



## A framework for determining unsaturated zone water quality time lags at catchment scale



Sara E. Vero<sup>a,b</sup>, Mark G. Healy<sup>b</sup>, Tiernan Henry<sup>c</sup>, Rachel E. Creamer<sup>a,d</sup>, Tristan G. Ibrahim<sup>a</sup>, Karl G. Richards<sup>a</sup>, Per-Erik Mellander<sup>e</sup>, Noeleen T. McDonald<sup>e</sup>, Owen Fenton<sup>a,\*</sup>

<sup>a</sup> Teagasc Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland

<sup>b</sup> Civil Engineering, National University of Ireland Galway, Co. Galway, Ireland

<sup>c</sup> Earth and Ocean Sciences, National University of Ireland Galway, Co. Galway, Ireland

<sup>d</sup> Department of Environmental Sciences, Wageningen University, Wageningen, Netherlands

<sup>e</sup> Agricultural Catchments Programme, Teagasc, Environmental Research Centre, Johnstown Castle, Co. Wexford, Ireland

### ARTICLE INFO

#### Article history:

Received 8 April 2016

Received in revised form 29 November 2016

Accepted 1 December 2016

Available online xxx

#### Keywords:

Time lag

Soil

Unsaturated

Water framework directive

Nitrate

### ABSTRACT

The responses of waterbodies to agricultural programmes of measures are frequently delayed by hydrological time lags through the unsaturated zone and groundwater. Time lag may therefore, impede the achievement of remediation deadlines such as those described in the EU Water Framework Directive (WFD). Omitting time lag from catchment characterisation renders evaluation of management practices impossible. Time lag aside, regulators at national scale can only manage the expectations of policy-makers at larger scales (e.g. European Union) by demonstrating positive nutrient trajectories in catchments failing to achieve at least 'good' status. Presently, a flexible tool for developing spatial and temporal estimates of trends in water quality/nutrient transport and time lags is not available. The objectives of the present study were first to develop such a flexible, parsimonious framework incorporating existing soil maps, meteorological data and a structured modelling approach, and to secondly, to demonstrate its use in a grassland and an arable catchment (~10 km<sup>2</sup>) in Ireland, assuming full implementation of measures in 2012. Data pertaining to solute transport (meteorology, soil hydraulics, depth of profile and boundary conditions) were collected for both catchments. Low complexity textural data alone gave comparable estimates of nutrient trajectories and time lags but with no spatial or soil series information. Taking a high complexity approach, coupling high resolution soil mapping (1:10,000) with national scale (1:25,000) representative profile datasets to <5 m depth, indicated trends in nutrient transport of 10–12 months and 13–17 months throughout the grassland and arable catchments, respectively. For the same conditions, regulators relying on data from groundwater sampling to test the efficacy of the present measures would be delayed by 61–76 months and 46–79 months, respectively. Variation in meteorological datasets enabled temporal analysis of the trends in nutrient transport and time lag estimates. Such a tool could help catchment scientists to better characterise and manage catchments, determine locations for monitoring or mitigation, assess the efficacy of current measures, and ultimately, advise policy makers and regulators.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

The European Union Water Framework Directive (WFD) (WFD; 2000/60/EC, [Official Journal of the European Communities, 2000](#)) requires that all waterbodies attain 'good' chemical qualitative status (amongst other stipulations) within set reporting periods (e.g. 2015, 2021, 2027). Attainment of this status is attempted

through implementation of programmes of measures (POM), such as those described by the Nitrates Directive ([European Commission, 1991](#)), which remediate pollution from agricultural sources via land and fertiliser management strategies. Quality status is determined via environmental monitoring implemented by the Environmental Protection Agency (EPA) in accordance with Annex II of the WFD. In Ireland, POM include the implementation of buffer zones, timing of fertiliser application, and prescribed application rates – derogation to which is critical for attainment of national production goals (Food Harvest 2020 ([Dept. of Agriculture, Food and the Marine, 2010](#)) and Food Wise 2025 ([Dept. of Agriculture,](#)

\* Corresponding author.

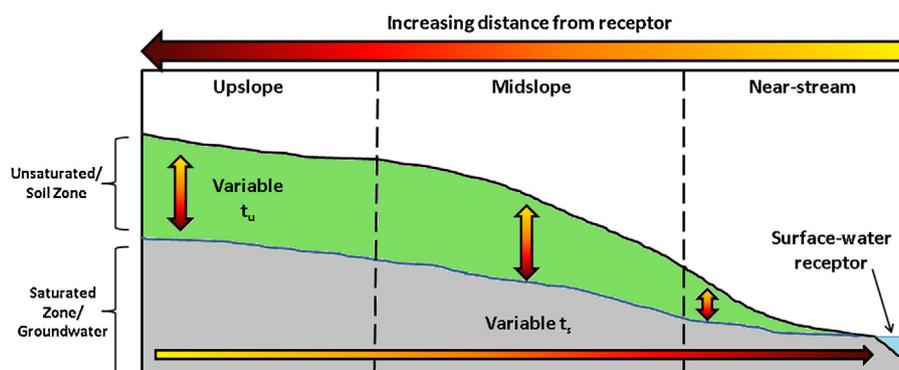
E-mail addresses: [owen.fenton@teagasc.ie](mailto:owen.fenton@teagasc.ie), [ofenton1111@gmail.com](mailto:ofenton1111@gmail.com) (O. Fenton).

Food and the Marine, 2015)). However, the inherent delay or ‘time lag’ (Sousa et al., 2013) that surplus nutrients (or other potential contaminants such as heavy metals or pesticides) encounter through subsurface pathways renders correlation between POM efficacy and waterbody status challenging (Cook et al., 2003; Schulte et al., 2006; Bechman et al., 2008; Fenton et al., 2011a,b; Huebsch et al., 2013; Van Meter and Basu, 2015). Total time lag ( $t_T$ ), not including the attenuation of nutrients or other pollutants during transport (Huebsch et al., 2013; Jahangir et al., 2013), may be subdivided into unsaturated ( $t_u$ ) and saturated ( $t_s$ ) zone components (Fig. 1) (Fenton et al., 2011a,b; Sousa et al., 2013). As the unsaturated zone offers an early indication of trends in water quality concentration and POM efficacy, it is a critical zone to monitor in order to guide the expectations of policymakers and stakeholders (Kronvang et al., 2008; Dworak et al., 2005; Wahlin and Grimvall, 2008; Huebsch et al., 2013). Transport of water and solutes through this region may occur relatively slowly through the soil matrix or rapidly as a result of preferential transport through macropores (Richards et al., 2005; Keim et al., 2012; Kramers et al., 2012). Matrix flow may present the greatest impediment to the achievement of deadlines, as it indicates the slowest rate of solute flushing from the catchment. Hence, it may contribute to prolonged elevation of solute concentration at an abstraction point or surface waterbody, as opposed to rapidly observed peaks resulting from preferential flow (Mellander et al., 2016). Both pathways can and do occur concurrently within a catchment, but the focus of the current paper is on the matrix component, and where  $t_u$  is mentioned hereafter, it is this portion which is referred to. Although the effects of soil properties on  $t_u$  are acknowledged as a potential impediment to applied POM (EPA, 2015), no framework exists to assess these limitations and associated timeframes in catchments and sub-catchment areas which are vulnerable to nutrient loss through the soil and groundwater pathway. While biogeochemical attenuation factors are also important (Jahangir et al., 2013; Van Meter and Basu, 2015), the current paper addresses the hydrological component of  $t_u$ , which may be differentiated into the following stages: initial breakthrough or trends (IBT/Trend), peak breakthrough (Peak), centre of mass (COM – indicating the bulk effect of POM), and complete exit of the solute from the profile (Exit) (Vero et al., 2014; Fenton et al., 2015). The IBT/Trend is particularly critical as it represents the first instance in which conservative nutrients transported by water may be observed at the base of the soil profile subsequent to implementation, and thereby indicates the general direction of water quality response. IBT/Trend reflects initial effects of POM, as might be ascertained from monitoring networks in the unsaturated zone or shallow groundwater.

