 for Irish sand and gravel aquifers, time lags ranged from 1.5 to 5.3 years (Fig. 2a) and from 5.4 to 13.6 years (Fig. 2b) for aquifers with mean initial groundwater nitrate of 40 and 50 mg NO_3^- L^{-1}, respectively. The ranges of time lags in sand and gravel aquifers are generally longer than the 1.9 year calculated horizontal travel time for an aquifer with a S_y of 0.14 presented in Table 4.

The results of the modelling of groundwater flushing indicate that the time required when reducing groundwater nitrate to below the threshold value is strongly influenced by the initial groundwater nitrate concentration. There is a linear increase in time lag with increasing aquifer S_y such that doubling S_y doubles the saturated zone time lag. Further complicating the up-scaling of the model is the relationship between time lag and aquifer recharge quantity. Time lag and recharge quantity are negatively correlated. For example, time lag calculation for: groundwater (50 mg NO_3^- L^{-1}), bedrock aquifer (100 m thick, S_y of 0.02), ER of 200, 400 and 600 mm yr^{-1} (35 mg NO_3^- L^{-1}) would be 18.2, 9.2 and 6.2 years, respectively.

3.4 Uncertainty Analysis

For the unsaturated zone travel time, the uncertainty analysis (Fig. 3) shows that travel times should amount to two years or less for the vast majority of scenarios. This suggests that longer travel times for the unsaturated zone, evident in Fig. 1 and Table 3, while conceivable at local scale, should be rare at national scale, and only occur where in worst case scenarios, with thick soils, high effective porosity and low effective rainfall.

For the aquifer flushing times, the uncertainty analysis (Fig. 4) shows a wide range of responses. For most scenarios, flushing should be completed within 5-10 years. However, significantly longer flushing times may occur at the local scale, in worst-case scenarios on high-yielding very thick aquifers.

4. Discussion

Vertical Time lag

For all low η_e conditions (Table 3) compared with fully saturated conditions (Table 2.) *Tt* seem faster than expected for <3 m and 3 – 5 m thicknesses but are at or slightly slower than fully $Tt_{(sat)}$ for moderate and low classes. This seems plausible as low η_e mimics unsaturated conditions best. With high ER and high η_e travel times are comparable for saturated conditions for > 10 m thicknesses. In Table 2 *Tt* for ER of 1 m mimics *Tt (sat)* as η_e is high at 40%, but also because of the *dh/dx* created by the ER. To have all the *Tt* values under the threshold set by the fully saturated conditions, more ER is needed (which is doubtful to occur in Ireland) or the η_e is too small in some cases. Such η_e values would allow the inclusion of immature tills. The *dh/dx* under saturated conditions should also be varied to compare results.

Sand and gravels from 3 to 5 m thick and with η_e of 10, 20 and 30% are comparable to tills with 5 to 10 m thicknesses.

Tt calculations seem to work well for the low ER for η_e >10% where *Tt* are slower than the $Tt_{(sat)}$ equivalent. Doubling the ER does not allow the correct *Tt* to be achieved. Bringing the η_e to 20% still achieves slower *Tt* than $Tt_{(sat)}$ conditions.

In general, η_e values for gravel and sand are 25% to 40% and 25% to 50%, respectively. When sand and gravel are mixed this η_e decreases, giving a range from 20% to 30%. The results from Table 3 agree with this. Stephens et al. (1998) showed that depending on the methodology used to determine η_e in sands and gravels the subsequent results and interpretation may differ considerably. The η_e estimated from geologic logs, measured particle size, and other means were 32%, 31% and 25%

respectively. In Ireland, a typical value of η_e for permeable sand and gravels is approximately 20%.

Horizontal Travel Time

The horizontal travel time in the Karst aquifer was difficult to estimate as considerable data (S_y, fracture density, fracture truncation, fracture orientation, fracture trace length, fracture spacing, mechanical aperture, effective hydraulic aperture, and aperture opening size) was required to estimate K_{sat} values. A K_{sat} range was available from slug injection tests but was not indicative or comparable with actual horizontal flow travel times. Instead, tracer breakthrough data in several wells originating from the vertical travel time study were used to calculate horizontal travel times. The horizontal travel time to the receptor 500 m away from the source following this pathway was estimated from 2 to 3 months (Fenton et al., 2009).

