Sources, sinks and stores of Nitrogen and Phosphorus associated with public water supply and the vadose zone

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Acknowledgements

Abstract

Reactive Nitrogen (N) and Phosphorus (P) in the environment remain a considerable problem for both ecosystems and drinking water quality. Although public water supply processes and the vadose zone are well known components of the anthropogenically perturbed hydrological cycle, the impact of these components on N and P cycling is poorly understood. The aim of this thesis was to improve the understanding of sources, sinks and stores of N and P associated with public water supply and the vadose zone, to support the development of integrated nutrient management approaches. Mains water leakage is shown to be an important source of P, which will increase in importance in the future. Mains water leakage of P has significant temporal variability associated with winter burst events, summer shrink-swell leakage and active leakage control. Mains water leakage has also been shown to be an important source of N in urban areas, contributing up to 20% of all N loads. Abstraction for public water supply has been shown to be a considerable temporary sink of N, equivalent to up to 39% of denitrification. The unsaturated zone has also been shown to be an important store of nitrate, with the quantity of nitrate stored in the vadose zone being equivalent to 200% of estimates of inorganic N stored in soils globally. The results of this thesis have important implications for the development of integrated nutrient management approaches. The sources, sinks and stores associated with public water supply and the vadose zone quantified in this thesis should be considered in future macronutrient budgets and models. Continued use of existing models which do not consider these additional N and P sources, sinks and stores should be tempered with the knowledge gained from this research.

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1   Introduction

1.1   Background

The macronutrients nitrogen (N) and phosphorus (P) are essential for life, stimulating metabolism in both plants and animals (Schlesinger, 2005). The important roles that these macronutrients play in metabolism has resulted in the intensive use of inorganic N and P for both fertilizers to increase crop yields and as feed additives in livestock production. Agricultural intensification associated with synthetic fertilizer applications has supported the growth of the world's population since the mid-20th century (Galloway and Cowling, 2002). As a result of this, humans have considerably altered global N and P cycles. Historic and recent data for industrial N fixation and P mining and processing show that reactive N and P fluxes in the environment are over double pre-industrial levels (Filippelli, 2008; Vitousek et al., 1997). The majority of reactive P is derived from mining and processing of non-renewable phosphate rocks (Sattari et al., 2012), and studies suggest that increasing demand for P and reducing resources will result in global production deficits in the next 100 years (Cooper et al., 2011). Increased levels of reactive N and P may also result in environmental and human health impacts. N and P have both been shown to be limiting nutrients in freshwater and marine ecosystems (Elser et al., 2007). Eutrophication associated with excess N and P inputs has resulted in increases in algal blooms worldwide (Glibert and Burford, 2017), potentially causing fish kills and impacts on animals (Main et al., 1977) and human health (Funari and Testai, 2008). The costs of eutrophication have been estimated at billions of dollars per year (Dodds et al., 2009; Pretty et al., 2000). Reactive N in the form of nitrate (NO_3) has also been shown to be a potential environmental endocrine disruptor, impacting the hormone balance of aquatic fauna (Poulsen et al., 2018). Nitrate is also subject to a drinking water standard of 50 mg NO_3/L (World Health Organisation, 2011). Whilst this standard is associated with the potential risks of methaemoglobinemia ("blue baby syndrome", Fewtrell (2004)),

epidemiological studies have also shown relationships between ingestion of nitrate through drinking water and colorectal cancer (Schullehner et al., 2018), thyroid disease and neural tube effects (Ward et al., 2018). Within the UK alone the cost of public water supply treatment to meet the standard has been estimated to be millions of pounds per year (House of Commons Environmental Audit Committee, 2018; UK Water Industry Research Ltd, 2004).

National and international policies have been implemented to reduce N and P water pollution. In Europe, the Nitrates Directive (European Union, 1991a), Urban Wastewater Treatment Directive (European Union, 1991b) and subsequently the Water Framework Directive (European Union, 2000) have all been developed to improve water quality. Similar legislation is in place in the USA (United States Environmental Protection Agency, 1972) and Canada (Government of Canada, 1970), with recent revisions in legislation in newly industrialised countries such as China (He et al., 2013). To meet regulatory targets within this body of legislation, budgets and models are often developed which quantify components of N and P cycles as fluxes of mass per unit time (e.g. kg N/day). These are associated with nutrient sources (e.g. agricultural N losses, wastewater discharges), sinks (e.g. denitrification) and transfers between environmental compartments of interest (N flux from soils to groundwater, from river to sea). Beyond the soil zone there is often limited quantitative information on the size of N and P stores in different environmental compartments (Chen et al., 2018), and as a result approaches are often time invariant (Leip et al., 2011). In this thesis an explicit distinction is made between a nutrient *sink* as the amount of nutrient that enters a store per unit time (e.g. kg N/day), and a *store* (often also referred to as a stock, reservoir or pool), which is the actual mass of nutrient (e.g. kg N) within that environmental compartment. These steady state approaches are useful for providing an overview of the relative significance of the processes occurring in N and P cycles. Models and budgets based on these approaches (e.g. Source Apportionment-GIS (SAGIS, Comber et al. (2013)) and SEctor Pollutant AppoRtionment

for the AquaTic Environment (SEPARATE, Zhang et al. (2014)) in the UK and the SPAtially Referenced Regressions On Watershed attributes model (SPARROW, Hoos and McMahon (2009)) in the USA) have been used within policy frameworks (e.g. the Water Framework Directive (European Union, 2000)) to determine priorities for investment decisions for macronutrient source control to reduce N and P concentrations in aquatic ecosystems.

However, anticipated changes in N and P concentrations as a result of reductions in macronutrient source terms have often not been realised over timescales originally envisaged (Sharpley et al., 2013; Van Meter et al., 2016). It is now considered this is the result of two factors: (1) additional fluxes (sources and sinks) of N and P not previously considered in nutrient budgets (Holman et al., 2008; Meinikmann et al., 2015); and (2) the build-up and subsequent release of legacy stores of macronutrients which invalidate steady state budget approaches (Haygarth et al., 2014). If neither these additional fluxes nor legacy stores are incorporated into the models and budgets used to make decisions regarding how to prioritise investment in mitigation of N and P pollution, then anticipated timescales for water quality improvements associated with these decisions may not be met. Recently, "Integrated Nutrient Management strategies" (Grizzetti et al., 2015) have been suggested as a future approach for tackling N and P pollution. The philosophy behind such an approach is that integrated strategies should consider all possible processes potentially affecting macronutrients in a management unit such as a river basin. Recent research has contributed evidence to support this approach by identifying both new N and P fluxes (e.g. mains water leakage as source of P (Ascott et al., 2016a; Gooddy et al., 2017); abstraction as a sink of organic N (Finlay et al., 2016)) and novel quantifications of known macronutrient stores (soils, groundwater (Bouwman et al., 2013a; Worrall et al., 2015a)). However, despite these advances in understanding of N and P cycles, there remain substantial gaps in our knowledge

of both N and P fluxes (sources and sinks) and stores, which must be addressed to underpin Integrated Nutrient Management strategies.

Historically, research has focussed on N and P fluxes from diffuse agricultural and single point sources (Carpenter et al., 1998; Edwards and Withers, 2008). Anthropogenic changes to the hydrological cycle associated with public water supply processes (abstraction, treatment and distribution and leakage of water) are a global phenomenon. The impact of abstraction on groundwater resources is well established, with global depletion during 1900-2008 estimated to be c. 4,500 km^3, equivalent to 12.6 mm of sea level rise (>6% of the total) (Konikow, 2011). Depletion rates have doubled in recent decades associated with increases in demand (and abstraction), and are predicted to increase further to 2050 (Wada et al., 2012). Mains water leakage (MWL) has been estimated to cost billions of pounds per year in wasted abstraction, treatment and distribution (World Bank, 2006). MWL has been shown to be a large contributor to groundwater recharge in urban areas, providing 30 – 65% of total recharge under cities in the UK (Yang et al., 1999), the Americas and Asia (Lerner, 1986; Lerner, 2002; Yang et al., 1999). Despite the magnitude of these water fluxes and the clear impact of public water supply processes on the hydrological cycle, the impact of these processes on N and P sources and sinks is poorly understood. MWL has been identified as an important urban multi-point source of P to the environment (Gooddy et al., 2017), but the temporal variability of this source and its future significance have not been quantified to date. Further, sources and sinks of N associated with public water supply process are poorly constrained. Both the source flux of N from mains water leakage and sink flux associated with N removal from the environment by abstraction are not well understood. Despite water transfers being considered to be essential for future supply resilience (Water UK, 2016), the impacts of future transfers on macronutrient cycles have not been quantified to date. Given the importance of the water

fluxes detailed above, public water supply processes may have a highly significant but as yet largely unquantified impact on N and P cycles.

In addition to macronutrient sources and sinks, a number of legacy macronutrient stores in the environment are also poorly constrained (Chen et al., 2018). The soil zone and groundwater are well established as important stores of both water (Gleeson et al., 2016) and macronutrients (Durand et al., 2011), although actual quantifications of the size of these legacy macronutrient stores are relatively scant (Chen et al., 2018). In contrast to soil water above and groundwater below, the deep vadose zone has been subject to little research, despite it playing a critical role in solute transport processes at the regional scale (Harter and Hopmans, 2004). Recently, it has been suggested that water stored in the deep vadose zone is an important missing component of global hydrological and land surface models, temporarily storing up to 27% of annual water fluxes from rainfall (Rempe and Dietrich, 2018). In spite of the size of this water store, biogeochemical cycling in the vadose zone remains relatively unexplored (Rempe and Dietrich, 2018). No estimates of the size and spatiotemporal distribution of legacy macronutrient stores in the vadose zone at national or global scales have been made to date. Given the magnitude of water stored in the vadose zone from rainfall, the vadose zone also represents a potentially highly important, but as yet unquantified store of macronutrients. Without an improved understanding of N and P sources, sinks and stores associated with public water supply processes and the vadose zone, continued use of conventional nutrient budgets and models for catchment planning may result in implementation of misinformed policy decisions, with potentially large delays in improvements in water quality.

1.2 Aims, Objectives and Scope

The overarching aim of this research is to develop an improved understanding of N and P sources, sinks and stores associated with public water supply and the vadose zone to support the development of Integrated Nutrient Management strategies. To achieve this aim, this thesis has the following objectives:

1. To review – in the context of conventional macronutrient models and budgets - the current state of the science regarding N and P sources, sinks and stores associated with public water supply and the vadose zone, and identify targeted research needs that must be addressed to underpin Integrated Nutrient Management approaches.

2. To quantify seasonality and future scenarios associated with P fluxes from mains water leakage.

3. To quantify nitrate sources and sinks associated with public water supply abstraction, leakage and planned water transfers.

4. To quantify the amount of nitrate stored in the vadose zone in England and Wales.

5. To quantify the amount of nitrate stored in the vadose zone at the global scale.

It should be noted that whilst carbon, hydrogen and oxygen are highly important macronutrients (Schlesinger and Bernhardt, 2013), they are considered to be out of the scope of this thesis.

1.3   Thesis Structure

The five objectives detailed in section 1.2 are delivered through five thesis chapters. Chapter 2 provides a review of the literature corresponding to objective 1. Chapters 3 – 6 consist of published papers in the peer reviewed literature which correspond to objectives 2 – 5. Details of the published papers are listed in Table 1.1. Chapter 7 provides a concluding discussion of the unique scientific contribution this research makes to the field, as well as policy implications of this research and recommendations for further work.

Table 1.1 Published papers corresponding to chapters and objectives

Objective/Chapter	Name of Paper	Journal and DOI
2/3	Phosphorus fluxes to the environment from mains water leakage: Seasonality and future scenarios	Science of the Total Environment 10.1016/j.scitotenv.2018.04.226
3/4	Public water supply is responsible for significant fluxes of inorganic nitrogen in the environment	Environmental Science & Technology 10.1021/acs.est.8b03204
4/5	Quantification of nitrate storage in the vadose (unsaturated) zone: a missing component of terrestrial N budgets	Hydrological Processes 10.1002/hyp.10748
5/6	Global patterns of nitrate storage in the vadose zone	Nature Communications 10.1038/s41467-017-01321-w

2 Sources, sinks and stores of N and P associated with public water supply and the vadose zone: State of the science and future research needs

2.1 Introduction

2.1.1 Background and Motivation

The macronutrients Nitrogen (N) and Phosphorus (P) are essential for life. Biogeochemical cycles transfer macronutrients between forms of differing bioavailability and between different compartments within the environment. Humans have significantly modified natural N and P cycles for the purpose of increasing human prosperity. The use of N and P in fertilizers and livestock feed additives has resulted in increases in food production (Galloway and Cowling, 2002). Reactive N and P are also used in detergents and as additives in the food industry (Appl, 1999), and P is used as a corrosion inhibitor in treated drinking water supplies (Edwards et al., 1999; Schorr and Valdez, 2016). It is estimated that reactive N and P fluxes are now double pre-industrial levels (Fowler et al., 2013). These anthropogenic changes have had significant environmental and human impacts. Eutrophication associated with increased N and P fluxes to aquatic ecosystems has resulted in fish kills (Vollenweider, 1968) and animal and human health impacts (Funari and Testai, 2008). High nitrate concentrations in drinking water have been linked to "blue baby syndrome" (methaemoglobinaemia) and as a result of this the World Health Organisation has set a standard of 50 mg NO_3/L for drinking water (World Health Organisation, 2011). The costs of both the environmental damage and water treatment for N and P are estimated to be of the order of billions of pounds per year globally (Dodds et al., 2009; House of Commons Environmental Audit Committee, 2018; Pretty et al., 2000; UK Water Industry Research Ltd, 2004).

In order to reduce eutrophication and drinking water nitrate exceedances, measures to reduce N and P fluxes to the environment have been implemented (Conley et al., 2009). Implementation of measures historically has been informed by analysis of nutrient budgets and models, many of which adopt a steady-state approach (Chen et al., 2018; Hoos and McMahon, 2009; Leip et al., 2011). However, there is increasing evidence that such measures have had less than anticipated impact over predicted timescales, as a result of: (1) macronutrient fluxes which have previously not been considered and (2) catchment processes which invalidate the steady state assumption. These catchment processes result in the formation of previously unconsidered legacy macronutrient stores (Sharpley et al., 2013; Van Meter et al., 2016). In the short term, release of N and P from these stores into aquatic ecosystems reduces the efficacy of land surface measures to reduce N and P losses (Melland et al., 2018).

Recently, "Integrated Nutrient Management (INM)" (Grizzetti et al., 2015) has been suggested as an approach to dealing with eutrophication resulting from N and P pollution. INM moves beyond the steady-state approach and considers all possible macronutrient processes in a catchment and how these change through time. Whilst conceptually straightforward, implementation of the INM philosophy beyond small exemplar catchments has been limited, in part due to a dearth of detailed information on macronutrient processes at large scales. Moreover, there are a number of significant research gaps regarding macronutrient sources, sinks and stores which currently limits the adoption of INM approaches. Despite groundwater abstraction resulting in significant perturbations to hydrological (Konikow, 2011) and element cycles (Stahl, 2018), the impact of public water supply processes on macronutrient cycles is poorly understood. The influence of the vadose zone on macronutrient cycling is also poorly constrained (Chen et al., 2018). The purpose of this literature review is - in the context of conventional macronutrient budgets and models - to present the state of the science

regarding sources, sinks and stores of N and P associated with public water supply and the vadose zone, and to identify key research needs to be addressed to underpin Integrated Nutrient Management strategies. It should be noted that in this thesis, a detailed analysis of N and P cycling associated with well-established nutrient sources such as agriculture and wastewater treatment is beyond the scope of the literature review.

2.2 Conventional macronutrient models and budgets

2.2.1 Fundamental principles

Nutrient budgets and models are well-established approaches to quantifying N and P fluxes in the environment, with the first budgets developed in the 1960s (Vollenweider, 1968). Budgets and models have been developed at a wide range of scales from farm and catchment to country and global. A central tenet of almost all approaches is the quantification of input and output fluxes (mass per unit time, e.g. kg N/year) to the environmental compartment of interest. Approaches can be transient or steady state. Steady state approaches are built on the assumption that there is no net change in the amount of macronutrients stored in each compartment, i.e.

$$\sum Inputs - \sum Outputs = 0 \qquad (2.1)$$

Whereas transient approaches calculate changes in storage through time, i.e.

$$\sum Inputs - \sum Outputs = \Delta Storage \qquad (2.2)$$

The adoption of either steady state or transient approaches depends on the question to be addressed by the model, which in turn may affect both the model extent (spatial, temporal, number of environmental compartments) and which macronutrients are considered. For example, approaches focussing on the soil zone have quantified changes in soil N and P stores (Plaza et al., 2018; Post et al., 1985; Prentice, 2008). The nature of P as a finite resource has also focussed approaches to quantify the magnitude of other stores (Yuan et al., 2018), as

detailed in section 2.2.3. It is beyond the scope of the literature review to present an exhaustive account of all the different macronutrient budgets and models, and the reader is referred to reviews by Wellen et al. (2015), Borah and Bera (2004) and Chen et al. (2018) for further details. This section provides an overview of different types of conventional budgets and models previously developed from the catchment to national/regional/global scales. Subsequently, in section 2.3, evidence for N and P fluxes and stores not considered in conventional approaches is reviewed.

2.2.2   Catchment scale models

A wide range of catchment models have been developed and applied worldwide with the aim of quantifying nutrient fluxes in catchments and evaluating the potential effectiveness of changes in management practices. In broad terms, these models can be divided into two categories: (i) lumped conceptual or statistical models, and (ii) physically-based models. Within both these categories, most conventional catchment scale models do not include explicit mechanisms to represent changes in macronutrient storage in the environment other than in the soil zone (Chen et al., 2018).

Lumped conceptual models have been used extensively for estimation of nutrient loads to receiving waters (Glibert et al., 2010). A number of models (e.g. Global Nutrient Export from WaterSheds (GlobalNEWS, Seitzinger et al. (2005)), Generalized Watershed Loading Function (GWLF, Haith and Shoenaker (1987)), Pollutant Flow (PolFlow, Wit (2001)), SPAtially Referenced Regressions On Watershed attributes (SPARROW, Smith et al. (1997))) adopt the steady state assumption either annually or over a 5-year period. In the UK, Source Apportionment-GIS (SAGIS, Comber et al. (2013)) and SEctor Pollutant AppoRtionment for the AquaTic Environment (SEPARATE, Zhang et al. (2014)) are two source apportionment tools

developed for N and P loadings in rivers. Both of these models are driven by pre-existing

models for N and P sources (Davison et al., 2008; Lord and Anthony, 2000). A similar approach

has recently been developed for the Republic of Ireland by Mockler et al. (2017). These tools

do not calculate a time lag between changes in macronutrient source terms and riverine

concentrations. Given that lag times of up to decades between changes in macronutrient

inputs and outputs have been reported (Howden et al., 2011; Wang et al., 2012), application

of these modelling approaches alone to quantify the likely impacts of changes in management

practices on riverine N and P concentrations is likely to be challenging. Where there is

continued release of N and P from legacy stores such as the vadose zone, these lags will delay

the predicted response in riverine N and P concentrations to land management changes.

Physically based models such as the Soil and Water Assessment Tool (SWAT, Arnold et al.

(2012)), AGricultural Non-Point Source Pollution Model (AGNPS, Young et al. (1989)) and the

Hydrological Simulation Program - FORTRAN (HSPF, Mishra et al. (2009)) have been widely

used to quantify N and P fluxes in catchments (Chen et al., 2018). Legacy nutrient dynamics

are often highly simplified within these models (Hrachowitz et al., 2016). For example, SWAT

uses a single parameter to represent lags in groundwater (Arnold et al., 2012) and the

magnitude of legacy stores in groundwater and the vadose zone are not calculated.

Application of these models is challenging where riverine nutrient fluxes are derived from

water sources with a range of ages (e.g. a mixture of runoff, shallow groundwater, deep

groundwater (Wellen et al., 2015)).

In addition to representation of legacy stores, both lumped and physically based models

poorly represent a number of macronutrient processes. In-stream P sources and sinks, major

river modifications such as damming are generally not represented in these models (Chen et

al., 2018). Recently quantified macronutrient sources and sinks associated with public water

supply such as mains water leakage (Gooddy et al., 2017) and abstraction (Finlay et al., 2016; Stahl, 2018) are also not explicitly represented, although mains water leakage is being considered in future model development in Ireland (Mockler et al., 2017). Where these fluxes are important, the application of existing models may be limited. Development of revised model structures that integrate these processes in existing lumped and physically based modelling approaches is a significant challenge.

2.2.3   Large-scale conceptual approaches

Conventional large-scale conceptual nutrient budgets consider a range of different N and P sources and fluxes between different environmental compartments. For each compartment the inflows and outflows are quantified. Estimates of N and P sources may be derived from models relating to the source term of interest (e.g. soil N and P balances, export coefficient models (Johnes, 1996; Worrall and Burt, 1999)).

Numerous large-scale analyses have quantified stores in the soil zone for both N (Post et al., 1985; Prentice, 2008) and P (Chen and Graedel, 2016; Sattari et al., 2012) for the purpose of quantifying the impact of fertilizer applications on soil macronutrient cycles. However, beyond the soil zone, there are differences between the large-scale budgets developed for N and for P in the representation of stores. Large-scale P budgets have often been developed using substance flow analysis (SFA) methods and the principles of mass balance to calculate the absolute magnitude of a number of P stores (Yuan et al., 2018) and how these change. In contrast, whilst a few novel national-scale substance flow analyses (Antikainen et al., 2005; Chen et al., 2016) and budgets (Worrall et al. (2009); Worrall et al. (2016a), reviewed in detail in section 2.3.2) have quantified the magnitude of N stores, in general conventional large scale budgets have focussed on quantifying fluxes between stores (Fowler et al., 2013; Galloway et

al., 2004). The focus on quantifying fluxes between stores in N budgets is likely to reflect two differences between N and P cycling; (1) the source of unreactive P (apatite and other P minerals) is finite and decreasing, resulting in the "global phosphorus crisis" (Sattari et al., 2012), whereas the Haber-Bosch process draws unreactive N from a larger and replenishing unreactive N source (atmospheric N_2) (Erisman et al., 2008), and (2) P is less mobile in the environment than N, with P likely to sorb to soils and sediments (Guppy et al., 2005).

These differences between N and P cycles have historically provided a greater impetus to quantify the magnitude of P stores. Global P budgets which calculate P stores have been developed by numerous workers (Liu et al., 2008; Ruttenberg, 2003; Smil, 2000; Smit et al., 2009). Figure 2.1 shows a global P budget recently developed by Yuan et al. (2018), where data for P fluxes and stores were drawn from a meta-analysis of previous studies. In these studies, fluxes of P associated with public water supply processes (mains water leakage and abstraction) were not included, which limits the application of these budgets when these fluxes are likely to be important. Global P flows and changes in stores have also been quantified by Chen and Graedel (2016), when comparing anthropogenic influences on the P cycle between 1961 and 2013. Budgets have also been developed at national, continental (Ott and Rechberger, 2012; van Dijk et al., 2016; Worrall et al., 2016b), basin (McCrackin et al., 2018) and regional and city scales (Chowdhury et al., 2014). Chowdhury et al. (2014) reviewed 21 P budgets covering city, regional and country scales, showing that 20 of the 21 studies reviewed calculated P stores. However, most of the studies did not quantify the spatial distribution of P stores, which is considered to be important for the development of policies to manage P pollution (Chowdhury et al., 2014).
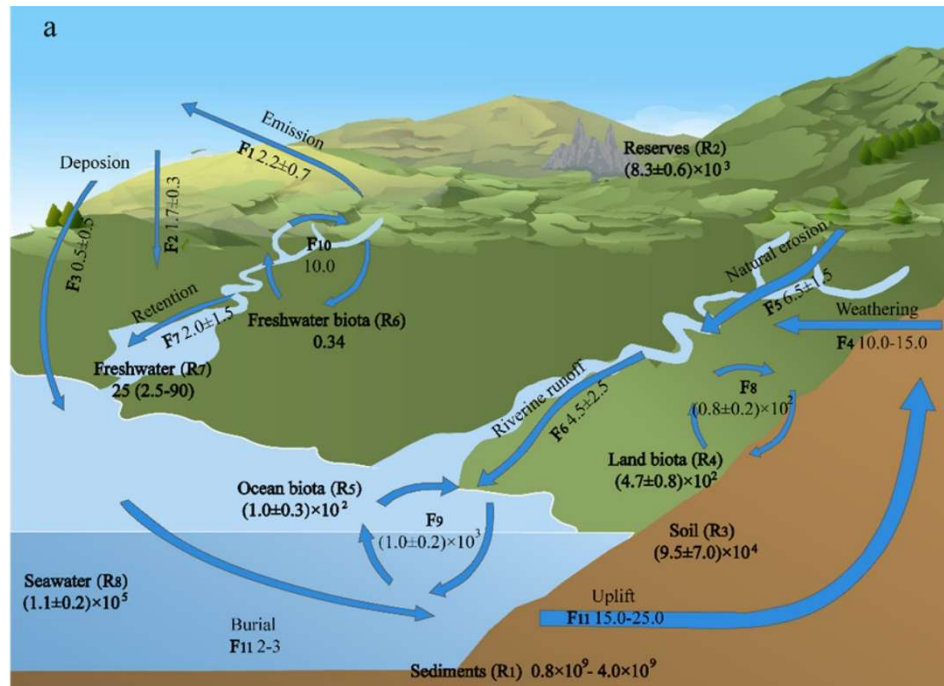
Figure 2.1 A global conceptual P budget. The budget includes both fluxes and stores. Public water supply processes are not explicitly included. Reprinted with permission from Yuan et al. (2018). Copyright 2018, American Chemical Society.

Large-scale N budgets have also been developed at national, continental and global scales. There is little consistency regarding approaches used within these budgets. In contrast to P budgets, in many studies the absolute magnitude of N stores excluding the soil zone is often not calculated. Moreover, where budgets have been reported in the grey literature (Sutton et al., 2011; United States Environmental Protection Agency, 2011), detail of the methodologies used has been limited. Figure 2.2 shows an example of a conceptual N budget at the national scale for the United Kingdom as reported by Leip et al. (2011). In this budget, and the other national- and continental-scale budgets reported by Leip et al. (2011), no net change in N storage across the whole environmental system is assumed, and differences between N sources and sinks were assumed to be the result of either denitrification or other sink processes. The principle of no change in storage has also been adopted by the Eurostat and the European Environment Agency in the development of the soil N surplus as a national-scale indicator of potential N pollution (European Environment Agency, 2019; Eurostat, 2018).

Due to lack of available data, current Eurostat/OECD guidance (Eurostat, 2013) indicates that the soil N surplus should be calculated without estimating changes in soil N storage. Eurostat (2013) recognised this limitation in areas where soil N accumulation is likely and recent work by Özbek and Leip (2015) has developed novel methods for accounting for changes in soil N storage in soil N budgets.
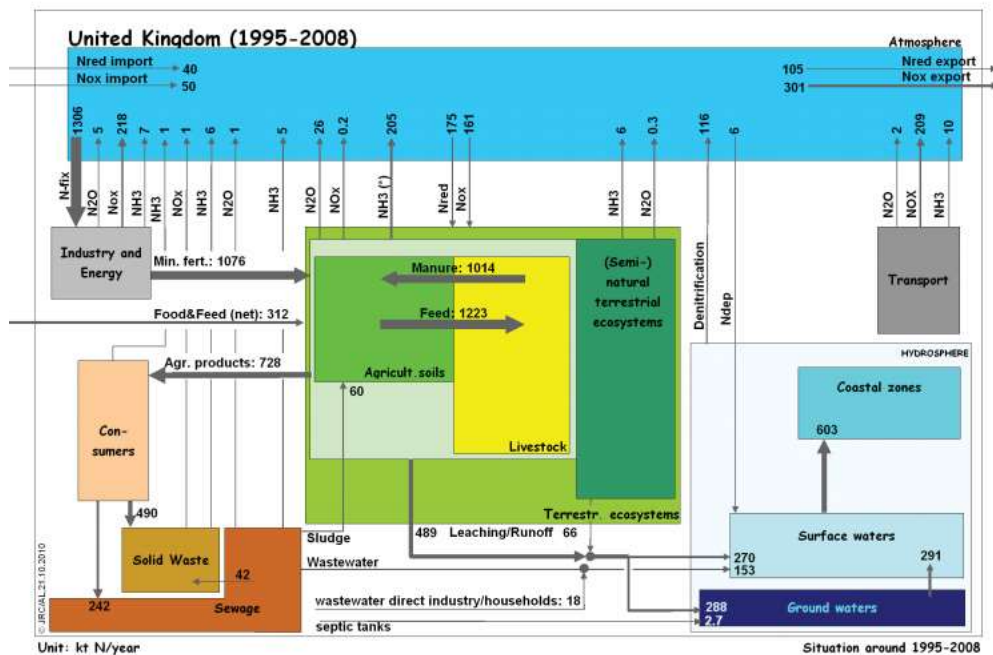
Figure 2.2 A large-scale conceptual N budget for the United Kingdom, reproduced after Leip et al. (2011) with permission from Cambridge University Press. Similar budgets have been developed at the continental and global scale. No estimates of either accumulation rates or absolute N storage are made, and public water supply processes are not included.

In contrast, in China, Gu et al. (2015) calculated N accumulation rates for the hydrosphere and other N stores based on differences in N inflows and outflows for each store. However, they did not calculate the absolute magnitude or net accumulation of each store. In the USA, total national-scale N fluxes to groundwater, soils and vegetation were estimated by United States Environmental Protection Agency (2011). However, no detail was provided as whether these are N inflows or accumulation rates, and, despite being reported as a flux (mass/year) were referred to as "stores". It was found that the total N source flux was significantly greater than

the sum of N export and fluxes to groundwater, soils and vegetation. The difference was assumed to be due to denitrification. A similar approach was developed for the UK by Worrall et al. (2012), who calculated, based on the difference between total N sources and the fluvial N flux at the tidal limit, that significant in-stream losses of N were occurring. It was postulated that these losses were due primarily to denitrification.

Budgets have also been developed at the global-scale (Battye et al., 2017; Fowler et al., 2013; Fowler et al., 2015; Razon, 2018). These budgets are typically derived from a compilation of estimates of N sources and sinks from previous studies. Fowler et al. (2013) recognised groundwater may be an important N store due to long residence times, but no quantification of this (or any N stores) was made. The lack of quantification of N stores limits the use of these budget approaches beyond simply highlighting particular N sources of concern. Moreover, fluxes of N associated with mains water leakage and abstraction have not been included in national, continental and global N budgets to date. Previously these budgets have been considered to be useful for highlighting the magnitude of anthropogenic influences on the N cycle (Galloway et al., 2004),. However, application of these budgets in areas where public water supply processes may significantly impact N cycling is likely to be limited.

2.3 Evidence for N and P fluxes and stores not considered in conventional approaches

Whilst the nutrient budgets and models highlighted in section 2.2 give a useful indication of relative importance of different well constrained macronutrient sources, the application of such approaches to making decisions regarding source control has been challenging. There are a number of instances where decisions regarding N and P source control made on the basis of these approaches have not resulted in anticipated changes in water quality (Haygarth et al., 2014; McIsaac et al., 2001; Sharpley et al., 2013; Van Meter et al., 2018). In the US, for

example, millions of dollars have been spent over the past 20-30 years on conservation measures in the Mississippi, Lake Erie and Chesapeake bay basins to reduce N and P loadings from agricultural sources (Haygarth et al., 2014; Van Meter et al., 2018). Despite these interventions, eutrophication remains an issue in these catchments. In the Chesapeake Bay catchment, annual riverine N fluxes are 5000 kt N/yr over 2017 goals (Chesapeake Progress, 2017). In the Gulf of Mexico, the outlet of the Mississippi, the hypoxic zone in 2017 was the largest ever measured and the target year for water quality improvements has been pushed back to 2035 (Van Meter et al., 2018). It is now understood that the two primary reasons why anticipated improvements in water quality have not occurred are: (1) macronutrient fluxes (sources and sink terms) not previously considered and (2) catchment stores invalidating the steady state assumption built into a number of modelling approaches. In this section the evidence for the role of these additional N and P sources, sinks and stores is reviewed.

2.3.1 Macronutrient fluxes not previously considered

2.3.1.1 Overview

If models and tools used for decision making for macronutrient source control are to be effective, it is essential that emerging pressures such as additional sources and sinks are taken into account (Mockler et al., 2017). Previous research has predominantly focussed on N and P fluxes from either diffuse agricultural or single point sources (e.g. wastewater treatment works discharges) (European Environment Agency, 2005). This focus is well justified, as historically in the UK >90% of both P (White and Hammond, 2009) and N (Hunt et al., 2004) loads have been derived from these sources. However, with significant decreases in N and P fluxes from these sources associated with improvements in agricultural management practices (European Environment Agency, 2019; Lord and Anthony, 2000; Wang et al., 2016) and wastewater treatment (e.g. Kinniburgh and Barnett (2010)), the relative importance of other anthropogenically derived fluxes is likely to grow in importance. Despite the fact that

groundwater abstraction has been shown to significantly perturb both the hydrological (Konikow, 2011; Rodell et al., 2018) and element cycles (Stahl, 2018), to date limited research has been undertaken to quantify the impact of public water supply on N and P cycles. In particular, leakage of mains water has been given little attention as a potential diffuse, multi-point macronutrient source (Holman et al., 2008) and has been represented simplistically in N and P flux models (e.g. Zhang et al. (2014)). Moreover, removal of macronutrients from the aquatic environment by abstraction has also been subject to little research.

2.3.1.2   *Public Water Supply and Macronutrient Cycles: Mains Water Leakage and Abstraction as sources and sinks of N and P*

Whilst interaction between public water supply processes and macronutrient cycles has been recognised for decades (Wilkinson et al., 1982; Yeoman et al., 1988), historically almost all research has focussed on the impacts of N and P cycles on public water supply, rather than the reverse. This research has focussed on controlling N concentrations in raw (untreated) waters to meet drinking water standards (see, for example, Beeson and Cook (2004)) and controlling P concentrations in wastewater discharges (de-Bashan and Bashan, 2004). Recently, mains water leakage (MWL) has been identified as a potentially important source of P to the environment. Phosphate is routinely added to mains water to reduce the release of lead from both customer supply pipes and household plumbing into drinking water ("plumbosolvency") (Hayes, 2010). Lead consumption is a public health concern which has been shown to result in cognitive development problems in children and increased risks of heart attacks and stroke (Bellinger et al., 1987; Pocock et al., 1988). Phosphate dosing replaces soluble lead carbonate with an insoluble lead phosphate precipitate (Edwards et al., 1999). The spatial extent of lead fixtures and fittings in household plumbing is poorly understood at the national scale (UK Water Industry Research Ltd, 2012), and as a consequence in the UK a precautionary approach has been adopted where >95% of water supplies are phosphate dosed (Chartered Institute for

Water and Environmental Management, 2011). In the USA over half of supplies are dosed (Dodrill and Edwards, 1995) and dosing strategies are being developed in the Republic of Ireland (Irish Water, 2015; Mockler et al., 2017) and South Korea (Lee, pers. comm.). Dosing typically results in tap water concentrations of c. 1 mg P/L (Chartered Institute for Water and Environmental Management, 2011; Gooddy et al., 2015).

As previously discussed in chapter 1, leakage is a globally important problem costing billions of pounds per year (World Bank, 2006). Leakage is well known to be a large contributor to groundwater recharge in urban areas (Lerner, 1986; Yang et al., 1999), providing up to 65% of total recharge under cities in the UK, Asia and Americas (Lerner, 1986; Lerner, 2002; Yang et al., 1999). Holman et al. (2008) and Holman et al. (2010) were the first to identify leakage of phosphate dosed mains water as a potentially important source of P to groundwater. Gooddy et al. (2015) made the first national scale quantification of the P flux from mains leakage for the UK based on the percentage of water distributed that was lost as leakage and conservative estimates of drinking water P concentrations. This showed that approximately 1000 tonnes of P per year (t P/year) enter the environment annually. Using more detailed water company level leakage data, Ascott et al. (2016a) estimated the national scale P flux as 1200 t P/year, with major cities such as London making the largest contribution to this flux. Gooddy et al. (2017) subsequently made the first comparison between P fluxes from mains water leakage and other P sources, using the River Thames catchment as an exemplar. MWL-P was shown to be equivalent to up to 24% of the P loading from wastewater treatment works.

In addition to P, MWL has been identified as a considerable source of N to the environment in urban areas. Early work by Lerner et al. (1999) showed that 36% of the N loading to groundwater could be attributed to leaking water mains in the city of Nottingham, UK. Building on research in Nottingham, Lerner (2003) presented generic methods for quantifying

urban N loads to groundwater, including from MWL using a simple export coefficient approach. These approaches have been adopted by the Environment Agency (2013) in England when estimating urban N loads to groundwater for designation of Nitrate Vulnerable Zones. Cross-sectoral modelling tools developed for N and P source apportionment (e.g. SAGIS (Comber et al., 2013) and SEPARATE (Zhang et al., 2014)) use simple lumped runoff models to estimate loads from urban sources. These models adopt similar approaches, using estimates of rainfall to derive average annual runoff from urban sources. Published representative concentrations for urban runoff for all sources (industrial, residential, open urban, highways etc.) are averaged to derive single representative concentrations for N and P. The derived concentrations and runoff rates are used to estimate N and P fluxes. These approaches do not consider mains leakage explicitly, and thus application of these models in areas where this source is important (e.g. the Thames Basin, Gooddy et al. (2017)) may be seriously constrained.