Numerical models simulate water flow and solute transport in the unsaturated zone (Saxena and Jarvis, 1995; Pang et al., 2000; Pachepsky et al., 2004; Schoups et al., 2008; Konikow, 2011), and can therefore be used to assess  $t_u$  (Bourououi and Grizzetti, 2014). Such models require input data pertaining to soil hydraulic properties (Durner and Lipsius, 2006; Vero et al., 2014; Fenton et al., 2014), temporal meteorological data (Mertens et al., 2002; Gladnyeva and Saifadeen, 2013; Vero et al., 2014) and boundary conditions (Jacques et al., 2008; Vereecken et al., 2010). Vero et al. (2014) examined the consequences of soil and meteorological input data complexity on  $t_u$  estimates produced using the Hydrus 1D model (Šimůnek et al., 2013). Results indicated that low-complexity soil data (textural properties and bulk density ( $\rho_d$ )) were sufficient to indicate trend response at the base of a soil profile to POM. Further soil hydraulic parameter evaluation (Fenton et al., 2015) indicated that three popular laboratory textural analyses methods (pipette, laser diffraction and hydrometer) perform equally well as sources of low-complexity data. Previously, Fenton et al. (2010) estimated ranges of  $t_u$  for Ireland using default values from the literature to simulate the unsaturated and saturated zones. Since then, more extensive soil datasets have become available via the Irish Soil Information System (SIS) (Creamer et al., 2014), and the Irish Agricultural Catchment Programme (ACP) (Wall et al., 2011) is currently testing the efficacy of agricultural POM implemented under the Nitrates Directive. Therefore, the primary objective of the current paper was to develop a parsimonious, readily implementable framework for the estimation of unsaturated soil time lag ranges in agricultural catchments. This framework will provide a mechanism by which catchment scientists can distinguish between various stages of  $t_u$ , and hence increase the detail included in projections of time lag trajectories. To fulfil this objective, the current study utilised onsite meteorological (from 2012 onwards to match implementation of POM) and soil data (from the Irish SIS) for two agricultural catchments, as inputs to the Hydrus 1D numerical model (Šimůnek et al., 2013). The secondary objective was to examine long-term  $t_u$  under future moderate rainfall scenarios, in order to comment on the achievability of subsequent WFD deadlines (e.g. 2021, 2027) within these catchments.

## 2. Materials and methods

In the development of the modelling framework, the following tasks were performed for both catchments: identification of catchment boundaries using GIS, collation of SIS soil and meteorological datasets, validation of the soil series via a soil survey and auguring campaign, numerical modelling using Hydrus



**Fig. 1.** Total time lag ( $t_T$ ) from source to receptor, including the unsaturated soil pathway ( $t_u$ ) and the saturated groundwater pathway ( $t_s$ ). Arrows indicate the variable duration of  $t_u$  and  $t_s$ , depending on the depth of the soil profile and proximity to a receptor, respectively.

1D and pertinent hydraulic parameter datasets (ranging from low-to high-complexity soil data and site specificity), and analysis and interpretation of model outputs. Other unsaturated zone numerical models (e.g. VLEACH or STANMOD) may also be suitable for implementation within the current framework.

2.1. Description of the modelling framework and data sources

The assessment of  $t_u$  followed the structure summarised in Fig. 2. The modelling framework consists of a protocol for the selection of input data resolution (meteorological data) and complexity (soil data), identification of appropriate boundary conditions, modelling of vertical water/solute transport and division of the resulting breakthrough curves into markers indicating the various indicative stages of  $t_u$ . Simulations were conducted using Hydrus 1D, coupled with appropriate meteorological and soil physical data, and boundary conditions, and resulting breakthrough curves were subdivided in accordance with Vero et al. (2014). Many studies have demonstrated the capacity of the Hydrus 1D model to successfully reflect real-life water and solute transport scenarios (Tafteh and Sepaskhah, 2012; Vero et al., 2014; Zeng et al., 2014, amongst others). Model stability is maintained in accordance with Perrochet and Berod (1993). Regarding the meteorological input data (Fig. 2 Step 1), Met Éireann (the Irish meteorological service) operates 25 synoptic stations, in addition to over 400 rainfall recording stations (Met Éireann, 2015) from which data may be requested. The ACP also operate weather stations within their study catchments. As indicated by Vero et al. (2014), daily or hourly data should be selected based on the stage of  $t_u$  in question; for IBT/trend assessment, daily data are sufficient. Atmospheric boundary conditions are applied within the model, to correspond with these meteorological inputs (Jacques et al., 2008).

Regarding the soil input data (Fig. 2 Step 2 and Fig. 3), the SIS provides an online national soil map at 1:250,000 scale (Creamer et al., 2014) (<http://gis.teagasc.ie/soils/>). A practitioner may select a map area (the SIS divides Ireland into polygons covering areas of >250 ha) in this database, and will be presented with a number of soil associations likely to occur within this polygon area. A soil association is a mapping unit which aggregates soil types co-

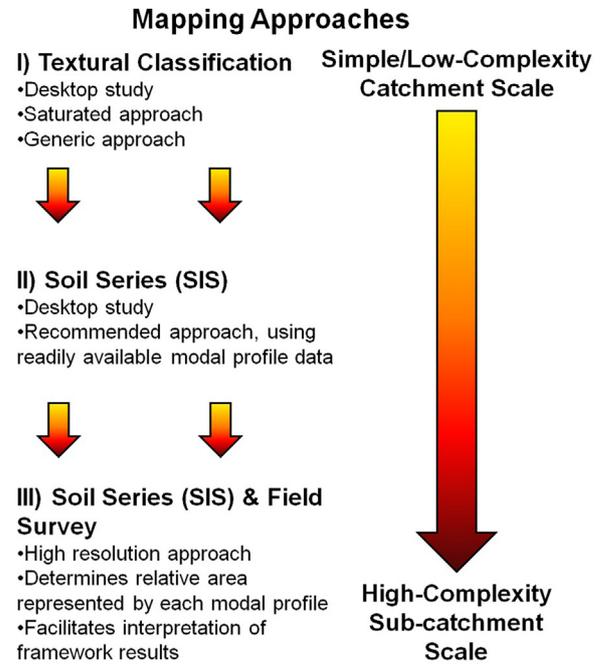


Fig. 3. Schematic of the catchment soil mapping approaches, from desktop to field survey. Increasing the complexity (by moving from top to bottom) aids in interpretation and contextualisation of results. These approaches correspond to Stage 2 in the time lag framework (Fig. 2). Maps of the grassland and arable catchments corresponding to each approach are available as Supplementary materials.

occurring within the same landscape pattern. Extracted from a soil association map Simo et al. (2016) defined a soil textural map of Ireland, based on the dominant textural class for the lead soil type of the soil association. Within the current study, clips of the catchment areas were obtained from the soil texture map (Simo et al., 2016) to derive a low-complexity soil textural class for each study catchment (Fig. 3, approach I). Hence, generic  $t_u$  estimates may be produced based on these data alone (Vero et al., 2014) (Fig. 2, Step 2–1st option). The database associates each soil series