Time to complete flushing of aquifer

The simple model used for estimating aquifer flushing time clearly highlights the importance of nitrate concentration in groundwater, ER and S_y. Increasing the groundwater initial nitrate concentration from 40 to 50 mg NO_3^- L^{-1}, increased the time lag by between 2.5 and 3.6 fold depending on ER nitrate concentration. Temporal variation in both recharge and groundwater nitrate concentration makes refining the model further problematic. The model proposed does not account for denitrification along the nitrate transport pathway. Denitrification in the saturated and unsaturated zones can further reduce ER and groundwater nitrate concentrations. This can reduce the time required to achieve the mean annual threshold value of 37.5 mg $NO_3^-L^{-1}$. Groundwater denitrification has been shown to be an important attenuation process and is controlled by substrate availability (N and C), oxygen/redox status and denitrifier occurrence. These conditions vary both temporally and spatially and denitrification has been shown to be important in controlling groundwater nitrate occurrence (Fenton et al. 2009).

Cumulative time lag

Integrating the estimated unsaturated zone travel times and the time lag in reducing groundwater nitrate concentrations as estimated by the groundwater mixing model gives an idea of the total time lag that can be expected. Integrated cumulative travel times have been calculated (Fig. 5). Unsaturated zones Tt were based on η_e 0.3 and unsaturated zone depths of 3, 5 and 10 m. Aquifer time lag was calculated for bedrock aquifers with S_y of 0.01 and 0.02 and gravel aquifers with S_y of 0.2, the criteria for the mixing model were that initial groundwater nitrate was 50 mg $NO_3^-L^{-1}$ and ER nitrate concentration of 35 mg $NO_3^-L^{-1}$. The estimated cumulative time lags are based on the current state of knowledge and data availability. Increasing the temporal and spatial understanding of hydrogeological characteristics will improve the accuracy of the time lag estimation.

Based on the scenario outlined above cumulative time lag for areas with unsaturated zone depths of 3 m were 6.9, 11.3 and 15.9 years for bedrock aquifers with S_y of 0.01 and 0.02 and gravel aquifers. Thus groundwater bodies with these characteristics with measures introduced in 2012 the minimum likely year to achieve good status between 2019 and 2028. For measures introduced in 2009 then minimum likely year to achieve good status between 2016 and 2025. Increasing unsaturated zone depth to 5 m increases the time lag slightly to between 8.4 and 17.4 years from the introduction of measures and this only slightly increases cumulative time as it only influences the Tt

in this zone. Further increasing the unsaturated zone depth to 10 m increases the cumulative time lag to between 12.1 and 21.1 years. In areas with thicker unsaturated zone thicknesses of 10 m the minimum likely year to achieve good status for measures introduced in 2012 would be between 2024 and 2033 (Fig. 6).

The minimum year for groundwater nitrate to reduce from 50 to below 37.5 mg L^{-1}, based on the unsaturated and saturated zone time lags, are presented for each aquifer by S_y combination. Karstified or fracture rock aquifers, with low S_y of 0.01, the minimum year to reduce nitrate concentrations are between 2019 and 2024 depending on the unsaturated zone thickness. In the same bedrock aquifers, with higher S_y of 0.02, this minimum time increases to between 2023 and 2029, depending on the unsaturated zone depth.

Failure of the WFD to recognise climate change remains a major short coming of such a legislative instrument. Climate change will have implications for mitigation option efficacy and groundwater response time lags. Expected changes in hydrology as a consequence of climate change may involve rainfall, evapotranspiration, runoff and effective rainfall alterations specific to a geographical location. In carbonate aquifers across Europe, research under the Groundwater Resources and Climate Change Effects (GRACE) program shows that factors such as recharge increase and lowering of the watertable are possibilities due to climate change. This coupled with heightened CO_2 levels in the atmosphere could cause increased dissolution of carbonate aquifers thereby changing their permeability and storage. In other areas, increased rainfall intensity could reduce recharge as more rainfall moves by overland flow rather than infiltrating into the soil. Such matters would re-define hydrological time lags over time but would still be within the ranges estimated in this paper.

Application of spatially explicit estimates of model input parameters will help catchment managers identify catchment specific time lags. Realistic timescales for groundwater quality improvements should be communicated with land managers so that they can appreciate the time required for their land management practices to impact on groundwater quality.

The time lag between introducing protection measures to reduce N inputs in 2012 and first improvements in water quality in 2015 is therefore likely to occur at different rates in different catchments comprising different soils and geologies and should be considered by policy makers and catchment managers (Kronvang et al., 2008).

Uncertainty Analysis

The outcomes of the uncertainty analyses depend to a significant degree on the assumed distribution of the model variables, and the associated parameters of these distributions. In other words, if different distribution parameters had been assumed, different outcomes may have been expected.