To meet increasing demand for water associated with population growth, transfers of treated drinking water between water companies are increasingly being considered (Water UK, 2016). These transfers range from planned and costed engineering schemes that will be implemented by 2020, through to more speculative schemes such as large inter-regional transfers. The implications for both drinking and environmental water quality of these transfers is poorly constrained (Water UK, 2016). Transfers of water of different quality have potentially highly important, but as yet unquantified, implications for the N cycle in the future. The transfer and subsequent leakage of treated drinking water may alter the spatial distribution of MWL macronutrient fluxes. To date no research has quantified the impact of this public water supply process on the N cycle.

In contrast to mains water leakage as a macronutrient source, very little research has quantified the role of abstraction for public water supply as a flux to remove macronutrients from aquatic environments. Macpherson (2009) made the first estimate of global C fluxes to the atmosphere associated with groundwater abstraction, with further estimates made at national (USA (Wood and Hyndman, 2017); India (Mishra et al., 2018)) and regional scales (Walloon Region, Belgium (Jurado et al., 2018)). Finlay et al. (2016) estimated the net flux of carbon associated with public water supply abstraction from UK rivers, and made the first estimate of the sink of organic N by this process. Figure 2.3 shows schematically the N fluxes reported by Finlay et al. (2016). It was estimated that 4 kt N/year of total organic N is removed by abstraction, greater than estimates of particulate organic N sinks in floodplain and in channels (1.5 and 3 kt N/yr respectively). Fluxes of inorganic N species associated with abstraction were not estimated. Recently, Stahl (2018) estimated the global removal of a number of elements from groundwater associated with abstraction. The global flux of N associated with groundwater abstraction was estimated to be 3.68 Tg N/year, which is also reported to contribute >10% of crop N requirements where croplands are irrigated with groundwater. However, it should be noted that a simplistic methodology was used to estimate these fluxes, using global water abstraction data and assuming groundwater quality data held by the United States Geological Survey (USGS) is representative of groundwater globally. Stahl (2018) suggests that country and regional level estimates of element fluxes associated with groundwater abstraction are needed to refine the initial global estimates made.
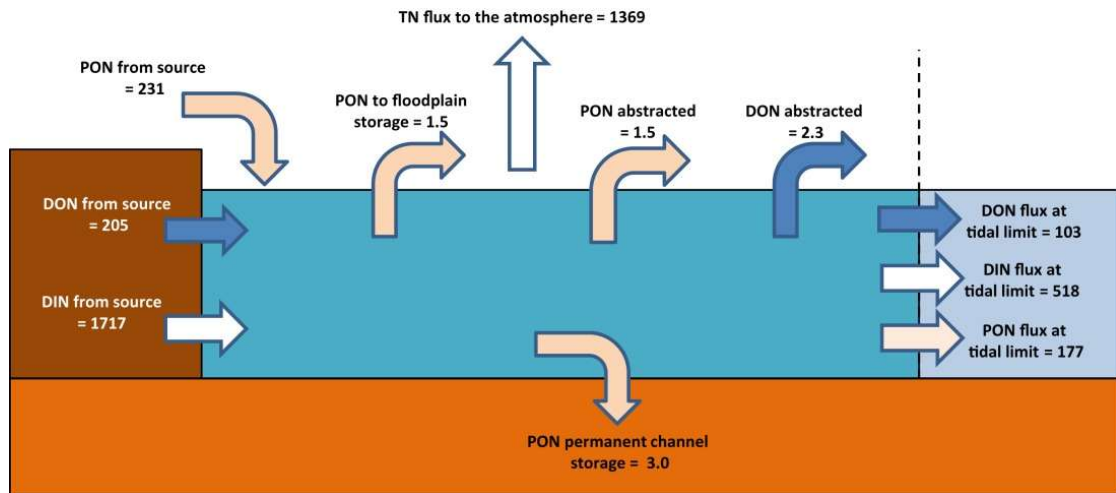
Figure 2.3 Schematic representation of fluvial N fluxes into and out of UK rivers. Reproduced after Finlay et al. (2016) with permission from Wiley. DON, DIN, PON, and TN are Dissolved Organic Nitrogen, Dissolved Inorganic Nitrogen, Particulate Organic Nitrogen and Total Nitrogen respectively.

2.3.2 Catchment stores invalidating the steady state assumption

2.3.2.1 Overview

Large-scale evaluation of N and P fluxes in the environment has often involved the development of nutrient budgets. Due to lack of quantitative information on the magnitude and distribution of macronutrient stores, these budgets have had to invoke the steady state assumption (Bouwman et al., 2013a; Chen et al., 2018; Leip et al., 2011). However, over the past 40 years a substantial body of work has been developed which indicates that the steady state assumption is invalid in a number of different environments when considering relatively short (<50 years) timescales. There is extensive evidence of N and P accumulating in temporary storage in the terrestrial environment such as soil zones (Sharpley et al., 2013; Van Meter et al., 2016), lentic and fluvial sediments (Chen et al., 2018), groundwater (Stuart and Lapworth, 2016; Vero et al., 2018) and the vadose zone (Walvoord et al., 2003). Despite this, quantification of the size of legacy macronutrient stores are scant. Of the 37 published estimates of the magnitude of legacy N and P stores at the regional or global scale reviewed by Chen et al. (2018), the majority were for the soil zone, with only seven reported estimates for groundwater and none explicitly for the vadose zone. Accurate quantification of the

magnitude of N stores, such as the vadose zone, and how they change through time is likely to be important in understanding future changes in macronutrient cycles.

2.3.2.2   N storage in the vadose zone

In areas with deep groundwater tables, delays between N leaching from the base of the soil zone and the groundwater table can be of the order of decades, resulting in significant nitrate stores accumulating in the vadose zone (Foster et al., 1982; Howden et al., 2011; Wang et al., 2012). Nitrate storage in the vadose zone (defined as between the base of the soil zone and the saturated zone) is illustrated conceptually in Figure 2.4. The accumulation and subsequent release of N from these stores can delay the impact of land management measures to reduce N pollution (Melland et al., 2018).
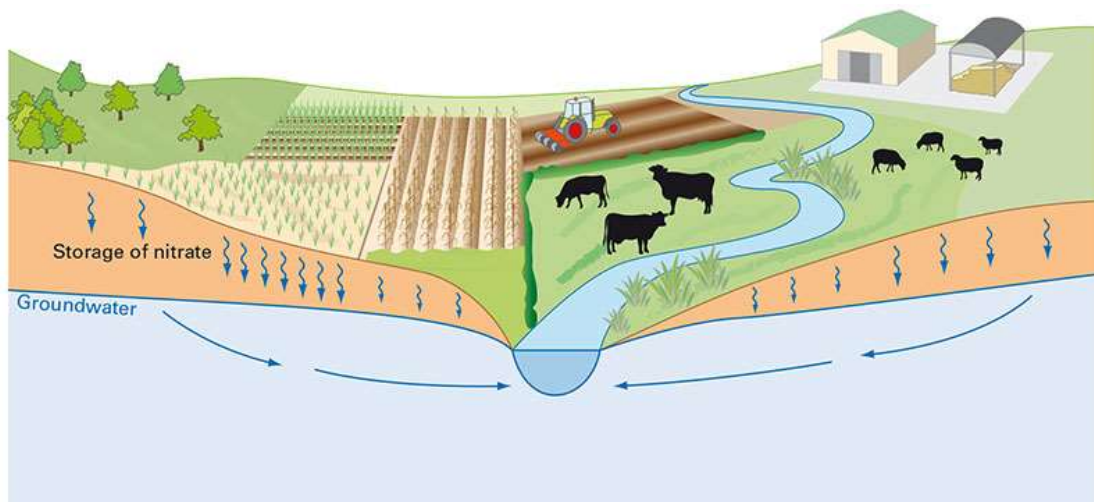
Figure 2.4 Conceptual model of nitrate stored in the vadose zone

Storage of N in groundwater and the unsaturated zone has been recognised for decades (Foster et al., 1982; Worrall et al., 2009), and research has been undertaken to quantify the time lags between management changes and measureable water quality improvements associated with this store. In the USA, extensive programmes of implementation of agricultural best management practices have resulted in minimal improvements in surface

water quality primarily due to time lags (Meals et al., 2010). Figure 2.5 (Vero et al., 2018) shows

the distribution of recent publications related to macronutrient time lags in Europe and North

America, where lags are reported to be from 4 to > 100 years.
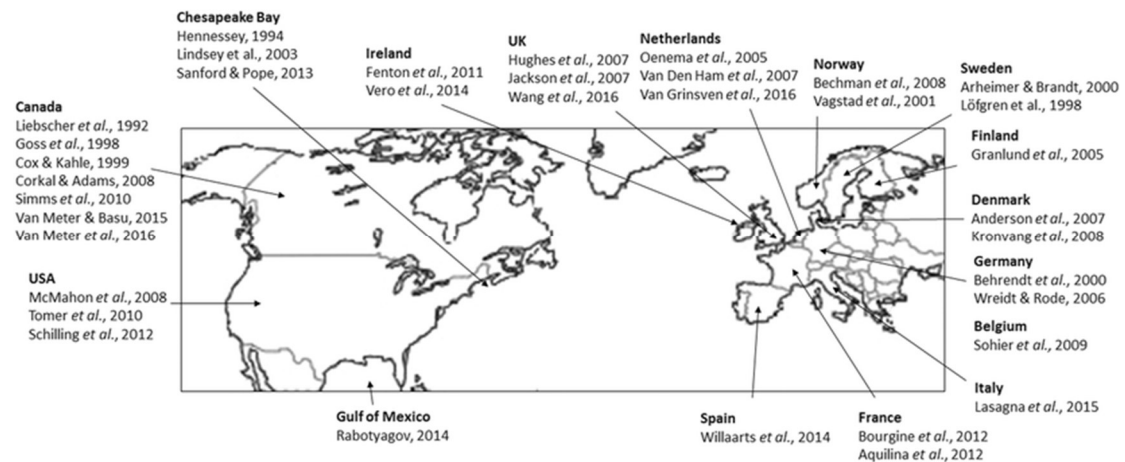
Figure 2.5 Recent publications showing evidence of N accumulation and time lags in Europe and North America. Reproduced after Vero et al. (2018) with permission from Springer and references included therein.

Estimates of time lags are useful for understanding timescales for responses in N

concentrations in aquatic ecosystems resulting from changes in soil N leaching associated with

changes in agricultural practices. However, time lag gives no indication of the legacy N already

in the vadose zone and groundwater, which will impact aquatic ecosystems before any

responses due to changes in leaching. To quantify the importance of legacy N, integrated

metrics of both time lag and historic N leaching are required. The absolute magnitude of N

stored in the vadose zone or groundwater is one such metric, which can also be compared to

the magnitude of other stores of N in the terrestrial environment. Despite the extensive

research on both time lags and N leaching, there are few estimates of the absolute magnitude

of N accumulation in either the vadose zone or groundwater. At the point scale, a number of

workers have quantified nitrate stored in the vadose zone based on porewater profiles (Foster

et al., 1982; Izbicki et al., 2015; Jia et al., 2018; McMahon et al., 2006; Mercado, 1976; Pratt et

al., 1972; Turkeltaub et al., 2015; Walvoord et al., 2003). However, there remains a paucity of

measured vadose zone and groundwater N data in a number of regions (Jia et al., 2018). This

lack of data has resulted in the few estimates of subsurface N storage at regional, national and global scales to be reliant on either extrapolation or modelling approaches, some of which do not consider the vadose zone explicitly, if at all. Walvoord et al. (2003) estimated the N store in global desert and arid subsoils to be 3,000,000 to 15,000,000 kt N. Jackson et al. (2004) subsequently questioned the validity of the approach used by Walvoord et al. (2003), which consisted of global extrapolation from 5 vadose zone profiles. In the USA, estimates of the groundwater N store have been made in the Mississippi Basin (Van Meter et al., 2017) and basins in the Atlantic and New Jersey Coastal Plains (Böhlke and Denver, 1995; Modica et al., 1998). In the UK, Worrall et al. (2015a) estimated the total N stored in the Thames Basin in both the vadose zone and saturated zone. Using a numerical solution to 1D transport in porous media, Worrall et al. (2015a) estimated concentration profiles for nitrate in groundwater. These profiles were then combined with estimates of aquifer geometry and porosity to derive estimates of nitrate storage in the Thames Basin. Nationally, Worrall et al. (2009) and Worrall et al. (2016a) used a simple approach to estimate nitrate accumulation in groundwater in Great Britain. By assuming that between 10-50% of the UK land area is underlain by groundwater bodies, and that a groundwater body represents a depth of water between 1 and 10 m, Worrall et al. (2009) equate a 1 mg N/L increase in groundwater concentration to be equivalent to 300 kt N additional storage. Bouwman et al. (2013a) used estimates of N leaching fluxes derived from soil N balances in combination with a simplistic model of groundwater travel time to quantify the groundwater N store globally. Bouwman et al. (2013a) estimated the global groundwater store to be 376,000 kt N, but did not consider the unsaturated zone. To the author's knowledge, no estimates of the mass of nitrate stored explicitly in the deep vadose zone have been made at national or global scales. Developing an improved understanding of the magnitude and distribution of this legacy N store is considered to be a major knowledge gap which much be addressed if management practices are to be developed to reduce N and P pollution (Chen et al., 2018).

2.4 Integrated nutrient management – Principles and key research needs

In response to the challenges faced in the application of conventional nutrient budgets and models in areas where unexpected nutrient sources, sinks and stores are present, numerous workers have suggested the development of "integrated nutrient management" approaches (see review by Oenema et al. (2011)). There is little consensus within the literature regarding the definition of "integrated" in the context of macronutrient budgets (Oenema et al., 2011). However, in the context of N and P sources, sinks and stores, the definition provided by Grizzetti et al. (2015) is useful. Grizzetti et al. (2015) suggest that integrated nutrient management strategies should consider all possible nutrient processes (i.e. sources, sinks, stores and time lags) in a river basin. Application of this holistic definition is likely to be highly challenging and ambitious. Whilst a number of studies have highlighted the importance of newly identified N and P sources (Gooddy et al., 2017; Holman et al., 2008), sink terms (Finlay et al., 2016), stores (Worrall et al., 2015a) and time lags (Van Meter et al., 2016; Vero et al., 2018), to achieve this definition requires a detailed understanding of all relevant N and P sources, sinks and stores and time lags within a catchment. Incorporating all processes affecting macronutrients into management strategies may not be feasible in practice, and there may be "unknown unknown" processes also occurring. Nevertheless, if any progress is to be made towards integrated nutrient management strategies (in the sense of Grizzetti et al. (2015)), there are large areas of uncertainty associated with N and P sources, sinks and stores associated with public water supply and the vadose zone which need to be addressed. These research gaps are illustrated schematically in Figure 2.6 and are listed below.

1. MWL-P has recently been identified as an important source of P to the environment (Gooddy et al., 2017). However, the temporal dynamics of MWL-P relative to other sources is poorly understood. Moreover, no research to date has quantified how the importance of MWL-P will change in the future associated with changes in leakage and improvements in wastewater treatment.

2. Early work by Lerner et al. (1999) has shown that MWL-N may be an important N source in urban areas. However, research to date has used simple literature values to estimate this source. Robust estimates of the importance of this source at local, national and global scales are lacking. Moreover, given the spatial variability in drinking water nitrate concentrations , it is likely that any changes in the water distribution network will result in changes in the distribution of MWL-N. No research has quantified the impact of future water transfers on MWL-N.

3. Public water supply abstraction has been shown to be a considerable temporary sink for organic N (Finlay et al., 2016). No research to date has quantified the size of the sink of inorganic N by public water supply abstraction.

4. Evidence for N stored in the vadose zone has been present since the 1980s (Foster et al., 1982). However, the spatiotemporal distribution of nitrate stored in the vadose zone at both national and global scales has not been quantified to date.
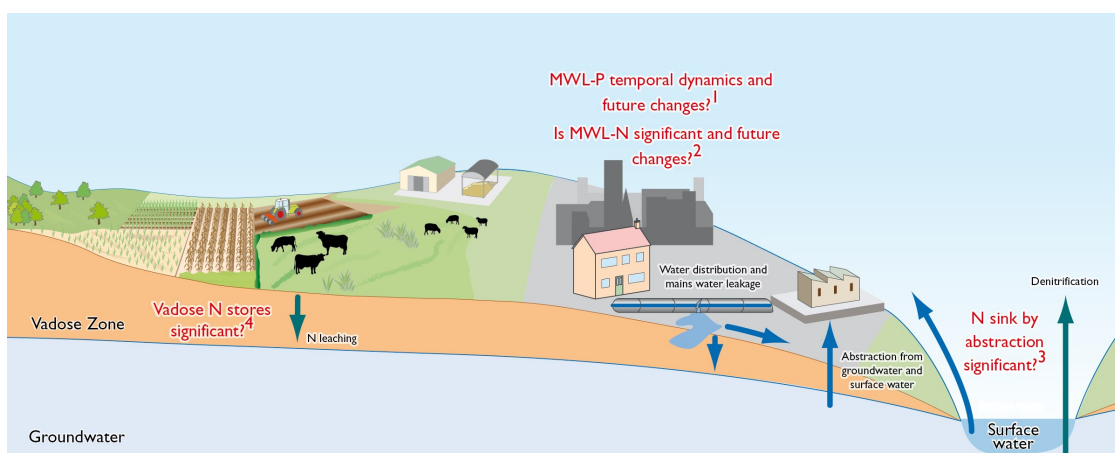
Figure 2.6 Key research gaps related to sources, sinks and stores of N and P associated with public water supply and the vadose zone to be addressed by this thesis

2.5   Conclusions

Despite recognition for over 30 years, eutrophication associated with N and P fluxes in the environment remains an important issue. To address this and concerns regarding nitrate concentrations in drinking water, nutrient budgets and models have been developed, many of which invoke steady-state assumptions. These approaches provide a useful indication of the relative contribution of well constrained N and P sources to total nutrient loads. However, application of these tools to make decisions regarding N and P source control has proved difficult, with limited improvements in water quality observed over predicted timescales following implementation of changes in management practices. Small improvements in water quality are due to (1) N and P sources and sinks not considered in conventional models and budgets and (2) build-up and release of legacy macronutrient stores in the environment through time, invalidating the steady state approach. To address these problems, "integrated nutrient management" approaches have been suggested which consider all nutrient processes in a river basin. Such approaches are highly ambitious and in their infancy, and there remain substantial gaps in our understanding of N and P sources, sinks and stores which need to be addressed prior to development of fully integrated approaches. Previous research developing N and P budgets and models has focussed primarily on agricultural and point sources of macronutrients.   Limited attention has been paid to the impact of public water supply processes on N and P sources and sinks. Recent research has suggested that mains water leakage may be an important macronutrient source, however N and P fluxes associated with mains water leakage are poorly constrained. Anthropogenic nutrient sinks are also poorly understood, such as the removal of N by public water supply abstraction. Whilst legacy stores of N and P in soils, groundwater and the vadose zone have been identified in previous research, the size and spatiotemporal distribution of N stored in the vadose zone is poorly constrained. Only by improving our understanding of these N and P sources, sinks and stores

can integrated nutrient management approaches be developed which can be used to support

policy decisions to reduce macronutrient pollution.

3   Phosphorus fluxes to the environment from mains water leakage: Seasonality and future scenarios

A version of this chapter has been published as ASCOTT, M.J., GOODDY, D.C., LAPWORTH, D.J., DAVIDSON, P., BOWES, M.J., JARVIE, H.P. AND SURRIDGE, B.W.J., 2018. Phosphorus fluxes to the environment from mains water leakage: Seasonality and future scenarios. *Science of the Total Environment*, 636, 1321-1332.
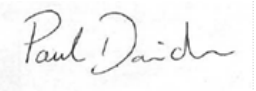
Author contributions are as follows:

Ascott conceived the idea to quantify seasonality and future scenarios of phosphorus fluxes from mains leakage. Ascott collated the data for water company leakage rates, river flow and phosphate concentrations. Ascott undertook the data analysis, interpretation and wrote and edited the manuscript. Davidson provided unprocessed wastewater treatment (WWT) flow and phosphate concentration data, outputs from SAGIS modelling and future WWT upgrades and commented on the manuscript. Bowes and Jarvie provided guidance on the use of concentration-flow relationships in deriving P flux time series and commented on the manuscript. Gooddy, Lapworth and Surridge contributed to the general review of the results during project meetings and commented on the manuscript.
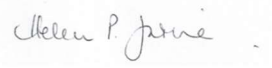
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Daren Gooddy

Dan Lapworth

Paul Davidson

Mike Bowes

Helen Jarvie

Ben Surridge

Abstract

Accurate quantification of sources of phosphorus (P) entering the environment is essential for the management of aquatic ecosystems. P fluxes from mains water leakage (MWL-P) have recently been identified as a potentially important source of P in urbanised catchments. However, both the temporal dynamics of this flux and the potential future importance relative to P fluxes from wastewater treatment works (WWT-P) remain poorly constrained. Using the River Thames catchment in England as an exemplar, we present the first quantification of both the seasonal dynamics of current MWL-P fluxes and future flux scenarios to 2040, relative to WWT-P loads and to P loads exported from the catchment. The magnitude of the MWL-P flux shows a strong seasonal signal, with pipe burst and leakage events resulting in peak P fluxes in winter (December, January, February) that are >150% of fluxes in either spring (March, April, May) or autumn (September, October, November). We estimate that MWL-P is equivalent to up to 20% of WWT-P during peak leakage events. Winter rainfall events control temporal variation in both WWT-P and riverine P fluxes which consequently masks any signal in riverine P fluxes associated with MWL-P. The annual average ratio of MWL-P flux to WWT-P flux is predicted to increase from 15 to 38% between 2015 and 2040, associated with large increases in P removal at wastewater treatment works by 2040 relative to modest reductions in mains water leakage. Further research is required to understand the fate of MWL-P in the environment and the role of other public water supply processes on macronutrient sources and sinks. Future research and management programmes should more fully consider MWL-P and its seasonal dynamics, alongside the likely impacts of this source of P on water quality.

Keywords

Graphical Abstract
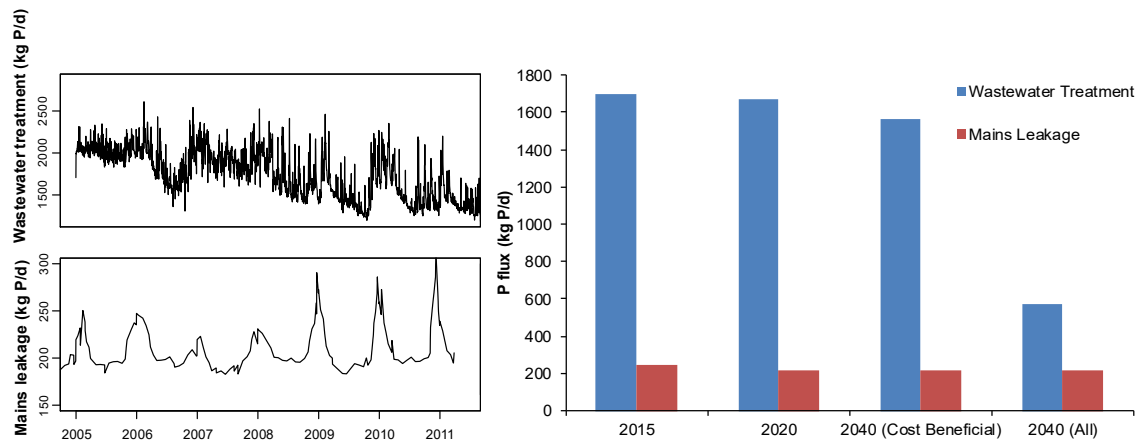
Highlights

- Seasonality + scenarios in P fluxes from mains water leakage (MWL-P) quantified

- MWL-P compared to wastewater P flux (WWT-P) and catchment P export

- Winter burst MWL-P >150% of spring/autumn flux, equal to up to 20% of winter WWT-P

- MWL-P/WWT-P ratio predicted to increase to 38% by 2040 due to WWT P removal

- MWL-P flux and seasonality should be considered in future P research and management

3.1 Introduction

Eutrophication associated with phosphorus (P) export from agricultural land and with wastewater treatment effluent is a well-known cause of water quality impairment (Elser et al., 2007; Hilton et al., 2006; Vollenweider, 1968), that can result in harmful algal blooms, fish kills and adverse impacts on animal and human health (Funari and Testai, 2008). Effluent from wastewater treatment works has been recognised as a major source of P at the global scale (Morée et al., 2013) which has been shown to impair water quality in rivers in Europe (Jarvie et al., 2006), Asia (Li et al., 2015), and the USA (Dubrovsky et al., 2010). In the UK in 2006, P fluxes from wastewater effluent have been estimated to account for 78% of annual river P loads (White and Hammond, 2009). The implementation of the Urban Wastewater Treatment Directive (European Union, 1991b) resulted in substantial decreases in P loads from UK wastewater treatment works (WWT-P), leading to large decreases in fluvial P fluxes. For example, in 2015, fluvial fluxes of P in England and Wales were estimated to have declined to less than 50% of 1974 fluxes (Worrall et al., 2015b).

In response to the challenges of eutrophication associated with macronutrient pollution, some workers have suggested the development of "integrated nutrient management strategies" (Grizzetti et al., 2015), which consider all macronutrient processes (sources, sinks, stores and time lags) in a catchment. Such approaches are in their infancy, and there are substantial gaps in our knowledge which currently limit implementation of integrated nutrient management approaches. Recent studies have shown that in catchments with a large proportion of urban landcover, public water supply processes may alter macronutrient cycles. In particular, leakage of P added to mains water (MWL-P) as phosphate has been shown to be a potentially important but previously largely overlooked source of P within the environment (Gooddy et al., 2017). Phosphate is added to mains water to reduce plumbosolvency (Hayes, 2010), with

the risks associated with lead in drinking water derived from pipework being a public health concern (Edwards et al., 2009). Lead consumption in humans has been associated with cognitive development problems in children (Bellinger et al., 1987) as well as increased risk of heart disease and stroke (Pocock et al., 1988). Phosphate is added to mains water to convert lead carbonate to lead phosphate. Lead phosphate is an order of magnitude less soluble than lead carbonate and results in the formation of lead phosphate precipitates on internal pipe surfaces (Hayes, 2010). In the UK it is estimated that >95% of water supplies are dosed with phosphate (Chartered Institute for Water and Environmental Management, 2011). In the USA, over half of supplies are dosed (Dodrill and Edwards, 1995). Dosing achieves final P concentrations in tap water that are estimated to be between 700 – 1900 µg P/L (UK Water Industry Research Ltd, 2012), with phosphate dosing having been a highly successful engineering solution to reduce lead concentrations in drinking water. For example, in 2011, 99.0% of random tap water samples in England and Wales met the drinking water limit of 10 µg Pb/L (Chartered Institute for Water and Environmental Management, 2011).

Leakage of mains water is a global challenge, with the cost of non-revenue water (leakage and unbilled consumption) estimated to be $14 billion per year (World Bank, 2006). National-scale leakage rates in England and Wales are reported to be up to 25% of the water that enters the distribution network and water companies plan future leakage rates over a 25-year planning horizon (2015-2040). Leakage of phosphate-dosed mains water as a potentially important source of P in the environment was first hypothesised by Holman et al. (2008). Gooddy et al. (2015) made the first quantification of this flux on an annual basis for England and Wales, which was subsequently refined by Ascott et al. (2016a).

However, understanding the temporal variability of MWL-P is also important, because biological impacts of P in aquatic ecosystems also show temporal variability, with autotrophic

biomass growth occurring in many systems primarily during spring (March, April, May) and early summer (June, July, August) (Bowes et al., 2012a). A number of studies (Birek et al., 2014; Cocks and Oakes, 2011; UK Water Industry Research Ltd, 2007; UK Water Industry Research Ltd, 2013) have highlighted seasonal dynamics in leakage of water from mains supplies. Higher rates of both bursts and low-level continuous "invisible" leakage occur during winter (December, January, February), due to pipe contraction and expansion. However, work on P to date has only quantified the annual flux of P from mains water leakage and the temporal dynamics of this source are poorly constrained. Whilst substantial reductions in WWT-P loads to rivers have been achieved (Worrall et al., 2015b), elevated P concentrations remain a concern, with 40% of the water bodies in England not achieving "good status" under the Water Framework Directive (European Union, 2000) due to high reactive P concentrations (Environment Agency, 2015). Consequently, in England and Wales, substantial further investment in wastewater treatment is planned to 2020 with an estimated total expenditure of £2.1 billion (Global Water Intel, 2014). Similar programmes exist internationally, for example in the USA (Sewage World, 2016) and across Europe (Water Technology, 2016). In parallel, water companies continue to reduce leakage based on water saving drivers, which will in turn reduce MWL-P fluxes. Despite these programmes, no estimates of how the relative contributions of MWL-P and WWT-P to the environment may change in the future have been made. If integrated approaches to managing macronutrient pollution are to be developed, and the impacts of MWL-P reduced, it is essential that the temporal dynamics of MWL-P and potential future changes in fluxes from this source of P are better constrained. The research reported here was undertaken to examine the following hypotheses:

1. MWL-P fluxes show seasonal trends, with increased fluxes in winter associated with increased bursts and invisible leakage

2. Seasonality in MWL-P fluxes can be distinguished from temporal variability in other P sources such as wastewater treatment works effluent

3. The relative importance of MWL-P fluxes will increase in the future, as WWT-P fluxes decrease due to improvements in tertiary treatment.

Using the River Thames, a large lowland catchment in the UK, as an exemplar, we tested these hypotheses by deriving historic, daily MWL-P, WWT-P and riverine P fluxes. Subsequently we validated this novel approach by comparing our derived annual fluxes of P from MWL and WWT sources to fluxes reported in previous studies. We then undertook time series analysis using multiple linear regression modelling to develop an improved understanding of the temporal dynamics and the processes controlling MWL-P, WWT-P and riverine P fluxes. Further, we derived future scenarios for MWL-P and WWT-P, based on 25 year plans for leakage reduction and WWT-P removal respectively as published by the UK environmental regulator and water companies. Finally, we provide a summary of key research priorities in the context of MWL-P, and consider how to manage this source of P across a range of different hydro-socioeconomic settings.

3.2   Materials and Methods

3.2.1   Study area

We quantified daily MWL-P, WWT-P and riverine P fluxes for the non-tidal Thames catchment (Figure 3.1). The Thames is a relatively large (9948 km^2) lowland catchment in southern England. The catchment is predominantly underlain by the Cretaceous Chalk, with Oolitic limestones at the head of the catchment and areas of low permeability clays around Oxford and London. Mean annual rainfall in the catchment at Oxford is 745 mm (Marsh and Hannaford, 2008). Although the catchment is relatively rural, with approximately 45% of land classified as arable (Fuller et al., 2013), there are also a number of major urban areas (London, Oxford, Reading) resulting in a high catchment population density (960 people/km^2 (Merrett,

2007) and relatively small agricultural P losses (<10% of all total P sources (White and Hammond, 2009)).

Water supply in the catchment is provided by four different water companies (Thames Water, Affinity Water, Sutton and East Surrey Water and South East Water) which operate across a total of 10 largely self-contained water resource zones (WRZs, Environment Agency (2012)). Each individual water company reports annual leakage rates. Leakage rates are reported to be high, reaching up to 26% of water input to the distribution network (Committee on Climate Change, 2015). The catchment has been subject to previous research to estimate the annual contribution of MWL-P and WWT-P to the River Thames (Ascott et al., 2016a; Gooddy et al., 2017), showing that approximately 30% of the MWL-P flux in England and Wales was derived from the river basin district in which the non-tidal Thames catchment is located. Wastewater treatment occurs throughout the catchment and 137 water company wastewater treatment works serving > 2000 population equivalents (p.e) are present. Since the late 1990s, P fluxes from WWTs have been reduced in the catchment through the introduction of tertiary treatment, primarily driven by the EU Urban Waste Water Treatment Directive (Kinniburgh and Barnett, 2010; Powers et al., 2016). Consequently, P concentrations in the River Thames fell by approximately 90% between 1992 and 2005 (Kinniburgh and Barnett, 2010). Despite this, there is scant evidence that eutrophication risk in the Thames has reduced (Bowes et al., 2014), with a number of rivers in the catchment exhibiting excessive phytoplankton biomass and P concentrations above those at which the growth of autotrophs can be expected (> 80 µg SRP/l, Bowes et al. (2012b)).
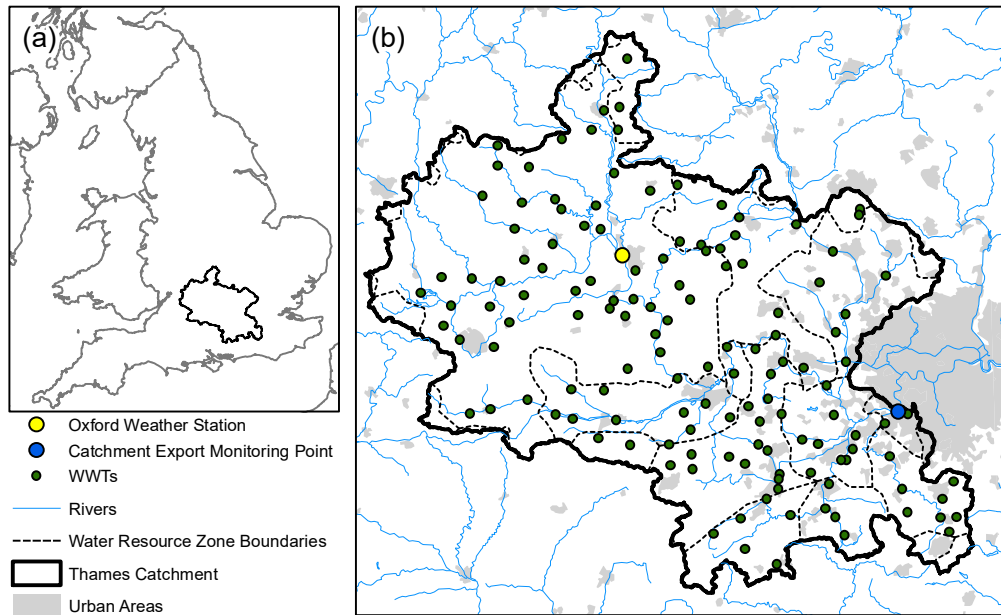
Figure 3.1 Location of the non-tidal Thames catchment within England (a) and the water resource zones, wastewater treatment works serving > 2000 p.e, catchment export monitoring point and the Oxford weather station within the catchment (b). Contains Ordnance Survey data © Crown copyright and database right (2017).

3.2.2   P flux time series derivation and analysis

3.2.2.1   Data sources

Table 3.1 summarises the data sources used to derive daily time series of MWL-P, WWT-P and riverine P fluxes in this study for the period 2001 - 2011. MWL-P was estimated based on published leakage rates and estimates of P concentrations in drinking water. Water quality sampling of WWT discharges and the River Thames occurs at a much lower frequency (around every 10 days to monthly) in comparison to the daily flow data that are available. Consequently, to derive daily WWT-P and riverine P fluxes, missing concentration data were estimated using concentration-flow relationships, as detailed in section 3.2.2.3.

Table 3.1 Data sources used to derive daily time series of MWL-P, WWT-P and riverine P fluxes for 2001 - 2011.