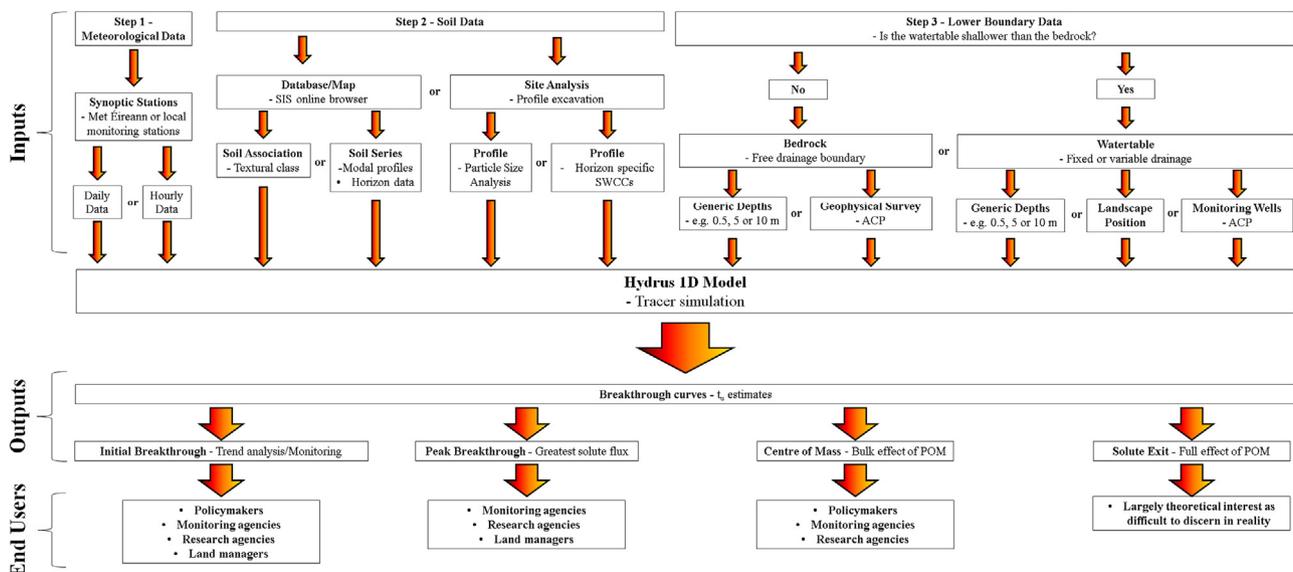


Fig. 2. Modelling framework for assessment of unsaturated zone time lag, including data-sources and outputs. Input data complexity within each step is increased by moving from left to right. Step 2 is further developed in Fig. 3.

with ‘modal soil profiles.’ These profiles describe the pedological characteristics that are considered representative of each series within a soil association. Modal profiles indicate horizon-specific characteristic data, including particle size distribution and  $\rho_d$  information, from which soil hydraulic parameters can be derived via pedotransfer functions (PTF) (e.g., ROSETTA) (Schaap et al., 2001). Moving from the generic soil association approach (indicating a single textural class for the entire profile depth) to the modal profile approach (indicating horizon-specific soil characteristics) (Fig. 2, Step 2–2nd option, Fig. 3, approach II) allows the influence of both vertical and horizontal heterogeneity of soil properties to be considered (Mohanty and Zhu, 2007). It is important to note that areas defined by polygons do not necessarily correspond to surface- or groundwater hydrological catchments. In order to derive soil data for specific catchment or sub-catchment areas, it is therefore necessary to transpose the outline of the area in question onto the SIS map using GIS (ArcGIS version 10.2) – as in the study catchments of the current study. This degree of site characterisation corresponds to the soil series mapping approach shown in Fig. 3. To increase the resolution of the soil type delineation, validation via ground-truthing was conducted. This involved identification of priority areas within each catchment (determined from landscape, proximity to receptors and soil association borders, etc.). Soil auguring and series identification was then performed in these areas in accordance with Creamer et al. (2014). This represents approach III depicted in Fig. 3, and is the highest level of site characterisation.

Lower boundary data (Fig. 2, Step 3) is determined according to either known or assumed watertable or bedrock depths. The hydraulic properties of unsaturated bedrock cannot be quantified using the PTF approach, and so only the soil component of the unsaturated zone may be accounted for. It is acknowledged that the full depth to groundwater may include unsaturated bedrock. Where the watertable is deeper than the soil/bedrock interface (i.e. no part of the soil profile is saturated), a free drainage lower boundary condition should be imposed. This condition assumes that water and solute outflow at the base of the profile is unimpeded. As soil pits are not typically excavated to bedrock due to safety concerns and practical challenges, the bottom-most surveyed soil horizon is assumed to account for the remainder of this region, unless geophysical data (if available) indicate otherwise. This assumption reflects the increased homogeneity observed in deep soil horizons (e.g. C horizons), which are less subject to the weathering, biological and management practices which influence shallower horizons, and more closely resemble the parent material (van Breemen and Buurman, 2002). For example, a soil pit is excavated to a depth of 1.8 m, and the bedrock interface is assumed at a depth of 2.5 m. The profile built within Hydrus should equate to 2.5 m in depth, with the properties of the bottom-most horizon extrapolated across this unaccounted-for region. Where no data are available, indicative bedrock depths may be identified from geophysical survey, or generic depths may be used. Within the context of Irish environmental policies, it is appropriate to use depths corresponding to the subsoil thickness vulnerability rating depths (3, 5 or 10 m) (DELG, 1999). Where the watertable is shallower than the bedrock, a fixed pressure head may be imposed at the base of the simulated soil profile. A variable pressure head may alternately be applied, although this requires additional data pertaining to watertable depth fluctuations at a similar resolution to the meteorological input data. There are three approaches by which watertable depths may be derived: a) assume generic depths e.g. 0.5, 5 or 10 m (Fenton et al., 2011a,b), b) estimate depths based on landscape position, or c) groundwater monitoring wells. While greatest temporal and spatial accuracy is obtained via monitoring wells, they may not be readily available in

many catchments, and so a landscape position approach may be preferred.

## 2.2. Implementation of the modelling framework in two study catchments

The two study catchments (Grassland and Arable) have been previously investigated as part of the ACP (Fealy et al., 2010; Mellander et al., 2012; ACP, 2013; Mellander et al., 2014, 2016). Site summaries are presented in Table 1, and SIS association maps (Creamer et al., 2014) (derived from the online resource) are available as Supplementary data.

### 2.2.1. Meteorological data

Two modelling exercises were conducted, using separate meteorological datasets. In the first exercise,  $t_u$  at the study sites was estimated in response to POM applied in 2012 (as in the Irish scenario) at each site, and so to comment on the 2015 reporting period, a 3-yr daily meteorological dataset (rainfall and evapotranspiration) was obtained from onsite weather recording stations. As this study was conducted in 2015, data for that year were incomplete and so omitted; data spanned from 1st January 2012 to 10th December 2014. In the second exercise, an example year, 1991, having median rainfall (865 mm), evapotranspiration (443 mm), and hence effective rainfall (ER) (422 mm) values, and exhibiting stereotypical annual rainfall patterns, was selected (due to its moderate meteorological conditions), and duplicated to provide a 13-yr dataset of moderate meteorological conditions, by which long-term simulations were conducted.