The lognormal distribution and associated parameters were calibrated and employed to one of the most important variables, i.e. effective porosity, against empirical data by Kilfeather et al. (2008) and Lind and Lundin (1990). For the distributions of the remaining data, we based our range (maxima and minima) on empirical data. In absence of detailed information on the probability density distributions of these variables, we employed the uniform distribution as the most parsimonious distribution.

In summary, the frequency distributions of both the unsaturated and aquifer flushing times should be interpreted as indicative distributions only that demonstrate the range of travel and flushing times that may reasonably be expected. Further empirical studies have now been initiated and are ongoing to collect empirical distribution data on some of the remaining model input variables.

Total Nitrogen

At present the EQS for European freshwaters and salt waters are set. Moves towards setting EQS for total nitrogen (TN) are being considered across much of Europe as nitrate only accounts for 50-60% of the TN flux especially in lowland permeable groundwater fed catchments. TN is composed of total kjeldahl nitrogen (organic and reduced nitrogen), ammonia, nitrates and nitrites. Proposed limits or EQS emerging from work reviewed by the European Nitrogen Assessment (ENA) are 2 mg TN L^{-1} for Lakes and 1.3 mg L^{-1} to 2 mg L^{-1} for salt waters (Johnes, 2010). This reflects a key change point in freshwater systems where reactive nitrogen becomes the dominant fraction of the TN load. Moving forward, this has challenging consequences for estimation of time lag. With such EQS, denitrification, nitrification and mineralisation would need to be accounted for in time lag estimation.

Benefits for policy makers

A lack of relevant and timely “lag” estimation, hamper the effective dissemination of results to relevant stakeholders. From uncertainty analysis the efficacy of mitigation measures will not manifest themselves for up to 10 years. Incorporation of time lag principles into future water quality regulations will provide regulators with realistic expectations when implementing policies. In Ireland, the Nitrates Directive is the main POM in place to meet the goals of the WFD. The Agricultural Catchments

Programme aims to pick up on early changes in water quality and in doing so can give guidance with regard to the efficacy of measures (Fealy et al., 2010).

5. Conclusions

The issue of hydrogeological time lag is not addressed within the WFD between implementation of catchment mitigation measures and expectations towards target dates. This period of time is related to the implementation of management rather than an appraisal of catchment hydrogeological processes and characteristics. Realistic timescales for achievement of good status for groundwaters or groundwater dominated surface waters must be based on estimates of catchment specific time lags. The simplified methodology in this paper provides reasonable estimates of time lags that could be anticipated in common Irish hydrogeological settings. Based on the simplified unsaturated zone travel time and aquifer mixing models achieving the WFD of good status for all waters by 2015 is unrealistic for groundwater bodies with reasonably long transport pathways but with reasonable expectations within future reporting cycles. This work highlights, that the minimum year for measures introduced in 2012 to reduce groundwater nitrate concentrations to mean annual threshold values, ranges from 2019 to 2033 depending on the specific unsaturated zone depth and aquifer thickness and S_y. Therefore, time lags offer justification in some scenarios to extend target dates for achieving good water quality status based on present POM. Furthermore, incorporation of these principles into regulations that may require more challenging N standards in the future (other than drinking water standards), and especially in groundwater fed surface waters such as some river and estuarine systems, will provide regulators with realistic expectations when managing towards target dates.

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Captions for Tables

Table 1 Scenarios used for unsaturated and flushing travel time

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Table 3 Travel time for recharge to move through varying till of unsaturated subsoil at 0.4, 0.8 and 1 m ER at η_e of 2.5, 5, 10, 20 30 and 40%.

Table 4 Horizontal travel time to a receptor 500 m away- this reflects first arrival. Flushing times should always be longer than this time (for 2% dh/dx)

Captions for Figures

Fig 1 - Unsaturated zone travel time (yrs) through varying unsaturated zone depths at a range of ER amounts (m yr^{-1}) for (a) η_e of 30%, (b) η_e of 20%, (C) η_e of 10% and (d) η_e of 5%.

Fig 2 - Time lag to reduce groundwater nitrate concentrations in areas with annual recharge rates of 400 mm yr^{-1} for aquifers with mean initial nitrate concentrations of A: 40 mg NO_3^- L^{-1} and B: 50 mg NO_3^- L^{-1}, to below the EPA groundwater mean annual nitrate threshold of 37.5 mg NO_3^- L^{-1}for bedrock aquifers (rock) 100 m thick with S_y of 0.01 and 0.02 and gravel aquifers (gravel)15 m thick with S_y of 0.15 and 0.2 at ER nitrate concentrations of 25, 30 and 35 mg NO_3^- L^{-1}.