Flux	Data	Time period	Frequency	Units	Source
MWL-P	WRZ level leakage rates for WRZs in non-tidal Thames catchment	2011 - 2013	Annual	ML/day	WRMP tables
	Leakage rates for Thames Water	2001 - 2011	Daily	ML/day	Cocks and Oakes (2011)
	PO_4-P dosing concentration	2001 - 2011	Annual	mg P/L	Comber et al. (2011)
	PO_4-P dosing extent	2001 - 2011	Annual	-	Hayes et al. (2008), Chartered Institute for Water and Environmental Management (2011)
Riverine P	PO_4-P concentration for Thames at Teddington	2000 - 2015	Monthly	mg P/L	Environment Agency
	Flows for the Thames at Teddington	2000 - 2015	Daily	m³/s	
WWT-P	PO_4-P WWT discharge concentrations	2005 - 2011	Variable (mean frequency = 10 days, median frequency = 27 days)	mg P/L	Environment Agency
	WWT discharge flows	2005 - 2011	Daily	m³/s	

3.2.2.2   MWL-P

Annual water resource zone level leakage rates (in ML/day) for 2011-2013 were extracted from water resources planning tables available on water company websites (Affinity Water, 2014; Southeast Water, 2014; Sutton and East Surrey Water, 2014; Thames Water, 2014). Daily leakage data for 2001 to 2011 (as reported by Cocks and Oakes (2011)) for the whole Thames Water supply area were used as the basis for estimating the MWL-P flux. The leakage data reported by Cocks and Oakes (2011) is the only publicly-available sub-annual leakage data for both the catchment and the UK. The Thames Water supply area covers 76% of the non-tidal Thames catchment that is the focus for the research reported here, but also includes London in the downstream tidal Thames catchment. To account for this discrepancy, we calculated the ratio of the annual leakage rates in the water resources planning tables for the whole Thames Water supply area versus the 10 WRZs in the non-tidal Thames catchment. We

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then used this ratio to scale the daily Thames Water leakage time series (Cocks and Oakes, 2011) to provide a daily leakage time series for the non-tidal Thames catchment to Teddington for the same period. Over the period 2001 to 2011, the extent of P dosing of mains water and the concentrations used have increased. Based on published reports of dosing concentrations (Comber et al., 2011) and the spatial extent of dosing (Chartered Institute for Water and Environmental Management, 2011; Hayes et al., 2008; UK Water Industry Research Ltd, 2012), we used the conservative approach adopted by Gooddy et al. (2017) to estimate the historic changes in P dosing concentrations and extents within the non-tidal Thames catchment.

3.2.2.3 Riverine P and WWT-P flux derivation, flux comparison and time series analysis

Riverine P flux derivation

The daily net export of P (2001-2016) from the catchment was derived using observed orthophosphate-P (PO_4-P) concentration and daily flow data for the River Thames at Teddington (Figure 3.1). To infill missing concentration data to derive a daily P flux time series, we first undertook single change point detection to determine whether there was a statistically significant change in the mean and variance of the concentration time series associated with historic reductions in P loads from WWTs (Kinniburgh and Barnett, 2010). We used the univariate informational approach for a single change in mean and variance detailed by Chen and Gupta (2011). The method tests the hypothesis H_0: no change point, against H_1: there is a change point at position k. Maximum likelihood estimation is used to derive regression models for H_0 (the full time series with no change) against H_1 for all possible positions of k. For all possible positions of k, the Schwarz Information Criterion (SIC) is used to determine if removing the change point results in information loss. H_0 is rejected when $SIC(H_0) > min(SIC(k)) + c_\alpha$, where c_α is a critical value based on the asymptotic null distribution of the test statistic used to ensure the location of the change point is statistically significant. When H_0 is rejected, the change point k is located where $min(SIC(k))$. We used this method in

R using the package "changepoint", implemented as the "at most one changepoint" method (Killick and Eckley, 2014) and used using an asymptotic penalty value (α in Chen and Gupta (2011)) of 0.05 (Chen and Gupta, 2011; Killick and Eckley, 2014). Within each of the datasets divided by the change point, we examined whether concentration-flow relationships also change associated with season and flow conditions (Moatar et al., 2017; Zhang, 2018; Zhang et al., 2016).   No significant differences were found under different season and flow conditions, and so single concentration-flow relationships before and after any change points were used for each following the non-linear least-squares regression approach of Bowes et al. (2014):

$$C = AQ^B \qquad\qquad (3.1)$$

Where C is concentration (mg P/L) and Q is flow (m^3/s). A and B are constants with no physical meaning that are empirically derived by automated fitting of the regression model of equation 3.1 in R. The derived relationships were used to estimate P concentrations where data were missing before and after the change point. The complete concentration and flow time series was then used to derive a daily P flux time series.

Wastewater Treatment Works P Flux Estimation

Wastewater treatment works in the Thames catchment fall into two categories: (1) monitored sites where flows are > 50m^3/d; and (2) unmonitored, small sites with flows <50m^3/d. Outputs from the Thames Source Apportionment Geographical Information Systems (SAGIS, Comber et al. (2013)) tool using population equivalent data and concentration estimates have shown that small unmonitored sites contribute <1% of the total WWT-P load to the River Thames. Consequently, these sites have not been considered further in the research reported here.

For the monitored WWT sites, daily flow monitoring data for 2005 – 2011 were used in conjunction with PO$_4$-P concentration data to derive daily P fluxes for each site. A similar

approach to that described above for the riverine P flux estimates was used for infilling of missing concentration data using concentration-flow relationships of the form of equation 3.1. The dates for implementation of P removal schemes at WWTs in the Thames catchment were provided by the environmental regulator for England. Where P removal schemes were implemented at a WWT during the study period, separate concentration-flow relationships were estimated for before and after implementation. Where no changes in treatment processes for P removal at WWTs occurred during the study period, a single concentration-flow relationship for the WWT was used. The derived daily P fluxes for each individual WWT were then summed to derive a total, daily catchment flux of WWT-P.

Flux comparison and time series analysis

To validate our daily estimates of MWL-P and WWT-P, we derived annual mean fluxes for each of these P sources and then compared these to previously published estimates of the same fluxes for the Thames catchment (Comber et al., 2013; Gooddy et al., 2017; Haygarth et al., 2014). We also calculated a daily time series of the ratio of MWL-P to WWT-P. The derived MWL-P, WWT-P and riverine P time series were initially compared by visual inspection to assess the timing and magnitude of peaks in fluxes. We then assessed whether there were statistically significant long term trends and changes in the variance in MWL-P and MWL-P/WWT-P ratios. Our data were non-normally distributed (Shapiro-Wilk test, $p < 0.01$), so we used the non-parametric Mann Kendall test (Pohlert, 2018) and a change point analysis using an asymptotic penalty value = 0.01 (Killick and Eckley, 2014).

To assess the control of cold weather events on temporal variability in MWL-P, we undertook correlation analyses using historic daily minimum temperature data for the Oxford weather

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station in the Thames catchment (Figure 3.1). We also quantified correlations between daily rainfall and daily WWT-P and daily riverine P loads to assess the role of short term rainfall events in controlling P fluxes. Finally, to determine how much of the variation in daily riverine P load could be explained by daily MWL-P and daily WWT-P, we developed parsimonious multiple linear regression models using (1) WWT-P only and (2) WWT-P + MWL-P as explanatory variables. To determine the impact of adding the MWL-P variable on model predictive power we initially compared the model results by visual inspection. We then compared the coefficient of determination between the two models and finally used a partial F-test (R Development Core Team, 2016). There is substantial uncertainty in the fate of MWL-P in the environment associated with the relative importance of different P retention (clay sorption, soil and sediment accumulation) and transport processes (groundwater, surface water and the sewer network) (Gooddy et al., 2017). In this context, our research does not aim to make a direct causal link between time series variability in WWT-P, MWL-P and riverine P fluxes. The purpose of the comparison of fluxes described here is threefold: (1) to provide indications of the relative contributions of these sources to the environment; (2) to improve understanding of the processes controlling temporal variability and seasonality in these sources; and (3) to improve understanding of the relationships between the sources.

3.2.3   Derivation of future scenarios of MWL-P and WWT-P

Scenarios for future reductions in both MWL-P and WWT-P were constructed on the basis of existing water company and environmental regulator investment plans. Planned leakage reductions for each of the 10 WRZs in the Thames catchment for 2015-2040 were extracted from water company water resource planning tables (Affinity Water, 2014; Southeast Water, 2014; Sutton and East Surrey Water, 2014; Thames Water, 2014). Estimates of future reductions in WWT-P were provided by the environmental regulator as new discharge permit limits for P (in mg P/L). In England and Wales investments in wastewater treatment are

planned on a five-year Asset Management Programme (AMP) cycle. Investments over 2015 – 2020 (Asset Management Programme 6 (AMP6)) are fully planned and costed. Further into the future, a provisional "long list" of improvements in WWTs that are potentially required in order to meet good ecological status in the catchment has been derived based on source apportionment modelling (Comber et al., 2013). This list has been subject to a cost benefit analysis which has divided sites into those at which enhanced P removal is cost beneficial and those at which this is not. In total, four WWT improvement scenarios were developed, as detailed below:

1. Baseline (2015)

2. AMP6 (2020) – planned and costed WWT improvements and leakage reduction programmes for 2015 – 2020

3. Cost beneficial planning period (2040a) – planned leakage reductions and cost beneficial WWT improvements for 2015 – 2040

4. Full planning period (2040b) – planned leakage reductions and all potential WWT improvements for 2015 – 2040

Scenarios were implemented by applying the new discharge permit limits for WWTs to the baseline observed concentration-flow data in 2015. Given the uncertainty in future WWT and leakage reduction beyond 2020, an annual average approach was used to derive annual fluxes from MWL-P and WWT-P in 2015, 2020 and the two 2040 scenarios.

3.3   Results

3.3.1   MWL-P flux estimation

Figure 3.2 shows the evolution of the MWL-P flux over the period 2001 to 2011 for the Thames catchment. Figure 3.2 (c) shows the total daily leakage (Cocks and Oakes, 2011) for 2001 – 2011 for Thames Water.   Over the period 2001 – 2011, the volume of leakage has declined due to water companies actively locating and fixing leaks in the distribution network. After accounting for this reduction, the leakage time series shows a relatively strong correlation at lag = 0 with daily minimum temperature (Pearson correlation, r = 0.63, p < 0.001). The time series shows a clear seasonal signal associated with increased bursts and invisible leakage in winter. The winters of 2009, 2010 and 2011 were particularly cold, with mean December temperatures 1.1, 2.0 and 4.8 degrees below long term average (1971-2000) respectively (Met Office, 2016). Cold winters resulted in large increases in leakage of up to 50% compared to the preceding autumn months (September, October, November). In summer (June, July, August), small increases of up to 6% compared to spring (March, April, May) values were also observed, which has been attributed to soil expansion and contraction resulting in pipe failure (Cocks and Oakes, 2011). Figure 3.2 (d) shows the estimated daily flux of MWL-P for 2001-2011 for the Thames catchment. Whilst the volumetric leakage rate (Figure 3.2 (c)) has reduced substantially, increases in the spatial extent of dosing and in phosphate dosing concentrations counteract these reductions, resulting in significant (Mann Kendall trend test, p < 0.001) net increases in MWL-P fluxes of 300% over the period 2001 to 2011. Seasonality increases through time with a significant change in variance identified at 08/09/2008 (single change point detection using an asymptotic penalty value = 0.01) and the ratio of daily annual maximum/minimum MWL-P rates increasing from 130% in 2002 – 2008 to 150% in 2008 – 2011.
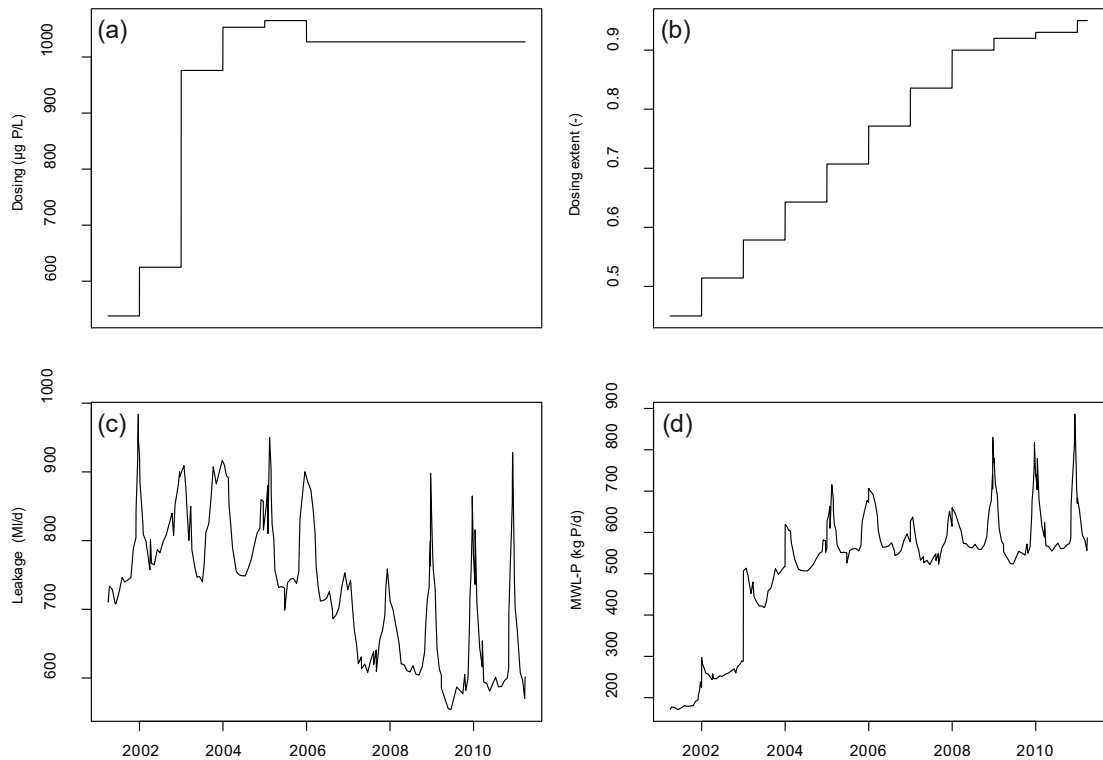
Figure 3.2: Estimates of P dosing concentrations (a) and extents (b) for 2001 – 2011, daily leakage rates reported by Cocks and Oakes (2011) (c), and the derived MWL-P flux (d).

3.3.2 WWT-P flux estimation

Figure 3.3 reports data related to the WWT-P flux for the Thames catchment. Substantial decreases in P concentration in WWT effluents occurred between 2005 and 2007, associated with the introduction of P removal technology. From March 2008 to 2012, no significant further P removal was implemented in the catchment. Consequently, effluent P concentrations have been relatively stable and the frequency of P monitoring reduced. The slight increase (5.4 to 5.6 mg P/L) in effluent P concentrations over this period may reflect an overall decrease in P removal efficiency in existing WWTs due to changes in plant operation and influent P loads (Tchobanoglous and Burton, 2013). There is considerable variation in the WWT flows (Figure 3.3 (a)) particularly during high flow periods in winter associated with rainfall events when flows can be up to twice as large as dry weather flows (DWF). The derived WWT-P flux (Figure 3.3 (c)) reflects both long term changes in P concentrations following

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investment in P removal technologies and short term variability in WWT flows associated with rainfall events.
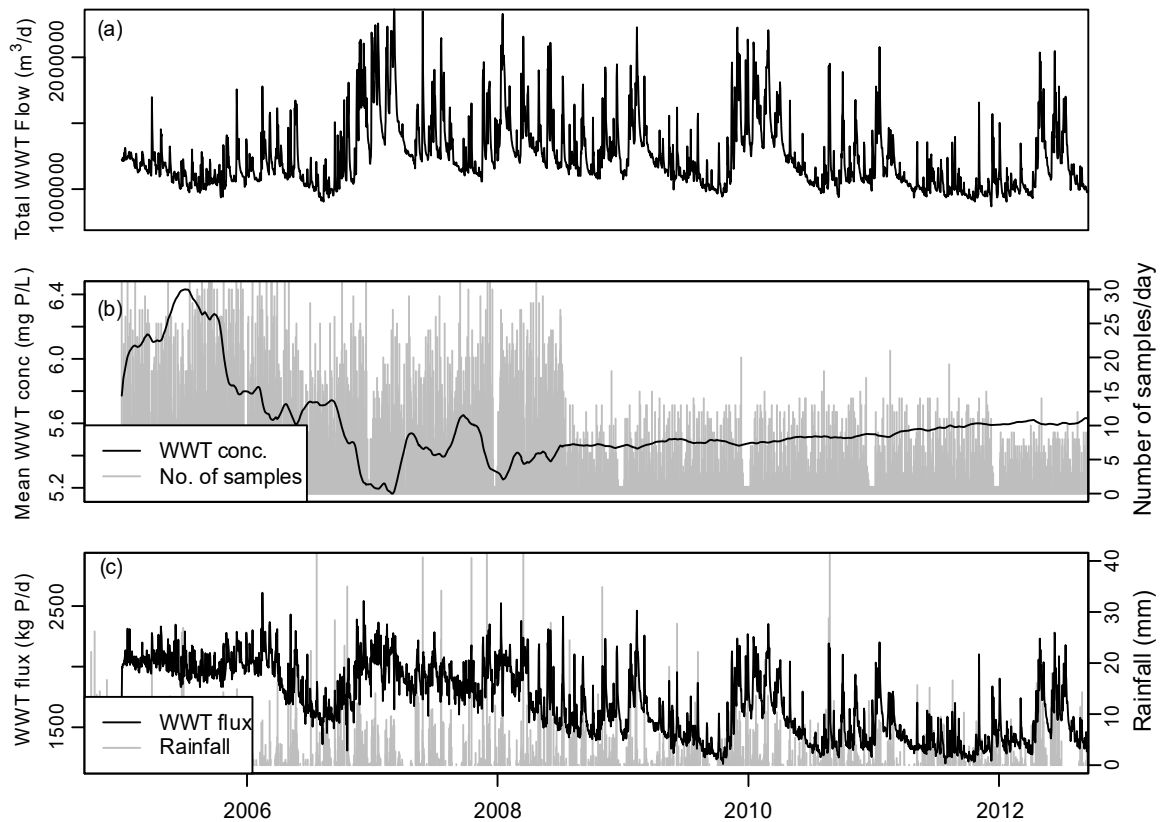
Figure 3.3 Total WWT flows (a), mean daily P concentrations and number of samples (b) and the derived WWT-P flux and rainfall time series for Oxford (c)

3.3.3   Flux comparison

Table 3.2 reports the annual mean MWL-P and WWT-P fluxes derived in the research reported here and in previous studies of the Thames catchment. The annual estimates of MWL-P derived from the daily flux time series in this study are within the range of values reported by Gooddy et al. (2017) who used annual average WRZ-level leakage rates directly and considered a range of different plausible historic mains water dosing extents. WWT-P fluxes broadly corroborate previous findings reported by Haygarth et al. (2014) and Comber et al. (2013). Fluxes estimated in the current study for 2006-2008 are somewhat higher (29%) than estimates made using observed soluble reactive P concentrations in WWT discharges in

conjunction with source apportionment tools (Comber et al., 2013). Fluxes from the source apportionment modelling were adjusted by the UK environmental regulator (Environment Agency, 2016b) to take into account new and enhanced P removal (and hence lower WWT-P fluxes) which is the likely cause of this discrepancy. Our estimates are also larger (50%) than those calculated by Haygarth et al. (2014), who used a simple approach based on population equivalents and assumed total P concentrations to estimate WWT-P flux for the catchment.

Table 3.2 Annual mean MWL-P and WWT-P fluxes derived in this study and previous studies

Period	MWL-P (kt P/year)		WWT-P (kt P/year)		
	Gooddy et al. 2017	This study	Haygarth et al. 2014	Comber et al. 2013	This study
2001	0.019 - 0.029	0.025	1.18	-	-
2006-2008	-		-	0.52	0.67
2011	0.068 - 0.089	0.082	0.38	-	0.58

3.3.4   Flux comparison between MWL-P and WWT-P with Riverine P Export

3.3.4.1   Riverine P flux estimation

Figure 3.4 shows the results of the change point detection analysis and the derived concentration-flow relationships before and after the change point for the River Thames at Teddington. A decrease in the mean and variance of riverine phosphate concentrations was observed in 2006, associated with reductions in P loads from WWTs. For the period 2000 – 2006, the concentration-flow relationship shows decreases in concentrations with increasing flow, associated with dilution of WWT inputs. This corroborates concentration flow relationships derived by Bowes et al. (2014) in the Thames basin. From 2006 to 2015, the variability in concentration with flow is substantially reduced. Between 0 and 100 m^3/d decreases in concentration with increasing flow are observed, associated with dilution of point source P inputs. However, from 100 to 500 m^3/d, there is limited change in concentration with

increasing flow which reflects a balance of both point source dilution and mobilisation of diffuse P sources across this range of discharges.
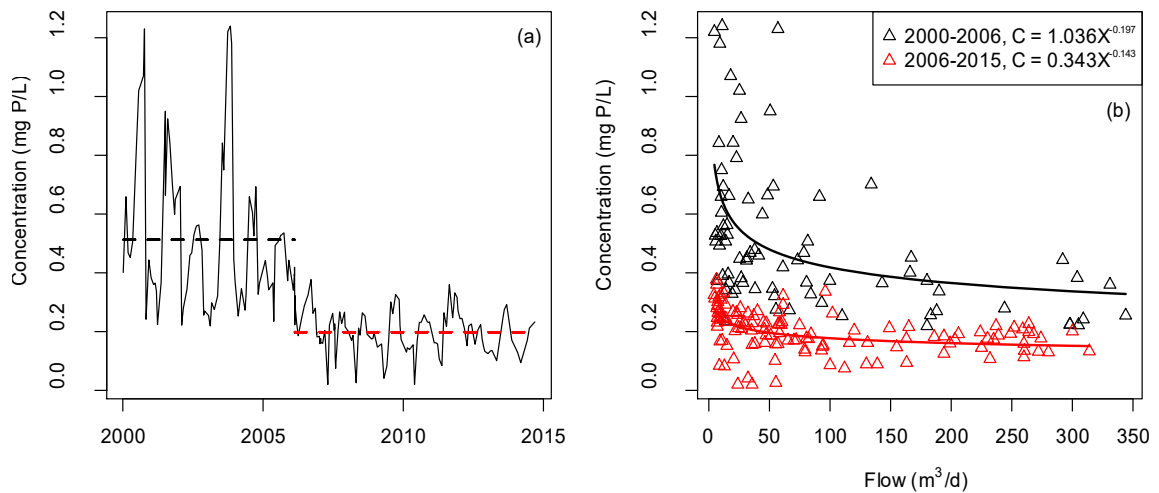
Figure 3.4 Observed phosphate concentrations (mg P/L) in the River Thames at Teddington and mean concentrations (dashed line) before and after the change point (a) and concentration-flow relationships for each of these periods (b).

3.3.4.2 Comparison of MWL-P, WWT-P and riverine P fluxes

Figure 3.5 shows the ratio of MWL-P and WWT-P fluxes ("MWL-P/WWT-P") and their relationship with P flux in the River Thames at Teddington. From 2005 to 2011 there is a significant trend in MWL-P/WWT-P (Mann-Kendall trend test, $p < 0.001$). The ratio of MWL-P to WWT-P increases from 7-10 in 2005 to 15% in 2011. This increase is due to two factors: (1) an increase in the extent of mains water P dosing through the period, as shown in Figure 3.2; and (2) a decrease in WWT-P loads due to investment in P removal technology.

Seasonality in the ratio of MWL-P to WWT-P increases through the period, due to the increased extent of dosing (Figure 3.2 (b)). There is a significant increase in the variance of MWL-P/WWT-P from 22/11/2008 onwards (single change point detection using an asymptotic penalty value = 0.01 (Chen and Gupta, 2011; Killick and Eckley, 2014)). Peaks in MWL-P/WWT-P of up to 20% occur in the winters of 2009 and 2011 in comparison to values around 10% in 2005-2008. Figure 3.5 (a) and (d) show the daily WWT-P flux and catchment P export. There

are weak but significant correlations between WWT-P and daily rainfall (Pearson correlation, r = 0.23, p < 0.001) and catchment export and daily rainfall (Pearson correlation, r = 0.18, p < 0.001). Figure 3.6 and Figure 3.7 show observed and modelled riverine P fluxes using regression models considering: (1) WWT-P only; and (2) WWT-P and MWL-P together. Figure 3.8 shows modelled and observed riverine P fluxes in detail for winter months from 2005 to 2011. Adding MWL-P as a predictor variable increases the modelled riverine P flux associated with increased MWL-P fluxes in winter. This is particularly the case in the winters of 2008/9, 2009/10 and 2010/11 where increases in winter leakage were particularly large (Figure 3.2). The multiple linear regression model used to determine whether the riverine P load can be explained by MWL-P and WWT-P resulted in a relatively modest coefficient of determination (adjusted R^2 = 0.41). The MLR model suggested that WWT-P and MWL-P are both significant explanatory variables (p < 0.001). Removing MWL-P from the regression significantly reduced the predictive power of the model (F = 242, p < 0.001, for partial F-test between MLR models considering WWT-P only and WWT-P + MWL-P) resulting in a lower coefficient of determination (adjusted R^2 = 0.33).
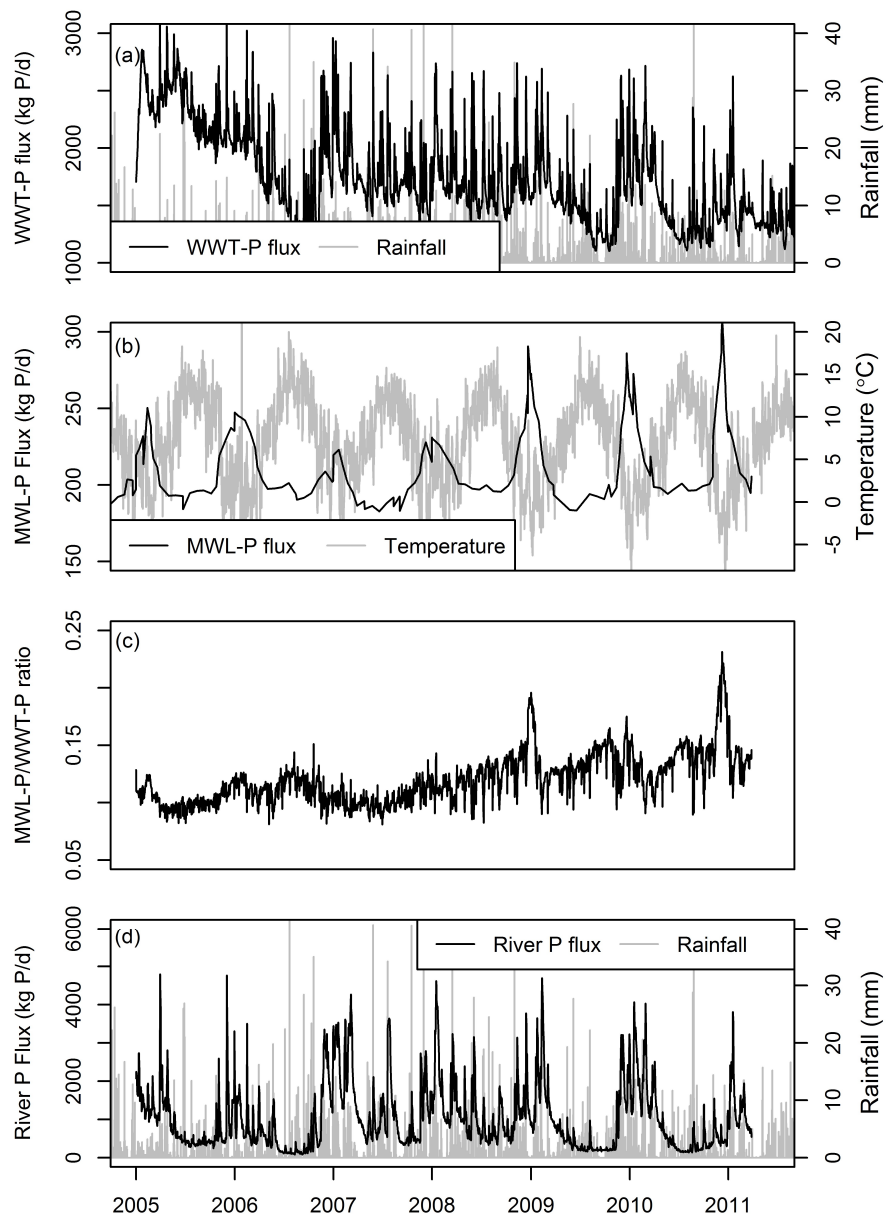
Figure 3.5 Daily fluxes of WWT-P and rainfall (a), MWL-P and temperature (b) for the Thames catchment, the ratio of MWL-P to WWT-P (c) and the riverine flux of P out of the catchment and rainfall (d)
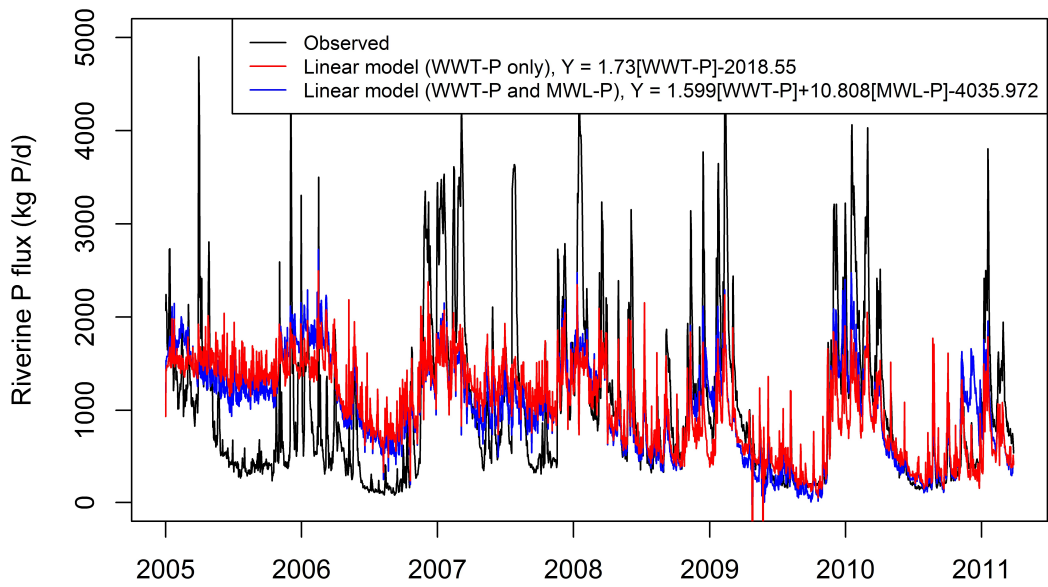
Figure 3.6: Observed (black) and modelled riverine P fluxes for the export of the Thames catchment using the MLR model considering WWT-P only (blue) and WWT-P and MWL-P (red)
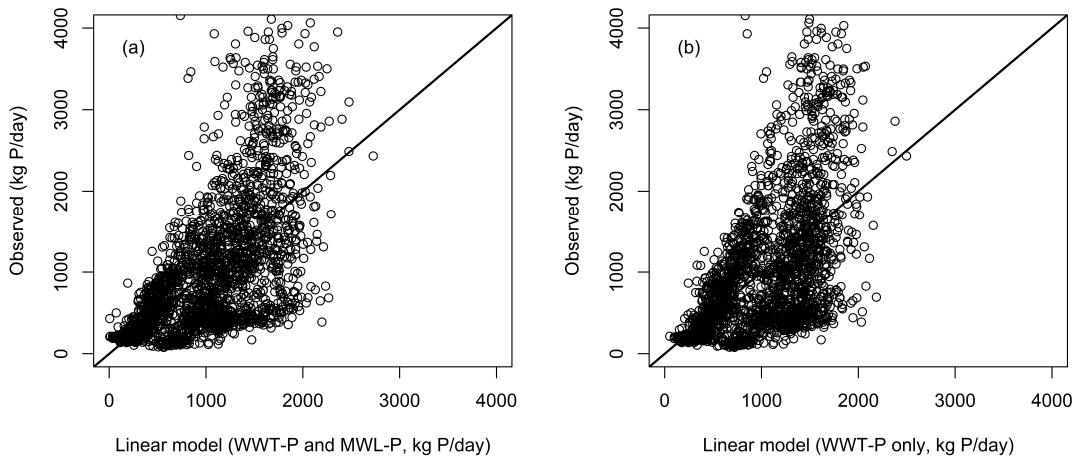
Figure 3.7 Observed and modelled riverine P fluxes for linear model considering WWT-P and MWL-P (a) and WWT-P only (b)

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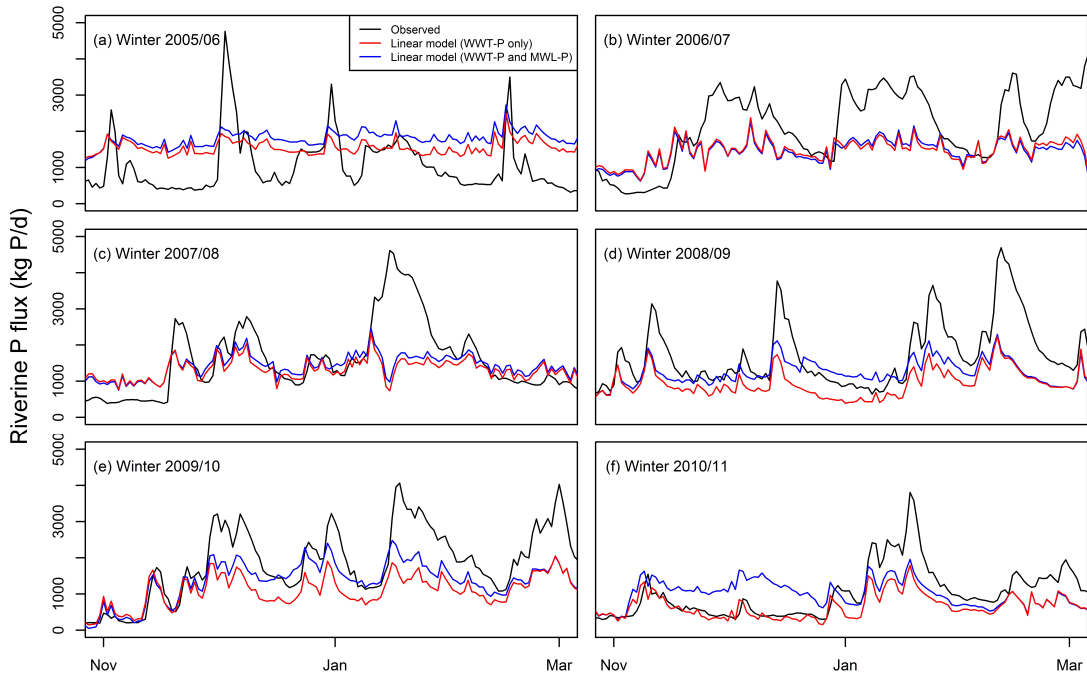
Figure 3.8 Riverine P flux time series for winter months for 2005/06 (a) to 2010/12 (f)

3.3.5   Future loads of MWL-P and WWT-P

Table 3.3 reports the derived future MWL-P and WWT-P loads for annual average conditions. WWT-P fluxes are predicted to decrease to 2020 associated with the AMP6 programme, with further decreases predicted to 2040. When considering all WWT improvements to 2040, a total decrease in WWT-P flux of 0.41 kt P/year is estimated. Small reductions in MWL-P of 0.01 kt P/year are predicted to occur to 2040. In total, the reduction in MWL-P loading is approximately 2% of the reduction in WWT-P. Consequently, the ratio of MWL-P to WWT-P is predicted to increase from 15% to 38% under average conditions.

Table 3.3 Future MWL-P and WWT-P loadings

Scenario Information				Fluxes (kt P/year)		MWL-P/WWT-P (%)
Scenario Name	Time Slice	WWT Improvements	MWL Improvements	MWL-P	WWT-P	
Baseline	2015	-	-	0.09	0.62	14.52
AMP6 Programme	2020	AMP6 Programme	AMP6 Leakage Programme	0.08	0.61	13.11
2040 Plan (Cost Beneficial)	2040	CBA "Long List"	2040 Plan Leakage Programme	0.08	0.57	14.04
2040 Plans (All sites)		Full "Long List"		0.08	0.21	38.10

3.4 Discussion

3.4.1 Seasonal dynamics and relative importance of MWL-P and WWT-P to riverine P loads

Estimates of MWL-P and WWT-P fluxes for the Thames catchment made in the research reported here illustrate that MWL-P is a potentially important source of P in the environment which has so far been largely overlooked in P source apportionment and management strategies. In particular, the distinct seasonal signal (Figure 3.2) in MWL-P results in higher ratios of MWL-P to WWT-P through the winter periods. The seasonality in MWL-P that was hypothesized in section 3.1 has not been reported to date. This research therefore represents a novel development in our understanding of this particular P source, and contributes to our overall understanding of the impact of public water supply processes on P cycling required for integrated nutrient management approaches.

The processes controlling seasonality in MWL-P are complex. Whilst correlations between minimum air temperatures and MWL-P are reported in this paper, it should be noted that other non-meteorological processes also have a potentially large impact on MWL-P variability. Cold weather is the predominant control on the timing and magnitude of the initial outbreak of water mains bursts during a winter leakage event. As temperatures increase, there is likely to be some natural reduction in invisible leakage associated with pipe expansion. However, rather than any meteorological factor, the majority of the reduction in leakage after an event is the result of active repairs to burst water mains (UK Water Industry Research Ltd, 2007). This combination of meteorological and engineering processes is likely to be broadly applicable in developed countries with significant temperature fluctuations and consequently a similar seasonality in MWL-P would be expected. Phosphate dosing is starting to be developed in other temperate countries (e.g. Ireland (Irish Water, 2015; Mockler et al., 2017)).

In these countries, as dosing extents and concentrations increase, an increase in the both the absolute magnitude and seasonality of MWL-P fluxes, as reported in Figure 3.2, would be anticipated.