### 2.2.2. Soil data

The SIS online database was used to obtain soil association, subgroup and series data by overlaying the outline maps of the two study catchments on the SIS map using GIS (Supplementary data). Horizon-specific data (particle size distribution and  $\rho_d$ ) for each of the modal profiles were processed using ROSETTA (Schaap et al., 2001) to derive soil hydraulic properties via PTF. Hydraulic parameters are available as Supplementary data.

### 2.2.3. Boundary data

Interpretation of ground penetrating radar (GPR) was used to estimate bedrock depths along two hillslope transects in each catchment. Hence, maximum and minimum profile depths were determined (Mellander et al., 2014). For the grassland site, four soil depths were simulated (0.5, 3, 5 and 10 m), while three depths were simulated at the arable site (1, 3 and 5 m). At the grassland site, the shallowest depths correspond to near-stream or low-slope positions, in which the watertable was present within the soil profile, while the deeper scenarios reflect mid- or upslope positions. At the arable site, GPR revealed undulating rockhead along the hillslope. Consequently, slope position and distance from the receptor cannot be correlated to depth of the soil profile, and each scenario may occur at various slope positions.

**Table 1**

Summary of Grassland and Arable characteristics. Rainfall data was obtained from the nearest Met Eireann synoptic stations (Johnstown Castle and Cork, respectively).

	Grassland	Arable
Area (ha)	758	1117
30-Year (1989–2020) Average Rainfall (mm)	1228	1060
Dominant Soil Permeability	Moderate	High
Dominant Subsoil Permeability	High	High
Bedrock Permeability	High	Low
Unsat. Soil Depth (m)	0.5–10	1–5
Dominant pathway	Subsurface	Subsurface

### 3. Results and discussion

#### 3.1. Catchment mapping and soil parameters

Soil association maps of the grassland and arable catchments, respectively, are available as Supplementary data. The broad textural class of both catchments is loam, and both are dominated by the Ballylanders series, and in the arable catchment – the highly similar Clonroche series (Table 2). The arable site exhibits a greater total diversity of series (Mellander et al., 2014), however, many of these series represent a very minor proportion of the total catchment and so may not be indicative of the dominant hydrological behaviour of the area (e.g. the Duarrigle and Kilrush series represent only 1% and 3% of the arable catchment, respectively). The relative area represented by each soil series in each catchment is shown in Table 2. Extensive characterisation of these study catchments in conjunction with the ACP rendered this possible; however, for most Irish catchments, further soil survey (auguring campaigns) would be required. This information is helpful in determining which modal profiles exert the greatest control over  $t_u$  within a catchment. However, even without such information, the ranges of  $t_u$  are indicative of overall catchment behaviour. In the absence of this high level of characterisation, the modelling framework may be implemented in accordance with the second approach depicted in Fig. 3, and that these data only lend context to model results. In some circumstances, for example the grassland catchment, preliminary high resolution mapping coupled with targeted field survey, suggests greater complexity than that suggested by the SIS maps (Murphy et al., 2015). Apropos to the objective of integrating soil and meteorological data at the available scales, as inputs to a modelling framework for  $t_u$  assessment, the approach herein is effective in establishing

catchment-specific temporal ranges using only existing available data-sources. With respect to catchment scale and practicalities regarding national implementation, use of SIS (or similar 1:25,000 scale soil maps) presents as optimum, with the caveat that refining to the 1:10,000 scale may be desirable where a high degree of characterisation is required.

The dominant series in both catchments were brown earths, and exhibited similar characteristics, although in the arable catchment, minor series exhibited a greater diversity of hydraulic properties. This implies that certain areas within a catchment may exhibit unique hydrological behaviours, which are consistent with the critical source area concept (Pionke et al., 2000; Galzki et al., 2011; Shore et al., 2014; Thomas et al., 2016), and which may be identified via catchment characterisation approaches (e.g. those described by Packham et al., 2013). Implementation of the methodological framework described herein may thus be targeted towards specific areas within a catchment identified by these approaches as prone to exhibit prolonged  $t_u$ .

#### 3.2. Time lag estimates – 2012 implementation

Results of the modal profile simulations subsequent to 2012 POM implementation scenario are shown in Table 2. The IBT/trends at the base of the soil profile were observed between 1 and 27 months, and 3 to 17 months depending on profile depth, for the grassland and arable sites, respectively. The wider range in IBT/trend observed in the grassland catchment reflects the depth of the soil zone, which exceeded that of the arable catchment. Exit of the solute was only achieved at shallow depths in either catchment (7–25 and 15–24 months, for grassland and arable, respectively) within the three-year simulation period. For deeper profiles, total exit of the solute from the soil was not achieved.

**Table 2**  
Results of modal profile simulations, subsequent to 2012 implementation, according to various profile depths indicative of slope position. X indicates failure to achieve marker within simulation period and  $t_u$  (unsaturated zone time lag) is reported in months.

Site	Association	Series	Area %	Depth m	Breakthrough (months) (subsequent to 2012 implementation)				Moderate Rainfall Conditions			
					IBT/Trend	Peak	COM	Exit	Long-term $t_u$	Saturated $t_u$		
Grassland	Rosscarbery	Ballylanders	50	0.5	1	3	3	7	13	4		
				3	6	11	12	25	46	48		
				5	11	16	X	X	63	80		
		10	22	X	X	X	104	160				
		Rosscarbery	34	0.5	<1	1	3	7	12	8		
				3	6	11	11	24	42	46		
	5			10	15	19	3	61	77			
	Driminidy/Newport	16	0.5	1	2	3	7	12	6			
			3	7	12	14	25	51	38			
			5	12	22	X	X	76	64			
	10	27	X	X	X	132	127					
	Arable	Ballylanders & Clonroche	Ballylanders	75	1	4	7	8	15	22	15	
3					9	14	X	X	23	46		
5					13	27	X	X	46	77		
Clonroche					1	1	4	8	9	22	24	14
						3	10	16	X	X	48	42
						5	14	28	X	X	66	69
Duarrigle			1	1	3	7	9	24	25	12		
				3	11	22	X	X	55	37		
				5	16	33	X	X	78	61		
Kilpierce			7	1	4	8	9	24	26	13		
				3	11	22	X	X	55	39		
				5	16	X	X	X	78	65		
Kilrush			3	1	5	8	9	16	22	10		
				3	11	24	X	X	54	31		
				5	17	X	X	X	79	52		
Other			14	Series representing minor land area								

Differences in  $t_u$  within either catchment was greater for the latter markers (COM and Exit), but IBT/Trend ranged between 14 and 26 months, depending on soil depth. This suggests that identification of the area represented by each soil series within a catchment is of greater importance where the soil is deeper (in upslope positions), or when solute exit, rather than trends, is the primary interest. It must be considered that in both study catchments, the prevalent soil series represent a relatively small range of soil types (brown earths). In catchments exhibiting more diverse soilscapes, the differences between series are likely to be greater. Taking a lower-complexity textural class approach (Fig. 3–Approach I) indicated IBT/trends in 0–24 months and 1–13 months, for the grassland and arable catchments, respectively, depending on profile depth. While these ranges roughly agree with those determined via the modal profile approach (Fig. 3. – Approach II and III) and may be useful for generally approximating catchment behaviour, they are implicitly less informative than the modal profile approach. Selection of the appropriate approach should therefore, be informed by the degree of characterisation required and data availability.