Fig 3 - Frequency distribution of vertical travel times due to different ER, η_e and unsaturated zone thicknesses

Fig 4 - Frequency distribution of time lags due to flushing in bedrock and sand and gravel aquifers based on the scenario outlined in Table 1.

Fig 5 - Cumulative time lag for reducing groundwater nitrate to below the mean annual threshold of 37.5 mg NO_3^- L^{-1} for bedrock aquifers with S_y of 0.01 and 0.02 and for gravel aquifers (S_y - 0.2) with 400 mm ER, groundwater nitrate of 50 mg NO_3^- L^{-1}and ER nitrate of 35 mg NO_3^- L^{-1}at a range of unsaturated zone depths of 3, 5 and 10 m.

Fig 6 - Minimum year for reducing groundwater nitrate concentrations to below the mean annual threshold of 37.5 mg NO_3^- $L^{-1}$for two bedrock aquifers (S_y of 0.01 and 0.02) and a gravel aquifer (S_y - 0.2) with measures introduced in 2012. For each aquifer type the three points relate to unsaturated zone depths of 3, 5 and 10 m.

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Table 1. Scenarios used for unsaturated and flushing travel time

Unsaturated zone

Scenario	Soil depth (*d*)	Effective porosity (η_e)	Effective Rainfall (ER)
	m	%	m
1-30	0.5, 2, 3, 5, 10	2.5, 5, 10, 20, 40	0.4, 0.8, 1.0

Aquifer flushing

Scenario	Aquifer	Sy	Aquifer thickness	Nitrate $_{(I)}$
		(%)	(m)	(mg L^{-1})
1	Bedrock	1	100	40
2	Bedrock	2	100	40
3	Bedrock	1	100	50
4	Bedrock	2	100	50
5	Sand and Gravel	20	15	40
6	Sand and Gravel	20	15	50
7	Sand and Gravel	20	100	40
8	Sand and Gravel	20	100	50

Table 2 Summary of four methods used to estimate the vertical travel time through variable unsaturated zone thicknesses of 0.5 to 10 m with an η_e of 37% under saturated conditions (hydraulic gradient =1) representing the fastest vertical travel times. *Tt* under unsaturated conditions will be longer than these best case scenarios.

	Gibbons et al (2006) Method 1	Gibbons et al (2006) Method 2	Fenton et al (2009) Method 3	Misstear et al (2009) Method 4
	Travel time (*Tt*) (yr)			
Depth (m)				
0.5	0.5	0.5	0.5	0.2
2	1.9	2.2	1.9	0.9
3	2.8	3.2	2.8	1.4
5	4.7	5.4	4.6	2.4
10	9.4	10.8	9.3	4.7

Method 1	Gibbons et al. (2006) Pore velocity =2.9mm yr^{-1} which is calculated based on pore velocity/number of days drainage
Method 2	Gibbons et al. (2006) T(t)= ER (400 mm) /depth (m) *n_e (37%)
Method 3	Fenton et al. (2009) Depth/((ER/η_e *time))
Method 4	Misstear et al. (2009) Darcian flux method with k=5*10^{-8}, η_e of 37% and hydraulic gradient of 1

Table 3 Travel time for recharge to move through varying till of unsaturated subsoil at 0.4, 0.8 and 1 m ER at η_e of 2.5, 5, 10, 20 30 and 40%.

Depth (m)*	η_e %	Travel time (yr) for variable Effective rainfall (m)		
		0.4	0.8	1.0
0.5	40	0.5	0.3	0.2
2	40	2.0	1.0	0.8
3	40	3.0	1.5	1.2
5	40	5.0	2.5	2.0
10	40	10.0	5.0	4.0
0.5	30	0.4	0.2	0.2
2	30	1.5	0.8	0.6
3	30	2.3	1.1	0.9
5	30	3.8	1.9	1.5
10	30	7.5	3.8	3.0
0.5	20	0.3	0.1	0.1
2	20	1.0	0.5	0.4
3	20	1.5	0.8	0.6
5	20	2.5	1.3	1.0
10	20	5.0	2.5	2.0
0.5	10	0.1	0.1	0.1
2	10	0.5	0.3	0.2
3	10	0.8	0.4	0.3
5	10	1.3	0.6	0.5
10	10	2.5	1.3	1.0
0.5	5	0.1	0.0	0.0
2	5	0.3	0.1	0.1
3	5	0.4	0.2	0.2
5	5	0.6	0.3	0.3
10	5	1.3	0.6	0.5
0.5	2.5	0.0	0.0	0.0
2	2.5	0.1	0.1	0.1
3	2.5	0.2	0.1	0.1
5	2.5	0.3	0.2	0.1
10	2.5	0.6	0.3	0.3