Rainfall events have an impact on the observed correlations between WWT-P, MWL-P and riverine P fluxes. Winter rainfall events cause short term increases in both WWT-P and riverine P fluxes but through different processes. High rainfall results in increased inflows to wastewater treatment works. There may be some dilution of influent P during these events due to increased contributions from runoff and groundwater infiltration (De Bénédittis and Bertrand-Krajewski, 2005), but these are unlikely to be captured in the flux estimates due to the paucity of concentration measurements. Influent flows below the peak storm flow treatment design criteria (typically 3 x DWF (Saul et al., 2007)) will be treated and discharged to watercourses. Excess flows will be temporarily diverted to storm tanks and flows > 6 x DWF will be directly discharged to rivers. Winter rainfall events can cause increases in riverine P fluxes through a number of processes. Increased agricultural runoff, in-stream mobilisation of P associated with sediments, combined sewer overflows (CSOs) and wastewater treatment works discharges can all contribute to increasing P loads during winter storm events (Bowes et al., 2008; Jarvie et al., 2006). These processes controlling short term temporal changes in both riverine P fluxes and WWT-P fluxes mask any correlation between MWL-P and riverine P.

In the context of MWL-P, there is some uncertainty in the extent of P dosing and the concentrations used. In this study, we used a conservative approach to estimate historic changes in P dosing concentrations and extents. It is plausible, however, that dosing extents and concentrations may have been higher than estimated here, which would result in greater flux seasonality. Just as water companies publically release water resource planning data, making historic P concentrations and dosing extents available would be beneficial to refining

MWL-P estimates. Given the potential importance of this flux, assessment of MWL-P using observed leakage and P concentration data at the local scale using district metered area (DMA) data could provide important new insights. Further, the uncertainty surrounding the ultimate fate of MWL-P following leakage is substantial. As discussed previously, comparisons with WWT-P and riverine P fluxes such as those presented in Figure 3.5 are beneficial as they provide indications of the relative contribution of different sources to the environment. It is likely that MWL-P makes some direct contribution to riverine P fluxes, but the relative importance of groundwater, surface water and the sewer network as pathways for MWL-P are largely unknown at this time. Moreover, the spring and summer growing period is often perceived to be the most biologically-critical period in many receiving waters (Jarvie et al., 2006), meaning that winter peaks in MWL-P which do directly contribute to riverine P loads may have a limited immediate impact on riverine ecosystems. However, there are likely to be time lags between the flux of P from a water mains leak and this flux reaching a river, with a range of transit times depending on catchment size, transport pathway and change in P concentration along the pathway. Consequently, it is plausible that winter peaks in leakage of P from water mains only reach a river network in more biologically-critical periods of the year. Long transit times are likely in catchments with a thick unsaturated zone and long groundwater flow paths. In these catchments it is plausible that MWL-P contributes to legacy P stores in groundwater (Holman et al., 2008) as has been observed for nitrate (Howden et al., 2011; Worrall et al., 2015a). River sediments can also accumulate P (Sharpley et al., 2013), with time lags of < 1 year associated with in-stream P remobilisation during high river flow events. These in-stream accumulation-remobilisation processes will result in further lags between MWL-P that reaches a river and P riverine exports. Whilst not considered in this study, agriculture remains a considerable P source to the environment in many catchments (White and Hammond, 2009) and should clearly be accounted for in future P management strategies. Much of the likely temporal dynamics of the fate of MWL-P (higher winter fluxes with potential

catchment legacy stores and lags) are analogous to the fate of nonpoint P sources such as agriculture (Sharpley, 2016). Improved understanding of the fate of these P sources could be developed through high frequency riverine P monitoring and application of data driven modelling tools (e.g. Chen and Chau (2016); Olyaie et al. (2015); Taormina et al. (2015); Wang et al. (2014)). The anticipated impact of measures to reduce P fluxes from both mains leakage and agriculture should be tempered with knowledge that catchment lags and P sources from existing nonpoint legacy P stores may significantly delay any water quality improvements.

3.4.2 MWL-P and WWT-P Scenarios: Implications for drinking water and wastewater management

Table 3.3 illustrates that future WWT-P reductions are likely to be substantially larger than MWL-P reductions, and consequently this will result in a greater relative contribution of MWL-P to P loads delivered into the environment in the future. This change in the relative contributions of P sources has not been quantified to date and is a novel contribution of this study. Whilst policy responses to minimise MWL-P were previously discussed by Gooddy et al. (2017), the implications of future increases in the relative contribution of MWL-P have not been considered to date. Such increases are likely to occur in countries where P dosing is currently being considered in future lead reduction strategies (e.g. Ireland (Irish Water, 2015) and South Korea (Lee, pers. comm.)). In these countries, the potential impacts of MWL-P should be considered in environmental impact assessments. Moreover, in less developed countries, current wastewater P removal and mains water P dosing may be less extensive. As both environmental and public health standards improve, it is plausible that in these countries mains water P dosing and WWT P removal may increase substantially, resulting in increases in the relative importance of MWL-P.

A number of European countries have adopted policies that actively avoid phosphate dosing on environmental grounds (Chartered Institute for Water and Environmental Management, 2011). Countries such as the Netherlands undertake pH correction and centralized water softening to ensure lead concentrations are below the required standard (Hayes, 2012). P has been shown to be a limiting nutrient to biofilm growth in a number of different drinking water systems (Liu et al. (2016) and references therein) and concern has been raised historically that the presence of P in water mains (through dosing or otherwise) would result in increased bacterial counts in water mains (Miettinen et al., 1996). The current and future importance of MWL-P in comparison to other P sources identified in this study adds to the body of evidence to support policies that avoid phosphate dosing, where the extent of lead piping in the distribution network is small enough to safeguard human health without dosing.

Across these different hydro-socioeconomic settings, future management of MWL-P and WWT-P is likely to be a challenge. Both water utilities and environmental regulators have often historically been divided between clean water and wastewater (Ofwat, 2017). Within the clean water sector, the industry has often been further divided between drinking water quality (responsible for P dosing) and water resources management (responsible for leakage) (Deloitte, 2014). Moreover, regulatory drivers for changes in water management have typically addressed single issues (e.g. drinking water quality via the EU Drinking Water Directive (European Commision, 1998), environmental quality via the EU Water Framework Directive (European Union, 2000)), whereas addressing MWL-P requires policy interventions across multiple fields. Where P dosing and WWT P removal are in their infancy, water and environmental managers will need to engage stakeholders from across these disciplines at an early stage of development. Cross-discipline engagement will ensure that strategies for managing P sources to the environment consider both WWT-P and MWL-P, and that reductions in WWT-P are not offset by increases in MWL-P. Where these practices are already

well established, integration of MWL-P into leakage targets and catchment P permits may be an effective policy intervention (Gooddy et al., 2017). Adopting these strategies will ensure that P sources to the environment are managed effectively, whilst safeguarding human health.

3.4.3   Research priorities for nutrient fluxes associated with mains water leakage and public water supply

Based on the uncertainties highlighted above, there are a number of key research priorities which need to be addressed if MWL-P and its associated seasonality are to be effectively integrated into P management strategies. The fate of water following a leak is currently poorly understood. It can be hypothesised that the fate will vary depending on the type of leak as follows: (1) Visible winter bursts causing rapid transport to rivers, groundwater and sewers, (2) Invisible winter leakage with a greater recharge to groundwater, (3) Summer leakage associated with changes in soil moisture deficit (SMD) causing possible loss by evapotranspiration and to groundwater, (4) Background leakage with a slower transport and greater recharge to groundwater. Background leakage is likely to have the largest impact in the long term, because these leaks are relatively difficult to locate and stop relative to bursts (Edie, 2016; Lambert, 1994).

The fate of P within the subsurface following a leak adds further uncertainty. The pH of mains water is often increased compared to raw untreated waters (Flem et al., 2015) which will inhibit formation of iron and aluminium phosphate precipitates, resulting in increased P mobility. However, after release into the environment MWL-P has a wide range of potential fates (clay sorption, soil/sediment accumulation, and flow to rivers, groundwater or the sewer network). Depending on the time of year and the type of leak identified above, the fate of MWL-P may vary substantially. Visible winter bursts and invisible winter leakage not captured by the sewer network may result in rapid P transport to rivers and groundwater, potentially

accelerated by high rainfall events following cold weather. Summer leakage associated with changes in soil moisture and background leakage is likely to result in slow transport and potentially sorption and accumulation of P in soils. Understanding the relative importance of these different fates and lags in the hydrological system is essential if MWL-P is to be managed in the future.

Changes in seasonality of P fluxes have not been quantified in this study and should be considered in future research. Long term changes in intra-annual variability in MWL-P are likely to occur due to climate change. Climate projections (UKCP09 2080s, Medium emissions scenario) show increases in daily mean, maximum and minimum temperatures across the UK, with slightly greater increases in summer than winter. Whilst changes to annual precipitation total are predicted to be small, winter and summer precipitation are predicted to increase by up to 33% and decrease by up to 40% respectively (Met Office, 2010; Murphy et al., 2009). Warmer winters may reduce winter bursts, and warmer summers may increase leakage related to soil movement. Consequently, it is plausible that the seasonal component of MWL-P may become more bimodal, with peaks in both winter and summer. Differences in the temporal rainfall distribution are also likely to impact the fate of P within the wider catchment. Increased winter rainfall may result in more pronounced winter P flushing (Johnson et al., 2009). Interactions between climate change induced temperature and rainfall effects on P fluxes are likely to be complex and require further investigation.

More broadly, the importance of public water supply processes such as mains water leakage on macronutrient sources and sinks remains poorly constrained. Mains water leakage may also represent an important source of N to the environment (Lerner et al., 1999), although quantifications of this source are scant. Furthermore, abstraction and treatment of nitrate in public water supply may represent a considerable N sink term which has never been

estimated. Further research evaluating the importance of these processes on macronutrient budgets would be beneficial to support the development of integrated approaches to managing anthropogenic influences in N and P cycles.

3.5   Conclusions

This study has quantified seasonality and future scenarios of fluxes of P from mains water leakage (MWL-P) to the environment for the first time. MWL-P shows a strong seasonality, with peak fluxes during burst and leak events in winter > 150% of fluxes during other seasons. During peak events, MWL-P is equivalent to approximately 20% of P fluxes from wastewater treatment works (WWT-P). A moderate cross correlation between WWT-P and riverine P fluxes is observed as the short term temporal variations in both of these fluxes are the result of winter rainfall events. This masks any potential correlation between MWL-P and riverine P fluxes. A substantial increase in the ratio of MWL-P to WWT-P is predicted to 2040 associated with implementation of substantial wastewater P removal and minimal mains water leakage reduction. Further research is required to understand the fate of MWL-P in the environment, future changes in MWL-P loadings, potential approaches to integrate this P source into water management strategies, and the impact of other public water supply processes on macronutrient sources, sinks and stores.

3.6   Data availability

WRZ level leakage rates for water companies in the Thames catchment, daily leakage, dosing concentration and extent data are directly available from the references cited in section 3.2. PO_4-P concentration and flow data for the Thames at Teddington are publically available at https://environment.data.gov.uk/water-quality/view/landing and https://nrfa.ceh.ac.uk/data/station/info/39001. Data for the Oxford weather station are available at https://www.metoffice.gov.uk/pub/data/weather/uk/climate/stationdata/oxforddata.txt.

The following datasets for wastewater treatment in the Thames catchment are available from the Environment Agency on request:

- PO_4-P concentration and effluent flow data for wastewater treatment works

- Dates of historic wastewater treatment works upgrades

- Future discharge permit limits for P for different scenarios

3.7   Acknowledgements

4 Public water supply is responsible for significant fluxes of inorganic nitrogen in the environment

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Author contributions are as follows:

Ascott conceived the idea to quantify nitrate abstracted from the aquatic environment and lost via mains leakage and the implications of water transfers. Ascott designed the data analysis and modelling approach and collated the input datasets (tap water nitrate concentration, raw water nitrate concentration, leakage and supply volumes, planned water transfers, SEPARATE model outputs). Ascott undertook the modelling, data analysis and interpretation and wrote and edited the paper. All co-authors contributed to the general review of the results during project meetings and commented on and edited the manuscript.

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Abstract

Understanding anthropogenic disturbance of macronutrient cycles is essential for assessing risks facing ecosystems. For the first time, we quantified inorganic nitrogen (N) fluxes associated with abstraction, mains water leakage and transfers of treated water related to public water supply. In England, the sink of nitrate-N removed from aquatic environments by abstraction (ABS-NO_3-N) was estimated to be 24.2 kt N/year. ABS-NO_3-N is equal to six times estimates of organic N removal by abstraction, 15 times the sink flux to in-channel storage of organic N and 30 times the sink flux to floodplain storage of organic N. ABS-NO_3-N is also between 3-39% of N removal by denitrification in the hydrosphere. Mains water leakage of nitrate-N (MWL-NO_3-N) returns 3.62 kt N/year to the environment, equating to approximately 15% of ABS-NO_3-N. In urban areas, MWL-NO_3-N can represent up to 20% of total N inputs. MWL-NO_3-N is predicted to increase by up to 66% by 2020 following implementation of treated water transfers. ABS-NO_3-N and MWL-NO_3-N should be considered in future assessments of N fluxes, to accurately quantify anthropogenic disturbances to N cycles. The methodology we developed is transferable, using widely-available datasets and could be used to quantify N fluxes associated with public water supply across the world.

Abstract Art
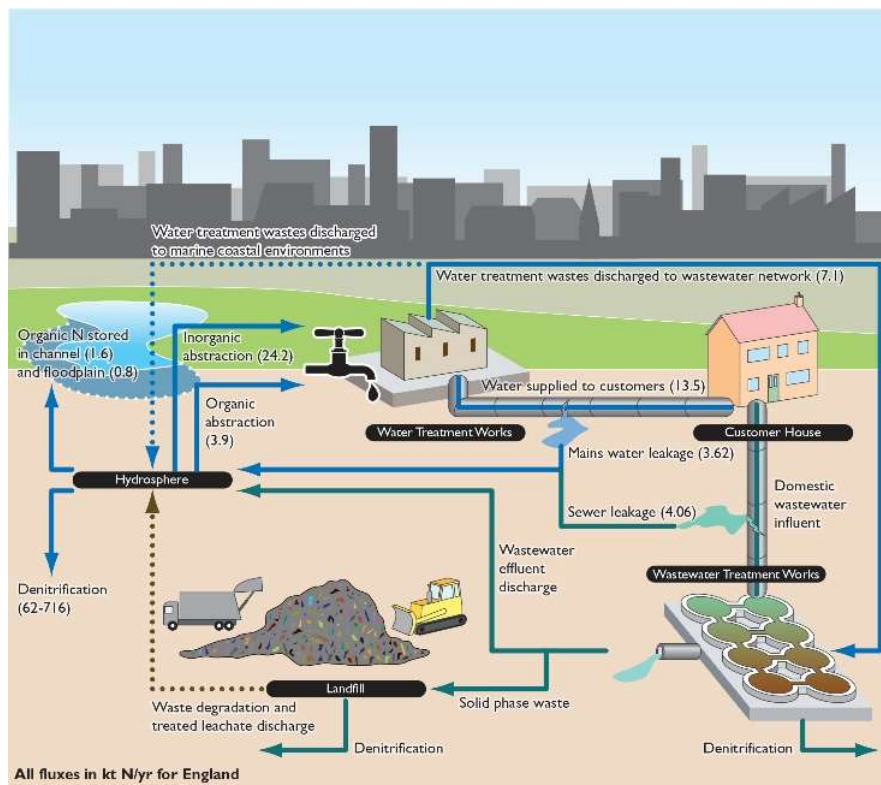
4.1 Introduction

Eutrophication associated with anthropogenic disturbance to nitrogen (N) and phosphorus (P) cycles within aquatic ecosystems is a widespread environmental challenge that has been recognised for over 50 years (Vollenweider, 1968). In response, substantial efforts have been made to reduce both point (Jarvie et al., 2006) and diffuse (Cherry et al., 2008) source nutrient inputs to the environment, for example through implementation of national and international legislation (e.g. the USA Clean Water Act (United States Environmental Protection Agency, 1972), EU Water Framework (European Union, 2000), Nitrates (European Union, 1991a) and Urban Wastewater Treatment (European Union, 1991b) Directives). Despite such efforts, there are multiple instances in which the reductions in riverine concentrations and fluxes of N and P after the implementation of mitigation activities have been lower than expected (Sharpley et al., 2013). The release of nutrients, both from previously unidentified sources and from legacy stores (e.g. groundwater, soils or the riparian zone (Haygarth et al., 2014)), is a potentially important contributor to unexpected trajectories of catchment nutrient balances. In this context, we sought to constrain the previously unquantified influence of public water supply on inorganic N fluxes.

Recent research has suggested that the public water supply processes (water abstraction, treatment, distribution and subsequent leakage) may have impacts on both nutrient sources and nutrient retention, particularly in urban areas. For example, previous research suggests that leakage of phosphate-dosed mains water (MWL-P) can be an important source of P in urban environments, with MWL-P fluxes now reaching up to 24% of wastewater treatment P loads in some catchments (Ascott et al., 2016a; Gooddy et al., 2017; Gooddy et al., 2015), and the relative importance of MWL-P estimated to increase in the future (Ascott et al., 2018a). Methods have also been developed to quantify N fluxes to groundwater from mains water

leakage at the city-scale (Lerner, 2003; Lerner et al., 1999; Wakida and Lerner, 2005), suggesting that approximately 36% of the total N loads in urban areas could be attributed to this source.

In the context of aquatic ecosystems, retention (also referred to as losses, sinks or removal) can be conceptualised as transient (e.g. nutrient accumulation within floodplains or groundwater) or permanent N removal (e.g. denitrification) (Grizzetti et al., 2015). Based on the difference between N fluxes from terrestrial to aquatic ecosystems and N fluxes at the tidal limit of the fluvial system, Worrall et al. (2012) concluded that substantial in-stream N retention occurs in Great Britain. Whilst detailed understanding of in-stream retention mechanisms at the national-scale remains to be developed, it has been postulated that these losses of N are primarily due to permanent N removal via denitrification (Worrall et al., 2012). However, the processes associated with public water supply may also contribute significantly to N retention within aquatic ecosystems. For example, Finlay et al. (2016) estimated the flux of organic N removed by water abstraction, suggesting that this flux is greater than N retention associated with the sink flux to transient floodplain storage.

However, important gaps remain in our understanding of how macronutrient fluxes are perturbed by the processes associated with public water supply (Ascott et al., 2018a). Whilst Finlay et al. (2016) calculated organic N removal, the mass of inorganic N removed during abstraction and the importance of this N retention process relative to other forms of in-stream retention have not been quantified to date. Further, previous methods developed for nutrient source apportionment either do not consider mains leakage (Comber et al., 2013; Zhang et al., 2014), or use simplistic approaches (Lerner, 2003; Lerner et al., 1999; Wakida and Lerner, 2005) based on export coefficients and literature values rather than observed leakage and concentration data. Finally, potential changes in inorganic N fluxes due to mains water leakage

associated with future treated drinking water transfers have not been quantified. Water transfers are considered essential if future water demand is to be met, but the water quality implications of water transfers remain poorly constrained (Water UK, 2016). Previous studies have called for the development of integrated nutrient management approaches which consider all macronutrient sources, sinks, stores and time lags in a river basin (Grizzetti et al., 2015). If such approaches are to be developed, it is essential that nutrient fluxes associated with abstraction, leakage and water transfers are quantified and the locations where these fluxes are enhanced in the future are identified. Within this context, in the research reported here we hypothesized that:

- Abstraction of raw untreated water removes a large, but spatially heterogeneous, flux of nitrate (ABS-NO_3-N) from the aquatic environment (defined here as groundwater, rivers and coastal marine environments);

- A considerable proportion of ABS-NO_3-N is returned to the environment through leakage of treated mains water containing nitrate (MWL-NO_3-N), particularly within urban areas;

- Treated drinking water transfers will substantially alter the future magnitude and spatial distribution of MWL-NO_3-N fluxes.

4.2 Materials and Methods
4.2.1 Study Area

The research reported here was developed at the national-scale for the country of England (Figure 4.1). Water is supplied by 21 water companies across England. Water company areas are divided into water resource zones (WRZs) within which water supplies are largely self-contained (Environment Agency, 2012). These WRZs are further divided into water supply zones (WSZs) which correspond to areas with uniform water quality, supplying up to 100,000

people (Drinking Water Inspectorate, 2017a). WSZs in England derived in this research (see supporting information) and principal regions referred to in this research are shown in Figure 4.1.
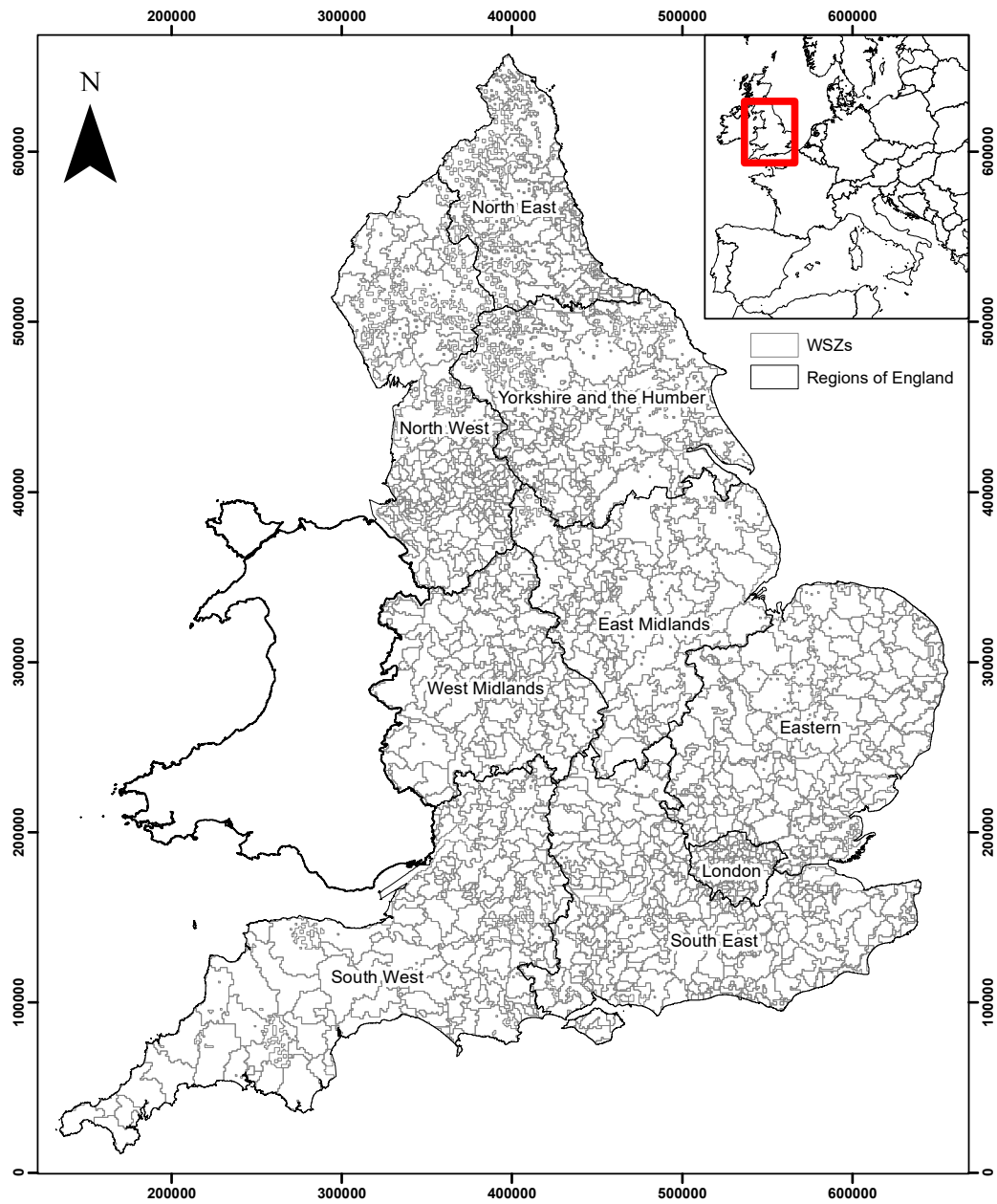
Figure 4.1 Water Supply Zones (WSZs) and principal regions in England

4.2.2 Quantification of ABS-NO$_3$-N and MWL-NO$_3$-N

4.2.2.1 ABS-NO$_3$-N

We derived ABS-NO$_3$-N using estimates of the rates at which treated water enters the distribution network from water treatment works (referred to herein as "distribution input") and raw water quality data for each WSZ. Distribution input rates are not reported nationally at the WSZ level, so these were derived as follows using estimates of treated water supplied to customers (referred to herein as "water supplied"). The total distribution input, DI (m^3/day) into a WSZ was divided into water supplied, S (m^3/day), and leakage, L (m^3/day):

$$DI = S + L \qquad (4.1)$$

S for each WSZ was extracted from published data submitted by the drinking water regulator for England to the European Commission (Eionet, 2016). For 12% of WSZs, values of S were not reported by the drinking water regulator. For these WSZs, S was estimated using WRZ-level estimates of per capita water consumption (PCC, L/h/d) published by Water UK (2016) and the total population (P, unitless) for each WSZ area, based on 1 km gridded population density mapping (Reis et al., 2017):

$$S = \frac{\text{PCC} \cdot \text{P}}{1000} \qquad (4.2)$$

Because WSZ-level leakage rates were not available, these were derived based on published WRZ-level leakage rates (Water UK, 2016). Assuming that the percentage leakage rate in a WSZ is equal to the percentage rate in the corresponding WRZ, L was derived as a fraction of the DI:

$$L = \text{DI} \cdot f_{\text{WRZ}} \qquad (4.3)$$

where f_{WRZ} (unitless) is the fractional leakage rate of the WRZ. Combining equations 4.1 and 4.3, DI was derived as:

$$DI = \frac{\text{S}}{1 - f_{\text{WRZ}}} \qquad (4.4)$$

As no national scale datasets on WSZ raw water quality were available, mean raw water nitrate concentrations for each WSZ were estimated using a heuristic approach based on data held in the English environmental regulator's water quality monitoring database. Following previous studies of national pollutant transport (Ascott et al., 2016a) and groundwater use maps (UK Groundwater Forum, 2018), WSZs were classified as either groundwater or surface water sources using national-scale hydrogeological mapping (British Geological Survey, 2014). If a WSZ is underlain by a moderate or highly productive aquifer, then the WSZ was considered to be a groundwater WSZ. If underlain by a low productivity aquifer or rocks with essentially no groundwater resource, then the WSZ was considered to be a surface water WSZ. In this research it was assumed that WSZs supplied by untreated surface water reservoirs would have the same water quality as the river and groundwater sources feeding the reservoirs. For each WSZ, raw water nitrate concentrations were estimated using the following rules: (1) only samples taken within a WSZ; (2) only samples that correspond to the derived WSZ source water (i.e. groundwater or surface water); (3) only samples taken in 2015 for direct comparability with drinking water quality data for the same year (see section 4.2.2.2 and supporting information); and (4) only samples for routine environmental monitoring, to avoid samples taken specifically for pollution investigations unduly impacting the analyses. Where no water quality samples were present within a WSZ (4.5% of WSZs in England by area) the mean raw water nitrate concentration of the nearest groundwater or surface water sample point was used. Where WSZs are fed by existing water transfers, the receiving WSZ was assigned the raw water nitrate concentration of the donor WSZ. After estimating DI and raw water nitrate concentrations (C_R, mg N/L) for each WSZ, the mass of nitrate-N removed from the aquatic environment through water abstraction, ABS-NO_3-N (kg N/day), was calculated as:

$$\text{ABS-NO}_3\text{-N} = \frac{C_R \cdot DI}{1000} \tag{4.5}$$

4.2.2.2 MWL-NO₃-N

We calculated MWL-NO$_3$-N at the WSZ level using existing datasets for nitrate concentrations in treated drinking water and the water supply rates and WRZ-level leakage rates detailed in section 4.2.2.1. Combining equations 4.3 and 4.4, L was calculated as:

$$L = \frac{S \cdot f_{WRZ}}{1 - f_{WRZ}} \qquad (4.6)$$

Nitrate concentration data were extracted from national-scale databases of WSZ drinking water quality reports for 2015 (see supporting information). All water company laboratories are required to be accredited by the UK Accreditation Service to the Drinking Water Testing Specification (United Kingdom Accreditation Service, 2013).   Accreditation includes interlaboratory proficiency testing for all parameters including nitrate concentrations, and thus any differences in nitrate concentrations between water companies associated with different laboratory methods were assumed to be minimal. Using the mean treated drinking water nitrate concentration for each WSZ for 2015, C$_T$ (mg N/L), MWL-NO$_3$-N$_{WSZ}$ (kg N/day) was calculated as:

$$MWL\text{-}NO_3\text{-}N_{WSZ} = \frac{C_T \cdot L}{1000} \qquad (4.7)$$

4.2.2.3 Changes in MWL-NO₃-N associated with future transfers of treated drinking water

Transfers of treated drinking water at the WRZ level that are planned to be implemented by 2020 were provided by the environmental regulator for England (Figure S1). These transfers are all located in South East and Eastern England, where current water stress is greatest (Water UK, 2016). To assess the impact of future transfers on the spatial distribution of MWL-NO$_3$-N, the WSZ-level MWL-NO$_3$-N$_{WSZ}$ estimates derived in section 4.2.2.2 were aggregated to the WRZ level (MWL-NO$_3$-N$_{WRZ}$, kg N/day) to obtain a baseline flux for 2015:

$$MWL\text{-}NO_3\text{-}N_{WRZ} = \sum MWL\text{-}NO_3\text{-}N_{WSZ} \qquad (4.8)$$

The impacts of aggregation of WSZ MWL-NO_3-N fluxes to WRZ level, in addition to impacts of using WRZ percentage leakage rates at the WSZ level and the impacts of estimating raw water nitrate concentrations using national environmental regulator water quality databases, are considered in section 4.4.3.

For each water transfer, the future leakage rate for the transferred water in the receiving WRZ was assumed to equal the existing leakage rate in the receiving zone. This assumption is reasonable because all water companies in England have current leakage rates at or below the sustainable economic level of leakage (Chartered Institute for Water and Environmental Management, 2015) and leakage rates are not forecast to change substantially over the next 25 years (Ascott et al., 2018a; Water UK, 2016). The volumetric leakage rate for a transfer, L_T (m^3/day), can therefore be estimated as:

$$L_T = DI_T \cdot f_R \tag{4.9}$$

where f_R is the leakage fraction (unitless) for the receiving WRZ and DI_T (m^3/day) is the additional distribution input associated with the transfer. The nitrate concentration in the transferred water in the future was assumed to equal to the current drinking water nitrate concentrations in the donor WRZ. Nitrate concentrations in drinking water in England are consistently below the European drinking water standard, with 99.99% of test samples compliant (Drinking Water Inspectorate, 2017b). Consequently, there is unlikely to be any additional treatment for nitrate removal associated with future treated water transfers. The flux of N from mains water leakage associated with an individual planned transfer, MWL-NO_3-N_T (kg N/day), was estimated as:

$$MWL\text{-}NO_3\text{-}N_T = L_T \cdot C_{T-D} \tag{4.10}$$

where C_{T-D} is the mean treated drinking water nitrate concentration in the donor WRZ (mg N/L). Some WRZs are expected to receive a number of different water transfers in the future.

In these cases, the individual transfers were combined to derive the total additional flux of N from mains leakage resulting from all transfers, MWL-NO$_3$-N$_{WRZ-T}$ (kg N/day):

$$MWL\text{-}NO_3\text{-}N_{WRZ-T} = \sum MWL - N_T \qquad (4.11)$$

Using the baseline WRZ-level estimates of MWL-NO$_3$-N$_{WRZ}$ for 2015, the percentage change in MWL-NO$_3$-N$_{WRZ}$ expected after the implementation of the planned transfers by 2020, ΔMWL-NO$_3$-N$_{WRZ}$ (unitless) was calculated as:

$$\Delta MWL\text{-}NO_3\text{-}N_{WRZ} = \frac{MWL\text{-}NO_3\text{-}N_{WRZ-T} + MWL\text{-}NO_3\text{-}N_{WRZ}}{MWL\text{-}NO_3\text{-}N_{WRZ}} \cdot 100 \qquad (4.12)$$

4.2.3 Comparison between ABS-NO$_3$-N, MWL-NO$_3$-N and estimates of other N sources and N retention in the aquatic environment

Our estimates of ABS-NO$_3$-N were compared with previous, national-scale estimates of the retention of organic N made by Finlay et al. (2016). These consist of N sink fluxes associated with water abstraction for public supply, floodplain storage and in-channel storage. We also compared ABS-NO$_3$-N with estimates of N removal via denitrification in the entire English hydrosphere (groundwater, surface water and the coastal marine environments (Leip et al., 2011)) and total in-stream losses (assumed to be dominated by denitrification (Worrall et al., 2012)). Organic N retention by abstraction was reported as a per-capita flux (kg N/h/yr) which was transformed to a total flux for England using the current population of England (Office for National Statistics, 2017) . All other fluxes were reported either as an absolute flux or flux per unit area. Where necessary, fluxes at the scale of England were calculated using the percentage of the UK land area which England comprises (54%).

To quantify the importance of MWL-NO$_3$-N, this flux was compared with other datasets aggregated to both the national and the WRZ level. To compare with previous estimates of urban N fluxes, we used estimates of N fluxes to groundwater at 1 km grid scale from water mains and the sewer network derived by the UK Environment Agency (2013) following the

export coefficient approach of Lerner (2003). We also used previous catchment-scale estimates of both urban diffuse (roads, residential zones, open urban spaces, industrial and commercial areas) N fluxes to rivers and from all N sources provided under the SEPARATE framework (Zhang et al., 2014). We calculated ratios of both current and future (post-transfers) MWL-NO_3-N made in our research to these estimates of N inputs from other sources.

4.3 Results

4.3.1 ABS-NO_3-N

Figure 4.2 reports the spatial distribution of ABS-NO_3-N across England. Blank areas denote locations in which no public water supplies are present (typically in sparsely populated upland areas in the north of England) or where data were unavailable (a small number of WSZs in southern England). Substantial spatial variation in the distribution of ABS-NO_3-N is revealed, with ABS-NO_3-N broadly greater in the Midlands and the South East than in the far North and Southwest of England. There are also additional hotspots of high ABS-NO_3-N in Yorkshire and the Humber, the West and East Midlands and near to London. The broad spatial trends and the hotspots are primarily related to variations in ABS-NO_3-N associated with high nitrate concentrations in some raw groundwaters and surface waters.