It is important to note that rapid groundwater response to agricultural practices may also be observed due to preferential flow, particularly on soils exhibiting high macroporosity (Keim et al., 2012; Kramers et al., 2012). For catchments (or sub-catchment regions) in which such soils predominate,  $t_u$  is unlikely to prevent attainment of WFD deadlines, hence, assessment using the present framework is unnecessary and not recommended. A user may, however, wish to model such soils using appropriate model settings (dual-porosity/permeability). As the focus of the current paper is on the prolonged aspects of  $t_u$ , approaches to preferential flow modelling are not discussed in detail herein. However, some guidance as to the identification of those latter scenarios is beneficial. Vervoort et al. (1999) noted that quantification of the relationship between the structure of a soil and its propensity for preferential flow is challenging – visual assessment or cracks and biopores, dye tracer tests (Kramers et al., 2012), tomography (Bacher et al., 2015) and inverse modelling (Arora et al., 2011) have all been successfully used; however, these require access to the soils in question, which may not be feasible where existing quantitative map data (such as from the SIS) are relied upon. Morphological characteristics included in map or soil survey data may provide useful qualitative indicators. Profile or horizon characteristics such as aggregation (Quisenberry et al., 1993), structure and landscape position (Vervoort et al., 1999), can suggest tendencies towards preferential flow. At a catchment scale, soil-based hydrologic classification systems, such as the UK's HOST (Boorman et al., 1995) may also be employed. Although it is beyond the scope of the present research to integrate preferential flow to the framework, this aspect recommends itself as a prime area for further research and development.

The results (Table 2) demonstrate that a single  $t_u$  figure cannot quantify the range of  $t_u$  durations exhibited across a catchment, with varying soil series and water-table depths. Hence, remediation of water quality from applied mitigation strategies may not be directly observable where specific areas within a catchment are transmitting solutes over a prolonged period, despite flushing in shallower or more rapidly drained regions. This is consistent with Mellander et al. (2015), who reported temporal and spatial variation in groundwater response in these catchments. Regarding the initial 2015 WFD deadline, these results indicate that assuming implementation of POM at a latest date of 2012, achieving full effects (indicated by Exit) within this timeframe is unrealistic, even when  $t_s$  is omitted. While this result is consistent with earlier research (Fenton et al., 2011a,b), the current framework offers the advantage of differentiating between the various stages of  $t_u$ . In particular, assessment of trend response better informs policy decisions relating to POM efficacy in the immediate future.

### 3.3. Time lag estimates – long-term simulations

The results of long-term simulations, using a moderate meteorological dataset, are shown in Table 2 (representing the Exit stage only). For the grassland site, long-term  $t_u$  (indicating complete effect of POM) exceeded 100 months/8 yr in deep profiles. Even under moderate profile depths (3–5 m) (likely at mid-slope positions), Exit ranged from 42 to 63 months (3.5–5 yr). In the arable catchment, maximum long-term  $t_u$  was less than that observed in the grassland catchment, and ranged between 46 and 79 months (3 to c. 6.5 yr), due to the relative shallowness of the soil profiles. This demonstrates that depth of the soil profile is a critical control on  $t_u$  ranges, and geophysical data should be preferred over generic values, particularly where groundwater quality is of poor or declining status.

These results indicate that even under moderate meteorological conditions, for many soil depths, it may take in excess of a 6-yr reporting period for the full effects of POM to be observed at groundwater, with a subsequent delay imposed by  $t_s$  prior to marked changes at a surface water receptor or abstraction point. While this is a relatively simplistic approach to meteorological scenario testing, the results are indicative of the timeframes in which  $t_u$  operates, and in which policy and subsequent evaluation of POM efficacy should be designed. Specific meteorological factors that should be considered in future scenario testing include the intensity and timing of precipitation, as these directly influence  $t_u$  and subsequently,  $t_s$ . Wendroth et al. (2011) correlated depth of leaching of bromide (which is frequently used as a proxy for conservative solutes such as nitrate) at a field scale with the proximity of precipitation events to solute application. The degree of influence exerted by meteorological conditions, land use or soil parameters on leaching rates varies by depth. Yang et al. (2013) revealed that  $t_u$  in the upper soil horizons (< 10 cm) is dictated primarily by rainfall intensity, while the timing of solute application is the dominant factor in the subsequent horizon (10–20 cm), and soil physical parameters becoming the increasingly important drivers deeper within the profile. These results should guide model users as to the importance of meteorological versus soil input data, depending upon the depth of the soil in question.

Assuming the scenario whereby POM were implemented by the end of 2012, trends should be observed within the first reporting period in both catchments. However, considering COM as an indicator of the bulk effect of POM (Vero et al., 2014), it is towards the latter stages of the first reporting period that substantial changes in groundwater quality are expected. Temporal trend analysis may therefore, be a more useful and informative indicator of POM efficacy. As indicated by Vero et al. (2014), the saturated approach of Fenton et al. (2011a,b) is useful as an indicator  $t_u$ ; however, it cannot distinguish between the various stages (IBT/Trend, Peak, COM, Exit) and so provides a general description only. The results of that paper (under ER conditions of c. 800 mm yr<sup>-1</sup> and  $n_e$  of 40%) are in good agreement with the results presented here. Exit of the solute from the soil (potentially challenging to discern *via* monitoring due to low concentrations) approached or exceeded 72 months/6 yr for many soil series and profile depths. This indicates that although the reporting periods suffice for trend assessment, they are too short to observe the full effects of POM. Although these temporal results may be considered unsurprising in light of the existing literature, the utility of this modelling framework is in incorporating both an input data decision support system and a structure for breakthrough curve analysis into an integrated system. Using this system, a model user can maximise the utility of their available data within the context of the stage of solute transport with which they are concerned.

While it is not within the scope of this paper to indicate  $t_s$  and hence,  $t_T$ , the similarity between the results herein and those of

Fenton et al. (2011a,b) suggest that their assertion of remediation timeframes between 2019 and 2033, depending on unsaturated zone depth and proximity to receptor, are realistic. While estimates produced under the saturated assumption provide a useful first estimate of  $t_u$ , they produce only a single figure, and cannot differentiate between the various stages of solute breakthrough, unlike the framework presented herein, which provides a more comprehensive description of  $t_u$ . Regarding  $t_s$ , transition zone delineation consistency and thickness, bedrock type, thickness and degree of fracturing controls the duration of this component of  $t_T$ . Within the Irish context, preliminary estimates of minimum  $t_s$  (contingent upon  $k_s$  and specific yield) over a distance of 500 m ranged between 0.06 and 6.85 years (Fenton et al., 2011a,b). However, it is important to note, that these are minimum values, and will be exceeded in many catchments. Further research into the  $t_s$  component and methodologies for its assessment are forthcoming.

### 3.4. Implications for policy and monitoring

That  $t_u$  should preclude attainment of WFD deadlines is not new; Fenton et al. (2011a,b) indicated this in advance of the first reporting period. The utility of this framework lies in its ability to disentangle the various stages of  $t_u$ , and, based upon the areas represented by a specific soil series, to anticipate the overall trends likely to be observed within a catchment over the forthcoming reporting periods. Hence, catchment scientists can provide policymakers with early indicators of likely trends and responses to mitigation measures through the judicious use of existing data. This removes time lag from the category of 'generic excuse' (Scheure and Naus, 2010), by adding both spatial and temporal specificity.