Table 4. Horizontal travel time to a receptor 500 m away- this reflects first arrival. Flushing times should always be longer than this time (for 2% *dh/dx*)

Aquifer Class	Class		S_y	K_{sat} m day^{-1}	*dh/dx** %	v m day^{-1}	v_e m day^{-1}	to 500 m yr
Rk	Regionally important	Pure limestone	0.01	5	2	0.1	10.0	0.14
Rf	Regionally important		0.02	5	2	0.1	5.0	0.27
Rg	Regionally important	Sand & gravel	0.2	5	2	0.1	0.5	2.74
Lm	Locally important		0.010	2	2	0.04	2.4	0.57
Lg	Locally important	Sand & gravel	0.200	2	2	0.04	0.2	6.85
Ll	Locally important		0.016	1	2	0.02	1.2	1.13
Pl	Poorly productive	Impure limestone	0.009	1	2	0.02	2.2	0.62
Pu	Poorly productive	Unweathered granite	0.0009	1	2	0.02	22.2	0.06

*dh/dx will change depending on $K_{sat.}$

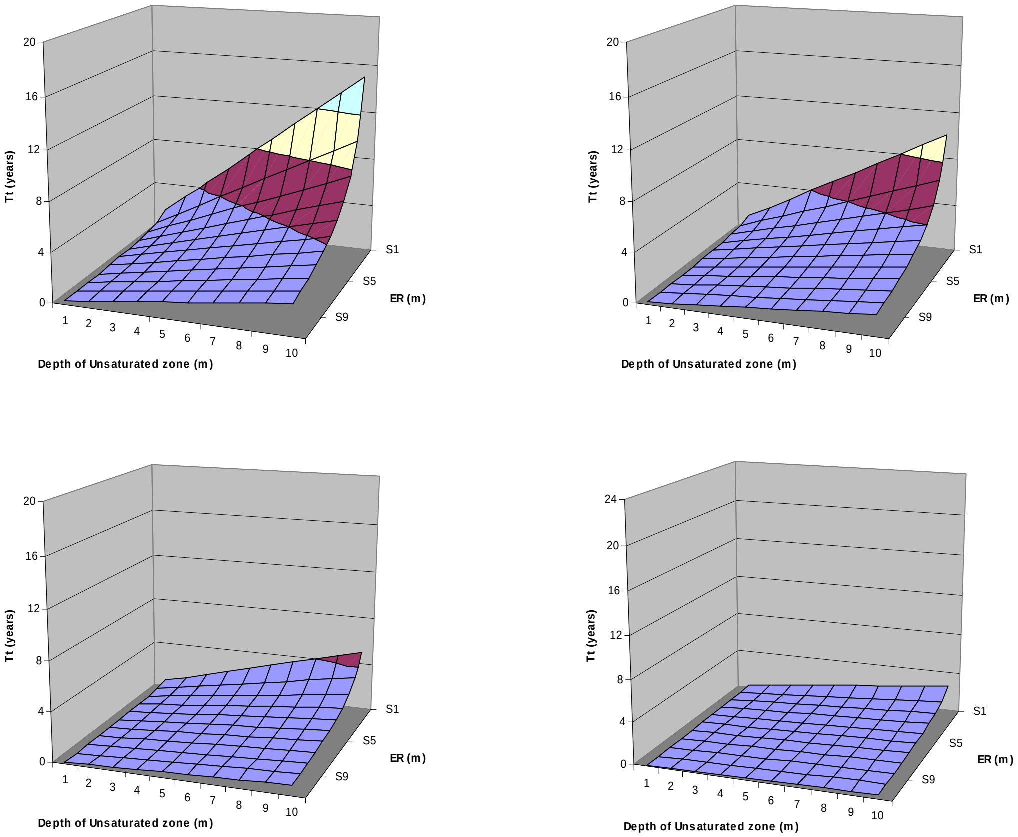


Fig 1 - Unsaturated zone *Tt* (yr) through varying unsaturated zone depths at a range of ER amounts (m in a particular time period) for (a) η_e of 30%, (b) η_e of 20%, (C) η_e of 10% and (d) η_e of 5%.