Table 4.1 reports national-scale estimates of ABS-NO_3-N for England in comparison to previous studies estimating N retention in aquatic environments in England. For 2015, we estimated total ABS-NO_3-N for England to be 24.2 kt N/year. Finlay et al. (2016) suggest that the total mass of organic N removed during water abstraction for public supply in the UK is 0.07 kg N/h/year, equating to a total flux in England of 3.9 kt N/year. ABS-NO_3-N therefore removes approximately six times more N from the environment as nitrate than is associated with abstraction of organic N. ABS-NO_3-N is also 30 and 15 times greater than estimates of organic N sink fluxes to floodplain and in-channel storage made by Finlay et al. (2016). The range of

estimates for the magnitude of denitrification within aquatic environments in England is substantial, from 62 kt N/year for the complete hydrosphere (surface water, groundwater and marine coastal environments) (Leip et al., 2011) to 716 kt N/year within the stream network alone (Worrall et al., 2012). Based on this range of available estimates, ABS-NO_3-N is equivalent to between 3 – 39% of current estimates of denitrification in aquatic environments.
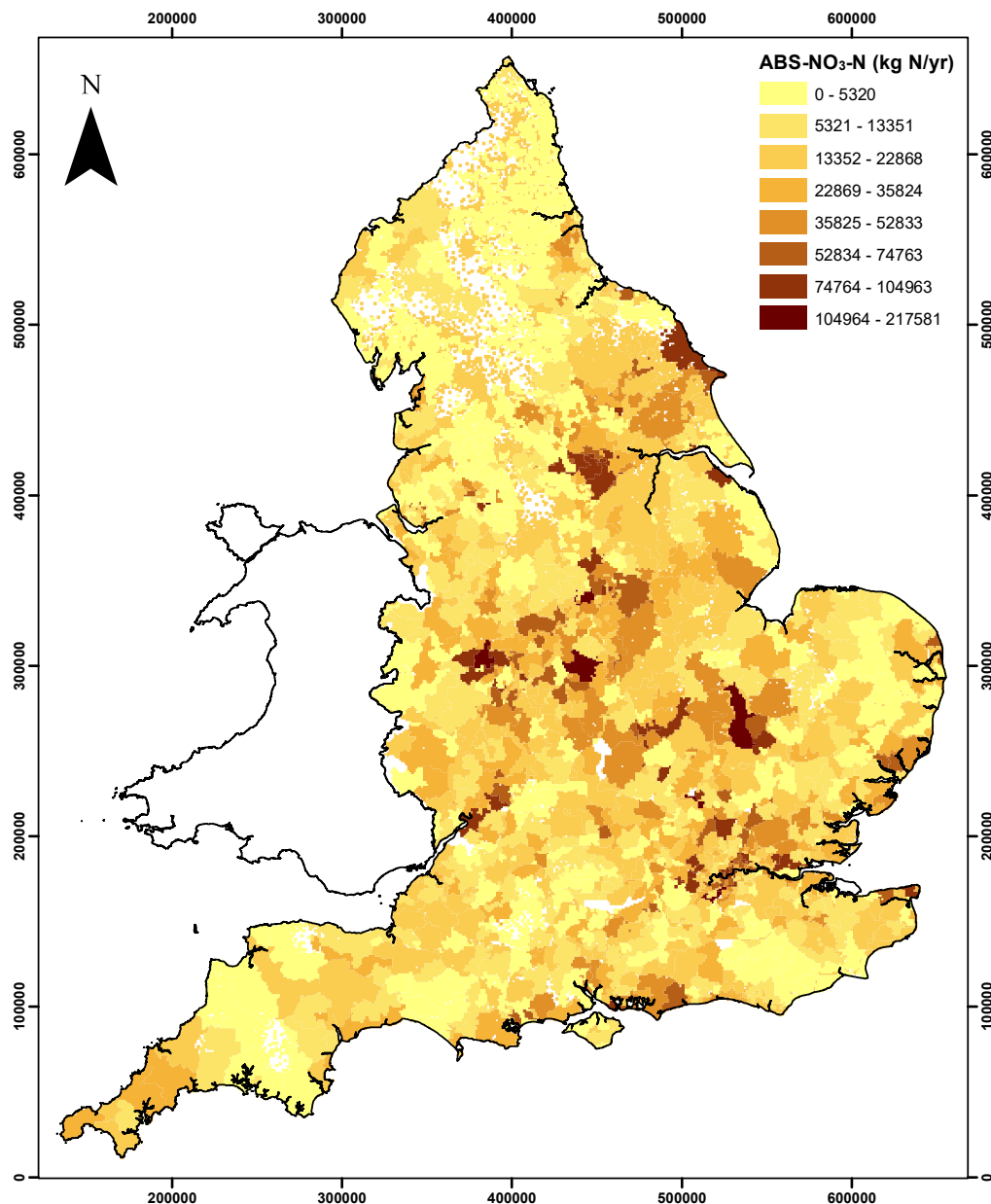
Figure 4.2 Distribution of ABS-NO_3-N in England for 2015

Table 4.1 Total flux of nitrate removed from the aquatic environment by abstraction (ABS-NO_3-N) in England for 2015 in comparison to previous estimates of aquatic N retention (organic N retention and sink fluxes to stores) and removal processes (denitrification)

Flux Name	Reference	Flux Value (kt N/year)	ABS-NO$_3$-N/Flux Value (-)
ABS-NO$_3$-N	This study	24.2	-
Organic N retention by abstraction	Finlay et al. (2016)	3.9	6.21
Organic N sink to floodplain storage	Finlay et al. (2016)	0.8	30.03
Organic N sink to in-channel storage	Finlay et al. (2016)	1.6	15.02
Denitrification in the hydrosphere (rivers, groundwater and coastal marine environments)	Leip et al. (2011); Worrall et al. (2012)	62 - 716	0.39 – 0.03

4.3.2 MWL-NO$_3$-N

The distribution of MWL-NO$_3$-N across WSZs in England is reported in Figure 4.3. Substantial spatial variation is also revealed in the MWL-NO$_3$-N fluxes, reflecting both the spatial distribution of leakage rates and drinking water nitrate concentrations. Large N fluxes from mains leakage are present in urban areas with high leakage rates such as London and the West Midlands. Relatively high MWL-NO$_3$-N fluxes are also observed in Eastern England and the Humber and along parts of the south coast, where particularly high nitrate concentrations have been observed in drinking water (Ascott et al., 2019).

Table 4.2 reports the total MWL-NO$_3$-N flux for England alongside previous national-scale N flux estimates. The estimate of national-scale MWL-NO$_3$-N in our research (3.62 kt N/year) is below previous estimates of this flux made by the Environment Agency (2013) and relatively similar to estimates of fluxes from sewer leakage (4.07 kt N/year). Based on previous N source apportionment studies (SEPARATE (Zhang et al., 2014)), the return of MWL-NO$_3$-N to the environment is small (c. 1%) at the national-scale relative to all other N sources, but much more important (c. 160%) relative to urban diffuse N sources.
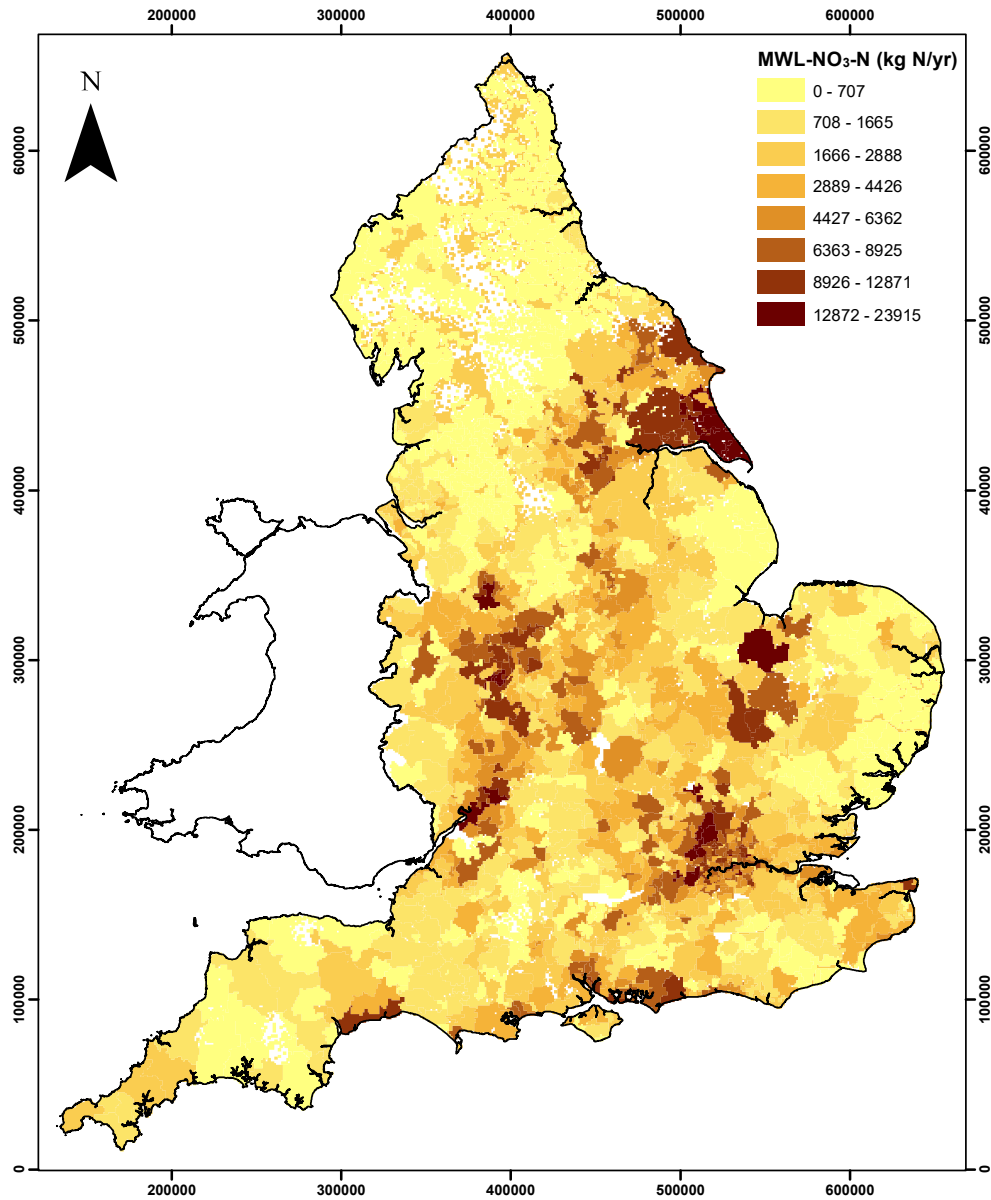
Figure 4.3 MWL-NO$_3$-N fluxes for WSZs in England for 2015

Table 4.2 Total flux of nitrate entering the environment from mains water leakage (MWL-NO$_3$-N) in England for 2015 in comparison to previous estimates of N sources (MWL-NO$_3$-N, N from leaking sewers, all N sources, urban diffuse N sources). MWL-NO$_3$-N/Flux Value refers to the MWL-NO$_3$-N estimate made in this study.

Flux Name	Reference	Flux Value (kt N/year)	MWL-NO$_3$-N/Flux Value (-)
MWL-NO$_3$-N	This study	3.62	-
MWL-NO$_3$-N	Environment Agency (2013)	20.31	0.178
SEWER-N	Environment Agency (2013)	4.06	0.891
All N sources	Zhang et al. (2014)	277	0.013
Urban diffuse N sources	Zhang et al. (2014)	2.31	1.567

Figure 4.4 reports our estimates of MWL-NO_3-N as a percentage of the total N flux from all sources derived from Zhang et al. (2014), aggregated to the WRZ level. MWL-NO_3-N is generally small relative to total N fluxes, at 2 – 5% of the total flux in the majority of WRZs in Southeast England and the Midlands. MWL-NO_3-N is <1% in large WRZs in Northern, Southwest and Eastern England, where agricultural land is extensive and urban areas are small relative to the total land area. However, in London and the surrounding area where urban land area is more extensive, MWL-NO_3-N grows in importance. For example, MWL-NO_3-N fluxes are estimated to be c. 15%, 16% and 20% of total N sources in WRZs in London, the south coast and Kent (east of London) respectively.
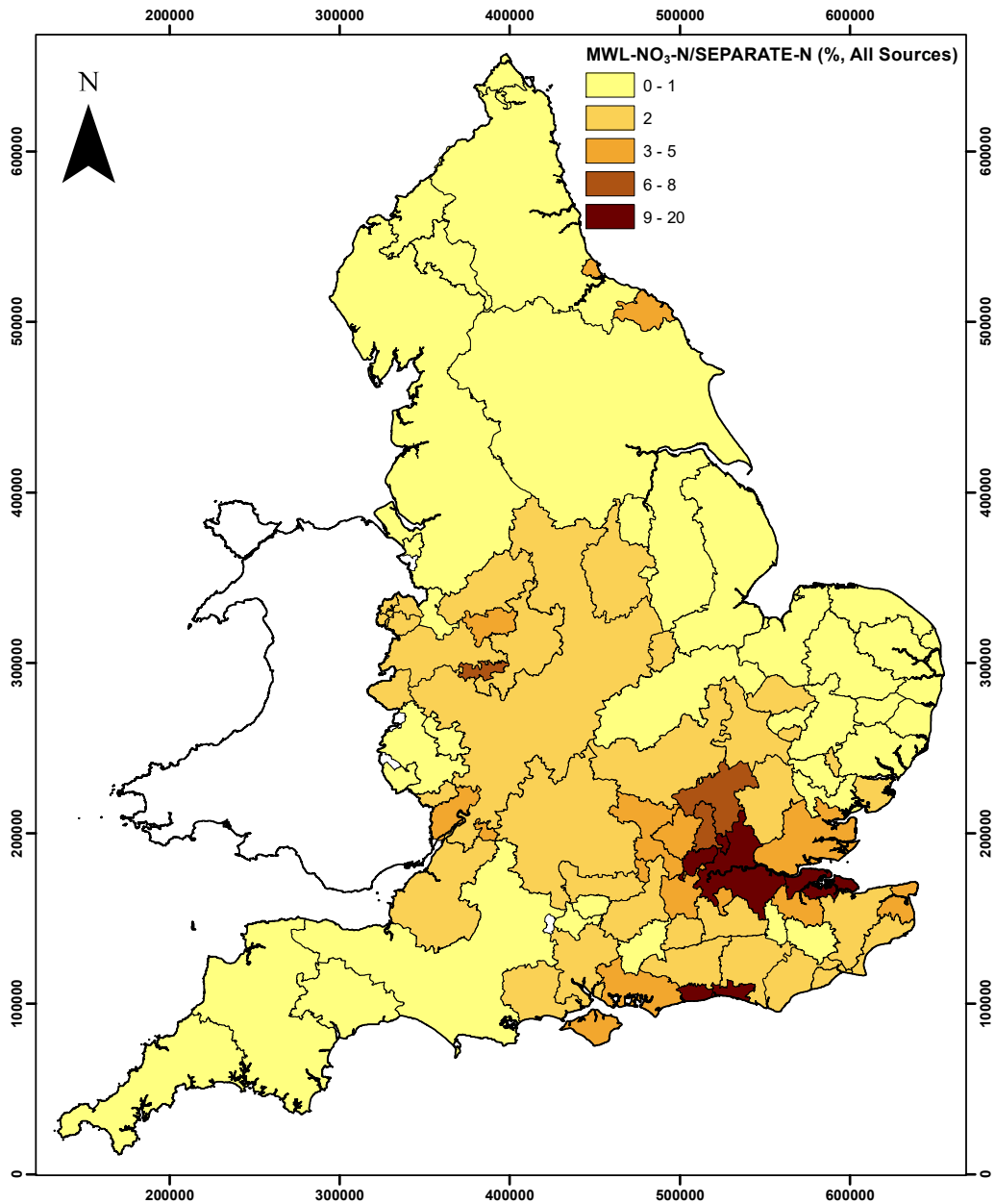
Figure 4.4 Percentage of MWL-NO$_3$-N to all N sources (as derived from SEPARATE (Zhang et al., 2014)) at the WRZ scale in England for 2015

4.3.3 Changes in MWL-NO$_3$-N associated with future treated water transfers

Figure 4.5 reports the percentage change in the MWL-NO$_3$-N flux in receiving WRZs after implementation of planned treated water transfers by 2020. In some WRZs on the south coast of England, MWL-NO$_3$-N fluxes are predicted to increase by up to 66% compared to 2015 levels, although implementation of water transfers is generally predicted to increase MWL-

NO$_3$-N fluxes by a relatively small amount (5 – 15%) compared to the 2015 baseline. MWL-

NO$_3$-N remains small relative to other N sources in the majority of WRZs where transfers are

implemented. However, in WRZs to the west of London, MWL-NO$_3$-N is expected to rise after

the implementation of planned water transfers to the equivalent to up to 20% of all N sources

(Figure S2).
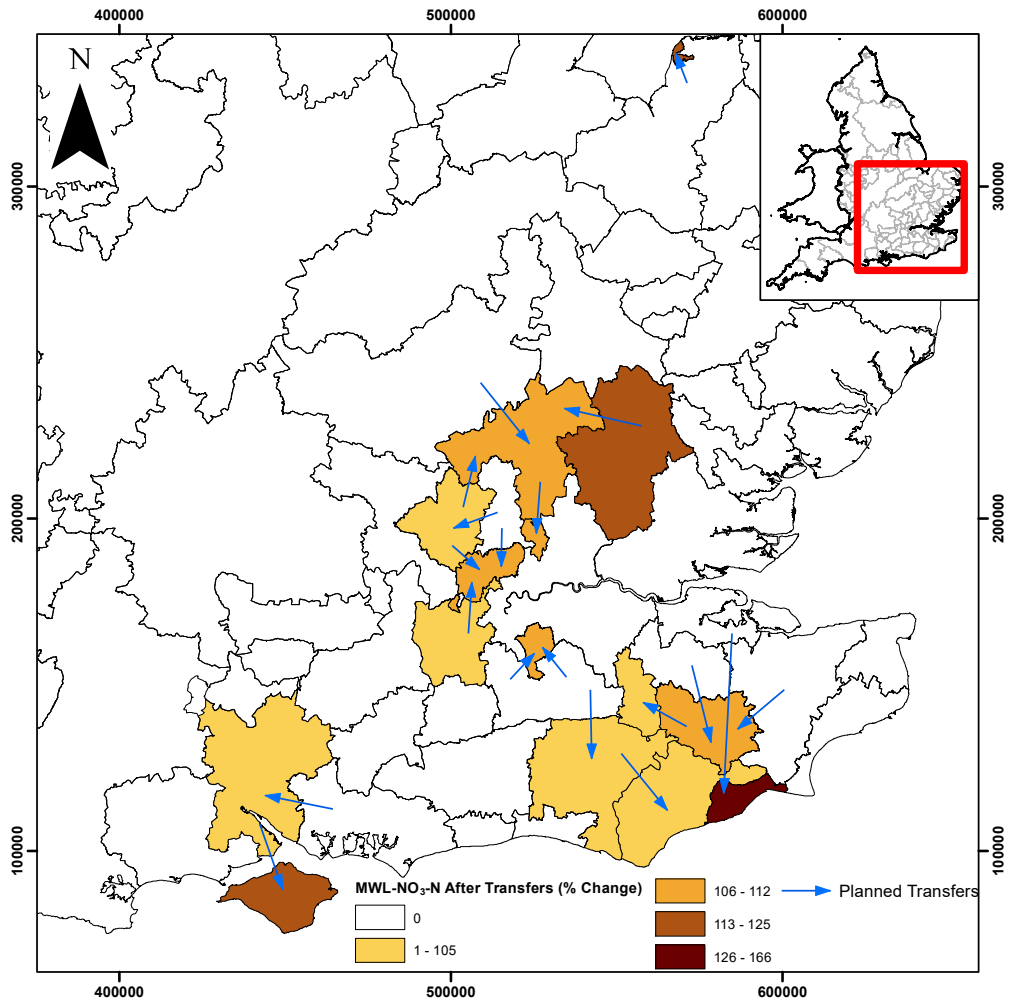
Figure 4.5 Percentage change in MWL-NO$_3$-N flux compared to 2015 baseline in receiving WRZs following implementation of treated drinking water transfers by 2020

4.4   Discussion

4.4.1   ABS-NO$_3$-N: An important sink for N within the environment?

N retention (sink fluxes) within the aquatic environment contributes to the differences between the N flux from the terrestrial biosphere and the fluvial flux of N to the oceans (Bernot and Dodds, 2005). Assuming net growth and decay of riverine biota at the national-scale is negligible (Worrall et al., 2012), denitrification has previously been considered the primary mechanism for N removal in aquatic ecosystems (Alexander et al., 2009; Durand et al., 2011). Only recently has research begun to quantify direct N removal from the environment through anthropogenic processes such as water abstraction (Finlay et al., 2016).   In the context of N retention, a unique contribution of our research is the quantification of nitrate removed from aquatic environments by water abstraction. ABS-NO$_3$-N is a significantly greater N flux than the estimate of organic N removal by abstraction, and the sink fluxes to floodplain and in-channel storage made by Finlay et al. (2016).   The wide range of estimates for the magnitude of aquatic denitrification means that quantifying the relative importance of ABS-NO$_3$-N is challenging. Further research is needed to better constrain these highly variable estimates to more accurately evaluate the importance of ABS-NO$_3$-N. Nevertheless, given that the upper limit for ABS-NO$_3$-N represents c. 40% of denitrification in the hydrosphere of England, including ABS-NO$_3$-N in future catchment N budgets appears to be important.

Whilst ABS-NO$_3$-N removes more N than is associated with abstraction of organic N, and may also be important relative to the N flux associated with denitrification, ABS-NO$_3$-N may only represent a transient retention process. The ABS-NO$_3$-N flux can be divided into: (1) N removed by water treatment processes; (2) N lost through mains water leakage; and (3) N supplied within treated water that reaches households. Mains water leakage will return N directly into the environment, although it is likely to be delayed before finally reaching receiving waters. Using drinking water nitrate concentrations and the WSZ supply rates estimated in this

research, we estimate that 13.5 kt N/year enters treated public water supply. The extent of ion exchange for nitrate removal of raw waters is poorly constrained at the national scale. However based on the difference between ABS-NO$_3$-N and the sum of MWL-NO$_3$-N and N in treated public water supply, we estimate that 7.1 kt N/year is removed by the treatment of raw water before distribution. Much of the N that enters treated water will ultimately move into the wastewater network (Sedlak, 1991). Waters that are highly enriched in nitrate produced by nitrate removal from raw water through ion exchange during drinking water treatment will also enter the wastewater network, although in coastal areas direct discharge to the marine environment may occur (Crittenden et al., 2012). Following wastewater treatment, N will be partitioned between solid phase waste sent to landfill or returned to agricultural land and dissolved or particulate N discharged directly to receiving waters. The return flux of N to the environment via these different pathways has not been quantified in this research. Whilst these processes are likely to have varying timescales for return of N into the environment, critically they are all likely to be substantially longer than the mean residence time for water within UK rivers (26.7 hrs (Finlay et al., 2016)). Therefore, whilst ultimately a transient retention processes, ABS-NO$_3$-N will significantly alter the spatial and temporal distribution of N inputs into aquatic ecosystems.

4.4.2 MWL-NO$_3$-N: An important N source in urban areas

At the national-scale, our research suggests that MWL-NO$_3$-N is equal to approximately 15% of ABS-NO$_3$-N. This estimate is likely to be reasonable because leakage rates in England have been reported to be up to 20% of water entering the distribution network (Gooddy et al., 2015) and treated waters show substantial variation in nitrate concentrations. MWL-NO$_3$-N is small compared to all other N sources in large WRZs, where agriculture is the most important N source. However, in urban areas MWL-NO$_3$-N may account for up to 20% of all N loads. These findings are in the same order of magnitude as initial city-scale studies reported

previously for Nottingham, UK (Lerner et al., 1999). Previous work that adopts relatively simple estimates of MWL-NO$_3$-N using export coefficient approaches (Environment Agency, 2013) substantially overestimates MWL-NO$_3$-N compared to our approach which uses observed leakage and concentration data. The flux of N associated with MWL should be considered in more detail in urban N source apportionment studies. The methodology we report here is transferable and could be applied where the necessary data are available, delivering an increase in accuracy and spatial resolution of estimates of MWL-NO$_3$-N compared to alternative approaches.

Previous research has suggested that incorporation of the environmental cost of P fluxes from mains water leakage within methodologies to estimate the sustainable economic level of leakage (SELL) could result in more stringent leakage targets, and consequently lower P fluxes to the environment (Gooddy et al., 2017). Extending the SELL approach to consider the environmental impact of MWL-NO$_3$-N would also be of environmental benefit. However, whilst MWL-NO$_3$-N represents a substantial N flux to the environment, concentrations in mains leakage are lower than in sewer leakage (Wakida and Lerner, 2005). Consequently, mains leakage to groundwater may dilute high nitrate sewer leakage. Integrating N sources into SELL would require an evaluation of the trade-off between the negative environmental impact of MWL-NO$_3$-N as an N source and any environmental benefit associated with dilution of sewer N leakage. Additional nitrate removal from raw waters to reduce MWL-NO$_3$-N fluxes whilst continuing to dilute sewer N leakage is unlikely to be a viable solution, given that concentrations of nitrate in drinking water within England are already below the European drinking water standard (Drinking Water Inspectorate, 2017b).

It should be noted that MWL-NO$_3$-N, rather than representing a new input of reactive N to the terrestrial environment (as would be associated with the application of inorganic N fertilisers

or N fixation for example), instead represents a return of N to the environment after water abstraction. Return of N via MWL therefore represents a potential alteration to the distribution and residence time of N in different environmental compartments. In this context, it should also be noted that the ultimate fate of MWL-NO_3-N currently remains uncertain. The MWL-NO_3-N flux may be mediated by the soil microbial community and by plants following leakage. MWL-NO_3-N may also be subject to denitrification, although this is unlikely near to the site of a leak as treated water has been shown to be low in organic carbon (Drinking Water Inspectorate, 2017a) and is unlikely to be anaerobic due to oxidation processes during water treatment (e.g. ozonation producing dioxygen (Camel and Bermond, 1998)) and extensive contact with the atmosphere (Goncharuk et al., 2010). It is likely that the fate of MWL-NO_3-N can be broadly divided between fluxes to groundwater, surface water and the sewer network. Based on the national-scale hydrogeological mapping described in section 4.2.2.1, the MWL-NO_3-N flux on moderate and highly productive aquifers is estimated to be 1.67 kt N/year. Given the long residence times in the unsaturated and saturated zones (Gooddy et al., 2006; Loáiciga, 2004), it is likely that legacy MWL-NO_3-N from previous decades has accumulated within both groundwater and the vadose zone, although estimates of the mass of nitrate stored in these environmental compartments are scant (Chen et al., 2018). Moreover, historical leakage rates have been much higher than at present, with rates falling by a third between 1994 and 2015 (Ofwat, 2015). Consequently, the rate of MWL-NO_3-N accumulation within the vadose zone and groundwater is likely to have been greater in the past compared to the present day.

Our research predicts relatively small changes in the spatial distribution of MWL-NO_3-N fluxes associated with treated drinking water transfers. These transfers are fully costed, planned and will be implemented by water utilities by 2020 in England. Larger-scale transfers which may result in larger differences in water quality (and changes in MWL-NO_3-N fluxes) are currently

being evaluated (Water UK, 2016), although these transfers are yet to be formally included in the water resources plans. However, it should be noted that for both planned and speculative transfers of treated water, implementation of additional treatment for nitrate removal is unlikely because concentrations are already below the European drinking water limit. With mitigation measures to control other N pollution sources being implemented (Environment Agency, 2016a), and limited changes planned for mains water leakage rates (Ascott et al., 2018a), it is likely that the relative importance of MWL-NO_3-N will increase in the future, as has been reported for MWL-P in the Thames catchment (Ascott et al., 2018a).

4.4.3 Local and global research priorities for ABS-NO_3-N and MWL-NO_3-N

By deriving the first national-scale estimates of N fluxes associated with public water supply abstraction, leakage and water transfers, this study makes a unique contribution to our understanding of macronutrient sources and sinks required for integrated nutrient management approaches (Grizzetti et al., 2015). There are a number of outstanding research priorities within this field which remain to be addressed. To date the only published national estimates of aquatic N retention by abstraction are for organic N compounds (Finlay et al., 2016), and comparing ABS-NO_3-N with other temporary retention processes that influence inorganic N would be helpful. Our research has quantified the flux of nitrate associated with water treatment processes as the difference between ABS-NO_3-N and the sum of MWL-NO_3-N and N in treated water supplied. Direct quantification of N removal during water treatment at the national-scale using observed concentration and flow data for process losses could be used to further validate the approach reported here. Water abstraction for public supply is also likely to be associated with fluxes of other inorganic N species, for example meaning that quantifying the mass of N removed via abstraction of ammonium may also be important. Further research should also evaluate the ultimate fate of MWL-NO_3-N, including

accumulation of nitrate stored in the vadose zone from this and other N sources. Understanding the timescales for re-release of N to the environment from transient stores associated with the water treatment cycle would also be of benefit.

The research reported here at the national-scale highlights the particular importance of MWL-NO_3-N in urban areas. However, due to the dearth of data at the WSZ level, there are a number of uncertainties in this study which should be considered when evaluating future research priorities. It should be noted that WSZ level leakage rates were estimated by applying percentage leakage rates from the corresponding WRZ. Whilst treated drinking water nitrate concentrations are reported at the WSZ level, there is likely to be some uncertainty in estimates of raw water nitrate concentrations as these have been made based on environmental regulator water quality databases and a heuristic assessment of water sources based on hydrogeological mapping and existing water transfers. Treated drinking water transfers are reported at the WRZ level and thus the impact of transfers on MWL-NO_3-N fluxes has been reported at the WRZ level in this research. As a consequence of these factors, it is plausible that there may be more detailed local variability in MWL-NO_3-N, ABS-NO_3-N and the impact of treated water transfers in urban areas than reported in this research. Additional local-scale work should focus on these areas, drawing on datasets such as detailed raw water quality data, District Metering Area leakage data and information on water transfers.

Further research to quantify both ABS-NO_3-N and MWL-NO_3-N fluxes globally is also likely to be of importance. For example, water abstraction for all uses at the global-scale has been estimated at c. 4000 km^3/year in 2010 (FAO, 2016). Using a conservative assumption that nitrate concentrations in raw abstracted water are half of the World Health Organisation guideline value (i.e. 5.65 mg N/L), global ABS-NO_3-N would remove 22.6 Tg N/year from the aquatic environment. This global estimate of ABS-NO_3-N is equivalent to between 5 and 39%

of denitrification in soils, groundwater and riparian zones globally (Bouwman et al., 2013a).

Global leakage rates have been estimated at 32 billion m^3/year (World Bank, 2006). Assuming the same nitrate concentration in leakage as in treated drinking water, leakage of N would contribute 0.525 Tg N/year into the environment. This equates to approximately 1% of the global leaching and riverine N flux (Fowler et al., 2013). Whilst small in absolute terms, this ratio at the global-scale is similar to that reported above for England. Given the importance of MWL-NO_3-N in urban areas in England we report above, it is plausible that MWL-NO_3-N may be an important N source in urban areas across the world. Further, both ABS-NO_3-N and MWL-NO_3-N may be more important N fluxes in developing countries where nitrate concentrations and leakage rates (World Bank, 2006) are likely to be higher than those reported here for England (World Health Organisation, 2011). Therefore, accurately quantifying N fluxes associated with public water supply represents an important challenge to be addressed across the globe in the development of integrated approaches to managing macronutrient pollution.

4.5 Data availability

1 km gridded population density mapping, national scale hydrogeological maps and estimates of water supplied at the WSZ are directly available from the references cited in section 4.2. WSZ boundaries and nitrate concentrations in treated drinking water are available from water company websites (summarised at https://www.ofwat.gov.uk/households/your-water-company/map/). WRZ level estimates of leakage rates and per-capita consumption reported by Water UK (2016) are available from Water UK on request. Data for N sources to rivers derived using the SEPARATE framework (Zhang et al., 2014) are available at https://catalogue.ceh.ac.uk/documents/8dc7c876-90ca-4886-bd0a-9b3a99b09f64. The following datasets are available from the Environment Agency on request:

- Raw water nitrate concentration data

- Maps of existing and planned transfers of treated drinking water

- Estimates of N fluxes to groundwater at 1 km grid scale from water mains and the sewer network derived by the UK Environment Agency (2013) following the approach of Lerner (2003).

4.6 Acknowledgements

4.7 Supporting Information

4.7.1 Methodology for Water Supply Zone mapping and extraction of treated drinking water nitrate concentration data

Following Drinking Water Inspectorate (2017a) regulations, water supply utilities in England provide the results of routine treated drinking water quality sampling to customers as PDF reports via their websites. These reports include nitrate concentration data. Water utility supply areas are divided into water supply zones (WSZ) which supply up to 100,000 people and have uniform water quality. Each WSZ has its own water quality report. All customers in a WSZ receive the same report based on a postcode search on water utility websites. We downloaded nitrate concentration data for all WSZ water quality reports for England in 2015 and collated these in a MS Access database.

A number of water companies publically provide information on the boundaries of WSZ. Where these are not available, we derived WSZ areas using postcode data. England was divided into a series of 1 km^2 grid cells. In each cell the postcode in the centre was extracted and the corresponding WSZ name returned from water utility websites recorded. Grid cells returning the same WSZ name were merged to derive the WSZ outlines reported in Figure 4.1.

4.7.2 Supporting Figures
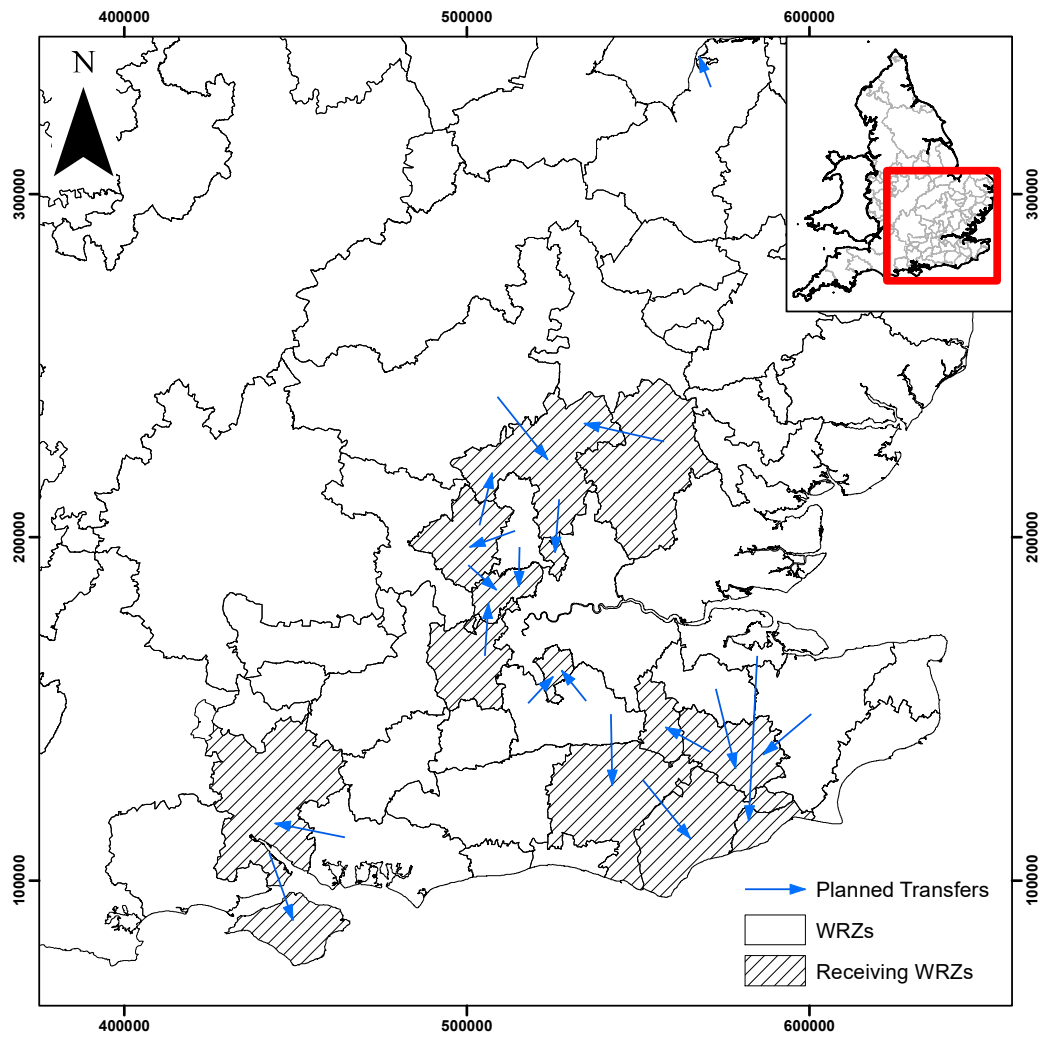
Figure S 1 Location of planned water transfers by 2020 and receiving water resource zones (WRZs) in England
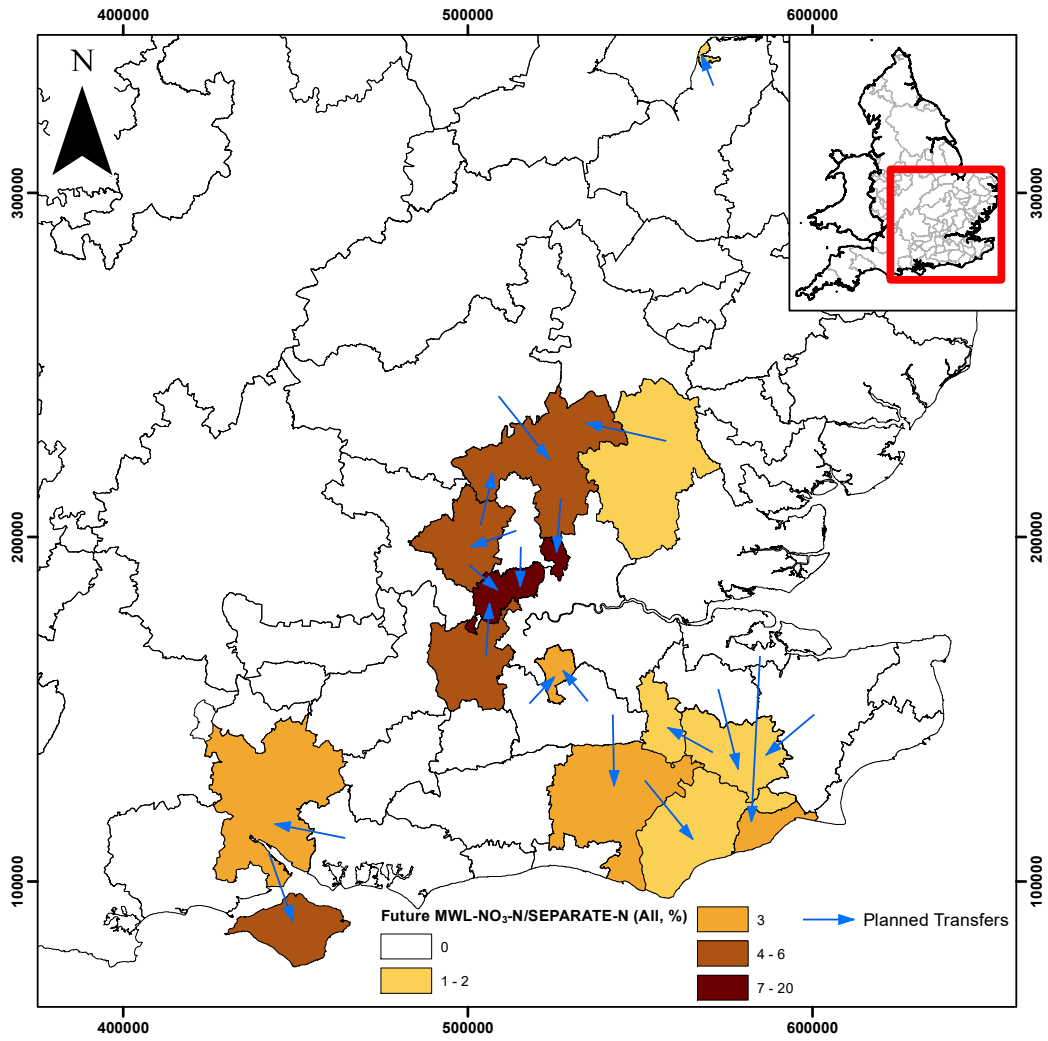
Figure S 2 MWL-NO$_3$-N as a percentage of all N sources (as derived from Zhang et al. (2014)) in receiving WRZs following implementation of water transfers by 2020
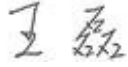
5 Quantification of nitrate storage in the vadose (unsaturated) zone: a missing component of terrestrial N budgets

A version of this chapter has been published as ASCOTT, M.J., WANG, L., STUART, M.E., WARD, R.S. AND HART, A. 2016. Quantification of nitrate storage in the vadose (unsaturated) zone: a missing component of terrestrial N budgets. *Hydrological Processes*, 30, 1903-1915

Author contributions are as follows:

Ascott conceived the idea to quantify the nitrate stored in the vadose zone in England and Wales in conjunction with Ward. Ascott designed the approach of linking NEAP-N soil leaching data with travel time estimates to estimate nitrate storage in the vadose zone and validation using porewater profile data. Ascott undertook the modelling, data analysis and interpretation and wrote and edited the manuscript. Stuart gave access to the nitrate porewater dataset. Hart gave access to the NEAP-N data. All co-authors contributed to project meetings when discussing the results and provided comments and edited the manuscript.