Thomas et al. (2016) used a digital elevation model (DEM) to define and map CSAs for nutrient loss via overland flow. Those same maps may be also used to inversely identify those areas which are prone to persistent, low concentration nutrient transport due to vertical transport through the unsaturated zone. This information is valuable in determining which areas within a catchment should be targeted for the implementation of mitigation or remediation techniques, which has implications for their efficacy and cost-effectiveness. It should further be noted that in line with the functional land management concept (Schulte et al., 2014; Coyle et al., 2016), a soil fulfils multiple functions, one of which is water purification. Understanding  $t_u$  durations alone does not account for subsurface transformational processes e.g. denitrification (Seitzinger et al., 2006; Green et al., 2009; Jahangir et al., 2013). Saturated hydraulic conductivity of soils/subsoils/bedrock have been correlated with nitrate concentration and  $N_2/Ar$  ratios at field scales (Fenton et al., 2009; Fenton et al., 2012) and indeed at landscape scales (Jahangir et al., 2012). Therefore, an understanding of soil type and soil physical parameters can guide not only time lag estimates at catchment scale but also provide appropriately scaled information required for translation into environmental policy, in accordance with the DPSIR (drivers, pressures, states, impacts and responses) approach (Bouma and Droogers, 2007).

Mapping endeavours (e.g. Creamer, 2014) demonstrated that a variety of distinct soil series may be observed within a single catchment, and so a specific slope position may exhibit one of several different  $t_u$  durations, dependant on which soil series is present. For example, in the arable catchment, the range of soil series and the undulating depth to bedrock (3 m–5 m) across the entire slope, indicates up to ten different  $t_u$  durations. Therefore, a range of potential  $t_u$  (for each marker: IBT/Trend/Peak/COM/Exit) provides a more realistic tool to assess timescales within a catchment. Analysis of trends in water quality response to POM is inherently limited by spatio-temporal factors; namely, the position

of monitoring points within the landscape and the stage of time lag which may be assessed at those locations. For example, surface-water quality is influenced by the sum of all hydrological processes in the catchment, including surface run-off, lateral subsurface flow, baseflow etc. Consequently, it is challenging to disentangle the trend effects of recent POM from the legacy of past practices, or those effects arising from measures implemented in different parts of the catchment. Likewise, monitoring of groundwater will indicate chemical concentrations reflective of both past and present measures, and at low-slope positions, will be subject to the import of water/contaminants from higher along the transect. As such, monitoring of waterbodies represents  $t_T$ , or  $t_u$  plus some portion of  $t_s$ , and cannot discriminate between the components of time lag (saturated versus unsaturated), or its various stages (IBT/Peak/COM/Exit). Unsaturated zone modelling according to the present framework enables trends at the base of the soil profile to be determined independently of confounding influences. This provides an earlier indication of trend responses than is possible via monitoring of ground- or surface-waters. Considering both ranges and stages of  $t_u$  may, with further research, facilitate examination of the potential for nitrate attenuation and dilution in the subsurface. For example, prolonged  $t_u$  may suggest greater attenuation than is likely in more rapid profiles. Conversely, where a catchment is dominated by very shallow soil profiles, or by overland flow pathways, long term  $t_u$  values are less informative, and attenuation potential may be lower. Such theories present as important areas for further research.

## 4. Conclusions

The results of this study indicate a range of potential unsaturated time lags within each catchment, depending on the stage of transport in question, soil series, and depth of the soil profile (or slope position). In the study catchments, trends were first observed at the base of the soil profile up to 27 months subsequent to the 2012 implementation of POM scenario, while the full effects may exceed 11 and 6 yr within the grassland and arable catchments, respectively. These lags should be considered as long, in light of the 6-yr reporting period cycles defined by the WFD. Under a scenario whereby POM implementation occurred in 2012, the 2015 deadline therefore allowed an insufficient period of time to bear full effect on water quality. However, based on the long-term simulations, response at groundwater should be observed at these sites within the subsequent reporting period (2021). This basic modelling framework can, in future, be built upon in order to account for additional delays due to nutrient attenuation and may be integrated with other tools for the characterisation of catchment hydrology.

## Acknowledgements

This research was funded by the Teagasc Walsh Fellowship Scheme. The authors gratefully acknowledge the assistance of Brian Reidy, Simon Leach, Edward Burgess, Dermot Leahy and the landowners.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.agee.2016.12.001>.

## References

- Arora, B., Mohanty, B.P., McGuire, J.T., 2011. Inverse estimation of parameters for multidomain flow models in soil columns with different macropore densities. *Water Resour. Res.* 47 (4) doi:<http://dx.doi.org/10.1029/2010wr009451>.