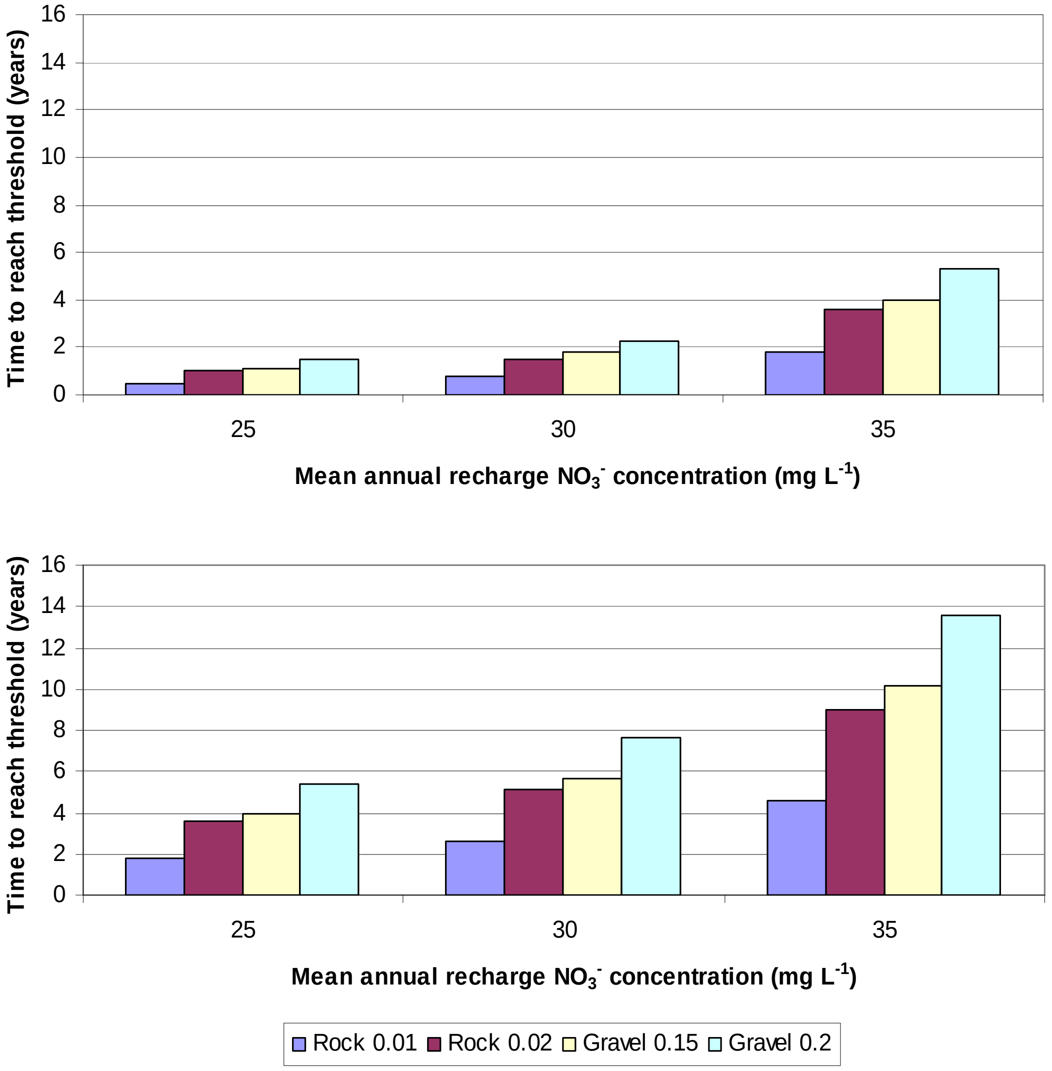


Fig 2 - Time lag to reduce groundwater nitrate concentrations in areas with annual recharge rates of 400 mm yr^{-1} for aquifers with mean initial nitrate concentrations of (a) 40 mg NO_3^- L^{-1} and B: 50 mg NO_3^- L^{-1}, to below the EPA groundwater mean annual nitrate threshold of 37.5 mg NO_3^- $L^{-1}$for bedrock aquifers (rock) 100 m thick with S_y of 0.01 and 0.02 and gravel aquifers (gravel)15 m thick with S_y of 0.15 and 0.2 at ER nitrate concentrations of 25, 30 and 35 mg NO_3^- L^{-1}.