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Alwyn Hart

Abstract

National terrestrial nitrogen (N) budgets for many developed countries have been calculated as part of the management of impacts of N on the environment, but these rarely represent the subsurface explicitly. Using estimates of vadose zone travel time and agricultural nitrate loading, we quantify, for the first time, the total mass of nitrate contained in the vadose zone of aquifers in England and Wales. This mass peaked in 2008 at 1400 kt N (800 to >1700 kt N from sensitivity analyses) which is approximately 2.5 to 6 times greater than saturated zone estimates for this period and indicates that the subsurface is an important store of reactive N. About 70% of the nitrate mass is estimated to be in the Chalk, with the remainder split between the Permo-Triassic sandstones, the Jurassic Oolitic limestones and minor aquifers. Current controls on fertiliser application mean that the vadose zone is now a nitrate source and in 2015 we estimate the net flux from the unsaturated zone to groundwater to be 72 kt N/year. The mass of nitrate in the vadose zone should be included in future terrestrial N budgets at national and global scales to improve ecosystem management.

Keywords: Nitrate; Nitrate budget; Groundwater; Unsaturated zone; Vadose zone

5.1 Introduction

Modern intensive agriculture has greatly affected the earth's nitrogen (N) cycle (Vitousek et al., 1997). It is estimated that input rates of reactive nitrogen to the terrestrial biosphere are now over double pre-industrial levels (Galloway et al., 2004) through changes in agricultural land use practices, including the development and application of N fertilizers. This reactive N cascades through the environment with a number of deleterious and costly effects (Galloway et al., 2003). Groundwater and surface water quality for public supply has deteriorated, resulting in expensive "end-of-pipe" solutions such as nitrate removal or blending of waters (Kapoor and Viraraghavan (1997); Pretty et al. (2000); UK Water Industry Research Ltd (2004)) and this has been recognised in the UK and elsewhere for several decades (ENDS, 2004). As a result, legislation such as the Nitrates Directive (European Union, 1991a) and Water Framework Directive (WFD) (European Union, 2000) have been introduced to control farming practices in order to reduce pollution of ground and surface water. In addition to drinking water impacts, groundwater discharges to rivers, wetlands and marine systems have also contributed to long term ecological degradation (Vitousek et al., 1997). However, whilst a drinking water standard for nitrate has been developed in Europe (50 mg/L, European Union (1991a)), no standard currently exists for surface water.

To manage public water supplies and protect aquatic ecosystems, estimates of N budgets and fluxes at both national and continental scales have been developed. Recent studies have begun to quantify at the national scale N fluxes which have not previously been considered, such as mains water leakage and abstraction (Ascott et al., 2018b). Whilst a few national-scale substance flow analyses (Antikainen et al., 2005; Chen et al., 2016) and budgets (Worrall et al. (2009); Worrall et al. (2016a)) have quantified the magnitude of N stores, N budget approaches often assume the N cycle is in a steady state with no net change in terrestrial N

storage (Galloway et al., 2004). Bouwman et al. (2013b), for example, developed steady-state soil N budgets to explore changes in global N cycles. Budget inputs are from biological N fixation (N_{fix}), atmospheric deposition (N_{dep}), fertilizer applications (N_{fert}) and animal manure (N_{man}) and outputs are from withdrawals (N_{withdr}) from harvesting, cutting and animal grass consumption. The soil budget (N_{budget}) was derived from:

$$N_{budget} = N_{fix} + N_{dep} + N_{fert} + N_{man} - N_{with} \qquad (5.1)$$

In such a steady state approach, positive N_{budget} values represent a loss of N to the environment and negative values indicate depletion of soil N. Whilst this may be appropriate at the global scale over a long timescale, these assumptions do not consider changes at national and regional scales. There is now a growing body of evidence for N accumulation in soils, the subsurface, riverine and lentic sediments (Chen et al., 2018) which limits the application of models and budgets invoking the steady state assumption. Recently, integrated approaches (Grizzetti et al., 2015) which consider all macronutrient processes (sources, sinks, stores and time lags) in a catchment have been suggested as a possible solution to eutrophication associated with N and P sources. However application of this approach has been limited to date due to a lack of quantitative information on the size and distribution of macronutrient stores. Worrall et al. (2009) showed that Great Britain is a net sink of reactive N. They postulated that the sink is associated with reactive N storage in groundwater and made the first attempt at quantifying the amount of transient N storage. By considering that approximately 10 – 50% of the land surface of Great Britain is underlain by aquifers with an effective depth of water of between 1 to 10 m, they equate a 1 mg N/L increase in average groundwater concentration to be equivalent to a store of 300 kt of N. Subsequently, Worrall et al. (2015a) estimated the storage of total N in the unsaturated and saturated zones of the Thames Basin, a lowland agricultural catchment in England. Whilst the individual storage of N in each zone was not presented, they presented a range of maximum accumulation rates for the unsaturated zone of 1.4 to 5.5 kt N/year and state the time series for the flux into

unsaturated zone storage will reflect that of the saturated zone. Given this range of maximum accumulation rates and the range and time series of accumulation rates to the saturated zone presented by Worrall et al. (2015a), we estimate the peak in total accumulation in the unsaturated zone derived by the approach of Worrall et al. (2015a) in 2000 to 2004 to be between 16.4 to 195 kt N.

At the catchment scale, Chen et al. (2014) developed a dynamic watershed model which demonstrated the importance of transient N storage when evaluating catchment management measures. Hale et al. (2015) developed a model to evaluate the roles of nutrient inputs, infrastructure and runoff on N and P fluxes. They acknowledge that a considerable data limitation in their study was the lack of information on subsurface nutrient transport via groundwater. Further national scale work has shown that there are substantial delays in the leaching of N from the base of the soil zone reaching groundwater in some areas (Howden et al. (2011); Wang et al. (2012)). This delay can be of the order of decades, which is the result of the thick vadose zones and slow travel times present above aquifers of the United Kingdom (Foster et al., 1982).

Representation of this delay and the associated vadose zone storage in national and continental scale N budgets has not been attempted to date. Figure 5.1 shows the global distribution of thick vadose zones (> 20 m) and cropland areas as estimated by Fan et al. (2013) and Ramankutty et al. (2010) respectively. Thick vadose zones in England and Wales as derived using the river base level model discussed in this study are also shown. There are large areas of Europe, Asia and the Americas where vadose zones are likely to be thick and agricultural N losses to the environment may be important. In these areas transient N storage in the vadose zone may seriously constrain the usage of conventional nitrate budget approaches.

Consequently it is crucial that a generic, simple-to-apply approach to estimating this storage is available.
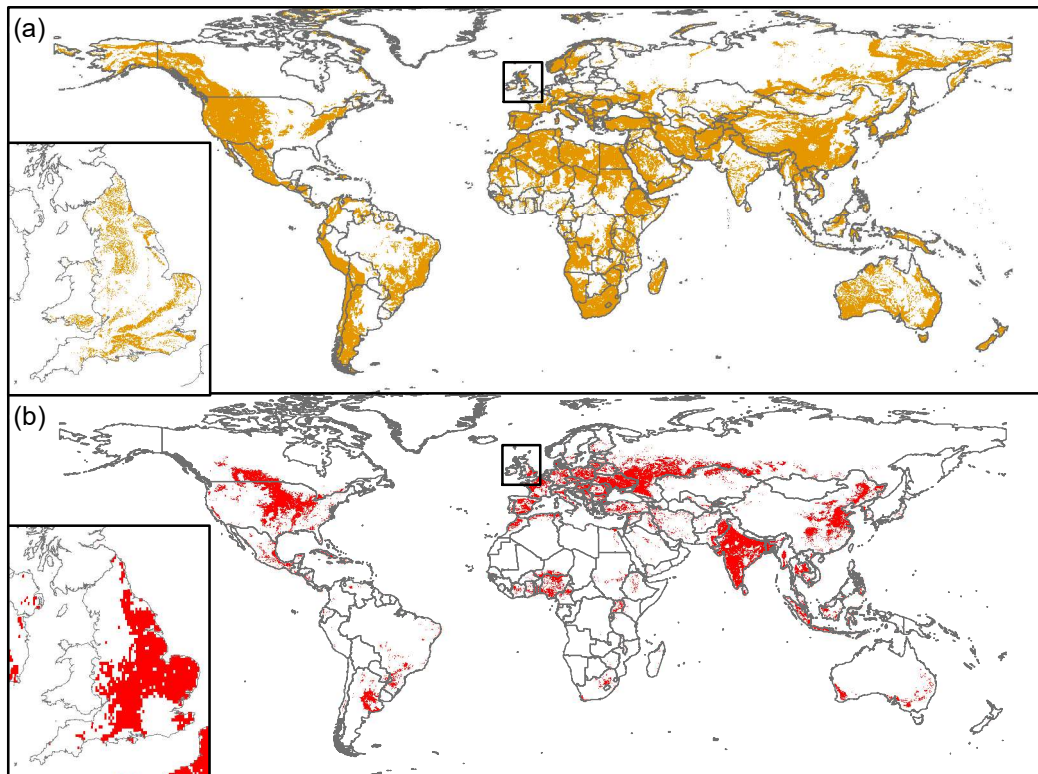
Figure 5.1: (a) Areas where depth to groundwater is estimated to be > 20 m. From Fan et al. (2013). Reprinted with permission from AAAS. (b) Areas where proportion of cropland is > 40% (reproduced after Ramankutty et al. (2010)).

Sutton et al. (2011) detail methods for national nitrate budgeting using a range of approaches across Europe. Most of these adopt a simple leaching and runoff factor approach to agricultural nitrate losses. They conclude that the largest uncertainties in budgets are associated with N leaching to groundwater and that future research should focus on this area. If integrated nutrient management approaches considering all N processes are to be developed, accurate quantifications of nitrate stored in the vadose zone are urgently required. This study presents a first quantification of the vadose zone nitrate budget at the national scale. We hypothesise that the lag between nitrate loss at the base of the soil zone and its impact on groundwater results in the vadose zone being an important store of nitrate in the terrestrial environment which needs to be properly considered for effective ecosystem management. We use a conceptually straightforward and generic approach which can be

readily adopted in other locations to improve national and continental scale N budgets. By linking estimates of nitrate leaching at the base of the soil zone with depth-to-groundwater maps and vadose zone velocities, we use a simple summation approach to derive the total unsaturated zone nitrate mass at the national scale.

5.2   Materials and Methods

5.2.1   Study Area

The countries of England and Wales were used as the study area; this together with the overall methodology is outlined in Figure 5.2. England and Wales have extensive areas of agricultural land (70% of the total area of the United Kingdom (DEFRA, 2012)) and are underlain by numerous important groundwater bodies (British Geological Survey, 2010). The three primary aquifers in England and Wales are the Chalk in Southern and Eastern England, the Permo-Triassic Sandstone in the Midlands and Northern England and the Jurassic Oolitic Limestones in Western England and the East Midlands. These aquifers provide the majority of the 35% of public water supply derived from groundwater in England and Wales (DETR, 1997) and support numerous groundwater-dependent ecosystems and the baseflow to many major rivers. Stuart et al. (2007) assessed long term trends in groundwater nitrate data across the aquifers of the UK and found an average annual rise in concentration of 0.34 mg NO_3 l^{-1} a^{-1}, with 34% of sites analysed exceeding the 50 mg NO_3 l^{-1} EU drinking water standard. Consequently, understanding the storage of nitrate in the vadose zone above these aquifers is of critical importance if future nutrient loadings to public water supply abstractions, groundwater dependent ecosystems and marine environments are to be suitably managed.

Wang et al. (2012) derived predictions of peak nitrate concentrations for the study area which were validated against historic nitrate trend data (Stuart et al., 2007). In this study we further

develop the verified approach of Wang et al. (2012) with additional datasets to derive the mass of nitrate in the vadose zone across England and Wales.
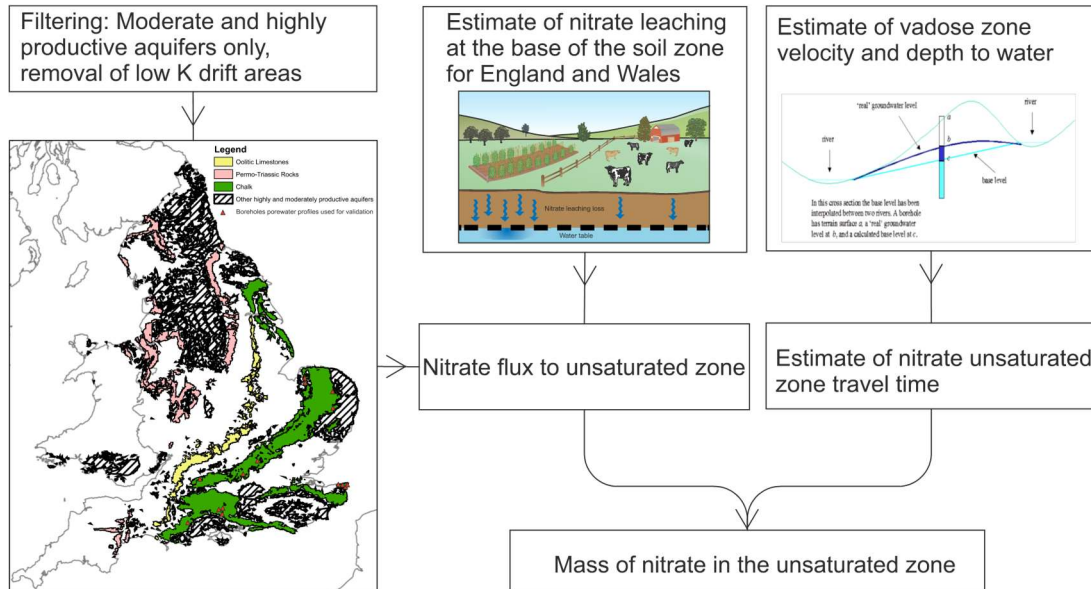
Figure 5.2: Methodology used to derive the mass of nitrate in the vadose zone in England and Wales. Based upon 1:625,000 scale digital hydrogeological mapping, British Geological Survey © NERC. Depth to water model reproduced after Wang et al. (2012).

5.2.2   Identification of Aquifers

High and moderate productivity aquifers (as defined by borehole yields > l L/s) were selected for this study using 1:625,000 scale digital hydrogeological mapping by the British Geological Survey (2010). Where bedrock aquifers are overlain by low permeability superficial deposits, recharge rates will be restricted and denitrification may occur (Jørgensen et al. (2004); Fragalà and Parkin (2010)). Consequently, these areas were excluded from the analysis using a national scale model of the recharge potential of superficial deposits (SNIFFER (2006); Griffiths et al. (2011); Wang et al. (2012)). Recharge potential mapping undertaken by Griffiths et al. (2011) used a domain-based methodology considering both primary and secondary lithological characteristics for each formation. Areas north of the limit of glaciation, where primary and secondary recharge potentials are low, were assumed to have no nitrate

transport to underlying aquifers. Figure 5.2 shows the aquifer areas used in this study derived from the hydrogeological bedrock and superficial mapping. The total outcrop area of these aquifers excluding areas overlain by low permeability superficial deposits is 43805 km^2 or approximately 29% of the land surface of England and Wales.

5.2.3   Nitrate Input to the Vadose Zone

It was assumed that the dominant form of reactive N in the subsurface is nitrate. This assumption is supported by national surveys of groundwater quality across England and Wales (Shand et al., 2007) showing that median nitrate-N concentrations are at least an order of magnitude higher than median ammonium-N and nitrite-N concentrations. Dissolved organic nitrogen (DON) concentrations in the subsurface are generally considered to be low in comparison to nitrate as evidenced by low levels of dissolved organic carbon (Durand et al., 2011). Data for Chalk baseflow dominated streams in lowland agricultural catchments show lower DON than inorganic N concentrations even where affected by wastewater treatment work effluents (10 – 20%, Yates and Johnes (2013)). DON may be locally important in more pristine or peat-rich environments (e.g upland moors; Lapworth et al. (2008)) and should be taken into consideration when reviewing results at small scales.

It was assumed that diffuse nitrate inputs to the vadose zone are primarily from agriculture. It has been shown that over 70% of nitrate in groundwater and surface water in England is derived from agricultural land (Foster (2000); Hunt et al. (2004); DEFRA (2006)). Point source discharges have been considered as insignificant at the national scale given the high potential for dilution in groundwater (Gooddy et al., 2001) and have been estimated as contributing < 1% of the total nitrate flux to groundwater in the United Kingdom (Sutton et al., 2011). Consequently these discharges have not been considered further in this study. At the local

scale in urban areas, non-agricultural diffuse nitrate sources (e.g. sewer leakage (Misstear and

Bishop, 1997), mains water leakage (as detailed in Chapter 4)) may be significant (Wakida and

Lerner, 2005) but have not been considered given the national scale of the work presented in

this study. The modelling approach of Lord and Anthony (2000) was adopted which derives

nitrate losses from agriculture at the base of the soil zone. Within the model (NEAP-N),

cropping and livestock data from agricultural censuses are integrated with land cover, soils,

climate data and interpolated to a 1 km grid for England and Wales for 5 specific years (1980,

1995, 2000, 2004 and 2010). Annual, spatially distributed, diffuse nitrate inputs for

intermediate years were derived by interpolation. Inputs back to 1925 and forward to 2050

were derived by scaling those of Lord and Anthony (2000) using a time variant nitrate input

function (NIF) (Wang et al., 2012). This scaling produced spatially distributed annual estimates

of nitrate inputs for 1925 to 2050. A time series of the total annual nitrate input for England

and Wales and the NEAP-N years is shown in Figure 5.4 (a). The NIF was based on estimates

of historic nitrate loading trends based on land use data detailed by numerous workers (Foster

et al. (1982); Lord et al. (1999); ADAS (2003); Addiscott (2005) and summarised by Wang et al.

(2012)).

5.2.4   Vadose Zone Nitrate Transport and Total Mass

Figure 5.2 outlines the methodology for the derivation of nitrate flux, travel time and total

mass in the vadose zone. Transport of nitrate through the unsaturated zone on a 1 km scale

was derived using the approach of Wang et al. (2012). We assume that nitrate is conservative

in the vadose zone above aquifers. This assumption is supported by studies which suggest

that denitrification in the unsaturated zone is likely to be very limited Kinniburgh et al. (1994);

Rivett et al. (2007). Field data indicate that vadose zone denitrification results in decreases in

concentrations which represent just 1 – 2 % of nitrate input (Rivett et al., 2007). We also

assume that nitrate moves through the vadose zone with a constant vertical velocity, no

hydrodynamic dispersion and undergoes vertical transport through the matrix when in dual porosity media.

Depth to water table was derived from observation borehole data, where available, and from a model deriving groundwater levels from river base levels and a digital terrain model (NEXTMap; Intermap Technologies (2007)). The river base level model derives an interpolated groundwater level surface on the assumption that groundwater is in direct hydraulic connection with rivers. This model is shown conceptually in Figure 5.2. The spatial distribution of depth to water across moderate and highly productive aquifers is shown in Figure 5.3.

Vadose zone velocities for each groundwater body were derived from historic work assessing water flows through the unsaturated zone (Chilton and Foster, 1991). Historic literature data for vadose zone travel times were available for the Chalk, Permo-Triassic Sandstones, Oolitic Limestones and Oxford Clay. For all other formations, a heuristic approach was adopted and vadose zone velocities were attributed based on expert judgement considering aquifer layering, permeability and grain size (Wang et al., 2012). The velocities used for moderate and highly productive aquifers are shown in Table 5.1.
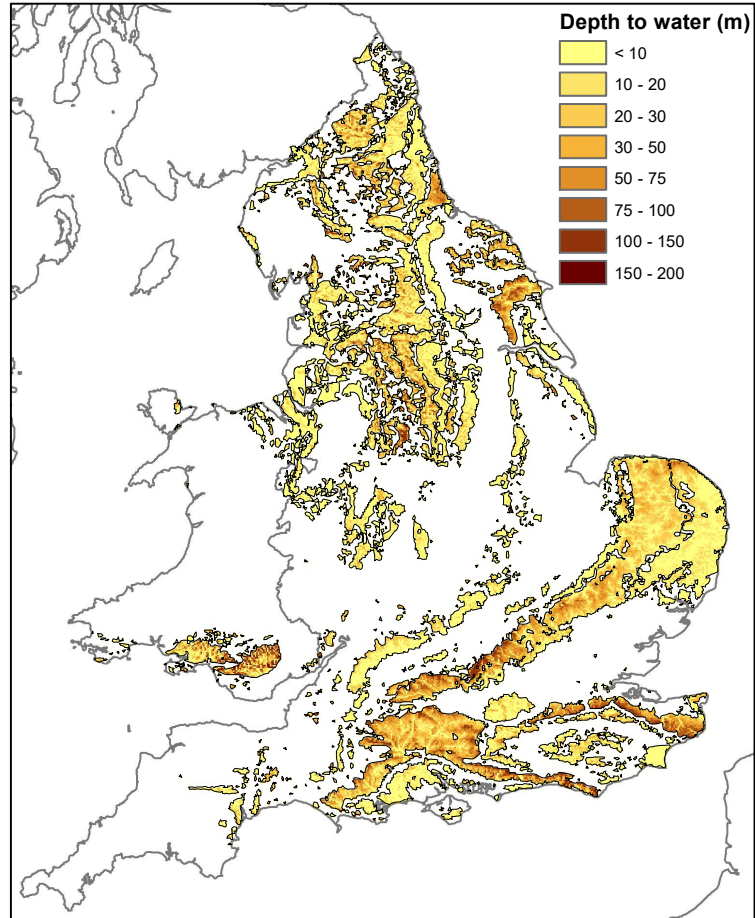
Figure 5.3: Estimates of depth to water derived from the River Base Level model for moderate and high productive aquifers. Based upon 1:625,000 scale digital hydrogeological mapping, British Geological Survey © NERC.

Table 5.1: Mean unsaturated zone velocities for moderate and highly productive aquifers used in the model. Observed velocity ranges for the Chalk, Limestone and Sandstone are derived from Chilton and Foster (1991).

Class	Formation	Unsaturated zone velocity (m/year)	
		Range	Mean
Fractured aquifers	White Chalk	0.3 - 1.4	0.76
	Grey Chalk		0.9
	Oolitic Limestone	0.6 - 2.5	1.1
	Other Karstic formations		10
	Layered Mesozoic formations		1
	Palaeozoic formations, igneous and metamorphic rocks		1
Aquifers with intergranular flow	Sherwood Sandstone	0.6 - 1.3	1.06
	Sands		3
	Silts		0.3

The total mass of nitrate in the vadose zone was derived for each year (1925 to 2050) for each 1 km grid cell using a conceptually simple summation approach and aggregated to the national scale by aquifers. For any year, *t (years)*, the total nitrate in vadose zone, N_{VZ} (kt N) for a given grid cell with a vadose travel time, TT_{VZ} (year) and a time-variant nitrate input function, *NIF (kg N)*, can be calculated as:

$$N_{VZ} = \frac{\sum_{i=t-TT_{VZ}}^{t} NIF_i}{10^6}$$
(5.2)

We derive changes in nitrate storage in the vadose zone through time using a simple mass balance approach;

$$NIF_t - Nout_t = \Delta N_{VZ}$$
(5.3)

Where $Nout_t$ is the nitrate flux from the vadose zone to the saturated zone and ΔN_{VZ} is the change in vadose zone nitrate storage for any year *t*.

5.2.5   Sensitivity Analysis

A number of assumptions have been made regarding nitrate inputs and transport in the vadose zone. To address the uncertainty in nitrate losses from agriculture at the base of the soil zone and transport in the vadose zone, a sensitivity analysis has been undertaken. Sensitivity of the nitrate storage to vadose zone travel time was assessed by considering ranges of travel times. A conservative sensitivity analysis was undertaken using a heuristic approach by deriving the total mass using travel times 15% greater and less than the baseline travel time distribution. Additionally, a wide range travel time sensitivity analysis was undertaken using the maximum and minimum vadose zone velocities reported in the published literature. For the Chalk, unsaturated zone velocities of 40% and 180% of the mean velocity have been reported (Chilton and Foster (1991); Wang et al. (2012)) and this range of values has been used to estimate the sensitivity of the nitrate storage to vadose zone. It should be noted that it is highly unlikely that these maximum and minimum velocities are

extensive nationally and consequently represent worst/best case scenarios for nitrate storage in the vadose zone. Uncertainty in the nitrate input from the base of the soil zone is likely to be temporally variable. Between 1980 and 2010 the nitrate input is reasonably well constrained by the NEAP-N data. Uncertainty in the nitrate input is likely to increase going forward from 2010 and back from 1980. Consequently a time variant error distribution was used. This is shown in Figure 5.4 (b). A stationary error of +/- 15% is used between 1980 and 2010. This is increased to +-30% to 2050 and back to 1940.
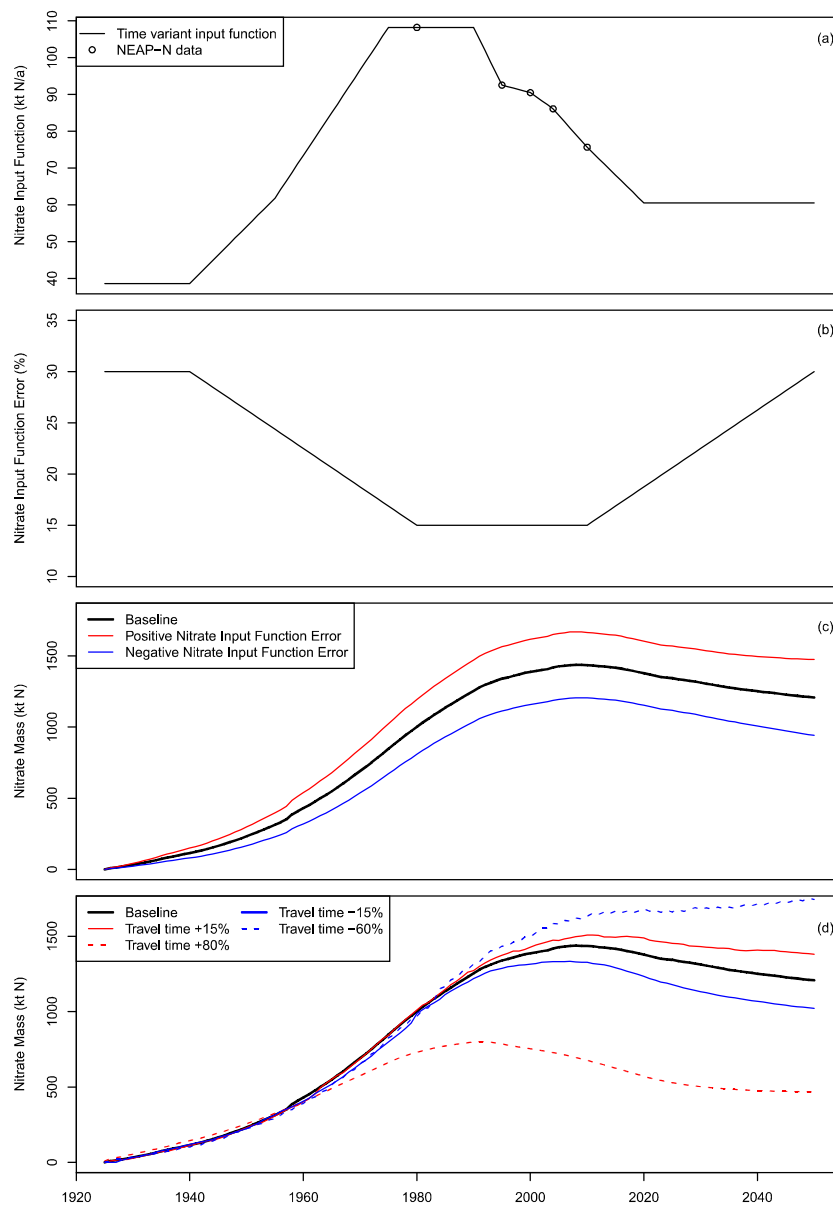
Figure 5.4: (a) Time variant nitrate input function, (b) nitrate input function error, (c) vadose zone nitrate mass considering input function uncertainty and (d) vadose zone nitrate mass considering travel time uncertainty.

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5.2.6 Model Validation

Validation of national scale models should be ideally undertaken at the same scale. However, there is very limited empirical data for vadose zone nitrate storage at the national scale. Howarth (2008) and Chen et al. (2014) highlight that it is nearly impossible to measure transient N storage at the watershed scale due to landscape heterogeneity. It should be noted that the primary input datasets to the modelling approach (depth to water estimates, unsaturated zone velocities and nitrate input (NEAP-N) data) have been validated against empirical observations in previous studies (Lord and Anthony (2000); Wang et al. (2012)). In this study, two approaches were taken to model validation. Model estimates of vadose zone storage were compared with estimates of storage in this zone in the Thames basin as undertaken by Worrall et al. (2015a) and discussed in section 5.1. Additional validation of model outputs was undertaken at the site scale where a body of vadose zone observation data exists. Model results for nitrate storage in the vadose zone at a 1 km grid scale were compared with estimates of nitrate storage derived from observed porewater concentration profiles from cored boreholes in England and Wales (Stuart, 2005). Over 400 boreholes are present in the database and an extensive screening process was undertaken to ensure the boreholes used in validation would be representative. The following criteria were used to select boreholes for validation; (1) Boreholes within the model area (where moderate and highly productive aquifers outcrop), (2) Boreholes where the full thickness of the vadose zone was sampled (98 boreholes in the model area), (3) Exclusion of boreholes where point source pollution issues were known. These criteria resulted in 43 borehole nitrate profiles remaining for validation. It should be noted that validation at this scale is itself challenging as site-scale heterogeneity will not be captured on a 1 km grid scale. Consequently, this approach to validation can be considered as a "sense-check" for model results using empirical data.

By assuming a fully saturated matrix and that the borehole porewater data reflect the concentration within the corresponding 1 km grid cell which is underlain by agricultural land, the vadose zone nitrate storage was calculated by numerical integration. For a given vadose zone borehole porewater profile with n sampling intervals each of thickness b (m) with observed concentration $[NO_3]$ (mg/L N) and porosity data $\emptyset$ (-), the total observed nitrate stored in the vadose zone N_{VZOBS} (tonnes/km^2) for the corresponding 1 km cell can be calculated as:

$$N_{VZOBS} = \sum_{i=1}^{n} \emptyset_i . b_i . [NO_3]_i . f_a \qquad (5.4)$$

Where f_a is the proportion of agricultural land in each 1 km grid cell as derived from the NEAP-N model (Lord and Anthony, 2000). This approach assumes that the fraction of each grid cell not underlain by agriculture does not contribute nitrate to the vadose zone. In a large number of cases, multiple borehole profiles were present at the same site and within the same 1 km grid cell. In these cases an average of these boreholes was taken. This averaging resulted in 15 sites being used for model validation, as shown in Figure 5.2. The sites cover the Chalk which is the principal aquifer of England.

5.3   Results and Discussion

5.3.1   Vadose zone nitrate storage in England and Wales

Figure 5.4 (c and d) shows the total nitrate mass in the vadose zone above aquifers in England and Wales. The total mass of nitrate in the vadose zone has increased substantially through time, peaking at approximately 1400 kt N in 2008. From 2008 onwards, the mass of nitrate in the vadose zone has been decreasing (i.e. the unsaturated zone is now a net source of nitrate to groundwater). The temporal change in nitrate storage in the vadose zone in 2015 is estimated to be approximately -5 kt N/year. In 2015, the flux from the vadose zone to groundwater ($Nout_t$, equation 5.2) was approximately 72 kt N/year.

Figure 5.4 (c) shows the variability in total nitrate mass associated with using greater or smaller nitrate inputs as shown in Figure 5.4 (b). Nitrate mass peaks of 1700 and 1200 kt N are estimated for the greater and smaller nitrate inputs respectively. Using conservative estimates of longer and short vadose zone travel times (Figure 5.4 (d), +/- 15%) results in nitrate mass peaks of 1500 and 1300 kt N respectively. Using these travel times also results in the peak nitrate mass occurring earlier (2007) for the shorter travel time distribution and later (2011) for longer travel times. Using a wider range of vadose zone travel times based on reported maximum and minimum unsaturated zone velocities (Figure 5.4 (d), + 80%/-60%) results in a wider range of unsaturated zone nitrate masses. Using the -60% travel time, the peak mass is reduced to 800 kt N and occurs in 1991. The +80% travel time results in a nitrate mass of 1750 kt N in 2050 however this is still increasing.

Figure 5.5 shows the temporal change in total nitrate stored in the vadose zone expressed by aquifers. The increase in vadose zone nitrate storage is dominated by the Chalk, containing an estimated 70% of the total mass in 2015. Increases are also observed in other aquifers such as the Permo-Triassic Sandstones (4% total mass in 2015), Oolitic Limestones (3% total mass) and numerous other locally important formations (23%). The Chalk, Permo-Trias and Oolites have peak mass years of 2015, 1991 and 1992 respectively. The year in which the total peak mass of vadose zone nitrate for England and Wales occurs is considerably affected by the majority of mass being in the Chalk.
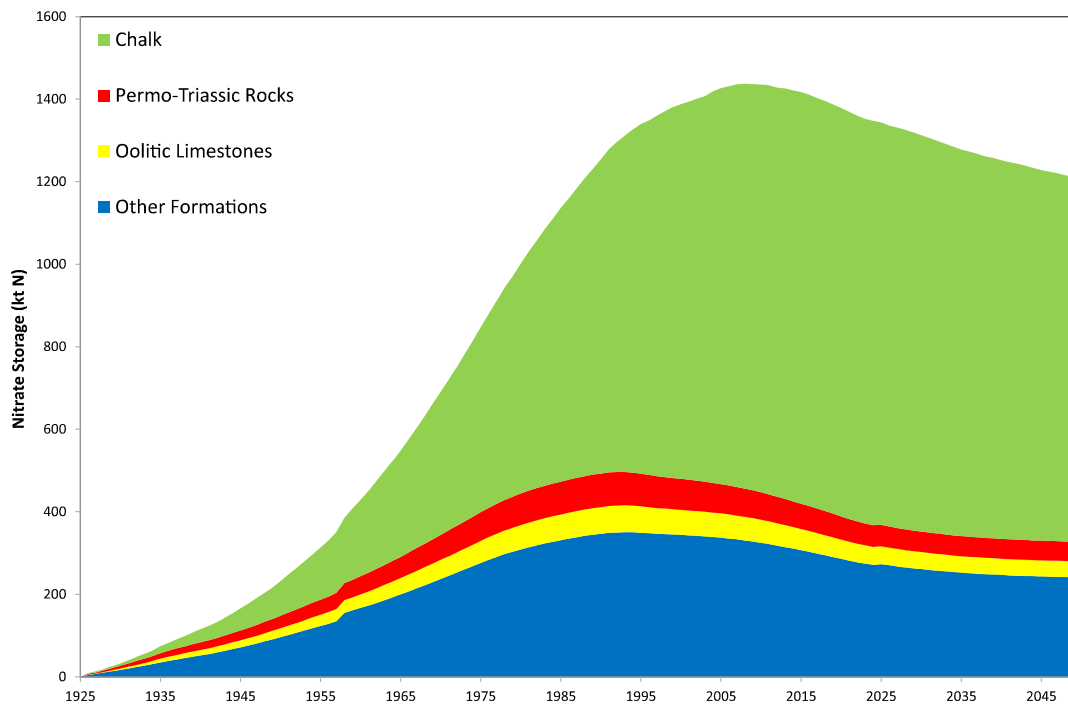
Figure 5.5: Change in vadose zone nitrate storage for 1925 – 2050 for moderate and highly productive aquifers.