- Bacher, M., Schwen, A., Koestel, J., 2015. Three-dimensional printing of macropore networks of an undisturbed soil sample. *Vadose Zone J.* 14 (2) doi:<http://dx.doi.org/10.2136/vzj2014.08.0111>.
- Boorman, D.B., Hollis, J.M., Lilly, A., 1995. Report No. 126. Hydrology of Soil Types: a Hydrologically Based Classification of the Soils of the United Kingdom. Institute of Hydrology, Oxfordshire, United Kingdom.
- Bouma, J., Droogers, P., 2007. Translating soil science into environmental policy: a case study on implementing the EU soil protection strategy in The Netherlands. *Environ. Sci. Policy* 10 (5), 454–463.
- Bourauoi, F., Grizzetti, B., 2014. Modelling mitigation options to reduce diffuse nitrogen water pollution from agriculture. *Sci. Total Environ.* 468–469, 1267–1277.
- Cook, P.G., Jolly, I.D., Walker, G.R., Robinson, N.I., 2003. From drainage to recharge to discharge: some time lags in subsurface hydrology. In: Alsharhan, A.S., Wood, W. W. (Eds.), *Water Resources Perspectives: Evaluation, Management and Policy*. Elsevier Science, Amsterdam, pp. 319–326.
- Coyle, C., Creamer, R.C., Schult, R.P.O., O'sullivan, L., Jordan, P., 2016. A functional land management conceptual framework under soil drainage and land use scenarios. *Environ. Sci. Policy* 56, 39–48.
- Creamer, R., 2014. Irish SIS Final Technical Report 10: Soil Profile Handbook. Associated Datasets and Digital Information Objects Connected to This Resource Are Available At: Secure Archive for Environmental Research Data (SAFER) Managed by Environmental Protection Agency Ireland. <http://erc.epa.ie/safer/resource?id=a1b872a2-3b8c-11e4-b233-005056ae0019> (Last Accessed: 19 March 2015).
- DELG, 1999. Groundwater Protection Schemes. Department of the Environment and Local Government, Environmental Protection Agency and Geological Survey of Ireland, Ireland.
- Dept. of Agriculture, Food and the Marine, 2010. Food Harvest 2020. A Vision for Irish Agri-Food and Fisheries. <https://www.agriculture.gov.ie/media/migration/agri-foodindustry/foodharvest2020/2020FoodHarvestEng240810.pdf> (Last downloaded 1/11/15).
- Dept. of Agriculture, Food and the Marine, 2015. Food Wise 2025. A 10-year Vision for the Irish Agri-food Industry. <http://www.agriculture.gov.ie/media/migration/agri-foodindustry/foodwise2025/report/FoodWise2025.pdf> (Last downloaded 15/10/15).
- Durner, W., Lipsius, K., 2006. Chapter 75: determining soil hydraulic properties. In: Anderson, M.G. (Ed.), *Encyclopaedia of Hydrological Sciences*. John Wiley and Sons Ltd.
- Dworak, T., Gonzalez, C., Laaser, C., Interwies, E., 2005. The need for new monitoring tools to implement the WFD. *Environ. Sci. Policy* 8 (3), 301–306.
- European Commission, 1991. Council Directive (1991/676/EC). EC Directive of the European Parliament and of the Council of 12 December 1991 on the Protection of Waters Against Pollution Caused by Nitrates from Agricultural Sources. European Commission, Brussels, pp. 1–8.
- Fealy, R., Buckley, C., Mechan, S., Melland, A., Mellander, P.-E., Shortle, G., Wall, D., Jordan, P., 2010. The Irish Agricultural Catchments Programme: catchment selection using spatial multi-criteria decision analysis. *Soil Use Manage.* 26, 225–236.
- Fenton, O., Richards, K., Kirwan, L., Khalil, M.I., Healy, M.G., 2009. Factors affecting nitrate distribution in shallow groundwater under a beef farm in South Eastern Ireland. *J. Environ. Manage.* 90 (10), 3135–3146.
- Fenton, O., Healy, M.G., Henry, T., Khalil, M.I., Grant, J., Baily, A., Richards, K., 2011a. Exploring the relationship between groundwater geochemical factors and denitrification potentials on a dairy farm in southeast Ireland. *Ecol. Eng.* 37 (9), 1304–1313.
- Fenton, O., Schulte, R.P.O., Jordan, P., Lalor, S.T.J., Richards, K.G., 2011b. Time lag: a methodology for estimation of vertical and horizontal travel and flushing timescales to nitrate threshold concentrations in Irish aquifers. *Environ. Sci. Policy* 14 (4), 419–431.
- Fenton, O., Vero, S.E., Ibrahim, T.G., Murphy, P.N.C., Sherriff, S., Ó'hUallachain, D., 2015. Consequences of using different soil texture determination methodologies for soil physical quality and unsaturated zone time lag estimates. *J. Contam. Hydrol.* 182, 16–24.
- Galzki, J.C., Birr, A.S., Mulla, D.J., 2011. Identifying critical agricultural areas with three-meter LiDAR elevation data for precision conservation. *J. Soil Water Conserv.* 66 (6), 423–430.
- Gladnyeva, R., Saifadeen, A., 2013. Effects of hysteresis and temporal variability in meteorological input data in modelling of solute transport in unsaturated soil using Hydrus-1D. *J. Water Manage. Res.* 68, 285–293.
- Green, M.B., Wollheim, W.M., Basu, N.B., Gettel, G., Rao, P.S., Morse, N., Stewart, R., 2009. Effective denitrification scales predictably with water residence time across diverse systems. *Nature Precedings*, <http://hdl.handle.net/10101/npre.2009.3520.1>.
- Huebsch, M., Horan, B., Blum, P., Richards, K.G., Grant, J., Fenton, O., 2013. Impact of agronomic practices of an intensive dairy farm on nitrogen concentrations in a karst aquifer in Ireland. *Agric. Ecosyst. Environ.* 179 (1), 187–199.
- Jacques, D., Šimunek, J., Mallants, D., van Genuchten, M. Th., 2008. Modelling coupled water flow, solute transport, and geochemical reactions affecting heavy metal migration in a podzol soil. *Geoderma* 145 (3–4), 449–461.
- Jahangir, M.M.R., Johnston, P., Khalil, M.I., Richards, K.G., 2012. Linking hydrogeochemistry to nitrate abundance in groundwater in agricultural settings in Ireland. *J. Hydrol.* 448–449, 212–222.
- Jahangir, M.M.R., Johnston, P., Barrett, M., Khalil, M.I., Groffman, P.M., Boeckx, P., Fenton, O., Murphy, J., Richards, K.G., 2013. Denitrification and indirect N<sub>2</sub>O emissions in groundwater: hydrologic and biogeochemical influences. *J. Contam. Hydrol.* 152, 70–81.
- Keim, D.M., West, L.J., Odling, N.E., 2012. Convergent flow in unsaturated fractured chalk. *Vadose Zone J.* 11 (4) doi:<http://dx.doi.org/10.2136/vzj2011.0146>.
- Konikow, L.F., 2011. The secret to successful solute-transport modelling. *Ground Water* 49 (2), 144–159.
- Kramers, G., Holden, N.M., Brennan, F., Green, S., Richards, K.G., 2012. Water content and soil type effects on accelerated leaching after slurry application. *Vadose Zone J.* 51 (1) doi:<http://dx.doi.org/10.2136/vzj2011.0059>.
- Kronvang, B., Andersen, H.E., Børgesen, C., Dalgaard, T., Larsen, S.E., Bøgestrand, J., Blicher-Mathiasen, G., 2008. Effects of policy measures implemented in Denmark on nitrogen pollution of the aquatic environment. *Environ. Sci. Policy* 11 (2), 144–152.
- Mellander, P.-E., Melland, A.R., Jordan, P., Wall, D.P., Murphy, P.N.C., Shortle, G., 2012. Quantifying nutrient transfer pathways in agricultural catchments using high temporal resolution data. *Environ. Sci. Policy* 24, 44–57.
- Mellander, P.-E., Melland, A.R., Murphy, P.N.C., Wall, D.P., Shortle, G., Jordan, P., 2014. Coupling of surface water and groundwater nitrate-N dynamics in two permeable agricultural catchments. *J. Agric. Sci.* 152, 107–124.
- Mellander, P.-E., Jordan, P., Shore, M., Melland, A.R., Shortle, G., 2015. Flow paths and phosphorus transfer pathways in two agricultural streams with contrasting flow controls. *Hydrol. Processes* 29 (16), 3504–3518.
- Mellander, P.-E., Jordan, P., Shore, M., McDonald, M.T., Wall, D.P., Shortle, G., Daly, K., 2016. Identifying contrasting influences and surface water signals for specific groundwater phosphorus vulnerability. *Sci. Total Environ.* 541, 292–302.
- Mertens, J., Raes, D., Feyen, J., 2002. Incorporating rainfall intensity into daily rainfall records for simulating runoff and infiltration in soil profiles. *Hydrol. Processes* 16 (3), 731–739.
- Met Éireann, 2015. Current Synoptic Stations. <http://www.met.ie/about/weatherobservingstations/synopmap.asp> (Last accessed 22 October 2015).
- Mohanty, B.P., Zhu, J.T., 2007. Effective hydraulic parameters in horizontally and vertically heterogeneous soils for steady-state land-atmosphere interaction. *J. Hydrometeorol.* 8 (4), 715–729.
- Murphy, P.N.C., Mellander, P.-E., Melland, A.R., Buckley, C., Shore, M., Shortle, G., Wall, D.P., Treacy, M., Shine, O., Mechan, S., Jordan, P., 2015. Variable response to phosphorus mitigation measures across the nutrient transfer continuum in a dairy grassland catchment Agriculture. *Ecosyst. Environ.* 207, 192–202.
- Official Journal of the European Communities, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 Establishing a Framework for Community Action in the Field of Water Policy. , pp. 72.
- Pachepsky, Y.A., Smettem, K.R.J., Vanderborght, J., Herbst, M., Vereecken, H., Wösten, J.H.M., 2004. Reality and fiction of models and data in soil hydrology. In: Feddes, R.A., de Rooij, G.H., van Dam, J.C. (Eds.), *Unsaturated Zone Modelling. Progress, Challenges and Applications*, Vol. 6. , pp. 231–260.
- Packham, I., Mockler, E., Bruen, M., 2013. Development of a Catchment Management Tool to assess environmental risk from nutrient loadings using open source GIS. In: Hřebíček, J., Schimak, G., Kubásek, M., Rizzoli, A.E. (Eds.), *Environmental Software Systems: Fostering Information Sharing*. Springer, Berlin Heidelberg, pp. 262–270.
- Pang, L., Close, M.E., Watt, J.P.C., Vincent, K.W., 2000. Simulation of picloram, atrazine, and simazine leaching through two New Zealand soils and into groundwater using HYDRUS-2D. *J. Contam. Hydrol.* 44 (1), 19–46.
- Perrochet, P., Berod, D., 1993. Stability of the standard Crank-Nicolson-Galerkin scheme applied to the diffusion-convection equation: some new insights. *Water Resour. Res.* 29 (9), 3291–3297.
- Pionke, H.B., Gburek, W.J., Sharpley, A.N., 2000. Critical source area controls on water quality in an agricultural watershed located in the Chesapeake Basin. *Ecol. Eng.* 14 (4), 325–335.
- Quisenberry, V.L., Smith, B.R., Phillips, R.E., Scott, H.D., Nortcliff, S., 1993. A soil classification system for describing water and chemical transport. *Soil Sci.* 156, 306–315.
- Richards, K.G., Coxon, C.E., Ryan, M., 2005. Unsaturated zone travel time to groundwater on a vulnerable site. *Irish Geogr.* 38 (1), 57–71.
- Saxena, R.K., Jarvis, N.J., 1995. Measurements and modelling of tracer transport in a sandy soil. In: Černý, J., Novák, M., Pačes, T., Wieder, R.K. (Eds.), *Biogeochemical Monitoring in Small Catchments*, pp. 409–425 Reprinted from *Water, Soil and Air Pollution*, 79 (1–4).
- Schaap, M.G., Leij, F.J., van Genuchten, M.Th., 2001. ROSETTA: A computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions. *J. Hydrol.* 251, 163–176.
- Scheure, S., Naus, J., 2010. In: Hontelez, J. (Ed.), 10 Years of the Water Framework Directive: A Toothless Tiger? A Snapshot Assessment of EU Environmental Ambitions. European Environmental Bureau, Brussels, Belgium.
- Schoups, G., van de Giesen, N.C., Savenije, H.H.G., 2008. Model complexity control for hydrologic prediction. *Water Resour. Res.* 44, W00B03. doi:<http://dx.doi.org/10.1029/2008WR006836>.
- Schulte, R.P.O., Richards, K., Daly, K., Kurz, I., McDonald, E.J., Holden, N.M., 2006. Agriculture, meteorology and water quality in Ireland: a regional evaluation of pressures and pathways of nutrient loss to water. *Biol. Environ.: Proc. R. Irish Acad.* 106B (2), 117–133.
- Schulte, R.P.O., Creamer, R.E., Donnellan, T., Farrelly, N., Fealy, R., O'Donoghue, C., Ó'hUallachain, D., 2014. Functional land management: a framework for managing soil-based ecosystem services for the sustainable intensification of agriculture. *Environ. Sci. Policy* 38, 45–58.
- Seitzinger, S., Harrison, J.A., Böhlke, J.K., Bouwman, A.F., Lowrance, R., Peterson, B., Tobias, C., Van Drecht, G., 2006. Denitrification across landscapes and waterscapes: a synthesis. *Ecol. Appl.* 16 (6), 2064–2090.