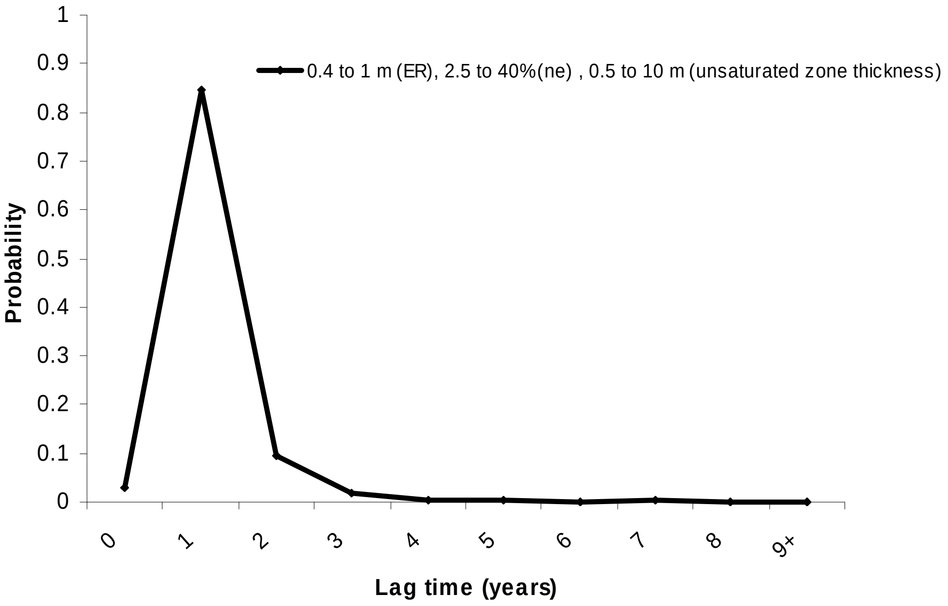
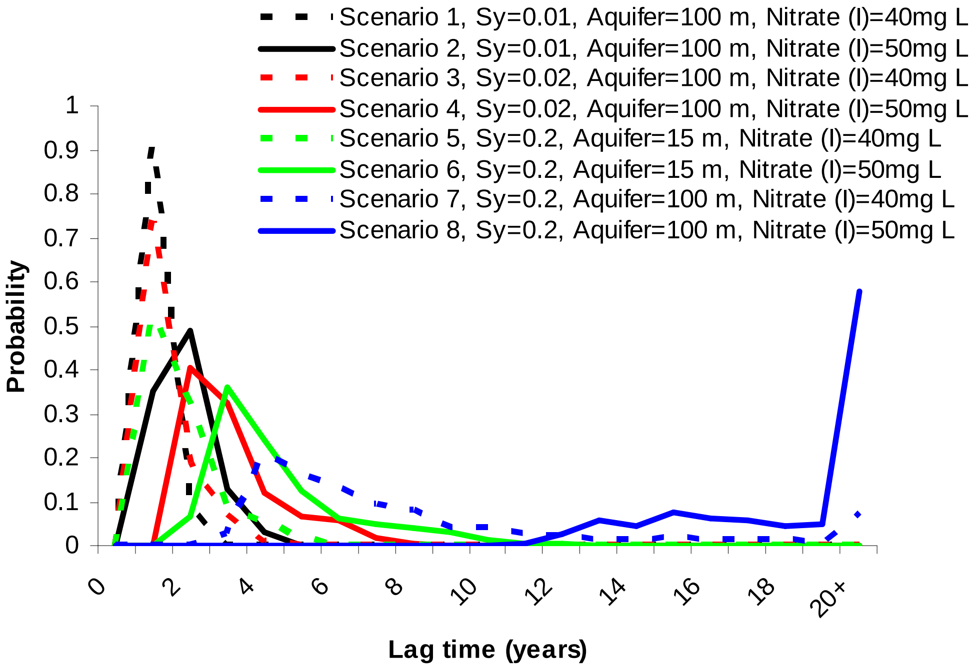


Fig 3 - Frequency distribution of vertical travel times due to different ER, η_e and unsaturated zone thicknesses