The Chalk dominates the increase in vadose zone storage because of its large outcrop area (Figure 5.2), extensive agricultural land use (87%) and extensive thick unsaturated zone (Wang et al., 2012). Thick vadose zones result in long travel times and consequently a large increase in nitrate storage. Figure 5.6 shows the spatial distribution of nitrate estimated to be stored in the vadose zone in 1960 and 2015. Increases in nitrate storage in the Chalk of southern and north east England can be observed. Increases are particularly large in interfluve areas where travel times are very long due to thick vadose zones.
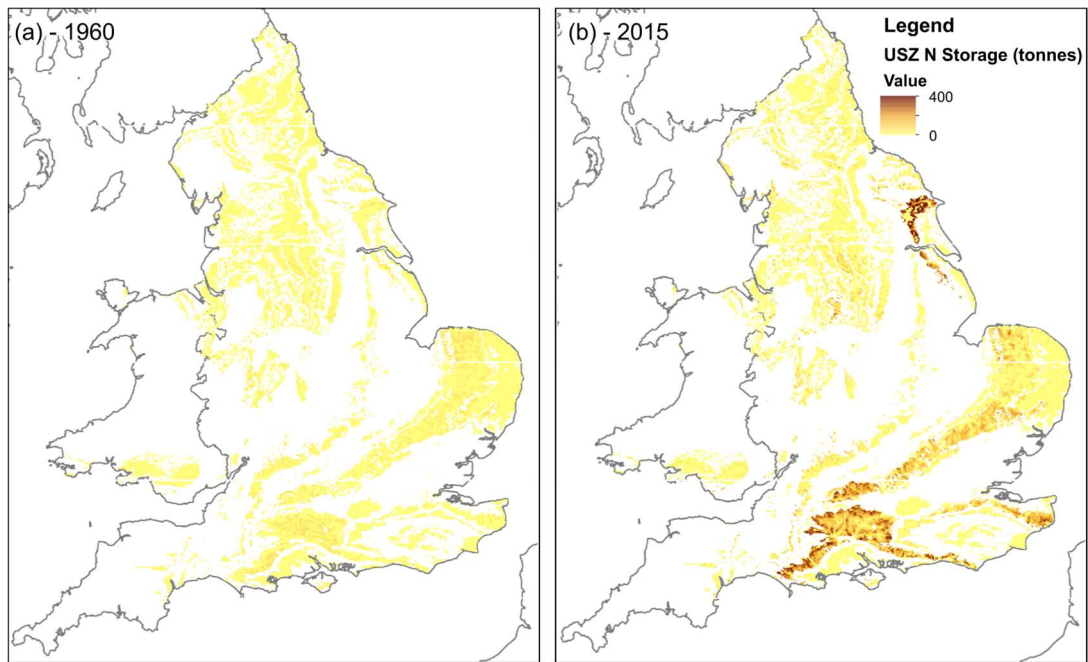
Figure 5.6: Spatial distribution of total vadose zone nitrate mass (as tonnes N per 1 km grid cell) in England and Wales in (a) 1960 and (b) 2015.

5.3.2   Validation

The total nitrate storage in the Thames catchment as derived in this study is estimated to be 198 kt N.   Considering the range of peak nitrate storage values for England and Wales estimated using the maximum and minimum unsaturated zone velocities (800 to >1750 kt N) compared to the best estimate mass (1400 kt N), we estimate the equivalent range for the Thames catchment to be 113 to 240 kt N.   This generally corroborates work undertaken by Worrall et al. (2015a) from which a range of N storage values of 16 to 195 kt N has been estimated.   Figure 5.7 shows nitrate storage for the 15 boreholes as derived from the model and from porewater data as discussed in section 5.2.6.   There is substantial scatter in the relationship between nitrate storage derived from the model and from pore-water data, resulting in a poor coefficient of determination (R_2= 0.16). This coefficient of determination is not surprising as the model has been developed at the national scale and does not capture the site-specific heterogeneity which is present at the borehole scale. Local scale hydrogeological complexities such as stratigraphic variability in aquifer properties which may enhance or inhibit nitrate transport and storage have not been considered in the national scale model.

Moreover, boreholes have been drilled for porewater profiles for specific investigations related to nitrate, and consequently are likely to show bias towards both particularly high and low concentrations. Boreholes have been drilled in areas where overlying land use is known to have had either extensive fertilizer applications or areas which are permanently unfertilised. Consequently, estimates of nitrate storage derived from point porewater profiles may be expected to both over and underpredict the amount of nitrate stored relative to model outputs at the 1 km scale.

Given the uncertainties in relating borehole-scale estimates of nitrate storage with national scale model outputs discussed above, it is encouraging that model results for a number of sites in the Chalk appear to be reasonably close to porewater results (10 sites with difference of less than 30 tonnes NO_3-N). This sense-check suggests that the model results may be reasonable at the national scale. However, model results at the local scale should be treated with caution and require further site-specific assessment and validation prior to use to inform decision making.
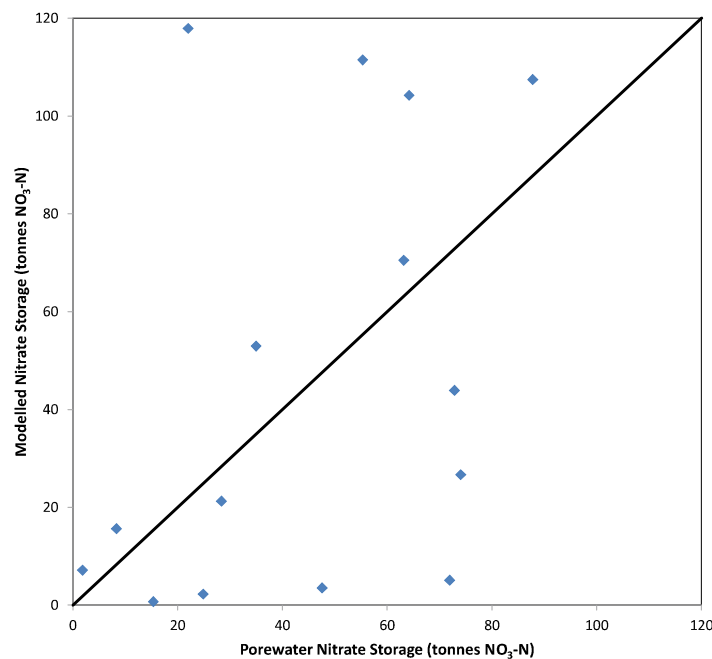
Figure 5.7: Nitrate storage in the vadose zone (tonnes NO_3-N) for 1 km grid cells as derived from the model and observed porewater profiles for 15 borehole sites.

5.3.3   Implications

5.3.3.1   Methodologies for derivation of national scale N budgets

This study corroborates previous work (Worrall et al. (2009); Chen et al. (2014)) suggesting that the subsurface is an important store of reactive N and that the steady state assumption at a national scale over one year is unlikely to be valid. The estimated peak nitrate mass in the vadose zone of 1400 kt N (range of 800 to >1700 kt N from sensitivity analysis) is 2.5 to 6 times greater than the first approximations for the saturated zone of 300 kt N (Worrall et al., 2009). Whilst the total nitrate storage in the vadose zone is now likely to be decreasing, travel times in the saturated zone can also be considerable. Consequently, peak nitrate concentrations at aquifer discharge points such as public water supply wells, rivers and groundwater dependent terrestrial ecosystems may not have occurred yet in some areas.

As discussed in section 5.2, the approach adopted in this study builds on a verified methodology used to derive peak nitrate concentrations at the water table (Wang et al., 2012). We have adopted a deterministic approach to the derivation of vadose zone nitrate storage and undertaken sensitivity analyses to assess the uncertainty in these estimates. However, we consider that further work to refine model inputs such as nitrate loadings and travel times will reduce the uncertainty in derived vadose zone budgets. Nevertheless, the methodology presented here for estimation of nitrate storage in the vadose zone is an important first step in improving nutrient budget estimations. To achieve integrated nutrient management approaches (Grizzetti et al., 2015) considering all N processes, further research is required to assess how this storage compares with other postulated terrestrial stores such as in-stream N retention, terrestrial N uptake in land not in agricultural production and N accumulation in subsoils (Worrall et al. (2009); Worrall et al. (2015a)). Future terrestrial N budgets at the national scale and at timescales of < 10 years should consider incorporation of these nutrient stores for effective management of N in the environment.

5.3.3.2   Targeting catchment management: From national to catchment scale

The approach adopted in this study is also likely to be beneficial for high-level targeting of catchment management activities at a wide range of scales. For example, Figure 5.5 illustrates that legacy nitrate in the vadose zone at a national scale in England and Wales is dominated by the Chalk. Figure 5.6 shows at a regional scale there is a substantial historical mass of nitrate in the unsaturated zone of the Chalk of southern England. At the catchment scale, nitrate mass is concentrated in interfluve areas where travel times are long due to thick vadose zones.

Environmental managers should take into account this mass when considering the implementation of catchment mitigation measures in attempts to improve groundwater, surface water and ecological quality. These measures typically consist of changes to agricultural practices through on-farm approaches (Zhang et al., 2012) and larger scale interventions such as nitrate vulnerable zones (Johnson et al., 2007). At the national scale, assessing where there is considerable vadose zone N storage would be useful in setting timescales and objectives for improvements in waterbody environmental status. The approach used in this study can help managers understand whether such improvements due to catchment measures are likely to be delayed by the flux of legacy N stored in the vadose zone to groundwater and surface water.

The approach can also be used at the basin and catchment scale, although estimates of vadose zone N storage should be reviewed in the context of site and catchment scale groundwater conceptual models (Allen et al., 2014). As detailed in section 5.3.2, site-scale outputs of the modelling approach presented here should be treated with caution, particularly in complex hydrogeological settings such as the Permo-Triassic Sandstones. Other forms and sources of reactive N should also be taken into consideration depending on the overlying land use. To

maximise the benefits to stakeholders it is suggested that the approach presented here should be integrated with outputs from existing flow and transport models for the saturated zone. This could include public water supply borehole capture zones (e.g. Wellhead Protection Areas (United States Environmental Protection Agency, 2014) and Source Protection Zones (Environment Agency, 2014)) and flow paths to groundwater dependent terrestrial ecosystems (e.g. Batelaan et al. (2003)). Having identified environmental receptors and potential polluting land uses, the vadose zone N mass can be helpful in assessing the likely timescales for improvements in water quality associated with catchment measures. Without proper consideration of legacy nitrate in the vadose zone and an understanding of saturated zone flow pathways, expectations of the timescales for the impacts of measures to improve water quality may be unrealistic.

Such measures have been implemented to meet recent environmental legislation such as the Water Framework Directive (WFD) (European Union, 2000). However, it has been widely acknowledged that WFD targets may not be met due to both socio-economic and hydrogeological delays (Cherry et al., 2008). The approach used in this study can show where vadose zone nitrate storage due to hydrogeological delays is likely to be most important, and consequently where it may be challenging to meet environmental objectives and policy targets. The methodology has the potential to be implemented across other countries in Europe implementing the Water Framework Directive and also internationally in areas where new environmental pollution targets have been set such as China (He et al. (2013); Yang (2014)).

5.3.3.3   Vadose zone nitrate storage: A global outlook

At the global scale, transient vadose zone storage in N budgets is likely to be important. To illustrate this and the importance of the approach detailed here internationally, we briefly

upscale our methodology to the USA. Based on mapping in Figure 5.1, we estimate the area of land in the USA where vadose zones are thicker than 20 m and cropland is greater than 40% total land use to be approximately 860,000 km^2. These areas have an average vadose zone thickness of approximately 35 m (based on Fan et al. (2013)). Using these estimates with a vadose zone velocity of 1 m/year and the nitrate input function shown in Figure 5.4 (a) converted to kg N/ km^2 and scaled to 40% of the European input (based on (van Grinsven et al., 2015)), we estimate a peak vadose zone nitrate mass for the USA of 29,000 kt N in 2001. This first approximation of vadose zone nitrate storage for the USA is likely to be highly uncertain but highlights the importance of this storage globally. The method we present here is generic and conceptually simple, with the most complex aspects of the approach associated with the input data. Recent global scale work on depth to groundwater (Fan et al., 2013), groundwater recharge (Döll et al., 2014) and soil N budgets (Bouwman et al., 2013b) should allow for the first global estimates of transient vadose zone nitrate storage to be derived. It is suggested that the approach could be particularly useful in areas where thick vadose zones are present above major aquifers. By doing this future N budgets are likely to be more accurate, enabling more informed management decisions to be made regarding groundwater quality and terrestrial and marine aquatic ecosystems.

5.4   Conclusions

This study has presented a generic approach to derive the storage of nitrate in the vadose zone above aquifers at the national scale, validated against observed porewater data and previous basis scale modelling approaches. The peak total mass in England and Wales in 2008 is estimated as 1400 kt N (range 800 to >1700 from sensitivity analysis) which is approximately 2.5 to 6 times greater than previous approximations for the saturated zone (300 kt N). The majority of this mass (>70%) is within the Chalk. This research supports the hypothesis that

the subsurface is an important terrestrial N store which needs to be considered in integrated nutrient management approaches which consider all catchment processes associated with N cycling. The methodology is a first step in reducing the uncertainty in national scale N budgets. In conjunction with saturated zone flow model outputs, the methodology can assist environmental managers and policymakers in decision making with regards to national and regional scale catchment mitigation measures to improve water quality. Vadose zone N storage is likely to be an international issue and it is suggested that recently published work on depth to groundwater, recharge and soil budgets could be used to derive a first global estimate of this storage.

5.5   Data availability

Global estimates of vadose zone thickness, agricultural land use, and national scale hydrogeological maps are directly available from the references cited in section 5.2. Nitrate leaching from the base of the soil zone derived from the NEAP-N model is available from the Environment Agency on request. The national database of nitrate profiles in the unsaturated zone is available from BGS on request.

5.6   Acknowledgements

6 Global patterns of nitrate storage in the vadose zone

Author contributions are as follows:

Ascott conceived the idea to quantify nitrate storage in the vadose zone globally. Ascott designed the modelling approach and collated the input datasets (nitrate leaching, vadose zone travel times). Ascott developed the model, analysed the model outputs and wrote and edited the paper. Ascott, Gooddy and Ward devised the cluster analysis approach during project meetings. All co-authors contributed to the general review of the results during project meetings and commented on and edited the manuscript.

Matthew Ascott
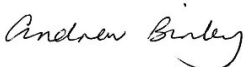
Daren Gooddy

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Andy Binley

Abstract

Global-scale nitrogen (N) budgets developed to quantify anthropogenic impacts on the N cycle do not explicitly consider nitrate stored in the vadose zone. Here we show that the vadose zone is an important store of nitrate which should be considered in future budgets for effective policymaking. Using estimates of groundwater depth and nitrate leaching for 1900-2000, we quantify the peak global storage of nitrate in the vadose zone as 605 - 1814 Teragrams (Tg). Estimates of nitrate storage are validated using basin and national scale estimates and observed groundwater nitrate data. Nitrate storage per unit area is greatest in North America, China and Europe where there are thick vadose zones and extensive historical agriculture. In these areas long travel times in the vadose zone may delay the impact of changes in agricultural practices on groundwater quality. We argue that in these areas use of conventional N budget approaches is inappropriate.

6.1 Introduction

It is estimated that inputs of reactive nitrogen (N) into the terrestrial biosphere are currently more than double pre-industrial levels due to modern agricultural practices and application of N fertilisers (Galloway et al., 2004). Reactive N cascades through the environment and has resulted in deterioration in quality of groundwater and surface water used for public supply (Kapoor and Viraraghavan, 1997) and ecological degradation of freshwater and marine systems (Vitousek et al., 1997). To manage the impacts of additional reactive N, N budgets have been developed at a wide range of scales to quantify man's impact on the N cycle (Bouwman et al., 2013b; Fowler et al., 2013; Galloway et al., 2004). Whilst estimates of N stored in soils have been made (Post et al., 1985; Prentice, 2008), and a few substance flow analyses (Antikainen et al., 2005; Chen et al., 2016) and budgets (Worrall et al. (2009); Worrall et al. (2016a)) have quantified the magnitude of N stores, in general N budgets often assume a steady state over a 1 year timescale, with no net accumulation of N. However, recent work at both national and catchment scales has shown this to be inappropriate, as there can be substantial storage of nitrate in soils, the vadose zone and groundwater (Ascott et al., 2016b; Van Meter et al., 2016; Worrall et al., 2009; Worrall et al., 2015a). The slow travel time for solutes through the vadose zone means that significant amounts of dissolved reactive N may be stored. This slow travel time can also result in a large lag between any changes in agricultural practices to reduce N loadings and subsequent impacts on groundwater and surface water quality (Wang et al., 2012). The problems associated with time lag and storage of nitrate in the vadose zone have been identified at local (Costa et al., 2002; Gvirtzman and Magaritz, 1986; Kurtzman et al., 2013; McMahon et al., 2006; Pratt et al., 1972; Rudolph et al., 2015; Spalding and Kitchen, 1988; Wellings and Bell, 1980), regional (Foster et al., 1982; Johnston et al., 1998; Mercado, 1976) and national scales (Ascott et al., 2016b; Fenton et al., 2011; Wang et al., 2013; Wang et al., 2012; Wang et al., 2016). Recently suggested "integrated

nutrient management approaches" (Grizzetti et al., 2015) aspire to incorporate these and all other N sources, sinks, stores and time lags in models and budgets used for decision making. However, the global importance of N storage in the vadose zone has not yet been quantified. In this study we hypothesised that long travel times in the vadose zone make it an important store of nitrate not considered at a global scale to date.

We quantified the nitrate stored in the vadose zone globally by linking numerical models and published datasets of nitrate leaching (Beusen et al., 2015), depth to groundwater (Fan et al., 2013), recharge rate and porosity (Gleeson et al., 2014) (see Methods section). We considered the sensitivity of model outputs to changes in model inputs by varying nitrate leaching inputs, vadose zone effective saturation and travel time. Results are aggregated by lithology and basins and analysed using k-means cluster analysis (Webster and Oliver, 1990). The model was validated by comparing the model storage against previous national and catchment scale vadose zone storage estimates (Ascott et al., 2016b; Worrall et al., 2015a) and by comparing model nitrate concentrations in recharge at the water table with observed concentrations in Europe (European Environment Agency, 2015) and the USA (USGS, 2015). It is shown that the vadose zone is an important store of nitrate at the global scale, with large storage in areas with extensive historical agricultural development and large depths to groundwater. Use of conventional N budgets in these areas is likely to be highly limited and policymakers should consider vadose zone nitrate storage when planning pollution mitigation measures.

6.2   Results
6.2.1   Global spatiotemporal distribution of vadose zone nitrate

Our modelling shows a substantial continuous increase in the amount of nitrate stored in the vadose zone (Figure 6.1). This increase implies the steady state assumption adopted by

conventional nutrient budgets is not appropriate at relatively short timescales (<50 years). Based on the sensitivity analysis, for the year 2000 we estimate the total global storage to be between 605 and 1814 Tg N (Figure 6.1).   The range of values of nitrate storage associated with uncertainty in nitrate leaching inputs (605 - 1814 Tg N) is significantly greater than that for uncertainty in unsaturated zone travel time (1007 – 1496 Tg N) or vadose zone saturation (778 – 1227 Tg N).   Modelled estimates of nitrate stored in vadose zones of all types of carbonate rocks are estimated to be 9.6% (58 – 174 Tg) of total N storage. In these areas rapid transport may occur and observed storage may be limited due to low matrix porosity, and consequently model estimates are likely to be overestimates. Total vadose zone N storage is small (<3%) in comparison to estimates of total soil N (68,000 (Prentice, 2008) – 280,000 (Lin et al., 2000) Tg N), but potentially significant (7 – 200%) in comparison to estimates of more labile soil inorganic N (NO_3^- + NH_4^+, 940 (Prentice, 2008) – 25,000 (Lin et al., 2000) Tg).   The modelled spatio-temporal distribution of nitrate stored in the vadose zone (Figure 6.2) shows increases between 1950 and 2000 associated with increased global use of N fertilizers and subsequent leaching.   Basins in North America, China and Central and Eastern Europe have developed large amounts of nitrate stored in the vadose zone due to thick vadose zones, slow travel times and high nitrate loadings.

Comparisons between estimates of nitrate storage made in this study with previous works go some way to validating the modelling undertaken. Previous studies have derived the amount of nitrate stored in the vadose zone for the Thames Basin (Ascott et al., 2016b; Worrall et al., 2015a) England and for the countries of England and Wales and the USA (Ascott et al., 2016b). The calculated peak store of 0.059 Tg N for the Thames catchment in this study agrees broadly with the range of peak nitrate storage values reported in previous work in this area (0.016 – 0.24 Tg N). For England and Wales, we calculated a peak store of 1.7 Tg N which agrees with previous calculations estimating the store to be 0.8 – 1.75 Tg N. For the USA, a first estimate

of 29 Tg N was previously made (Ascott et al., 2016b) and our modelling suggests a store of 191 Tg N. This large discrepancy can be accounted for by the modelling approach of the previous study which only considered land areas where agriculture was greater than 40% of the overall landuse.

The distributions of observed groundwater nitrate concentrations and modelled concentrations in groundwater recharge show reasonably good agreement for both European Union and United States (Figure 6.3). It should be noted that comparison between observed groundwater concentrations and concentrations in recharge do not take into account dilution of recharge by low-nitrate groundwater. Consequently, comparison between these datasets should be considered to be a sense-check, but nonetheless useful, validation. The distributions of nitrate concentrations in the USA appear to be more similar than those for Europe, which reflects the much larger observational dataset for the USA than for Europe (see Methods).
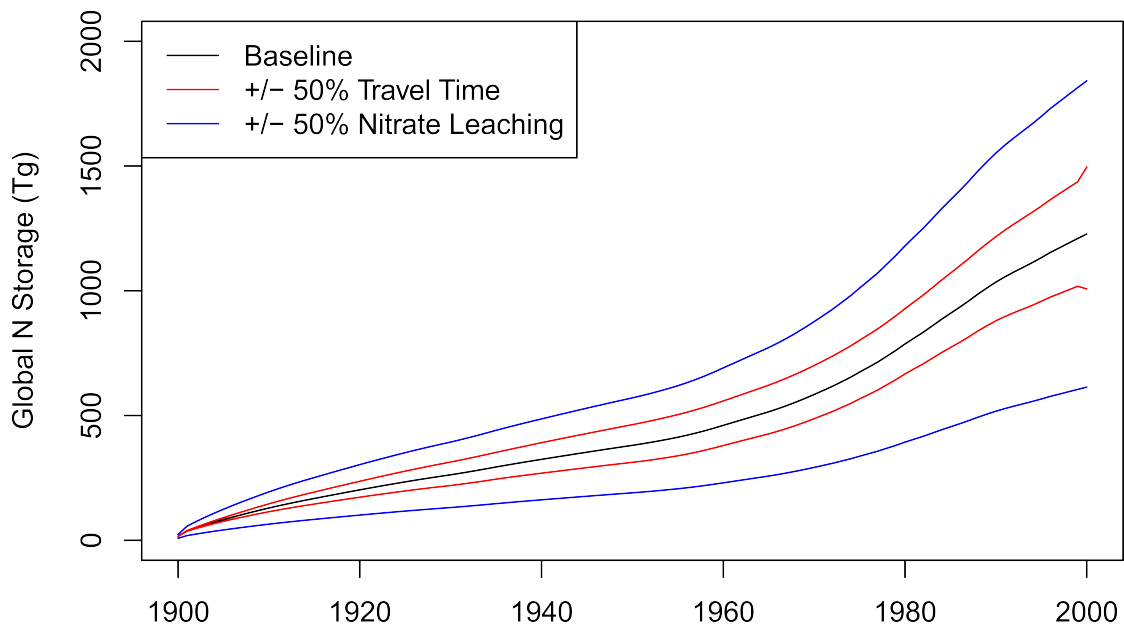
Figure 6.1: Modelled global increase in nitrate (Tg N) stored in the vadose zone for 1900-2000 under the baseline model run (black) and from sensitivity analyses (red and blue for +/- 50% travel time and nitrate leaching respectively)
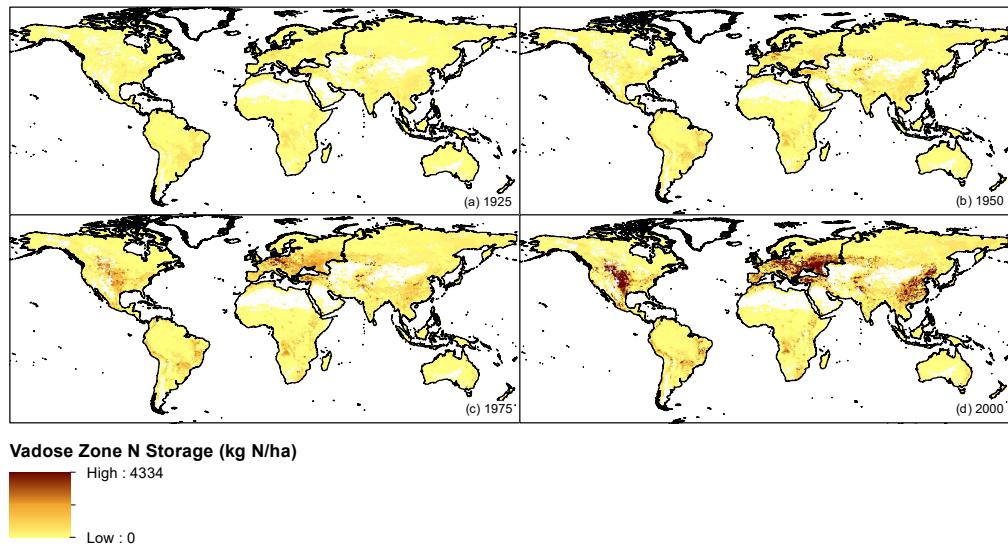
Figure 6.2: Spatial distribution of nitrate stored in the vadose zone in kg N ha-1 for 1925 (a), 1950 (b), 1975 (c) and 2000 (d)

6.2.2   Coherent basin scale nitrate storage trends

k-means cluster analysis revealed 3 spatially coherent responses in basin nitrate storage (Figure 6.4 a and b) reflecting differences in vadose zone travel time (c) and nitrate leaching inputs (d). In all the clusters, the time taken for the impact of stopping N leaching inputs from the base of the soil zone (i.e. $N_{leach} = 0$, see Methods) to reach groundwater ($N_{out} = 0$) will equal the vadose zone travel time. The majority of basins fall within clusters 1 and 2. These clusters show a continuous increase in the nitrate stored in the vadose zone. The vadose zones in some areas of the basins in these clusters accumulate nitrate with no loss to groundwater as the travel time through the vadose zone is long (Figure 6.4 c) due to deep water tables and low recharge rates. In these catchments some legacy nitrate may not have reached the water table yet and anticipated improvements in groundwater and surface water quality due to catchment management may be delayed. It should also be noted that there may also be large lags in the saturated zone between recharge at the water table and discharge at receptors such as public water supply wells and streams where there are long groundwater flow paths. Additionally, in some areas where groundwater recharge is estimated to be very low, modelled

estimates of vadose zone nitrate are likely to represent storage in both the soil and vadose zone.

Cluster 3 shows a substantially different nitrate storage response to the other clusters. This response a result of shorter vadose zone travel times throughout each basin. In these basins, storage rapidly increases initially until the travel time is reached and nitrate is present across the full depth of the vadose zone. After this point the basin moves to a quasi-steady state where any input of nitrate from the base of the soil zone is accompanied by an equivalent loss from the base of the vadose zone to groundwater. This dynamic balance results in minimal increases in nitrate storage and a relatively rapid response to changes in N loadings in comparison to other clusters. In these catchments, nitrate loss at the base of the soil zone > 10 years ago is likely to now be present in groundwater.

The nitrate leaching time series for each cluster (Figure 6.4 d) show distinct differences associated with the extent of historical agricultural and population development. Cluster 1 shows a continuous increase in nitrate leaching inputs through time associated with increased development and intensification of agriculture to maximise crop yields. Basins in cluster 1 form a spatially coherent pattern, covering large parts of the developing world including Africa, Southeast Asia and South America. Cluster 2 shows an increase in nitrate leaching to c. 1985, followed by decreases to 2000. Such an input can be characterised by historical agricultural development followed by implementation of catchment measures to reduce nitrate losses in the last decade. Spatially this cluster reflects large parts of the developed world including the USA and Europe. The nitrate leaching time series for cluster 3 shows large variability associated with the small number of catchments averaged but generally shows an increase to 2000. Recent studies have shown evidence that N losses from agriculture follow an Environmental Kuznets Curve (EKC), with a number of developed countries having reduced

N losses since the 1980s associated with increased GDP (Zhang et al., 2015). The spatiotemporal patterns of nitrate leaching inputs between the different clusters (Figure 6.4 c) corroborate this.
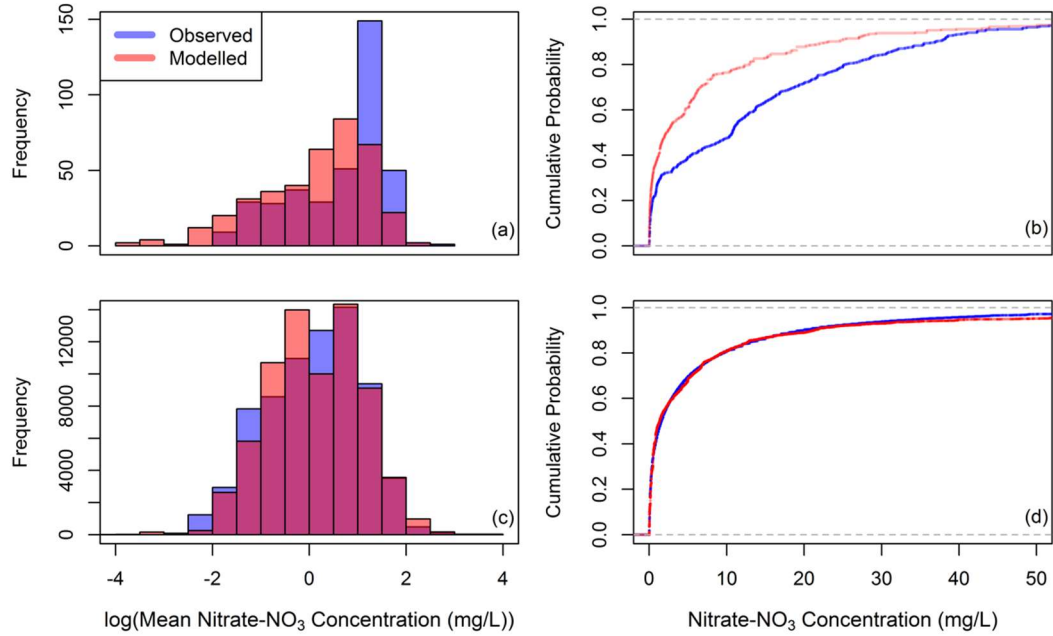
Figure 6.3: Distributions of observed (blue) nitrate concentrations in groundwater and modelled (red) nitrate concentrations in recharge at the water table for the European Union (European Environment Agency, 2015) ((a) and (b)) and the United States (USGS, 2015) ((c) and (d)). Purple colour in the histogram indicates where the model and observed concentration distributions overlap.
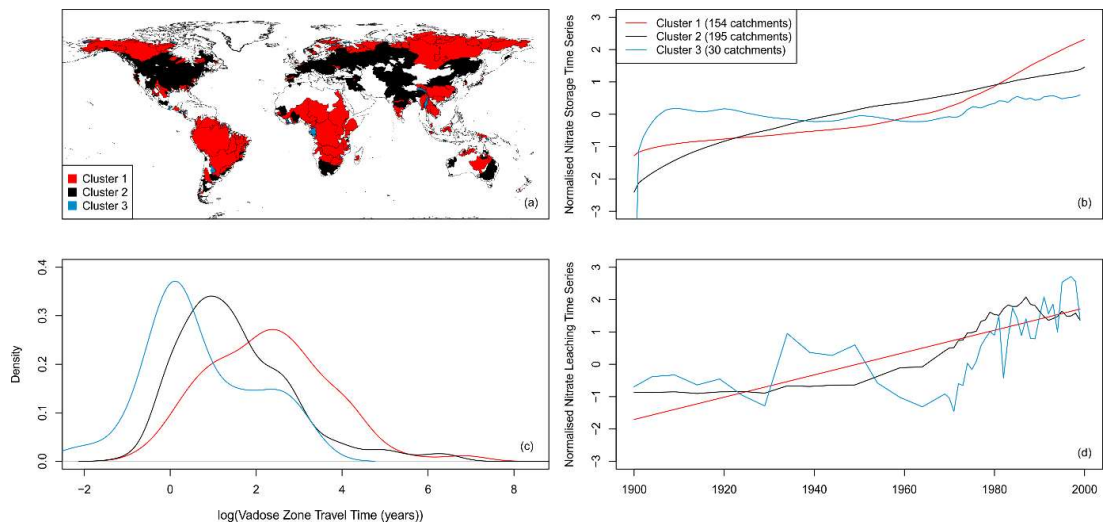
Figure 6.4: Spatial distribution of the nitrate storage clusters (a), nitrate storage cluster centroids (b), distribution of vadose zone travel times (c) and mean annual nitrate leaching input time series (d) for each cluster.

6.3   Discussion

There is a well-established discourse on the balance between increasing agricultural productivity to improve human health and feed growing populations and the negative impact of N leaching on aquatic ecosystems (Fowler et al., 2013). A central tenet of future N management is that agricultural productivity can be increased in a cost effective manner with limited environmental impacts through increased N use efficiency (NUE) and reduced soil N surplus (N_{sur}) (Stefan et al., 2016; Zhang et al., 2015). Several recent studies have continued to assume that N_{sur} is directly analogous to nitrate pollution (Mekonnen and Hoekstra, 2015; Oita et al., 2016; Zhang et al., 2015) and recently developed models that do consider groundwater explicitly still ignore the vadose zone (Beusen et al., 2015). Given the substantial lags present in the transport of nitrate from the soil zone to groundwater and surface water, we argue that use of N_{sur} alone as a metric to quantify impacts of agriculture on the aquatic environment is inappropriate. Our modelling shows that the vadose zone is a globally significant store of nitrate which needs to be considered in future N budgets for more effective long-term nutrient management. N storage in the vadose zone is most important in areas where agricultural development and intensification occurred first and where there is a large depth to groundwater. The vadose zone is one of a number of temporary catchment stores, which also include soil organic matter (Van Meter et al., 2016), subsoils, land not in agricultural production (Worrall et al., 2009), the riparian zone and in rivers (Grizzetti et al., 2015; Worrall et al., 2015a). These possible N stores and how they change through time (e.g N release through mineralisation of soil organic matter) should also be compared with storage in the vadose zone to determine whether they are significant enough to be incorporated into future nutrient budgets. In combination, these processes will result in substantial delays in the impacts of changes in agricultural management practices on groundwater and surface water quality.

Nitrate storage in the vadose zone has significant implications for environmental policy. The need for internationally cooperative policy responses to N pollution to avoid shifting of pollution sources to areas with less stringent environmental controls has been established (Bodirsky et al., 2014). However, development of such policies is in its infancy (Oita et al., 2016). Moreover, established policies in the developed world have been shown to be difficult to implement in areas where vadose zone lags are present. For example, it is now widely acknowledged (Cherry et al., 2008; Fenton et al., 2011) that original environmental targets set under the European Water Framework Directive (European Union, 2000) and Nitrates Directive (European Union, 1991a) may not be met due to storage of nitrate in the vadose zone. As a result, many river basin managers have been forced to consider new planning timescales accounting for these lags (Fenton et al., 2011).