- Shore, M., Jordan, P., Mellander, P.-E., Kelly-Quinn, M., Wall, D.P., Murphy, P.N.C., Melland, A.R., 2014. Evaluating the critical source area concept of phosphorus loss from soils to water-bodies in agricultural catchments. *Sci. Total Environ.* 490, 405–415.
- Simo, I., Creamer, R.E., O'sullivan, L., Reidy, B., Schulte, R.P.O., Fealy, R.M., 2016. Irish soil information system: soil property maps. *SIS Final Technical Report 18, (2007-S-CD-1-S1) EPA STRIVE Programme 2007–2013, . . . (Available for download from) <http://erc.epa.ie/safer/reports>*.
- Šimunek, J., Šejna, M., Saito, H., Sakai, M., van Genuchten, M. Th., 2013. The HYDRUS 1D software package for simulating the movement of water, heat and multiple solutes in variably saturated media. Version 4.16 HYDRUS Software Series 3. Department of Environmental Science, University of California Riverside, Riverside, California, USA, pp. 340.
- Sousa, M.R., Jones, J.P., Frind, E.O., Rudolph, D.L., 2013. A simple method to assess unsaturated zone time lag in the travel time from ground surface to receptor. *J. Contam. Hydrol.* 144 (1), 138–151.
- Tafteh, A., Sepaskhah, A.R., 2012. Application of hydrus 1D model for simulating water and nitrate leaching from continuous and alternate furrow irrigated rapeseed and maize fields. *Agric. Water Manage.* 113, 19–29.
- Thomas, I.A., Jordan, P., Mellander, P.-E., Fenton, O., Shine, O., O'hUallachain, D., Creamer, R.E., McDonald, N.T., Dunlop, P., Murphy, P.N.C., 2016. Improving the identification of hydrologically sensitive areas using LiDAR DEMs for the delineation and mitigation of critical source areas of diffuse pollution. *Sci. Total Environ.* 556, 276–290.
- Van Meter, K.J., Basu, N.B., 2015. Catchment legacies and time lag: a parsimonious watershed model to predict the effects of legacy time lag on nitrogen export. *PLoS One* 10 (5), e0125971. doi:<http://dx.doi.org/10.1371/journal.pone.0125971>.
- Vereecken, H., Weynants, M., Javaux, M., Pachepsky, Y., Schaap, M.G., van Genuchten, M. Th., 2010. Using pedotransfer functions to estimate the van Genuchten-Mualem soil hydraulic properties: a review. *Vadose Zone J.* 9 (4), 795–820.
- Vero, S.E., Ibrahim, T.G., Creamer, R.E., Grant, J., Healy, M.G., Henry, T., Kramers, G., Richards, K.G., Fenton, O., 2014. Consequences of varied soil hydraulic and meteorological complexity on unsaturated zone time lag estimates. *J. Contam. Hydrol.* 170, 53–67.
- Vervoort, R.W., Radcliffe, D.E., West, L.T., 1999. Soil structure development and preferential solute flow. *Water Resour. Res.* 35 (4), 913–928.
- Wahlin, K., Grimvall, A., 2008. Uncertainty in water quality data and its implications for trend detection: lessons from Swedish environmental data. *Enviro. Sci. Policy* 11 (2), 115–124.
- Wendroth, O., Vasquez, V., Matocha, C.J., 2011. Field experimental approach to bromide leaching as affected by scale-specific rainfall characteristics. *Water Resour. Res.* 47 (6), W00L03. doi:<http://dx.doi.org/10.1029/2011WR010650>.
- Yang, W., Wendroth, O., Walton, R.J., 2013. Field-scale bromide leaching as affected by land-use and rain characteristics. *Soil Sci. Soc. Am. J.* 77 (4), 1157–1167.
- Zeng, W.Z., Xu, C., Wu, J.W., Huang, J.S., 2014. Soil salt leaching under different irrigation regimes: hydrus 1D modelling and analysis. *J. Arid Land* 6 (1), 44–58.
- van Breemen, N., Buurman, P., 2002. *Soil Formation*, second ed. Netherlands, Springer.