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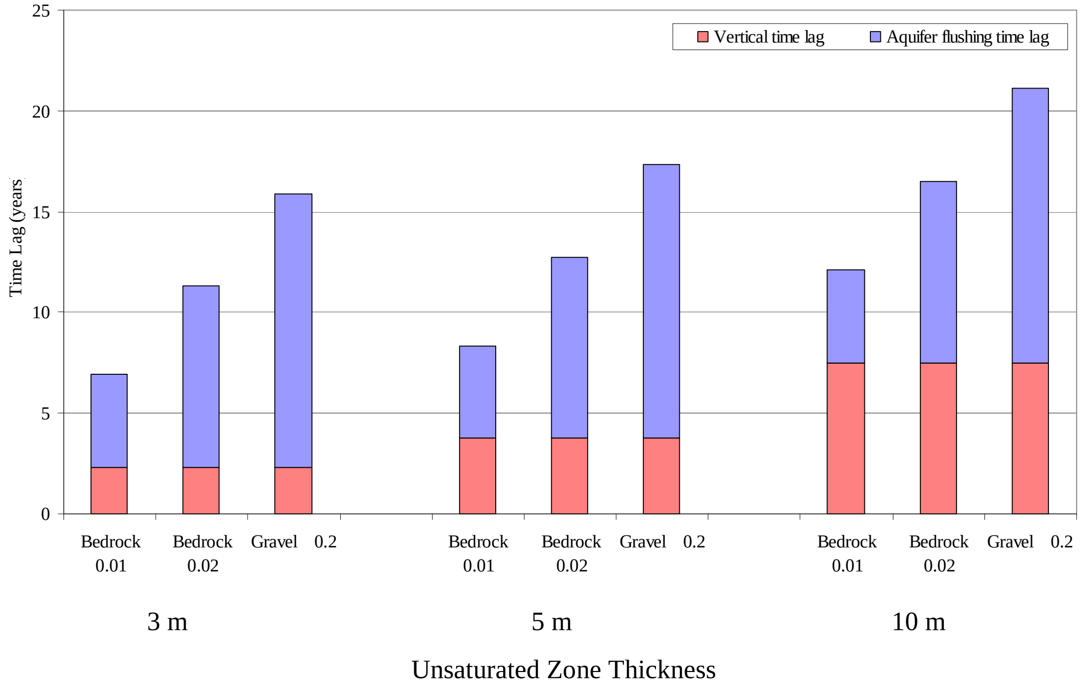

Fig 5 - Cumulative time lag for reducing groundwater nitrate to below the mean annual threshold of 37.5 mg NO_3^- L^{-1} for bedrock aquifers with S_y of 0.01 and 0.02 and for gravel aquifers (S_y - 0.2) with 400 mm ER, groundwater nitrate of 50 mg NO_3^- $L^{-1}$and ER nitrate of 35 mg NO_3^- L^{-1}at a range of unsaturated zone depths of 3, 5 and 10 m.

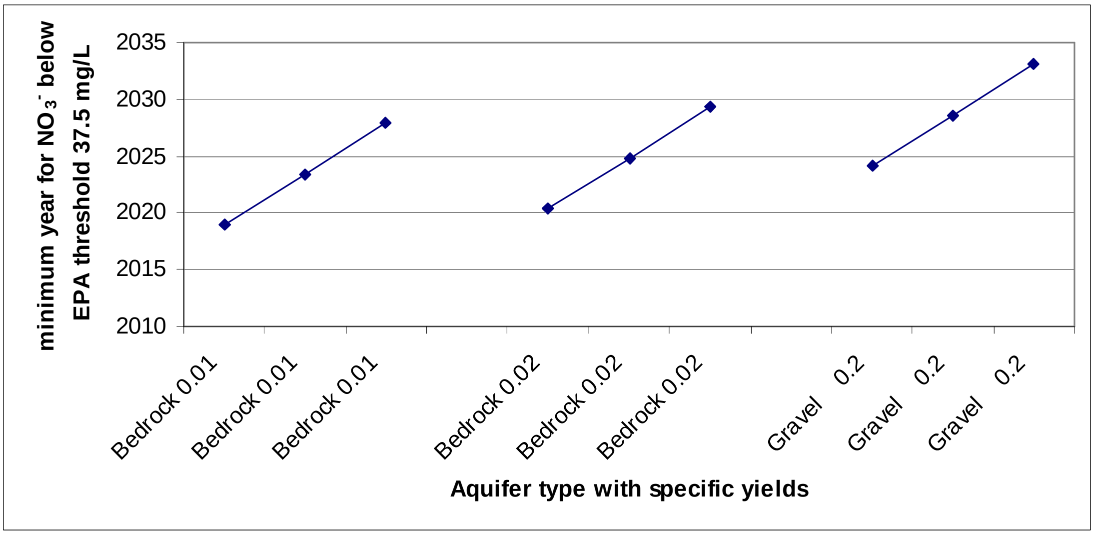

Fig 6 - Minimum year for reducing groundwater nitrate concentrations to below the mean annual threshold of 37.5 mg NO_3^- $L^{-1}$for two bedrock aquifers (S_y of 0.01 and 0.02) and a gravel aquifer (S_y - 0.2) with measures introduced in 2012. For each aquifer type the three points relate to unsaturated zone depths of 3, 5 and 10 m, respectively.