Recent work (Grizzetti et al., 2015) has called for the development of integrated pollution management policies which consider both all macronutrient processes (sources, sinks, stores and time lags). This research provides a critical contribution to the literature in that we make the first global scale quantification of one of these temporary stores. The spatial distribution of vadose zone N storage in 2000 (Figure 6.2) can give a first global indication to policymakers and decision-makers of where N legacy issues may be significant and delay improvements in groundwater and surface water quality. In these areas, an understanding of nitrate storage in the vadose zone can help managers in planning mitigation measures and the timescales and expectations for improvements in water quality. With this quantification of vadose zone N storage and further research to quantify other N stores at the global scale, development of integrated pollution management strategies at an international level should be possible. Such an approach is critical for a realistic assessment of environmental impacts of global N flows associated with economic development and international trade (Oita et al., 2016).

The spatial coherence of the nitrate storage clusters (Figure 6.4) highlights the need for different management strategies to tackle nitrate pollution across developing and developed countries. In the developed world, a number of countries are already on a trajectory of declining soil N losses associated with sustainable intensification of agriculture (Zhang et al., 2015). In the developing world, soil N losses are increasing associated with rapid early development of fertilized agriculture (Zhang et al., 2015). However, in both cases, catchment processes such as vadose zone storage must be considered. Without consideration of these lags, which is often the case, nitrate pollution control policy may appear not to be working. This may lead to more stringent but unnecessary measures that may adversely impact agricultural production and/or lead to disproportionate costs.

6.4   Methods
6.4.1   Estimates of Vadose Zone Travel Time

Travel time in the vadose zone was derived by estimating the depth to groundwater and nitrate velocity. Depth to groundwater mapping at 0.5 degree scale was derived from previously published global groundwater model forced by modern climate, terrain and sea level (Fan et al., 2013). Velocity of nitrate (V_{NO3}, m year^{-1}) in the vadose zone was calculated as follows:

$$V_{NO3} = \frac{R}{\varnothing} \qquad (6.1)$$

Where R is the recharge rate (m year^{-1}) and $\varnothing$ is effective porosity (dimensionless). Global groundwater recharge mapping was derived from the PCR-GLOBWB model (Wada et al., 2010) which has been used extensively in global scale hydrological modelling (Bierkens, 2015; Gleeson et al., 2016; Gleeson et al., 2012). PCR-GLOBWB calculates vertical water fluxes between 2 soil layers and groundwater based on unsaturated hydraulic conductivity estimates for each layer (Van Beek and Bierkens, 2009). Unsaturated hydraulic conductivity was

calculated using the degree of saturation of each layer. The degree of saturation was calculated based on average, saturated and residual soil moisture content, in turn derived by depth of water storage in each layer and the layer thickness. Global soil mapping (Sanchez et al., 2009) and soil moisture characteristic curves (Clapp and Hornberger, 1978) were used to derive soil physical relationships for each layer, tabulated moisture retention, matric potential and unsaturated hydraulic conductivity values.

Whilst recharge estimates derived using PCR-GLOBWB account for increased hydraulic conductivity with increased saturation, vadose zone velocities can also decrease with increased saturation associated with an increased cross-sectional area of flow (Sousa et al., 2013). Based on previous catchment and regional scale approaches (Fenton et al., 2011; Sousa et al., 2013; Vero et al., 2014; Wilson and Shokri, 2015), we accounted for this process separately from recharge in the calculation of deep vadose zone travel times.   Estimates of travel time through the deep vadose zone calculated using equation 6.1 assumes a fully saturated matrix. This assumption is supported by work which shows that vadose zone velocities calculated using this method agree well with observed velocities derived from vadose zone porewater profiles in limestone and sandstone aquifers (Wang et al., 2012). However, in partially saturated media, assuming 100% effective saturation will result in unsaturated zone velocities being underestimated and hence vadose zone storage being overestimated. N storage in vadose zones of strongly karstified aquifers with limited matrix porosity will also be overestimated using this method.   Global geological maps do not differentiate between karst and non-karst sedimentary carbonate rocks (Gleeson et al., 2011), so we explored the impact of these assumptions on model results through sensitivity analysis (see below).

6.4.2 Estimates of Nitrate Leaching from the base of the soil zone

Nitrate leaching (N_{leach}, kg N 0.5 degree grid cell^{-1} year^{-1}, same units for all N budget terms) at the base of the soil zone was derived from the global nutrient model IMAGE (Beusen et al., 2015) for 1900 to 2000. IMAGE has been detailed extensively elsewhere (Beusen et al., 2015; Bouwman et al., 2013b; Van Drecht et al., 2003) and the key soil zone N inputs, outputs and processes are described here for clarity and illustrated in Supplementary Fig. 1. IMAGE uses the concept of an annual steady state soil N budget surplus, defined as the balance between soil N inputs and outputs for a unit land area. Storage and release of N associated with changes in soil organic matter through time are not considered. Historic land cover data (Zuidema et al., 1994) at the 0.5 degree scale which distinguishes between 9 agricultural land use types and 17 different natural ecosystems was used as a basis to derive 5 broad land use groups for the soil N budget estimation (Supplementary Fig. 1). The soil N budget (N_{budget}) is calculated as follows:

$$N_{budget} = N_{fix} + N_{dep} + N_{fert} + N_{man} - N_{withdr} - N_{vol} \qquad (6.2)$$

Where N_{fix} is biological N fixation, N_{dep} is atmospheric N deposition, N_{fert} is application of N fertilizer, N_{man} is addition of manure and N_{withdr} and N_{vol} are loss terms for N withdrawal from harvesting and ammonia volatilisation respectively.

Biological N fixation in leguminous (pulses and soybeans) crops and natural ecosystems was estimated by crop production data and N content (Bouwman et al., 2013b; FAO, 2008). It was assumed that total biomass of leguminous crops was twice that of the harvested product, and that N is also released to the soil during the growing season (Van Drecht et al., 2003). Fixed N is available for harvesting, or volatilisation and leaching if released to the soil. Total N fixation during the growing season was therefore derived by multiplying the N in harvested product by 3 to account for this additional unharvested biomass and the plant-soil N flux (Van Drecht et al., 2003). Atmospheric N deposition for the year 2000 was estimated from an ensemble

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of global atmospheric chemistry models (Dentener et al., 2006) and estimated for 1900 to 2000 by scaling the N deposition field with historic emissions inventories (Bouwman et al., 2013b). Country level N fertilizer application rates divided by land use for 1900 to 2000 were derived from global databases (FAO, 1951; FAO, 2008) and data on fixed N use in 1913 (Cressy, 1937). Country animal population data in conjunction with N excretion rate estimates (Van der Hoek, 1998) were used to estimate addition of N in manure form. Animal populations back to 1900 were derived from statistical compilations by Mitchell (Mitchell, 1993a; Mitchell, 1993b; Mitchell, 1998) and scaling of human population data (Goldewijk et al., 2010) for poultry and camels where data was limited. N loss through ammonia volatilisation was estimated using an empirical model of c. 1700 field measurements across a range of different crop types, fertilizer types and applications and environmental conditions (Bouwman et al., 2002). Removal of N through harvesting was estimated from country crop production data, crop dry matter and N content estimates(Bouwman et al., 2005). N budget inputs and outputs derived from crop type and production data (N_{fix}, N_{man}, N_{withdr}, N_{vol}) were estimated back to 1900 by scaling 1960 crop production data with population numbers and land use data in the HYDE database (Klein Goldewijk et al., 2011).

It is assumed that all reduced N compounds are nitrified to nitrate such that N_{budget} = soil nitrate (Van Drecht et al., 2003). When N_{budget} is positive, leaching, surface runoff and denitrification can occur. N leaching (N_{leach}) at the base of the soil zone is a fraction of the soil N budget excluding N loss via surface runoff (N_{sro}):

$$N_{\text{leach}} = f_{\text{leach}}\left(N_{\text{budget}} - N_{\text{sro}}\right) \tag{6.3}$$

Where the soil leaching fraction, f_{leach}, is complementary to the fraction of soil N lost by denitrification (f_{den}):

$$f_{\text{den}} = 1 - f_{\text{leach}} \tag{6.4}$$

f_{leach} is estimated empirically using 5 denitrification factors, each with a range from 0 to 1, with a maximum value of 1:

$$f_{\text{leach}} = \left[1 - MIN[(f_{\text{climate}} + f_{\text{text}} + f_{\text{drain}} + f_{\text{soc}}), 1]\right]f_{\text{landuse}} \tag{6.5}$$

Where $f_{climate}$, f_{text}, f_{drain}, f_{soc} and $f_{landuse}$ are factors representing climate, soil texture, aeration, soil organic carbon content and landuse respectively(Beusen et al., 2015). $f_{climate}$ uses the Arrhenius equation and estimates of soil water capacity and potential recharge to estimate the effects of temperature and residence time on root zone denitrification (Beusen et al., 2015). f_{text}, f_{drain}, f_{soc} were estimated using global scale mapping of soil texture, drainage and organic carbon content (Batjes, 1997; Van Drecht et al., 2003). $f_{landuse}$ was set to 1 for arable land areas, with grassland and natural vegetation having a value of 0.36 (Keuskamp et al., 2012). For further detail on soil N budget inputs, outputs and processes the reader is referred to previous modelling studies (Bouwman et al., 2013b; Van Drecht et al., 2003).

6.4.3 Calculation of Nitrate Storage in the Vadose Zone

Nitrate storage in the vadose zone was calculated using a simple summation approach. It was assumed that nitrate undertakes conservative transport in the vadose zone. This assumption is supported by numerous studies (Rivett et al., 2008) which showed that the evidence for vadose zone denitrification is very limited, with just 1-2% of the nitrate leached from the soil zone removed (Rivett et al., 2007). In some specific local hydrogeological environments (e.g. where anaerobic conditions and organic carbon are present (Rivett et al., 2008)) vadose zone denitrification may occur, and in these areas the model may overestimate nitrate storage. However, at the global scale this was considered negligible. For a year t (years), the nitrate stored in vadose zone, N_{VZ} (Tg N) for a grid cell with a vadose travel time, TT_{VZ} (year) and a time-variant nitrate leaching input, N_{leach} (kg N), can be calculated as:

$$N_{\text{VZ}} = \frac{\sum_{i=t-TT_{\text{VZ}}}^{t} N_{\text{leach}}}{10^9} \tag{6.6}$$

Global maps of the model input datasets and the derived vadose zone storage for the year 2000 are shown in Supplementary Fig. 2. We derive changes in nitrate storage in the vadose zone through time using a simple mass balance approach;

$$N_{\text{leach}_t} - N_{\text{out}_t} = \Delta N_{\text{VZ}} \qquad (6.7)$$

Where N_{out} (kg N) is the nitrate flux from the unsaturated zone to the saturated zone and ΔN_{VZ} (kg N) is the change in nitrate storage in the vadose zone.

6.4.4 Sensitivity and Cluster Analysis

We undertook a heuristic sensitivity analysis by running the model using different inputs. We separately varied the vadose zone travel time and nitrate leaching input by +/-50%. We also varied vadose zone effective saturations (0.25, 0.5, 0.75 and 1) to account for variable cross-sectional area of flow in partially saturated media.

We aggregated vadose zone N storage data by lithology and catchments. We separated areas underlain by sedimentary carbonate rocks (Gleeson et al., 2014) to account for rapid vadose zone transport in karstic aquifers with limited matrix porosity, and hence limited N storage. We normalised the catchment nitrate storage responses for 1900 – 2000 and used k-means clustering (Webster and Oliver, 1990) to identify spatial patterns of N storage responses. We adopted a parsimonious approach by incrementally testing k = 2 to k = 4 and evaluating the spatial coherence of the clusters. k = 3 was shown to have the most spatially coherent patterns. For each of the clusters we calculated the mean annual nitrate leaching input for 1900 – 2000 and the kernel density distribution of travel times for the catchments within the cluster.

6.4.5 Model Validation

We undertook a 2 step model validation: (1) Comparison against previously published national and catchment scale estimates of nitrate storage in the vadose zone and (2) Comparison against nitrate concentrations in groundwater. Recent work has given estimates of nitrate storage in the vadose zone for the United Kingdom and the USA (Ascott et al., 2016b) and for the Thames catchment (Worrall et al., 2015a), England. We estimated nitrate concentrations in recharge at the water table as follows:

$$Conc = \frac{N_{\text{out}}}{Recharge} \qquad (6.8)$$

Modelled estimates of nitrate concentrations in recharge were compared against observed groundwater nitrate data for Europe (European Environment Agency, 2015) and America (USGS, 2015). It should be noted that this comparison does not directly validate estimates of nitrate storage. Comparison against observed nitrate concentrations in groundwater provides a sense-check that the nitrate inputs and vadose zone travel time estimates are reasonable.

6.4.6 Data Availability

Global input datasets (depth to groundwater table, recharge rate, porosity and nitrate leaching) and model validation data (groundwater nitrate concentrations) are publically available from the references cited in the section 6.4.

6.5 Acknowledgements

6.6   Supplementary Information
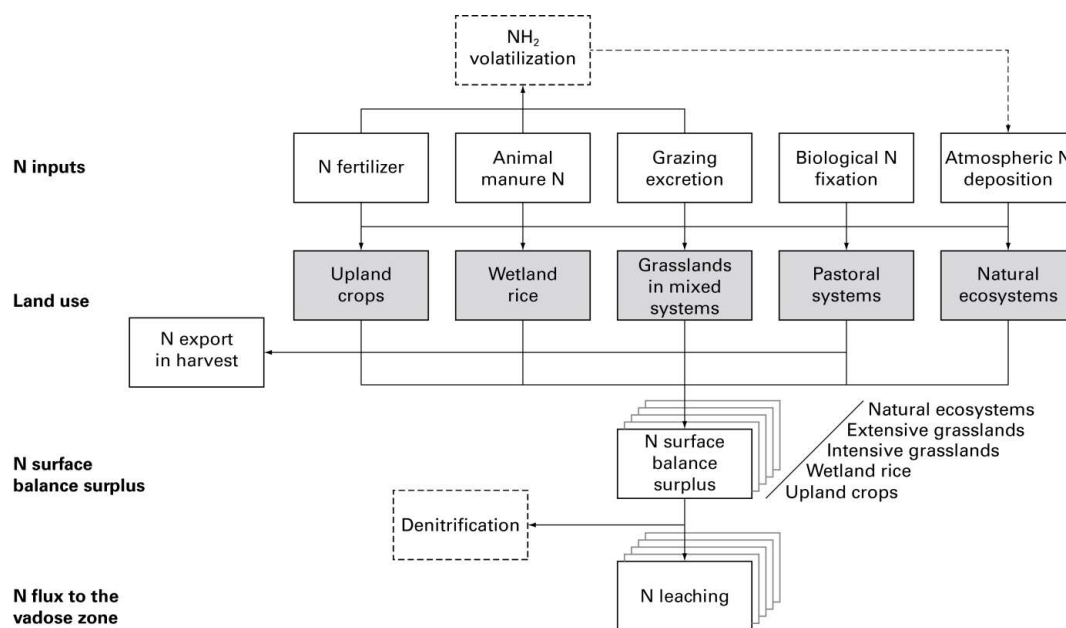
Supplementary Fig. 1: Scheme used to calculate N leaching at the base of the soil zone. Modified after Van Drecht et al. (2003) with permission from Wiley.
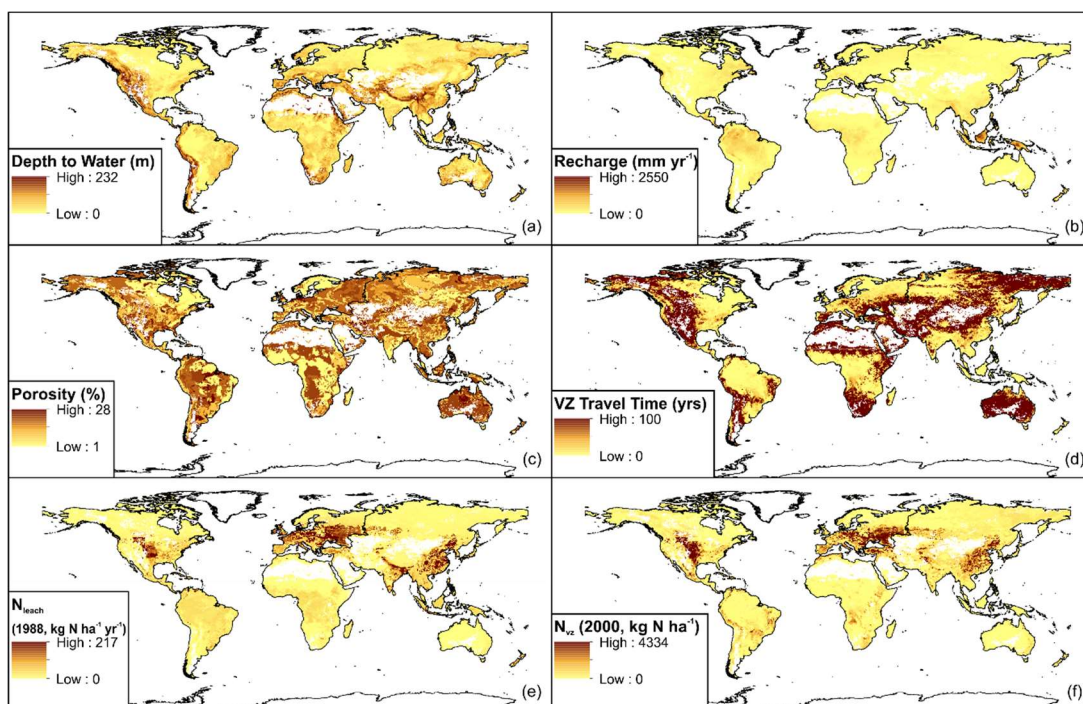
Supplementary Fig. 2: Global depth to water (reproduced after Fan et al. (2013), with permission from AAAS) (a), groundwater recharge (reproduced after Wada et al. (2010), with permission from Wiley) (b), porosity (reproduced after Gleeson et al. (2014) with permission from Wiley) (c) input datasets and derived vadose zone (VZ) travel times (d), nitrate leaching (Nleach) for 1988 (Beusen et al., 2015) (e), and vadose zone nitrate-N storage (Nvz) in 2000 (f)

7 Concluding Discussion

7.1 Discussion

7.1.1 Fundamental contributions of this research to scientific knowledge in relation to thesis objectives

The overarching aim of this research was to develop an improved understanding of N and P sources, sinks and stores associated with public water supply and the vadose zone, to support integrated nutrient management strategies. Figure 7.1 shows the conceptual model initially developed in Figure 2.6 with the significant conclusions of this research shown in red. In relation to the initial research objectives set in section 1.2, this thesis has made the following fundamental contributions to scientific knowledge:

- Mains water leakage is an important source of P to the environment in urban areas and this source exhibits significant seasonality. This is an important and novel contribution to our understanding of the P cycle. Winter fluxes of P from mains water leakage are > 150% of spring/autumn fluxes, and equivalent to up to 20% of winter fluxes of P from wastewater treatment works. The relative importance of mains water leakage as a source of P will increase in the future, with the ratio of P fluxes from mains water leakage to wastewater treatment predicted to increase to 38% by 2040. This change in importance is associated with large reductions in P fluxes from wastewater treatment and modest reductions in mains water leakage and no reductions in P dosing. (*Objective 2*)

- The impact of public water supply processes on inorganic N fluxes in the environment is a highly novel scientific outcome of this thesis with important implications for our understanding of the N cycle. Abstraction of inorganic N for public water supply is a highly significant temporary sink, equal to six times the estimates of organic N removal by abstraction, 15 times in-channel storage of organic N, and 30 times floodplain storage of organic N. Abstraction of inorganic N is also between 3 and 39% of N

removal by denitrification in the hydrosphere. Given that estimates of denitrification have been derived from the difference between N source fluxes and the fluvial flux at the tidal limit, it is plausible that some of the N losses previously ascribed to be denitrification may in reality be temporary sinks as ABS-N. This potential shift from permanent N removal by denitrification to a temporary sink by abstraction (and, considering long timescales, potential re-release into the aquatic environment) is a highly significant research result which challenges the assumption that in-stream N losses are solely due to denitrification *(Objective 3).*

- Mains water leakage is an important source of inorganic N in urban areas, representing up to 20% of total N inputs. Approximately 15% of ABS-N is returned to the environment as MWL-N. Water transfers are predicted to increase MWL-N fluxes in the future by up to 66%. (*Objective 3*).

- Estimates of storage of nitrate in the unsaturated zone at the national and global scales have important scientific implications for our understanding of the N cycle.   In England and Wales, estimates of nitrate stored in the vadose zone are 2.5 – 6 times greater than previous estimates for the saturated zone, with the majority of the mass stored in the Chalk (*Objective 4*). Globally, total peak vadose zone storage is estimated to be between 7 and 200% of soil inorganic N stores, with the most N stored in areas with significant historical agricultural development and deep water tables *(Objective 5)*.   This research has shown that conventional steady-state nutrient budget approaches are likely to be invalid in areas where significant N is stored in the unsaturated zone, and that this store of reactive N needs to be considered in future N budgets.
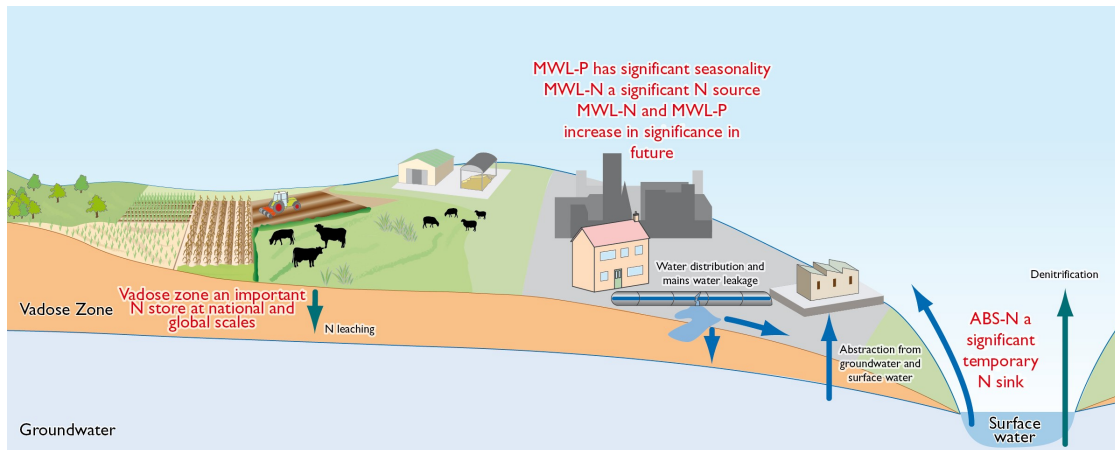
Figure 7.1 Conceptual model of improved understanding of N and P sources, sinks and stores associated with public water supply and the vadose zone. Significant conclusions of this research are shown in red.

7.1.2 Implications for macronutrient budgets and integrated nutrient management approaches

7.1.2.1 Novel estimates of sources and sinks of N and P

The overarching philosophy of integrated nutrient management approaches is to consider all macronutrient processes (sources, sinks, stores and time lags) in a river basin (Grizzetti et al., 2015). The research undertaken in this thesis has important implications for these approaches. This thesis makes a critical contribution to knowledge by providing the first national and global scale estimates of nitrate stored in the vadose zone. To date, inclusion of public water supply processes in macronutrient budgets and models has been limited (Finlay et al., 2016; Lerner, 2003) and future research should consider N and P sources and sinks associated with these processes. The research reported in this thesis is critical in that it makes the first estimate of temporal variation and future scenarios of MWL-P and the first estimates of ABS-N and MWL-N at the national scale. Grizzetti et al. (2015) also suggest that one of the most significant research challenges that must be addressed in the development of integrated nutrient management approaches is quantifying the split between permanent and temporary sinks. To this end, this thesis makes a critical contribution to this discourse by calculating the temporary N sink associated with public water supply abstraction relative to all in-stream N losses (assumed to be a permanent N sink in the form of denitrification).

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Grizzetti et al. (2015) define integrated nutrient management to include all processes affecting nutrient cycles. Soil N and P budgets have quantified N and P stores (Plaza et al., 2018; Post et al., 1985; Prentice, 2008; Sattari et al., 2012) and substance flow analyses have quantified P (Chen and Graedel, 2016) (and to a limited extent, N (Chen et al., 2016)) stores in other compartments of the environment. Whilst a few national (Worrall et al., 2009; Worrall et al., 2016a) and global scale budgets (Bouwman et al., 2013a) have quantified the magnitude of the groundwater N store, in many large scale N budget studies limited attention has been paid to quantifying actual N *stores* (the mass of N, i.e. kg N) in comparison to N *sinks* (i.e. a flux in kg N/day). More broadly, there is some inconsistency in the N cycling literature regarding the use of the term "store", with some referring to it as a flux (United States Environmental Protection Agency, 2011), and some as a mass (Chen et al., 2018; Van Meter et al., 2016). Given the importance of N stored in the vadose zone both nationally and globally as shown in this thesis, it is suggested that a clear distinction between stores and sinks is made in the N cycling community in the future, as defined in section 1.1 and reiterated above.

Having made this distinction, it is suggested that N budgets need to better take into account macronutrient stores in the environment and how these change both spatially and temporally, as well as sources and sinks. As discussed in section 2.2.3, numerous P budgets based on substance flow analysis already calculate P stores other than the soil zone on the basis that P is a finite resource. It is suggested that future N budgets could adopt similar approaches to P budgets (e.g. Yuan et al. (2018)), estimating the size of N stores. To this end this thesis makes a critical contribution to scientific knowledge by calculating the magnitude of one of these temporary stores (the vadose zone).

7.1.3 Implications for management and decision making

This research has important implications for N and P source apportionment and decision making related to macronutrient source control. Models used for source apportionment (e.g. SAGIS (Comber et al., 2013), SEPARATE (Zhang et al., 2014), SPARROW (Hoos and McMahon, 2009), Source Load Apportionment Model (SLAM, Mockler et al. (2017))) should better take into account N and P sources and sinks associated with public water supply processes such as ABS-N, MWL-N and MWL-P. Given the highly simplified approaches used to represent processes in existing models (if included at all), incorporating ABS-N, MWL-N and MWL-P in detail is likely to require structural changes to the models, rather than changes in parameter sets.

Given the importance of MWL-N and MWL-P, development of policy responses that consider both the environmental costs and benefits of these fluxes is required. For MWL-P, a simplistic policy response to lowering this flux would be the wholesale removal of lead pipework, thus removing the requirement to undertake P dosing. However, this approach is likely to be prohibitively expensive. It has been estimated that the market price of P used for dosing would have to increase by a factor of 20 before removal of lead piping becomes a financially viable option (UK Water Industry Research Ltd, 2012). This approach also has no impact on MWL-N fluxes. Given that nitrate concentrations in drinking water are below the drinking water standard (Drinking Water Inspectorate, 2017b) and there is no driver to reduce this standard further, additional nitrate removal from raw waters to reduce MWL-N fluxes is unlikely to be realistic.

MWL-P and MWL-N could be addressed by integrating the potential impact of these fluxes into calculations of the Sustainable Economic Level of Leakage (SELL). For MWL-N, this would require a trade-off analysis between the environmental damage of MWL-N as an N source against the benefits of dilution of high nitrate sewer leakage. Most water companies in England and Wales operate at leakage rates at or below the SELL (Chartered Institute for Water and Environmental Management, 2015), however there is a broad aspiration to reduce leakage rates further, with current research evaluating whether reductions to zero by 2050 are feasible (UK Water Industry Research Ltd, 2018). Consideration of the impacts of MWL-P and MWL-N in leakage cost-benefit analyses should provide more impetus to achieve these goals.

An alternative approach to tackling MWL-N and MWL-P could be to integrate these fluxes into catchment scale macronutrient permitting processes. Permitting processes which estimate the total maximum daily load of P have been developed in the USA and the UK (Gooddy et al., 2017) and permit schemes for N have recently been developed in Australia (Smart et al., 2016). If total loads exceed those specified in catchment permits, water companies may reduce these through reductions in individual source terms. By integrating MWL into estimates of total loads, water utilities may choose to reduce MWL as a macronutrient source, or make reduction in loads from other sources (e.g. wastewater treatment). However, there are likely to be challenges associated with this approach. If MWL is diluting high N sewer leakage, reduction in MWL may result in increases in N concentrations in receiving groundwater and/or surface water. Moreover, integration of MWL would also require a detailed understanding of the ultimate fate of MWL-N and MWL-P in the environment, which is considered to be a significant uncertainty at present.

As previously discussed, a number of models and budgets used for macronutrient source control adopt a steady state approach. This research has shown that the vadose zone is a significant temporary store of N. The accumulation and subsequent release of macronutrients from this store may give the appearance that N and P source control is not working. Future development of models used for N and P source control should consider incorporating this store. Incorporating this store is likely to be a challenging task, and thus at the very least the results of existing models which do not incorporate macronutrient storage in the unsaturated zone should be viewed in light of the results of this research. Predicted timescales for changes in macronutrient fluxes in aquatic ecosystems which are derived from models which do not incorporate this store will need to be extended.

7.1.4   Further research

This research has made a number of advances towards the aim of gaining an improved understanding of N and P sources, sinks and stores associated with public water supply and the vadose zone, to support the development of integrated nutrient management strategies. However, further research is required to gain a better understanding of the fluxes and stores quantified in this thesis and to integrate them into improved models of N and P cycles. To this end, the following specific areas of further research would be of benefit:

- Understanding the environmental fate of MWL-N and MWL-P. For the first time, the research in this thesis has developed robust estimates of MWL-N and MWL-P fluxes now and in the future. However, the ultimate fate of both MWL-N and MWL-P is poorly constrained. Further research to understand the fate of MWL nutrient fluxes would be highly beneficial. Combining localised leakage rates and tap water N and P concentrations with sewer and surface water flow and concentration data could provide insights into the split of MWL nutrient fluxes between groundwater, surface water and the sewer network. Nitrate-nitrogen, nitrate-oxygen and phosphate-

oxygen isotopes may also be of use in characterising the biogeochemical fate of MWL nutrient sources. MWL-P has been shown to have one of two distinct phosphate-oxygen isotope signatures (Gooddy et al., 2015). MWL-N is unlikely to have a unique nitrate isotope signature at the national scale as N in tap water is derived from a range of sources. Depending on whether any fractionation occurs during water abstraction and treatment, nitrate isotopes of MWL-N may reflect the local source water. Further work exploring how these isotopic signatures change as MWL moves away from a leak site may provide some indication of the fate of both N (biotic uptake, denitrification) and P (sorption, biotic uptake).

- Improved understanding of storage processes and timescales. This research has shown that there are large amounts of nitrate stored in the unsaturated zone. However, the results reported in this research represent first estimates of this store at the national and global scales. In order to improve these estimates, it is suggested that models are refined considering heterogeneity in subsurface transport processes (for example, in karstic environments (Hartmann et al., 2015; Hartmann et al., 2017)) and changing water table depth (de Graaf et al., 2015). Refined global models should also be evaluated against existing modelling studies and observations at the regional scale (e.g. the studies summarised by Vero et al. (2018)). It should be noted, however, that such modelling and observational studies are limited and only cover a small proportion of the land uses and hydrogeological settings across the globe. Consequently, targeted field campaigns to estimate N storage in the vadose zone, soil zone and groundwater in catchments which are in less well studied land use-hydrogeological settings (e.g. crystalline basement aquifers overlying agricultural land), would also be of benefit to validate the models developed in this research.

- It has also been shown that relative to denitrification, public water supply abstraction is a potentially significant temporary sink for inorganic N. Denitrification has been

assumed to be equal to all in-stream losses, estimated based on the difference between the sum of N source terms and the N flux at the tidal limit (Worrall et al., 2012). Consequently, it is plausible that some of the in-stream N losses associated with denitrification may, in fact, be due to public water supply abstraction. Given the very wide range of published estimates of denitrification, further work to quantify these in-stream losses directly would be highly beneficial. Pinay et al. (2015) developed a framework for upscaling denitrification estimates from individual hotspots to the drainage basin scale based on catchment topography, landscape pattern and dynamic hydrological modelling. Integrating this framework with catchment similarity concepts (Krause et al., 2014) to derive denitrification estimates in catchments with limited monitoring data could support the development of national scale denitrification estimates to compare with the in stream loss fluxes reported by Worrall et al. (2012) and Leip et al. (2011).

- It should also be noted that the timescales for inorganic N sinks by abstraction are poorly understood. It is likely that within abstracted N the timescales for return of N to the environment will vary from relatively rapid (mains water leakage) to slow (N storage in landfill). Monitoring to develop an N budget of a complete water treatment (clean and waste) network would be beneficial for this.

In addition to these specific research needs, there are a number of broader gaps which need to be addressed if integrated nutrient management strategies are to be developed. In general, estimates of N and P stored in different parts of the terrestrial environment are scant. Previous workers have postulated N and P stores in soils, wastewater sludge, landfills, subsoils, land not in agricultural production and in-streams (Worrall et al., 2009; Worrall et al., 2015a; Worrall et al., 2015b; Worrall et al., 2016b). Future research needs to quantify other stores in the environment and compare the relative significance of these stores.

Having developed an understanding N and P stores as well as source and sink fluxes, further work would then be required to integrate this understanding into existing or new macronutrient cycle models and budgets. For practitioners, integration of all macronutrient stores, sources and sinks in catchment models is likely to be highly ambitious and potentially unrealistic, particularly in areas where existing models and data on N and P fluxes are limited. Consequently, research should focus on a range of different catchment typologies, to identify which stores and processes are most significant in each catchment typology. These typologies should consider a range of different land uses (e.g agriculture, urban) and hydrogeological settings (e.g. groundwater dominated, surface water dominated). Identification of the likely relevant macronutrient sources, sinks and stores in each typology could act as a screening tool to aid practitioners to identify which processes are relevant in their catchment of interest, with a view to determining priority areas for further investigation.

7.2   Conclusions

Despite being recognised for years, the conversion of unreactive forms of N and P to reactive forms and the resulting transfer of reactive N and P in the environment remains a considerable problem for both ecosystems and drinking water quality. In order to address both eutrophication of aquatic ecosystems and nitrate concentrations in drinking water, N and P budgets and models have been developed, many of which adopt a steady-state approach. These budgets can give an indication of the relative contribution of different well constrained nutrient sources to N and P loads, and can inform measures to control sources. However, despite implementation of source control measures, improvements in water quality have often not been realised over predicted timescales. It is now understood this is due to (1) macronutrient fluxes (sources and sinks) not previously considered, and (2) accumulation and subsequent release of legacy stores of N and P, resulting in the steady state assumption invoked in these budgets being invalid. To address these limitations of conventional steady

state approaches, "integrated nutrient management (INM)" has been suggested as an approach which considers all macronutrient processes in a catchment. However, to achieve this, there are still major gaps in our understanding of N and P processes related to the 2 limitations identified above. Although groundwater abstraction is well known to perturb the hydrological cycle, the impact of public water supply processes on N and P cycling is poorly understood. The importance of the vadose zone as a macronutrient store is also not well constrained.

The overarching aim of this thesis was to improve the understanding of sources, sinks and stores of N and P associated with public water supply and the vadose zone to support the development of INM. This aim has been achieved by addressing 4 targeted research objectives which have been identified as key research needs which must be addressed if INM approaches are to be developed. Mains water leakage has recently been identified as a potentially important source of P. However, understanding of the temporal variability in this source and how the importance of this source will change in the future is poorly understood (objective 2). There is also a very limited understanding of the importance of public water supply abstraction and mains water leakage as sinks and sources of N (objective 3). No estimates have been made of the size and spatiotemporal distribution of N stored in the vadose zone to date (objectives 4 and 5).

This thesis has shown that mains water leakage is an important source of P, which will increase in importance in the future. Mains water leakage of P has significant temporal variability associated with winter burst events, summer shrink-swell leakage and active leakage control. Mains water leakage has also been shown to be an important source of N in urban areas, contributing up to 20% of all N loads. Abstraction for public water supply has been shown to be an important temporary sink of N, equivalent to up to 39% of denitrification. This research

has shown that the unsaturated zone is also an important store of nitrate, with the quantity of nitrate stored in the vadose zone being equivalent to 200% of estimates of inorganic N stored in soils globally.

The results of this research have implications for the development of integrated nutrient management approaches. N and P sources and sinks associated with mains water leakage and abstraction for public water supply should be considered in future macronutrient budgets and models. Storage of nitrate in the vadose zone should also be included. Continued use of existing models which do not consider these additional N and P sources, sinks and stores should be tempered with the knowledge gained from this research. Whilst definitions of INM consider all macronutrient processes, little attention has been paid to estimates of N stores, and the term store has not been used consistently in the literature to date, particularly in the N cycling literature.   Given the importance of nitrate stored in the vadose zone shown in this thesis, a clearer definition of N stores as the actual mass within an environmental compartment would be beneficial. This should be followed by integration of these stores into models and budgets used in INM approaches.

This thesis provides a unique contribution towards INM, but further work considering other possible N and P sources, sinks and stores is required to achieve INM. Integration of this new knowledge in to models used for decision making is likely to be challenging. It is suggested that future research adopts a catchment typology approach.   For a range of different typologies, future work can identify the relevant macronutrient sources, sinks and stores. This can act as a screening tool to support practitioners in the prioritisation of which processes to consider in specific catchments of interest.

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